

## Supporting Information (SI)

For

**Subnanoporous Highly Oxygen Permselective Membranes  
from Poly(conjugated hyperbranched macromonomer)s Synthesized  
by One-pot Simultaneous Two-mode Homopolymerization of  
1,3-Bis(silyl)phenylacetylene Using a Single Rh Catalytic System:  
Control of their Structures and Permselectivities**

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# Experimental

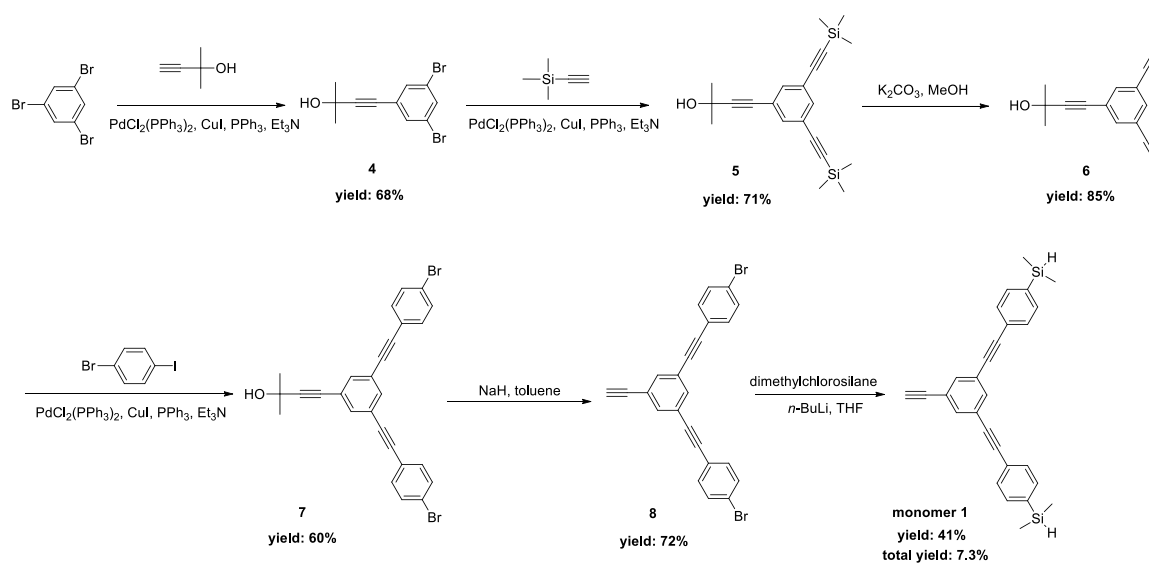
## 1. Materials

All the solvents used for synthesis and polymerizations of the monomers were distilled as usual. The polymerization initiator,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  (nbd = 2,5-norbornadiene) and polyaddition (hydrosilylation) catalyst,  $\text{RhCl}(\text{PPh}_3)_3$  purchased from Aldrich Chemical were used as received. (*R*)-phenylethylamine, (*S*)-1-cyclohexylethylamine, (*S*)-*N,N*-dimethyl-1-phenylethylamine, 2-methylbutan-2-amine and diisopropylamine were purchased from Tokyo Chemical Co., Ltd., and used as received. All the solvents used for synthesis of the monomers and polymerizations were distilled as usual.

## 2. Synthesis of monomers (1-3; Chart 1)

All the reaction procedures were conducted under nitrogen.

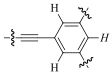
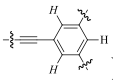
### 2.1 Synthesis of 3,5-bis{(4'-dimethylsilyl)phenylethynyl}phenylacetylene (**1**)(Scheme S1)



**Scheme S1. Synthesis of AB<sub>2</sub> type monomer(1)**

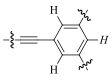
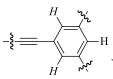
### (1) 4-(3',5'-Dibromophenyl)-2-methyl-3-butyn-2-ol (**4**)

A mixture of 2-methyl-3-butyn-2-ol (2.8 mL, 30 mmol), 1,3,5-tribromobenzene (9.4 g, 30 mmol), bis(triphenylphosphine)palladium(II) chloride (0.14 g, 0.20 mmol), triphenylphosphine (0.24 g, 0.92 mmol) and copper(I) iodide (0.12 g, 0.63 mmol) in dry triethylamine (150 mL) was stirred at 90°C for 16 h. After the mixture was filtered, the solvent was removed by evaporation and the crude product was purified by silica-gel column chromatography to give **4** as a yellow liquid. Yield: 68% (6.5 g).  $R_f$  = 0.40 (ethyl

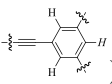
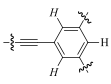
acetate/hexane = 1/4 (v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.60 (t, 1H, *J* = 2.0 Hz, , 7.49 (d, 2H, *J* = 2.0 Hz, , 2.10 (s, 1H, OH), 1.60 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>).

(2) 4-{3',5'-Bis(trimethylsilylethynyl)phenyl}-2-methyl-3-butyn-2-ol (**5**)

Trimethylsilylacetylene (3.5 mL, 38 mmol) was added to a mixture of **4** (6.0 g, 19 mmol), bis(triphenylphosphine)palladium(II) chloride (0.26 g, 0.34 mmol), triphenylphosphine (90 mg, 0.34 mmol) and copper(I) iodide (60 mg, 0.34 mmol) in dry triethylamine (120 mL). The reaction solution was stirred at 80°C for 24h and filtered. The solvent was removed by evaporation and the crude product was purified by silica-gel column chromatography to give **5** as a brown solid. Yield: 71% (4.7 g). *R<sub>f</sub>* = 0.35 (ethyl

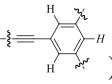
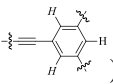
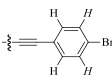
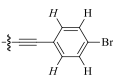
acetate/hexane = 1/4 (v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.49 (t, 1H, *J* = 1.6 Hz, , 7.45 (d, 2H, *J* = 1.6 Hz, , 2.04 (s, 1H, OH), 1.59 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 0.23 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>).

(3) 4-(3',5'-Diethynylphenyl)-2-methyl-3-butyn-2-ol (**6**)

To a mixture of K<sub>2</sub>CO<sub>3</sub> (2.5 g, 24 mmol) in methanol (40 mL), a methanol solution (10 mL) of **5** (8.4 g, 24 mmol) was added at room temperature. This reaction mixture was stirred for 12h at room temperature followed by treating with 10% HCl(aq) and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times. The organic layer was combined and dried over anhydrous MgSO<sub>4</sub> for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **6** as a white solid. Yield: 85% (4.2 g). *R<sub>f</sub>* = 0.35 (ethyl acetate/hexane = 1/4 (v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.52 (t, 1H, *J* = 1.6 Hz, , 7.50 (d, 2H, *J* = 1.6 Hz, , 3.09 (s, 2H, HC≡C), 2.01 (s, 1H, OH), 1.60 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>).



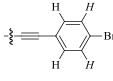
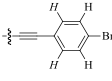
(4) 4-{3',5'-Bis(4''-bromophenylethynyl)phenyl}-2-methyl-3-butyn-2-ol (**7**)

A mixture of **6** (3.2 g, 15 mmol), bis(triphenylphosphine)palladium(II) chloride (0.26 g, 0.34 mmol), copper(I) iodide (65 mg, 0.34 mmol), triphenylphosphine (90 mg, 0.34 mmol) and 1-bromo-4-iodobenzene (10 g, 34 mmol) in dry triethylamine (150 mL) was stirred at 90°C for 24 h. After the mixture was filtered, the solvent was removed by evaporation and the crude product was purified by silica-gel column chromatography to give **7** as a brown viscous liquid. Yield: 60% (4.7 g). *R<sub>f</sub>* = 0.30 (ethyl acetate/hexane =



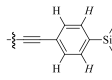
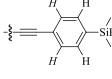
1/4 (v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.60 (t, 1H, *J* = 1.6 Hz, , 7.54 (d, 2H, *J* = 1.6 Hz, , 7.51 (d, 4H, *J* = 8.8 Hz, , 7.38 (d, 4H, *J* = 8.8 Hz, , 2.00 (s, 1H, OH), 1.61 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>).

(5) 3,5-Bis(4'-bromophenylethynyl) phenylacetylene (**8**)

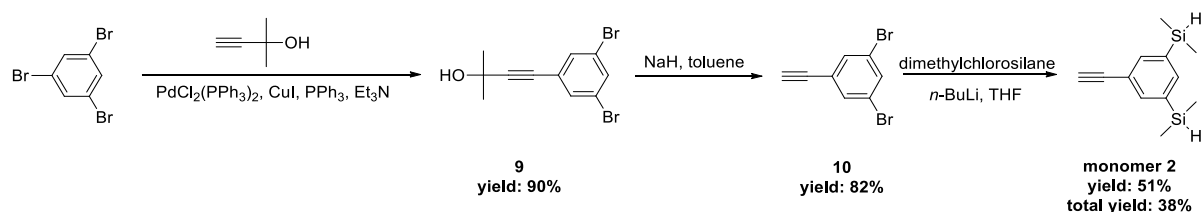
To a mixture of sodium hydride (0.31 g, 7.1 mmol) in toluene (100 mL), a toluene solution (20 mL) of **7** (3.7 g, 7.1 mmol) was added. The reaction solution was stirred at 90°C for 2h and the temperature was lowered to room temperature slowly. This solution was treated with 10% HCl(aq) and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times. The organic layers were combined and dried over anhydrous MgSO<sub>4</sub> for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **8** as a white solid. Yield: 72% (2.4 g). *R<sub>f</sub>* = 0.35 (ethyl acetate/hexane = 1/20 (v/v)).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.65 (t, 1H, *J* = 1.6 Hz, , 7.60 (d, 2H, *J* = 1.6 Hz, , 7.50 (d, 4H, *J* = 8.4 Hz, , 7.38 (d, 4H, *J* = 8.4 Hz, , 3.11 (s, 1H, HC≡C).

(6) 3,5-Bis{(4'-dimethylsilyl)phenylethynyl}phenylacetylene (**1**)

To a THF solution (34 mL) of **8** (1.6 g, 3.4 mmol), 1.57 mol/L of *n*-butyllithium hexane solution (6.4 mL, 10 mmol) was added dropwise at -75°C. The solution was stirred at -75°C for 4h and a THF solution (5 mL) of chlorodimethylsilane (0.75 mL, 6.7 mmol) was added dropwise. The temperature of the reaction solution was enhanced to slowly and kept overnight. The stirring was continued for another 1h after an excess of water was added to the solution. This reaction solution was extracted with diethyl ether, washed with brine, and dried over anhydrous sodium sulfate for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give monomer **1** as a colorless liquid. Yield: 41% (0.58 g). *R<sub>f</sub>* = 0.35 (ethyl acetate/hexane = 1/20 (v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.68 (t, 1H, *J* = 1.6 Hz, , 7.60 (d, 2H, *J* = 1.6 Hz, , 7.54 (d, 4H, *J* = 8.4 Hz, , 7.50 (d, 4H, *J* = 8.0 Hz, , 4.44 (hept, 2H, Si(CH<sub>3</sub>)<sub>2</sub>H), 3.11 (s, 1H, HC≡C), 0.37 (d, 12H, -Si(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>28</sub>H<sub>26</sub>Si<sub>2</sub>: C, 80.32; H, 6.26. Found: C, 80.34; H, 6.29. IR (KBr): 3310 (HC≡C), 2120 (SiH), 1250 (SiC) cm<sup>-1</sup>.

2.2 Synthesis of 3,5-bis(dimethylsilyl)phenylacetylene (**2**)(Scheme S2)

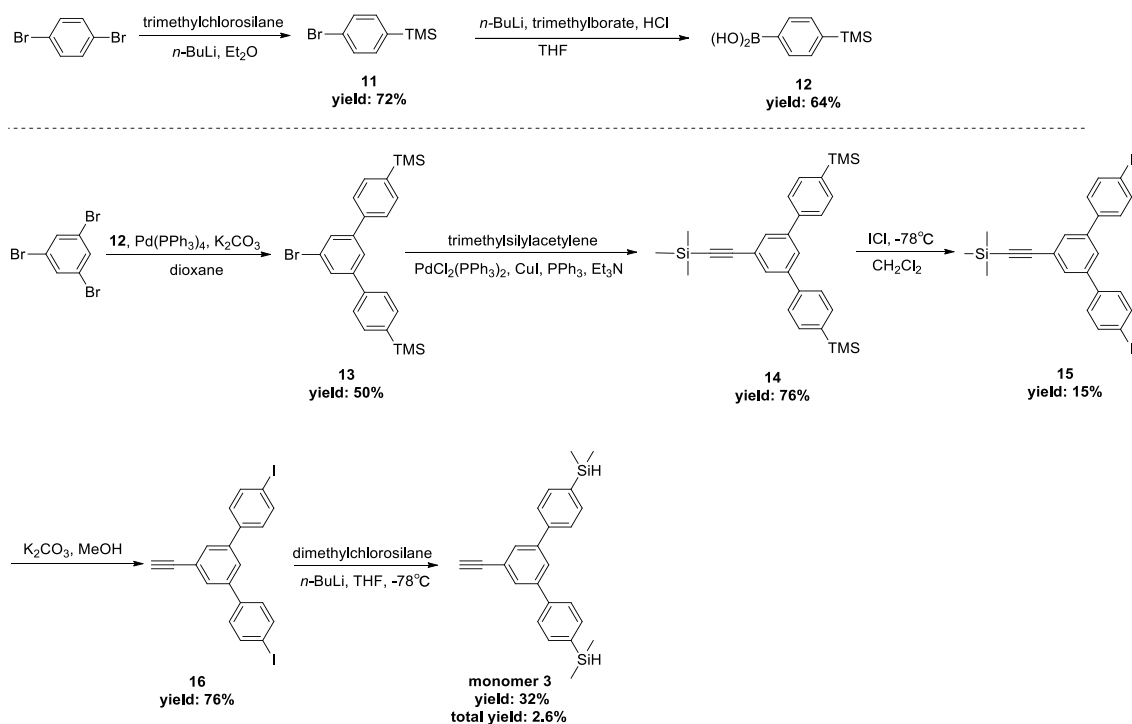


Scheme S2. Synthesis of AB<sub>2</sub> type monomer(2).

According to our report<sup>20</sup>, monomer **2** was synthesized. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.67 (t, 1H, *J* = 1.6 Hz, ArH), 7.50(d, 2H, *J* = 1.6 Hz, ArH), 4.44 (hept, 2H, Si(CH<sub>3</sub>)<sub>2</sub>H), 3.11 (s, 1H, HC≡C), 0.35 (d,

12H, Si(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>12</sub>H<sub>18</sub>Si<sub>2</sub>: C, 65.98; H, 8.31. Found: C, 66.01; H, 8.30. IR (KBr): 3311 (HC≡C), 2120 (SiH), 1252 (SiC) cm<sup>-1</sup>.

### 2.3 Synthesis of 3,5-bis{(4'-dimethylsilyl)phenyl}phenylacetylene (**3**) (Scheme S3)



**Scheme S3. Synthesis of AB<sub>2</sub> type monomer(3).**

#### (1) 1-Bromo-4-trimethylsilylbenzene (**11**)

To a diethyl ether solution (50 mL) of 1,4-dibromobenzene (5.9 g, 25 mmol), 1.56 mol/L of *n*-butyllithium hexane solution (16 mL, 25 mmol) was added dropwise at 0 °C. This solution was stirred for 2h at 0 °C and a diethyl ether solution (10 mL) of trimethylchlorosilane (3.0 mL, 28 mmol) was added dropwise. The temperature of the reaction solution was enhanced to room temperature slowly with stirring for another 1 h. An excess of water was added to the solution. The water layer was extracted with diethyl ether three times. The organic layers were combined and dried over anhydrous MgSO<sub>4</sub> for 1h. After filtration and concentration, the crude product was purified by distillation under reduced pressure (74°C, 5×10<sup>2</sup> Pa) to give **11** as a colorless liquid. Yield: 72% (4.1 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.44 (d, 2H, *J* = 8.4 Hz, ArH), 7.32 (d, 2H, *J* = 8.4 Hz, ArH), 0.24 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

#### (2) 4-(Trimethylsilyl)phenylboronic acid (**12**)

To a THF (50 mL) solution of **11** (5.7 g, 25 mmol), 1.56 mol/L *n*-butyllithium hexane solution (16 mL, 25

mol) was added dropwise at  $-78^{\circ}\text{C}$ . The solution was maintained under this condition for 2.5h. Trimethyl borate (3.4 ml, 30 mmol) in THF (20 ml) was added dropwise to the solution. Hydrochloric acid (10%, 20 mL) was added to the solution at room temperature and stirred for 2h. The resulting aqueous layer was extracted with diethyl ether (100 ml) and the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude product was recrystallized from hexane to give **12** as a white powder. Yield: 64% (3.1 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  8.21 (d, 2H,  $J = 8.0$  Hz, ArH), 7.69 (d, 2H,  $J = 8.0$  Hz, ArH), 0.33 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ).

(3) *1-Bromo-3,5-bis(4'-trimethylsilylphenyl)benzene (13)*

A mixture of 1,3,5-tribromobenzene (7.8 g, 25 mmol), 4-trimethylsilylphenylboronic acid (**12**) (9.7 g, 50 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (2.9 g, 2.5 mmol) and  $\text{K}_3\text{PO}_4$  (11 g, 50 mmol) in dioxane (100 mL) was stirred at  $85^{\circ}\text{C}$  for 24 h. The solution was extracted with diethyl ether three times at room temperature. The organic layers were combined and dried over anhydrous  $\text{MgSO}_4$  for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **13** as a white solid. Yield: 50% (9.0 g).  $R_f = 0.42$  (hexane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.76 (t, 1H,  $J = 1.6$  Hz, ArH), 7.66 (d, 2H,  $J = 1.6$  Hz, ArH), 7.63 (br, 8H, ArH), 0.33 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).

(4) *1-Trimethylsilylethynyl-3,5-bis(4'-trimethylsilylphenyl)benzene (14)*

A mixture of **13** (11 g, 25 mmol), bis(triphenylphosphine)palladium(II) chloride (0.28 g, 0.50 mmol), copper(I) iodide (0.28 g, 1.5 mmol), triphenylphosphine (0.26 g, 1.0 mmol) and trimethylsilylacetylene (4.0 mL, 28 mmol) in dry triethylamine (150 mL) was stirred at  $80^{\circ}\text{C}$  for 24 h. After the mixture was filtered, the solvent was removed by evaporation and the crude product was purified by silica-gel column chromatography to give **14** as a brown viscous liquid. Yield: 76% (8.9 g).  $R_f = 0.40$  (chloroform).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.67 (t, 1H,  $J = 1.6$  Hz, ArH), 7.59 (d, 2H,  $J = 1.6$  Hz, ArH), 7.56 (br, 8H, ArH), 0.40 (s, 18H,  $\text{ArSi}(\text{CH}_3)_3$ ), 0.31 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ).

(5) *1-Trimethylsilylethynyl-3,5-bis(4'-iodophenyl)benzene (15)*

$\text{ICl}$  (2.8 mL, 2.8 mmol) in dichloromethane (20 mL) was added dropwise to a dichloromethane solution (300 mL) of **14** (0.23 g, 0.50 mmol) at  $0^{\circ}\text{C}$  and the solution was stirred for 1h under this condition. Aqueous  $\text{Na}_2\text{S}_2\text{O}_5$  solution (150 mL, 150 mmol) was added to the solution which was stirred for another 1h. The resulting solution was extracted with dichloromethane three times and the organic layers were combined and dried over anhydrous  $\text{MgSO}_4$  for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **15** as a pink solid. Yield: 15% (43 mg).  $R_f = 0.34$  (ethyl acetate/hexane = 1/9 (v/v)).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.70 (t, 1H,  $J = 1.6$  Hz, ArH), 7.61 (d, 2H,  $J = 1.6$  Hz, ArH), 7.58 (br, 8H, ArH), 0.34 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ).

(6) *3,5-Bis(4'-iodophenyl)phenylacetylene (16)*

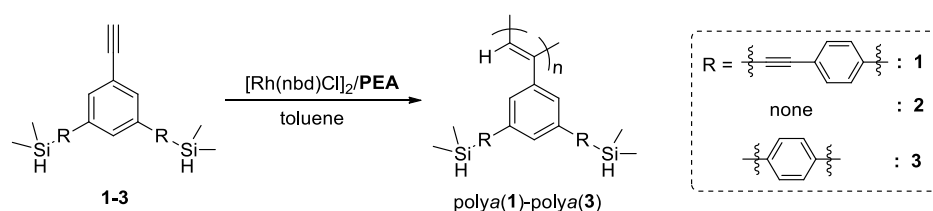
A methanol solution (5.0 mL) of **15** (1.4 g, 2.4 mmol) was added to K<sub>2</sub>CO<sub>3</sub> (0.25 g, 2.4 mmol) in methanol (30 mL) at room temperature. The solution was stirred for 12h at room temperature and treated with 10% HCl(aq). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The organic layers were combined and dried over anhydrous MgSO<sub>4</sub> for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **16** as a white solid. Yield: 76% (0.92 g). *R<sub>f</sub>* = 0.25 (ethyl acetate/hexane = 1/10 (v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.78 (t, 1H, *J* = 1.6 Hz, *ArH*), 7.68 (d, 2H, *J* = 1.6 Hz, *ArH*), 7.62 (br, 8H, *ArH*), 3.11(s, 1H, *HC*≡C).

(7) 3,5-Bis{(4'-dimethylsilyl)phenyl}phenylacetylene (**3**)

To a THF solution (34 mL) of **16** (5.0 g, 10 mmol), 1.56 mol/L of *n*-butyllithium hexane solution (19 mL, 30 mmol) was added dropwise at -75°C. After 4h a THF solution of dimethylchlorosilane (2.2 mL, 20 mmol) was added dropwise to the solution and the solution was stirred for 1h. The temperature of the reaction solution was enhanced to room temperature slowly and kept overnight. It was stirred for 1h after an excess of water was added to the solution. This reaction mixture was extracted with diethyl ether, and the organic layer was washed with brine, and dried over anhydrous sodium sulfate for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give monomer **3** as a colorless liquid. Yield: 32% (1.2 g). *R<sub>f</sub>* = 0.28 (ethyl acetate/hexane = 1/10 (v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.78 (t, 1H, *J* = 1.6 Hz, *ArH*), 7.70 (d, 2H, *J* = 1.6 Hz, *ArH*), 7.62 (br, 8H, *ArH*), 4.44 (hept, 2H, Si(CH<sub>3</sub>)<sub>2</sub>H), 3.11 (s, 1H, *HC*≡C), 0.37 (d, 12H, Si(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>24</sub>H<sub>26</sub>Si<sub>2</sub>: C, 77.77; H, 7.07. Found: C, 77.80; H, 7.04. IR (KBr): 3315 (*HC*≡C), 2123 (SiH), 1251 (SiC) cm<sup>-1</sup>.

### 3. Polymerization of monomers (1-3) in different catalytic systems (Schemes 1 and 2, and Figures 3 and 4)

#### 3.1 Synthesis of poly(**1**)-poly(**3**) by addition polymerization of **1-3** (Schemes 2 and S4)



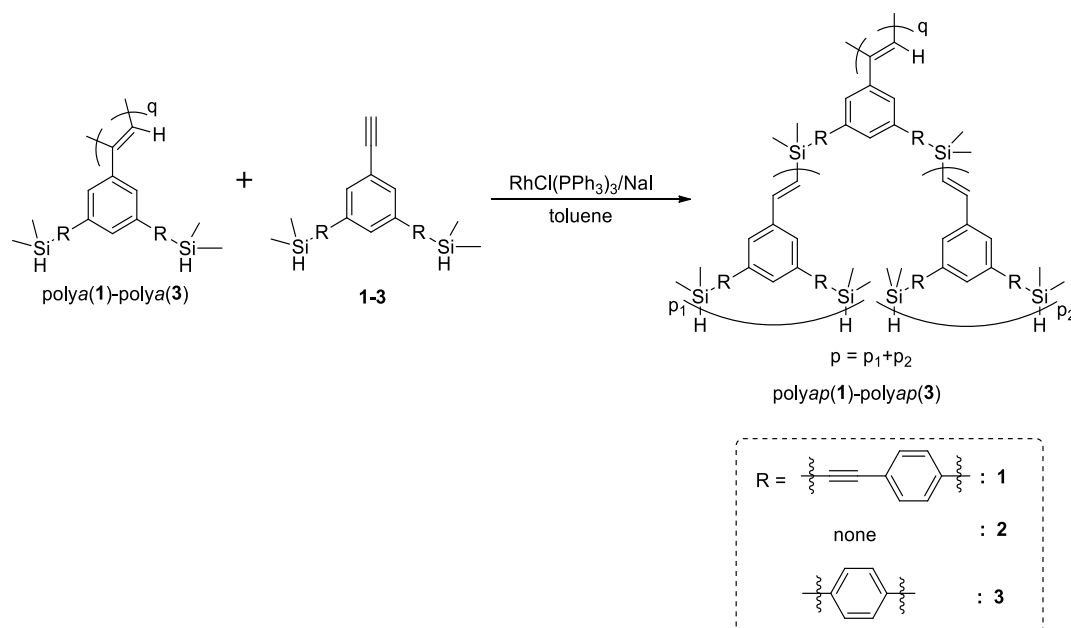
**Scheme S4. Synthesis of poly(**1**) - poly(**3**) by addition polymerization of AB<sub>2</sub> type monomers (1-3).**

A typical polymerization procedure was as follows: A solution of [RhCl(nbd)]<sub>2</sub> (0.37 mg, 8.0 μmol) in toluene (1.0 mL) was added to a toluene solution (1.0 mL) of **1** (84 mg, 0.20 mmol) and phenylethylamine (**PEA**) (48.4 mg, 0.40 mmol). The reaction solution was stirred at room temperature for 12h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and the



formed solid was dried in *vacuo* for 24h to give polya(**1**) as a red solid. Yield: 87%.  $M_n = 3.3 \times 10^4$  (Table 3, no. 5).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  8.0-5.5 (several broad peaks for aromatic and olefinic protons), 4.41 (br, 0.1H, SiH), 4.21 (br, 2.0H, SiH), 0.40-0.22 (br, 0.6H, Si( $\text{CH}_3$ )<sub>2</sub>), 0.22-0.03 (br, 12H, Si( $\text{CH}_3$ )<sub>2</sub>). (Figure 4 c)) Other addition polymerizations of the other monomers( **2** and **3**) were carried out similarly.

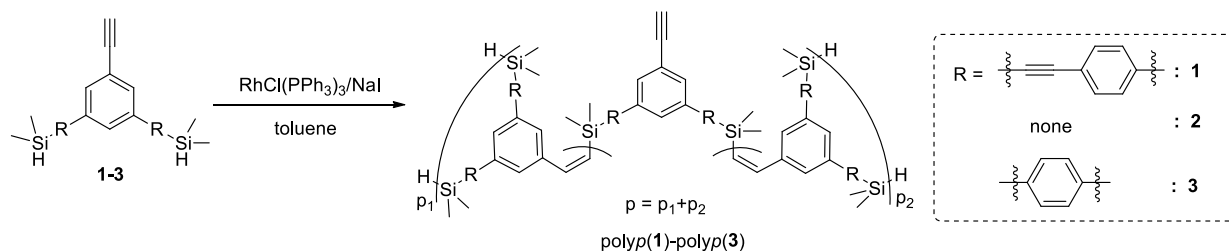
### 3.2 Synthesis of polyap(**1**)-polyap(**3**) by polyaddition (hydrosilylation) of **1-3** from polya(**1**)-polya(**3**) with **1-3** (Schemes 2 and S5)



**Scheme S5. Synthesis of polyap(**1**) - polyap(**3**) by polyaddition of polya(**1-3**) with **1-3**.**

A typical polymerization procedure was as follows: A solution of  $\text{RhCl}(\text{PPh}_3)_3$  (0.74 mg, 8.0  $\mu\text{mol}$ ) / NaI (0.15 mg, 8.0  $\mu\text{mol}$ ) in toluene (1.0 mL) was added to a toluene solution (1.0 mL) of **1** (0.12 mg, 0.20 mmol) and polya(**1**) (21 mg). The reaction solution was stirred at 80°C for 4h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and the formed solid was dried in *vacuo* for 24h to give polyap(**1**) as a red solid. Yield: 62%.  $M_n = 5.0 \times 10^4$  (Table 3, no. 4).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  8.0-5.5 (several broad peaks for aromatic and olefinic protons), 4.41 (br, 0.2H, SiH), 4.21 (br, 2.2H, SiH), 0.55-0.40 (br, 2.6H, Si( $\text{CH}_3$ )<sub>2</sub>), 0.40-0.22 (br, 1.2H, Si( $\text{CH}_3$ )<sub>2</sub>), 0.22-0.03 (br, 13.1H, Si( $\text{CH}_3$ )<sub>2</sub>). (Figures 3 2) and 4 b)) Other polyadditions of the precursor polymer (polya(**2**)) were carried out similarly.

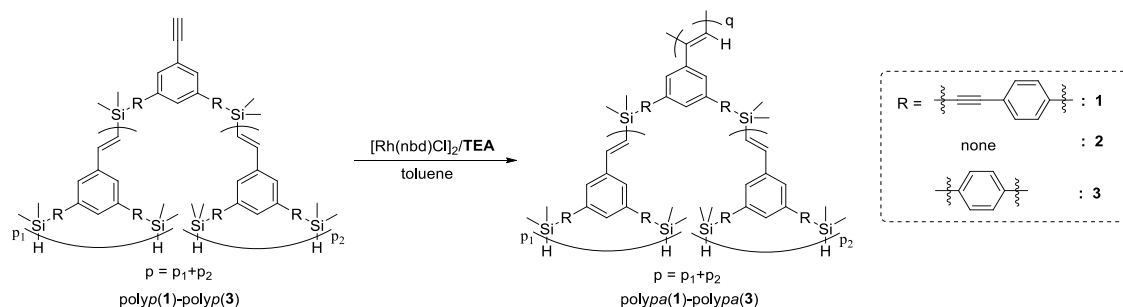
### 3.3 Synthesis of polyp(**1**)-polyp(**3**) by polyaddition (hydrosilylation) of **1-3** (Schemes 2 and S6)



**Scheme S6. Synthesis of polyp(1) - polyp(3) (macromonomers) by polyaddition of AB<sub>2</sub> type monomers(1-3).**

A typical polymerization procedure was as follows: A solution of  $\text{RhCl}(\text{PPh}_3)_3$  (0.74 mg, 8.0  $\mu\text{mol}$ ) / NaI (0.12 mg, 8.0  $\mu\text{mol}$ ) in toluene (1.0 mL) was added to a toluene solution (1.0 mL) of **1** (84 mg, 0.20 mmol). The reaction solution was stirred 80°C for 4h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and the formed solid was dried in *vacuo* for 24h to give the polyp(1) as a yellow solid. Yield: 90%.  $M_n = 3.0 \times 10^3$  (Table 3, no. 7). <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  8.0-5.5 (several broad peaks for aromatic and olefinic protons), 4.41 (br, 1H, SiH), 0.55-0.40 (br, 6.6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.40-0.22 (br, 5.6H, Si(CH<sub>3</sub>)<sub>2</sub>). (Figure 4 e)) Other polyadditions of the other monomers (**2** and **3**) were carried out similarly.

### 3.4 Synthesis of polypa(1)-polypa(3) by addition homopolymerization of polyp(1)-polyp(3) (macromonomers) (Schemes 2 and S7)

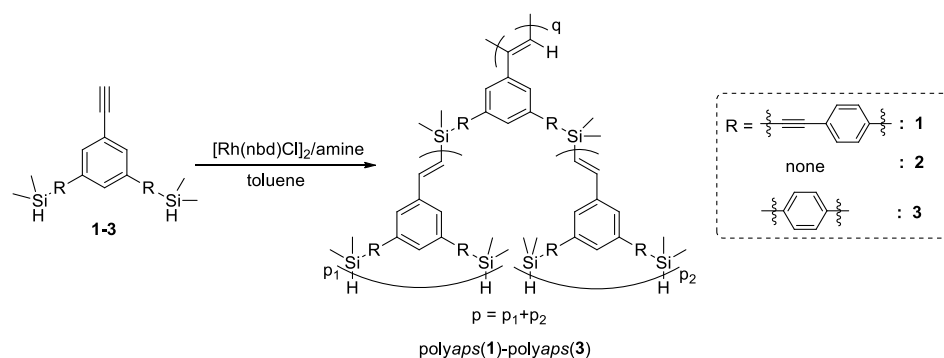


**Scheme S7. Synthesis of polypa(1) - polypa(3) by addition homopolymerization of polyp(1-3) (macromonomers).**

A typical polymerization procedure was as follows: A solution of  $[\text{RhCl}(\text{nbd})]_2$  (0.37 mg, 8.0  $\mu\text{mol}$ ) and triethylamine (TEA) (40 mg, 0.40 mmol) in toluene (1.0 mL) was added to a toluene solution (1.0 mL) of

polyp(1) (84 mg, 0.20 mmol). The reaction solution was stirred at room temperature for 12h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and dried in *vacuo* for 24h to give polypa(1) as a red solid. Yield: 94%.  $M_n = 1.2 \times 10^4$  (Table 3, no. 6).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  8.0-5.5 (several broad peaks for aromatic and olefinic protons), 4.41 (br, 3.6H, SiH), 4.21 (br, 3.2H, SiH), 0.55-0.40 (br, 26H,  $\text{Si}(\text{CH}_3)_2$ ), 0.40-0.22 (br, 21H,  $\text{Si}(\text{CH}_3)_2$ ), 0.22-0.03 (br, 19H,  $\text{Si}(\text{CH}_3)_2$ ). (Figures 3 3) and 4 d)) Other addition polymerizations of the precursor polymer (polyp(2)) were carried out similarly.

### 3.5 Synthesis of polyaps(1)-polyaps(3) by one-pot simultaneous two-mode homopolymerization(S) of 1-3 (Schemes 1, 2 and S8)



#### Scheme S8. Synthesis of polyaps(1) - polyaps(3) by simultaneous homopolymerization of AB<sub>2</sub> type monomers(1-3).

A typical polymerization procedure was as follows: A solution of  $[\text{RhCl}(\text{nbd})]_2$  (0.37 mg, 8.0  $\mu\text{mol}$ ) and triethylamine (**TEA**) (40 mg, 0.40 mmol) in toluene (1.0 mL) was added to a toluene solution (1.0 mL) of **1** (84 mg, 0.20 mmol). The reaction solution was stirred at room temperature for 12h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and the formed solid was dried in *vacuo* for 24h to give polyaps(1) as a red solid. Yield: 76%.  $M_n = 2.4 \times 10^5$  (Table 3, no. 1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  8.0-5.5 (several broad peaks for aromatic and olefinic protons), 4.41 (br, 2.0H, SiH), 4.21 (br, 2.7H, SiH), 0.55-0.40 (br, 16H,  $\text{Si}(\text{CH}_3)_2$ ), 0.40-0.22 (br, 12H,  $\text{Si}(\text{CH}_3)_2$ ), 0.22-0.03 (br, 16H,  $\text{Si}(\text{CH}_3)_2$ ). Other simultaneous two-mode homopolymerization(S) of the monomers( **2** and **3**) were carried out similarly.

#### 4. Model reactions of phenylacetylene with dimethylsilylbenzene in different catalytic systems (Figure 5 and Scheme 3)

A typical procedure was as follows: A solution of  $[\text{RhCl}(\text{nbd})]_2$  (0.37 mg, 8.0 mol) and triethylamine (**TEA**) (40 mg, 0.40 mmol) in toluene (1.0 mL) was added to a toluene solution (1.0 mL) of phenylacetylene (10 mg, 0.10 mmol) and dimethylsilylbenzene (14 mg, 0.10 mmol). The reaction solution was stirred at room temperature for 12h. Other model reactions by using different cocatalysts were carried

out similarly.

## 5. Membrane preparation

A toluene solution (1.0 mL) of the polymer (50 mg) was casted on a poly(tetrafluoroethylene) sheet. After the solvent was evaporated for 24h at room temperature, the membrane was detached from the poly(tetrafluoroethylene) sheet and dried in *vacuo* for 24h at room temperature.

## 6. Measurements of oxygen and nitrogen permeation

Oxygen and nitrogen permeability coefficients ( $P_{O_2}$  and  $P_{N_2}$ :  $\text{cm}^3(\text{STP})\cdot\text{cm} / \text{cm}^2\cdot\text{s}\cdot\text{cmHg}$ ) of mixed gases of oxygen and nitrogen ( $O_2 / N_2 = 20 / 80$  (v/v)) were measured by gas chromatographic method using YANACO GTR-10. The permeability coefficients ( $P$ ), the oxygen separation factors ( $\alpha$ ) and the diffusion coefficients ( $D$ ) ( $\text{cm}^2 / \text{s}$ ) were calculated by the following equations:

$$P = \frac{Q \times l}{A \times \Delta p \times t}$$

$$\alpha = P_{O_2} / P_{N_2}$$

$$D = l^2 / 6T$$

where  $Q$  ( $\text{cm}^3$ ),  $l$  (cm),  $A$  ( $\text{cm}^2$ ),  $\Delta p$  (cmHg),  $t$  (s), and  $T$  (s) are the amount of the permeated gas, the thickness of the membrane, the permeation area of the membrane, the pressure difference across the membrane, the permeation time and the time lag, respectively. The  $A$  and  $l$  of the membranes were  $1.77 \text{ cm}^2$  and  $60\text{-}120 \text{ }\mu\text{m}$ , respectively.

## 7. Other measurements

### 7.1 Density of polyaps(1)s

Density of the polymers were determined by floating method in ethanol / water as follows. A polymer was immersed into ethanol / water with a certain ratio and the ratio was changed until the polymer was floating in the middle of the mixed liquid. The density of the polymer was that of the mixed liquid.

### 7.2 Fractional free volume (FFV) of polyaps(1)s

The FFV values were calculated using the following relationship:

$$V_f = V_{sp} - 1.3V_w$$

$$FFV = V_f / V_{sp}$$

where  $V_f$  ( $\text{cm}^3/\text{g}$ ) is the free volume,  $V_{sp}$  ( $\text{cm}^3/\text{g}$ ) =  $1 / \text{density (g / cm}^3\text{)}$  is the specific volume, and  $V_w$  ( $\text{cm}^3/\text{g}$ ) is the specific van der Waals volume.  $V_w$  ( $\text{cm}^3/\text{g}$ ) =  $0.5407$  was calculated from  $V_w = V_{wi} (\text{cm}^3/\text{mol}) / M(\text{molecular weight})(\text{g/mol})$ .  $V_{wi}$  ( $\text{cm}^3/\text{mol}$ ) is the molar van der Waals volume of polyaps(1).  $M$  was  $495.8$  and the  $V_{wi}$  value was  $268.08$  which was calculated by using the group contribution method of Bondi.

**Table S1. Fractional free volume (FFV) of polyaps(1)**

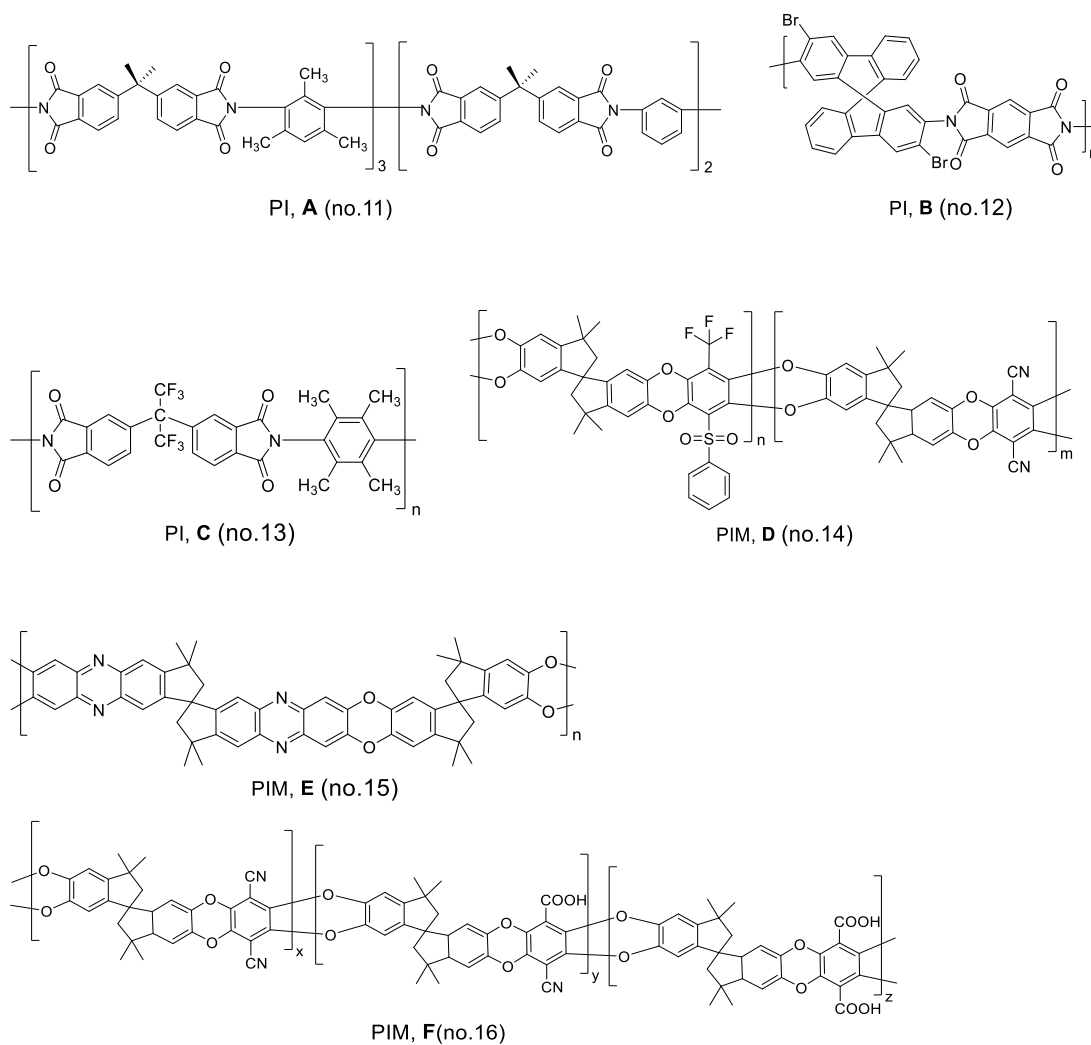
No. <sup>a</sup>	Density (g/cm <sup>3</sup> ) <sup>b</sup>	V <sub>sp</sub> (cm <sup>3</sup> /g)	V <sub>f</sub> (cm <sup>3</sup> /g)	FFV
1	0.9823	1.017	0.3140	0.3081
2	0.9758	1.025	0.3221	0.3142
3	0.9680	1.033	0.3301	0.3195

<sup>a</sup> The numbers correspond to those in Table 2; <sup>b</sup> Determined by floating method in ethanol / water.

## 8. Apparatus

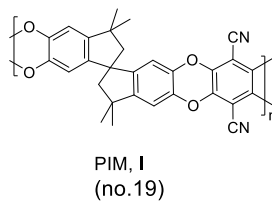
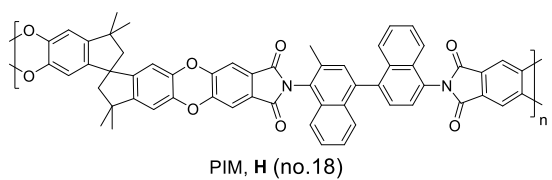
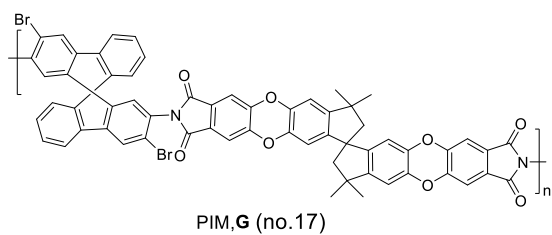
<sup>1</sup>H NMR (400 MHz) spectra were recorded on a VARIAN-400 spectrometer. The average molecular weights (*M<sub>n</sub>* and *M<sub>w</sub>*) were evaluated by gel permeation chromatography (GPC) using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration).

## Supporting charts and figures



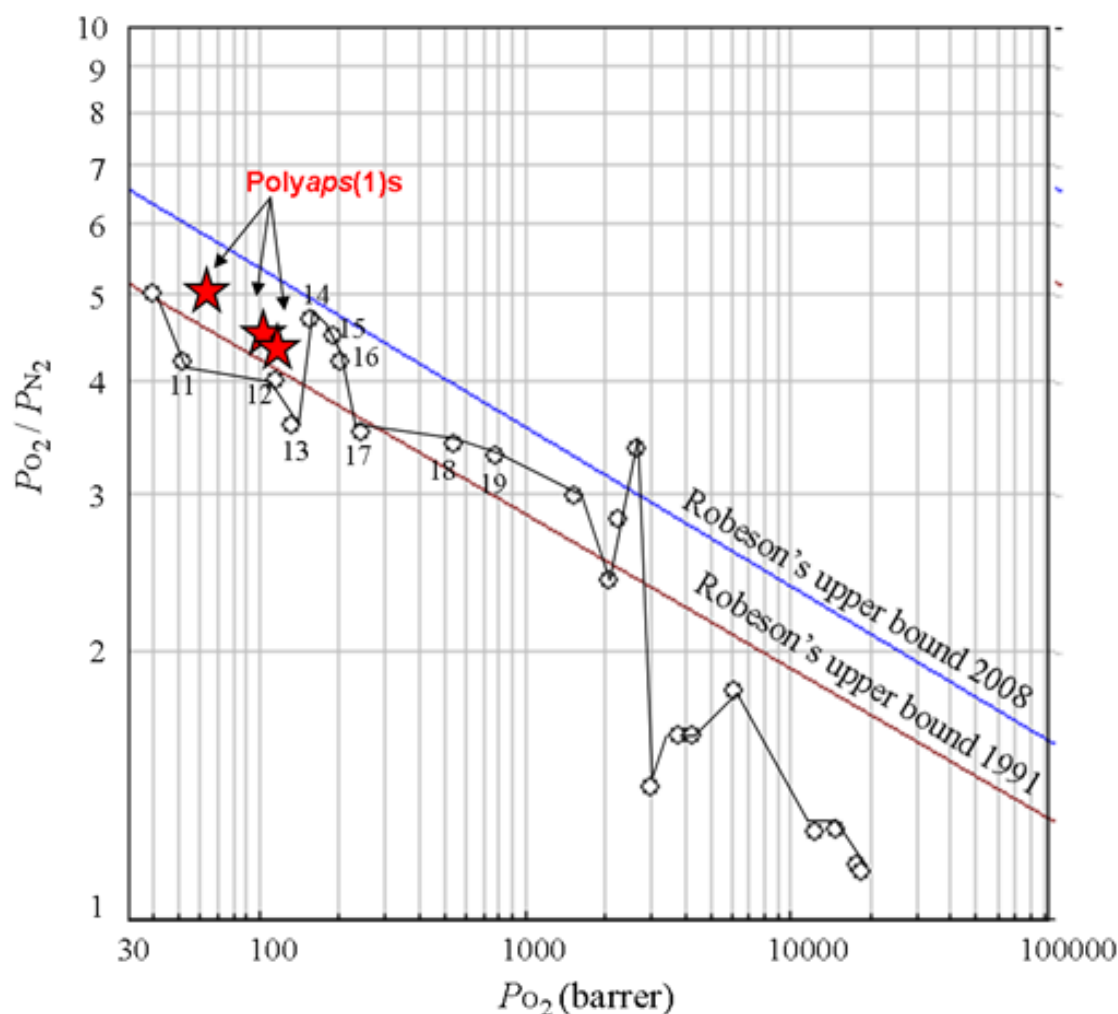
**Chart S1. Chemical structures of polymers showing the best permselectivity in the literatures.**

For their permselectivities and permeabilities, see Table 6 and Figures 5 and S1, nos. 11-16.



**Chart S2. Chemical structures of polymers showing the best permselectivity in the literature.**

For their permselectivities and permeabilities, see Figure S1, nos. 17-19.



**Figure S1. Actual upper plots for oxygen permeation of homopolymer membranes in the literature searched by our group.** The numbers in the figure correspond to those of the following papers we searched. For nos.11-16, see Table 6, Figure 5, and Chart S1, and for nos.17-19 see Chart S2. (\*Robeson's upper bounds from refs. 6 and 7)

*Note: As shown in Figures 5 and S1, judging from Robeson's paper in 2008, there are not many polymers over the upper bound 1991. Also judging from our searching this time, there are only a few polymers over the upper bound 1991 especially at the region of  $P_{O_2} = 40 - 150$  and  $> 3000$  barrer.*

no.11 (ref.74). Qiu, W.; Xu, L.; Chen, C.; Paul, D.; Koros, W. Gas Separation Performance of 6FDA-Based Polyimides with Different Chemical Structures. *Polymer*, **2013**, 54, 6226-6235.

no.12 (ref.75). Ma, X.; Salinas, O.; Litwiller, E.; Pinnau, I. Novel Spirobifluorene- and



Dibromospirobifluorene-Based Polyimides of Intrinsic Microporosity for Gas Separation Applications. *Macromolecules*, **2013**, *46*, 9618-9624.

no.13 (ref.76). Lin, W. H.; Chung, T. S. Gas permeability, Diffusivity, Solubility, and Aging Characteristics of 6FDA-Durene Polyimide Membranes. *J. Membr. Sci.*, **2001**, *186*, 183-193.

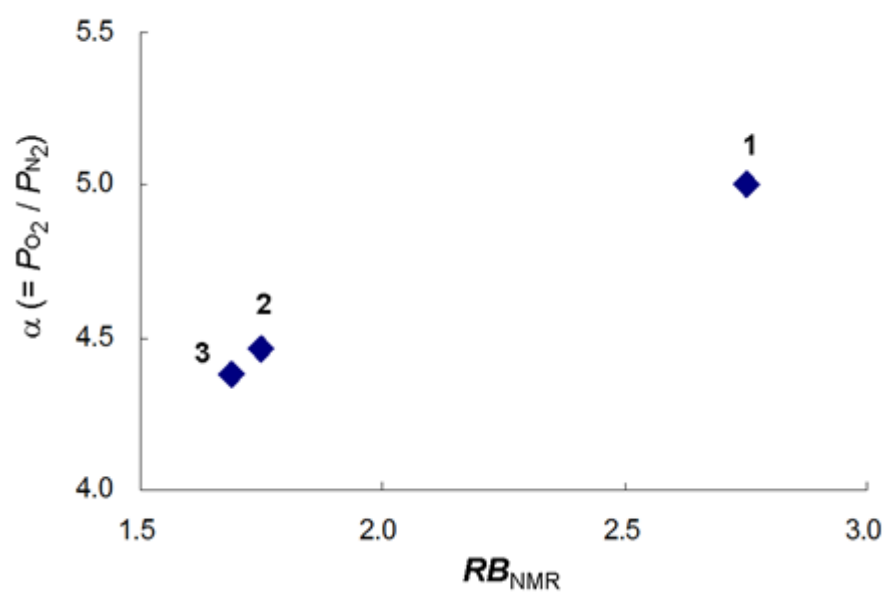
no.14 (ref.78). Du, N.; Robertson, G. P.; Song, J.; Pinnau, I.; Thomas, S.; Guiver, M. D. Polymers of Intrinsic Microporosity Containing Trifluoromethyl and Phenylsulfone Groups as Materials for Membrane Gas Separation. *Macromolecules*, **2008**, *41*, 9656-9662.

no.15 (ref.79). Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Ghanem, B. S.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D. Gas Separation Membranes from Polymers of Intrinsic Microporosity. *J. Membr. Sci.*, **2005**, *251*, 263-269.

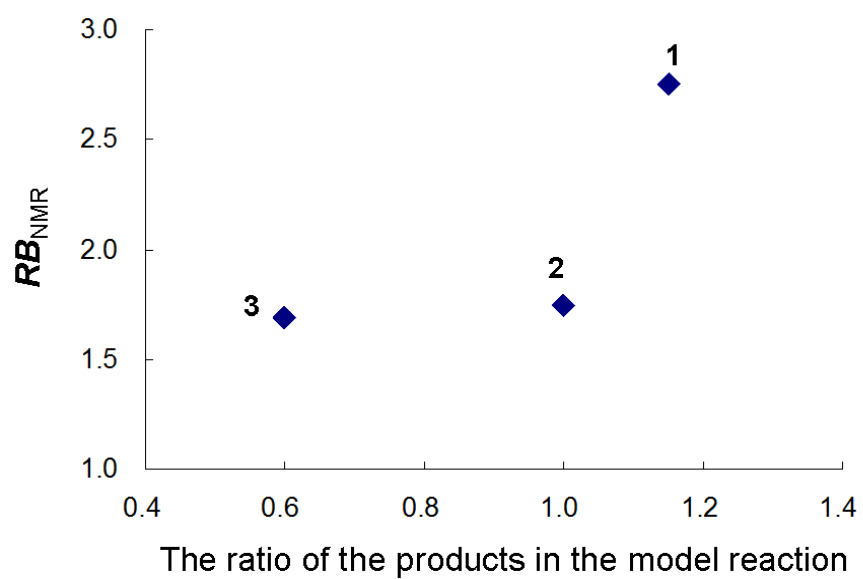
no.16 (ref.80). Du, N.; Robertson, G. P.; Song, J.; Pinnau, I.; Guiver, M. D. High-Performance Carboxylated Polymers of Intrinsic Microporosity (PIMs) with Tunable Gas Transport Properties. *Macromolecules*, **2009**, *42*, 6038-6043.

no.18. Ghanem, B.S.; McKeown, N.B.; Budd, P.M.; Selbie, J.D.; Fritsch, D. High-Performance Membranes from Polyimides with Intrinsic Microporosity. *Adv. Mater.*, **2008**, *20*, 2766-2771.

no.19. Staiger, C.L.; Pas, S.J.; Hill, A.J.; Cornelius, C.J. Gas Separation, Free Volume Distribution, and Physical Aging of a Highly Microporous Spirobisindane Polymer. *Chem. Mater.* **2008**, *20*, 2606-2608.



**Figure S2. Plots of  $\alpha (= P_{O_2}/P_{N_2})$  versus  $RB_{NMR}$  of polyaps(1).** For the numbers, see Table 6.



**Figure S3. Plots of  $RB_{\text{NMR}}$  of polyaps(1) versus the ratio of the products by hydrosilation and polymerization for phenylacetylene and dimethylsilylbenzene in the model reaction.** For the model reaction, see Figure 4 and Scheme 3. For the numbers see Tables 2 and 6.