

**DESIGN OF MOLECULAR CONFIGURATION  
OF POLYIMIDE NANOCOMPOSITE  
MEMBRANE FOR CO<sub>2</sub>/N<sub>2</sub> SEPARATION**

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**UNIVERSITI SAINS MALAYSIA**

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NANOCOMPOSITE MEMBRANE FOR CO<sub>2</sub>/N<sub>2</sub> SEPARATION**

**by**

**TAN PENG CHEE**

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## LIST OF ABBREVIATIONS

|          |  |
|----------|--|
| 6FDA     | 4,4'-(hexafluoroisopropylidene)diphthalic anhydride                                  |
| 6FpDA    | 4,4'-(hexafluoroisopropylidene)dianiline   |
| APTES    | (3-aminopropyl)triethoxysilane   |
| APTMS    | (3-aminopropyl)trimethoxysilane  |
| ATR-FTIR | Attenuated total reflectance-Fourier transform infrared                              |
| BAFM     | $\alpha,\alpha$ -bis(4-amino-3,5-dimethylphenyl)-1-(4'-fluorophenyl)methane          |
| BAPAF    | 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane                                    |
| BAPM     | $\alpha,\alpha$ -bis(4-amino-3,5-dimethylphenyl)-1-phenylmethane                     |
| BATFM    | $\alpha,\alpha$ -bis(4-amino-3,5-dimethylphenyl)-1-(3',4',5'-trifluorophenyl)methane |
| BDA      | Benzidine  |
| BDC      | 1,4-benzenedicarboxylate   |
| BET      | Brunauer-Emmett-Teller   |
| BisP     | 4,4'-(1,4-phenylenediisopropylidene) bisaniline                                      |
| BTC      | Benzene-1,3,5-tricarboxylate   |
| BTDA     | Benzophenone-3,3',4,4'-tetracarboxylic dianhydride                                   |
| CFC      | Chlorofluorocarbon   |
| CNT      | Carbon nanotube  |
| COMPASS  | Condensed-phase optimized molecular potentials for atomistic simulation studies      |
| CVFF     | Consistent-valence forcefield  |
| DABA     | 3,5-diaminobenzoic acid  |
| DAM      | 2,4,6-trimethyl- <i>m</i> -phenylenediamine  |
| DAP      | 2,4-diaminophenol dihydrochloride  |
| DLS      | Dynamic light scattering   |

|               |  |
|---------------|--|
| DMMDA         | 3,3'-dimethyl-4,4'-diaminodiphenylmethane                            |
| DPPD          | 3,8-diphenylpyrene-1,2,6,7-tetracarboxylic dianhydride               |
| DPt           | 3,8-di(4-tert-butylphenyl)pyrene-1,2,6,7-tetracarboxylic dianhydride |
| EDX           | Energy dispersive X-ray  |
| EMT           | Hexagonal Faujasite  |
| FAU           | Cubic Faujasite  |
| FESEM         | Field emission scanning electron microscopy                          |
| FFV           | Fractional free volume   |
| GC            | Gas chromatograph  |
| GCMC          | Grand canonical Monte Carlo  |
| GDP           | Gross domestic product   |
| GHG           | Greenhouse gases   |
| GONRs         | Graphene oxide nanoribbons   |
| GPC           | Gel permeation chromatography  |
| HBD           | Hydrogen bond donation   |
| Hmim          | 2-methylimidazole  |
| IR            | Infrared   |
| MD            | Molecular dynamics   |
| MFC           | Mass flow controller   |
| <i>m</i> -HAB | 4,4'-dihydroxybiphenyl-3,3'-diaminobiphenyl                          |
| MOF           | Metal organic framework  |
| MSD           | Mean square displacement   |
| <i>m</i> -TDA | 2,4-toluenediamine   |
| MWCNT         | Multi-walled carbon nanotube   |
| NMP           | 1-methyl-2-pyrrolidinone   |
| NPT           | Constant number of particles, pressure and temperature               |

|                          |  |
|--------------------------|--|
| NVT                      | Constant number of particles, volume and temperature           |
| <i>o</i> -BAT            | 1,4-bis(2-aminophenoxy)tritycene                               |
| ODA                      | 4,4'-oxydianiline  |
| ODPA                     | 4,4'-oxydiphthalic anhydride                                   |
| PAA                      | Polyamic acid  |
| <i>p</i> -BAT            | 1,4-bis(4-aminophenoxy)tritycene                               |
| PCFF                     | Polymer-consistent forcefield                                  |
| PDI                      | Polydispersity index   |
| <i>p</i> -DMPD           | 2,5-dimethyl-1,4-phenylenediamine                              |
| PEBA                     | Polyether-block-amide  |
| PEBA 1657                | Poly(amide-6-b-ethylene oxide)                                 |
| PES                      | Polyethersulfone   |
| PFDAB                    | 2-(perfluorohexyl)ethyl-3,5-diaminobenzoate                    |
| <i>p</i> -HAB            | 3,3'-dihydroxy-4,4'-diaminobiphenyl                            |
| PI                       | Polyimide  |
| PIM                      | Polymers of intrinsic microporosity                            |
| PMDA                     | Pyromellitic dianhydride                                       |
| <i>p</i> -PDA            | 1,4-phenylenediamine   |
| PSf                      | Polysulfone  |
| SO <sub>3</sub> H-MCM-41 | Sulfonic acid functionalized ordered mesoporous silica spheres |
| TEM                      | Transmission electron microscopy                               |
| TEOS                     | Tetraethyl orthosilica   |
| THF                      | Tetrahydrofuran  |
| UiO-66                   | Universitet i Oslo-66  |
| XRD                      | X-ray diffraction  |
| ZIF                      | Zeolitic imidazolate framework                                 |

## LIST OF SYMBOLS

|                  |  |   |
|------------------|--|---|
| $A$              | Area of membrane sample  | $\text{cm}^2$   |
| $a$              | Slope of mean square displacement versus time plot                     | $\text{\AA}^2/\text{ps}$                              |
| $\alpha_{a/b,B}$ | Binary gas selectivity   | dimensionless   |
| $\alpha_{a/b,I}$ | Ideal selectivity  | dimensionless   |
| $C$              | Concentration of ZIF-8 units   | $\text{mol}/\text{cm}^3$                              |
| $C_i$            | Gas concentration in polymer matrix                                    | $\text{cm}^3(\text{STP})/\text{cm}^3 \text{ polymer}$ |
| $C_o$            | Equilibrium concentration of ZIF-8 units                               | $\text{mol}/\text{cm}^3$                              |
| $D$              | Gas diffusivity  | $\text{cm}^2/\text{s}$                                |
| $D_o$            | Pre-factor of diffusivity  | $\text{cm}^2/\text{s}$                                |
| $D_s$            | Diffusion coefficient of solid particle                                | $\text{m}^2/\text{s}$                                 |
| $dp/dt$          | Permeation rate  | $\text{cmHg}/\text{s}$                                |
| $\Delta E$       | Binding energy of membrane system                                      | $\text{kcal}/\text{mol}$                              |
| $\Delta G_v$     | Gibbs free energy per unit volume                                      | $\text{J}/\text{m}^3$                                 |
| $\Delta p$       | Differential pressure  | $\text{cmHg}$   |
| $E_a$            | Electron affinity  | dimensionless   |
| $E_{complex}$    | Total energy of a membrane system comprising of different components   | $\text{kcal}/\text{mol}$                              |
| $E_d$            | Diffusion activation energy  | $\text{kcal}/\text{mol}$                              |
| $E_{individual}$ | Energy of individual component present in a particular membrane system | $\text{kcal}/\text{mol}$                              |
| $k$              | Boltzmann constant   | $\text{J}/\text{K}$                                   |
| $l$              | Membrane thickness   | $\text{cm}$   |
| $l_c$            | Initial membrane casting thickness                                     | $\mu\text{m}$   |
| $M$              | Mass of membrane or polyimide chain                                    | $\text{g}$  |
| $M_w$            | Molecular weight   | $\text{g}/\text{mol}$                                 |

|          |   |   |
|----------|---|---|
| $N$      | Number of diffusing molecules                                     | dimensionless                                   |
| $\eta$   | Viscosity   | Pa·s  |
| $\Omega$ | Atomic volume   | m <sup>3</sup>                                  |
| $P_a$    | Pure gas permeability of gas $a$                                  | Barrer  |
| $P_b$    | Pure gas permeability of gas $b$                                  | Barrer  |
| $P_{bf}$ | Pure gas permeability obtained from bubble flow permeation method | Barrer  |
| $P_{br}$ | Pure gas permeability obtained from barometric permeation method  | Barrer  |
| $P/P_o$  | Relative pressure   | dimensionless                                   |
| $P$      | Gas permeance   | GPU   |
| $P_a$    | Permeance of gas $a$  | cm <sup>3</sup> (STP)/(cm <sup>2</sup> ·s·cmHg) |
| $p$      | Operating pressure  | bar   |
| $p_d$    | Downstream pressure   | Pa  |
| $p_i$    | Sorbent pressure  | cmHg  |
| $\rho$   | Membrane density  | g/cm <sup>3</sup>                               |
| $R$      | Universal gas constant  | cm <sup>3</sup> ·cmHg/mol·K                     |
| $r$      | Radius of diffusing particle                                      | m   |
| $r^*$    | Minimum size to form a stable ZIF-8 nucleus                       | m   |
| $r(0)$   | Initial position vector of gas molecule                           | Å   |
| $r(t)$   | Final position vector of gas molecule over time interval $t$ .    | Å   |
| $S_i$    | Solubility of gas $i$   | cm <sup>3</sup> (STP)/(cm <sup>3</sup> ·cmHg)   |
| $\sigma$ | Supersaturation   | dimensionless                                   |
| $T$      | Temperature   | °C or K   |
| $T_g$    | Glass transition temperature                                      | °C  |
| $t$      | Simulation run time   | ps  |
| $\mu$    | Dipole moment   | D   |

|           |   |                        |
|-----------|---|------------------------|
| $\mu_x$   | Dipole moment in $x$ direction              | D                      |
| $\mu_y$   | Dipole moment in $y$ direction              | D                      |
| $\mu_z$   | Dipole moment in $z$ direction              | D                      |
| $V$       | Downstream reservoir volume                 | $\text{cm}^3$          |
| $V_{ds}$  | Volume of dope solution                     | mL                     |
| $V_e$     | Specific volume of sample                   | $\text{cm}^3/\text{g}$ |
| $V_o$     | Volume occupied by polymer chains           | $\text{cm}^3/\text{g}$ |
| $V_T$     | Total membrane volume                       | $\mu\text{m}^3$        |
| $V_w$     | Van der Waals volume                        | $\text{cm}^3/\text{g}$ |
| $\dot{V}$ | Permeate flow rate                          | $\text{cm}^3/\text{s}$ |
| $x_a$     | Mole fraction of gas $a$ in feed stream     | dimensionless          |
| $x_b$     | Mole fraction of gas $b$ in feed stream     | dimensionless          |
| $y_a$     | Mole fraction of gas $a$ in permeate stream | dimensionless          |
| $y_b$     | Mole fraction of gas $b$ in permeate stream | dimensionless          |
| $\gamma$  | Surface energy of ZIF-8 formed              | $\text{J}/\text{m}^2$  |

# REKA BENTUK KONFIGURASI MOLEKUL MEMBRAN NANOKOMPOSIT POLIIMIDA UNTUK PEMISAHAN CO<sub>2</sub>/N<sub>2</sub>

## ABSTRAK

Aplikasi luas membran poliimida (PI) untuk pemisahan CO<sub>2</sub> perindustrian telah dihadkan oleh keseimbangan intrinsik antara kebolehtelapan dan kememilihan. Sehubungan itu, kajian ini menerokai reka bentuk molekul polimer PI dan pembangunan membran nanokomposit PI/partikel kerangka imidazolat zeolitik-8 (ZIF-8) untuk meningkatkan prestasi pemisahan gas. Secara prinsipnya, berat molekul asid poliamik (PAA) dan PI yang sepadan sangat bergantung pada kereaktifan monomer yang dikawal oleh halangan sterik gantian monomer tetapi bukan sifat elektroniknya. Ia juga didapati bahawa perilaku reologi dan berat molekul PAA boleh bertindak sebagai garis panduan untuk menyaring protokol sintesis membran yang sesuai untuk struktur PI tertentu. Khususnya, PAA dengan kelikatan yang tinggi (> 81 cP) dan berat molekul yang tinggi ( $\geq 5.39$  Mg/mol) adalah prasyarat untuk membentuk membran PI tanpa kecacatan melalui penuangan larutan PI yang diimidai secara kimia. Ia juga mendapati bahawa kesan kesekerjaan antara konfigurasi atom dan kekutuban monomer harus dipertimbangkan dalam menganalisa pecahan isipadu bebas (FFV) membran PI. Suatu monomer dengan struktur tak sesatah dan kekutuban yang rendah adalah lebih baik untuk mencapai membran PI dengan FFV yang tinggi. Membran 4,4'-(heksafluoroisopropilidena)diftalik anhidrida (6FDA)-2,4,6-trimetil-*m*-fenilen diamina (DAM):asid 3,5-diaminobenzoik (DABA) (3:2) yang mempunyai FFV tinggi pada 0.212 telah menunjukkan prestasi pemisahan yang terbaik antara struktur PI yang dikaji. Ia mempunyai kebolehtelapan CO<sub>2</sub> sebanyak 63 Barrer (0.60 GPU) dan

kememilihan CO<sub>2</sub>/N<sub>2</sub> setinggi 57 dalam ujian penelapan pada 3 bar. Simulasi dinamika molekul (MD) juga dijalankan untuk meramalkan kelakuan pengangkutan gas membran PI. Sesungguhnya, kebolehharian model PI yang dibina menggunakan *Materials Studio* telah disahkan kerana kebolehtelapan CO<sub>2</sub> dan N<sub>2</sub> yang diramalkan hanya berbeza daripada keputusan ujikaji dengan faktor 1.86 dan 1.76 masing-masing. Kemudian, ZIF-8 telah diletakkan di atas membran PI yang disokong oleh alumina melalui penyalutan celup untuk menghasilkan membran nanokomposit PI/ZIF-8. Keberkesanan (3-aminopropil)trietoksisilan (APTES) untuk meningkatkan keserasian antara alumina-PI-ZIF-8 telah diramal dengan menggunakan simulasi molekul berdasarkan pengiraan tenaga pengikat. Hasil simulasi juga disahkan selanjutnya dengan ujikaji. Dalam pemisahan gas perduaan, telapan CO<sub>2</sub> dan kememilihan CO<sub>2</sub>/N<sub>2</sub> yang optimum adalah 93.47 GPU dan 7.50 dengan penyalutan celup ZIF-8 sebanyak 5 kali. Secara keseluruhan, kajian ini memberikan gambaran asasi tentang peranan reka bentuk molekul dan membran nanokomposit PI/ZIF-8 dalam penyesuaian prestasi pemisahan gas membran. Kajian pada masa hadapan boleh ditumpukan kepada pengubahsuaian permukaan ZIF-8 untuk mengurangkan kecenderungan penggumpalan ZIF-8 dan seterusnya menambahbaik prestasi pemisahan gas membran nanokomposit PI/ZIF-8.