Preparation of two-dimensional materials and their application in thin film composite membranes





Dissertation

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List of Abbreviations

ACM	Aspen Custom Modeling
ACOF	Azine-linked covalent organic framework
AGMD	Air gap membrane distillation
APTS	3-(aminopropyl)triethoxysilane
BD	Benzidine
BET	Brunauer-Emmett-Teller
BI	Benzimidazole
BPrB	2-bromopropionyl bromide
BTA	Benzene-1,3,5-tricarboxaldehyde
bwGO	Base-washed Graphene oxide
cam	D-camphoric acid
CAU	Chung-Ang University
CGO	Conventional graphite oxide
CNT	Carbon nanotube
СО	Methylspirobisindane monomer
COF	Covalent organic framework
СР	Cross-polarization
CTF	Covalent triazine framework
CuBDC	Copper 1,4-benzenedicarboxylate
CVD	Chemical Vapor Deposition
dabco	1,4-diazabicyclo(2.2.2)octane
DCIBAO	2,4-dichlorobenzamidoxime
dClpf	1,1-bisdichlorophosphino-ferrocene
DCMD	Direct contact membrane distillation
DEAEMA	2-diethylaminoethyl methacrylate
DHF	9,9-dihexylfluorene-2,7-diamine
dMbpy	4,4'-dimethyl-2,2'-dipyridyl
DMBIM	5,6-dimethylbenzimidazole
DMF	N, N-dimethylformamide
DMPPA	2,5-dimethyl-6-phenylpyrazolo[1a]-pyrimidin-7-amine
EA	Elemental analysis

EB	3,8-diamino-5-ethyl-6-phenylphenanthridinium bromide
EDX	Energy-dispersive X-ray analysis
F	Phenylalanine
FGO	Functionalized graphene oxide
FTIR	Fourier transform infrared
GIC	Graphite-intercalated compound
GO	Graphene oxide
GO-CI	Chlorinated graphene oxide
h-BN	Hexagonal boron nitride
HKUST	Hong Kong University of Science and Technology
HZG	Helmholtz-Zentrum Geesthacht
IL	Imine-linked
ImGO	Imidazole functionalized graphene oxide
IR	Infrared
JLU	Jilin University
LB	Langmuir-Blodgett
LbL	Layer-by-layer
LSNMR	Liquid state nuclear magnetic resonance
LZU	Lanzhou University
MAS	Magic angle spinning
MB	Methylene Blue
MEHQ	4-methoxyphenol
MF	Microfiltration
MFP	Mean free path
MIL	Matériaux de l'Institut Lavoisier
MMM	Mixed Matrix Membrane
MOF	Metal-organic framework
MSB	Magnetic suspension balance
NF/RO	Nanofiltration/reverse osmosis
NIPAM	N-isopropylacrylamide
NMP	N-Methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
NUS	National University of Singapore

OD	Oxidative debris
ОМе	Monomethylethers
Ра	<i>p</i> -phenylenediamine
ΡΑ	Polyamide
PAA	Poly(acrylic acid)
PAI	Poly(amide-imide)
PAN	Polyacrylonitrile
PBI	Polybenzimidazole
PDA	Terephthaldehyde
PDEAEMA	Poly (2-diethylaminoethyl methacrylate)
PDEMA	Poly(2-(2-ethoxyethoxy) ethyl methacrylate)
PDMS	Polydimethylsiloxane
PEBA	Polyether block amide
PEEK	Polyetheretherketone
PEEMA	Poly(2-ethoxyethyl methacrylate)
PEG	Poly(ethylene glycol)
PEGDMA	Poly(ethylene glycol) dimethacrylate
PEI	Poly(ethylene imine)
PEMA	Poly(ethyl methacrylate)
PET	Polyethylene terephthalate
PGMD	Permeate gap membrane distillation
PhChGO	Phosphochlorinated graphene oxide
PIM	Polymers of Intrinsic Microporosity
РМА	Polymethacrylate
РММА	Poly(methyl methacrylate)
PMPS	Polymethylphenylsiloaxe
PP	Polypropylene
PtBMA	Poly(tertiary-butyl methacrylate)
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PVDF	Polyvinylidene difluoride
PXRD	Powder X-ray diffraction
R	Arginine

rbwGO	Base-washed and reduced Graphene Oxide		
rGO	Reduced Graphene Oxide		
SDU	Shandong University		
SE	Secondary electron		
SEC	Size exclusion chromatography		
SEM	Scanning electron microscopy		
SGMD	Sweeping gas membrane distillation		
SI-ATRP	Surface-initiated atom transfer radical polymerization		
SI-GO	Surface-Initiator functionalized Graphene Oxide		
SIP	Surface-initiated polymer		
SI-PDEAEMA	Surface-initiated poly(2-diethylaminoethyl methacrylate)		
SNW	Schiff base networks		
SSNMR	Solid-state nuclear magnetic resonance		
ТАРВ	1,3,5-tris(4-aminophenyl) benzene		
TEA	Triethylamine		
TEM	Transmission electron microscopy		
TFCM	Thin-film composite membrane		
TFP	1,3,5-triformylphloroglycinol		
TGA	Thermal gravimetric analysis		
TGA-FTIR	Fourier transform infrared spectroscopy-coupled thermal		
	gravimetric analysis		
ТНВА	Trihydroxybenzoic acid		
THEIC	1,3,5-tris(2-hydroxyethyl)isocyanurate		
THF	Tetrahydrofuran		
ΤΗΡΤΑΜΑ	Tris(3-hydroxypropyltriazolylmethyl)amine		
ТМВ	3,3´,5,5´-tetramethylbenzidine		
ТМС	1,3,5-benzenetricarbonyl chloride		
TMD	Transition metal dichalcogenide		
ТМО	Transition metal oxide		
Тр	1,3,5-triformylphloroglucinol		
ТРРМ	Two-pulse phase-modulated		
TR	Thermally rearranged		
ТХІ	Triple Resonance		

Ultrafiltration
Universitetet i Oslo
University of Texas at San Antonio
Ultraviolet
Ultraviolet-visible
Vacuum multi-effect membrane distillation
Vacuum membrane distillation
Cross-linked poly(ethylene glycol diacrylate)
X-ray photoelectron spectroscopy
X-ray diffraction
Zeolitic Imidazolate Framework
Zn ₂ (cam) ₂ dabco

List of Symbols

b	Dimensionless constant
C ₁	Gas concentration in the permeate side of the membrane
C ₂	Gas concentration in the polymer feed
D	Concentration-averaged diffusivity
Dij	Binary diffusion coefficient (m·s ⁻¹)
d _{gas}	Diameter of the gas molecule
<i>d</i> _{pore}	Characteristic length
$d[R^*]/dt$	Change in the radical concentration at the substrate surface
	with time
$ar{f}$	Average functionality
G	Molar concentration of a gas dissolved (mol m ⁻³)
G	Gas adsorption amount (m ³ m ⁻³)
Gm	Saturated gas adsorption amount at the reference
	temperature (m ³ m ⁻³)
J_k	Flux
k	Empirical constant (dimensionless)
<i>k</i> a	Gas equilibrium adsorption rate (m Pa ⁻¹ s ⁻¹)
kв	Boltzmann constant (1.38x10 ⁻²³ J K ⁻¹ molecule ⁻¹)
<i>k</i> _c	Henry constant (mol m ⁻³ Pa ⁻¹)
<i>k</i> _d	Gas equilibrium desorption rate (m Pa ⁻¹ s ⁻¹)
1	Membrane thickness
Μ	Molecular mass
$\overline{M_0}$	Average molar mass of the repeating unit
$\overline{M_w}$	Weight average molecular weight
т	Gas mass adsorbed by the mass of an adsorbent (kg/kg)
Ν	Steady-state penetrant flux through the membrane
NA	Avogadro's number
N_i^F	Molar diffusive flux with respect to the bulk velocity of a gas
	mixture
n	Molecular density (molecule m ⁻³)
n	Empirical constant (dimensionless)

Ρ	Permeability coefficient	
Pc	Permeability coefficient of the composite	
P _{ic}	Permeability coefficient of component i in the continuous	
	phase	
P _{id}	Permeability coefficient of component i in the dispersed	
	phase	
Pimm	Permeability coefficient of component <i>i</i> in the mixed matrix	
P_m	Permeability coefficient of the neat polymer	
p	Partial gas pressure (Pa)	
p_0	Gas saturated vapor pressure at the reference temperature	
	(Pa)	
<i>p</i> ₁	Permeate pressure	
<i>p</i> ₂	Feed pressure	
q	Volumetric flux per unit area (m·s ⁻¹)	
R	Universal gas constant (0.08314 m ³ bar K ⁻¹ kmol ⁻¹)	
R or P _c /P _m	Relative permeability coefficients	
S	State of the filler alignment in the composite membrane	
Т	Temperature of the gas (K)	
ν	Specific volume of the polymer	
$v - v_{\infty}$	Distance from the equilibrium specific volume	
VT	Mean thermal molecular speed (m sec ⁻¹)	
W	Probability of a gas molecule that enters the pore and flows	
	along the pore to the other side	
α	Aspect ratio of the filler dimensions	
α	Conversion degree	
θ	Gas coverage of the porous black rock surface	
	(dimensionless)	
τ	Relaxation time for the specific volume	
φd	Volume fraction of the dispersed phase	

Chapter 1

Introduction

Energy-efficient gas separation becomes more and more critical due to the current status of global warming leading to climate change. Such a disrupting phenomenon is a global challenge that does not respect national borders. This issue requires solutions to be implemented in order to convert the modern industry into a low-carbon economy. Two-dimensional materials have received considerable attention due to their unique properties in different fields such as optoelectronics [1], nanoelectronics [2], energy storage devices [3], pharmaceutics [4], composites [5], multifunctional textiles [6], biosensors [7], etc. These materials are referred to graphene, graphene oxide, transition metal dichalcogenides (TMDs), graphitic carbon nitride, MXenes, hexagonal boron nitride (h-BN), transition metal oxides (TMOs), covalent organic frameworks (COFs), metal-organic frameworks (MOFs), and other materials are good candidates for molecular separation.

Gas separation and storage is one of the main topics in modern energy concerns. Different approaches, such as polymer membrane-based separation and adsorption techniques, have been implemented for this kind of task. Having a great impact on CO₂ capture [8], natural gas sweetening [9, 10], hydrogen purification [11], and water vapor separation [12], polymer membrane-based gas separation has received significant attention since 1980 [13]. On the one hand, most of the polymers cannot surpass the Robeson upper bound [14], which was proposed for a better understanding of the gas transport phenomenon through the polymer membrane. On the other hand, the polymer membranes age physically within their utilization period and become useless. This is a big problem for the Polymers of Intrinsic Microporosity (PIMs) membranes whose permeability and selectivity for CO₂/N₂ is high and could be one of the well-exploited polymer membranes. Due to the aging problem of PIMs, it has not found its place in the industry since its discovery [15]. The task, to increase the gas transport phenomenon through the membrane sparation science into the direction of mixed matrix membrane preparation, where polymer membranes

and adsorbent particles meet. This requires the preparation of new types of materials that are compatible with the polymers and increase their transport properties.

In this dissertation, the preparation and characterization of mixed matrix membranes comprising of a PIM-1 polymer matrix, graphene-like nanosheets, and metal-organic frameworks (MOFs) are attained. Additionally, novel two-dimensional covalent organic frameworks (COFs) were synthesized, and their gas adsorption properties were tested to extend further such kinds of materials in membrane science. Moreover, for the first time, the possibility to use single-layer graphene oxide for grafting-from polymerization using a controlled radical polymerization technique was developed.

1.1. Objective

The aim of this research project is the preparation of 2D nanomaterials and their effect on the gas transport properties of thin-film mixed matrix composite membranes. To implement this task, the following approaches were conducted:

- Chemical approach.
 - a) Synthesis and characterization of graphene oxide. As a twodimensional material, graphene oxide has great potential in membrane science; thus, the structural investigation will widen its manufacturing, usage, and modification.
 - b) Surface-initiator functionalized graphene oxide layers in the SI-ATRP technique. Initiator-mounted graphene layers open up a new avenue in the field of polymer synthesis.
 - c) Synthesis of metal-organic frameworks (MOFs). The MOF particles containing defined pore sizes are one of the best candidates for the preparation of mixed matrix membranes.
 - d) Synthesis of covalent organic frameworks (COFs). Although metalorganic frameworks possess defined pore sizes, the metal sites might be irresistible to water vapor in the industry. Thus, the synthesis of novel water vapor durable compounds with defined pore sizes is highly desirable.
- Physical approach.

- a) Preparation of mixed matrix membranes. Here, the synthesized particles were incorporated into a PIM-1 polymer matrix to understand the effect of particles on the gas transport properties of the thin-film composite membranes.
- b) Preparation of thin film membranes for membrane distillation experiments. The synthesized surface-initiated polymers were tested for the membrane distillation techniques.

1.2. Outline of the thesis

The thesis is divided into five chapters, including the introduction. Chapter 2 is devoted to the theoretical background on membranes and their types. Additionally, the gas transport properties of the mixed matrix membranes are also discussed in this chapter. Chapter 3 sketches the experimental procedures employed during the research. In this chapter, characterization techniques for graphene oxide analysis, its modification into different graphene particles, and surface-initiator functionalized graphene oxide layers, synthesis, and characterization of metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are detailed. The results and discussion of the research are summarized in Chapter 4. This chapter is subdivided as follows: a) Chapter 4.1 reveals information about the synthesis, surface functional group analysis of the graphene oxide (GO) layers, and its use in membrane science; b) Chapter 4.2 contains information about chemical modification of GO into functionalized GO (FGO) particles, and their use in the PIM-1 polymer matrix as 2D nanofillers; c) Chapter 4.3 summarizes details on the surface-initiated atom transfer radical polymerization of methacrylate derivatives from graphene oxide particles and single-layer graphene oxide layers, and the application of such kind of polymer in membrane distillation; d) Chapter 4.4 gives details about the synthesis, characterization of the MOFs, and their usage as the fillers in mixed matrix membranes; e) Chapter 4.5 describes the synthesis, characterization of the novel 2D COFs, and their usage as adsorbents for gas uptake experiments. Finally, Chapter 5 concludes all the results of this research and gives an outlook for the future.

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Chapter 2

Theoretical background and state-of-the-art

2.1. Membranes

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments [1]. The main advantages of membrane technology as compared with other unit operations in (bio)chemical engineering are related to this unique separation principle, i.e., the transport selectivity of the membrane. Separations with membranes do not require additives, and they can be performed isothermally at low temperatures and— compared to other thermal separation processes—at low energy consumption. Also, upscaling and downscaling of membrane processes, as well as their integration into other separation or reaction processes, are secure.

Passive transport through membranes occurs as the consequence of a driving force, i.e., a difference in chemical potential by a gradient across the membrane, e.g., concentration or pressure, or by an electrical field (Figure 2.1). The barrier structure of membranes can be classified according to their porous character. Active development is also concerned with the combination of nonporous or porous membranes with additional separation mechanisms, and the most important ones are electrochemical potentials and affinity interactions.



Figure 2.1. Different driving forces present in a membrane separation process. Reprinted from [2]. ΔC , ΔP , ΔT , and ΔE are the differences in concentration, pressure, temperature, and electrical potential, respectively.

Separation of the components of the gaseous and liquid mixtures is a critical step in several important industrial, biological, and chemical processes, including natural gas purification, hydrogen production, carbon dioxide sequestration, and oxycombustion. The membrane separation method possesses definite benefits compared to conventional cryogen and sorption based methods. It employs no moving parts, requires no exotic chemicals, exhibits low energy requirements, and flexibility in configuration.

Being a permeable or semipermeable interphase material, membranes have gained a remarkable role in the chemical and pharmaceutical industries, since they occupy 40-70% of both the capital and operational costs [3]. In the aforementioned industries, chemical synthesis performs in organic solvents, which need to be recovered or discarded after the reaction. Discarding the organic solvent would contribute to environmental problems and increase operational costs. Membrane technology offers a benefit in such kind of problem, where the membrane filtration process employs for the recovery of organic solvents and the purification of the synthesized valuable compounds (Figure 2.2).

(a) Concentration

Defining feature: at least one solute and one solvent



(b) Solvent exchange

Defining feature: at least one solute and two solvents





Defining feature: at least two solutes and one solvent



Figure 2.2. Membrane filtration processes for liquid applications: a) concentration, b) solvent exchange, and c) purification processes. Reprinted with permission from [4]. *Copyright* © *2014, American Chemical Society.*

2.2. Classification of membranes

According to their origin, membranes are divided into two main classes: a) natural and b) synthetic.

Natural membranes are generally biological membranes, and they act as a selectively permeable barrier within the living organisms. All natural membranes are composite in the sense that they contain both a lipoid-like and non-lipoid like components. Mostly, these kinds of membranes are called "cell membranes". In a cell membrane, the bulk of lipids provides the fluid matrix for proteins to rotate and laterally diffuse for physiological functioning. A fluid membrane model for the phospholipid bilayer is shown in Figure 2.3.



Figure 2.3. The illustration of a cell membrane. The image was reprinted from [5].

Synthetic membranes are inspired by natural membranes. The main idea of the preparation of synthetic membranes is to control the molecular flow and selectively separate one component from a liquid or a gaseous mixture. They can be categorized into two main classes corresponding to the constituents of the membranes:

 Inorganic membranes. Such kinds of membranes are made of ceramic, carbon, silica, zeolite, various oxides (alumina, titania, zirconia), as well as metals such as palladium, silver, and their alloys. Table 2.1 shows the main advantages and disadvantages of the use of inorganic membranes.

Advantage	Disadvantage
High-temperature long term stability	High capital costs
Resistance to harsh environments	Brittleness
Resistance to high-pressure drops	Low membrane surface per module
	volume
Inertness to microbiological degradation	Difficulties in achieving high selectivities
	in large scale microporous membranes
Easy cleanability after fouling	Generally low permeability of the highly
	selective membranes (dense
	membranes) at medium temperatures
Easy catalytic activation	Baffling membrane-to-module sealing at
	high temperatures

The main factors that hinder the use of inorganic membranes are high capital costs, low permeability, and difficulties in achieving high selectivities. For the membrane industry, the membranes that possess low capital costs, high permeability coefficients, and selectivities are desirable. This demand started the exploration boom of organic membranes.

 Organic membranes. Under the term "organic membrane", mainly, all kinds of polymeric membranes are considered. Nowadays, almost all of the membranes operated in the membrane industry are made of synthetic or natural polymers. Natural polymers used as the membranes are wool, rubber (polyisoprene), and cellulose. Polyamide, polyimide, polystyrene, polyvinylidene difluoride, and polytetrafluoroethylene are examples of the synthetic polymers used as membranes for different purposes. Table 2.2 describes the membrane processes and the polymers used in those fields.

Membrane application	Polymeric materials
Microfiltration (MF)	Cellulose acetate, cellulose esters,
	cellulose nitrate, polyvinyl alcohol,
	polyvinyl chloride (PVC), PVC
	copolymers, aromatic and aliphatic
	polyamides, polysulfone, polyimide,
	polyetheretherketone (PEEK),
	polycarbonate, polyester, polyethylene,
	polypropylene, polytetrafluoroethylene
	(PTFE), polyvinylidene difluoride (PVDF)
Ultrafiltration (UF)	Cellulose acetate, polyacrylonitrile, PVC
	copolymers, Aromatic and aliphatic
	polyamides, polysulfone, polyimide,
	polyetheretherketone (PEEK),
	polytetrafluoroethylene (PTFE),
	polyvinylidene difluoride (PVDF)
Nanofiltration/reverse osmosis (NF/RO)	Cellulose acetate, aromatic polyamide,
	polyimide
Gas separation	Cellulose acetate, polyimide,
	polyetheretherketone (PEEK),
	polydimethylsiloxane (PDMS)
Pervaporation	Cellulose acetate, polyacrylonitrile,
	polyethylene, polypropylene,
	polytetrafluoroethylene (PTFE),
	polyvinylidene difluoride (PVDF),
	polydimethylsiloxane (PDMS)
Membrane distillation	Polyethylene, polypropylene,
	polyvinylidene difluoride (PVDF)

Table 2.2. Application of polymeric materials in the membrane industry.

All synthetic membranes can be classified as symmetric (isotropic) and asymmetric (anisotropic) corresponding to their cross-sectional structure. The illustration of this kind of classification is shown in Figure 2.4.



Figure 2.4. The schematic representation of the typical membrane structure. The image was adapted with permission from [6]. *Copyright* © 2012 WILEY-VCH Verlag *GmbH* & Co. KGaA, Weinheim.

Nowadays, such kinds of membranes are used for different purposes in the modern industry. In Table 2.3, the separation processes and mechanisms conducted by the membranes are summarized.
Table 2.3. Classification of the separation processes and mechanisms of the membranes.

Process	Size	of	the	Driving fo	orce	Separation	
	retained materials					mechanis	m
Microfiltration	0.1-10		μm	Pressure	difference	Sieve effect	
	microparticles		(0.2-2 bar)				
Ultrafiltration	1-100 nm Pressur		Pressure	difference Sieve effect			
	macromolecules		(1-5 bar)				
Nanofiltration	0.5-50		nm	Pressure	difference	Sieve	effect,
	molecules		(5-20 bar)		solution-diffusion,		
						exclusion	
Reverse osmosis	<1 nm ions		Pressure	difference	Solution-di	iffusion,	
				(10-100 bar)		exclusion	
Dialysis	ialysis <1 nm molecules		Concentration		Diffusion		
				difference			
Electrodialysis	<1 nm molecules		Electric	potential	Exclusion		
				difference			
Pervaporation	<1 nm m	<1 nm molecules		Concentration		Solution-diffusion	
				difference			
Gas separation	<1 nm molecules		Partial	pressure	Sieve	effect,	
			difference	(10-100	solution-di	ffusion	
				bar)			
Membrane	<1 nm molecules		Temperature and		Evaporation		
distillation			partial	pressure	pressure		
			difference				

2.3. Membranes for molecular separation

Membrane technology is a powerful tool for solving modern problems and developing industrial growth. Gas separation membranes are competitive separation technology since 1980 and prevail over some other conventional separation technologies such as cryogenic distillation and adsorption processes. These kinds of technology for gas separation do not need a phase change, and the absence of moving parts makes them peculiar for different critical remote operations. However,

membranes required for gas separation must be made from long-term, stable, and highly permeable materials and depend on several factors [7]:

- The materials with high permeability and separation factors.
- The membrane structure and thickness profoundly influence the permeability of the membrane.
- The membrane configuration (flat or hollow fiber).
- The module and system design.

Permeability is the rate, which determines the permeation of any compound through the membrane. It depends upon two main factors: a thermodynamic factor and a kinetic factor. The thermodynamic factor is the distribution of compounds between feed and membrane phase, while the kinetic factor summarizes diffusion or surface diffusion of the species in the dense and microporous membranes, respectively. Another critical factor in membrane science is selectivity. The selectivity is the relative permeability of the membrane for the feed side to accomplish the separation of one compound. A list of commercial membranes according to their polymeric nature used for gas separation in the industry is shown in Table 2.4.

Table 2.4. Rubbery and glassy polymers used for gas separation in the industry [8].

Rubbery polymers	Glassy polymers
Polydimethylsiloxane (PDMS)	Cellulose acetate
Ethylene oxide/propylene oxide-amide copolymers	Polycarbonates
	Polyperfluorodioxoles
	Polyimides
	Poly(phenylene) oxide
	Polysulfone

Although there are a lot of studied polymers for membrane science, they offer slow progress. Existing challenges in this field are the low selectivity and permeability of the suggested polymer membranes. The primary purposes for the membranes being used in the industry are described in Table 2.5.

Table 2.5. Membrane applicationCommon gas separation	ons for gas separation. Application
O ₂ /N ₂	Oxygen enrichment, inert gas
	generation
H ₂ /Hydrocarbons	Refinery hydrogen recovery
H ₂ /N ₂	Ammonia purge gas
H ₂ /CO	Syngas ratio adjustment
CO ₂ /Hydrocarbons	Acid gas treatment, landfill gas
	upgrading
H ₂ O/Hydrocarbons	Natural gas dehydration
H ₂ S/Hydrocarbons	Sour gas treating
He/Hydrocarbons	Helium separation
He/N ₂	Helium recovery
Hydrocarbons/Air	Hydrocarbons recovery, pollution control
H ₂ O/Air	Air dehumidification

In their work, L.M. Robeson *et al.* showed in detail the main highlights of the glassy and rubbery polymers used as a membrane [9]:

- The diffusion coefficients in rubbery polymers are higher than in glassy polymers
- The diffusion selectivity of glassy polymers is modest.
- Rubbery polymers have a low dependence on diffusion selectivity.
- Glassy polymers have higher solubility coefficients.

The relationship between membrane selectivity and membrane permeability is recognized as Robeson upper bound [10, 11], and it is desirable to develop highly permeable and selective membranes (Figure 2.5).



Figure 2.5. Schematic representation of Robeson upper bound. Figure (a) reprinted with permission from [12], while Figure (b) from [13].

Figure 2.5a describes the desirable continuous, highly selective, and permeable membranes. Up to now, several research groups have targeted the desirable zone; however, research in this field needs further investigations. The progress in the field of highly permeable and selective polymer membrane preparation is very slow, as it is seen from Figure 2.5b, which shows that the excellent members for the membrane separation technology are inorganic membranes. Moreover, these materials have drawbacks such as high cost, modest reproducibility, brittleness, low membrane area to module volume ratio, and sealing difficulties [7]. Thus, to improve the effectiveness of the polymer membranes, research has been focused on the preparation of mixed matrix membranes. This thesis is mainly concentrated on mixed matrix membranes.

When it comes to the comparison of the rubbery and glassy polymeric membrane properties, it would be noted that the rubbery polymers show lower permeability than the glassy polymers (Figure 2.6).



Figure 2.6. Comparison between the glassy and the rubbery polymers for O_2/N_2 upper bound. Figure reprinted with permission from [14]. *Copyright* © 2014 Elsevier B.V.

2.3.1. Polymers of intrinsic microporosity (PIM) as membrane materials

The microporous materials defined by IUPAC corresponds to the solid compounds that contain pore sizes less than 2 nm, and consequently, they possess a large surface area (300-3000 m² g⁻¹) measured by techniques based on analysis of gas adsorption isotherms. These materials are usually used as adsorbents, heterogeneous catalysts, and molecular sieves. The IUPAC adsorption isotherms are shown in Figure 2.7.



Figure 2.7. IUPAC classification of adsorption isotherms. n_a is the quantity of adsorbed gas, p/p_0 is the relative pressure. The image was reprinted from [15].

Figure 2.7 reveals six different adsorption isotherms. The isotherm type I is for microporous materials, while type II, III, and VI correspond to the non-porous or macroporous materials. Mesoporous materials show the IV and V isotherms.

The term "intrinsic microporosity" in polymers was firstly introduced by Ilinitch and co-workers [16]. It refers to a continuous network of interconnected intermolecular microcavities [17]. PIM-1 possesses such kinds of intermolecular voids that arise from the shape and rigidity of the polymer chains, which prevents very close packing, and these voids are not related to any thermal and processing history of the polymer [18]. The structural model of PIM-1 is shown in Figure 2.8.



Figure 2.8. Chemical structure of PIM-1 and its 3D model showing the rigid structure and contortion site. Adapted with permission from [19]. *Copyright 2016, Springer-Verlag Berlin Heidelberg.*

PIM-1 displays excellent chemical, mechanical, and thermal stabilities. Budd *et al.* [20] revealed that while the molecular structure of the polymer remains intact, its microporosity is maintained. Brunauer-Emmett-Teller (BET) analysis conducted on PIM-1 showed 500-900 cm² g⁻¹ inner surface areas with the 0.4-0.8 nm intrinsic microporosity determined by the Howarth-Kawazoe method [21-23]. This polymer has good solubility even at high molecular weights (200000 g mol⁻¹) in tetrahydrofuran or chloroform allowing the preparation of a robust, free-standing PIM-1 film, which is used as a membrane for the selective separation of a desirable compound from a liquid or a gas mixture.

PIM-1 possesses a ladder structure due to the existence of contorted sites, and therefore, the rotation and tightly packing of the polymeric chains are prevented. This results in the formation of nanopores with a large inner surface area [22]. PIM-1 membranes show a large fractional free volume (24-26% [24]) and higher permeability for many gases. In particular, the PIM-1 membrane shows very high solubility against CO₂. Several research groups [25-28] reported high permeability of CO₂ through the PIM-1 membrane (2000-15000 Barrer). Research on PIM-1 has resulted in the

preparation of several PIM family polymers. Table 2.6 summarizes the permeability data of several PIM family polymers for different gases.

PIM polymers	Gas	Permeability (Barrer)	Ref.	
	O ₂	370		
	N ₂	92	[29]	
P1IVI-1	CH_4	125		
	$\rm CO_2$	2300		
	O ₂	190		
	N ₂	42	[29]	
PIIVI-7	CH_4	62		
	$\rm CO_2$	1100		
	O2	1360	[30]	
	N ₂	490		
	CH ₄	830		
	CO_2	9270		
	O2	2180	[31]	
	N ₂	850		
	CH ₄	1525		
	CO ₂	14180		

Table 2.6. The permeability data of PIM family polymers for several gases.

Several reference data show higher solubility and permeability for CO₂. Halder *et al.* showed that PIM-1 postmodified by vinyl groups exceeds the Robeson upper bound [31], which is shown in Figure 2.9.



Figure 2.9. Robeson 2008 upper bound for the gas pair CO₂/N₂ showing various modified PIM-1 membranes. Reprinted with permission from [31]. *Copyright* © 2018, *American Chemical Society.*

Aging of PIM-1. PIM-1 is a glassy polymer, and unlike rubbery polymers, gas transport and sorption properties of such kinds of polymers change over time towards an unattainable equilibrium. This process, referred to as "physical aging", often accompanies the increase of selectivity resulting in reduced gas permeability. During this process, the polymer matrix densifies volumetrically, which is attributed to the small molecular motions below the glass transition temperature of the polymer [32]. The phenomenon of physical aging is described by the equation shown below:

$$\frac{dv}{dt} = -\left(\frac{v - v_{\infty}}{\tau}\right) \tag{2.1}$$

where v is the specific volume of the polymer, v_{∞} is the equilibrium specific volume, and τ is the relaxation time for the specific volume in the polymer matrix. Over time PIM-1 membrane ages, which means the polymer chains merge, leading to the collapse of the void spaces. Figure 2.10 shows some data related to the decrease of the permeabilities for several gases.



Figure 2.10. Gas permeability of the original PIM-1 membrane as a function of aging time. Reprinted with permission from [33]. *Copyright* © *2013 Hydrogen Energy Publications, LLC. Published by Elsevier Ltd.*

Figure 2.10 shows that PIM-1 loses its permeability substantially over time, and within 100 days, almost 60% of the PIM-1 permeability for methane decreased. This has a significant impact on the commercialization of PIM-1, as for an industrial application of a polymer membrane, one of the key parameters is the long-term operation stability. In their work, F. Y. Li *et al.* [33] conducted positron annihilation lifetime experiments for the prepared membranes and showed that over 100 days original PIM-1 reduces its fractional free volume by 11%, while UV-irradiated PIM-1 reveals only a 2% drop. The results are shown in Figure 2.11.



Figure 2.11. O-Ps lifetime (a) and intensities (b) of the original and UV-rearranged PIM-1 membranes as a function of aging time. Reprinted with permission from [33]. *Copyright* © *2013 Hydrogen Energy Publications, LLC. Published by Elsevier Ltd.*

Interestingly, the aging of PIM-1 is faster in thin films in comparison with their thick counterparts. It is explained that free volume elements diffuse and escape from the surface faster than from thick films. Moreover, when glassy films become thinner, the relaxation rate is to be accelerated due to the reduction of constrains on the relaxation time [34].

2.3.2. Graphene and graphene oxide membranes

Graphene is a new and promising carbon nanomaterial for future applications. Since its discovery by K.S. Novoselov *et al.* in 2004 [35], research activities related to graphene-based materials have been increased. It is an allotropic modification of carbon in the form of a single-layer atom in a two-dimensional hexagonal lattice. In this lattice, one atom forms each vertex and shows excellent mechanical, electrical, and optical properties.

Being a transparent material, graphene is the only form of carbon, which possesses the chemical reactivity for every atom from two sides due to its 2D structure. Diankov et al. showed that the single-layer graphene etches hydrogen 100 times stronger than thicker layers [36]. However, there is still an opportunity to improve the use of advantages of the single-layer graphene. The main problem in graphene production is its transfer. For this reason, all single-layer graphene experiments are carried out on the substrates such as SiO₂, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDs) to get better results [37]. Another difficulty of the graphene fabrication is the π - π stacking and van der Waals interactions of the sheets causing aggregation. One can overcome this issue by chemical attachment of functional groups, small molecules, and even polymer chains to a graphene sheet via 'grafting to' or 'grafting from' methods [38]. Another interesting point in the development of the single-layer graphene technology is the oxidation of graphene into graphene oxide (GO). After the transformation of graphite into conventional graphite oxide (CGO), it is much easier to transfer the CGO into the graphene layer via the reduction process to get large-scale graphene layers at a low cost.

Oxidation of graphite leads to the formation of GO, whose structure and the mechanism of formation are still unclear and need further investigation. The structural examination of GO is a necessary step for further functionalization, for the reduction and for determining the structure of its origin-graphene. This helps to reduce the

manufacturing expenses of graphene production and to synthesize new types of graphene nanoparticles for future applications such as lithography, biosensing, drug delivery, etc. [39, 40]. The molecular structure of graphene, graphene oxide, and its reduction are shown in Figure 2.12.



Figure 2.12. Transformation of graphite into graphene oxide and the reduction of graphene oxide to reduced graphene oxide. The image was reprinted from [41]. *Copyright* © *1969, Elsevier.*

Graphene offers an advantage for membrane science due to its infinitesimal thickness, chemical stability, flexibility, and mechanical strength. In general, graphene layers are impermeable to all gases; however, they render a new platform for the realization of mass transport, if they are precisely perforated. Theoretical studies conducted to understand the mass transport through graphene nanopores have indicated that these kinds of membrane materials can be superior to state-of-the-art polymer-based filtration membranes [42, 43]. Yuan *et al.* [44] using molecular dynamics simulations predicted that gas transport through graphene nanopores could vary depending on pore diameter. Thus, a pore diameter less than 0.7 nm can allow transport of gas molecules by a translocation dominated mechanism, while a surface pathway and direct pathway dominated gas transport mechanisms can appear only in the case of pore diameters 1-2 and > 4 nm, respectively. As it is seen from the computational simulations, porous graphene holds great promise for membrane separation. If the nanopores could be controlled upon the sizes of gas molecules, then

at the nanolevel, the gas molecules could be selectively separated. To separate hydrogen from carbon dioxide, the perforated graphene nanopores must be in the range of the kinetic diameter of the hydrogen molecule (0.289 nm). Unfortunately, precise control of the pore sizes down to 0.3 to 0.5 nm is still challenging.

The main methods for drilling holes into the graphene layers are ultravioletinduced oxidative etching [45], ion bombardment [46-48], and oxygen-plasma etching [49] techniques. Graphene membranes used for drilling are usually prepared by mechanical exfoliation or chemical vapor deposition (CVD) methods [50]. Both approaches have drawbacks:

- Mechanical exfoliation. This procedure is a time-consuming approach, and the lateral dimensions of the resulting graphene flakes are several micrometers. Unfortunately, the yield of this method is rather low; therefore, its practical application is hindered except for laboratory-scale fundamental research.
- Chemical vapor deposition (CVD). Although, this method is a promising technique for the preparation of large-area and high-quality graphene membranes, the unintentionally introduced cracks, tears, and/or damages during transfer and pore-drilling processes will degrade the mechanical strength of graphene.

Furthermore, current state-of-the-art drilling techniques produce irregular pores. The existence of such pores in the graphene may cause stress concentration on the graphene matrix and weaken its mechanical strength. They are the main reasons that prevent the application of these kinds of novel membranes in the industry. Theoretical calculations showed that graphene membranes over a substrate possessing pore sizes less than 1 μ m could withstand high hydraulic pressures nearly 10 times higher than conventional polymer membranes in typical reverse osmosis operations [51].

Another problem in graphene science is the π - π stacking of graphene layers, which follows with the agglomeration. To prevent agglomeration of graphene layers, oxidation is one of the options. Oxidation leads to the formation of graphene oxide (GO). In view of the structure, graphene oxide is decorated with different oxygen functional groups such as phenolic hydroxyl, epoxy, carboxyl, lactonic, ketone, and quinone both on basal planes and edges of the graphene structure. This compound can be easily dispersed and exfoliated in water by sonication. Using various methods,

such as vacuum and pressure filtration, spin-casting, drop-casting, dip-coating, spraycoating, doctor blade coating, layer-by-layer (LbL) assembly, and Langmuir-Blodgett (LB) assembly, GO membranes can be prepared [52]. Although nanoporous graphene membranes transport the molecules and ions via size exclusion and electrostatic interactions, ion adsorption is additionally introduced to graphene layers due to the presence of oxygen functionalities distributed on the surface of graphene (Figure 2.13).



Figure 2.13. Transport through graphene and graphene oxide membranes. Reprinted with permission from [53]. *Copyright* © *2017, Springer Nature.*

Preparation of GO membranes requires much attention; thus, GO membrane can possess pinhole defects that will reduce the membrane performance. To get a better membrane process, Hu *et al.* suggested to crosslink the GO membrane on the membrane support. Although this process improves the stability of GO layers to prevent their dispensability in water, the membrane has a low rejection (6-46%) for monovalent and divalent salts but exhibited a moderate rejection (46-66%) of Methylene Blue (MB), and a high rejection (93-95%) of Rhodamine-WT [54]. Nature-inspired GO-RF8 (R and F represent arginine and phenylalanine, respectively) membranes [55] showed superior flux and high rejection, similar to the aquaporin membranes. Moreover, such kind of membrane can reject 94% of MB from water at 5 bar driving force. Membranes prepared by the incorporation of GO into the

poly(ethylene glycol) diamine polymer matrix showed high CO₂ permeance and selectivity of ~70 for CO₂/CH₄ gas pair, which is the highest performance reported for dry-state-GO-stacking membranes [56]. Due to the assembly of the graphene oxide nanosheets, the lamellar structure originates, and they support the fast and selective transport of the molecules.

2.3.3. Metal-organic framework (MOF) membranes

Metal-organic frameworks are a class of porous coordination polymers and have become one of the fastest-growing fields in chemistry. Such kinds of frameworks are constructed from metal nodes and organic linkers. This feature gives the MOFs structural and chemical tunability. Having an inorganic and organic nature, the MOFs can be used in different research areas such as fuel storage (hydrogen and methane) [57], carbon dioxide capture [58], catalysis and photocatalysis [59], gas separation [60], biomedical imaging and drug delivery [61], ion conduction [62], and enzyme carrier [63].

Tailorable pore sizes, pore geometries, high void fractions, and large surface areas make them unique for different fields. In particular, the extensive study and upscaling of the industrial production of MOFs have become attractive in the field of fuel cells and supercapacitors [64, 65]. Their surface area can reach as high as 10000 m² g⁻¹, which is substantially higher than zeolites (1000 m² g⁻¹) and activated carbon (3500 m² g⁻¹) [66, 67].

Up to now, approximately 70000 MOF structures have been envisioned. The crystallographic data from the Cambridge Crystallographic Data Centre (CCDC) is shown in Figure 2.14.



Figure 2.14. The variation of the Cambridge Structural Database (CSD) and MOF entries between 1972 and 2016. The inset shows the MOF assembly from building blocks: red spheres are metals, while organic linkers are blue struts. Reprinted with permission from [68]. *Copyright* © 2017, *American Chemical Society.*

Figure 2.14 shows that the number of entries has abruptly increased over 44 years; however, the number of MOFs among these entries has reached approximately 70000. The trend shows that the research in the field of MOFs increases rapidly even further as the building block approach to MOFs synthesis opens up the possibility to create more and more materials.

Owning the large variety in their chemistry, structure, and pore sizes, MOFs offer a new platform for novel membranes. Methods such as seeding and microwave heating can be deployed for the preparation of MOF membranes. Although the MOF membranes offer better mass transport, they often suffer from possessing pinholes and/or cracks during membrane preparation. Another drawback of such kinds of membranes is the grain boundary effects. They have a significant impact on the packing of the MOF nanoparticles that reduce the membrane selectivity dramatically.

In general, for the fabrication of thin-film polycrystalline MOF membranes, there are two main steps: in situ growth and secondary or seeded growth [69]. In situ growth refers to a film formation method where the pure substrate at first is immersed in the growth solution, and then the nucleation, growth, and intergrowth of the MOF crystals occur on the substrate. Secondary or seeded growth mechanism differs from that

mechanism in the way that the film growth occurs from the pre-attached seed crystals [70]. There are also various fabrication techniques for the MOF membranes, such as layer-by-layer growth, chemical solution deposition, or electrospinning technology [71].

Having the nanometer-scale pore sizes, MOF membranes could be useful for membrane separation technology. Thus, Bux et al. [72] reported the preparation of a ZIF-8 (ZIF stands for Zeolitic Imidazolate Framework) membrane on porous titania support and demonstrated that this membrane is a potential candidate for hydrogen purification. The ZIF-8 MOF nanoparticles possess a sodalite-related structure with a pore diameter of 0.34 nm, and this material could separate hydrogen molecules from larger molecules. Another benefit of the ZIF-8 membrane is the hydrophobicity of the MOF nanoparticles. In gas separation technology, all gas molecules often follow with water vapor, which deteriorates the hydrophilic membrane performances gradually. Having a hydrophobic nature, ZIF-8 membranes could resist water vapor and support continuous hydrogen transport. They reported that the ZIF-8 membranes show high hydrogen permeance (6.7x10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) and a moderate selectivity over CH₄ $(\alpha=11.2)$. The separation experiments revealed that in situ grown ZIF-8 membranes on α -Al₂O₃ disks showed a high C₃H₆/C₃H₈ selectivity of 50 for the 50/50 propylene/propane binary mixture [73]. Interestingly, the ZIF-8 membrane prepared on a porous α -Al₂O₃ capillary substrate by a counter diffusion method showed higher permeances for H₂ (9.1x10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹), and propylene (2.5x10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹) ¹) with the selectivity factors of 2000 and 59 for H_2/C_3H_8 and C_3H_6/C_3H_8 , respectively [74]. On the other hand, this kind of membrane shows a moderate selectivity of 7 for CO₂/CH₄ [75]. ZIF-8 membranes are potential candidates for ethane/propane separation. Thus, the experiments showed that this kind of membranes demonstrates a high separation factor of 80 for C₂H₆/C₃H₈ [76]. ZIF-7 membranes prepared on the α -Al₂O₃ disk also showed high permeance for hydrogen (4.5x10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) and the separation factors for the H_2/CO_2 , H_2/N_2 , and H_2/CH_4 were 13.6, 18.0, and 14.0, respectively [77]. High selectivities for H₂/N₂ (19.1) and H₂/CH₄ (14.5) were reported for the Zn-CD MOF (Zn-CD represents Zn₂(cam)₂dabco; cam is D-camphoric acid; dabco is described as 1,4-diazabicyclo(2.2.2)octane) membranes [78]. Membranes prepared on hollow ceramic fibers called CAU-1 (CAU is the abbreviation for Chung-Ang University) showed high hydrogen permeance over carbon dioxide, nitrogen, and methane with the separation factors of 12.3, 10.3, and 10.4 for H₂/CO₂, H₂/N₂, and

H₂/CH₄, respectively [79]. HKUST-1 MOF (HKUST refers to Hong Kong University of Science and Technology) membrane grown on the copper net performed higher permeance (\sim 1x10⁻¹ mol m⁻² s⁻¹ Pa⁻¹) and selectivity (7) for hydrogen over nitrogen [80]. Possessing a 1.6 nm pore size, Ni-MOF-74 membranes showed moderate selectivities of 9.1, 3.0, and 2.9 for H₂/CO₂, H₂/N₂, and H₂/CH₄, respectively [81]. A MOF membrane having a thickness of 360 nm on a polyacrylonitrile (PAN) support is shown as an example in Figure 2.15.



Figure 2.15. An example of the MOF membranes. The image shows the ZIF-8 membrane intergrown on PAN support. Reprinted with permission from [82]. *Copyright* © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

MOF membranes are also potential candidates for liquid separation. Hu et al. showed that the MIL-53 MOF (MIL stands for Matériaux de l'Institut Lavoisier) membrane selectively separates water from ethyl acetate with a separation factor 100 **ZIF-8-DMBIM-PMPS** (DMBIM higher than [83]. 5.6means dimethylbenzimidazole; PMPS describes Polymethylphenylsiloaxe) mixed matrix membrane was performed for the separation of isobutanol from water. It was revealed that when a feed containing 3.0 wt.% isobutanol employed on such a mixed matrix membrane, the permeate contained 58 ± 2 wt.% isobutanol [84]. The experiments showed that for the ZIF-8 membranes prepared on the α-Al₂O₃ disk, an ideal permselectivity of benzene over *n*-hexane could be predicted as 23 [85]. The selfrepairing ZIF-90 membranes effectively separate oil from water with efficiencies reaching ~100% [86] due to its high hydrophobicity.

Akpinar *et al.* [87] used three different MOFs for water purification from atrazine contamination. Experiments conducted on MOF supported polymers showed that the use of a continuous MOF layer exhibits much more technical barrier rather than a

polymer gutter layer in 30 nm-thick polymer membranes with a selectivity factor of 34 for CO₂/N₂ gas pair [88]. ZIF-8 membranes formed inside a porous γ - Al₂O₃ support showed a marked hydrogen separation performance with a maximum H₂/CO₂ separation factor of ~9.9 at 250 °C [89]. The exfoliated two-dimensional Zn₂(bim)₄ showed an H₂/CO₂ selectivity greater than 200 [90]. Recently synthesized UTSA-220 MOF (UTSA is University of Texas at San Antonio) nanoparticles exhibit high C₂H₂ uptake capacity, which is very interesting in terms of acetylene separation from light hydrocarbons in downstream industrial applications [91]. Go *et al.* [92] revealed that in-situ grown ZIF-7 membranes show higher selectivity (~16) for H₂/CO₂ than ZIF-7 membranes prepared by other methods.

Although the MOF membranes offer high permeance and selectivity for different applications, the preparation of such kinds of membranes is challenging. The common challenges for the MOF membrane preparation are 1) poor membrane-substrate bonding, 2) poor membrane stability, and 3) macroscopic crack formation during membrane fabrication or activation [70]. For this reason, during the preparation of such kinds of membranes, a proper substrate must be chosen, and problems with the crack formation must be solved.

2.3.4. Covalent organic framework (COF) membranes

Covalent organic frameworks are covalently bonded porous crystalline polymers. In 2005, Yaghi and co-workers firstly introduced the porous organic frameworks synthesized via covalent bonds using topological design principles [93]. Such kind of porous materials have periodic skeletons and ordered pores that are constructed from organic building blocks. Depending on the building blocks, the COFs can be characterized into 2D and 3D architectures. In 2D architecture, the covalently bonded structure is restricted to 2D sheets, in which the layers are eclipsed and formed periodically aligned columns.

From a chemistry perspective, the COFs are unique due to full control of the skeletons and pores. Depending on the aim of the COF usage, one can construct the structure and play with the pore sizes [94]. From a physics point of view, COFs offer a platform for the mechanistic studies in π systems. Thus, these systems facilitate interactions with excitons, electrons, holes, spins, ions, and molecules [95]. Having such kinds of abilities, these materials could be used in different fields, for instance,

semiconductors [96-99], CO₂ capture and storage [100, 101], proton conduction [102, 103], luminescence [104], and catalysis [105-108].



Figure 2.16. The three-dimensional image of a stacked covalent organic framework with the one-dimensional pore channels. The image was reprinted with permission from [109].

Figure 2.16 shows the model of a 2D covalent organic framework with a 1D pore structure. These layered compounds are beneficial for different purposes, where pore size plays an important role. In terms of nanotechnology, such kinds of stacked layers would be exfoliated into single layers, and the properties of single layers can be investigated in advance.

Another type of novel approach that could be useful in membrane science is the preparation of covalent organic framework membranes. These kinds of membranes have gotten extensive attention for gas separation and might even be extended to molecular sieving applications [110]. As it is described, COFs are the porous crystalline polymers, and their chemical structure is rigid due to enhanced cross-linking that prevents the solubility of the COFs for the membrane fabrication process [111]. Although such kind of materials has been deemed as potential membrane material, they have limitations such as chemical instability [112-114], synthetic complexity [115], scalability [116], and solubility [117] remain as obstacles for its development [118].

Fortunately, on the lab scales, different precursors have been used for the preparation of the COF membranes.

One of the most reliable COF membranes is based on triazine based frameworks (CTFs). The predictions showed that the two-dimensional CTF-0 membranes could be made as ultrathin nanomembranes after exfoliation, and employing the first-principle calculations revealed that a monolayer CTF-0 membrane could exhibit exceptionally high He and H₂ selectivities over Ne, CO₂, Ar, N₂, CO, and CH₄ [119]. In this work, the calculations describe that the solubility selectivities for H₂/CO₂, H₂/N₂, H₂/CO, and H₂/CH₄ should be 9×10¹³, 4×10²⁴, 1×10²², and 2×10³⁶, respectively. The synthesis of the covalent triazine-based frameworks has been conducted via the ionothermal method and requires high temperatures of ca. 400-600 °C [100, 120]. Zhu et al. demonstrated the CTF membrane synthesized by a superacid-catalyzed method. This method decreases the synthesis temperature of CTF significantly, and the prepared membranes show a CO_2/N_2 selectivity of 29 ± 2 with a CO_2 permeability of 518 ± 25 Barrer [121]. Boron-based COF-1 membranes were successfully prepared using exfoliated COF nanosheets with a small average pore size of ~1.5 nm [122]. This kind of membrane with a thickness of ~100 nm showed a 16.8x10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ permeance for hydrogen; however, the selectivity of H₂/N₂ was 3.3 due to random stacking manner of the nanosheets resulting in relatively large pore sizes. A computational study performed by Tong et al. [123] showed that the preparation of the few-layered COF membranes offers high CO₂ flux and CO₂/N₂ selectivity due to the formation of interlayer flow passages that have "gate-closing effect" on the selective transport of the molecules. Another computational study conducted on 298 CoRE COFs showed that COF membranes exceed the 2008 Robeson upper bound, and the CO₂/CH₄ selectivities range between 3.3 and 11458 [124]. It was also revealed that the functionalization of the COF membrane pores could enhance the selectivity of CO₂/CH₄. For example, when CTF-1 is functionalized with the chlorine atoms, the selectivity increases from 2.4 to 186 due to narrowing the pore size. ACOF-1 (ACOF stands for azine-linked covalent organic framework) membrane with an ~8 µm thickness prepared on porous Al₂O₃ support showed high selectivity of 86.3 for CO₂/CH₄ with favorable CO₂ permeance of 9.9x10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹, which explained with the molecular sieving effect of the membrane resulted from the crystal intergrown in the pores [125].

The COF membranes are excellent candidates, not only for gas separation technologies. The presence of the micropores (<2 nm), even ultramicropores (<0.7 nm), makes such kinds of membranes excellent candidates also for nanofiltration purposes. Thus, it was reported that an interfacially grown cationic two-dimensional COF EB-COF:Br (EB stands for 3,8-diamino-5-ethyl-6membrane. phenylphenanthridinium bromide), efficiently rejects ≥98% of anionic dye molecules or ions, while maintaining high solvent permeability [126]. With a thickness of only 400 nm, the COF-LZU1 (LZU represents Lanzhou University) membrane prepared on alumina tubes showed an excellent water permeance of ca. 760 L m⁻² h⁻¹ MPa⁻¹ and favorable rejection rates of water-soluble dyes exceeding >90% [127]. The computational studies showed that the modification of the COF membranes prepared via condensation of 1,3,5-triformylphloroglycinol (TFP) and p-phenylenediamine with different hydrophilic (-AMC2NH2, -OC3OH, and -AMCOOH) and hydrophobic (-AM2, -AM3, -OC4H9, and -OBn) groups influence water flux and salt rejection significantly. The results suggest that hydrophilic functionalities exhibit higher water flux than their hydrophobic counterparts with similar aperture sizes. Such kinds of membranes showed high water permeance ranging from 1216 to 3375 kg m⁻² h⁻¹ bar⁻¹ that are higher than the commercial reverse osmosis membranes, and the salt rejection of the membranes is calculated to be over 98%, except for the -AMCOOH functionalized COF membrane [128]. The TFP-DHF 2D COF (DHF describes 9,9-dihexylfluorene-2,7-diamine) membrane prepared on a porous anodic aluminum oxide support via the Langmuir-Blodgett method showed remarkable permeabilities for both polar and nonpolar solvents, which are suggested to be 100 times higher than those for the conventional polymer membranes fabricated via the same method. The membrane possesses a molecular sieving property with a molecular weight retention onset of ca. 600 Da and a molecular weight cutoff of approximately 900 Da [129]. Another example of the COF membranes deposited via the Langmuir-Blodgett method is described by Gadwal et al. [130]. They revealed that at the molecular size around 1.3 nm, this membrane outperforms as a molecular sieving membrane and selectively eliminates NaCl and MgSO₄ at the rejection rates of 64 and 71%. Kuehl et al. prepared twodimensional COF membranes with carboxylated pore walls that were highly permeable, as well as highly charged and size-selective. The research showed that this COF membrane has water permeance of ~2260 L m⁻² h⁻¹ bar⁻¹, which was ~300

times higher than pure GO membrane (~7.6 L m⁻² h⁻¹ bar⁻¹) [131]. Highly porous, selfstanding, and crystalline covalent organic frameworks showed an acetonitrile flux that was 2.5 times higher than the existing polyamide nanofiltration membranes even though the solute rejection was the same (~99%) [117]. Imine-linked highly porous and crystalline COFs were very stable in harsh environments such as concentrated H₂SO₄ (18 M), concentrated HCI (12 M), and NaOH (9 M) due to the presence of strong interlayer C-H····N hydrogen bonding among the individual layers. Such kinds of membranes were reported for the sulphuric acid recovery, and they exhibited unprecedented permeance for acetonitrile (280 L m⁻² h⁻¹ bar⁻¹), and acetone (260 L m⁻² h⁻¹ bar⁻¹) [132].



Figure 2.17. An illustration of the covalent organic framework (COF) membrane for molecular separation. Reprinted with permission from [125]. *Copyright* © *The Royal Society of Chemistry 2018.*

Figure 2.17 shows the illustration of the covalent organic framework membrane for molecular separation, and it shows that such kind of membrane can easily separate the molecules depending on pore sizes. The computational survey conducted on the COF membranes shows that the solvent fluxes through these membranes are to be governed by the aperture size and membrane functionality, as well as solvent properties [133]. They revealed that for membranes with comparable aperture sizes, the hydrophobic one (with the exception of n-hexane) exhibits higher fluxes than the hydrophilic counterpart for all solvents.

Although COF-based membranes offer better benefits than conventional polymer membranes, there are still some challenges to be overcome:

- 1. COFs with pore sizes less than 1 nm are required for gas separation, nanofiltration membranes for seawater desalination with a high rejection rate of salts, and the fabrication of organic solvent nanofiltration membranes with a small molecular weight cut-off. To achieve this, relatively small and short organic linkers must be chosen; however, there is a limitation of this method. Another method for the preparation of the COFs with pore size <1 nm is the post-modification of the inner walls of the frameworks.</p>
- 2. The design of the hydrophobic COF-based membranes for pervaporation processes has not been reported.
- 3. The practical application of the COF membranes in the industry is still challenging.
- 4. The studies on the long-term stability of the COF-based membranes in realistic separation conditions are still limited.
- 5. High-cost and time-consuming fabrication methods hinder their large-scale fabrication.

2.3.5. Mixed matrix membranes

The membranes applied for the gas separation technology in the industry must be processable. Such kinds of membranes require a thin selective layer, which is between 100 nm and 1.0 μ m, and the surface area of 1000-500000 m² [134]. In order to economically achieve such films at scale, all commercial membranes have been necessarily made from dense films. Unfortunately, most of the applied polymers can not surpass the Robeson upper bound shown in Figure 2.18. To harness the processability, and meanwhile, to surpass the upper bound, different kinds of fillers have been incorporated into polymers as composites to form hybrid materials known as mixed matrix membranes (Figure 2.18).



CO, permeability, P (barrer)

Figure 2.18. The relationship between the CO₂/N₂ selectivity and CO₂ permeability compared to the Robeson upper bound for pure polymeric membrane, mixed matrix membranes (MMMs), and pure MOF membranes. Reprinted with permission from [135]. *Copyright* © 2017 Springer Nature Limited.

In typical mixed matrix membranes (MMMs), the polymer acts as a continuous phase with the filler being dispersed in it. Material selection for such kinds of MMMs begins with the identification of a filler with attractive transport properties, preferably above the polymer upper bound. The next step is the matching of the filler with a high-performance polymer to achieve desirable selectivity and permeability in the hybrid matrix membranes. Thus, matching the filler with the polymer is often accompanied by the mixing of two phases, where the filler connects to the polymer via van der Waals forces and covalent or hydrogen bonding [136]. The transport property of the filler is one of the critical parameters for achieving desirable composite membranes. At least three options exist for the transport property determination of the filler [137]:

- Experimental diffusion and adsorption analysis of the fillers.
- Molecular simulation analysis.
- Filler permeability back-calculation.

The selected filler must exactly correspond to the shape, size, and other property difference of the targeted gas molecules. The compatibility of the filler must be high in order to get it well-dispersed inside the polymer matrix. Besides all this, the size of the

fillers should be comparatively small. The typical sizes for the fillers could range from dozens of nanometers to hundreds of nanometers. Depending on nature, the fillers can be classified as inorganic and organic nanomaterials. Inorganic nanofillers for this purpose can be solid or impermeable, and porous or permeable fillers. As the impermeable fillers, graphene, silica, and titania can be differentiated. Metal-organic frameworks, graphene oxide, carbon molecular sieve, carbon nanotubes, and zeolite can be mentioned as examples for the permeable fillers [138].

When porous fillers are incorporated into the selective layer, the transport and separation of the targeted gas is enhanced by the pore sizes of the nanofiller. Depending upon this factor, the transport should follow either the molecular sieving mechanism or surface diffusion mechanism [139]. When the pore size of the gas molecule is roughly the same as the kinetic diameter of the corresponding gas molecule, then the mechanism is the molecular sieving. If the pore size ranges between the kinetic diameter of the targeted gas and other gases, then the mass transport of the smallest gas molecule will be faster, leading to an efficient separation. When the pore size increases, the filler loses its molecular sieving properties, and another parameter becomes more important. This is the affinity of the filler toward target gas molecules. If the filler surface has a strong affinity towards the gas molecule, then the gas molecule adsorbs along the pore walls following the surface diffusion mechanism. The coexistence of these two mechanisms leads when the pore size of the filler is big enough. For the lamellar nanofillers such as graphene and graphene oxide, the transport of the gas molecules follows the molecular sieving mechanism. Such a mechanism could be achieved if the percolation index of nanosheets is determined.



Figure 2.19. Electrical conductivities for carbon nanotube (CNT) incorporated polyurethane sheets. Reprinted with permission from [140]. *Copyright* © *Published 2017 by the American Chemical Society.*

In Figure 2.19, Martinez-Rubi *et al.* describe the percolation index of carbon nanotubes in polyurethane nanocomposites. They revealed that with the increase of the CNT loading, the electrical conductivity of the nanocomposite increases, and after 35 wt.% stays almost the same, indicating the percolation index has reached [140]. Using this knowledge, one can predict the transport mechanism of the graphene incorporated polymer membranes, while graphene layers are the precursors for the carbon nanotubes, and they have high electrical conductivity.

The incorporation of poly(ethylene glycol)- and poly(ethylene imine)functionalized graphene oxide (PEG-PEI-GO) into the PEBAX[®] selective layer showed a high CO₂ permeability (1330 Barrer) surpassing the Robeson upper bound with the selectivity factors of 45 for CO₂/CH₄ and 120 for CO₂/N₂ [141]. Ha *et al.* [142] reported that the incorporation of 8 wt.% GO into the PDMS polymer matrix resulted in a 99.9% reduction in gas permeation values for H₂, N₂, O₂, CH₄, and CO₂ while enhancing the selectivities of CO₂/N₂ (24 vs. 9.5) and CO₂/CH₄ (10 vs. 3.0) compared to neat PDMS membrane. Another example of the mixed matrix membranes surpassing the Robeson upper bound was reported by Dai *et al.* [143]. They revealed that when 0.8 wt.% selectivity reaches 105.5 combined with CO₂ permeability of 76.2 Barrer. It was described that an addition of GO nanosheets in a concentration only 2 wt.% boosts the selectivity of water vapor over nitrogen (α =80000) in the PEBAX[®] layer [144]. The lateral size of GO nanosheets influences the membrane transport properties significantly. Thus, Shen et al. [145] revealed that the incorporation of 0.1 wt.% GO (with a lateral size of 1-2 µm) into the polyether block amide matrix (PEBA) enhances the CO₂ transport with a permeability coefficient of 110 Barrer and a CO₂/N₂ mixed gas selectivity of 80. Such a membrane also shows long-term stability under the operating test. An addition of *N*-isopropylacrylamide coated CNT into the PEBAX® mixed matrix membrane resulted in high CO₂ permeability of 567 Barrer with a CO₂/CH₄ selectivity of 35, and CO₂/N₂ selectivity of 70, which transcends the Robeson upper bound [146]. The functionalization of GO with alkylamines such as octylamine and octadecylamine causes the reduction of GO. When such kinds of nanoparticles were incorporated into the PIM-1 polymer matrix, separation of alcohol from binary mixtures (EtOH/water and butanol/water) showed an increasing trend. Thus, it was revealed that the incorporation of 0.1 wt.% reduced alkylamine-functionalized GO, increases an average separation factor of butanol from 13.5 for pure PIM-1 to 32.9 in the case of octylamine and 26.9 in the case of octadecylamine functionalization [147]. A novel nanofiltration-like poly(amide-imide)-polyethyleneimine (PAI-PEI) hollow fiber membrane whose surface was covered by GO served as a selective barrier material, and water permeability reached up to 86% without compromising the membrane selectivity [148]. Graphene nanoplatelets (less than 0.0075 wt.%) dispersed in PIM-1 reduce the permeability coefficients of gases by a factor of three [149, 150]. In the case of PET (Polyethylene terephthalate) coated with a low amount of graphene (0.4 wt.%), permeability fourfold reduced [151]. APTS (3oxygen was (aminopropyl)triethoxysilane)-functionalized graphene oxide (GO) incorporation into the PVDF membrane showed a perfect salt rejection (>99.9%). It was also reported that the PBI-GO (PBI stands for Polybenzimidazole) mixed matrix membranes were developed for organic solvent nanofiltration technique [152, 153]. Current research on thermally rearranged (TR) polymers showed that the incorporation of reduced graphene oxide (rGO) increased the permeance of CO₂ by a factor of 482 times, while the selectivity of the mixed matrix membrane remained at 35 as it was for the pure PBI membrane [154].

Mixed matrix membrane prepared via the facilitated cross-linking between hydroxyl groups of Mg-MOF-74, and the fluoride chain-ends of PIM-1 demonstrates improved permeabilities and selectivities for all gases. In particular, the permeability of CO₂ increased from 6500 Barrer to 21000 Barrer; meanwhile, the CO₂/CH₄ selectivity reached 19.1 [155]. Thin-film nanocomposite membranes comprising of aminemodified ZIF-8 and polyamide polymer matrix, which was prepared by in-situ interfacial polymerization show a high separation performance for different gas pairs as reported by Yu [156]. Another benefit of the incorporation of ZIF-11 into the 6FDA-DAM selective layer was seen in the high permeabilities of H₂, CO₂, and CH₄ [157]. Experiments conducted on 6FDA-Durene/ZIF-71 mixed matrix membranes revealed that the addition of nanoparticle increases the CO₂ permeability of the pristine 6FDA-Durene selective layer by three times [158]. Distribution of layered two-dimensional CuBDC (copper 1,4-benzenedicarboxylate) nanosheets inside the ultrathin PIM-1 polymer matrix exhibits a CO₂/CH₄ selectivity of 15.6, and CO₂ permeance surpasses the pure PIM-1 performance [159]. Mixed matrix membranes consisting of UiO-66 MOFs (UiO demonstrates Universitetet i Oslo) and PIM-1 selective layer show high selectivity for CO₂/CH₄ surpassing the Robeson upper bound [160]. Blending of a Tröger's Basecontaining microporous polyimide polymer matrix with ZIF-8 results in enhanced separation of hydrogen from nitrogen and methane, surpassing the state-of-the-art 2008 Robeson upper bound [161]. The MMMs prepared with the incorporation of the ultrathin α -Ni(im)₂ nanosheets into the PEBAX MH 1657 polymer matrix performed an enhanced CO₂/CH₄ selectivity based on molecular sieving properties. Thus, the addition of 2 wt.% α -Ni(im)₂ nanosheets increases the selectivity of CO₂ over CH₄ with a separation factor of 33.4 without compromising the CO₂ permeability [162]. The MMMs those were composed of the polyimide polymer matrix, and UiO-66 and hybrid UiO-66-GO fillers demonstrated high separation performances for H₂/CH₄ and CO₂/CH₄. However, the addition of UiO-66 resulted in the domination of H₂ permeability (73 Barrer) over CH₄ with an H₂/CH₄ selectivity of 151, while CO₂/CH₄ performance enhanced in the case of a hybrid UiO-66-GO incorporation (CO2 permeability 21 Barrer and CO₂/CH₄ selectivity value of 51) [163]. A mixed-matrix membrane composed of ZIF-94 filler and 6FDA-DAM polymer matrix presented the increasing trend in CO₂ permeability, depending on filler loading. It was revealed that at 40 wt.% loading, the CO₂ permeability reached at 2310 Barrer and the CO₂/N₂

mixed gas selectivity was ~22 [164]. The hollow fiber composite membrane prepared with the addition of ZIF-8 nanoparticles into the PEBAX[®] matrix has shown an increased CO₂ permeability and slightly reduced selectivities [165]. Another experiment showed that the incorporation of the PEG-ylated UiO-66 MOF nanoparticles into the Polyactive matrix influences the gas transport properties of these membranes significantly. Thus, with the addition of such kinds of nanoparticles, the gas transport properties of P@MOF/Polyactive MMMs increase gradually, and at 40 wt.% loading, the mass transport transcends the Robeson 2008 upper bound for CO₂/N₂ [166]. The PEBAX-ZIF-8@GO-6 mixed matrix membrane containing 6 wt.% ZIF-8@GO nanoparticles exhibited the optimum gas transport performance with a CO₂ permeability of 249 Barrer and a CO₂/N₂ selectivity of 47.6 [167]. Polysulfone-based mixed matrix membranes (MMMs) embodying ZIF-11 MOF nanoparticles showed a 43.5% and 160% increase in CO₂ permeability and CO₂/CH₄ diffusion selectivity, respectively, at 24 wt.% loading [168]. Good compatibility between ZIF-67 and PIM-1 matrix renders ideal interfacial morphology, and it demonstrated superior CO₂/CH₄ selectivity of 45 [169]. Blending of a narrow pore size CAU-21 MOF with the PIM-1 selective layer showed high selectivity for H₂ over N₂ with a memorable H₂ permeability of 7200 Barrer [170].

Having nanosized pores, COFs offer a significant promise for the improvement of membrane performance. The prepared PA-SNW-1 (SNW describes Schiff base networks) thin-film composite membranes exhibited an increased pure water flux from 100 L m⁻² h⁻¹ MPa⁻¹ to 193 L m⁻² h⁻¹ MPa⁻¹ compared to a pristine polyamide (PA) membrane with a Na₂SO₄ rejection above 80% [171]. The addition of such kind of a filler into the PIM-1 polymer matrix shows a 116% enhancement in CO₂ permeability. Such an improvement has increased the selectivities of CO₂/CH₄ and CO₂/N₂ by 27.4% and 37.6%, respectively [172]. Mixing the two-dimensional NUS-2 COF (NUS is defined as National University of Singapore) nanoparticles with the PBI polymer matrix showed an excellent H₂ separation over CO₂, which exceeded the Robeson 2008 upper bound due to selective gas sorption properties of the filler [110].

A hybrid membrane prepared from 60 wt.% 5, 10, 15, 20-tetrakis(1-methyl-4pyridinio) porphyrin (calculated with respect to dry rGO weight) and reduced GO (rGO) showed improved methanol permeance and high rejection for negatively charged organic dyes (>92%). Such a membrane exhibited a water permeance of 5.76 L m⁻² h⁻ ¹ bar⁻¹ with a rejection of 98.4% in the separation experiments of a B12 aqueous solution. These results were $4.40 \text{ Lm}^{-2} \text{ h}^{-1}$ bar⁻¹ and 91.0% in methanol solutions [173].

2.4. Application of membranes

2.4.1. Membrane distillation

The membrane distillation process is a thermally-driven process where hot water circulates on the feed side of a porous hydrophobic membrane, and only vapors pass through. This process is driven by the water vapor pressure difference between the membrane surfaces. The polymeric membranes used in such kind of a process are mostly based on polytetrafluoroethylene (PTFE), polyvinylidenefluoride (PVDF), and polypropylene (PP). These membranes contain many pores that cannot be wetted by feed solution. The vapor passing through the membrane condenses on the cold side to produce the distillate. A typical membrane distillation process is shown in Figure 2.20.



Figure 2.20. Schematic representation of the membrane distillation process. Reprinted with permission from [174].

The most common technologies used for membrane distillation are the following:

- Direct contact membrane distillation (DCMD). Here, hot feed is in direct contact with the hot membrane side surface. At this interface, the evaporation process takes place, and water vapor is passed through the membrane by the generated pressure difference across the membrane. The passed water vapor condenses inside the membrane module. The main drawback of this technique is the heat loss by conduction.
- Air gap membrane distillation (AGMD). In this method, hot feed solution circulates on the hot membrane side surface as described for DCMD process. The evaporated water vapor crosses immobile air filled between the surfaces of a cold membrane side and a condenser. This approach reduces heat loss by conduction; however, a hindrance for the mass transfer is created, which is assumed as a disadvantage.
- Vacuum membrane distillation (VMD). Mainly, this type of membrane distillation is prepared for the separation of volatile solutions. With a pump, a vacuum is generated at the permeate side, and the condensation of the vapor occurs outside of the membrane module. The heat loss is negligible here.
- Sweeping gas membrane distillation (SGMD). This technique is similar to the AGMD method. The main difference is the inserted mobile inert gas, which means instead of stationary air, the inert gas blows to sweep the vapors, and the condensation of the swept vapor takes place in outside of the membrane module.
- Vacuum multi-effect membrane distillation (V-MEMD). Such kind of a membrane distillation module consists of a steam-raiser, evaporation-condensation stages, and a condenser. The design of this system contains multi-effect membrane distillation frames, and the channels are created between the frames. The foil frames are the "distillate channels", the membrane frames are "vapor channels". Between these frames, the "feed channels" are created.
- Permeate gap membrane distillation (PGMD). In the following approach, the channel configuration consists of a condenser and an evaporator

channel. Both of the channels have inlet and outlet and are separated by a hydrophobic and microporous membrane.

2.4.2. Gas transport through membranes

Depending on the structural types of the membranes, gas transport can follow the pore flow or solution-diffusion models. The pore flow model is mostly observed in gas transport through porous membranes, and the flow is strongly dependent on the pore size of a porous membrane and the mean free path of the molecules. The ratio of the gas mean free path (MFP) to the pore size is considered as Knudsen number (K_n) [175]:

$$K_n = \frac{MFP}{d_{pore}}$$
(2.2)
$$MFP = \frac{RT}{\sqrt{2}\pi d_{gas}^2 N_A p}$$
(2.3)

 d_{pore} is the characteristic length, d_{gas} is the diameter of the gas molecule, N_A is the Avogadro's number, p is the gas pressure, R is the universal gas constant (0.08314 m³ bar K⁻¹ kmol⁻¹), and T is the temperature of the gas (K). In such kind of flow, the gas molecules can collide between themselves and the pore walls. Thus, collisions between the gas molecules and the pore walls occur in the case of $K_n > 10$. This process is called Knudsen diffusion. When $K_n < 0.1$, collisions, and interactions between the gas molecules are dominant over the interactions between the gas molecules and pore walls. In this case, Knudsen diffusion is negligible compared to molecular diffusion and viscous flow [176].

As it is seen from equation (2.3), when the pressure decreases, the mean free volume increases. Therefore, at 1 bar, the mean free path is 68 nm meaning that for the Knudsen type flux operation, the pore sizes need to be less than 50 nm [177]. The following equation describes the flux of the gas molecules from one side of the membrane to the other side, which is under vacuum [177]:

$$J_K = w \cdot n \cdot v_T \tag{2.4}$$

where J_k is the flux, *w* is the probability of a gas molecule that enters the pore and flows along the pore to the other side, *n* is the molecular density (molecule m⁻³), and v_T is the mean thermal molecular speed (m sec⁻¹). The last term, v_T , is described by the following expression [177]:

$$v_T = \sqrt{\frac{8k_BT}{\pi M}} \tag{2.5}$$

Here, k_B is the Boltzmann constant (1.38x10⁻²³ J K⁻¹ molecule⁻¹), *T* is the temperature in K, and *M* is the molecular mass. This parameter increases with the increase of the temperature and decreases with the increase of molecular mass. Considering equation (2.5) and the flow of a gas molecule from one side of the membrane to the vacuum side, the equation (2.4) is written by the following [177]:

$$J_{K1} = w \cdot n_1 \cdot v_T \qquad (2.4.1)$$
$$J_{K2} = -w \cdot n_2 \cdot v_T \qquad (2.4.2)$$

The negative sign of equation (2.4.2) indicates the direction of transport from right to left. In this case, the net flux of the gas molecule is [177]:

$$J_K = w \cdot (n_1 - n_2) \cdot v_T = w \cdot \sqrt{\frac{8k_BT}{\pi M}} \cdot \Delta n$$
(2.6)

The Knudsen diffusivity can be written in terms of operating conditions and the pore parameter, K_0 , as follows [177]:

$$D_k = \frac{4}{3} K_0 \sqrt{\frac{8R_g T}{\pi M}}$$
(2.7)

The equation (2.7) reveals that the Knudsen diffusion of two gases is strongly dependent on molecular weight ratios. Thus, it can be ascribed as below [177]:

$$\frac{D_{K1}}{D_{K2}} = \sqrt{\frac{M_2}{M_1}}$$
 (2.8)

The molar viscous flux for the gas in the porous medium is related to the pressure gradient and the gas permeability, which can be described as follows [178]:

$$N^V = -C \frac{B_{ka}}{\mu} \nabla p \tag{2.9}$$

where N^{V} is the molar viscous flux (mol m⁻² s⁻¹), μ is the viscosity (kg m⁻¹ s⁻¹), B_{ka} is the apparent gas permeability, *C* is the total molar density (mol m⁻³), and *p* is the pressure (Pa).

The second part of the equation gives the well-known Darcy equation [178]:

$$q = -\frac{B_{ka}}{\mu} \nabla p \tag{2.10}$$

q is the volumetric flux per unit area (m s⁻¹), and in this form of the equation, it is assumed that the gravity forces are negligible in comparison to the applied pressure gradient. The Darcy equation can be used for the determination of the apparent gas permeability of a porous medium.

The permeability of a polymer is dependent on the membrane thickness, feed, and permeate pressure. In a simple way, this dependence is written as follows [179]:

$$P = \frac{Nl}{P_2 - P_1}$$
(2.11)

Here *P* is the permeability coefficient, p_2 is the feed pressure, p_1 is the permeate pressure, *I* is the membrane thickness, and *N* is the steady-state penetrant flux through the membrane.

The gas transport through a nonporous membrane is usually described by a three-step solution-diffusion mechanism. For a two-component system, which contains *i* and *j*, the diffusive flux of gas *i* is obeyed Fick's first law [178, 180],

$$N_i^F = -D_{ij}C\nabla x_i \tag{2.12}$$

where N_i^F is the molar diffusive flux with respect to the bulk velocity of the gas mixture, *C* is the total molar density (mol m⁻³), D_{ij} is the binary diffusion coefficient (m s⁻¹), and ∇x_i is gradient in the mole fraction (mol⁻¹). When the gas flux obeys the Fick's law, the permeability coefficient can be expressed as [181]:

$$P = \left(\frac{C_2 - C_1}{P_2 - P_1}\right) \times D \tag{2.13}$$

D is the concentration-averaged diffusivity, and C_2 and C_1 are the gas concentration in the polymer at the feed and permeate sides of the membrane, respectively. According to Henry's law [182], a concentration (C_i) of a given gas in the polymer is proportional to the applied pressure (P_i) describing the gas solubility (S_i):

$$C_i = P_i \cdot S_i$$
(2.14)
$$S_i = \frac{C_i}{P_i}$$
(2.15)

When the permeate pressure is much less than feed pressure, then the second part of the parathesis in the equation (2.13) is negligible, and the gas flux follows Henry's law. Thus, the equation can be written as follows:

$$P = S \times D \tag{2.16}$$

The ideal selectivity of a polymer for penetrant *A* over the penetrant *B* is the ratio of the permeability coefficients of two penetrants [137]:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \cdot \frac{D_A}{D_B}$$
(2.17)

Diffusion selectivity is demonstrated by a quadratic ratio of jump lengths multiplied by the exponential difference in free energies of activation [137]:

$$\frac{D_A}{D_B} = \left[\frac{\lambda_A^2}{\lambda_B^2}\right] exp\left(\frac{\Delta S_{D(A,B)}^*}{R}\right) exp\left(-\frac{\Delta H_{D(A,B)}^*}{RT}\right)$$
(2.18)

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where λ is the jump lengths of the corresponding gas molecules, $\Delta S^*_{D(A,B)}$ is the differences in the diffusion transition state entropy, and $\Delta H^*_{D(A,B)}$ is the differences in the diffusion transition state of enthalpy.

The understanding of the gas transport properties of the mixed matrix membrane is the most important issue in order to achieve the best composite membranes that are industrially viable and more advantageous in gas separation technology. A theoretical framework [183] describes the hybrid mixed matrix membrane permeability of component *i*:

$$P_{imm} = P_{ic} \left[\frac{P_{id} + 2P_{ic} - 2\varphi_d(P_{ic} - P_{id})}{P_{id} + 2P_{ic} + \varphi_d(P_{ic} - P_{id})} \right]$$
(2.19)

Here, P_{imm} is the permeability of component *i* in the mixed matrix, φ_d is the volume fraction of the dispersed phase, and P_{id} and P_{ic} correspond the permeabilities of component *i* in the dispersed and continuous phases, respectively. For the explanation of gas transport of a mixed matrix membrane, the modified Nielson and Cussler models are widely used. Amongst these models, the modified Nielson model showed an accurate prediction in relative permeability coefficients (R or P_c/P_m) of the composite membranes possessing high aspect ratio randomly dispersed fillers at very diluted concentrations. The state of the filler alignment influences highly on the model accuracy, and the general expression of this equation is expressed as [184]:

$$\frac{P_c}{P_m} = \frac{1 - \varphi_d}{1 + \frac{\alpha}{3}(S + \frac{1}{2})\varphi_d}$$
(2.20)

where α represents the aspect ratio of the filler dimensions, φ_d is the filler volume, P_c and P_m are the permeabilities of the composite and neat polymer, respectively. *S* illustrates the state of the filler alignment in the composite membrane. *S*=0 is accepted for the randomly dispersed filler in the composite membrane, while *S*=1 for the fillers perfectly aligned to the gas flux direction. In these cases, equation (2.20) can be described as follows:

$$\frac{P_c}{P_m} = \frac{1 - \varphi_d}{1 + \frac{\alpha}{6} \varphi_d}, \quad S = 0$$
(2.20.1)
$$\frac{P_c}{P_m} = \frac{1 - \varphi_d}{1 + \frac{\alpha}{2} \varphi_d}, \quad S = 1$$
(2.20.2)

Such kind of prediction would give us a better understanding of the preparation of the high-performance composite membranes for membrane technology. Koros *et al.* [137] revealed that this ratio should be calculated on a case-to-case basis using the
pertinent polymer upper bound for each gas pair, and they reported a possible nextgeneration selective synthetic membrane, which is shown in Figure 2.21.



Figure 2.21. Mixed matrix composite membrane. **a**, Schematic, and SEM image illustrating the structure of mixed-matrix membrane. **b**, An example showing polymersieve matching for hybrid mixed matrix membrane (MMM). The dotted lines indicate transport properties of a hypothetical hybrid mixed matrix membrane made with ZIF-8 and different polymer matrices residing on the polymer upper bound. Reprinted with permission from [137] *Copyright* © *2017, Springer Nature.*

2.5. Adsorption models

Adsorption experiment is a helpful tool for the understanding of the filler-gas interactions. This would be very informative for the understanding of gas transport

through a mixed matrix membrane. There are four main adsorption models for the explanation of the adsorption process by the adsorbents [185].

The first adsorption model is the Henry model, where a straight line is passing through the origin of adsorbance G and equilibrium sorption pressure p. Such kind of relationship is described by the following equation [185]:

$$G = k_c p \tag{2.21}$$

where, *G* is the molar concentration of a gas dissolved (mol m⁻³), k_c is the Henry constant (mol m⁻³ Pa⁻¹), and *p* is the partial gas pressure (Pa). This model is only applicable to describe gas adsorption at low pressure.

Freundlich suggested a new adsorption model based on Henry model and the relationship is an exponential relationship [185]:

$$m = kp^n \tag{2.22}$$

where *m* is the gas mass adsorbed by the mass of an adsorbent (kg/kg), *p* is the gas partial pressure (Pa), and *k* and *n* are the empirical constants (dimensionless). *k* normally decreases with the increase of temperature, and *n* ranges between 0 and 1 that generally reflects the influence of pressure on adsorbance. At high pressure, 1/n approaches 0, and the adsorption is independent of pressure, but adsorbance is related to pressure.

Studying the gas adsorption onto solid surfaces based on molecular dynamics, Langmuir made these assumptions:

- The surface of an adsorbent is uniform, and the gas molecules on the solid adsorbent as a monolayer.
- The gas adsorption is a dynamic process.
- When the adsorption equilibrium is reached, the adsorption rate is equal to the desorption rate.
- The rate of gas molecule adsorption onto the solid surfaces is positively proportional to the gas partial pressure of this component.
- No interaction force occurs between adsorbed gas molecules at the solid surfaces.

The adsorption rate on the unit area of a rock surface (J_{ads}) is [185]:

$$J_{ads} = k_a p(1 - \theta) \tag{2.23}$$

The desorption rate on the unit area of a rock surface (J_{des}) is [185]:

$$J_{des} = k_d \theta \tag{2.24}$$

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When the equilibrium is achieved, the adsorption rate is equal to the desorption rate, and then the combination of equations (2.23) and (2.24) would be as follows [185]:

$$\theta = \frac{k_a p}{k_d + k_a p} \tag{2.25}$$

 Θ is the gas coverage of the porous black rock surface (dimensionless), *p* is the gas partial pressure (Pa), k_a is the gas equilibrium adsorption rate (m Pa⁻¹ s⁻¹), and k_d is the gas equilibrium desorption rate (m Pa⁻¹ s⁻¹). The ratio of k_a/k_d is equal to the Langmuir gas adsorption equilibrium constant (*b*), Pa⁻¹. Then, equation (2.25) can be transformed into the common Langmuir equation form [185]:

$$\theta = \frac{bp}{1+bp} \tag{2.26}$$

The multilayer adsorption of the gas molecules on the solid adsorbents can happen, and there are no interaction forces between the layers, which leads to the implementation of the Langmuir adsorption theory for each molecule adsorption layer. These assumptions extended the monolayer adsorption theory to the multilayer adsorption, and such kind of a multilayer model is named as BET adsorption model, which corresponds to the expression [185]:

$$\frac{G}{G_m} = \frac{b(p/p_0)}{(1 - p/p_0)[1 + (b-1)(p/p_0)]}$$
(2.27)

where *G* is the gas adsorption amount (m³ m⁻³), *G_m* is the saturated gas adsorption amount at the reference temperature (m³ m⁻³), *p* is the gas equilibrium partial pressure (Pa), p_0 is the gas saturated vapor pressure at the reference temperature (Pa), and *b* is the dimensionless constant. The BET adsorption model is valid for p/p_0 ranging from 0.005 to 0.35 [185]. If the value is smaller than the lower limit, then the model gets away from the straight line. This phenomenon is related to a non-uniform physical and chemical shape of a solid surface with the existence of the activated adsorption points. If the value is greater than the upper limit, then an infinite adsorption layer most likely occurs.

2.6. Step-growth polymerization

Step-growth polymerization is a type of polymerization where bifunctional or multifunctional monomers react to form first dimers, then trimers, longer oligomers, and eventually high-molecular-weight long-chain polymers or branched polymers or networks. Many polymers such as polyesters, polyamides, polyurethanes, PIMs, etc. are synthesized by such polymerization.

The Carothers theory is used to predict the molar mass of the polymers prepared via step-growth polymerization [186]. This can be used to derive the number average degree of polymerization \overline{X} given by

$$\bar{X} = \frac{2}{2-\alpha\bar{f}} \tag{2.28}$$

where 2 is the number of the used functional groups, α is the conversion degree of the monomer, and \overline{f} is the average functionality. Based on the Carothers equation, several results could be obtained:

 The functionalities of the monomers are 1, and all the monomers are consumed in the case of an alcohol and an amine (HO-X + NH₂-Y) (α=1):

$$\bar{f} = \frac{1+1}{2} = 1$$

 $\bar{X} = \frac{2}{2-1\cdot 2} = 0$

This means that even though all the monomers consumed, the high-molecularweight polymer formation is impossible.

 Polycondensation of equimolar (1:1) two bifunctional monomers in the case of a dialcohol and a diamine (HO-X-OH + H₂N-Y-NH₂).

$$\bar{f} = \frac{2+2}{2} = 2$$

 $\alpha = \frac{2}{2} - \frac{2}{2\bar{X}} = 1 - \frac{1}{\bar{X}}$

The result reveals that with the increase of number average degree of polymerization (\overline{X}), the degree of monomer conversion reaches 0.99, indicating high-molecular-weight polymer production.

 Polycondensation of three equivalents of bifunctional monomer and two equivalents of trifunctional monomers in the case of a dialcohol and a triamine (3(HO)₂-X + 2(H₂N)₃-Y).

$$\bar{f} = \frac{3 \cdot 2 + 2 \cdot 3}{3 + 2} = \frac{12}{5} = 2.4$$
$$\alpha = \frac{2}{2.4} - \frac{2}{2.4\bar{X}} = 0.83 - \frac{1}{1.2\bar{X}}$$

It means that at the infinite number of number average degree of polymerization $(\bar{X}=\infty)$ the consumption of the functional groups is 83%.

The difference between step-growth, anionic living, and radical chain-growth polymerization is shown in Figure 2.22.



Conversion

Figure 2.22. Molecular weight vs. conversion diagrams of the step-growth polymerization (1), anionic living polymerization (2), and the non-living radical polymerization (3). Reprinted with permission from [187]. *Copyright* © 2015, *Royal Society of Chemistry*.

For the predictions of the PIM synthesis, the number average molecular weight, $\overline{M_n}$, can be used as a measure of reaction success:

$$\overline{M_n} = \overline{M_0} \times \overline{X_n} \tag{2.29}$$

where $\overline{M_0}$ is the average molar mass of the repeating unit. According to the equation (2.29) the weight average molecular weight $\overline{M_w}$, can also be used for the identification of the polymerization success:

$$\overline{M_w} = \overline{M_0} \times \frac{(1+p)}{(1-p)}$$
(2.30)

2.7. Surface-initiated atom transfer radical polymerization (SI-ATRP)

Surface-initiated atom transfer radical polymerization (SI-ATRP) is a sub-division of atom transfer radical polymerization, where the polymerization starts from substrate surfaces. Scheme 2.1 shows the accepted mechanism of atom transfer radical polymerization, while Scheme 2.2 describes the radical formation, termination after polymerization, and backbiting reactions during atom transfer radical polymerization.



Scheme 2.1. Accepted mechanism of atom transfer radical polymerization. Reprinted with permission from [188]. *Copyright* © 2016 Elsevier Inc.



Scheme 2.2. Bimolecular radical termination of two chain-end radical acrylate radicals (\dot{P}_2) , proceeding either combination or disproportionation, and formation of tertiary midchain radicals (\dot{P}_3) via backbiting and subsequent termination with another midchain radical or secondary chain-end radical, both resulting in disproportionationed chains. Reprinted with permission from [189]. *Copyright* © 2017, American Chemical Society.

In general, the SI-ATRP follows the same mechanism even though the polymerization initiates from the surface-mounted radicals. The general mechanism of SI-ATRP is shown in Scheme 2.3.



Scheme 2.3. The general mechanism of the SI-ATRP through radical formation, polymer growth, and termination of the macroradicals in the presence of CuBr/dMbpy (1:1) catalyst/ligand system (dMbpy=4,4'-dimethyl-2,2'-dipyridyl).

Considering the abovementioned mechanism, the polymer growth can be conducted from different surfaces. As reported previously, such kind of polymers have been successfully synthesized on Au [190], SiO₂ [191], clay [192], mica [193], cellulose [194, 195], multi-walled carbon nanotubes [196], graphene oxide [197, 198] and other surfaces. Due to the presence of the oxygen functionalities on the graphene oxide layers, these groups can be further modified to get different graphene-like nanoparticles with different functional groups. However, modification of the graphene oxygen functionalities with initiator groups converts them into macro initiators that can initiate the polymerization of the monomers. This opens a new route in the so-called surface-initiated atom transfer radical polymerization (SI-ATRP) technique that gives the opportunity to use these layers for different purposes.

In a common way, the rate law for ATRP can be derived as follows using the assumption that contribution of termination becomes insignificant due to persistent radical effect, and fast equilibrium approximation, which is necessary for the low molecular weight dispersities [199]:

$$R_p = k_p[M][P^*] = k_p K_{eq}[M][I]_0 \times [Cu^I] / [X - Cu^{II}]$$
(2.31)

where R_p is the rate of polymerization, k_p is the rate constant of propagation, K_{eq} is the equilibrium constant, [M] is the concentration of a monomer, [P*] is the concentration of the propagated macroradicals, [I]₀ is the initial concentration of an initiator, [Cu^I] is the concentration of Cu(I) in the reaction system, and [X-Cu^{II}] is the concentration of CuX₂ in the reaction system.

In terms of SI-ATRP, equation (2.31) can be derived in order to describe the change in the radical concentration (at the substrate surface) with time $(d[R^*]/dt)$ [200]:

$$\frac{d[R^*]}{dt} = k_a [RBr] [CuX] - k_d [R^*] [CuX_2] - k_t [R^*]^2$$
(2.32)

where $d[R^*]/dt$ is the change in the radical concentration with time, k_a , k_d , and k_t are the activation, deactivation, and termination constants, [*RBr*] is the concentration of an initiator, [*CuX*] is the concentration of a catalyst, [*CuX*₂] is the concentration of a deactivated catalyst, and [*R**] is the concentration of radicals.

The radical concentration change can be described in three terms:

- The rate of radical generation via the reaction of Cu(I) with the initiator.
- The loss of radicals through deactivation.
- The loss of radicals through bimolecular termination.

The time-dependent concentration of RBr in equation (2.32) is calculated by the following function:

$$\frac{d[RBr]}{dt} = -k_a[RBr][CuX] + k_d[R^*][CuX_2]$$
(2.33)

Within the reaction time, the molecular weight of the polymer increases with the corresponding decrease of the dispersity index. This evolution is shown in Figure 2.23.



Figure 2.23. Evolution of molecular weight and molecular weight dispersity of polymethacrylate (PMA) in the ATRP in the presence of MBP/CuBr/dTbpy (1:1:2) initiator/catalyst/ligand system (MBP=methyl 2-bromopropionate; dTbpy=4,4'-di-*tert*-butyl-2,2'-bypyridine). Reprinted with permission from [199]. *Copyright* © 2001, *American Chemical Society.*

Considering Figure 2.23, the drop in the dispersity index can be described by the following equation:

$$\frac{M_w}{M_n} = 1 + \left(\frac{[RX]_0 k_p}{k_{deact}[D]}\right) \left(\frac{2}{\alpha} - 1\right)$$
(2.34)

where M_w/M_n is the dispersity index, $[RX]_0$ is the initial concentration of an initiator, k_p and k_{deact} are the rate constants of propagation and deactivation, respectively, [D] is the concentration of a deactivator, and α is the conversion degree.

2.8. Reticular chemistry

Reticular chemistry is the chemistry of linking molecular building blocks to make crystalline open frameworks. Research in this field started first with linking inorganic clusters into extended porous frameworks with the following linkage of organic molecules and metal ions into metal-organic frameworks (MOFs), and organic molecules together into covalent organic frameworks (COFs) [201]. Such kind of an approach opens a new direction in chemistry beyond the molecule, and the advantages of this chemistry are [202]:

- The existence of well-defined structure and geometry, molecular building blocks provide control in the construction of frameworks.
- Strong bonds provide architectural, mechanical, and thermal stability.
- Crystallinity, which was the challenge for the realization of such kind of frameworks, is overcome.

Since the molecular building blocks can be manipulated by chemical reactions and/or stimuli to cause a change, the molecule orientation, geometry, and spatial arrangement play a substantial role in the preparation of 0D, 1D, 2D, and 3D frameworks. The crystallinity of these MOF/COF and permanent porosity allow to use them for different kind of purposes. Possessing permanent porosity demonstrates the move of gaseous molecules in and out of the frameworks without destroying their structure. Today, MOF and COF compound families have been designed for high porosities such as 500-10000 m² g⁻¹, high thermal stability (300-500 °C), and exceptional chemical stability in organic and aqueous media, acids, and bases.

Reticular Chemistry in Zirconium MOFs



Figure 2.24. An example of MOF types employing different organic linkers and zirconium ions. Reprinted with permission from [203]. *Copyright* © *2019 Elsevier B.V.*

Compared to MOFs, crystalline covalent organic frameworks are a maturing field in reticular chemistry. Since the first discoveries of 2D and 3D COFs in 2005 [93], and in 2007 [204] have taken place, the field of COFs has increased rapidly so far. This phenomenon is caused by two major factors:

- The ability to use different types of linkages, especially those thought to be less reversible.
- The success of making their reticulated structures in crystalline forms.

a Conventional approach to COFs with one-type linkage and same vertices units



b Double-stage approach to COFs with two-type linkages and different vertices units



Figure 2.25. An example of COFs constructed from different organic linkers. Reprinted with permission from [205]. *Copyright* © *2015, Springer Nature.*

2.9. References

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Chapter 3

Experimental part

3.1. Materials

Graphite (natural, crystalline, briquetting grade, -100 mesh, 99.9995%, Ultra "F" purity), sulfuric acid (H₂SO₄, ACS, 95.0–98.0%), potassium permanganate (KMnO₄, ACS, 99.0%) and potassium hydrogen phthalate (C₈H₅KO₄, primary standard, ACS, 99.95–100.05%), 2,4-dichlorobenzamidoxime (DCIBAO, 97%), tetrahydrofuran (THF) "for synthesis" grade, 2-bromopropionyl bromide (BPrB, 97 %), 3,3',5,5'tetramethylbenzidine (TMB, 98%), 1,3,5-benzenetricarbonyl chloride (TMC, 98+%), benzimidazole (BI, 99%) and glacial acetic acid (CH₃CH₂COOH, 99+%) were purchased from Alfa Aesar (Heysham, UK). Sodium nitrate (NaNO₃, ACS, 99.5%), sodium carbonate (Na₂CO₃, anhydrous grade for analysis, 99.9%), sodium hydroxide solution (NaOH, Titrisol, 1 M) and hydrogen chloride (HCl, reagent grade for analysis, 37%), N,N-dimethylformamide (DMF) "for synthesis" grade were purchased from Merck (Kenilworth, NJ, USA). Milli-Q ultrapure water (>18 MΩ·cm at 25 °C) and aluminum chloride (AlCl₃, anhydrous powder sublimed for synthesis, 98.0%) were purchased from Merck Millipore (Darmstadt, Germany). Hydrogen peroxide (H₂O₂, Ph. Eur. Stabilized, 30%) was purchased from Carl Roth (Karlsruhe, Germany). During the research, some part of ultrapure water was collected from Millipore Direct-Q®3 water purification system supplied from Merck Millipore (Darmstadt, Germany). Hydrazine monohydrate (N₂H₄·H₂O, reagent grade, 98%), sodium bicarbonate (NaHCO₃ crystalline, reagent grade, 99.5%), parafilm[®], DAX-8 resin and 50WX2-100 Dowex ion exchanger, 2,5-dimethyl-6-phenylpyrazolo[1a]-pyrimidin-7-amine (DMPPA, 98%), (R_p)-1-[(1S)-(1-Aminoethyl)]-2-(diphenylphosphino) ferrocene (AEDPPF, 97%), 1,1bisdichlorophosphino-ferrocene (dClpf, ≥96%), N-Methyl-2-pyrrolidone (NMP, >99%), thionyl chloride (SOCI₂, 99%), 2-diethylaminoethyl methacrylate (DEAEMA, contains 1500 ppm MEHQ (4-methoxyphenol) as an inhibitor, 99%), Cu(I)Br (99.999% trace metals basis), 4,4'-dimethyl-2,2'-dipyridyl (dMbpy, 99%), methyl iodate (CH₃I, ≥99.0%, Sigma-Aldrich), and tris(3-hydroxypropyltriazolylmethyl)amine (THPTAMA, 95%),

triethylamine (Et₃N, 99%), thionyl chloride (SOCI₂, 99%), Zn(NO₃)₂ ·6 H₂O (98%) and 1,3,5-tris(2-hydroxyethyl) isocyanurate (THEIC, 97%), benzene-1,3,5tricarboxaldehyde (BTA, 97%), 1,3,5-trimethylbenzene (mesitylene, 98%), *N,N*dimethylformamide (DMF, anhydrous, 99.8%), tetrahydrofuran (THF, anhydrous, 99.8%) and 1,4-dioxane (anhydrous, 99.8%) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Benzene "for synthesis" grade was purchased from AppliChem (Darmstadt, Germany), while triethylamine (Et₃N, 99%) was purchased from ABCR (Karlsruhe, Germany). All materials were used as received.

3.2. Synthesis of Conventional Graphite Oxide (CGO)

Conventional graphite oxide (CGO) was synthesized from natural crystalline graphite by the Hummers method [1]. Thus, the mixture of 4.0 g of graphite powder and 2.0 g of NaNO₃ was added into 92.0 mL of concentrated H₂SO₄ in a round-bottom flask placed into an ice bath and stirred for 30 minutes. Then, 12.0 mg of KMnO₄ was added into the mixture by portions to prevent the temperature rise above 20 °C and stirred for 2 hrs. Subsequently, the temperature of suspension was brought to 35 °C and maintained at this level for an hour. The obtained brownish-grey paste was diluted with Milli-Q ultrapure water (>18 MΩ·cm at 25 °C, 184 mL), causing violent effervescence and an increase of temperature to 98 °C. The obtained diluted, brown color suspension was kept at this temperature for several minutes, during this time the suspension changed its color to bright yellow and after this, the suspension was further diluted with 300 mL of warm distilled water and treated with 80 mL of H₂O₂ to reduce the residual permanganate and manganese dioxide. Synthesized CGO was vacuumfiltered through a qualitative Grade 1 filter paper (pore size 11 µm, Whatman, Maidstone, UK) when the suspension was still warm to avoid precipitation of side products [2]. The filter cake was washed with warm water, centrifuged at the speed of 11,000 rpm in a Sigma 6-16 K machine (Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany) and freeze-dried in a Gamma 1–16 LSC plus machine (Martin Christ Gefriertrocknungsanlagen GmbH, Osterode am Harz, Germany).

3.3. Preparation of Base-Washed Graphene Oxide (bwGO)

CGO was dispersed in 1.0 M NaOH, shaken for 3 hours, refluxed for an hour at 80 °C, vacuum-filtered in order to remove ~30 wt.% oxidative debris (OD) from the 72

CGO dispersion and after the filter cake was washed until a neutral pH, it was freezedried on a Gamma 1-16 LSC plus machine. Then, the Na-form of the base-washed graphene oxide (bwGO) was re-dispersed in 1.0 M HCl solution and refluxed at 80 °C for an hour to regenerate the acidic groups [3, 4].

3.4. Synthesis of the Reduced Graphene Oxide Forms (Reduced GO (rGO), and Base-Washed and Reduced GO (rbwGO))

2.0 grams of CGO and 2.0 grams of bwGO were separately dispersed in ultrapure water (1.0 L) in two different flasks, sonicated and reacted with hydrazine monohydrate (10 mL) at 100 °C for 24 hours [5].

3.5. Exfoliation Experiments of Graphene Oxide and Base-Washed Graphene Oxide Samples

Exfoliation experiments were conducted both for OD-containing graphene oxide and OD-stripped graphene oxide samples, base-washed GO (bwGO), in order to detect the effect of oxidative debris on the agglomeration of graphene layers. 10 aqueous dispersions of both graphene samples were prepared ranging from 0.002 wt.% to 0.1 wt.%, and their UV absorbance was analyzed on an UVmini-1240 spectrophotometer (Shimadzu Europe, Duisburg, Germany) at 600 nm after sonication in a bath. According to the results, the correlation curves were plotted (Figure 3.1). Using correlation curves, we were able to determine the concentration of the singlelayer containing graphene oxide dispersion.



Figure 3.1. Correlation between absorbance and concentration of GO (a) and bwGO (b) aqueous solutions obtained at 600 nm on an UVmini – 1240 spectrophotometer.

3.6. Isolation, Fractionation, and Purification of OD Using a Precipitation Procedure

OD was isolated, fractionated, and purified by methods shown elsewhere [3, 6]. The filtrate, which contains OD, was acidified until pH 1.0 from pH 14.0 with 4.0 M HCl aqueous solution and poured into a glass column (25 mm internal diameter, 650 mm length) prefilled with ca. 300 mL DAX-8 resin. The eluted non-adsorbed fraction was collected, adjusted to pH 5.0, and treated with 0.1 M AlCl₃ solution to precipitate the colored solution resulting in a clear supernatant. Then, the white dispersion was passed through a 50WX2-100 Dowex ion exchanger column to regenerate the acidic groups. The slimy yellowish sediment was separated from the solution via a separator funnel and freeze-dried (OD-1). The column was eluted successively with 1 L of 0.1 M HCl, 1 L of ultrapure water, and 500 mL of 0.1 M NaOH sequentially. All fractions were treated by passing through a 50WX2-100 Dowex ion exchanger corresponding to OD-1 and labeled as OD-2, OD-3, and OD-4, respectively.

3.7. Synthesis of Chlorinated Graphene Oxide (GO-CI)

Chlorinated graphene oxide was synthesized according to the procedure reported elsewhere [7]. Briefly, 0.5 g of GO, 10 mL of benzene, and 50 mL of SOCl₂ were mixed together in a 500 mL round flask and stirred at 70 °C for 24 hr. Afterward, the excess of SOCl₂ was removed by vacuum distillation, and the solid was dispersed in acetone. Then, the suspension was filtered, washed twice with acetone, and vacuum dried at 60 °C for 24 hrs.

3.8. Synthesis of (R_p)-1-[(1S)-(1-Aminoethyl)]-2-(Diphenylphosphino) Ferrocene Modified GO (GO-AEDPPF)

In the presence of 60 mL of DMF, 0.2 g of GO-CI and 3 mL of triethylamine were allowed to react with 0.02 g of $(R_p)-1-[(1S)-(1-aminoethyl)]-2-(diphenylphosphino)ferrocene (AEDPPF) at 130 °C for 3 days to obtain GO-AEDPPF [8]. After the reaction, the solution was allowed to cool down to ambient temperature and vacuum filtered. The filter cake was washed with DMF, a small amount of distilled water (to remove Et₃N·HCI) and acetone, and vacuum dried at 60 °C for 24 hrs.$

3.9. Synthesis of 2, 4-Dichlorobenzamidoxime Modified GO (GO-DCIBAO)

0.2 g of GO-CI was dispersed in 50 ml of NMP in a 500 mL round-bottom flask. Then, into the suspension, in the presence of 3 mL of trimethylamine (TEA), 0.02 g of 2, 4-dichlorobenzamidoxime (DCIBAO) was added, reaction temperature set at 157 °C and maintained for 72 hours to obtain GO-DCIBAO. After the reaction, the suspension was filtered under vacuum, washed with NMP, a small amount of distilled water (to remove Et₃N·HCI), and vacuum dried at 40 °C for 24 hrs.

3.10. Synthesis of 2, 5-Dimethyl-6-Phenylpyrazolo [1, 5-a]-Pyrimidin-7-Amine (GO-DMPPA)

In the presence of 60 mL of DMF, 0.2 g of GO-CI and 3 mL of triethylamine were allowed to react with 0.054 g of 2,5-dimethyl-6-phenylpyrazolo[1,5-a]-pyrimidin-7amine (DMPPA) at 130 °C for 3 days to obtain GO-DMPPA. After the reaction, the suspension was allowed to cool down to ambient temperature and vacuum filtered. The filter cake was washed with DMF, a small amount of distilled water (to remove Et₃N·HCI) and acetone, and vacuum dried at 60 °C for 24 hrs.

3.11. Synthesis of 1, 1-Bisdichlorophosphinoferrocene Modified GO (GO-dClpf)

In a 500 mL round-bottom flask, 0.2 g GO was dispersed in 20 mL of benzene. Then 0.02 g of 1,1-bisdichlorophosphinoferrocene (dClpf) was added into the suspension, and the mixture was heated to 70 °C for 24 hrs. in an oil bath. Afterward, the suspension was cooled to room temperature and filtered under vacuum to obtain a brownish-black precipitate of GO-dClpf, and vacuum dried at 60 °C for 24 hrs.

3.12. Synthesis of Phosphochlorinated GO (PhChGO)

0.5 g of GO was dispersed in 10 mL of chloroform in a 50 mL triple-neck round bottom flask. 4 mL of PCl₃ (phosphorus trichloride) was added by portions in order to keep the temperature stable, and the mixture was refluxed for 3 hours at ambient temperature under oxygen flow (8 L h⁻¹). The final sediment was washed with distilled water up to pH 7, vacuum filtered, and dried in vacuum at 50 °C for 24hrs.

3.13. Surface Functional Groups Determination

The general titration procedure was carried out by a "standardized" Boehm titration method [9, 10]. A known mass of approximately 0.01 g of GO samples was added to 25.0 mL of one of three 0.05 M reaction bases: sodium bicarbonate (NaHCO₃), sodium carbonate (Na₂CO₃), and sodium hydroxide solutions (NaOH). The vials were nitrogen-purged for 2 hours, sealed and placed in a shaking incubator (Incutec K30-300, EquipNet, Canton, MA, USA, at ambient temperature) at 90 min⁻¹ frequency for 24 hours. Samples were then filtered through qualitative Grade 1 filter paper (Whatman, pore size 11 μ m), and 10 ± 0.02 mL aliquots were taken by pipette from the solutions. The aliquots of the reaction bases NaHCO₃ and NaOH were acidified by 20 mL 0.05 M HCI (reagent grade for analysis, 37%, Merck). However, the aliquots of Na₂CO₃ were acidified by the addition of 30 mL 0.05 M HCl solution. During titration, all aliquots are covered with a seal of parafilm[®], which maintained around the electrode and burette and bubbled continuously with nitrogen flow to ensure sufficient removal of CO₂. 0.05 M NaOH solution was used as a titration base for these experiments and the correctness of NaOH was controlled by potassium hydrogen phthalate (0.2 g) solution in 20 mL Milli-Q ultrapure water (>18 MΩ cm at 25 °C). Blank samples were also titrated for the accuracy of the measurements.

3.14. Synthesis of Polymer of Intrinsic Microporosity

A Polymer of Intrinsic Microporosity (PIM-1) was synthesized by the route described in the references [11-15]. The synthesized polymer was dried under vacuum at 70 °C for 2 days before being used for characterization and preparation of thin-film composite membranes (TFCMs). The molecular weight and dispersity of PIM-1 were 200 kg mol⁻¹ and 4-5, respectively, as determined by size exclusion chromatography. During membrane preparation, only one synthesis batch was used due to the controversial permeability properties of the PIM membranes.

3.15. Synthesis of surface-initiator functionalized graphene oxide (SI-GO)

Synthesized by the Hummers method [1], graphene oxide (GO) was modified into surface-initiator functionalized graphene oxide (SI-GO) using the method initially

reported in previous works [16, 17]. In general, GO (1.0 g) was dispersed in DMF (100 mL, anhydrous, 99.8%, Sigma-Aldrich) in a 250-mL round-bottom flask in the sonication bath for 1 hour and a brownish-black dispersion was obtained. After triethylamine (TEA, 10 mL, 0.072 mol, \geq 99%, Sigma-Aldrich) was added to the dispersion, the flask was immersed in an ice bath placed in the sonication bath and then, using a dropping funnel, which was mounted on the flask, 2-bromopropionyl bromide (BPrB, 15 mL, 0.142 mol, 97%, Alfa Aesar) was added dropwise into the dispersion at 0 °C. After the addition, the resulting dispersion was stirred at room temperature for 24 hours. The product was vacuum-filtered on a qualitative Grade 1 filter paper (Whatman, pore size 11 µm), washed with chloroform (200 mL), ultrapure water (100 mL, to remove Et₃N·HBr) and methanol (300 mL) sequentially. The product was dried under high vacuum at 50 °C for 2 days.

3.16. Exfoliation of SI-GO

In order to use the single-layer SI-GO in SI-ATRP, the study on exfoliation was performed for the SI-GO nanoparticles. For the preparation of a calibration curve, ten different concentrations (between 0.002 and 0.1 wt.% of SI-GO in DMF) were used. After sonication, the samples were investigated using a Genesys 10S UV-Vis spectrophotometer (Thermo Scientific[™], Ottawa, Canada) in absorbance mode with a 10 mm cuvette at a wavelength of 600 nm. Then, the samples were centrifuged on a Heraeus Biofuge primo centrifuge (Thermo Scientific[™], Ottawa, Canada) at the speed of 5000 rpm for 30 minutes to remove the large particles for obtaining only the single-layer SI-GO dispersion. The concentration of the single-layer SI-GO containing dispersion was calculated on the base of the calibration curve (Figure 3.2). The maximum concentration obtained for the single-layer SI-GO dispersion was 0.0015 wt. % even though the dispersions were not stable in DMF after several hours.



Figure 3.2. Correlation between absorbance and concentration of SI-GO solution in DMF obtained at 600 nm on a Genesys 10S UV-Vis spectrophotometer.

3.17. Polymerization of 2-diethylaminoethyl methacrylate from SI-GO

Two approaches were applied for the polymerization of 2-diethylaminoethyl methacrylate (DEAEMA, contains 1500 ppm MEHQ (4-methoxyphenol) as an inhibitor, 99%, Sigma-Aldrich) monomer. The first method, called "bulk" polymerization, was performed using the polymerization method reported by Rajendar et al. [17]. In a typical SI-ATRP experiment, Cu(I)Br (~18 mg, ~0.1 mmol, 99.999% trace metals basis, Sigma-Aldrich) and 4,4'-dimethyl-2,2'-dipyridyl (~23 mg, dMbpy, ~0.1 mmol, 99%, Sigma-Aldrich) were mixed in anhydrous DMF (0.6 mL) under argon flow in a round bottom flask with magnetic stirring until homogeneous solution. In another round bottom flask, after purification of the monomer through basic Alumina containing column (ICN Alumina B-Super I, VWR International, Germany), 2 mL DEAEMA was mixed with different concentrations of SI-GO (0.2, 0.4, 0.6, 0.8, and 1.0 wt.% SI-GO, with respect to DEAEMA monomer weight) and sealed under argon, followed by 30 minutes sonication in a sonication bath. The polymerization was carried out in an oil bath at 70 °C for 48 h. In this procedure, the weights of the bulk SI-GOs were 3.69, 7.38, 11.1, 14.8, and 18.4 mg, respectively. Taking into account our previous experiments [18] on surface functional group analysis of GO and considering the complete transformation of the -OH groups into initiator groups, it is assumed that the amount of the initiator on the surface of GO is about 3.69, 7.38, 11.1, 14.8, and 18.4 µmol, respectively. The synthesized polymer was dissolved in anhydrous THF (10 mL)

and precipitated in water-methanol (250 mL, 5:1) mixture in order to recover the polymer. The synthesized polymers were labeled as SI-PDEAEMA_GO_X (X means the weight percentage of the "bulk" SI-GO nanoparticles with respect to the monomer weight).

In the second method, 0.0015 wt.% exfoliated SI-GO dispersion in anhydrous DMF was used for the polymerization. Thus, under argon flow DEAEMA monomer (2 mL) was sealed in a round bottom flask. After argon purge, a homogeneous Cu(I)Br/dMbpy solution in DMF (0.6 mL) was injected into the monomer-containing flask, and then the injection of different volumes of the exfoliated SI-GO dispersion in anhydrous DMF (0.25, 0.50, 0.75, 1.00, and 2.00 mL) was conducted. In this procedure, the weights of the single-layer SI-GOs were 0.0034, 0.0068, 0.0101, 0.0135, and 0.0270 mg, respectively. It is assumed that the amount of the initiator on the surface of GO is about 0.0034, 0.0068, 0.0101, 0.0135, and 0.0270 µmol, respectively. The polymerization and the polymer recovery procedures were the same as reported for the "bulk" polymerization. The synthesized polymers were labeled as SI-PDEAEMA_exf.GO_X (X means the added volume of the exfoliated SI-GO nanoparticles).

3.18. Cleavage of the polymer chains from SI-GO

Approximately 20 mg of SI-PDEAEMA_exf.GO_0.75 polymer was dissolved in THF (5 mL) and, after the addition of NaOH solution (0.1 M, 2 mL), the polymer solution was stirred for 24 h. The cleavage of SI-PDEAEMA_exf.GO_1 polymer was conducted in the interface of CHCl₃/water after successful dissolution of polymer in chloroform. Then, the cleaved polymers were precipitated in water-methanol (5:1) mixture. The obtained polymers were analyzed by SEC to identify the molecular weight.

3.19. Synthesis of Zn₂(bim)₄ nanosheets

Zn₂(bim)₄ nanosheets were synthesized via hydrothermal method [19]. Thus, 0.3 g (1.0 mmol) of Zn(NO₃)₂ ·6 H₂O was mixed with 0.77 g (6.52 mmol) of benzimidazole in a 250 ml round-bottom flask and dissolved in 100 mL anhydrous DMF. After dissolution, the flask stirred for 48 hours at room temperature, and it was subsequently kept still for another 2 days. The product was centrifuged at 10000 rpm for 30 minutes in order to separate synthesized ZIF-7 nanocrystals from DMF. The ZIF-7 nanocrystals 79

washed carefully with ultrapure water and methanol. The yield was 55% with respect to Zn²⁺ salt.

After drying, 0.15 g of ZIF-7 nanocrystals placed in a 100 mL round-bottom flask and refluxed for 24 hours at 100 °C. The product was vacuum-filtered on Qualitative Grade 1 Whatman filter paper, washed with ultrapure water, methanol, and dried. The product donated as $Zn_2(bim)_4$, and the yield was 75% with respect to ZIF-7 nanocrystals.

3.20. Synthesis of COF-HZG1

For the synthesis of COF-HZG1 covalent organic frameworks, approximately 0.05 g benzene-1,3,5-tricarboxaldehyde (BTA, ~0.3 mmol) and ~0.11 g 3,3´,5,5´- tetramethylbenzidine (TMB, ~0.45 mmol) were dissolved in 5 mL mesitylene and in 5 mL 1,4-dioxane, respectively, in two different 20 mL sealed bottles. In the next steps, the BTA solution was added into a 25 mL round-bottom flask, following 1 mL glacial acetic acid and the TMB solution addition. After addition all reagents, the flask was mounted to a reflux condenser, and the reaction started at 60°C. The obtained yellow powder was vacuum-filtered, sequentially washed with methanol, THF, and water, and the resulting material vacuum dried.

3.21. Synthesis of COF-HZG2

The synthesis of COF-HZG2 was conducted in a 25 mL round-bottom flask through the reaction of 10 mL 1,3,5-benzenetricarbonyl chloride (TMC, ~0.05 g, ~0.2 mmol) solution in mesitylene and 10 mL tris(3-hydroxypropyltriazolylmethyl)amine (THPTAMA, ~0.08 g, ~0.2 mmol) solution in DMF in the presence of TEA (1 mL) at 70 °C for 24 hours. The obtained red COF nanoparticles was vacuum-filtered, sequentially washed with methanol, THF, and water, and the resulting material was vacuum dried.

3.22. Synthesis of COF-HZG3

COF-HZG3 synthesis was conducted with the reported protocol for COF-HZG2. However, the 1,3,5-benzenetricarbonyl chloride (TMC, ~0.1 g, ~0.4 mmol) solution (10 mL) in mesitylene was reacted with the 1,3,5-tris(2-hydroxyethyl)isocyanurate (THEIC, ~0.1 g, ~0.4 mmol) solution (10 mL) in THF. The synthesized greenish-white powder was vacuum-filtered, sequentially washed with methanol, THF, and water, and the resulting material vacuum dried.

3.23. Thin-film composite membrane preparation

3.23.1. PIM-1 thin-film membrane preparation

The coating of the selective layer on microporous PAN support was done on an in-house designed dip-coating machine. Figure 3.3 shows the set-up details of the device. In a general process, microporous PAN having approximately 1 m length and 10 cm width rolled on the machine and interacted with the polymer solution that is placed in the experimental reservoir. The dipped substrate gradually is raised, and the solution cast on support slowly drawn out, leaving a thin film adhered to its surface. To achieving a uniform thin film coating on the PAN surface, the reservoir is frequently raised to a position where the solution was in contact with the substrate surface, enabling the formation of a meniscus for coating. The speed of the coating process was 1.56 m min⁻¹.



Figure 3.3. Representation of in-house dip-coating machine. The lengths are in mm. Reprinted with permission from [20]. *Copyright* © 2016 Elsevier B.V. All rights reserved.

3.23.2. PIM-1 and graphene oxide based mixed matrix membranes

The thin-film composite membranes with the hybrid selective layer of graphene compounds and PIM-1 were prepared on microporous polyacrylonitrile (PAN) support (made in-house, average pore size of 22 nm and 15% surface porosity) [21] using a laboratory-scale membrane casting machine [20]. The nanoparticles of GO, GO-AEDPPF, and GO-DCIBAO were dispersed in the PIM-1 solution (1 wt.% in THF) at 9, 33, 50, 76, and 84 wt.% loadings with respect to dry polymer weight. Before casting, all solutions were tip sonicated (using Bandelin Sonoplus sonicator, Berlin, Germany) for 1 hour.

The selective layer deposition was done by a modified dip-coating method when the porous support at first was brought into contact with the polymer solution and then rose for 1-2 millimeters to form a meniscus of the polymer solution between the porous membrane and solution surface. The selective layer was formed at ambient conditions by dragging the polymer solution (at 1.56 m min⁻¹ speed) out of the meniscus, thus achieving uniform, reproducible coating. The evaporation of the solvent was not controlled or influenced. The formed membrane was allowed to dry at ambient conditions.

3.23.3. MOF incorporated mixed matrix membranes

The thin-film composite membranes (TFCM) from Polymer of Intrinsic Microporosity and MOF nanoparticles were prepared according to the same protocol reported for graphene-based PIM-1 mixed matrix membranes. The nanoparticle of $Zn_2(bim)_4$ was dispersed in PIM-1 solution (1 wt.% in THF) at 2, 4, 6, 8, and 10 wt.% loadings with respect to polymer dry weight. After the preparation of the composite dispersions, they were sonicated for 30 minutes in the sonication bath before casting.

The selective layer deposition was done by the same method reported in subheading 3.23.2.

3.23.4. Thin-film composite membrane preparation of surfaceinitiated polymers

For the preparation of such kind of thin-film membranes, the SI-PDEAEMA_GO_X polymers were dissolved in THF (10 mL) in order to prepare 1 wt.% dispersions. The obtained dispersions contained some amount of graphene-polymer agglomerates, which were removed before the membrane casting. After the preparation of the black dispersions, they were kept for 30 minutes without stirring to settle down the large particles by gravitational forces, and the homogeneous part of the dispersion was taken for membrane casting. The concentration of the homogeneous dispersion was controlled by the UV-Vis spectroscopy using calibration curves shown in Figure 3.4 and Figure 3.5. The dispersions were stable during membrane casting, and no precipitation was observed.



Figure 3.4. Concentration versus Absorbance of SI-PDEAEMA_GO_0.6 dispersions. The value 0.6 denotes that during polymerization, 0.6 wt.% SI-GO was used with respect to monomer weight.



Figure 3.5. Concentration versus Absorbance of SI-PDEAEMA_GO_0.8 dispersions. The value 0.8 denotes that during polymerization, 0.8 wt.% SI-GO was used with respect to monomer weight.
The polymers synthesized from exfoliated SI-GO dissolved completely in THF, and the obtained solutions were used for membrane casting without the polymergraphene agglomerates removal. The polymer solutions were transparent, and no agglomerates were seen.

The selective layer deposition was done by a modified dip-coating method reported for PIM-1 thin-film composite membranes.

3.24. Quaternization of the SI-PDEAEMA_exf.GO_0.75 polymer membrane

Quaternization of the SI-PDEAEMA_exf.GO_0.75 membrane sample was conducted. Thus, methyl iodate (CH₃I, ≥99.0%, 2 mL, Sigma-Aldrich) was dissolved in methanol (10 mL) in the sample container, and the SI-PDEAEMA_exf.GO_0.75 polymer membrane sample soaked into the solution. After sealing the container, it was shaken overnight at 2.5 Hz in a shaking incubator (Incutec K30-300, EquipNet, Canton, MA, USA, at ambient temperature). On the next day, the polymer membrane was removed from the quaternization solution, washed 5 times with an excess of methanol, and dried in the vacuum oven overnight.

3.25. Characterization techniques

3.25.1. XPS analysis

The X-ray photoelectron spectroscopy (XPS) analysis of the graphene oxide samples was carried out on a Kratos AXIS Ultra DLD spectrophotometer (Kratos, Manchester, UK) using an Al-K α X-ray source operated at 225 W under ultra-high vacuum (UHV, <2.5 \cdot 10⁻⁹ Torr.). Before the experiments, the pre-load chamber was degassed, and the graphene oxide samples positioned in the UHV analytics chamber. The analysis was conducted in the area of 700 µm × 300 µm with an acceleration depth of approximately 5 nm. All the spectra were calibrated to the C1s signal maintained at 284.5 eV. For the evaluation and validation of the data, CASA-XPS version 2.3.18 was used. Before calculation, the background subtraction (linear or Shirley) was applied for the deconvolution of the different regions of the spectra.

3.25.2. FTIR analysis

Fourier transform infrared (FTIR) spectra were recorded in attenuated total reflectance (ATR) mode on a Bruker ALPHA FT-IR spectrometer (Bruker, Ettlingen, Germany). The transmittance measurements were collected at ambient temperature in a spectral range of 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹ and an average of 64 scans.

3.25.3. UV-VIS analysis

Ultraviolet-visible (UV-Vis) spectra were collected on an UVmini-1240 spectrophotometer (Shimadzu Europe, Duisburg, Germany) and a Genesys 10S UV-Vis spectrophotometer (Thermo Scientific[™], Ottawa, Canada) in the absorbance mode with a 10 mm cuvette in the wavelength range of 190–1100 nm applying 0.02 wt.% solutions. UV-Vis spectroscopy investigations of functionalized GO samples (GO-AEDPPF and GO-DCIBAO) were carried out on a Specord 210 Plus spectrophotometer (Analytik Jena AG, Jena, Germany) in absorbance mode with a 2 nm slit in the wavelength range of 190–1100 nm using an integrating sphere.

3.25.4. Nuclear magnetic resonance spectroscopy

Liquid state nuclear magnetic resonance (LSNMR) experiments were conducted on a Bruker Avance 300 nuclear magnetic resonance (NMR) spectrometer (Bruker, Ettlingen, Germany) operating at a frequency of 300 MHz using a 5 mm ¹H/¹³C TXI (Triple Resonance) probe at 298 K. ¹H spectra were recorded applying a 10 ms 90° pulse. ¹³C spectra measurements were done using dept-45 and dept-135 sequences, employing a waltz-16 decoupling scheme. The relaxation delay was chosen in that way that the samples were fully relaxed. Solid-state nuclear magnetic resonance (SSNMR) experiments were performed on a Bruker Avance II 400 spectrometer (Bruker, Rheinstetten, Germany) equipped with a 4 mm double resonance probe. Direct excitation ¹³C magic angle spinning (MAS) NMR spectra were obtained with a 45° pulse length of 2.05 µs and recycle delay of 30 s at an operating frequency of 100.66 MHz. ¹³C¹H} cross-polarization (CP) MAS spectra were acquired using a ramped polarization transfer with a ¹H 90° pulse length of 4.0 µs, the contact time of 1 ms, and a repetition delay of 2 s or 4s. Two-pulse phase-modulated (TPPM) decoupling was used during the acquisition of both experiments. All the experiments were conducted with a sample spinning frequency of 13 kHz at room temperature.

3.25.5. Elemental analysis

Elemental analysis (EA) was carried out with a EuroEA Elementar CHNSO Analyser (EuroVector, Pavia, Italy). The amounts of carbon, hydrogen, nitrogen, and oxygen were quantitatively determined by the dry combustion method.

3.25.6. Surface functional group analysis

The standardized Boehm titration method was carried out on a fully automatized Titrino Plus 848 (Metrohm, Filderstadt, Germany) equipped with a 20 mL burette using a 0.05 M NaOH solution. Before experiments, the NaOH solution was standardized with potassium hydrogen phthalate.

3.25.7. Raman spectroscopy

Raman spectra were obtained using a Senterra (Bruker, Ettlingen, Germany) Raman spectrometer equipped with a 532 nm excitation laser and 10 fold objective lens. The results were estimated by extracting every single spectrum, and the areas corresponding to the D mode (disorder-induced mode, centered around 1300 cm⁻¹) and the G mode (graphite mode, around 1550 cm⁻¹) have been evaluated by two Gaussian fits.

3.25.8. X-ray diffraction

A D8 discover X-ray diffractometer (Bruker, Ettlingen, Germany) with Cu K α radiation (λ = 1.54184 Å, 50 kV, 1000 mA) was applied for the X-ray diffraction (XRD) experiments of the graphene oxide, metal-organic, and covalent organic framework samples at a scanning rate of 1° min⁻¹. Air-tight sample holders (Bruker, Ettlingen, Germany) were used to prevent any contaminations of the samples.

3.25.9. Thermogravimetric analysis

Thermal gravimetric analysis (TGA) was used to investigate the mass loss of the synthesized samples as a function of temperature. The analysis was carried out on a

Netzsch TG209 F1 Iris instrument (Netzsch, Selb, Germany) under argon flow (50 mL min⁻¹) from 25 °C to 800 °C to 900 °C at 5 and 10 K min⁻¹. Fourier transform infrared spectroscopy-coupled thermal gravimetric analysis (TGA-FTIR) (Mettler-Toledo GmbH, Vienna, Austria) was applied to identify the evolved gaseous compounds during thermal degradation of surface-initiated polymers.

3.25.10. Contact angle experiments

Dynamic contact angle measurements were done on a KRUESS Drop Shape Analysis System DSA 100 using ADVANCE software (KRUESS GmbH, Hamburg, Germany). Each sample was measured four times. The average error for the measurements was $\pm 1^{\circ}$. The materials can be divided into three groups regarding their water contact angles (Θ) at solid surfaces (Figure 3.6).



Figure 3.6. Classification of surfaces based on water contact angle analysis. The image reprinted from [22].

3.25.11. Size exclusion chromatography

Size exclusion chromatography (SEC) measurement was performed at room temperature in CHCl₃ on a Waters instrument (Waters GmbH, Eschborn, Germany) using an ultraviolet (UV) detector and polystyrene as standards of different molecular weights (Polymer Standards Service, Mainz, Germany) for calibration.

3.25.12. BET analysis

Sample porosity and BET area were determined by N₂-adsoprtion on a Micrometrics ASAP2020MPHD analyzer (Micromeritics Instrumental Corp., Norcross (GA), USA). N₂-isotherms were measured at 77 K. Surface area was calculated by BET-Theory between 0.05 and 0.3 P/P₀. During the data fitting it was made sure that no negative BET constant occurs. The principles of the gas adsorption on the adsorbates are shown in Figure 3.7.



Figure 3.7. Representation of different states of the gas molecules in the adsorbates pores. Reprinted with permission from [23]. *Copyright* © *2008,* © *SAGE Publications.*

3.25.13. Adsorption

The gas adsorption analysis of the COF nanoparticles was conducted on a magnetic suspension balance (MSB, Rubotherm Series IsoSORP[®] sorption analyzer, TA® Instruments, New Castle, DE, USA) with an uncertainty of 10 μ g. The sample of COF nanoparticles in powder form was evacuated at 120 °C for 24 h in order to remove the residual gas. The density of the sample was estimated in situ with helium at 30°C with MSB in the pressure range from 10⁻⁵ bar to 50 bar. The adsorption measurements were conducted from high vacuum to 50 bar stepwise with an uncertainty ± 0.1% for CH₄, N₂, O₂, and CO₂ series. The specific uptake was analyzed considering gas buoyancy [24].

The equilibrium concentration *C* of gas in the polymer for a given gas pressure p was obtained from the equation:

$$C = \frac{C'_H \cdot b \cdot p}{1 + b \cdot p},\tag{3.1}$$

where C'_{H} is the Langmuir sorption capacity related to addition sorption owing to the non-equilibrium volume, and *b* is the Langmuir affinity parameter.

3.25.14. Scanning electron microscopy

Scanning electron microscopy (SEM) experiments were carried out on a Merlin (ZEISS, Oberkochen, Germany) equipped with an energy-dispersive X-ray (EDX) analysis system (Oxford, Wiesbaden, Germany) at an accelerating voltage of 1,3 kV. Before investigating the surface and cross-section morphology of the samples, they were coated with approx. 2 nm Pt and 6 nm carbon (for GO incorporated PIM-1 membranes) using a sputter coating device MED 020 (Bal-Tec/Leica Microsystems, Wetzlar, Germany). Secondary electron (SE) images and energy-dispersive X-ray (EDX) spectra were taken at accelerating voltages of 2–3 kV and at 10 kV during the experiments for different samples. The working principle of an SEM is shown in Figure 3.8.





3.25.15. Transmission electron microscopy

Transmission electron microscopy (TEM) was carried out on a Tecnai G2 F20 (Thermo Fisher Scientific, Eindhoven, The Netherlands) at 120 kV in the bright field mode. Graphene oxide was diluted in chloroform (0.001wt.%). A droplet of 3 μ L was put on a Lacey grid and dried. The working principle of a TEM is shown in Figure 3.9.



Figure 3.9. Schematic ray diagram for TEM for imaging mode. Reprinted from [27].

3.25.16. Membrane gas separation analysis

After membrane casting, the samples of 75 mm (for GO-incorporated PIM-1 membranes) and 20 mm (for the both SI-ATRP functionalized graphene oxide and MOF-incorporated PIM-1 membrane samples) in diameter were cut and placed into the measurement cell of the membrane testing facility, and the gas transport properties for CH₄, N₂, O₂, CO₂, and H₂ were determined at 30 °C and 500 mbar feed pressure. The feed pressure of a maximum 500 mbar and permeate pressure of a maximum 10 mbar give the possibility to consider all aforementioned gases as ideal for calculation of membrane permeance. The gas permeation experimental facility is described elsewhere in more detail [29]. The membrane permeance (L) of a gas can be calculated using the equation:

$$L = \frac{V \cdot 22,41 \cdot 3600}{RTAt} \ln \frac{(p_F - p_0)}{(p_F - p_{P(t)})}$$
(3.2)

where *L* is the gas permeance (m³(STP) m⁻² h⁻¹ bar⁻¹), *V* is the permeate volume (m³), 22.41 is the molar volume (m³(STP) kmol⁻¹), 3600 is a conversion factor (s h⁻¹), *R* is the ideal gas constant (0.08314 m³ bar K⁻¹ kmol⁻¹), *T* is the temperature (K), *t* is the time of measurement between permeate pressure points p_0 and $p_{P(t)}$ (s), *A* is the membrane area (m²), and p_F , p_0 and $p_{P(t)}$ are the pressures at the feed, permeate side at the start and at the end time of measurement, respectively (mbar). The ideal selectivity for a gas pair A and B ($\alpha_{A/B}$) can be calculated by the equation:

$$\alpha_{A/B} = \frac{L_A}{L_B} \tag{3.3}$$

The single gas transport properties of surface-initiated polymers were determined for H₂, N₂, O₂, CO₂, and H₂O vapor at feed pressures of 100, 250, 250, 250, and 1000 mbar, respectively. The pressure of the water vapor was predetermined by the temperature of the thermostated part of the facility, was 95% of water vapor activity at a given temperature, and lowered during the experiments due to consumption by vapor transport through the membrane. The cell temperatures during the experiments were between 30 °C and 80 °C. The described feed pressures and permeate pressure of a maximum of 10 mbar give the possibility to consider all aforementioned gases as ideal for the calculation of membrane permeance. Water vapor was considered as other gases, even taking into account that vapor activity on the feed side of the membrane changed during the experiment significantly. No experiments on possible water vapor concentration effects on the diffusion coefficient were carried out.

The equation oriented process simulator Aspen Custom Modeler[®] was employed for the description of water vapor permeance through the SI-PDEAEMA_exf.GO_0.75 membrane using the Free Volume Model equation [30]:

$$L_{i} = L_{\infty,i}^{0} \cdot \exp\left(\frac{-E_{i}}{RT} + \sum_{j=1}^{nc} \left(\frac{\sigma_{i}}{\sigma_{j}}\right)^{2} \cdot m_{0,j} \cdot f_{av,j} \cdot exp(m_{T,j} \cdot T)\right)$$
(3.4)

$$f_{av,j} = 0.5 \cdot \left(f_{R,j} + f_{P,j} \right) \tag{3.5}$$

where *L* is the permeance, L_{∞}^{0} is the permeance at infinite temperature and pressure approaching to zero, *E* is the sum of the activation energy of diffusion and heat of sorption, *R* is the universal gas constant, *T* is the temperature, and σ is the Lennard-Jones molecule diameter. f_{av} , f_{R} , and f_{P} are the average, retentate and

permeate fugacities, respectively. This model allows to predict the permeation of multicomponent gas mixtures based on the single gas experiments by accounting for the increase in flux of one component caused by the swelling induced by another. According to the model, these parameters were used: $E_0 = -174.266$, L = 2.52415, $L_0 = 14.0671$, $m_0 = 0$, $m_T = 0$, p = 0.487239 bar, R = 8.31433, T = 10.275 °C, $T_0 = 273.15$ for the no-swelling condition; $E_0 = -2087.48$, L = 2.52415, $L_0 = 5.66042$, $m_0 = 446380$, $m_T = -0.0352701$, p = 0.487239 bar, R = 8.31433, T = 10.275 °C, $T_0 = 273.15$ for the no-swelling condition. In case no swelling was caused by a component, m_0 and m_T are equal to 0 and the model becomes an Arrhenius type relationship.

3.26. References

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Chapter 4

Results and Discussion

4.1. Structural characterization of graphene oxide and its gas transport properties.

4.1.1. Summary

In this subchapter, the primary goal is to uncover the formation of GO and OD, and to analyze the structure of both and to propose a new structural model for GO layers. The model explains the origin of lactone peaks, the presence of defects, and quinone groups, which have never been discussed in the literature before. The experiments showed that during the synthesis, OD is generated, which increases the difficulties in terms of functional group determination of GO. For successful analysis, OD is extracted from GO layers and precipitated by the Hiradate method [1]. This method consists of the adsorption of OD on a hydrophobic resin (DAX-8) followed by complete elution using acidic, neutral, and basic solutions sequentially.

The proposed structure will help to modify the Lerf–Klinowski model [2] and open new directions in the field of graphene-like nanomaterials synthesis. Furthermore, based on exfoliated graphene oxide layers, thin-film membranes were prepared, and their gas separation properties were analyzed.

4.1.2. Synthesis of graphene oxide and its characterization

The formation of graphene oxide (GO) depends on several factors, such as the concentration of acids, the strength of oxidizer, and the decomposition of the intermediate compounds. By following the Hummers method, we used highly concentrated sulfuric acid (18 M) and sodium nitrate. The first intercalation occurs immediately by sulfuric acid after adding graphite, graphite bisulfate generates [3], and this state of graphite is called stage-1 GIC (graphite-intercalated compound). While HSO₄⁻ ions attack the edge of the graphene layers, Na⁺ ions enter between graphene layers removing Van der Waals and π - π stacking interactions, and the *d*-spacing increases between the layers. The next intercalation, after expanding the graphene 96

layers, occurs on basal planes. Simultaneously, nitric acid is generated in the sulfuric acid medium and intercalates into the graphite structure (Figure 4.1.2.1), yielding defective black graphene layers [4].



$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

Figure 4.1.2.1. Intercalation, oxidation and exfoliation of graphene oxide layers: • - HSO4⁻,• - NO_{3⁻};• - Na⁺;• - oxygen functionalities;• - oxidative debris.

The defective sites are also attacked by acids, which intercalate them. Gradually, amorphization proceeds, the interlayer distance between the graphene layers increases, the lattice parameter along the *c*-axis (axis perpendicular to the carbon layers) decreases, the number of layers reduces [5] and yields soluble and gaseous products. The decrease of the lattice parameter along the c-axis is related to the break of the large layers.

When KMnO₄ is added to the stage-1 GIC, which has a high intercalation potential in sulfuric acid, it starts to oxidize graphene layers thoroughly, and gas evolution is observed when the formed graphite foam heats up to 35 °C. The synthesized graphite-intercalated suspension is not stable when it is in contact with water. These processes finish with the formation of different functional groups (phenolic –OH, lactone, quinone, ketone, and carboxyl) at both peripheral edges and

defects on the basal planes. Due to incomplete removal of sulfuric and nitric residuals trapped between the graphene layers [6], XPS and EDX results (Figure 4.1.2.4) showed characteristic bands for both sulfur and nitrogen. Sulfuric moieties with 1.06 atomic percentage (at.%) and nitric moieties with 0.14 at.% recorded by XPS confirm this hypothesis. Considering the complete oxidation of stage-1 GIC into graphite oxide, the amount of the recorded sulfuric and nitric moieties are negligible. The C1s XPS spectrum of the GO samples is shown in Figure 4.1.2.2. As it is seen from this figure, all graphene samples exhibit four peaks. The peaks at around ~284.4 eV are assigned to C–C, and C=C of graphene lattices. Epoxy and phenolic –OH attached carbons show relevant binding energy at ~286.5 eV, while the corresponding signals of ketone, lactone, and carboxyl groups containing carbons are located at ~288–290 eV. The signals of carbons from ketone groups located at the defect areas of the GO samples are located at ~285.6 and ~285.8 eV [7].



Figure 4.1.2.2. C1s XPS spectra of graphene oxide samples: (a) GO, (b) bwGO, (c) rGO and rbwGO.

The results from the O1s spectra of GO samples confirm the C1s results according to which the graphite structure is strongly oxidized and contains different oxygen functionalities. Therefore, the signal around ~530 eV corresponds to quinone, ~532 eV (C=O and O–C=O from the carboxylic group), the signal around ~533 eV corresponds to phenolic –OH and epoxy groups, and ~534 eV to lactone groups (Figure 4.1.2.3). O1s XPS shows qualitatively that during reduction, some amount of oxygen functionalities remain on the surface. They are mainly phenolic hydroxyl groups 98

and epoxy groups. The reason for their incomplete reduction could be explained with the existence of oxidative debris on the surface of graphene oxide. However, during reduction, hydrazine hydrate molecules react with oxidative debris, and they are not able to reach the oxygen surface functionalities of the big layers. Furthermore, the reduction of base-washed graphene oxide (rbwGO) shows a different result than reduced graphene oxide (rGO). On the surface of the rbwGO, there is no indication of the existence of epoxy and phenolic –OH groups. The possible surface functionalities of the rbwGO are quinone, ketone, lactone, and carboxylic groups.



Figure 4.1.2.3. O1s XPS spectra of graphene oxide samples: (a) GO; (b) bwGO; (c) rGO and (d) rbwGO.



Figure 4.1.2.4. EDX results for graphene oxide samples.

Figure 4.1.2.5 shows the FTIR spectra of GO samples. It is clear from this figure that pristine GO (red color) has a transmission band near ~1620 cm⁻¹, assigned to physisorbed water [8, 9] by hydrogen bonds. The broad band at ~3300-3400 cm⁻¹ denotes C–OH stretching vibrations. The high-wavenumber shoulder (~3600 cm⁻¹) observed in the GO spectrum can be identified with the -OH stretching (high frequency) vibration of edge hydroxyl groups [9]. The C-OH stretching vibration in the base-washed graphene oxide (bwGO) spectrum is significantly higher than for GO, and the physisorbed water peak disappeared. This indicates that in the basic medium (pH 14), all non-covalently adsorbed OD is stripped off from the surface of GO, and carboxylic groups turned into the -COONa form. A reduction in the FTIR spectrum at ~3300 cm⁻¹ indicates the high hydrophilicity of bwGO. Stretching vibrations of carbonyl groups observed between 1718 and 1738 cm⁻¹ indicate the formation of carboxyl, quinone, and six-membered lactone moieties after oxidation of graphite. When GO is freed from OD, a strong peak at 1585 cm⁻¹ appeared, showing conjugated benzene rings. –OH bending and C–O stretching vibrations from –COOH groups of the samples can be observed at 1410 or 1370 cm⁻¹ and 1220 or 1230 cm⁻¹, respectively. Epoxy group (C–O–C) stretching vibrations are found at 1045 and 1050 cm⁻¹. After reduction with hydrazine hydrate, these peaks disappear.



Figure 4.1.2.5. FTIR spectra of GO samples.

The FTIR analysis of OD showed that it also contains oxygen functionalities. The broad band between 3300 and 3500 cm⁻¹ attributes to C–OH stretching vibrations mainly located at the edges. The peaks at 1524, 1525, 1526, and 1558 cm⁻¹ belong to benzene rings. The carbonyl (C=O) groups show the stretching vibrations at 1597, 1643, and 1673 cm⁻¹; however, the peak of lactone is at 1735 cm⁻¹. –OH bending and C–O stretching vibrations of –COOH groups of OD can be observed at 1400–1425 cm⁻¹ and 1230 cm⁻¹, respectively. The FTIR spectra of OD is shown in Figure 4.1.2.6.



Figure 4.1.2.6. FTIR spectra of oxidative debris.

From UV-Vis spectroscopic studies (Figure 4.1.2.7), it is seen that the dominant optical absorption of GO is located at ~230 nm. It belongs to the π - π * plasmon peak of nanometer-scale sp² clusters and C=C chromophore units. The shoulder peak at ~300 nm corresponds to an n- π * plasmon peak of carboxyl, other carbonyl and hydroxyl auxochromes. The rest of the samples do not show any peaks, which is explained by the reduction and substitution of oxygen functionalities.



Figure 4.1.2.7. UV-Vis spectra spectra of graphene oxide samples.

Solid-state NMR experiments were performed to study the molecular structure of the GO samples (Figure 4.1.2.8). Direct excitation ¹³C magic angle spinning (MAS) NMR spectra of GO and bwGO exhibit similar features, showing three dominant signals at 60, 70 and ~130 ppm, which can be assigned to the epoxide (C–O–C), hydroxyl group (C–OH, most likely tertiary alcohol), and sp² carbon of graphene, respectively. These characteristics are in good agreement with previous reports, demonstrating that graphite is highly oxidized. In bwGO, additional weak signals occur at 104, 175, and 190 ppm. The signals at ~100 ppm can be attributed to a six-/five-membered lactone ring containing hydroxyl groups (lactol) along the periphery of the GO layer [10]. The signals at ~170 and 190 ppm are ascribed to carboxylic moieties that are bound to aromatic rings and ketone/quinone type parts of GO, respectively. The broad overlapping shoulders at ~110 and ~140 ppm are also present, which can be attributed to the phenolic –OH group. Interestingly, two signals of sp² carbon are observed at 120 and 130 ppm for bwGO, suggesting the presence of sp² species in different local environments. ¹³C MAS NMR results of "washed" graphene oxides confirm that both H- and Na-form contain ketone, guinone, carboxyl, lactone with a hydroxyl group (lactol), epoxy and C-OH functional groups, which are distributed around the sp² graphene structure (Figure 4.1.2.9). To obtaining further structural information, ¹³C{¹H} CP MAS NMR spectra were measured (Figure 4.1.2.9). Since the CP efficiency

depends on the dipolar interaction between nuclear spin pairs, which is inversely proportional to the cube of the internuclear distance, the CP signal can be selectively enhanced for carbon centers nearby protons. The relative intensity of the signal at 130 ppm with respect to that of 120 ppm is stronger in ¹³C{¹H} CP MAS NMR spectrum than in the direct excitation spectrum, suggesting that the sp² carbon of GO nearby protons (C–OH or trapped water between the layers) is responsible for the signal at 130 ppm. Moreover, the signals corresponding to lactone with -OH moieties are clearly visible in the CP spectra. In contrast, reduced GO showed very different MAS NMR spectra. For both reduced GO (reduced graphene oxide (rGO), and base-washed and reduced graphene oxide (rbwGO), only a very broad sp² signal is observed at 120 ppm, which is lower than that of GO and the signals corresponding to other oxidative moieties are not visible. Furthermore, tuning and matching of ¹H and ¹³C channels to obtain MAS NMR spectra of reduced GO was extremely difficult, and CP MAS NMR spectra could not be acquired. It is likely that the reduction procedure yields highly conductive materials, which are similar to pure graphite. However, it is not clear whether all the oxidative moieties are completely eliminated due to the poor spectral quality.



Figure 4.1.2.8. Direct excitation ¹³C MAS NMR spectra of graphene oxide samples.



Figure 4.1.2.9. Direct excitation ¹³C MAS NMR (left) and ¹³C{¹H} CP MAS NMR (right) spectra of base-washed graphene oxide (sodium and hydrogen forms).

¹³C{¹H} CP MAS NMR experiment for OD-1 shows that ketone, carboxylic and hydroxyl groups are the mainly distributed functionalities (Figure 4.1.2.10).



Figure 4.1.2.10. ¹³C{¹H} CP MAS NMR spectrum of OD-1.

Elemental analysis shows that after oxidation, there is a moderate alteration in the weight percentage of the elements, and the results are depicted in Table 4.1.2.1.

Therefore, carbon being ~100% in graphite decreased to ~47 wt.% in GO, while oxygen increased by ~48 wt.%. The C/O ratio is 1.32 in the GO sample, which evidences the high level of oxidation of graphite. After stripping off the oxidative debris and reduction of graphene oxide, carbon increased to ~55, ~86 and ~79 wt.% and by contrast, the amount of oxygen decreased to ~39, ~10 and ~15 wt.% in bwGO, rGO, and base-washed and reduced graphene oxide (rbwGO), respectively.

Samples	Eleme	ents by %	weight	C/O ratio	C/H ratio	
	С	Н	0			
Graphite	99.6	0.4	-	-	0.4	
GO	47.1	4.4	47.6	1.32	0.89	
rGO	85.5	0.84	9.6	11.9	8.48	
bwGO	55.0	2.4	39.2	1.87	1.91	
rbwGO	78.8	1.27	14.8	7.1	5.17	

 Table 4.1.2.1. Elemental composition of graphene oxide samples.

The C/O ratio reaches its highest level in reduced graphene oxide by ~12, which results from the loss of most oxygen-containing functional groups.

Raman spectroscopy is widely used to measure some of the properties of graphene samples. As a non-destructive spectroscopic method, Raman spectroscopy is a promising tool for the characterization of the 2D allotrope of carbon, in particular the characterization of "vacancy defects" [11]. Vacancy summarizes the absence of one or several carbon atoms from the hexagonal honeycomb graphene lattice, as well as the edges of the structure (Figure 4.1.2.11). Pristine crystalline graphite shows only one Lorentzian G-band at ~1580 cm⁻¹. When graphite has a structural disorder, D, 2D, D + D', and 2D' bands are also activated [12]. In our measurements, graphite showed a G-band at ~1580 cm⁻¹. It gives information about the E_{2g} phonon at the Brillouin zone center. A small D-band at ~1360 cm⁻¹ attributes to the breathing mode vibration of six-atom benzene rings, or it is activated by the boundary of the larger crystallinity, explaining the scattering of electrons from armchair edges [13, 14].



Figure 4.1.2.11. Lattice model for the edges and round hole. Red and blue lines mark armchair and zigzag edges, respectively.

After oxidation of graphite to conventional graphite oxide (CGO), the degree of order of the structure alters, and the intensity of D-band increases in comparison with graphite, and the G-band in case of reduced forms decreases (Figure 4.1.2.12). The D peak in oxidized forms lies between 1342 and 1356 cm⁻¹. This shows that GO samples are in a distorted form of the sp² crystal structure and contain an enormous quantity of defects. In general, the activation of the D peak occurs within 3-4 nm size regions of the crystals that are close to defects or an edge [14]. Another band, which confirms the defect formation is the appearance of a D+D' band ($\sim 2920-2940$ cm⁻¹), corresponding to the backscattering of a phonon at a hole point, and it is much broader than other bands. This peak is significant evidence that distinguishes GO samples from graphite. No defects are required for the activation of 2D and 2D' bands [15]. Therefore, the 2D peak (~2700 cm⁻¹) shape can be useful for the determination of the number and orientation of graphene layers. A single sharp peak at 2D-band, the peak is considered to be the existence of single-layer graphene. During the experiments, a bulk form of graphene oxide samples was used, and the results show that GO samples contain many single layers (Table 4.1.2.2). This result suggests that the synthesized graphene oxide samples need to be exfoliated in order to get single-layer graphene oxide layers.



Figure 4.1.2.12. Raman spectra of graphene oxide samples.

Samples	D-band	G-band	2D-band	D+D'- band	2D'-band	ID/IG	I2D/IG
Graphite	1359	1578	2713	-	3240	~0.08	~5.6
GO	1356	1592	2683	2920	3204	~0.92	~0.05
rGO	1351	1584	2685	2939	-	~1.47	~0.19
bwGO	1342	1583	2708	2920	3183	~0.97	~0.11
rbwGO	1343	1575	2684	2916	3165	~1.2	~0.09

 Table 4.1.2.2. Raman results for graphene oxide samples.

Figure 4.1.2.13 depicts the XRD pattern of pristine graphite and GO samples. Graphite flakes exhibit a sharp 002 reflection at ~26.6°, corresponding to its interlayer spacing of 0.34 nm. Using the Scherrer equation for this sharp peak, it is revealed that the thickness of graphite flakes is about 12.9 nm, and the number of the layers in this crystal is 38. The Scherrer equation is described by the following equation [16, 17]:

$$D_p = \frac{\kappa\lambda}{\beta\cos\theta} \tag{4.1.1}$$

where D_p is a mean size of the ordered (crystalline) domains, K is a dimensionless shape factor with a value close to unity (~0.94), λ is the X-ray

wavelength, β is the broadening at half the maximum intensity (FWHM, in radians), and θ is the Bragg angle.

The Bragg angle is determined by the Bragg law [18], and using this equation the distance between graphene layers could be determined:

$$n\lambda = 2dsin\theta \qquad (4.1.2)$$

where *n* is a positive integer, λ is the wavelength of the incident wave, *d* is the spacing of the crystal planes, and θ is the Bragg angle.

In the case of GO and bwGO, the strong 20 peak is around ~10.7° and ~13.6° showing a 001 reflection, which amounts to 0.83 and 0.65 nm in basal spacing, respectively. These explain the existence of oxygen functionalities, increasing the interlayer distance between the layers. Furthermore, the XRD patterns of the reduced graphene oxide samples are different from GO, showing that the crystal sizes decreased by amorphization. This information confirms that the crystalline structure after oxidation is distorted, and these data correlate well with the Raman data (Table 4.1.2.3).



Figure 4.1.2.13. XRD patterns of graphene oxide samples.

Samples	2 0 max. (002)	FWHM(La)	La (nm)	d (nm)	N	2θ max. (100)	FWHM(L₀)	L _c (nm)
Graphite	26.6	0.66	12.9	0.34	38	44.6	0.66	13.6
GO	10.7	6.72	1.24	0.83	2	42.5	7.14	1.25
rGO	-	-	-	-	-	-	-	-
bwGO	13.8	11.37	0.74	0.65	1	42.9	13.19	0.68
rbwGO	-	-	-	-	-	-	-	-

Table 4.1.2.3. XRD analysis results.

Testing the thermal stability is also one of the methods to investigate the existence of oxygen-containing functionalities through the degradation of the investigated samples. In order to evaluate the oxygen-containing functional groups of GO samples, thermogravimetric analysis was performed under the argon atmosphere. Figure 4.1.2.14 shows the mass loss of the samples as a function of temperature. It is clear that graphite does not show any mass loss, thus explaining why there are no oxygen-containing functionalities. After oxidation, the graphite structure changes dramatically to CGO and contains an enormous amount of oxygen-containing functionalities. Experiments revealed that GO and bwGO samples degrade mainly in three steps, which show a high degree of oxidation. The first step (26–125 °C) of ~10% mass loss belongs to the evaporation of adsorbed water, which is located between the lamellar layers of CGO [19]. The major mass loss is between 130 and 220 °C by ~28% in GO and by ~18% in bwGO. In this range, decomposition occurs with the evolution of water molecules from neighboring hydroxyl groups and carbon dioxide and carbon monoxide from carboxylic and lactone groups [20]. In comparison with these results, reduced graphene oxide samples are stable at this stage. As for GO and bwGO, a sharp weight loss (between 30 °C and 100 °C) in the rbwGO sample is explained by the evaporation of trapped water molecules between the graphene layers. The third degradation range (220-400 °C) by ~12% weight loss in CGO and ~6% mass loss in the other graphene oxide samples could be explained by decomposition of quinone and ketone groups. Thermogravimetric analysis supported the thesis of Eigler et al. [21] that the small amount of sulfur recorded by XPS attributes to a covalently linked organosulfate moiety rather than a trapped sulfur species between the graphene layers, which besides quinone and ketone groups also decompose. After basewashing, those moieties reduce from the surface of the GO, which leads to the wrong interpretation of "partial reduced GO" [21]. In other GO samples, we clearly see the decomposition of oxygen functionalities.



Figure 4.1.2.14. Thermogravimetric results of graphene oxide samples between 25 and 800 °C under argon flow at 10 K min⁻¹.

Figure 4.1.2.15 shows scanning and transmission electron microscopic (SEM, TEM) images of GO and OD samples, respectively. The images prove that during graphite oxidation, the number of layers reduces, crystallinity decreases, and amorphization occurs. TEM images show that the obtained GO is a single-layer product and contains "more defective" OD (Figure 4.1.2.15h).



Figure 4.1.2.15. SEM (a–e) and TEM (f–i) images of graphene oxide and oxidative debris samples: (a)—graphite, (b)—GO, (c)—bwGO, (d)—rGO, (e)—rbwGO, (f)—bulk GO, (g)—single-layer GO, (h)—oxidative debris, (i)—stacked and wrinkled GO layers.

Exfoliation experiments were conducted for the analysis of the effect of oxidative debris [22] on the agglomeration of graphene layers.

The plots shown in Figure 3.1 were used for the calculation of the concentrations of graphene oxide dispersions. After centrifugation, it was found that, after OD-stripping, the graphene oxide layers are more stable than the OD-containing graphene oxide. An explanation could be that OD non-covalently adsorbed on graphene oxide layers and attracts more solvent molecules for a stable dispersion. Therefore, the existence of oxidative debris on graphene oxide layers leads to hydrogen bonding between the layers, and agglomeration starts. Moreover, during the experiments, it was revealed that at 0.01 wt.% concentration, the samples showed different concentrations after centrifugation. Hence, oxidative debris interacted between themselves, and the graphene layers became unstable. The concentration of OD-containing graphene oxide sample was 0.005 wt.%, while the concentration for OD-stripped graphene oxide layers was higher, with a concentration of 0.007 wt.%. The result of this experiment suggests that graphene oxide needs further purification after synthesis. The optical images of the dispersions of the GO samples are shown in Figure 4.1.2.16.



GO dispersions in THF



GO dispersions in water



bwGO dispersions in water

Figure 4.1.2.16. Optical images of the exfoliated GO dispersion in THF and water, and bwGO in water.

In Figure 4.1.2.17 and Figure 4.1.2.18, we propose a new structural model for GO nanolayers and OD with respect to the obtained results. The analysis shows that graphene oxide layers also contain ketone groups in some areas; ketone and hydroxyl groups are close enough to each other to show keto-enol tautomerism [23]. It is found that GO layers also contain lactone groups.



Figure 4.1.2.17. Proposed structure of a graphene oxide layer.



Figure 4.1.2.18. Possible structure of oxidative debris.

4.1.3. Surface functional group analysis of GO samples

Research on carbon blacks and other carbons conducted by Boehm considered that surface oxides are mainly at the periphery or vacant defect sites of graphitic basal planes [24].



Figure 4.1.3.1. Possible structures of surface oxygen groups on GO.

These surface functionalities can be divided into acidic and basic oxides: acidic oxides are bound to the edges of graphene layers, while basic groups can be distributed on basal planes. The plausible acidic groups on graphene layers can be carboxylic, lactonic, and phenolic –OH groups [25], which can be quantitatively analyzed (Figure 4.1.3.1).

In general, Boehm suggested that for the determination of surface functional groups, the carbon samples should react with the reaction bases such as NaOH (reacts with all surface functionalities), Na₂CO₃ (reacts with carboxyl and lactonic groups), and NaHCO₃ (reacts only with carboxylic groups). The aliquots taken after reaction can be titrated using two different methods: a) acidification of the aliquots by HCl solution and the back-titration of the samples; b) direct titration of the samples by the addition of HCl. In all cases, the possibility of CO₂ dissolution in the solutions must be taken into consideration. For this reason, before the titration experiments, the dissolved CO₂ needs to be removed from the solutions immediately. Depending on the titration method, the quantity of surface functional groups can be determined by the following equations [26, 27]:

a) Back-titration method

$$[HCl]V_{HCl} = [NaOH]V_{NaOH} + \left(\frac{n_{HCl}}{n_B}[B]V_B - n_{CSF}\right)\frac{V_a}{V_B}$$
(4.1.2.1)

$$n_{CSF} = \frac{n_{HCl}}{n_B} [B] V_B - ([HCl] V_{HCl} - [NaOH] V_{NaOH}) \frac{V_B}{V_a}$$
(4.1.2.2)

b) Direct titration method

$$n_{CSF} = [B]V_B - [HCl]V_{HCl}\frac{V_B}{V_a}$$
(4.1.2.3)

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where [B] and V_B are the concentration and volume of the reaction base mixed with the graphene oxide samples. n_{CSF} denotes the moles of surface functional groups that reacted with the reaction base during the mixing step. V_a is the volume of the aliquot taken from the V_B . [HCI] and V_{HCI} are the concentration and volume of the acid added into the aliquot taken from the original sample. [NaOH] and V_{NaOH} are the concentration and volume of the titrant.

Using a "standardized Boehm titration" method [26, 27], the surface oxygencontaining functionalities of the synthesized graphene flakes were calculated using equation (4.1.2.2) and the concentration of the carbon surface functional groups are given in Table 4.1.3.1. The quantity of the different possible surface functionalities are calculated through the difference in the calculated amounts of the surface functionality reacted (n_{CSF}). Thus, the difference between $n_{CSF, NaOH}$, and $n_{CSF, Na2CO3}$ gives the number of surface phenolic groups, while the difference between $n_{CSF, Na2CO3}$, and $n_{CSF, Na2CO3}$, and $n_{CSF, NaHCO3}$ result the number of the lactonic groups. The number of carboxylic groups is found directly from the reacted amount of NaHCO3.

<i>n</i> _{CSF} ± SD (μmol/g)						
Phenolic	Lactonic	Carboxylic				
0	0	0				
1017	565	5626				
0	2747	0				
985	2009	216				
0	2896	465				
	0 1017 0 985 0	ncsF ± SD (μm Phenolic Lactonic 0 0 1017 565 0 2747 985 2009 0 2896				

Table 4.1.3.1. Carbon surface functionalities (*n*_{CSF}) of graphene oxide samples.

4.1.4. Gas adsorption behavior of GO

Gas sorption, storage, and separation in carbon materials, especially graphene samples, undergo the physisorption on the surfaces and particularly van der Waals interactions. In general, the binding or adsorption strength of the gas molecules with the carbon nanostructures changes from relatively low for H₂ and N₂ to intermediate for CO, CH₄, and CO₂ to relatively high for H₂S, NH₃, and H₂O [28]. In order to investigate the possibility of using graphene oxide as a membrane material, the gas

adsorption experiments were conducted for CH₄, N₂, and CO₂ gas series. The results show that GO has an affinity towards CO₂, albeit the adsorption of CH₄ and N₂ was not observed during experiments. CO₂ adsorption fits in the Langmuir model, and the isotherm is shown in Figure 4.1.4.1.



Figure 4.1.4.1. Experimental (a) and model (b) CO₂ adsorption isotherms of GO.

The adsorptions of N₂ and CH₄ could not be detected during the experiments. The uptake behavior of these gases by GO can not be shown due to negative results, which means the adsorption strengths of N₂ and CH₄ with graphene oxide layers are considerably low. However, CO₂ adsorption is notably high, and the experimental points perfectly fit the Langmuir model showing the isotherm regarding the microporous materials (Figure 4.1.4.1a). Experiments conducted up to 20 bar show the following parameters according to equation 3.1: C'_{H} =29.9 cm³ (STP) g⁻¹, *b*=0.688 bar¹. Using this equation, the uptake of CO₂ by GO up to 50 bar was predicted, and the result is shown in Figure 4.1.4.1b. The model shows that at high pressures, the uptake can be reached 30 cm³ g⁻¹ due to the presence of oxygen functional groups that have an affinity towards CO₂, which corresponds to the high solubility selectivity for CO₂ over nitrogen and methane.

4.1.5. Pure GO membranes and GO-incorporated PIM-1 mixed matrix membranes

Pure gas permeance experiments for thin-film membranes are divided into two parts. The first part details data about the thin-film selective layer prepared from exfoliated graphene oxide. Three different concentrations (0.005, 0.01, and 0.015

wt.%) of GO in water was cast on microporous PAN support, and their gas permeances for H₂O, H₂, CO₂, O₂, N₂, and CH₄ were investigated. The data of single gas permeance and ideal selectivity according to the equations (3.2) and (3.3) were obtained for at least four stamps of the same batch of each TFCMs; the permeances were calculated as an average value from at least 20 experimental points. All permeance data is shown in Table 4.1.5.1.

Membrane	Permeability coefficients, Barrer					rer	Ref.	
samples	H ₂	N ₂	02	CH₄	CO ₂	H ₂ O	. Non	
GO	-	0.31	-	0.36	5.20	-	[29]	
GO-PEGDA2000	-	2.20	-	1.97	34.0	-	[29]	
GO	1100	5.00	6.00	9.00	0.40	-	[30]	
GO	1135	425	472	638	8500	-	[31]	
GO	2436	756	-	1217	685	-	[32]	
GO	90	-	-	-	4.50	-	[33]	
GO_5	411	111	104	146	88.0	249		
GO_10	22.0	6.20	5.48	8.00	4.75	358	This work	
GO_15	11.0	2.70	2.70	3.84	2.20	543		

Table 4.1.5.1. Single gas permeances of the thin-layer GO membranes with the comparison to reference data.

The permeance results confirm the outcome from the suspension balance experiments leading to a molecular-sieving separation of H₂ from CO₂ due to strong adsorption of CO₂ on GO layers. This suggests that the influence of GO membrane on H₂ permeance is negligible, which means only H₂ can permeate through the nanolayers. Due to the presence of oxygen functionalities on graphene layers, the water vapor permeance increases with the increase of the GO selective layer thickness (Figure 4.1.5.1).



Figure 4.1.5.1. Permeability of single gases with regard to their kinetic diameters through GO membranes prepared dip-coating method on microporous PAN support (a). H₂ Permeability versus H₂/CO₂ selectivity of GO membranes along in this study with several reference GO membranes listed in Table 4.1.5.1. The black line indicates the Robeson 2008 upper bound of pure polymeric for H₂/CO₂ separation, assuming a membrane thickness of 100 nm. The red line shows the 2010 Robeson upper bound of microporous inorganic membranes for H₂/CO₂ separation (b).

The obtained H₂ permeance for PAN is 376 m³ (STP) m⁻² h⁻¹ bar⁻¹ with an H₂/CO₂ separation factor of 4.46, which is in the range of the expectation of Knudsen diffusion through 22 nm pores of pure PAN support (4.69). The highest H₂ permeance through GO galleries was observed for GO_5 membrane sample (~5 nm thickness) with a permeance of 225 m³ (STP) m⁻² h⁻¹ bar⁻¹, which is 1.7 times lower than the permeance of the pristine PAN support. However, the separation factor for H₂ over CO₂ is ~4.7, explaining that the permeance of the gases follows the Knudsen flux. With the increase of the GO thickness, the permeance increases with the increase of the GO selective layer thickness due to the existence of oxygen functional groups on the layers. The membrane sample GO_15 showed an H₂/CO₂ selectivity of ~5 exceeding the Knudsen diffusion mechanism, which can be explained with the molecular sieving effect of the GO layers. Thus, the results are much lower than the results reported by other groups [30, 34].

Figure 4.1.5.1a verifies the molecular sieving separation mechanism of the GO membrane, which is identical to the previous reports [34]. Using a single gas permeance technique, we revealed that the GO membranes allow faster permeance

of the smaller gases (H₂O and H₂), but slow the permeance of the larger gases (CO₂, O₂, N₂, and CH₄). The permeance of the experimental gases follows such a particular pattern: H₂O >> H₂ >> CH₄ > CO₂ > N₂ \approx O₂, which is roughly the same as the kinetic diameters of the gases, except methane. This phenomenon could be explained by the molecular shape effect of the molecule. Thus, possessing sphere molecules, CH₄ can penetrate the GO nanopores much easier than the rod-shaped CO₂ and N₂ molecules. The molecular shape effect also affects the permeance of the oxygen through the GO layers as it is seen that the behavior of the rod-like molecules is the same during the molecular sieving separation mechanism. The low selectivities of the prepared membranes can be explained by the wrinkles of the GO layers revealed by TEM analysis (Figure 4.1.5.2).



Figure 4.1.5.2. TEM microscopic images of the GO layers on carbon grid (a), GO membrane with a thickness of 10 nm (b), and 15 nm (c) on microporous PAN support.

The figure shows the presence of wrinkles on the prepared GO membranes that open new opportunities for fast-passing channels, which increases the gas permeance through the GO membranes.

The H₂ permeability versus H_2/CO_2 selectivity is plotted in Figure 4.1.5.1b along with literature data described in Table 4.1.5.1 indicating their place in the 2008
Robeson upper bound for pure polymeric membranes and the 2010 Robeson upper bound for microporous inorganic membranes. Ultimately, the results are placed in Figure 4.1.5.3 to show the comparison with data reported by Celebi *et al.* [35].



Figure 4.1.5.3. H₂ Permeance versus H₂/CO₂ selectivity along with reported data from Celebi *et al.* [35]. Reprinted with permission from AAAS. The 2008 Robeson upper bound for pure polymeric membranes was assumed with a membrane thickness of 1 μ m.

Considering the figures, we can assume that the results are exceeding the Robeson upper bound. The main drawback of the results is the considerably lower selectivity of the prepared GO membranes. However, the permeabilities of the membranes are comparable with reported details by other groups.

The effect of the GO loading on the gas separation performances of the PIM-1 mixed-matrix membranes was also investigated. Pure gas permeances of thin-film composite membranes (TFCM) for CH₄, N₂, O₂, and CO₂ with pure PIM-1 and GO containing PIM-1 mixed-matrix membrane such as PIM-1/GO were determined at 30 °C on the home-built gas permeation facility. The data of single gas permeance and ideal selectivity according to the equations (3.2) and (3.3) were obtained for at least four stamps of the same batch of each TFC membranes; the permeance was calculated as an average value from at least 10 experimental points. The experimental error was determined from the accuracy of the measurement systems permeate

volume calibration, the accuracy of pressure sensors, and the standard deviation of experimental points. The error of the ideal selectivity was taken as a multiplication factor of experimental errors of corresponding gas permeances (Table 4.1.5.2).

Table 4.1.5.2. Permeance for the GO containing PIM-1 TFC membranes and th	e gas
permeance comparison with the state-of-the-art membranes.	

Membrane	Fillor	Wt.% of Permeance, m ³ (STP)m ⁻² h ⁻¹ bar ⁻¹					
code	Filler	filler	N2	CH ₄	CO ₂	02	NCI.
PolyActive™	-	-	0.08	0.35	4.8	0.24	[36]
Matrimid®	-	_	0.0083	0.010	0.304	0.058	[27]
5218							[37]
Polyetherimide	-	-	0.05	0.029	1.56	0.38	[38]
PIM1-	Graphene	0.00096	870	1450	12700	2260	[20]
0.00096G ¹	••••						[29]
Telechelic	GO	8	1.15	6.44	27.7	1.61	[40]
PDMS-GO ²		Ū.					[40]
PIM-1	-	-	0.52 ±	0.83 ±	11.04	1.69 ±	
			0.16	0.03	± 0.34	0.05	
PIM1-9GO		9	0.42 ±	0.58 ±	7.32 ±	1.25 ±	
		Ū	0.08	0.12	0.75	0.12	
PIM1-33GO		33	0.11 ±	0.16 ±	1.18 ±	0.24 ±	
		00	0.01	0.02	0.63	0.08	This
PIM1-50GO	GO	50	0.07 ±	0.1 ±	0.1 ±	0.07 ±	work
		00	0.02	0.03	0.03	0.02	
PIM1-76GO		76	0.8 ±	1.08 ±	0.7 ±	0.74 ±	
		10	0.57	0.76	0.5	0.53	
PIM1-84GO		84	1.3 ±	1.71 ±	1.43 ±	1.27 ±	
		04	0.52	0.68	0.36	0.48	

¹ For the gas permeability experiments of the PIM1-0.00096G membrane, the thick polymer film was used and the permeability is shown in barrer.

² For the gas permeability experiments of the Telechelic PDMS-GO membrane, the thick polymer film was used and the permeability is shown in barrer.

The data for the selectivities and the comparison of the achieved results with the state-of-the-art polymer membranes are presented in Table 4.1.5.3.

Membrane	Filler	Filler content	Selectivity					
Code		wt. %	O ₂ /N ₂	CH4/N2	CO ₂ /N ₂	CO₂/CH₄		
PolyActive™	-	-	3.0	4.4	60	14	[36]	
Matrimid® 5218	-	-	7.0	1.2	37	30	[37]	
Polyetherimid e	-	-	7.6	0.58	31	54	[38]	
PIM1- 0.00096G	Graphe ne	9.6 [.] 10 ⁻⁵	2.6	1.67	14.6	8.8	[39]	
Telechelic PDMS-GO	GO	8	1.4	5.6	24.1	4.3	[40]	
PIM-1	-	-	3.26 ± 0.02	1.61 ± 0.01	21.3 ± 0.02	13.2 ± 0.02		
PIM1-9GO		9	3.06 ± 0.35	1.40 ± 0.04	18.0 ± 2.82	12.9 ± 1.43		
PIM1-33GO		33	2.09 ± 0.52	1.38 ± 0.08	9.99 ± 4.33	7.24 ± 2.21	This	
PIM1-50GO	GO	50	0.99 ± 0.01	1.34 ± 0.01	1.32 ± 0.07	0.99 ± 0.04	work	
PIM1-76GO		76	0.93 ± 0.01	1.35 ± 0.02	0.86 ± 0.01	0.64 ± 0.02		
PIM1-84GO		84	0.98 ±1.00	1.32 ± 1.31	1.10 ± 0.69	0.84 ± 0.53		

 Table 4.1.5.3.
 Selectivity for the graphene containing PIM-1 TFC membranes.

In order to evaluate the influence of GO layers on the TFC membrane morphology, the surface and cross-sectional SEM images were taken and shown in Figure 4.1.5.4. The surface of the pure PIM-1 thin-film membrane is smooth and has no features except one chosen for focusing purposes, which would indicate the

presence of defects in the selective layer (Figure 4.1.5.4a). An increase in the loading amount of GO and its modifications in PIM-1 changes the appearance of the membrane surface (Figure 4.1.5.4c-g). At 76 wt.% and 84 wt.% solution loadings of GO (Figure 4.1.5.4f and 4.1.5.4g) agglomerated GO particles were observed. Since no visible breaks between the polymer and filler particles up to a solution loading of 50 wt.% can be observed, and one can assume that PIM-1 has good adhesion to graphene oxide and that the filler is relatively evenly distributed along the membrane surface. However, to really know about the homogeneity of the filler distribution within the polymer matrix, also the cross-section of the membranes was investigated.



Figure 4.1.5.4. Surface and cross-sectional SEM images of pure PIM-1 and GOincorporated PIM-1 mixed matrix membranes.

In Figure 4.1.5.4h-l, the cross-sectional morphologies of the prepared TFC membranes are shown. The images demonstrate that with the increase of the GO loading, the agglomeration of the particles starts.

The image of the TFC membrane having a pure PIM-1 selective layer demonstrates that the procedure implemented for coating on porous support gave a uniform layer of polymer with a thickness of ca. 200 nm using a polymer solution with 50 wt.% of concentration. At 9 wt.% of filler in the solution (9 wt.% to GO/polymer composition) GO particles are oriented along the membrane surface, which is expected due to the presence of shear force applied to the forming selective layer

during TFC membrane preparation. A competing additional force orienting the particles parallel to the membrane surface may arise from a strong suction of the solvent into the porous support by capillary force resulting in a complete wetting of the porous PAN sublayer. However, due to the high molecular weight of PIM-1, no significant penetration of polymer into the PAN pores was observed, as it can be seen by a border line between the continuous polymer layer and porous substrate in the SEM images of pure PIM-1 and PIM-1 with 9 wt.% of GO. At filler concentrations higher than 50 wt.% loading of GO, strong agglomerations of particles were observed with voids within the graphene agglomerates, which were not filled with the polymer. The presence of voids had led to the Knudsen type of gas flow through the membrane at filler loadings of \geq 50 wt.%.

Figure 4.1.5.5 demonstrates that the permeance of all gases decreases drastically when GO nanoparticles are incorporated into the selective layer of the TFC membrane.



Figure 4.1.5.5. Gas permeances of different gases as a function of GO-loading in PIM-1.

It can be seen that the integrity of the selective layer is lost in the case of filler loading exceeding 50 wt.%. At the same time, at filler content lower than 50 wt.%, differences in gas transport properties can be observed.

In the case of GO-containing TFC membranes, due to the presence of flat particles in the PIM-1 oriented along the membrane surface, and a significant decrease of permeances is observed already at 9 wt.% loading and the most significant permeance loss was observed for CO₂. The lowering trend is continued until filler loading 50 wt.%, and at higher loadings, the selective layer becomes strongly damaged by GO agglomerates, the permeance of all gases increases, and the selectivity doesn't differ from the Knudsen selectivity.

According to Figure 4.1.5.6, which supports Figure 4.1.5.5, the permeance loss increased in the line CH_4 - O_2 - CO_2 , meaning that "fastest" gases are the most affected. Correspondingly, the selectivity of CO_2 and O_2 over N_2 decreased with the increase of filler content in the polymer.



Figure 4.1.5.6. GO containing PIM-1 thin film composite membrane's selectivity for gas pairs.

In general, the results of the PIM-1/GO mixed-matrix membranes confirm the results of the pure GO membranes. Therefore, the oxygen functional groups strongly influence the permeance of CO₂ through the mixed-matrix membrane, and all selectivities reduce with the increase of loading. The loss of CH₄ selectivity over N₂ is approximately 20%.

4.1.6. Conclusions

The thorough analysis showed that graphene oxide layers contain a large variety of oxygen functionalities. During synthesis by an oxidation reaction, the interlayer distance increases, crystallinity decreases, the number of layers reduces, and soluble oxidative debris and gaseous products are obtained. Titration methods revealed that GO layers contain acidic surface oxygen functionalities, but the basic functional group analysis was not performed due to the possibility of experimental errors, which could arise from the π electron cloud of benzene rings. Spectroscopic tools showed that on graphene layers, there are also lactone, quinone, and ketone sites located mainly at peripheral and defect areas. The suggested structural model explains the existence of NMR peaks corresponding to lactones. The lactone groups have also been confirmed by the standardized Boehm titration method. Experiments showed that in some regions, the ketone groups are involved in keto-enol tautomerism with aromatic hydroxyl groups. Based on the obtained results, new possible structures for GO layers and for OD are implemented, the latter acting as a natural surfactant, which stabilizes GO layers in dispersions. Unlike previous structural models, our model gives answers to the remaining questions from the Lerf-Klinowski and Lee models mentioned in the summary. Experiments showed that the small amount of sulfur moiety covalently linked onto the graphene oxide surface is organosulfate, which is negligible for the proposed GO model. The proposed model does not abate the importance of the Lerf-Klinowski model; however, our model makes corrections on the weak points of the formerly proposed structure models. The newly proposed structure may be interesting for those researchers who work on graphene synthesis and functionalization and, moreover, for material scientists in order to prepare new types of composite materials.

Gas adsorption experiments showed that due to the presence of the oxygen functionalities, GO adsorbs CO₂ much higher than other tested gases. The experiments showed that the adsorption of methane, oxygen, and nitrogen is negative, indicating there is no interaction between GO layers and those gases. These support the results of the GO membranes cast on microporous PAN support. Such kinds of membranes work as a molecular-sieving membrane, and regarding the sizes of the gas molecules, they can be selectively separated. The investigations showed that GO membranes could be used for the separation of hydrogen from CO₂ surpassing the 2008 Robeson upper bound for polymeric membranes. The pristine GO acts as an

effective barrier material for single gas transport through the PIM-1/GO selective layer with both permeance and ideal selectivity decreasing with an increase of the GO loading. The PIM-1/GO TFC membranes with the filler loading 76 and 84 wt.% have shown low gas permeance, indicating that GO can be aligned along the membrane surface under the influence of forces available during the casting solution penetration into the porous support.

4.1.7. References

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4.2. Chemical modification of graphene oxide and their use as fillers in PIM-1 mixed matrix membranes

4.2.1. Summary

In subchapter 4.1, information about graphene oxide and its effect on gas separation as the pure GO membranes and PIM-1 mixed-matrix membranes were investigated. This part of the chapter focuses on chemical modification of GO layers with different small organic compounds that have an affinity towards O₂ and CO₂. The synthesized new GO flakes are incorporated into PIM-1, and their gas separation properties are investigated.

4.2.2. Functionalization of GO

The presence of the oxygen functionalities on GO layers opens opportunities for chemical modification in order to prepare novel graphene flakes that can be used for different purposes. Scheme 4.2.2.1 and Scheme 4.2.2.2 represent GO synthesis and its modification to GO-CI, and 1,1-bisdichlorophosphinoferrocene modified graphene oxide (GO-dClpf) and phosphochlorinated graphene oxide (PhChGO), respectively, while Scheme 4.2.2.3 describes GO-CI modification to GO-DMPPA, GO-DCIBAO and GO-AEDPPF with 2,5-dimethyl-6-phenylpyrazolo[1,5-a]-pyrimidin-7-amine (DMPPA), 4-dichlorobenzamidoxime (DCIBAO) (R_p)-1-[(1S)-(1-aminoethyl)]-2-2, and (diphenylphosphino)ferrocene (AEDPPF), respectively. The small organic modifiers are shown as illustrations, and only the bindings to the graphene oxide layers are demonstrated. The crosslinking between the layers might occur during synthesis. However, that case was excluded from the scheme descriptions for better visualization.



Scheme 4.2.2.1. Synthesis of chlorinated graphene oxide (GO-CI) via the Hummers method where (i) KMnO₄, NaNO₃, H₂SO₄, H₂O₂; (ii) SOCI₂.



Scheme 4.2.2.2. Synthesis of GO-dClpf and PhChGO from GO.



Scheme 4.2.2.3. Synthesis of GO-DMPPA, GO-AEDPPF, GO-DCIBAO from GO-CI.

Earlier reports revealed that GO contains oxygen functional groups both in basal planes and at the edges, which can undergo nucleophilic substitution reaction with *e. g.* amines [1, 2] and ferrocene [3]. In the present study, nucleophilic substitutions of graphene oxide with modified ferrocene and different amines are discussed.

The elemental composition of graphene oxide and products of its modifications were analyzed by elemental analysis, and the results are listed in Table 4.2.2.1.

Samples	Elem	ent co	ntent [wt.]%	C/O ratio	C/H ratio	C/N ratio	
Campico	С	Н	0	N		0/11 fallo		
GO	48.1	3.06	45.2	-	1.42	1.32	-	
GO-CI	53.6	2.83	-	-	-	1.59	-	
GO-DMPPA	71.5	3.44	17.0	5.73	5.61	1.74	14.6	
GO-AEDPPF	70.1	3.69	-	6.27	-	1.58	13.0	
GO-DCIBAO	71.9	3.26	18.7	5.65	5.12	1.85	14.9	
GO-dClpf	48.1	2.93	-	-	-	1.37	-	
PhChGO	54.5	2.56	-	-	-	1.79	-	

 Table 4.2.2.1.
 Elemental analysis of graphene oxide and its modifications

The elemental analysis gives information about the bulk composition of the prepared graphene-based samples. As can be seen from Table 4.2.2.1, after the synthesis, the C/O ratio for graphene oxide is 1.42, indicating a high degree of oxidation, which is accompanied by the largest interlayer spacing [4]. GO-DMPPA and GO-AEDPPF samples have a C/O ratio of 5.61 and 5.12, respectively indicating, together with the reduced oxygen content, successful grafting of amine compounds to GO sheet.

Consequently, we investigated graphite and GO by SEM and EDX analysis. The SEM images presented in Figure 4.2.2.1 show the difference in the graphite morphology before and after the oxidation process.



Figure 4.2.2.1. SEM images and EDX spectra show the morphology (left) and the detected elements (right) of graphite (up) and GO particles (down)

The EDX analysis (Figure 4.2.2.1) confirmed the change in the elemental composition of the graphite after its modification to GO. An increase in oxygen amount indicates the successful oxidation process.

Chemical modification and successful grafting of different compounds on GO were evaluated by spectroscopic methods such as FTIR, UV-Vis, and Raman spectroscopy. Figure 4.2.2.2 shows the FTIR spectra of GO, chlorinated GO, and chemically modified GO that provides information about chemical interactions between GO and other chemical compounds. The FTIR spectrum of graphite (Figure 4.2.2.2) appears flat and featureless in the IR region. Pristine GO showed major FTIR stretching vibrations at 3000-3700, 1725, 1628, 1226 and 1055 cm⁻¹ corresponding to the intermolecularly bonded -OH stretching vibrations of the hydroxyl group, -C=O stretching (-COOH group), unoxidized graphitic domains, C-O stretching (-COOH group) and C-O-C oxirane stretching (epoxy group) vibrations, respectively (Figure 4.2.2.2). After thionyl chloride treatment, the carboxylic sites of GO were converted to acid chlorides. This was indicated by peak shifts on the FTIR spectrum and almost disappearing of the broad peak at 3000-3700 cm⁻¹. Thus, the band representing -C=O stretching vibrations shifts from 1725 to 1717 cm⁻¹ indicating the negative inductive effect of the chlorine atom in -COCI group and the presence of quinones [5, 6], which results in vacancy defects [7] formation on GO sheet. A new band at around 1800 cm⁻ ¹ shows the reaction between –COOH and SOCl₂. Transmittance bands at 1210 cm⁻¹ and 717 cm⁻¹ describe the C-O stretching vibrations in –COCI group and C-CI formation in GO, respectively. However, stretching vibrations from C-O-C at 1050 cm⁻¹ are still observed.



Figure 4.2.2.2. FTIR spectra of GO and its modifications. Curves are shifted vertically for better clarity.

Compared to pristine GO and GO-CI, amine and imine-modified GO (GO-DMPPA, GO-AEDPPF, and GO-DCIBAO) showed the new peaks between 1500 and 1650 cm⁻¹ corresponding to reaction products between GO and amine, and imine compounds. The appearance of peaks at around 1560 cm⁻¹ shows N-H bending vibrations in –CONH group, and at 1240 cm⁻¹ represents C-N stretching (grafting to an aromatic ring). This confirms amide linkages during grafting. A slight broad peak at 3200-3600 cm⁻¹ belongs to N-H stretching vibrations, while peaks at 1700, 1717, and 1734 cm⁻¹ show the presence of quinones and lactones.

When it comes to GO-dClpf and PhChGO, stretching vibrations for the C-O-P group (connected to aromatic rings) are at 1054 cm⁻¹. The peak at 644 cm⁻¹ indicates P-Cl stretching vibration, while the peak at 1232 cm⁻¹ shows P=O stretching vibration describing the presence of –OH groups in phosphorus moiety.

Figure 4.2.2.3 depicts the UV-Vis spectra of GO and its modifications. π - π^* transition of carbonyl group was observed between ~190 and ~200 nm, while n- π^* transition of this group can be seen at ~265 and ~273 nm in GO and its modifications. The absorption peak at around ~248 nm attributes to the π - π^* transition of C=C bonds from an original graphitic structure. The range ~295-310 nm observed in UV-Vis

measurements is assigned to the n- π^* transitions due to the presence of C-O-C and C-O-P linkages (Figure 4.2.2.3).



Figure 4.2.2.3. UV-Vis absorption spectra of GO and its modifications. The whole spectra (b) for GO modifications were shown to describe the differences between the GO-like particles.

As a powerful technique, Raman spectroscopy was used for the characterization of sp^3 and sp^2 hybridization of the carbon atoms and examination of ordered vs. disordered crystal structures [8]. The Raman spectra of GO and its modifications display (Figure 4.2.2.4) the D-bands at ~1340 and ~1350 cm⁻¹, characteristic Lorentzian G-band at ~1580 and ~1585 cm⁻¹, and 2D-peaks at ~2700 cm⁻¹. The data are summarized in Table 4.2.2.2.

Sample	Ram				
Gample	D-band G-band		2D-band	10110	
Graphite	1359	1578	2713	-	
Graphene oxide	1342	1584	-	~0.92	
GO-CI	1340	1580	-	~0.96	
GO-AEDPPF	1350	1588	-	~1.02	
GO-DMPPPA	1346	1580	-	~1.05	
GO-DCIBAO	1342	1584	-	~1.12	
GO-dClpf	1352	1582	-	~0.99	
PhChGO	1340	1580	-	~0.94	

Table 4.2.2.2. Raman spectroscopy results of GO and its modifications

The D-band is attributed to local defects and disorders, while G-band assigned to the E_{2g} phonon of carbon sp^2 atoms of graphite lattice. The 2D-band gives information about the layers of graphene [8]. However, the 2D band of monolayer graphene shows a single sharp peak. The ratio of intensities of the D and G bands is often used for determining the number of layers: I_D/I_G for all samples was ~1, indicating that GO layers are multilayer (Figure 4.2.2.4).



Figure 4.2.2.4. Raman spectra of: a) Graphite, GO and GO-DCIBAO; b) GO-CI, GO-dClpf and GO-AEDPPF, and c) GO-DMPPA and PhChGO.

In order to investigate the thermal stability of GO and its modifications, the thermogravimetric analysis was carried out (Figure 4.2.2.5).



Figure 4.2.2.5. Thermogravimetric analysis results of modified GO samples. "GO iso" is the graphene oxide sample heated up to 125 °C and kept at this temperature for 30 minutes in argon flow at 10 K min⁻¹.

The pristine GO degraded in two main steps. The first step (25-140 °C) of 15% weight loss can be explained by the evaporation of absorbed water. Similar behavior is found for GO-CI with the weight loss of 6%, GO-AEDPPF - 2%, GO-DMPPPA - 1%, GO-DCIBAO, and GO-dClpf - 7%, and PhChGO - 11%. A further major weight loss of about 33% occurs in the temperature range 140-350 °C and corresponds to the decomposition of labile oxygen-containing functionalities. Grafting of amine and imines increased the thermal stability of GO in the temperature range of 200-500 °C [1]. The weight loss for these GO modifications is hovering around 35%. The major weight losses for GO-Cl, GO-dClpf, and PhChGO are seen in the second step: 100-240 °C for GO-Cl by 28%, 120-360 °C for GO-dClpf by 32% and 150-280 °C for PhChGO by 25%. The lower weight loss below 100 °C of modified GO indicates an enhanced hydrophobicity, which minimizes the amount of absorbed water in comparison with pristine GO.

Figure 4.2.2.6 shows the SEM images of GO and its modified derivatives. After functionalization, the morphology of graphene (Figure 4.2.2.6) was changed significantly, and it should be mentioned that the morphology of the graphene sheets observed by SEM is not planar. This observation is important for the formation of a thin

film composite membrane where a selective layer is often in the range of 100 nm [9]. In this procedure, graphene oxide layers can wrinkle in the polymer matrix under the shear forces and hinder the gas transport. The SEM images of modified graphene oxide samples show that their morphology is not plane, which gives us information that these modifications can resist the aforementioned forces.



Figure 4.2.2.6. SEM images of: a) GO, b) GO-CI, c) GO-DMPPA, d) GO-AEDPPF, e) GO-dClpf, f) GO-DCIBAO, and g) PhChGO.

4.2.3. Gas transport performances of functionalized graphene oxide (FGO)-incorporated thin-film composite membranes

Pure gas permeances of TFC membranes for CH₄, N₂, O₂, and CO₂ with pure PIM-1 and PIM-1 containing FGO, such as PIM-1/GO-AEDPPF and PIM-1/GO-DCIBAO were determined at 30 °C on the home-built gas permeation facility. The data of single gas permeance and ideal selectivity calculation were conducted with the same technique used for the PIM-1/GO thin-film composite membranes. The permeance results for the PIM-1/FGO TFCM are shown in Table 4.2.3.1 along with the comparison of the achieved results of state-of-the-art polymer membranes, while selectivities are described in Table 4.2.3.2.

Table 4.2.3.1. Permeance for the FGO-containing PIM-1 TFC membranes and the gaspermeance comparison with the state-of-the-art membranes.

Membrane	Filler	Wt.%	Permeance, m ³ (STP)m ⁻² h ⁻¹ bar ⁻¹				
code	Filler	filler	N2	CH4	CO ₂	O 2	Rei.
MP-MMM ³	PEG- PEI-GO	10	11.0	30.0	1330	-	[10]
PEBAX-ImGO ³	ImGO	0.8	0.72	3.00	76.2	-	[11]
PebaxMH1657-	NIPAM-	5	8 10	16.2	567	_	[12]
NIPAM-CNTs ³	CNTs	0	0.10	10.2	007		ניבו
PIM-1	_	_	0.52	0.83	11.04	1.69	
			± 0.16	± 0.03	± 0.34	± 0.05	
PIM1-9GO-		Q	0.18	0.26	4.55	0.83	
AEDPPF	GO-	9	± 0.02	± 0.03	± 0.51	± 0.1	
PIM1-33GO-		22	0.17	0.25	3.3	0.64	
AEDPPF		33	± 0.005	± 0.007	± 0.25	± 0.03	
PIM1-50GO-		50	0.83	1.13	3.43	1.2	
AEDPPF	AEDPPF	50	± 0.17	± 0.23	± 0.66	± 0.23	
PIM1-76GO-		70	30.98	44 . 44	26.85	29.1	
AEDPPF		76	± 10.58	41 ± 14	± 6.84	± 9.58	
PIM1-84GO-		0.4	63.58	85.12	49.13	59.22	This
AEDPPF		04	± 10.38	± 14.39	± 7.56	± 9.45	work
PIM1-9GO-		0	0.38	0.61	8.17	1.41	
DCIBAO		9	± 0.01	± 0.02	± 0.25	± 0.05	
PIM1-33GO-		22	0.39	0.62	8.16	1.41	
DCIBAO		33	± 0.02	± 0.04	± 0.3	± 0.07	
PIM1-50GO-	GO-	50	2.11	2.85	5.74	2.52	
DCIBAO	DCIBAO	50	± 0.57	± 0.65	± 1.07	± 0.51	
PIM1-76GO-		76	103.77	141	75.42	96.1	
DCIBAO		10	± 11.62	± 23.44	± 7.59	± 13.34	
PIM1-84GO-		0 /	127.52	176.65	97.22	118.74	
DCIBAO		04	± 2.85	± 2.5	± 0.93	± 3.23	

³ The permeability is shown in Barrer (1 Barrer= 10^{-10} cm³ (STP) cm⁻² s⁻¹ cm⁻¹ Hg).

Membrane	Filler	Wt.%					
Code	Filler	filler	O ₂ /N ₂	CH4/N2	CO ₂ /N ₂	CO ₂ /CH ₄	Ref.
MP-MMM	PEG- PEI-GO	10	-	2.7	121	44.0	[10]
PEBAX-ImGO	ImGO	0.8	-	4.2	106	25.4	[11]
PebaxMH1657- NIPAM-CNTs	NIPAM- CNTs	5	-	2.0	70	35.0	[12]
DIM 1			3.26	1.61	21.3	13.2	
F IIVI- I	-	-	± 0.02	± 0.01	± 0.02	± 0.02	
PIM1-9GO-		0	4.70	1.49	25.9	17.4	
AEDPPF		9	± 0.06	± 0.02	± 0.35	± 0.03	
PIM1-33GO-			3.86	1.49	19.7	13.2	
AEDPPF		33	± 0.14	± 0.01	± 1.24	± 0.02	
PIM1-50GO-	GO-	50	1.44	1.35	4.13	3.06	
AEDPPF	AEDPPF	50	± 0.04	± 0.01	± 0.24	± 0.12	
PIM1-76GO-		76	0.95	1.33	0.87	0.65	
AEDPPF		70	± 0.02	± 0.005	± 0.08	± 0.04	
PIM1-84GO-		84	0.93	1.34	0.77	0.58	This
AEDPPF		04	± 0.91	± 1.39	± 0.73	± 0.53	work
PIM1-9GO-		0	3.74	1.61	21.7	13.5	
DCIBAO		9	± 0.03	± 0.04	± 0.15	± 0.01	
PIM1-33GO-		22	3.63	1.59	21.1	13.3	
DCIBAO		33	± 0.06	± 0.05	± 0.45	± 0.03	
PIM1-50GO-	GO-	50	1.21	1.36	2.79	2.05	
DCIBAO	DCIBAO	50	± 0.07	± 0.03	± 0.54	± 0.29	
PIM1-76GO-		76	0.71	1.05	0.74	0.7	
DCIBAO		10	± 0.03	± 0.09	± 0.02	± 0.06	
PIM1-84GO-		<u>8</u> 1	0.93	1.39	0.76	0.55	
DCIBAO		04	± 1.13	± 0.88	± 0.33	± 0.37	

 Table 4.2.3.2.
 Selectivity for the graphene containing PIM-1 TFC membranes.

In comparison to the GO, GO-AEDPPF nanosheets influenced diversely the gas transport properties of MMM. In this case, gas permeances were at the lowest point at already 33 wt.% loading and remained at approximately the same value up to 50 wt.%. Above 50 wt.% filler content, the integrity of the selective layer was lost, and permeances of all gases increased tremendously due to the presence of non-selective defects as it is shown in Figure 4.2.3.1.



Figure 4.2.3.1. Gas permeances of different gases as a function of GO-AEDPPF-loading in PIM-1.

At 9 wt.% as well as at 33 wt.% loadings of $(R_p)-1-[(1S)-(1-Aminoethyl)]-2-$ (diphenylphosphino) ferrocene modified graphene oxide (GO-AEDPPF), selectivities of carbon dioxide and oxygen over nitrogen were higher than those of the pure PIM-1 membrane, which indicates a better interaction of the GO-AEDPPF with PIM-1 (Figure 4.2.3.2).



Figure 4.2.3.2. GO-AEDPPF containing PIM-1 thin film composite membrane's selectivity for gas pairs.

It was revealed that 2,4-dichlorobenzamidoxime containing graphene oxide (GO-DCIBAO) showed the same performance as it was found in the GO-AEDPPF case (Figure 4.2.3.3).



Figure 4.2.3.3. Gas permeances of different gases as a function of GO-DCIBAOloading in PIM-1.

The incorporation of 9 wt.% GO-DCIBAO decreased the gas transport through the PIM-1 based selective layer, and it stood at the same level up to 33 wt.% loading (Table 4.2.3.1). The selectivities of CO_2 and O_2 over N_2 were lower at these GO-

DCIBAO loadings when compared with the results for the GO-AEDPPF containing membranes and were almost the same as in pure PIM-1 membrane (Figure 4.2.3.4).



Figure 4.2.3.4. GO-DCIBAO containing PIM-1 thin film composite membrane's selectivity for gas pairs

An increase in permeance above 33 wt.% loading can be explained by loose aggregation of modified graphene oxide nanosheets that allow permeating gaseous molecules without any hindrance.

Figure 4.2.3.1 and Figure 4.2.3.3 prove that up to 33 wt.% incorporation permeance performance for all gases was leveled off at the same point after 9 wt.% loading. An increase in permeance above 33 wt.% loading for methane, oxygen, and nitrogen can be explained by the influence of defects on the modified graphene oxide monolayers. The increase above 50 wt.% indicates the aggregation of nanosheets.



Figure 4.2.3.5. Effect of different FGOs incorporation on permeance and selectivity of MMMs.

Figure 4.2.3.5 shows the effect of nanoparticle loading on CO₂ permeance and CO₂/N₂ selectivity for three types of MMMs. The effect of the GO modification on the membrane performance when the selective layer is loaded with more than 50 wt.% of filler can be observed. The GO nanoparticles appear to have a strong agglomeration tendency accompanied by the ability of these particles to effectively cover the surface of the membrane, creating an effective barrier for gas transport, when compared to the other two compounds resulting in mostly non-changing CO₂ permeance at 50 wt.% and 84 wt.% loadings. The GO-AEDPPF and especially GO-DCIBAO containing membranes showed a strong permeance increase at 76 and 84 wt.% loadings indicating properties of the modified GO particles much different from the properties of pure GO. The modification of GO with AEDPPF and DCIBAO lead to improved particle affinity toward the PIM-1 matrix at a particle content below 50 wt.% and to high permeances at 76 and 84 wt.% loadings. Taking into account low permeance of the GO containing PIM-1 TFC membrane at 84 wt.% GO loading and high permeances of both other membranes one can conclude that modification of the GO with bulky functional groups able to increase polymer-filler compatibility at low filler loadings can change the rigidity of the graphene sheets, which prevents effective alignment of particles along the membrane surface at the chosen conditions of TFC membrane preparation.

4.2.4. Conclusions

In this study, different functionalizing agents were grafted onto graphene sheets. By EDX and elemental analysis, elemental compositions of the samples are confirmed. Thermogravimetric analysis revealed that the grafting of amines and imines on graphene sheets increased their thermal stability. Raman investigations showed that functionalization leads to multilayer flakes formation. TFC mixed matrix membranes containing PIM-1 as a matrix polymer and three different graphene-based fillers synthesized in the course of the current work have demonstrated the difference of filler materials properties. Gas transport properties of the GO embedded into the PIM-1 matrix differ a lot from properties of the GO-AEDPPF and GO-DCIBAO, which have good compatibility to the PIM-1 at 9 and 33 wt.% loading and the MMMs show ideal selectivities overpassing those of the pure PIM-1 TFC membrane. When the loading of these two GO fillers is above 50 wt.% the TFC membranes show a significant increase of the permeance compared to GO-PIM-1 MMM, indicating that the PIM-1 polymer matrix and shear forces occurring during the membrane formation are not able to effectively align these particles along the membrane surface. The observation of high permeance, which is similar to the permeance of the porous PAN membrane, has lead us to the conclusion that the introduction of large amounts of bulky functional groups onto the surface of graphene sheets is leading to increase of the graphene rigidity.

4.2.5. References

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4.3. Surface-initiated atom transfer radical polymerization from GO and their use for membrane distillation

4.3.1. Summary

In this subchapter, graphene oxide is functionalized with poly (2diethylaminoethyl) methacrylate (PDEAEMA), and the resulting material is used as a selective layer of a thin-film composite membrane (TFCM). The polymer synthesis is carried out by surface-initiated atom transfer radical polymerization (SI-ATRP) from both the bulk and the single-layer graphene oxide (GO). The obtained membranes are utilized for gas and water vapor transport experiments in a wide temperature range. The water vapor permeability coefficient for the investigated materials is up to 4500 Barrer and the increase threefold when the amine groups of the membrane are quaternized. The high permeance and selectivity for water vapor make this type of thinfilm composite membranes a potential candidate for membrane distillation. The usage of the single-layer surface-initiator functionalized graphene oxide for polymerization of different monomers is a promising approach to prepare polymer brushes at the nanoconfined level.

4.3.1. Synthesis of surface-initiator functionalized graphene oxide nanosheets (SI-GO)

In the first step, the hydroxyl groups of graphene oxide layers were modified with 2-bromopropionyl bromide for the preparation of surface-initiator functionalized graphene oxide (SI-GO) layers (Figure 4.3.1.1), and the structure was confirmed by FTIR and MAS-NMR spectroscopies (Figure 4.3.1.2 and Figure 4.3.1.3). Figure 4.3.1.2 shows the FTIR spectra of the surface-initiator functionalized graphene oxide layers.



Figure 4.3.1.1. Synthesis of surface-initiator functionalized graphene oxide (SI-GO). GO means graphene oxide, while BPrB attributes to 2-bromopropionyl bromide.



Figure 4.3.1.2. FTIR spectra of SI-GO in comparison with GO.

As it can be seen from Figure 4.3.1.2, after functionalization with 2bromopropionyl bromide stretching vibrations of hydroxyl groups disappear and two alkane C-H stretching vibrations appear at 2975 and 2913 cm⁻¹. These were attributed to the $-CH_3$ and -CH groups of the 2-bromopropionyl bromide moiety covalently attached to the graphene oxide layers. The peak at 1724 cm⁻¹ corresponds to carbonyl groups of both graphene oxide, indicating the presence of carboxyl, ketone, quinone, and six-membered lactone functional groups and initiator moieties. Stretching vibration of conjugated benzene rings is observed at 1560 cm⁻¹. The -OH bending and C-O stretching vibrations from the -COOH group were observed at 1441 or 1379 cm⁻¹ and 1201 cm⁻¹, respectively. The peak at 1058 cm⁻¹ is corresponding to the epoxy group (C-O-C) stretching vibrations and is much broader than that of pristine graphene oxide.

¹³C MAS NMR (Figure 4.3.1.2) confirmed the successful modification of graphene oxide into surface-initiator functionalized graphene oxide nanoparticles. A broad peak at ~175 ppm belongs to carbonyl groups of graphene surface functionalities and initiator moieties. The peak at ~6 ppm was attributed to -CH₃ groups of initiator moieties (Figure 4.3.1.2), which confirmed the attachment of initiator moieties to the graphene.



Figure 4.3.1.3. ¹³C MAS NMR spectra of SI-GO.

EDX analysis showed that 2-bromoisopropionyl bromide moieties were attached to the graphene surface after chemical reaction (Figure 4.3.1.4). A characteristic band for bromine atoms is visible in Figure 4.3.1.4.



Figure 4.3.1.4. EDX spectrum of SI-GO particles.

4.3.2. SI-ATRP polymer functionalization of graphene oxide

The surface-initiated poly(2-diethylaminoethyl methacrylate) (SI-PDEAEMA) polymers were prepared using the SI-ATRP method, and the standard polymerization procedure is shown in Figure 4.3.2.1.



Figure 4.3.2.1. Schematic representation of 2-diethylaminoethyl methacrylate polymerization by surface-initiator functionalized graphene oxide. SI-GO indicates surface-initiator functionalized graphene oxide, DEAEMA represents 2-diethylaminoethyl methacrylate, and SI-PDEAEMA describes surface-initiated poly(2-diethylaminoethyl methacrylate).

The SI-PDEAEMA polymers were prepared using varying concentrations of SI-GO with respect to monomer weight and varying the volumes of the exfoliated SI-GO dispersions in DMF with the polymerization scheme described in Figure 4.3.2.1.

Since 2-diethylaminoethyl methacrylate (DEAEMA) is a CO₂-triggered monomer [1], our idea was to synthesize a polymer-graphene nanocomposite with an affinity toward carbon dioxide. For this purpose, two synthesis methods were utilized for the synthesis of poly(2-diethylaminoethyl methacrylate) (PDEAEMA) using the surface-initiated atom transfer radical polymerization (SI-ATRP) technique: a) the use of "bulk" SI-GO particles and b) exfoliated SI-GO dispersions in DMF. The composition and the characteristics of the polymers synthesized are given in Table 4.3.2.1.

Table 4.3.2.1. Composition and characteristics of PDEAEMA nanocompositessynthesized via SI-ATRP and conventional ATRP.

	SI-GO	Exfoliated		
Sample name	content	SI-GO	Conversion,	dMbpy:CuBr
Sample name	w/f 0/	content,	%	ampy.cabi
	WL.70	mL		
PDEAEMA ^{a)}	-	-	0.50	1:1
SI-PDEAEMA_GO_0.2	0.2	-	1.80	1:1
SI-PDEAEMA_GO_0.4	0.4	-	11.8	1:1
SI-PDEAEMA_GO_0.6	0.6	-	41.1	1:1
SI-PDEAEMA_GO_0.8	0.8	-	25.8	1:1
SI-PDEAEMA_GO_1	1	-	-	1:1
SI-		0.25		1.1
PDEAEMA_exf.GO_0.25	-	0.23	-	1.1
SI-	_	0.50	8 60	1.1
PDEAEMA_exf.GO_0.5	-	0.50	8.00	1.1
SI-	_	0.75	21.0	1.1
PDEAEMA_exf.GO_0.75	-	0.75	21.9	1.1
SI-	_	1 00	24.0	1.1
PDEAEMA_exf.GO_1	-	1.00	24.0	1.1
SI-	_	2.00	9.00	1.1
PDEAEMA_exf.GO_2 ^{b)}	-	2.00	9.00	1.1

Note: PDEAEMA – poly(2-diethylaminoethyl methacrylate); SI-PDEAEMA – surfaceinitiated poly(2-diethylaminoethyl methacrylate); dMbpy - 4,4'-dimethyl-2,2'-dipyridyl; ^{a)} = 2-diethylaminoethyl methacrylate was polymerized using 10 μ L 2-bromoisobutyryl bromide via ATRP; ^{b)} = this polymerization took 5 days.

Table 4.3.2.1 shows that during the polymerization of DEAEMA at the given conditions, the monomer conversion systematically increases with the increase of SI-GO contents (both bulk and exfoliated). The highest conversion of nearly 40% is achieved using 0.6 wt.% SI-GO initiator in SI-PDEAEMA_GO_0.6 compared to the 24% conversion for SI-PDEAEMA-exf.GO_1, even though both results are much higher than those for PDEAEMA homopolymer synthesized via the ATRP method. The

obtained 24% conversion degree is the best rate for the exfoliated samples. Interestingly, after 0.6 wt.% addition of SI-GO, the conversion of the monomer decreases, and when 1 wt.% SI-GO was added into the reaction, the precipitation of the synthesized polymer was impossible. This was attributed to the hydrophobic nature of SI-GO, implying that during the reaction, the initiator became less efficient with the catalyst-monomer complex [2], which needs to be investigated further.

When it comes to the exfoliated SI-GO dispersions used as initiators with the low concentration of the exfoliated SI-GO (0.25 mL), the polymerization did not occur. It is explained by the low amount of initiator centers in the used SI-GO dispersion. When high amounts of the exfoliated SI-GO dispersions between 0.5 and 2 mL were used, polymerization was successfully accomplished. In the case of the SI-PDEAEMA_exf.GO_0.5 sample, it was not possible to dissolve the synthesized polymer, a gel is formed when further diluted with THF. However, the other samples are completely soluble either in THF or in CHCl₃. The polymerization of SI-PDEAEMA_exf.GO_2 (2 mL exfoliated SI-GO dispersion was used during polymerization) sample was conducted within 5 days, suggesting that with the increase of the volume of the SI-GO dispersion, the initiator becomes inefficient and the possibility of polymer crosslinking increases.

For the molecular weight determination, the polymer chains were cleaved from the SI-GO surfaces. The cleavage was achieved by the attack of NaOH to the carbonyl bonds formed between graphene oxide layers and the polymer chains. For this purpose, the polymer solution was mixed with NaOH solution in a THF/water mixture. Unfortunately, this method did not work for SI-PDEAEMA_GO_X samples. It seems that during the cleavage procedure, the carbonyl groups of the side chains also degrade [3]. In the case of SI-PDEAEMA_exf.GO_X samples, the cleavage procedure was possible in the samples that were soluble in THF. The molecular weight of the synthesized polymer from 0.75 mL exfoliated SI-GO dispersion (used as an initiator) was $M_w = 39500 \text{ g}\cdot\text{mol}^{-1}$ with a dispersity index of 1.25. The obtained SI-PDEAEMA_exf.GO_1 polymer is not soluble in THF; therefore, the sample was completely dissolved in CHCl₃, and the cleavage reaction was conducted. The molecular weight of the cleaved polymer from SI-PDEAEMA_exf.GO_1 was $M_w =$ 39400 g·mol⁻¹ with a dispersity index of 1.20. This data confirms that the usage of the exfoliated SI-GO dispersions is a new approach in terms of controlled polymerization. Thus, the controlled nature of the SI-ATRP is confirmed. However, further experiments are required to understand the kinetics of the polymerization. In Figure 4.3.2.2, the SEC results for SI-PDEAEMA_exf.GO_0.75 and SI-PDEAEMA_exf.GO_1 is shown.



Figure 4.3.2.2. SEC chromatograms for SI-PDEAEMA_exf.GO_0.75 and SI-PDEAEMA_exf.GO_1 samples.

The structural characterization of the synthesized compounds using FTIR showed a sharp increase of stretching vibrations for C-H and $-CH_2$ between 2727 and 2967 cm⁻¹ compared to the FTIR spectra of the SI-GO particles (Figure 4.3.1.2). A sharp peak at 1725 cm⁻¹ represents the increase of the carbonyl group content, which can be attributed to the side chains of the synthesized polymers. C-H bending vibration of $-CH_3$ is observed at 1450 and 1384 cm⁻¹. The peaks at 1264 and 1146 cm⁻¹ correspond to the C=O stretching vibration of carbonyl groups. The C-N stretching vibration is seen at 1066 and 1022 cm⁻¹. The C-Br stretching vibration of the unreacted initiator moiety is at 750 cm⁻¹ (Figure 4.3.2.3). The results for other polymers are similar.



Figure 4.3.2.3. FTIR spectra for SI-PDEAEMA_GO_0.6 and SI-PDEAEMA_exf.GO_0.75 polymers.

The FTIR analysis (Figure 4.3.2.4) showed that after quaternization, the spectrum has changed, and additional peaks appear. The peak at 3450 cm⁻¹ is attributed to the intermolecular bonded –OH stretching vibration, where some methanol molecules are entrapped in the membrane, and it was impossible to remove them via overnight vacuum drying process. Amine salt formation at 2981 cm⁻¹ confirms the quaternization procedure. The deformation vibration of the amine group is visible at 1625 cm⁻¹, while the peak at 1400 cm⁻¹ reveals the formation of amine salts. The C-I stretching vibration is detected at 500 cm⁻¹.



Figure 4.3.2.4. FTIR spectra for SI-PDEAEMA_exf.GO_0.75 and quaternized SI-PDEAEMA_exf.GO_0.75 on PAN support.

To further confirm the structure of the polymers, ¹H- and ¹³C-NMR spectra were recorded for the soluble polymers (Figure 4.3.2.5 and Figure 4.3.2.6). Solid-state NMR was applied to confirm the structure of the "bulk" polymers (Figure 4.3.2.7).



Figure 4.3.2.5. ¹H-NMR spectra of the samples: a) SI-PDEAEMA_exf.GO_0.75 and b) SI-PDEAEMA_exf.GO_1.



Figure 4.3.2.6. ¹³C-NMR spectra of the samples: a) SI-PDEAEMA_exf.GO_0.75 and b) SI-PDEAEMA_exf.GO_1.


Figure 4.3.2.7. ¹³C CP MAS NMR analysis of the SI-PDEAEMA_GO_0.6 sample.

Figure 4.3.2.5a and Figure 4.3.2.5b show ¹H-NMR spectra for the SI-PDEAEMA_exf.GO_0.75 and SI-PDEAEMA_exf.GO_1 polymers, respectively. As can be seen from Figure 4.3.2.5 and Figure 4.3.2.6, a sharp peak at 1.00 ppm belongs to the side chain –CH₃ groups, while backbone –CH₃ groups are located between 1.00 and 1.5 ppm. The chemical shift at ~2 ppm belongs to the main chain –CH₂ groups, while side chain –CH₂ group of ethyl radical is at ~2.5 ppm. The characteristic resonance signal at ~4.0 ppm corresponds to the –OCH₂ groups. In addition, ¹³C-NMR spectra (Figure 4.3.2.6) showed that the SI-PDEAEMA_exf.GO_0.75 sample has a characteristic band for the C=C bond. The other polymers did not show the characteristic band for that double bond. This is explained by the assumption that the samples are in the cross-linked form (SI-PDEAEMA_exf.GO_0.5) or that termination occurred by the combination mechanism (SI-PDEAEMA_exf.GO_1 and SI-PDEAEMA_exf.GO_2).

Solid-state ¹³C CP MAS NMR analysis (Figure 4.3.2.7) shows signals of COO groups at ~176 ppm. The sharp peaks at ~50 and ~10 ppm belong to $-CH_2$ and $-CH_3$ groups of the N-CH₂CH₃ side chains, respectively. Signals at ~55 and ~65 ppm can be attributed to the $-CH_2$ groups attached to the nitrogen atom and carboxyl moiety of the side chain of the polymer, respectively. The $-CH_2$ and C (quaternary) of the main polymer chain yield signals are between ~45 and ~50 ppm. Solution and solid-state NMR results confirm the structure of polymeric methacrylate, demonstrating that the

polymerization was successful both on the single-layer exfoliated SI-GO and on bulky SI-GO particles. The ¹³C-NMR analysis is an excellent technique for the stereochemistry of the polymers. A peak at ~52 ppm shows that the polymer has isotacticity [4].

TGA results for the synthesized polymer, SI-GO, and GO nanoparticles are shown in Figure 4.3.2.8. There are two degradation steps for both SI-GO nanoparticles and SIPs; however, the weight loss of these systems occurs at significantly different temperatures. The curve of SI-GO shows that the synthesized surface-initiator functionalized nanoparticles are stable in the temperature range of 30-100 °C above, in which the pure GO starts to lose its weight. The first degradation step between 100 and 200 °C in an amount of ~25% corresponds to the elimination of 2bromoisopropionyl bromide moieties from GO layers and the evolution of carbon dioxide and carbon monoxide from lactone and carboxyl groups of the layers themselves. This step is followed by another degradation step with ~25% mass loss accompanied by the degradation of other oxygen functional groups such as guinone and ketone groups of the GO layers. Unlike GO and SI-GO, the synthesized polymers are stable up to 250 °C, meaning that GO layers are covered by polymer chains, which increases the thermal stability. The first weight loss occurs at 250-350 °C, with ~60% weight loss. The TGA curve at this step for the polymers has a steep decline, which can be attributed to the degradation of polymer's side chains. The second step is between 350 and 450 °C, with around 38% mass loss corresponding to the main chain destruction. The degradation of the oxygen functional groups of SI-GO coincides with the degradation of polymer chains, and it was not possible to differentiate.



Figure 4.3.2.8. Thermogravimetric analysis results of the synthesized polymer nanocomposites between 25 and 800 °C under argon flow at 5 K min⁻¹.

To support this interpretation, TGA-FTIR analysis was conducted, and the eliminated gaseous compounds were analyzed (Figure 4.3.2.9). The experiments strongly support the idea that degradation starts from the side chains. The strong C-H stretching vibrations for the side chain –CH₃ groups are recorded between 2820 and 2975 cm⁻¹. The peak at 1740 cm⁻¹ belongs to the C=O stretch vibration of methylformate, a possible degradation product of the polymer side chain. The experiment showed that during this degradation step, the bromine groups of the polymer end functionalities are eliminated, and the peaks at 1204 cm⁻¹ and 1164 cm⁻¹ correspond to the C-H wagging vibrations of CH₃Br. The C-N stretching vibration of the eliminated trimethylamine is seen at 1061 cm⁻¹.





Figure 4.3.2.9. TGA-FTIR spectra of SI-PDEAEMA_GO_0.6 (a-first degradation step, b-second degradation step) and SI-PDEAEMA_exf.GO_0.75 (c-first degradation step, d-second degradation step). The spectra with the red color correspond to our experimental results.

It was proposed that the second step is accompanied by the degradation of the main polymer chains. A small peak at 3091 cm⁻¹ is attributed to the =C-H stretching vibrations of the degraded –C=CH-Br moiety. The peaks for sp³ type C-H vibrations are smaller in intensity than that for the first degradation step, which strongly supports the interpretation as degradation of -CH₃ groups of the backbone. This method helped us to reveal that at this step, the degradation of graphene oxide layers starts. The increase of the peaks corresponding to CO₂ and CO gases suggests that those are the result of lactone, ketone, quinone, epoxy, and carboxyl group elimination. The peak for γ -lactone is at 1775 cm⁻¹, while the peak at 1748 cm⁻¹ belongs to acetaldehyde, a thermal degradation product of the unreacted mounted initiator groups. The vibrations recorded at 1721 and 1690 cm⁻¹ are the C=O stretching vibrations of carboxyl groups (Figure 4.3.2.9).

Figure 4.3.2.10 shows the water contact angle images of the exfoliated GO layers, SI-PDEAEMA_GO_0.6, and SI-PDEAEMA_exf.GO_0.75 polymer nanocomposites coated on the PAN porous membrane. The images show that the water contact angle for the exfoliated GO layers is 45°, which is smaller than the water contact angle of the porous PAN support (54°). This phenomenon can be explained by the high degree of oxygen functionality, making the graphene surface hydrophilic. In addition, pure graphene layers epitaxially grown on SiC showed a bad wettability with a water contact angle of 92° for single, bi- and multi-layer graphene [5]. For the polymer films, the contact angle is higher than for exfoliated GO, however, smaller than that of epitaxially grown graphene. Thus, a water contact angle of 80° was observed for SI-PDEAEMA_GO_0.6 and 77° for SI-PDEAEMA_exf.GO_0.75.



Figure 4.3.2.10. Images of a water droplet on a PAN membrane surface coated with exfoliated graphene oxide, SI-PDEAEMA_GO_0.6, and SI-PDEAEMA_exf.GO_0.75.

Scanning electron microscope (SEM) images show the effect of SI-GO particles on the polymerization of the DEAEMA monomer. As it can be seen in Figure 4.3.2.11, the SI-GO particles successfully polymerized DEAEMA monomer due to its surfacemounted initiator groups. In Figure 4.3.2.11c, it is clearly seen that SI-GO particles are in agglomerated form, and we suggest that the graphene layers are connected to SI-PDEAEMA polymer chains. The TEM image of the single-layer GO, and the SEM image of bulk SI-GO are shown in Figure 4.3.2.11a and Figure 4.3.2.11b, respectively. The cross-section of the membrane (Figure 4.3.2.11d) shows that the polymers cover the PAN support without significant penetration into the porous layer. Due to the atom size thickness of graphene, it is not possible to detect the polymer covered graphene layers by SEM. The image (Figure 4.3.2.11d) shows the SI-GO particles only in agglomerated form.



Figure 4.3.2.11. Electron microscopy investigation of studied materials: a) TEM image of single-layer graphene oxide (GO), b) SEM image of graphene oxide functionalized with an initiator for ATRP (SI-GO), c) SEM image of the surface and d) SEM image of the cross-section of SI-PDEAEMA_GO_0.6 polymer nanocomposite thin film coated on porous PAN support.

4.3.3. Gas transport properties of surface-initiated polymers (SIP)

Pure single gas transport performance of surface-initiated polymer (SIP) membranes for H_2O vapor, H_2 , N_2 , O_2 , and CO_2 was determined at 30 °C employing our home-build gas permeation facility. The data of single gas permeance (Table

4.3.3.1) and ideal selectivities were calculated according to the equations (3.2) and (3.3), and the permeance was calculated as an average value from at least 20 experimental points (for water vapor 150 points). The data for the ideal selectivities and the comparison of the achieved results with the different polymer membranes from the literature are shown in Table 4.3.3.2.

Table 4.3.3.1. Single gas permeability coefficients for the surface-initiated polymer

 (SIP) thin-film membranes compared to other amorphous methacrylate polymers.

Membrane	Perme	Rof					
code	H ₂ O	H ₂	N ₂	CO ₂	02	. itel.	
PMMA	-	-	0.079	1.1	0.31	[6]	
PEMA ^{a)}		24.0	0.73	15.0	3.5	[7]	
XLPEGDA	-	15.0	2.0	100	5.0	[8]	
PEGDMA	-	15.0	1.6	95.0	4.7	[9]	
PAA	-	-	1.4	1.3	1.3	[10]	
PtBMA	-	60	0.8	10.5	4.5	[11]	
PEEMA	-	-	0.40	8.56	1.45	[12]	
PDEMA	-	-	3.6	133	11.4	[12]	
SI-PDEAEMA_GO_0.6	3874	20	2	43	6		
SI-PDEAEMA_GO_0.8	4590	30	4	56	9	This work	
SI-PDEAEMA_exf.GO_0.75	3363	18	2	40	6		
SI-PDEAEMA_exf.GO_1	3158	12	1	28	4		

^{a)} Experiments have been done at 25 °C.

Membrane Code	Selectivity						
Membrane Code	H ₂ O/N ₂ ^{b)}	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /N ₂	H ₂ O/CO ₂ ^{b)}	INCI.	
PMMA	-	-	3.9	13.9		[6]	
PEMA ^{a)}		33.0	4.8	20.5	-	[7]	
XLPEGDA	-	7.5	2.5	50.0		[8]	
PEGDMA	-	9.4	2.9	59.0	-	[9]	
PAA	-	-	0.93	0.93	-	[10]	
PtBMA	-	75.0	5.6	13.0	-	[11]	
PEEMA	-	-	3.6	21.4	-	[12]	
PDEMA	-	-	3.2	37.0	-	[12]	
SI-PDEAEMA_GO_0.6	1937	10.0	3.0	21.5	90		
SI-PDEAEMA_GO_0.8	1148	7.5	2.3	14.0	82	Thia	
SI- PDEAEMA_exf.GO_0.75	1682	9.0	3.0	20.0	84	work	
SI-PDEAEMA_exf.GO_1	3158	12.0	4.0	28.0	113		

Table 4.3.3.2. Ideal selectivities for the surface-initiated polymer (SIP) TFC membranes in comparison to results from the literature.

^{a)} Experiments have been done at 25 °C; ^{b)} Selectivity at water vapor activity 90% obtained during the experiment.

The gas transport performances of the membranes prepared from surfaceinitiated polymers show an improved ideal selectivity in comparison to other amorphous polymer membranes. The membranes show high selectivity for water vapor, demonstrating that they are potential candidates for the dehumidification of various gases. Additionally, the experiments showed that when the amount of the SI-GO particles increases, the ideal selectivities decrease as it is demonstrated on SI-PDEAEMA_GO_0.6 and SI-PDEAEMA_GO_0.8 samples in Table 4.3.3.2.

Table 4.3.3.2 shows that the ideal selectivities for gas mixtures are significantly influenced by choice of the type of SI-GO, i.e., polymer grown on single-layer exfoliated SI-GO layers showed higher selectivities in comparison to the polymer synthesized from the bulky SI-GO particle. The ideal selectivities for H_2O/N_2 and H_2O/CO_2 gas pairs are 1682 and 84, respectively, in the case of SI-PDEAEMA_exf.GO_0.75 thin

film membrane. The SI-PDEAEMA_exf.GO_1 thin-film membrane showed higher selectivities for the aforementioned gas pairs with a selectivity factor of 3158 for H_2O/N_2 and 113 for H_2O/CO_2 . The ideal selectivity recorded for CO_2/N_2 is ~28 in the case of SI-PDEAEMA_exf.GO_1.



Figure 4.3.3.1. The variation in water vapor permeability of SI-PDEAEMA_exf.GO_0.75 polymer at different water vapor activities between 30 and 80 °C.

In order to understand the transport of water vapor through the prepared membrane, a series of experiments were conducted. Figure 4.3.3.1 shows the water vapor permeability versus water vapor activity in the temperature range of 30-80 °C. Metz *et al.* explained that when water vapor dissolves in polymer chain fragments that have interactions with the water molecule, the sorption isotherm shows a linear trend at low activities ($p/p_0 < 0.4$) and increases exponentially at higher activities [13]. The same trend is seen in our research explaining that the polymer might have low solubility for water vapor at $p/p_0 < 0.4$ (see the curve at 40 °C, Figure 4.3.3.1) and with the increase of the vapor activity, water vapor solubility increases due to the clustering or multilayer formation of water molecules [14]. Since our polymer is completely in the amorphous state, it is possible that water vapor molecules form clusters at the "free" polymer chains. With the increase in temperature, the polymer-penetrant interaction 165

becomes weak. Considering the recent work of Akhtar *et al.* [15], we can assume that at high temperatures where the vapor activity reaches ~1, this kind of membrane could transport water vapor with more than 2400 Barrer at high temperatures. To support this approximation, we conducted Aspen Custom Modeling (ACM) in order to understand the water vapor transport through the prepared membranes. The results are shown in Figure 4.3.3.2.



Figure 4.3.3.2. Experimental (a) and Free Volume Model modeling results (b) for water vapor permeability dependence on the mean pressure value.

The modeling showed that water vapor transport could be adequately described in terms of the Free Volume Model (Equation (3.4)). Due to experimental setup limitations, it was not possible to conduct vapor transport measurements at high water vapor activity on the feed side of a membrane. Since the Free Volume Model was found to be applicable for the description of water vapor transport through polymers under study, the estimation of permeability coefficient at $p/p_0=0.99$ was done. For data points obtained from this estimation at each temperature point, Arrhenius dependence showed a minor positive effect of temperature on water vapor transport. The calculated activation energy of water vapor transport was just 0.6 kJ mol⁻¹ (Figure 4.3.3.3). Assuming water vapor permeance at 100 °C, vapor activity $p/p_0=0.99$ as 2800 Barrer and transmembrane pressure 1000 mbar, for the studied membrane with the selective layer thickness of 400 nm one can calculate a permeation of approximately 13 kg h⁻¹ of pure water to the cold side of the 1 m² membrane.



Figure 4.3.3.4. Determination of the activation energy of water vapor transport through SI-PDEAEMA_exf.GO_0.75.

The quaternized SI-PDEAEMA_exf.GO_0.75 membrane showed higher water vapor transport than the same but non-quaternized SI-PDEAEMA_exf.GO_0.75 membrane. The experiments showed that at low temperatures and high vapor

activities, the permeability of water vapor is around 9000 Barrer (Figure 4.3.3.5), which at conditions described above up to 27 kg h⁻¹ of pure water that can be obtained from 1m² of the membrane.



Figure 4.3.3.5. The variation in water vapor permeability of quaternized SI-PDEAEMA_exf.GO_0.75 polymer at different water vapor activities between 30 and 80 °C.

According to the activation energy calculation, we assume that this kind of membrane can be useful for the lowering of the distillation cost by reducing the temperature on the hot side of the membrane. Graphene oxide has exhibited an advantage in water purification even though the large scale GO membrane preparation suffers from damage to the membrane, which needs to be solved for better performances. To avoid this, Chang *et al.* prepared hierarchically assembled GO-MOF composite membranes to achieve better results [16]. Growing polymer chains from the single GO layers affects the orientation of graphene nanoparticles significantly during the membrane preparation, and it helps to reduce the thickness of the selective layer below 100 nm as a consequence of increasing membrane performance by a factor of at least 4 compared to the membrane under study.

4.3.4. Conclusions

In this study, graphene oxide layers were transformed into surface-initiator functionalized graphene initiators and were used for the polymerization of 2diethylaminoethyl methacrylate. EDX, FTIR, and SSNMR analysis showed that the modification was successful. For the first time, an exfoliated graphene initiator dispersion was applied for polymerization. SEC results showed dispersity indexes of 1.25 and 1.20 for SI-PDEAEMA_exf.GO_0.75 and SI-PDEAEMA_exf.GO_1, respectively. The synthesized polymers were analyzed by FTIR, NMR, TGA, TG-FTIR, dynamic water contact angle measurement, and SEM analysis. Using the synthesized polymers, thin-film composite membranes were prepared on a porous PAN support, and their single gas and water vapor transport performances were investigated. Single gas transport experiments showed that the prepared amorphous polymer membranes are defect-free and show high selectivities such as 3158 for H₂O/N₂, 28 for CO₂/N₂, and 113 for H₂O/CO₂. According to the membrane water transport results, we can draw the following conclusions:

- Since the synthesized polymer is in the rubbery amorphous state, the polymer of the selective layer is in a fully relaxed, non-aging state.
- Single-layer surface-initiator functionalized graphene oxide gives us the opportunity to decrease the thickness of the membrane without defect formation during membrane preparation.
- The activation energy of the water vapor transport is low, which means the operational costs of the membrane distillation can be decreased by optimization of separation process conditions.
- The obtained data opens a new prospect for further development of the thin-film membranes for membrane distillation.

4.3.5. References

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4.4. Metal-organic framework incorporated mixed matrix membranes

4.4.1. Summary

This part of the work summarizes the findings of the synthesis of metal-organic frameworks and their influence on the gas transport properties of the PIM-1 mixed matrix membranes. Zn₂(bim)₄ nanosheets synthesized from the ZIF-7 nanoparticles were incorporated into the PIM-1 polymer matrix, and the effect of loading on the transport properties was also investigated.

4.4.2. Synthesis and characterization of Zn₂(bim)₄ nanosheets

In a general procedure, the synthesis of the $Zn_2(bim)_4$ nanosheets is done in the following way:



Scheme 4.4.2.1. The synthesis procedure of ZIF-7 from $Zn(NO_3)_2 \cdot 6H_2O$ and benzimidazole. The image was reprinted with permission from [1]. *Copyright* © *The Royal Society of Chemistry 2015.* The transformation of ZIF-7 nanoparticles into $Zn_2(bim)_4$ nanosheets. Reprinted with permission from [2]. *Copyright* © *2014, American Association for the Advancement of Science.*

Figure 4.4.2.1 shows the FTIR spectra of the synthesized MOF nanoparticles. The FTIR experiments were conducted for the synthesized ZIF-7 and $Zn_2(bim)_4$ particles to understand the coordination of benzimidazole molecules to Zn^{2+} metal centers. Infrared (IR) analysis of the benzimidazole molecules conducted by Pashchevskaya et al. [3] showed that in-plane and out-of-plane N-H stretching vibrations of the linker (benzimidazole molecule) are between 2540 and 3060 cm⁻¹. However, such stretching vibrations overlap with the combination bands of C=C stretching and C-H in-plane bending vibrations of the benzimidazole molecule, making separation of these vibrations complicated. The presence of the combination bands was firstly described by Mohan et al. [4]. They have indicated that the benzimidazole [4] shows the stretching vibrations between 2900 and 3100 cm⁻¹, which are the combination bands of C=C stretching and C-H in-plane bending vibrations. Those peaks at 2900-3100 cm⁻¹ are also seen for our materials. Since this stretching vibration range belongs to the aliphatic compounds and the synthesized compounds do not possess any aliphatic groups, they are assumed as the combination bands of two different vibrations. For example, the peak at 2900 cm⁻¹ is the combination band of the peaks at 1621 and 1273 cm⁻¹, which are C=C stretching and C-H in-plane bending vibrations of the benzene rings. The peak at 1772 cm⁻¹ is not a stretching vibration of the carboxylic groups; thus, it can be attributed to the combination band of the N-H inplane bending vibrations at 1545 cm⁻¹ and out-of-plane (C-C-C) bending of the organic linker at 228 cm⁻¹ [4]. Hence, the identification of the C-N and C=N stretching vibrations is a difficult task for the benzimidazole molecules. Mohan and Sundaraganesan [4] suggested that the C=N stretching vibration is at 1689 cm⁻¹; however, we did not observe this peak in the FTIR spectra of our materials. Moreover, the peak at 1675 cm⁻ ¹ likely belongs to the C=O stretching vibrations of the residual DMF molecules that are trapped in the pores of the ZIF-7 nanoparticles. After the transformation of the ZIF-7 nanoparticles into the Zn₂(bim)₄ particles, this peak reduces significantly, which we claim it is the effect of the solvent exchange. According to the FTIR experiment, the residual DMF content in the pores of the ZIF-7 nanoparticles is ~10%. The C=C stretching vibrations of the aromatic ring is observed in a broad range between 1241 and 1611 cm⁻¹. The strong peak at 750 cm⁻¹ is attributed to the C-H out-of-plane bending vibration of the organic linker. Full deprotonation of benzimidazole linker can occur in an alkaline medium. However, during the synthesis procedure, no alkaline medium was used. In finalizing the FTIR experiments, we can claim that some percentage of the benzimidazole linkers were not deprotonated. Additionally, it is not claimed that the reaction was unsuccessful; thus, FTIR peaks below 600 cm⁻¹ manifest

the Zn-N stretching vibrations. The change in the feature of the spectra of ZIF-7 and Zn₂(bim)₄ particles demonstrates the structural difference between the particles.

Thermogravimetric analysis showed that ZIF-7 nanoparticles degrade in three steps while $Zn_2(bim)_4$ nanoparticles degrade in only one step (Figure 4.4.2.3). The first degradation step for ZIF-7 is observed between 30 and 200 °C, with a mass loss of ~8%. This data overlaps with the FTIR and NMR data and confirms the existence of the trapped DMF molecules in the pores of the ZIF-7 nanoparticles. The second degradation step starts at 220 °C and ends at 700 °C with a ~37% mass loss, which corresponds to the decomposition of the framework. The last decomposition step could be attributed to the destruction of the benzimidazole molecules. Conversely, the $Zn_2(bim)_4$ nanoparticles are stable up to 550 °C. A plateau is followed by a ~46% mass loss between 550 and 800 °C, corresponding to the decomposition of the framework.



Figure 4.4.2.3. TGA analysis of the synthesized MOF nanoparticles between 25 and 800 °C under argon flow at 5 K min⁻¹.

Figure 4.4.2.4 depicts the X-ray powder diffraction spectra of ZIF-7 and $Zn_2(bim)_4$ nanoparticles. The spectra suggest that the transformation of the ZIF-7 nanoparticles into the $Zn_2(bim)_4$ nanoparticles leads to a strong alteration of the crystal structure. A sharp 001 reflection at ~7.8° suggests that there is a difference between the

nanoparticles. Using the Scherrer equation [5, 6], it was calculated that the crystal size of the ZIF-7 nanoparticles has significantly changed after transformation into the $Zn_2(bim)_4$ nanoparticles from 15 nm to 9 nm, respectively. The XRD pattern also confirms the existence of the ordered structure.



Figure 4.4.2.4. XRD pattern of the synthesized MOF nanoparticles.

SEM images support the results of the spectroscopic analysis (Figure 4.4.2.5). The images show that after the transformation of ZIF-7 nanoparticles, the product possesses the ordered structure with the dimensions of $1000 \times 1000 \times 200$ nm. Peng *et al.* [2] revealed that the Zn₂(bim)₄ nanoparticles have a layered structure.



Figure 4.4.2.5. SEM images of the ZIF-7 and Zn₂(bim)₄ nanoparticles.

4.4.3. Gas transport properties of the Zn₂(bim)₄-incorporated PIM-1 mixed matrix membranes

Prepared thin-film composite membranes whose selective layer consists of MOF incorporated PIM-1 composite layer was used to measure the single gas transport experiments of CH₄, N₂, O₂, and CO₂ gases using in-house built gas permeation facility at 30 °C. Data of the single gas transport properties and the ideal selectivities of the prepared mixed matrix membranes were obtained for at least four different stamps of the same batch TFC membranes, and the permeances of the gases were calculated as an average value of 20 experimental points. The standard deviations and the mean permeance values of the error of the ideal gas selectivity was taken as a multiplication factor of the corresponding gas permeances. The experimental errors were determined from the accuracy of the measurement systems permeate volume calibration, the accuracy of the sensors, and the standard deviations. The data for the permeabilities and selectivities and the comparison of the achieved results with the state-of-the-art polymer membranes are presented in Table 4.4.3.1 and Table 4.4.3.2.

Membrane		wt.% of	Pei					
code	filler	Barrer					Ref.	
			H ₂	N ₂	CH₄	CO ₂	O ₂	
PIM-1/UiO-66	UiO-66	9	3080	256	371	5940	1010	[7]
PIM-1/CAU-21-	CAU-21-	4.5	15 7295	186	-	-	-	[8]
ODB	ODB	15						
PIM-1/ZIF-67	ZIF-67	20	3500	219	315	5200	-	[9]
PIM-1	-	-	670	64	102	1350	207	
PIM1-	Zn₂(bim)₄	0	700	F 4	70	1000	047	
Zn2(bim)4_2		2	192	51	13	1000	217	
PIM1-		4	1059	77	110	1405	202	
Zn2(bim)4_4		4	1056	//	110	1425	302	This
PIM1-		6	4000	100	100	1040	204	work
Zn ₂ (bim) ₄ _6		ю	1222	100	100	1840	304	WOIN
PIM1-		0	4000	100	150	4050	204	
Zn2(bim)4_8		8	1220	100	150	1852	384	
PIM1-		10	1050	120	104	1000	126	
Zn₂(bim)₄_10		10	1308	130	194	1990	430	

Table 4.4.3.1. Permeability coefficients for the Zn₂(bim)₄ containing PIM-1 TFC membranes.

Membrane		wt.	Selectivities					
code	Filler	% of filler	H2/N2	CH4/N2	CO ₂ /N ₂	O2/N2	CO ₂ /CH ₄	Ref.
PIM-1/UiO- 66	UiO-66	9	12.0	1.45	23.0	3.95	16.0	[7]
PIM-1/CAU- 21-ODB	CAU-21- ODB	15	39.0	-	-	-	-	[8]
PIM-1/ZIF-67	ZIF-67	20	16.0	1.44	23.7	-	16.5	[9]
PIM-1	-	-	10.5	1.59	21.0	3.23	13.2	
PIM1- Zn ₂ (bim) ₄ _2		2	15.5	1.43	19.6	4.25	13.7	
PIM1- Zn ₂ (bim) ₄ _4		4	13.7	1.53	18.5	3.92	12.0	This
PIM1- Zn₂(bim)₄_6	Zn2(bim)4	6	12.2	1.60	18.4	3.84	11.5	work
PIM1- Zn₂(bim)₄_8		8	12.2	1.50	18.5	3.84	12.3	
PIM1- Zn ₂ (bim) ₄ _10		10	10.4	1.50	15.3	3.35	10.3	

Table 4.4.3.2. Selectivities for the Zn₂(bim)₄ containing PIM-1 TFC membranes.

As it is seen from the tables, with the increase of the $Zn_2(bim)_4$ loading, the permeabilities of the mixed-matrix membranes for all gases increases expect 2 wt.% loading. At this loading, the increase in the permeability coefficients is seen in the cases of H₂, CO₂, and O₂ while N₂ and CH₄ permeabilities decrease. This gives rise to the selectivities of hydrogen and oxygen over nitrogen. The selectivity of CO₂/N₂ is almost unchanged. Peng *et al.* [2] showed that $Zn_2(bim)_4$ nanoparticles are a stacked two-dimensional material, and the layers have ~0.21 nm pore diameter, which makes such kind materials potential candidates for hydrogen separation. When this nanoparticle is incorporated into the PIM-1 matrix, it is supposed to get a mixed-matrix membrane prone to hydrogen separation. The H₂/CH₄ selectivity is increased from ~6.6 for pure PIM-1 to ~11.0 for PIM1- $Zn_2(bim)_4_2$ mixed-matrix membrane.





Figure 4.4.3.1. Cross-sectional SEM images of pure PIM-1 (a) and 2 wt.% Zn₂(bim)₄ nanoparticle-loaded PIM-1 mixed-matrix membrane.

The cross-sectional SEM images of the thin-film composite membranes are shown in Figure 4.4.2.7. At 2 wt.% of filler in the casting solution $Zn_2(bim)_4$ nanoparticle are oriented along the membrane surface, which is expected due to the presence of shear force applied to the forming selective layer during TFC membrane preparation. A competing additional force orienting the particles parallel to the membrane surface may arise from a strong suction of the solvent into the porous support by capillary force resulting in a complete wetting of the porous PAN sublayer. However, due to the high molecular weight of PIM-1, no significant penetration of polymer into the PAN pores was observed, as it can be seen by a border line between the continuous polymer layer and porous substrate in the SEM images of pure PIM-1 and PIM-1 with 2 wt.% of $Zn_2(bim)_4$ nanoparticle.



Figure 4.4.3.2. Gas permeability as a function of penetrant kinetic diameter (a) and loading of nanofiller (b) for PIM-1/Zn₂(bim)₄ mixed-matrix membranes.

Although hydrogen possesses a small kinetic diameter (~0.289 nm), the permeability of pure PIM-1 follows the order of CO₂ (~0.33 nm) > H₂ (~0.289 nm) > O₂ (~0.346 nm) > CH₄ (~0.34 nm) > N₂ (~0.364 nm). It is worth to note that the reinforcement influences strongly on the gas transport properties of the mixed-matrix membrane (Figure 4.4.2.6a and b). With the loading of Zn₂(bim)₄ nanoparticles, the transport of hydrogen increases without any hindrance. In comparison to hydrogen, at 2 wt.% the transport of other gases is prohibited, which gives an increase in the corresponding selectivities. This can be explained by the exfoliation of layered nanoparticles, which allows the transport of hydrogen. With the increase of the nanoparticle loading, the stacking effect of the layers allows other gases to by-pass the nanoparticles giving rise in the permeabilities and decrease in the selectivities. The permeabilities of all gases stabilize between 6 wt.% and 8 wt.% that we claim after 8 wt.% loading the defect formation between the particles occurs and the gas molecules transport through such type of the defects.

4.4.4. Conclusions

In this study, ZIF-7 nanoparticles were transformed into $Zn_2(bim)_4$ layered nanoparticles, and their structures and morphologies were investigated. After synthesis of $Zn_2(bim)_4$ nanoparticles, they were incorporated into the PIM-1 polymer matrix in order to test the effect of the nanoparticle loading on the gas transport properties. It was revealed that at 2 wt.% of filler loading, due to exfoliation of the $Zn_2(bim)_4$ layers, they hinder the permeance of larger gas molecules, albeit to facilitate the transport of hydrogen. This gives an increase in the hydrogen selectivities and makes PIM-1/Zn_2(bim)_4 mixed-matrix membranes suitable the hydrogen purification.

4.4.5. References

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4.5. Novel covalent organic frameworks for gas adsorption

4.5.1. Summary

In this study, we synthesized novel covalent organic frameworks, and their effects on gas adsorption are investigated. The main task was to synthesize new type frameworks that can adsorb different gaseous products, as such kinds of products could be useful for membrane science in order to separate different gaseous mixtures.

4.5.2. Synthesis and characterization of novel covalent organic frameworks

In our research, three types of covalent organic frameworks were synthesized through a polycondensation reaction. The new covalent organic frameworks named COF-HZG1, COF-HZG2, and COF-HZG3 are described below (HZG is defined as Helmholtz-Zentrum Geesthacht):



Scheme 4.5.2.1. Synthesis route of COF-HZG1 comprising benzene-1,3,5-tricarboxaldehyde and 3,3',5,5'-tetramethylbenzidine.



Scheme 4.5.2.2. Synthesis route of COF-HZG2 comprising 1,3,5-benzenetricarbonyl tricholoride (TMC) and tris(3-hydropropyltriazolylmethyl)amine (THPTAMA).



Scheme 4.5.2.3. Synthesis route of COF-HZG3 comprising 1,3,5-benzenetricarbonyl tricholoride (TMC) and 1,3,5-tris(2-hyroxyethyl)isocyanurate (THEIC).

The reaction schemes (Scheme 4.5.2.1, Scheme 4.5.2.2, and Scheme 4.5.2.3) show that new COFs are imine- and ester-based. COF-HZG1 synthesis is carried out by the polycondensation reaction between benzene-1,3,5-tricarboxaldehyde and 3,3`,5,5`-tetramethylbenzidine with the elimination of two water molecules. The synthesis of COF-HZG2 and COF-HZG3 undergo with the elimination of HCl during the reactions of trimesoyl chloride with tris(3-hydropropyltriazolylmethyl)amine and 1,3,5-tris(2-hyroxyethyl) isocyanurate, respectively. In the cases of COF-HZG1 and COF-HZG3, twelve-membered imine and six-membered ester rings are formed by the dehydration and dehydrochlorination reactions, while in the case of COF-HZG2, the HCl elimination causes the formation of non-uniform rings.

Fourier-Transform Infrared spectroscopy experiments support the proposed structures of the synthesized covalent organic frameworks (Figure 4.5.2.1). In all samples, several characteristic vibration peaks are observed with significantly different intensity. C-H stretching vibrations of the alkane groups are visible at 2970 cm⁻¹ and benzene rings found at 3100 cm⁻¹, respectively. The –C=O stretching vibrations of the edge carbonyl groups are between 1727-1771 cm⁻¹. The C-H stretching vibrations of the methylene and methyl groups are seen at 1460 cm⁻¹. The peak at ~1230 cm⁻¹ shows the presence of the C-N and C-O stretching vibrations of the aromatic amine and ester linkages in the structures, respectively. For the COF-HZG1 sample, the peak corresponding to the –C=N stretching vibrations are seen at 1630 cm⁻¹, confirming the formation of imine linkage. In addition, the C-N stretching vibrations of aromatic amines is observed with significantly reduced intensity, indicating that small amount of the 3,3`,5,5`-tetramethylbenzidine moieties that have not formed a six-membered ring is also present in the COF-HZG1 sample. For COF-HZG2 and COF-HZG3, strong peak intensities of the C-N and C-O stretching vibrations imply the formation of alkyl aryl ether linkage.



Figure 4.5.2.1. FTIR results of the COF samples.

To verify the chemical structures of COF, ¹³C CP MAS NMR analysis was conducted, and the results and the peak assignments are shown in Figure 4.5.2.2.



Figure 4.5.2.2. ¹³C CP MAS NMR analysis of the COF samples.

The results suggest that all the reactions were successful, confirming the proposed structures for the COF samples. For COF-HZG1, the framework structure consisting of benzene and benzidine rings is represented by the aromatic carbon signals at 127 and 138 ppm and by a strong peak at 18 ppm resulting from the methyl groups (-CH₃) of the benzidine moieties. The peak at 150 ppm can be ascribed to the

aromatic amine moieties, and the imine moieties are seen at ~160 ppm, verifying the condensation reaction product [1]. At ~190 ppm, the edge carbonyl groups are also detected for COF-HZG1 (Figure 4.5.2.2a). For COF-HZG2 (Figure 4.5.2.2b), signals of THPTAMA units are shown at 30–63 ppm for aliphatic carbons and at 126 and 145 ppm for triazole moieties. The benzene rings resulting from trimesoyl chloride moieties are revealed at 131 ppm. A strong signal at 165 ppm is related to the –COO groups, confirming the condensation reaction. A small peak at 169 ppm belongs to the unreacted –COCI groups that are placed at the edges of the two-dimensional structure. For COF-HZG3 (Figure 4.5.2.2c), ¹³C NMR signals of THEIC units are visible at 42, 62, and 150 ppm as well as the signal of trimesoyl chloride moieties at 131 ppm. Again, the signals of –COO groups and –COCI groups at the edge are observed, indicating the condensation reaction.

The conducted EDX experiments on the COFs support the results of FTIR and SSNMR. Figure 4.5.2.3 shows all the atoms distributed through the structure of the synthesized particles.



Figure 4.5.2.3. EDX results of the synthesized COF particles.

COFs are crystalline powders in general, meaning that such kind of materials must show strong powder X-ray diffraction (PXRD) peaks during experiments.

However, it has been reported that during COF synthesis, a so-called "crystallization problem" can occur [2].



Figure 4.5.2.4. Experimental PXRD results of the COF samples.

As shown in Figure 4.5.2.4, our experiments revealed that the synthesized COF nanoparticles do not show the high crystallinity that was reported for the TpBD COF samples (Tp stands for 1,3,5-triformylphloroglucinol, while BD as benzidine) [3]. However, the samples show some PXRD reflections depraving us to claim that the COFs are amorphous, indicating less structural order, which was reported for superacid catalyzed low-temperature triazine-based frameworks [4]. The crystallinity disorder and the broadening of the reflections are most likely due to the deviation from the ideal stacking of the two-dimensional layers governed by the electrostatic and attractive dispersion forces [5-7]. Furthermore, such kind of staggered stacking can reduce the pore volume and thus, limit the uptake of the high molecular weight compounds.

Thermogravimetric analysis showed that the synthesized covalent organic frameworks are stable up to 400 °C in the case of COF-HZG1, while the thermal stability of COF-HZG2 and COF-HZG3 slightly is lower (Figure 4.5.2.5).



Figure 4.5.2.5. Thermogravimetric patterns of the COF samples between 25 and 800 °C under argon flow at 5 K min⁻¹.

In the case of COF-HZG1, at 400 °C the first degradation step starts, which can be attributed to the decomposition of edge carbonyl and amine groups from the structure with a ~10% mass loss. This is followed by a gradual mass loss of ~28% up to 800 °C, corresponding to the degradation of the six-membered rings. The residual mass at the end of the experiment is ~62%. The sample COF-HZG2 shows a different TGA curve compared to COF-HZG1. A small mass loss up to 100 °C could be explained by the evaporation of the residual water molecules that trapped in the pores of the framework after washing. A sharp degradation step between 250 and 550 °C is explained by the degradation of the structure, suggesting the elimination of CO₂. Up to 800 °C, approximately 90% of the structure is degraded. The degradation of COF-HZG3 is accompanied by the decomposition of the unreacted -OH and –COCI groups between 200 and 360 °C with a mass loss of ~10%. A steep decrease of the mass loss between 360 and 750 °C suggests the structural destruction of the sample.

Figure 4.5.2.6 shows the scanning electron microscope (SEM) images of the synthesized covalent organic frameworks. All compounds exhibit agglomerate of particles with irregular roundish shape possesses different microstructures.



Figure 4.5.2.6. SEM images of the novel covalent organic frameworks.

4.5.3. Gas adsorption experiments of the COF samples

For the evaluation of the permanent porosities and the surface areas of the synthesized COF-HZG1 and COF-HZG3, the nitrogen adsorption-desorption experiments were conducted at 77 K. Before the experiments, the samples were degassed at 120 °C for 24 h. As it is shown from Figure 4.5.3.1a-d, the isotherms of the covalent organic frameworks display type-I isotherm feature according to IUPAC classification [8].





Figure 4.5.3.1. Nitrogen adsorption-desorption isotherms of COF-HZG1 (a, and b), and COF-HZG3 (c, and d). The pore size distribution of COF-HZG1 (e), and COF-HZG3 (f).

Reversible isotherms, given in Figure 4.5.3.1a-d, show that the synthesized covalent organic frameworks possess a microporous nature. The isotherms exhibit that the synthesized materials have relatively small external surfaces. A steep uptake at low p/p₀ is observed for both of the samples (Figure 4.5.3.1b, and d). This is due to enhanced adsorbent-adsorptive interactions in narrow pores. The pore size distribution results (Figure 4.5.3.1e, and f) describe that COFs have micropores ranging between 1.77 and 2 nm. In the case of COF-HZG1, the main distributed pore size is 1.85 nm with different pore sizes, such as 1.77, 1.92, and 2.0 nm. COF-HZG3 displays a more uniform pore size distribution, where the majority of the micropores are 1.77 nm in diameter, and micropores of d=1.85 nm are present in minor amount. The presence of multiple pore sizes can be attributed to the topology and flexibility of the ligands used in the synthesis. This factor in our opinion affects the uniformity of the nanopores. The Brunauer-Emmett-Teller (BET) and Langmuir surface areas of the samples are SABET=70 m² g⁻¹ and SALang=85 m² g⁻¹ for COF-HZG1, and SABET=21 m² g⁻¹ and SA_{Lang}=27 m² g⁻¹ for COF-HZG3, respectively. The BET surface areas obtained are considerably lower than the previously reported COFs such as COF-42 (710 m² g⁻¹), COF-43 (620 m² g⁻¹) [9], COF-1 (711 m² g⁻¹) [10], COF-LZU1 (410 m² g⁻¹) [11], and (Et)₂₅-H₂P-COF (1326 m² g⁻¹) [12]. However, our results are higher than the amorphous TAPB-PDA COF (18 m² g⁻¹) (TAPB demonstrates 1,3,5-tris(4aminophenyl) benzene; PDA is terephthaldehyde) [13], and graphite (10 m² g⁻¹) [14] or close to some reported amine-functionalized microporous organic polymers (72 m² g⁻ ¹) [15]. This could be explained by the non-ordered packing of the 2D layers. It is assumed that the layers are packed in the staggered form, and the nitrogen molecules could not enter the pores. The total pore volume calculated at $p/p_0=0.99$ is to be 0.33 cm³ g⁻¹ and 0.07 cm³ g⁻¹ for COF-HZG1 and COF-HZG3, respectively, which is relatively lower than that COF-SDU3 (0.53 cm³ g⁻¹) [16] (SDU is Shandong University), ILCOF-1 (1.21 cm³ g⁻¹) [7] (IL is described as imine-linked), COF-JLU2 (0.56 cm³ g⁻¹) [17] (JLU stands as Jilin University), COF-42 (0.31 m³ g⁻¹) [9], COF-43 (0.36 m³ g⁻¹) [9], COF-1 (0.30 m³ g⁻¹) [18], and COF-6 (0.32 m³ g⁻¹) [18]. The possible lower surface area could be explained by the presence of the side functional groups that are covering the inner and outer surfaces of the COF samples. Chandra et al. [3] reported that the introduction of a functional group at the 3, 3' position in the biphenyl ring system disturbs the planarity of the diamine ligands. The diamine ligands of COF-HZG1 contain methyl groups at the 3,3,5,5 positions, which means the planarity of the diamine groups is disturbed which may be the reason for the low crystallinity and following lower surface area. Considering this factor, we claim that the presence of different functional groups in the ligands used for the synthesis of COF-HZG2 and COF-HZG3 affects to the crystallinity and packing of the two-dimensional nanolayers.

During the conceptualization of the work, it was planned to prepare covalent organic frameworks that have an affinity towards CO₂. Since novel COFs (COF-HZG1, COF-HZG2, and COF-HZG3) synthesized contain a variety of functional groups decorated through the frameworks, we performed the adsorption experiments for CH₄, N₂, O₂, and CO₂ gases at 303 K. The idea was to understand the behavior of the COFs toward the gas molecules and to lay a basis for the development of membranes from these covalent organic frameworks for separation of CO₂ in the industry at relevant pressures. In Figure 4.5.3.2, the experimental and the Langmuir model adsorption isotherms of the COFs are shown.



Figure 4.5.3.2. The experimental adsorption isotherms of CO2, CH4, O2, and N2 on (a, b) COF-HZG1, (c, d) COF-HZG2, (e, f) COF-HZG3. Solid lines represent the Langmuir model isotherms.

Although the BET surface areas of the synthesized covalent organic frameworks are low, they show high gas uptakes. For the CO₂ isotherm, it can be found that the
synthesized COFs are indeed CO₂-philic as expected. Thus, all the uptake curves fit the Langmuir model described with the equation 3.1.

The isotherm shows that with the increase of the pressure, the uptake of CO₂ increases and reaches 67 cm³ g⁻¹ for COF-HZG1, 19 cm³ g⁻¹ for COF-HZG2, and 46 cm³ g⁻¹ for COF-HZG3 samples. Amongst the synthesized covalent organic frameworks, COF-HZG1 and COF-HZG3 exceed the CO2 uptake values of SNW-1 (50 cm³ g⁻¹) [19]. Parallel experiments with CH₄, O₂, and N₂ were conducted as well. COF-HZG1 exhibited 4.75 cm³ g⁻¹ uptake for N₂, 5.55 cm³ g⁻¹ uptake for O₂, and 20 cm³ g⁻¹ for CH₄. Interestingly, nitrogen and oxygen adsorptions of COF-HZG2 and COF-HZG3 were very low and almost undetectable. The reason for such kind of a missing adsorption ability could be the polarizability and quadrupole moments of these molecules. COF-HZG2 does not adsorb oxygen at all, while COF-HZG3 adsorbs O2 at 5 bar with an uptake value of 0.53 cm³ g⁻¹ (with the increase of the pressure the adsorption value decreases and after 15 bar there are no detectable adsorption points). During experiments, the adsorption isotherm for O₂ was always negative, while the adsorption isotherm for N₂ was barely positive after filtering the major negative adsorption points, which means that such kind of materials does not have an affinity towards nitrogen. The maximum amounts of nitrogen adsorptions by COF-HZG2 and COF-HZG3 were 0.23 cm³ g⁻¹ at 40 bar and 0.55 cm³ g⁻¹ at 33 bar, respectively. Employing the Langmuir model, it was predicted that at 50 bar, COF-HZG2 must adsorb 0.25 cm³ g⁻¹ (Figure 4.5.3.2d), while the maximum nitrogen uptake value predicted for COF-HZG3 was 0.6 cm³ g⁻¹. These predictions were not supported by the experimental values. At 50 bar, the adsorbed amount of nitrogen by COF-HZG2 is 0.000765 cm³ g⁻¹, when the adsorption by COF-HZG3 is undetectable. The adsorption of methane was higher than nitrogen and reached 4.45 cm³ g⁻¹ and 9.28 cm³ g⁻¹ at 35 bar in the case of COF-HZG2 and COF-HZG3, respectively. In Table 4.5.1.1, the CO₂ capture results of the synthesized materials along with literature data is shown.

COFs	CO ₂ capacities, cm ³ g ⁻¹	CO ₂ /N ₂	CO ₂ /CH ₄	Ref.
SNW-1	50	10	5	[19]
CTF-1	55 ^{a)}	18 ^{b)}	-	[20]
TpPa-COF (MW)	111 ^{a)}	32 ^{c)}	-	[21]
COF-JLU2	110 ^{a)}	77 ^{c)}	5.7 ^{c)}	[17]
ACOF-1	90 ^{a)}	40 ^{c)}	15.4 ^{c)}	[22]
COF-HZG1	67	14 ^{d)}	3.4 ^{d)}	
COF-HZG2	19	76 ^{d)} ; 24836 ^{e)}	4.0 ^{d)}	This work
COF-HZG3	46	77 ^{d)}	4.5 ^{d)}	

Table 4.5.1.1. CO₂ capture results of the synthesized COFs along with literature data.

^{a)} Low-pressure CO₂ capacity was measured at 273 K at 1 bar; ^{b)} Determined from experiment breakthrough with CO₂/N₂ (10:90 v/v) at 298 K and 1 bar; ^{c)} Determined from Henry's law; ^{d)} Determined from the Langmuir model; ^{e)} Determined from the experimental values.

Table 4.5.1.1 shows that the newly synthesized covalent organic frameworks show high CO_2/N_2 selectivities exceeding the results of other reported COFs. Performing Langmuir adsorption model calculations based upon experimental data, COF-HZG2 and COF-HZG3 show the same selectivities for CO_2/N_2 reported for COF-JLU2, (COOH)₁₀₀-H₂P-COF [12], and FCTF-1 [20]. However, due to the low polarizability of nitrogen, the adsorption of this COF-HZG2 framework decreases drastically, while CO_2 and CH₄ adsorption increase reaching high selectivities for CO_2 and CH₄ over N₂ with a solubility sorption factor of ~25000 and ~5820, respectively.



Figure 4.5.3.3. Solubility selectivities of (a) COF-HZG1, (b) COF-HZG2, and (c) COF-HZG3 versus to applied pressure.

Figure 4.5.3.3 shows the evolution of solubility (adsorption) selectivities for CO₂/N₂, CH₄/N₂, O₂/N₂, and CO₂/CH₄ as a function of the applied pressure. The selectivities calculated based on the Langmuir sorption model uptake for every single gas. As it is described in the model, at 1 bar, the CO₂/N₂ selectivity is 10, 22, and 35 for COF-HZG1, COF-HZG2, and COF-HZG3, respectively. With the increase of the pressure, the selectivity also increases and reaches 14 for COF-HZG1, 76 for COF-HZG2, and 77 for COF-HZG3. The CH₄/N₂ selectivity is calculated to be 25 at 10 bar, and with the further increase of the pressure, the selectivity decreases slightly in the case of COF-HZG2. The higher CO₂/N₂ selectivities are related to the significantly high polarizability (29.1 x 10⁻²⁵ cm³) and quadrupole moment (13.4 x 10⁻⁴⁰ cm²) of CO₂ over those for N₂ (polarizability: 17.4 x 10^{-25} cm³; quadrupole moment: 4.7 x 10^{-40} cm²). When it comes to the selectivity of CH₄ over N₂, this data is five times lower for COF-HZG1 and ~1.5 times for COF-HZG3. The quadrupole moment of CH₄ is zero; however, the polarizability $(25.9 \times 10^{-25} \text{ cm}^3)$ is high [23]. These units confirm that the polarizability of CH₄ molecules by the synthesized COFs is in this order: COF-HZG2 > COF-HZG3 > COF-HZG1. It means that the separation of CH₄ from N_2 is solely corresponding to the adsorbent-adsorbate interactions where polarizability plays an important meaning. Thus, the modification of organic linkers with the molecules that can polarize methane could be a potential approach for high selective hydrocarbon upgrade purposes. Our adsorption-based results are significantly greater than the results reported for carbon molecular sieves (CMSs) (1.9), silicalite pellets (3.4), and activated carbons (3.0-4.0). Molecular simulation studies conducted on several MOFs (BERGAI01, PEQHOK, and GUSLUC) as potential candidates showed moderate selectivities between 7.7 and 8.8 for CH₄ separation [24]. Novel 2D COFs show better results experimentally than those simulations exceeding other reported adsorbents in this field (COF-HZG1 is exceptional). Table 2 describes the comparison between the synthesized COFs and other adsorbents such as zeolites, activated carbons, molecular sieves, and MOFs reported in the literature.

Adsorbents	S(ads),	Condition	Method	Ref.
	CH4/N2			
Linde 5A zeolite	2.20	298 K, 10 bar	а	[25]
SAPO-34 zeolite	3.00	298 K, 10 bar	а	[25]
MFI zeolite	9.50	298 K, 10 bar	b	[26]
LTA zeolite	5.00	298 K, 10 bar	b	[26]
DDR zeolite	10.5	298 K, 10 bar	b	[26]
F30-470 Degussa activated carbon	3.20	303 K, 10 bar	С	[27]
Anthracite based activated carbon	1.73	298 K, 10 bar	С	[28]
Xtrusorb A754 activated carbon	2.11	303 K, 10 bar	С	[29]
Bayer KEL2200 5A molecular sieve	1.90	303 K, 10 bar	С	[27]
Taixi anthracite based carbon	1.50	298 K, 10 bar	С	[30]
molecular sieve (CMS)				
Cu-BTC	3.00	298 K, 10 bar	b	[26]
IRMOF-11	4.00	298 K, 10 bar	b	[26]
BERGAI01	8.80	298 K, 10 bar	b	[24]
PEQHOK	8.40	298 K, 10 bar	b	[24]
GUSLUC	7.70	298 K, 10 bar	b	[24]
COF-HZG1	4.50	303 K, 10 bar	С	Thie
COF-HZG2	25.0	303 K, 10 bar	С	work
COF-HZG3	16.0	303 K, 10 bar	С	WOIN

Table 4.5.1.2. CH₄/N₂ selectivities of different adsorbents as a comparative study with our results.

Note: a-breakthrough experiments (CH₄/N₂, 50/50), b-mixture simulations (CH₄/N₂, 50/50), c-single-component adsorption experiments.

Table 2 shows that under the same conditions, COF-HZG2 and COF-HZG3 explicitly exceed the results of zeolites, activated carbons, carbon molecular sieves, and MOFs making these materials as potential candidates for CH₄ separation from N₂. The experiments showed that with the increase of the pressure, the O₂/N₂ selectivity decreases in the case of COF-HZG1. This selectivity was not detectable for COF-HZG2 due to the lack of interactions between the particles and oxygen molecules. COF-HZG3 shows low selectivity (~3) for oxygen over nitrogen at low pressures. The

increase of the pressure, the selectivity decreases below 1. The almost equal polarizabilities of nitrogen (17.4 x 10^{-25} cm³) and oxygen (15.8 x 10^{-25} cm³) [23] explain the lower O₂/N₂ selectivity. It seems that with the increase of the pressure, the polarization of nitrogen by the pores of COF-HZG3 increases leading to a 4-fold increase of adsorption capacity (from 0.15 cm³ g⁻¹ to 0.6 cm³ g⁻¹), while oxygen adsorption remains the same.



Figure 4.5.3.4. CO_2/N_2 selectivity as functions of pore diameter (a), and pore volume (b). For the plots, data was used from the references [31, 32].

Considering the results from Figure 4.5.3.4, we claim that the synthesized novel COFs, especially COF-HZG2 and COF-HZG3, show much better selectivity performances compared to the values reported for other COFs having high pore volume and BET surface areas. The relationships between CO_2/N_2 and CO_2/CH_4 selectivities and CO_2 uptake are described in Figure 4.5.3.5.



Figure 4.5.3.5. a) CO₂ uptake versus CO₂/N₂ selectivity along with data from [31], and b) CO₂ uptake versus CO₂/CH₄ selectivity along with data from [33-36].

As it is seen from Figure 4.5.3.5, the adsorption properties of the synthesized COFs are in good agreement with other covalent organic frameworks. Although the CO₂ uptake is lower in the case of COF-HZG2, it features high selectivity due to the nature of the synthesized compounds. Furukawa *et al.* showed that with the increase of the pore volume, the amount of the guest molecule storage increases as well [18]. However, the experiments showed that the adsorption (solubility) selectivity of gas mixtures could be decreased in this case. Possessing lower pore volume, COF-HZG3 showed a high separation factor among the synthesized COFs due to the dense packing of the layers.

The CO₂/CH₄ selectivity recorded for the synthesized COFs is almost the same as the results of other covalent organic frameworks (Figure 11b). Although the CO₂ uptake is low with the compared samples, the selectivity could be applicable for the effective separation of CO₂ from CH₄.

4.5.4. Conclusions

In this study, three novel COFs were synthesized, and their structures were characterized by FTIR and solid-state NMR spectroscopies. The XRD experiments showed the imperfections in the crystallinity of the synthesized materials, while TGA results suggest that such kind of materials are stable up to high temperatures. The N₂ adsorption-desorption experiments showed low BET surface areas and pore volume, which is related to the non-polarizability of nitrogen. It is supposed that during experiments, nitrogen molecules were not polarized by the COFs, and for this reason, these compounds demonstrated low surface areas and pore volumes. High-pressure adsorption experiments revealed that these novel COFs show comparable gas uptakes, and CO₂/N₂ selectivities are in a good agreement with other reported COF adsorbents. COF-HZG2 showed exceptionally high CO₂/N₂ and CH₄/N₂ selectivities with solubility separation factors of ~25000 and ~5820, respectively. This is related to the non-polarization nature of nitrogen under high pressure.

4.5.5. References

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Chapter 5

Summary and outlook

5.1. Summary and outlook

The main focus of this Ph.D. thesis was about the preparation of 2D materials and their application in thin-film composite membranes. Thus, graphene oxide, its modifications, and 2D Zn₂(bim)₄ MOF particles were successfully incorporated into the PIM-1 polymer matrix, and their effect on gas transport properties was investigated. Additionally, 2D COFs were synthesized and analyzed as adsorbents for gas uptake experiments.

Graphene oxide nanosheets were synthesized via the Hummers method, and its structure was determined by means of several techniques. It was revealed that after synthesis, graphene oxide nanosheets contain some amount of soluble oxidative debris that adsorbed on the surface of the layers, and it needs to be stripped off. The amount of oxidative debris is about 30% by weight and significantly influences the stability of the GO dispersion, which was proved by the exfoliation experiments. Thus, GO dispersion without oxidative debris showed higher concentration after centrifugation than that of as-synthesized graphene oxide.

After successful exfoliation, GO dispersions were dip-coated on microporous PAN support, and the potential use of such membranes in gas separation studies was tested. The experiments showed that the increase in thickness facilitates the permeance of hydrogen over CO_2 , N_2 , and CH_4 through the GO nanolayers. Due to the presence of the oxygen functional groups, GO layers adsorb CO_2 much higher than N_2 and CH_4 . The decrease in the permeability coefficients of CO_2 might be attributed to such a factor. However, it was suggested that GO is a promising material for the separation of hydrogen from carbon dioxide. The experiments showed that in a 15 nm GO layer, an H_2/CO_2 selectivity is 5. Plotting the obtained results in the 2008 Robeson upper bound, the surpass of the bound was achieved, showing that our results correspond to the previous results reported in the literature. The incorporation

of GO into the PIM-1 polymer matrix hinders the permeation of gas molecules through the mixed matrix membrane resulting in low selectivities.

However, the covalent modification of the GO layers opens up new possibilities in the synthesis of the novel graphene-like sheets. Thus, newly synthesized GO modifications (GO-AEDPPF and GO-DCIBAO) demonstrated ultimately different results rather than pure GO when they were incorporated in the PIM-1 polymer matrix. Although the functionalized GO (FGO) samples were not exfoliated, they showed an increased selectivity for CO_2/N_2 . At 9 wt.% FGO loading, the selectivity of the PIM-1 membrane was boosted from 21 to 26 or were not changed up to 50 wt.%. Unlike pure GO, FGO-loading showed exceeding gas permeances at high loadings, which is explained with the mass transfer through the graphene layers.

Graphene oxide layers were also transformed into initiators for performing surface-initiated atom transfer radical polymerization. For the first step, the GO layers were converted into surface-initiator functionalized graphene oxide (SI-GO) layers, and they were used for the polymerization of 2-diethylaminoethyl methacrylate (DEAEMA) as in bulk and in exfoliated forms. The exfoliated SI-GO is a new approach in the SI-ATRP polymerization method, and such kind of an initiator could polymerize the target monomer that was not achieved via anionic polymerization. The controlled polymerization was confirmed with several characterization techniques, and the molecular weight of the synthesized polymer was ~40000 g mol⁻¹ with a dispersity index of 1.2. The surface-initiated polymers were soluble in THF, and it was possible to dip-coat a membrane on the PAN support. Single gas transport experiments showed that the prepared amorphous polymer membranes are defect-free and show high selectivities such as 3158 for H₂O/N₂, 28 for CO₂/N₂, and 113 for H₂O/CO₂. Although the CO₂/N₂ selectivity is promising, the permeability coefficient of CO₂ is low, which fits with the results reported for other methacrylate membranes. The membranes showed high water vapor permeability coefficients, which would be beneficial for the membrane distillation in order to overcome water scarcity in the future.

The synthesis of the 2D metal-organic frameworks and their incorporation into the PIM-1 polymer matrix were also under consideration. In the experimental part of this section, ZIF-7 nanoparticles were synthesized, and they were transformed into $Zn_2(bim)_4$ nanosheets. With the pore diameter of 0.21 nm, $Zn_2(bim)_4$ nanosheets offer high hydrogen separation performance over other gases. For this reason, the $Zn_2(bim)_4$ nanosheets were incorporated into the PIM-1 polymer matrix. It was observed that the H_2/N_2 selectivity increased from 11 to 15 and decreased at further loadings. The prepared mixed matrix membranes could not surpass the 2008 Robeson upper bound even though such kind of a nanofiller boosted the PIM-1 performance.

Furthermore, the synthesis of two-dimensional novel covalent organic frameworks and their gas uptake experiments were realized. High-pressure adsorption experiments revealed that novel COFs show comparable gas uptakes, and CO_2/N_2 selectivities are in good agreement with the reported COF adsorbents. COF-HZG2 showed the exceptionally high CO_2/N_2 , and CH_4/N_2 selectivities with the solubility separation factor of ~25000 and ~5820 even though the BET surface areas and the pore volumes were lower than other COFs. This related to the non-polarization nature of nitrogen under high pressure.

As an outlook of this work, it is suggested to utilize the exfoliated nanolayers. Since graphene oxide is an insulating material, using conductive single-layer graphene, the percolation index can be detected. This gives us an interesting result for the explanation of gas transport through the PIM-1/G, PIM-1/GO, and PIM-1/FGO composite membranes. Exfoliated single-layer surface-initiated graphene oxide layers are promising initiators for the SI-ATRP polymerization, and the synthesis of block copolymers from exfoliated layers can be interesting for the membrane community. Another point for the pure GO membranes is to overcome the pinholes originated from the casting process that drastically decreases the performance of these membranes. Tuning the interlayer distance and the functional groups could be the next approach for the high-performance GO membranes as well. For the future, 2D MOF nanosheets, such as Zn₂(bim)₄, should be exfoliated to get better results even though the exfoliation is hurdle with the MOF nanosheets. Two-dimensional covalent organic frameworks offer a new prospect for the preparation of molecular sieving membranes to separate valuable components. It is worth noting that the pore size of the covalent organic frameworks must be tuned via post functionalization regarding the target gas molecules.

5.2. Zusammenfassung und Ausblick

Die Hauptmotivation der Arbeit war die Herstellung von 2D-Nanomaterialien und deren Anwendung in Dünnschicht-Kompositmembranen. Ein Teil der Arbeit befasste

sich mit der Herstellung von Graphenoxid (GO) und deren anschließende Funktionalisierung, die oberflächeninitiierte radikalische Atomtransferpolymerisation ausgehend von Graphenoxid-Oberflächen und die Synthese von metallorganischen und kovalenten organischen Rahmenstrukturen bzw. Gerüsten.

Als erstes wurden die Graphenoxid-Nanoblätter nach der Hummers-Methode funktionalisiert und ihre Struktur und Funktionalisierung bestimmt. Es konnte gezeigt werden, dass Graphenoxid-Nanoblätter nach der Synthese eine gewisse Menge an löslichen oxidativen Rückständen (OD) enthielten, die an der Oberfläche der Schichten adsorbiert sind und von der GO-Oberfläche entfernt werden müssen. Während der Experimente wurde berechnet, dass die Menge an oxidativen Verunreinigungen etwa 30 Gew.-% beträgt und die Stabilität der GO-Dispersion signifikant beeinflusst. Die Peeling-Experimente zeigten den Einfluss der OD auf die Stabilität der Dispersion. Somit zeigte die GO-Dispersion ohne oxidative Rückstände nach der Zentrifugation eine höhere Konzentration bzw. Stabilität.

Graphenoxid besitzt eine zweidimensionale Struktur aus einzelnen Schichten und konnte auf einen mikroporösen PAN-Träger aufgebracht werden. In durchgeführten Gastransportexperimenten konnte gezeigt werden, dass mit zunehmender GO-Dicke auf dem PAN-Träger die Permeanzen von CO₂, N₂ und CH₄ drastisch abnimmt, was den Durchgang von Wasserstoff durch die GO-Nanoschichten aber trotzdem noch weiterhin ermöglichte. Dies stützt die Ergebnisse der Suspensionsbilanz, bei der gezeigt werden konnte, dass CO2 aufgrund der vorhandenen Sauerstoffhaltigen funktionellen Gruppen GO viel stärker an GO adsorbiert wird als Stickstoff und Methan. Die Adsorptionen von N2 und CH4 wurden während der Experimente nicht nachgewiesen. Die Abnahme der Permeabilität von CO2 könnte auf einen solchen Faktor zurückgeführt werden. Es konnte gezeigt werden, dass GO ein vielversprechendes Material für die Trennung von Wasserstoff von Kohlendioxid ist. Es wurde gezeigt, dass in einer 15 nm dicken GO-Schicht der Trennfaktor für das Gasgemisch H₂/CO₂ 5 beträgt, was höher als die Knudsen-Diffusionsselektivität ist und es keinen Unterschied in der Permeanz des Wasserdampfs gab. Durch Auftragen der erhaltenen Ergebnisse in den Robeson-Plot von 2008 wurde die Überschreitung der Grenze erreicht, was zeigt, dass unsere Ergebnisse den in der Literatur angegebenen vorherigen Ergebnissen entsprechen. Wenn GO in die PIM-1-Polymermatrix eingebaut wird, ist der Durchgang der

Gasmoleküle verringert. Somit nimmt die Permeanz der Gasmoleküle allmählich mit der Schichtdicke ab und die Selektivitäten werden dadurch auch schlechter.

Im zweiten Teil der Arbeit ging es um die kovalente Modifikation der GO-Schichten, hierdurch ergeben sich neue Möglichkeiten von funktionalisierten Graphen-Schichten. Nach der Funktionalisierung änderte sich die Morphologie der GO-Schichten und ihre Auswirkungen auf die PIM-1-Mischmatrixmembran waren anders als bei reinem GO. Obwohl die modifizierten GO-Schichten nicht exfoliert wurden, zeigten sie eine erhöhte Selektivität für CO₂/N₂. Bei einer FGO-Beladung von 9 Gew.% wurde die Selektivität der PIM-1-Membran für CO₂/N₂ von 21 auf 26 erhöht. Eine weitere Erhöhung der Beladung behinderte den Fluss der Gasmoleküle durch die Mischmatrixmembran. Trotz reinem GO zeigte die FGO-Beladung bei hohen Beladungen übermäßige Gasdurchlässigkeiten, was mit dem Stoffübergang durch die Graphenschichten erklärt werden konnte.

Der dritte Teil der Arbeit befasste sich mit der Verwendung von mit Initiatoren funktionalisierten GO für kontrolliert radikalische Polymerisationen. Für den ersten Schritt wurden die GO-Schichten in Graphenschichten mit Initiatoren auf der Oberfläche (SI-GO) umgewandelt und zur Polymerisation 2von Diethylaminoethylmethacrylat (DEAEMA) im Bulk und in exfolierten Formen exfolierte SI-GO war SI-ATRPverwendet. Das ein neuer Ansatz im Polymerisationsverfahren, und eine solche Art von Initiator konnte das Zielmonomer polymerisieren, das nicht durch anionische Polymerisation erhalten werden konnte. Die mit kontrollierte Polymerisationsreaktion wurde verschiedenen Charakterisierungstechniken bestätigt und das Molekulargewicht des synthetisierten Polymers betrug ~ 40000 g mol⁻¹ mit einem Dispersitätsindex von 1,2. Die oberflächeninitiierten Polymere waren in THF gut löslich und es war möglich, aus solchen Lösungen eine Membran auf den PAN-Träger aufzutragen. Einzelgastransportversuche dass die hergestellten zeigten, amorphen Polymermembranen fehlerfrei sind und hohe Selektivitäten aufweisen, wie 3158 für H₂O/N₂, 28 für CO₂/N₂ und 113 für H₂O/CO₂. Obwohl die CO₂/N₂-Selektivität vielversprechend ist, ist die Permeabilität von CO2 viel geringer als erwartet und übertrifft die Robeson-Obergrenze von 2008 nicht, was mit den für andere Methacrylatmembranen angegebenen Ergebnissen übereinstimmt. Die Membranen zeigten eine hohe Wasserdampfdurchlässigkeit, was für die Membrandestillation und

somit für zukünftige Anwendungen (z.B. im Bereich der Wasseraufbereitung) von Interesse sein könnte.

Die Synthese der metallorganischen 2D-Gerüste und deren Einbau in die PIM-1-Polymermatrix war der vierte Teil der Arbeit. Im experimentellen Teil wurden ZIF-7-Nanopartikel synthetisiert und in Zn₂(bim)₄ -Nanoblätter umgewandelt. Mit einem Porendurchmesser von 0,21 nm bieten Zn₂(bim)₄-Nanoblätter eine hohe Wasserstoffpermeanz gegenüber anderen Gasen, und somit sind diese Systeme interessant für Gasgemische mit Wasserstoff. Unter Berücksichtigung dieses Merkmals wurden Zn₂(bim)₄-Nanoblätter in die PIM-1-Polymermatrix eingebaut. Es wurde beobachtet, dass die H₂/N₂-Selektivität von 11 auf 15 anstieg und bei weiteren Beladungen abnahm. Die hergestellten Mischmatrixmembranen konnten die Robeson-Obergrenze von 2008 nicht übertreffen, obwohl durch den Nanofüllstoff die PIM-1-Leistung gesteigerten werden konnte.

Der letzte Teil der Arbeit war die Synthese neuer kovalenter organischer Gerüste für den Einsatz als Füllstoffe in Membranen für die Gasseparation. In dieser Arbeit wurden drei neue kovalente organische Gerüste synthetisiert und ihre Gasadsorptionseigenschaften analysiert. Hochdruckadsorptionsexperimente zeigten, dass die neuartigen COFs vergleichbar gute Gasaufnahmen zeigen und die CO₂/N₂-Selektivitäten gut mit den angegebenen COF-HZG3 übereinstimmen. COF-HZG2 extrem hohen CO₂/N₂- und CH₄/N₂-Selektivitäten zeigte die mit einem Löslichkeitstrennungsfaktor von ~ 25000 und ~ 5820, obwohl die BET-Oberflächen und die Porenvolumina niedriger waren als bei anderen COFs. Dies hing mit der Nichtpolarisation von Stickstoff unter hohem Druck zusammen.

Als Ausblick für zukünftige Arbeiten wird empfohlen, mit den exfolierten Nanoschichten zu arbeiten. Da Graphenoxid ein Isoliermaterial ist, kann unter Verwendung von leitendem einschichtigem Graphen der Perkolationsindex ermittelt werden, der ein interessantes Ergebnis für die Erklärung des Gastransports durch PIM-1/G, PIM-1/GO und PIM-1/FGO-Verbundmembranen darstellt. Abgeblätterte, einschichtige Graphenoxidschichten sind vielversprechende Initiatoren für die oberflächeninitiierte SI-ATRP-Polymerisation. Die Synthese von Blockcopolymeren aus exfolierten Schichten kann zu einer neuen Klasse von Polymeren führen, die für Anwendungen in Membranen interessant sein können. Ein weiterer Punkt für die reinen GO-Membranen ist die Überwindung der durch den Gießprozess verursachten

Fehlstellen, die die Leistung dieser Membranen drastisch verringern. Das Einstellen des Zwischenschichtabstands und der funktionellen Gruppen könnte der nächste Ansatz auch für die Hochleistungs-GO-Membranen sein. Für die Zukunft sollten 2D-MOF-Nanoblätter wie Zn₂(bim)₄ exfoliert werden, um bessere Ergebnisse zu erzielen, obwohl das Peeling mit den MOF-Nanoblättern eine Hürde darstellt. Zweidimensionale kovalente organische Gerüste bieten eine neue Perspektive für die Herstellung von Molekularsiebmembranen zur Trennung wertvoller Komponenten. Es ist anzumerken, die Porengröße der kovalenten organischen Gerüste dass durch Nachfunktionalisierung in Bezug auf die Zielgasmoleküle eingestellt werden muss.

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First of all, I would like to cordially thank Prof. Dr. Volker Abetz for giving me a chance to conduct my Ph.D. project at Helmholtz-Zentrum Geesthacht in the Institute of Polymer Research under his supervision. I am greatly indebted to him for his help, guidance, valuable criticism, support, and understanding in all situations. He helped me in all cases related to science, and made great contributions to my work, improving the quality of the work.

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In the end, I want to deliver my frank thanks to my parents, fiancée, relatives, and siblings, whose eternal love, support, and motivation helped me turn this whole Ph.D. into a success.

Appendix

Toxicity of chemicals

In the following table, all the chemicals used in research with H- and P-data are given.

Chemicals	GHS	Hazard	Precautiona	iry
	Symbols	Statements	Statements	
Graphite	GHS02,	H228, H319,	P210,	P280,
	GHS07	H335	P337+P313,	
			P304+P340,	P312
Sulfuric acid	GHS05	H314	P260,	P280,
			P301+P330+	⊦P331,
			P305+P351-	⊦P338,
			P310,	
			P303+P361-	+P353
Potassium permanganate	GHS03,	H272, H302,	P210, P220,	P280,
	GHS07,	H314,	P301+P330+P331,	
	GHS08,	H316d,	P303+P361+P353,	
	GHS05,	H373, H410	P305+P351-	⊦P338,
	GHS09		P310	
Potassium hydrogen phthalate	-	-	-	
2,4-Dichlorobenzamidoxime	GHS07	H315, H319,	P302+P352,	
		H335	P337+P313,	
			P304+P340,	P312,
			P280, P332-	-P313
Tetrahydrofuran	GHS02,	H225, H302,	P210,	
	GHS07,	H319, H335,	P303+P361-	⊦P353,
	GHS08,	H336, H351	P301+P330-	+P331,
			P312, P304-	⊦P340,
			P280	
2-Bromopropionyl bromide	GHS07	H302, H314,	P280,	
	GHS05	H317	P301+P330-	⊦P331,
			P303+P361-	⊦P353,
			P305+P351-	⊦P338,
			P310	

3,3,5,5-Tetramethylbenzidine	GHS07,	H302, H315,	P201, P280,
	GHS08	H319, H335,	P301+P310,
		H341	P302+P352,
			P304+P340
1,3,5-Benzenetricarbonyl chloride	GHS05	H314	P301+P330+P331,
			P280,
			P305+P351+P338,
			P310
Benzimidazole	-	-	-
Glacial acetic acid	GHS02,	H226, H314	P210,
	GHS05		P303+P361+P353,
			P280,
			P301+P330+P331,
			P305+P351+P338,
			P310
Sodium nitrate	GHS03,	H272, H319	P220, P305 +
	GHS07		P351 + P338
Sodium carbonate	GHS07	H319	P305 + P351 +
			P338
Sodium hydroxide solution	GHS05	H290, H314	P234 + P264 +
			P280
Hydrogen chloride	GHS04,	H280, H314,	P261, P280,
	GHS05,	H331	P303+P361+P353,
	GHS06		P304+P340+P310,
			P305+P351+P338,
			P403+P233
N, N-dimethylformamide	GHS02,	H226,	P201, P210, P261,
	GHS07,	H312+H332,	P280, P308+P313,
	GHS08	H319,	P370+P378
		H360d	
Aluminum chloride	GHS05	H314,	P280,
		EUH014	P301+P330+P331,
			P305+P351+P338,
			P308+P310
			210

Hydrogen peroxide	GHS07	H302+H332,	P280,
	GHS05	H318, H412	P302+P352.0,
			P305+P351+P338,
			P310.0
Hydrazine monohydrate	GHS05,	H301+H311,	P201, P260, P273,
	GHS06,	H314, H317,	P280,
	GHS08,	H330, H350,	P304+P340+P310,
	GHS09	H410	P305+P351+P338
Sodium bicarbonate	-	-	-
2,5-Dimethyl-6-phenylpyrazolo[1a]-	-	-	-
pyrimidin-7-amine			
(R _p)-1-[(1S)-(1-Aminoethyl)]-2-	-	-	-
(diphenylphosphino) ferrocene			
1,1-Bisdichlorophosphino-	GHS05	H314	P280,
ferrocene			P305+P351+P338,
			P310
N-Methyl-2-pyrrolidone	GHS07	H302, H315,	P261,
		H319, H335	P305+P351+P338
Thionyl chloride	GHS05,	H302, H314,	P260, P280,
	GHS06	H331	P303+P361+P353,
			P304+P340+P310,
			P305+P351+P338,
			P403+P233
2-Diethylaminoethyl methacrylate	GHS07	H315, H317,	P280,
		H319, H332	P305+P351+P338
Cu(I)Br	-	-	-
4,4'-Dimethyl-2,2'-dipyridyl	GHS07	H315, H319,	P261,
		H335	P305+P351+P338
Methyl iodide	GHS06,	H301, H312,	P261, P280,
	GHS08	H315, H331,	P301+P310, P311
		H335, H351	
Tris(3-	GHS07	H315, H319,	P261,
hydroxypropyltriazolylmethyl)amine		H335	P305+P351+P338

Triethylamine	GHS02,	H225, H302,	P210, P261, P280,
	GHS05,	H311+H331,	P303+P361+P353,
	GHS06	H314, H335	P305+P351+P338,
			P370+P378
Zn(NO ₃) ₂ ·6 H ₂ O	GHS03,	H272, H302,	P210, P220, P221,
	GHS07,	H315, H319,	P301+P312+P330,
	GHS09	H335, H410	P305+P351+P338,
			P370+P378
1,3,5-Tris(2-	-	-	-
hydroxyethyl)isocyanurate			
Benzene-1,3,5-tricarboxaldehyde	GHS07	H302, H315,	P261,
		H319, H335	P305+P351+P338
1,3,5-Trimethylbenzene	GHS02,	H226, H304,	P210, P301+P310,
	GHS07,	H315, H319,	P305+P351+P338,
	GHS08,	H335, H411	P331, P370+P378
	GHS09		
1,4-Dioxane	GHS02,	H225, H319,	P210, P280,
	GHS07,	H335, H351	P305+P351+P338,
	GHS08		P370+P378,
			P403+P235
Benzene	GHS02,	H350, H340,	P201, P202, P210,
	GHS07,	H225, H319,	P233, P240, P241,
	GHS08	H315, H372,	P242, P243, P260,
		H304	P264, P270, P280,
			P281, P301+P310,
			P302+P352,
			P303+P361+P353,
			P305+P351+P338,
			P307+P311,
			P308+P313, P321,
			P331, P332+P313,
			P337+P313, P362,
			P370+P378,

P403+P235, P405, P501

Sworn declaration

I hereby declare that this doctoral dissertation is my own work and that I have not used any sources other than those listed. I also declare that I have not previously applied or pursued a doctorate (Ph.D. degree).

Elvin Aliyev Hamburg, 11.05.2020

Affidavit

I declare under penalty of perjury that the present dissertation was written independently and solely by me using the specified writing tools.

Elvin Aliyev Hamburg, 11.05.2020

List of publications

1. Covalently modified graphene oxide and Polymer of Intrinsic Microporosity (PIM-1) in mixed matrix thin film composite membranes

Elvin Aliyev, Muntazim Munir Khan, Afig Nabiyev, Rasim Alosmanov, Irada Bunyadzadeh, Sergey Shishatskiy, Volkan Filiz

Nanoscale Research Letters 2018, 13:359; doi.org/10.1186/s11671-018-2771-3.

2. Structural characterization of graphene oxide: surface functional groups and fractionated oxidative debris

Elvin Aliyev, Volkan Filiz, Muntazim Munir Khan, Young J. Lee, Clarissa Abetz, Volker Abetz

MDPI Nanomaterials 2019, 9(8), 1180; <u>https://doi.org/10.3390/nano9081180</u>.

3. SI-ATRP Polymer-functionalized Graphene Oxide for use in Membrane Distillation.

Elvin Aliyev, Sergey Shishatskiy, Clarissa Abetz, Young Joo Lee, Silvio Neumann, Thomas Emmler, and Volkan Filiz

Adv. Mater. Interfaces 2020, 2000443; doi: 10.1002/admi.2000443

Author contribution to the publications

I am the author of three papers indicated in the list of publications.

The outcomes of this thesis were published in different journals, as indicated below.

"Covalently modified graphene oxide and Polymer of Intrinsic Microporosity (PIM-1) in mixed matrix thin film composite membranes" (Subchapters 4.1 and 4.2)

Elvin Aliyev, Muntazim Munir Khan, Afig Nabiyev, Rasim Alosmanov, Irada Bunyadzadeh, Sergey Shishatskiy, Volkan Filiz

Nanoscale Research Letters 2018, 13:359; doi.org/10.1186/s11671-018-2771-3. (Journal Impact Factor: 3.159 (2018))

In this publication, I was involved in the conceptualization, synthesis, and covalently modification of graphene oxide, characterization of the prepared nanomaterials, preparation of mixed-matrix membranes, gas permeation measurements, and interpretation of data and preparation of the paper.

Muntazim Munir Khan synthesized Polymer of Intrinsic Microporosity (PIM) and helped with scientific discussions.

Afig Nabiyev synthesized phosphochlorinated graphene oxide samples and helped in paper preparation.

Rasim Alosmanov helped with scientific discussions.

Irada Bunyad-zadeh helped in the synthesis of phosphochlorinated graphene oxide samples.

Sergey Shishatskiy helped in providing very valuable scientific insights in discussion of the results.

Volkan Filiz supervised the project and helped in the discussion of the results.

"Structural characterization of graphene oxide: surface functional groups and fractionated oxidative debris" (Chapter 4.1)

Elvin Aliyev, Volkan Filiz, Muntazim Munir Khan, Young J. Lee, Clarissa Abetz, Volker Abetz

MDPI Nanomaterials 2019, 9(8), 1180; <u>https://doi.org/10.3390/nano9081180</u>. (Journal Impact Factor: 4.034 (2018)).

In this publication, I was involved in the conceptualization, synthesis, and characterization of graphene oxide, interpretation of data, and preparation of the paper.

Volkan Filiz supervised the project and helped in the discussion of the results.

Muntazim Munir Khan helped with scientific discussions.

Young J. Lee helped in the execution of solid-state nuclear magnetic experiments, their characterization, and discussion of the results.

Clarissa Abetz helped with the SEM, EDX, and TEM investigations and provided valuable comments in the preparation of the paper. Her hard work made it possible to analyze and characterize the morphology of the graphene samples.

Prof. Volker Abetz helped with valuable scientific discussions and manuscript preparation.

"SI-ATRP Polymer-functionalized Graphene Oxide for use in Membrane Distillation" (Subchapter 4.3)

Elvin Aliyev, Sergey Shishatskiy, Clarissa Abetz, Young Joo Lee, Silvio Neumann, Thomas Emmler, and Volkan Filiz

Adv. Mater. Interfaces 2020, 2000443; doi: 10.1002/admi.2000443

In this publication, I was involved in the conceptualization, synthesis, and characterization of the SI-ATRP functionalized graphene oxide, interpretation of data, and preparation of the paper.

Sergey Shishatskiy helped in providing a very valuable scientific discussion of the results.

Clarissa Abetz helped with the SEM and EDX investigations and provided valuable comments in the preparation of the paper. Her hard work made it possible to analyze and characterize the morphology of the graphene samples.

Young J. Lee helped in the execution of solid-state nuclear magnetic experiments, their characterization, and discussion of the results.

Silvio Neumann helped in the execution of thermogravimetric analysis and its characterization.

Thomas Emmler helped with liquid-state nuclear magnetic experiments and their characterization.

Volkan Filiz supervised the project and helped in the discussion of the results.