

Supporting Information

Internal Molecular Free Volume in Organic Porous Copolymers: Tunable Porosity, Highly Selective CO₂ Adsorption

Yindong Zhang,^a Yunlong Zhu,^a Jun Guo,^b Shuai Gu,^a Yuanyuan Wang,^a Yu Fu,^a Dongyang Chen,^a Yijun Lin,^a Guipeng Yu,^{*,a,c} and Chunyue Pan,^{*,a}

^a College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China.

^b School of Chemistry and Material Science, Guizhou Normal University, Guiyang 550000, China.

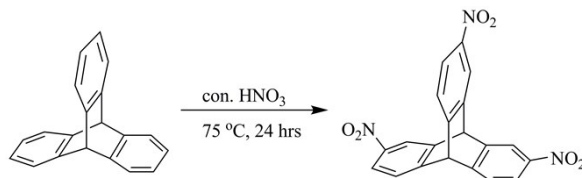
^c State Key Laboratory of Advanced Technology For Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

Table of Contents

1 General synthetic procedures	2
2 Molecular Modeling and “IMFV” Calculating	4
3 Infrared spectroscopy	5
4 Solid-state ¹³ C NMR	5
5 Water stability of NOP-34 series	6
6 Thermogravimetric analysis	6
7 XRD-pattern of NOP-34 series	7
8 SEM and TEM images of NOP-34@7030	7
9 BET plots for NOP-34 series	8
10 Gas adsorption data for NOP-34 series at 298 K	10
11 Additional gas adsorption data for NOP-34 series	10
12 Gas adsorption data and corresponding SSL fitting for NOP-34 series (273 K)	13
13 Gas adsorption selectivity study (CO ₂ /N ₂ , IAST, 298 K)	17
14 References	17

1 General synthetic procedures

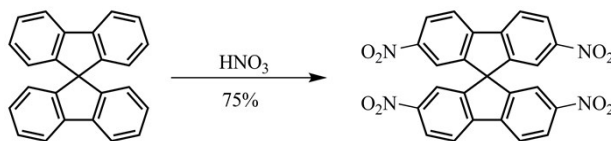
1.1. Synthesis of 2,7,14-trinitrotriptycene



Scheme 1 Schematic illustration of the targeted synthesis of 2,7,14-Trinitrotriptycene

2,7,14-Trinitrotriptycene was prepared by a modified procedure previously disclosed.¹ To triptycene (5 g, 20 mmol) was dropwise added concentrated HNO₃ (200 mL), and the mixture was heated at 75 °C for 24 h. The brown solution was cooled to room temperature, and then poured into H₂O (1000 mL) and vigorously stirred. The precipitate was collected, and washed with cooled water, and then dried under vacuum. The crude products were separated by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) as eluent, and a white solid was obtained in a yield of 47%. ¹H NMR (400 MHz, CDCl₃): δ 5.85 (s, 1H), 5.86 (s, 1H), 7.64-7.68 (m, 3H), 8.06-8.09 (m, 3H), 8.34-8.37 (m, 3H).

1.2. Synthesis of 2,2',7,7'-tetranitro-9,9'-spirobifluorene



Scheme 2 Schematic illustration of the targeted synthesis of 2,2',7,7'-Tetranitro-9,9'-spirobifluorene

2,2',7,7'-Tetranitro-9,9'-spirobifluorene was prepared by a known procedure.² A solution of fuming nitric acid (20 mL) was stirred at 0 °C, and 9,9'-spirobifluorene (3.6 g, 11.3 mmol) was added in small portions (20 times) during 10 min. The resulting mixture was kept at 0°C for 1 h, and a mixture of acetic anhydride (8 mL) and acetic acid (13 mL) was slowly charged. The resulting precipitate was filtered, and washed abundantly with water, and dried under vacuum. The crude products were separated by crystallization from tetrahydrofuran/hexane to obtain the light yellow solid in 77% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.58 (d, 4H, 3J) 8.5 Hz), 8.45 (dd, 4H, 3J) 8.5 Hz, 4J) 2.0 Hz), 7.63 (d, 4H, 4J) 2.0 Hz).

1.3. General procedure for azo polymerization

All copolymers were prepared by a known procedure.^{3,4} The detailed synthetic routes are as follows:

NOP-34@1000: 2,7,14-Trinitrotriptycene (0.778 g, 2 mmol) was dissolved in a mixture of THF (7 mL) and DMF (8 mL) in a three-necked round bottom flask equipped with a condenser, thermocouple and mechanical stirring. NaOH (1.38 g) in 3 mL de-ionized water and zinc powder (1.47 g) were added to the solution. The mixture was heated at 65 °C with vigorous stirring under N₂ atmosphere and kept at this temperature for 48 h then cooled to room temperature. The reaction mixture was poured into 200 mL 2 M HCl and stirred for 3h. The precipitate was filtered off and washed with distilled H₂O (150 mL), Me₂CO (150 mL), CHCl₃ (150 mL) and THF (150 mL) respectively. Subsequently, brown yellow precipitates were dried at 110 °C under vacuum for 12 h

to give NOP-34@1000 in 93 % yield.

NOP-34@7030: 2,7,14-Trinitrotriptycene (0.545 g, 1.4 mmol) and 2,2',7,7'- tetranitro-9,9'-spirobifluorene (0.298 g, 0.6 mmol) was dissolved in a mixture of THF (7 mL) and DMF (8 mL) in a three-necked round bottom flask equipped with a condenser, thermocouple and mechanical stirring. NaOH (1.38 g) in 3 mL de-ionized water and zinc powder (1.47 g) were added to the solution. The mixture was heated at 65 °C with vigorous stirring under N₂ atmosphere and kept at this temperature for 48 h then cooled to room temperature. The reaction mixture was poured into 200 mL 2 M HCl and stirred for 3h. The precipitate was filtered off and washed with distilled H₂O (150 mL), Me₂CO (150 mL), CHCl₃ (150 mL) and THF (150 mL) respectively. Subsequently, brownish red precipitates were dried at 110 °C under vacuum for 12 h to give NOP-34@7030 in 95 % yield.

NOP-34@3070: 2,7,14-Trinitrotriptycene (0.233 g, 0.6 mmol) and 2,2',7,7'- tetranitro-9,9'-spirobifluorene (0.694 g, 1.4 mmol) was dissolved in a mixture of THF (7 mL) and DMF (8 mL) in a three-necked round bottom flask equipped with a condenser, thermocouple and mechanical stirring. NaOH (1.38 g) in 3 mL de-ionized water and zinc powder (1.47 g) were added to the solution. The mixture was heated at 65 °C with vigorous stirring under N₂ atmosphere and kept at this temperature for 48 h then cooled to room temperature. The reaction mixture was poured into 200 mL 2 M HCl and stirred for 3h. The precipitate was filtered off and washed with distilled H₂O (150 mL), Me₂CO (150 mL), CHCl₃ (150 mL) and THF (150 mL) respectively. Subsequently, brownish red precipitates were dried at 110 °C under vacuum for 12 h to give NOP-34@3070 in 92 % yield.

NOP-34@0100: 2,2',7,7'-tetranitro-9,9'-spirobifluorene (0.992 g, 2 mmol) was dissolved in a mixture of THF (7 mL) and DMF (8 mL) in a three-necked round bottom flask equipped with a condenser, thermocouple and mechanical stirring. NaOH (1.38 g) in 3 mL de-ionized water and zinc powder (1.47 g) were added to the solution. The mixture was heated at 65 °C with vigorous stirring under N₂ atmosphere and kept at this temperature for 48 h then cooled to room temperature. The reaction mixture was poured into 200 mL 2 M HCl and stirred for 3h. The precipitate was filtered off and washed with distilled H₂O (150 mL), Me₂CO (150 mL), CHCl₃ (150 mL) and THF (150 mL) respectively. Subsequently, brownish red precipitates were dried at 110 °C under vacuum for 12 h to give NOP-34@0100 in 87 % yield.

1.4. High Performance Liquid Chromatography (HPLC) of TNTPC, TNSBF and the obtained filtrate solution (typically for NOP-5050)

For checking the synthesis of copolymers (typically for NOP-34@5050), the obtained filtrate solution during the polymerization after the generation of porous solids was analyzed by HPLC (Fig. S1). High performance liquid chromatogram (HPLC) was performed on a Hewlett–Packard (HP) 1100 liquid chromatography using a mixture of acetic acid (0.1 wt%) and actone (v/v ¼ 90:10) as eluting solvent and a 2.0 × 150 mm Microbore column (Waters Spherisorb® S5 ODS2) as a column. The retention time of TNTPC (2,7,14-trinitrotriptycene) and TNSBF (2,2',7,7'-tetranitro-9,9'-spirobifluorene) are about 6 minutes. And there is no corresponding signal (Retention time: from 1 to 12 minutes) detected for the filtrate solution. Thus we can conclude almost all TNTPC and TNSBF have take part in copolymerization. Most of TNTPC and TNSBF formed the polymer NOP-34@5050, and maybe a small proportion of them formed the oligomer precursors (Typically the retention time centered at 13~14 minutes) that are extracted off by the eluents subsequently.

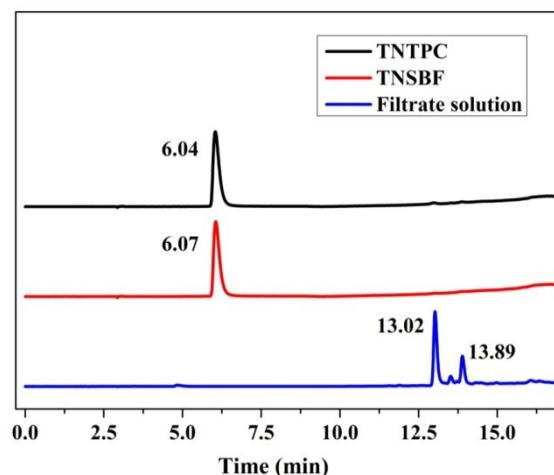


Fig. S1 HPLC image of monomers and filtrate solution

2 Molecular Modeling and “IMFV” Calculating

The “IMFV” is defined by Swager⁵ as “the gap of volume between that which is generated by the geometry of the structure and that occupied by the structure itself.” Accelrys Materials Studio modeling software was used to construct the spirobifluorene models. Discover dynamics smart minimizer with medium convergence for 5000 steps was used to determine the most energetically stable conformation of the structure. The software was also used to calculate the volume occupied by the spirobifluorene units using a van der Waals isosurface. This method is a direct geometric calculation of the internal cavities created by the structure. The different spaces defined in Figure S2b and Figure S2c represent the portions used to calculate the total IMFV. These volumes could be measured by using the symmetrical cavities labeled A, which are approximated as triangles or tetrahedrons defined by the van der Waals surfaces of the phenyls. As seen from Figure S2, the maximum width of the cavities is 7.4 Å. The IMFV by this model for an individual triptycene is $3 \times A \times 7.4 \text{ Å} \approx 93 \text{ Å}^3$. The IMFV for an individual spirobifluorene is $4 \times A \times 3.7 \text{ Å} \approx 24.4 \text{ Å}^3$.

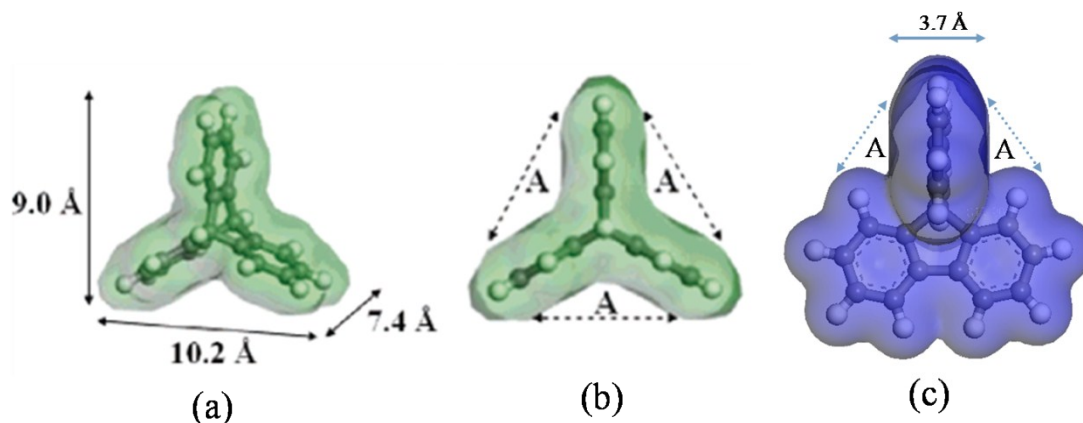


Fig. S2 Space-filling (van der Waals isosurface) triptycene and spirobifluorene models showing (a) width measurements along the triptycene axes, (b) IMFV three-dimensional view of triptycene, (c) IMFV three-dimensional view of spirobifluorene

3 Infrared spectroscopy

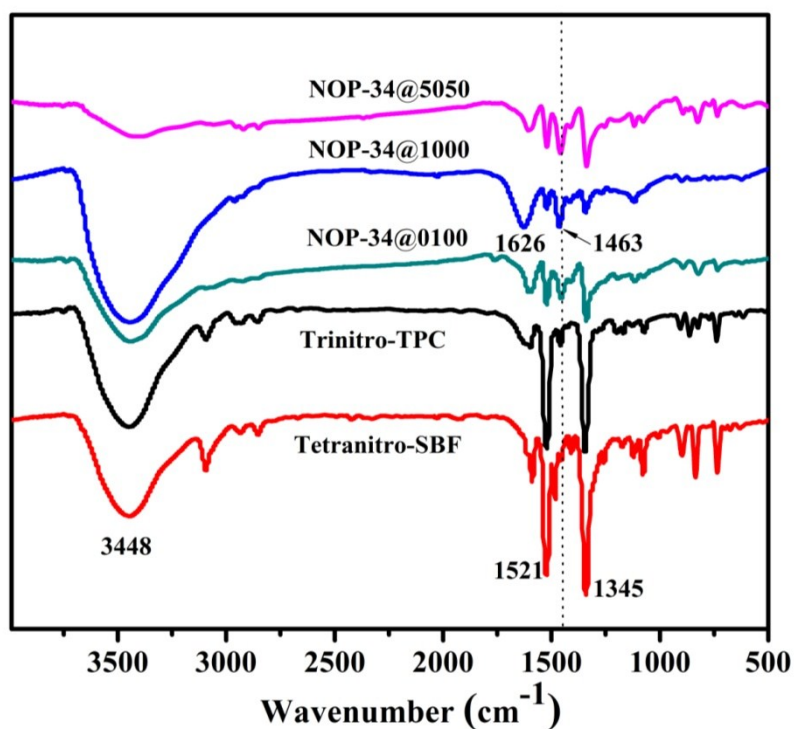


Fig. S3 FT-Infrared spectra of typical NOP-34 series and their monomers

4 Solid-state ^{13}C NMR

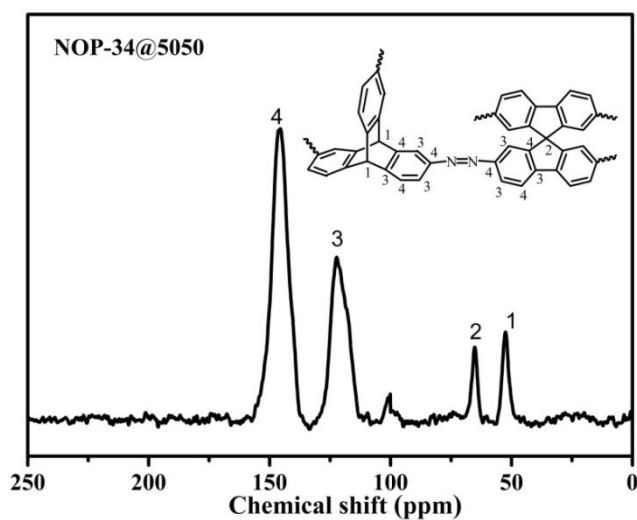


Fig. S4 Solid ^{13}C NMR spectrum of NOP-34@5050

5 Water stability of NOP-34 series

NOP-34s were dispersed in distilled H₂O (15 mL) and kept at 100 °C for three days. Afterwards, the solids were removed by filtration and dried at 110 °C under vacuum for 24 h. The BET surface areas (m² g⁻¹) of the samples after refluxing were measured from N₂ adsorption–desorption at 77 K. All NOP-34s showed no significant loss in their surface areas, thus proving their robust nature.

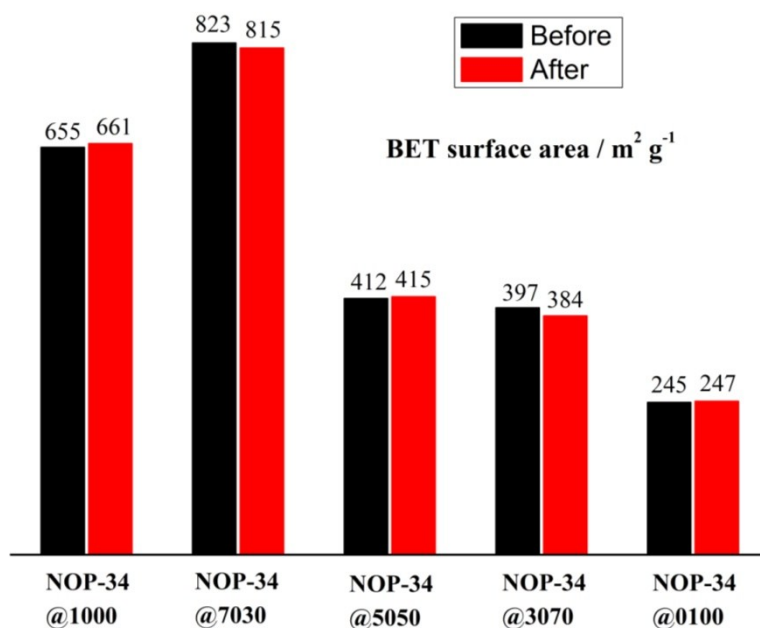


Fig. S5 Water stability of NOP-34 series

6 Thermogravimetric analysis

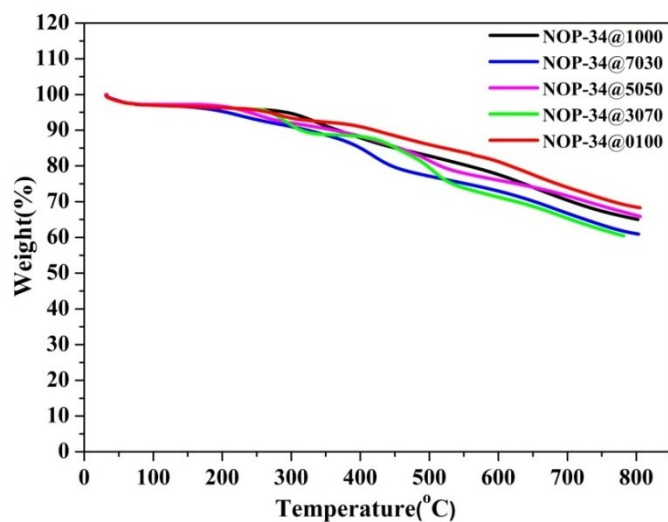


Fig. S6 Thermogravimetric analysis (TGA) for NOP-34 series

7 XRD-pattern of NOP-34 series

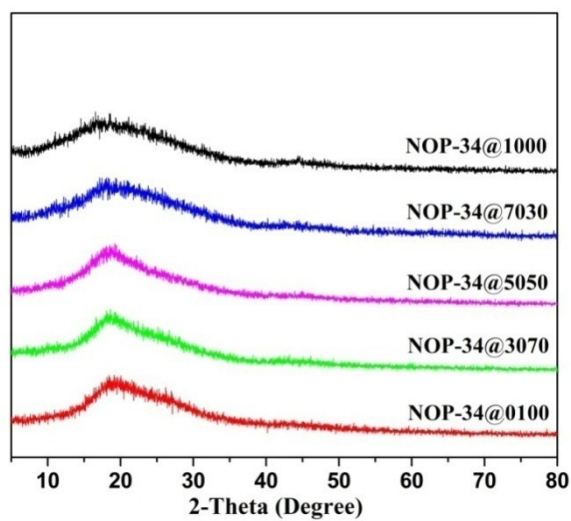


Fig. S7 Powdered XRD patterns of NOP-34 series

8 SEM and TEM images of NOP-34@7030

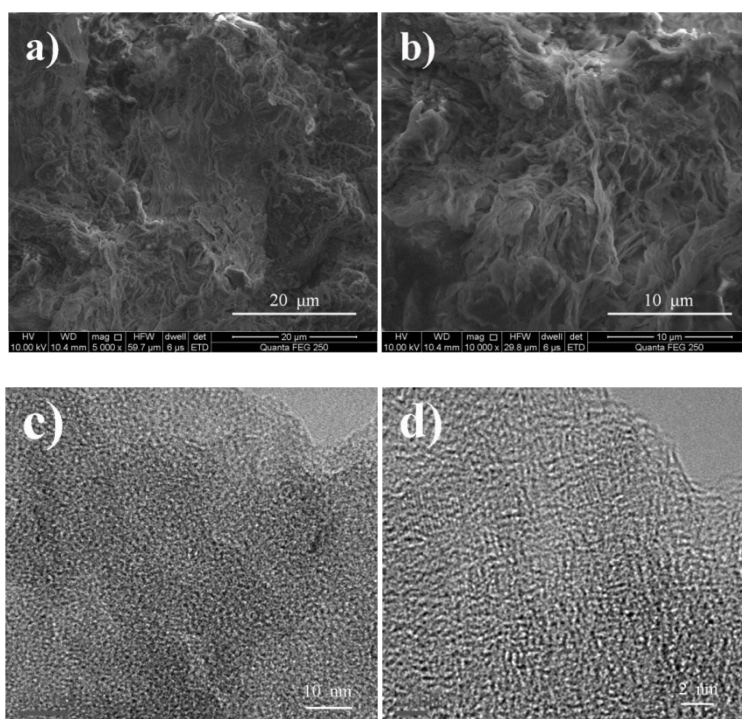


Fig. S8 FE-SEM and TEM images of NOP-34@7030 (a and b) SEM, (c and d) Low-magnification and high-magnification TEM images.

9 BET plots for NOP-34 series.

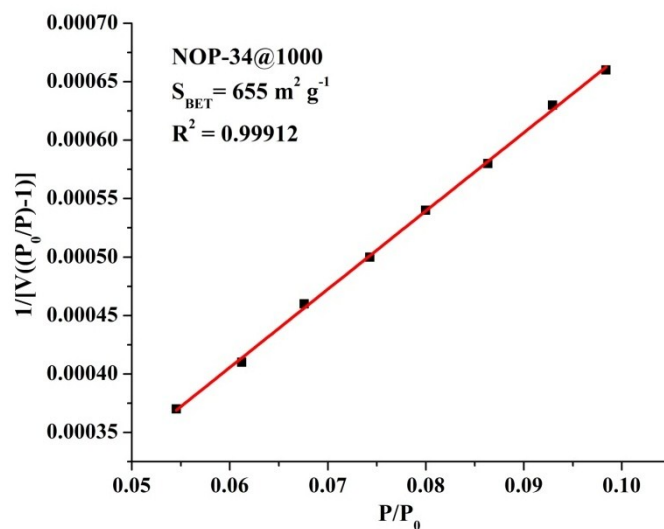


Fig. S9 BET plot ($P/P_0 = 0.05-0.1$) from N_2 isotherms at 77 K of NOP-34@1000. Correlation coefficient C constant was 2324.47.

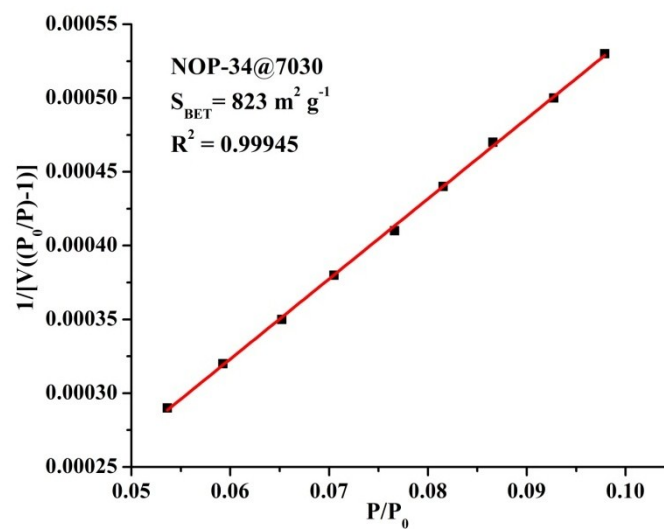


Fig. S10 BET plot ($P/P_0 = 0.05-0.1$) from N_2 isotherms at 77 K of NOP-34@7030. Correlation coefficient C constant was 817.15.

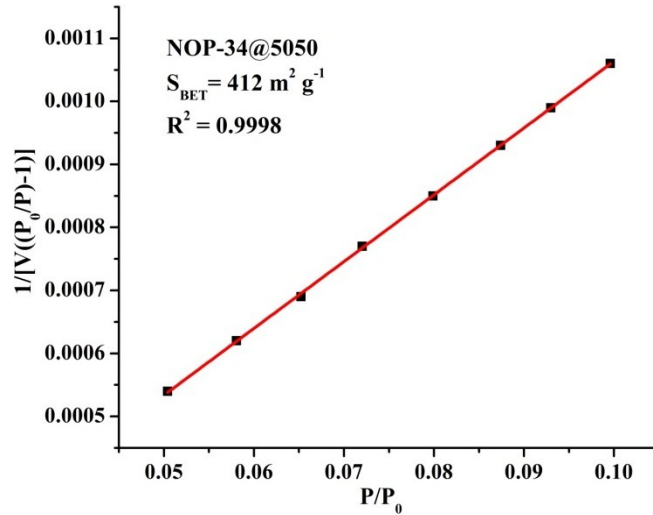


Fig. S11 BET plot ($P/P_0 = 0.05-0.1$) from N_2 isotherms at 77 K of NOP-34@5050. Correlation coefficient C constant was 3860.05.

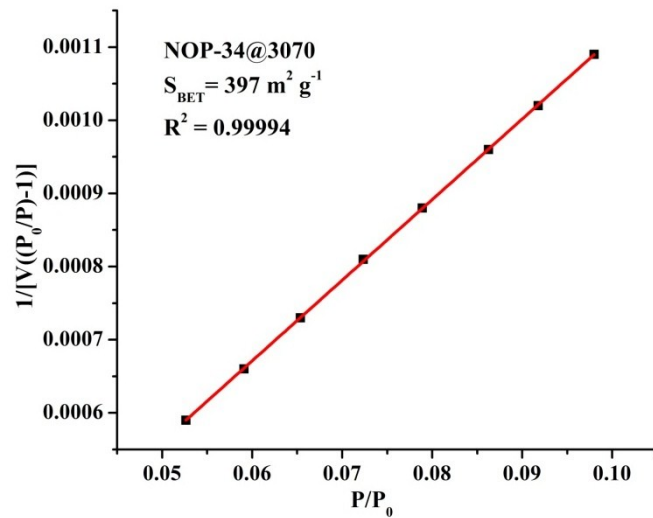


Fig. S12 BET plot ($P/P_0 = 0.05-0.1$) from N_2 isotherms at 77 K of NOP-34@3070. Correlation coefficient C constant was 1042.03.

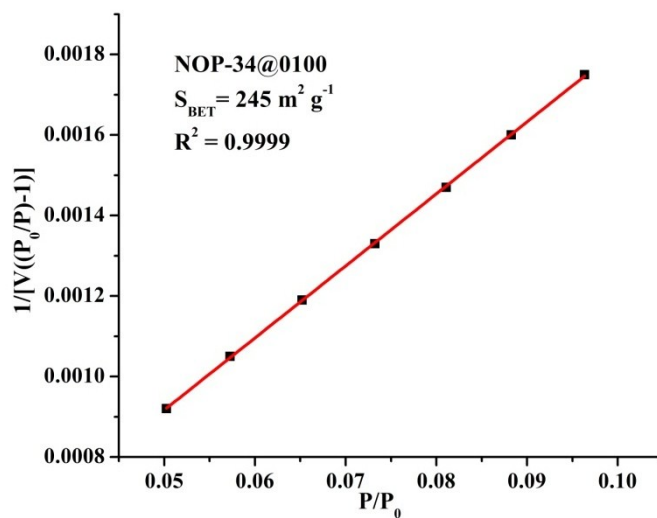


Fig. S13 BET plot ($P/P_0 = 0.05-0.1$) from N_2 isotherms at 77 K of NOP-34@3070. Correlation coefficient C

constant was 1138.97.

10 Gas adsorption data for NOP-34 series at 298 K

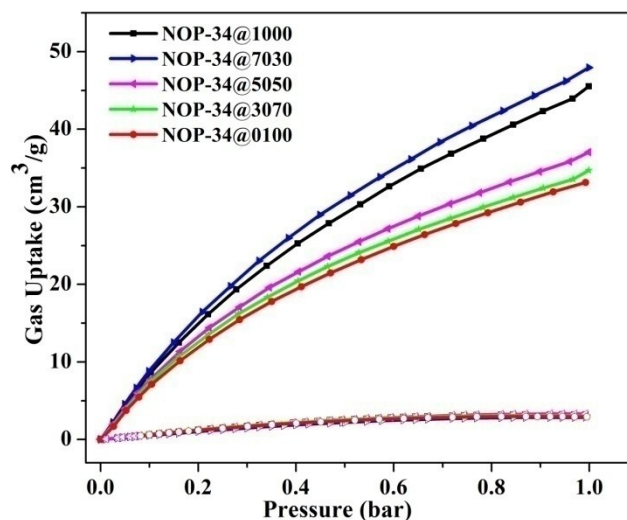


Fig. S14 CO₂ (filled symbols) and N₂ (open symbols) adsorption isotherms of NOP-34 series measured at 298 K

11 Additional gas adsorption data for NOP-34 series

The isosteric heats of adsorption were fitted to Clausius-Clapeyron equation:

$$Q_{st} = RT_1 T_2 (\ln P_1 / P_2) / (T_1 - T_2) \quad (1)$$

$$P = k_1 V_m^3 + k_2 V_m^2 + k_3 V_m + C \quad (2)$$

(where P, T, R, and C are the pressure, temperature at the equilibrium state, the gas constant, and equation constant, respectively).

Henry's law selectivities (S_H) were calculated by the ratio of Henry's law constants of CO₂ (H_C) and N₂ (H_N).

$$S_H = H_C / H_N \quad (3)$$

The Henry's law constants for CO₂ and N₂ were obtained by the slope of linear fitting of the initial data (pressure less than 0.1 bar) of the gas adsorption isotherms.

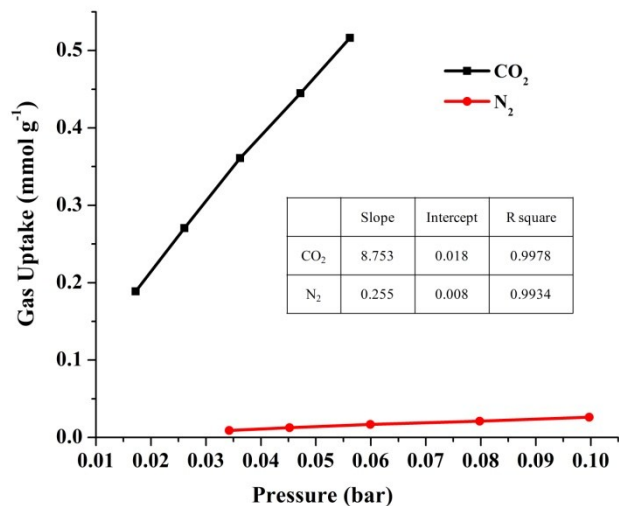


Fig. S15 CO₂-N₂ Initial slope selectivity (273 K) for NOP-34@1000

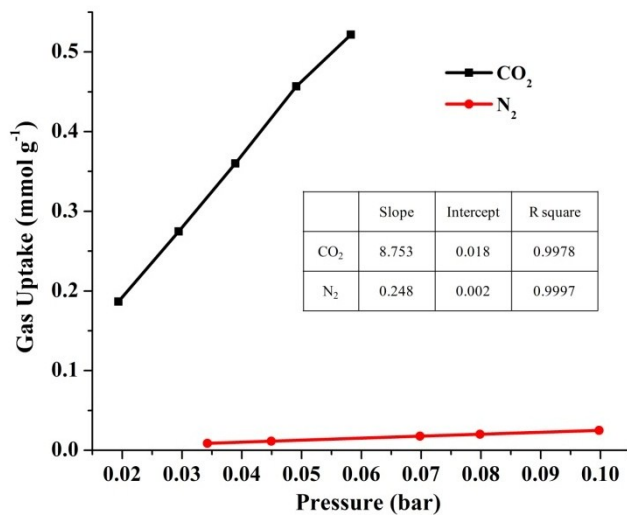


Fig. S16 CO₂-N₂ Initial slope selectivity (273 K) for NOP-34@7030

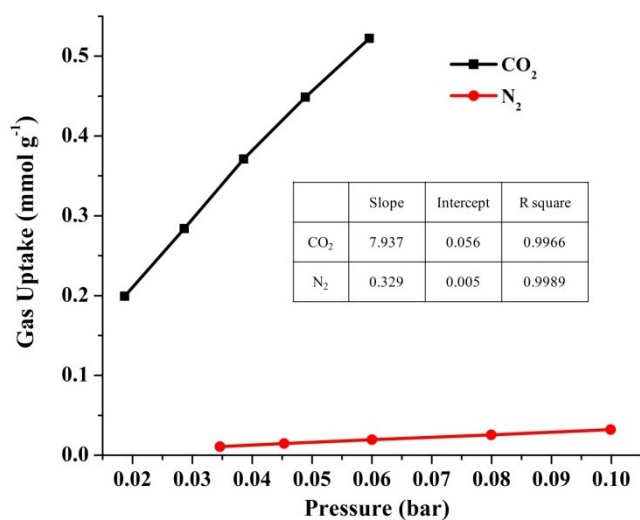


Fig. S17 CO₂-N₂ Initial slope selectivity (273 K) for NOP-34@5050

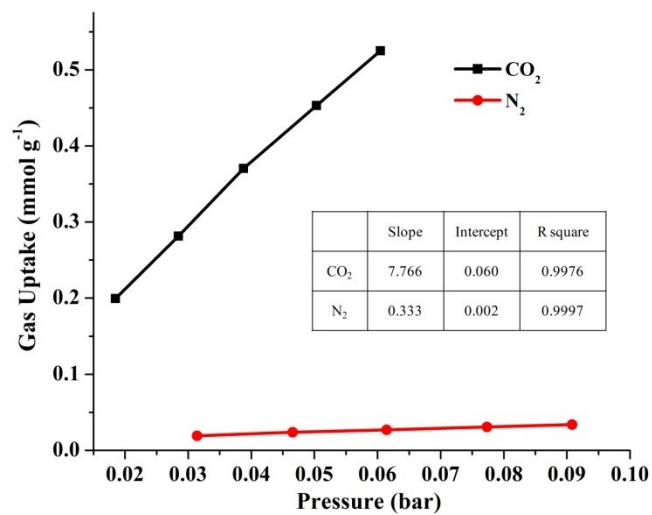


Fig. S18 CO₂-N₂ Initial slope selectivity (273 K) for NOP-34@3070

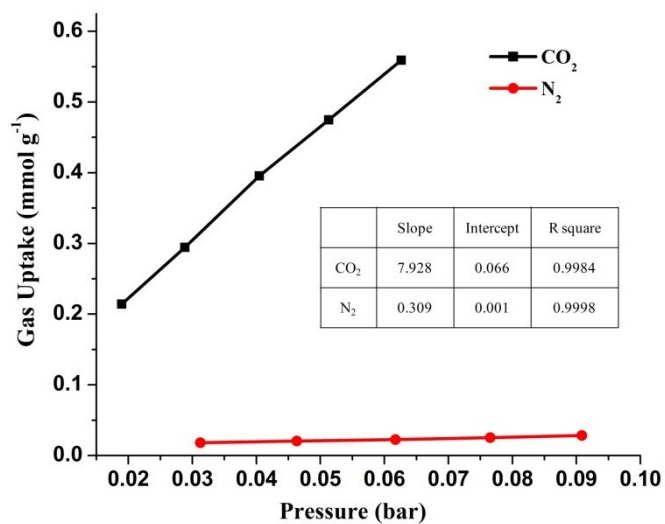


Fig. S19 CO₂-N₂ Initial slope selectivity (273 K) for NOP-34@0100

12 Gas adsorption data and corresponding SSL fitting for NOP-34 series (273 K)

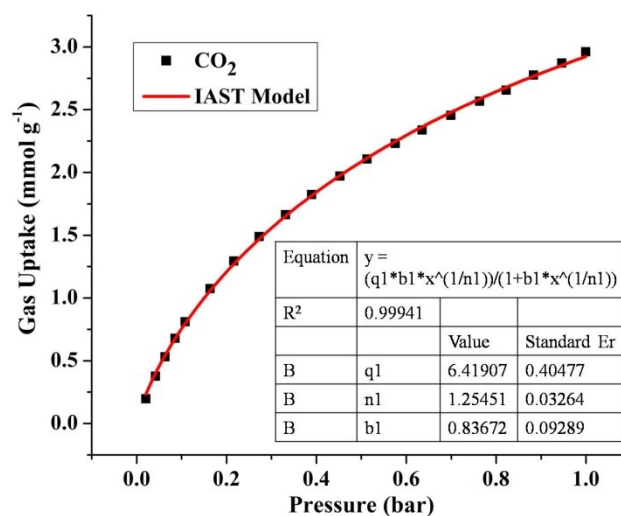


Fig. S20 CO₂ isotherm of NOP-34@1000 fitted by single-site Langmuir equation

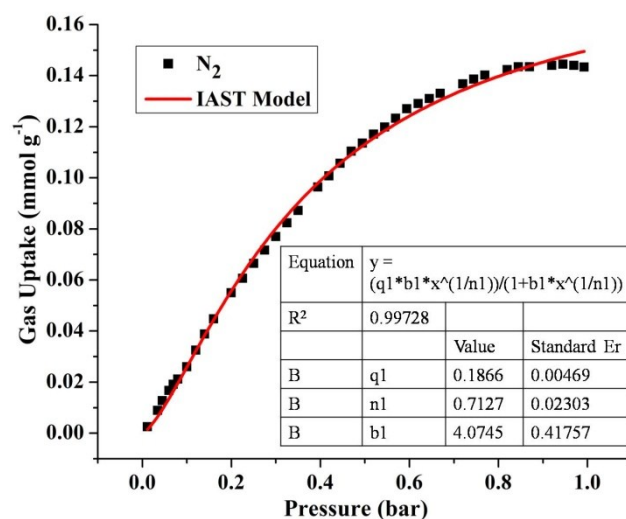


Fig. S21 N₂ isotherm of NOP-34@1000 fitted by single-site Langmuir equation

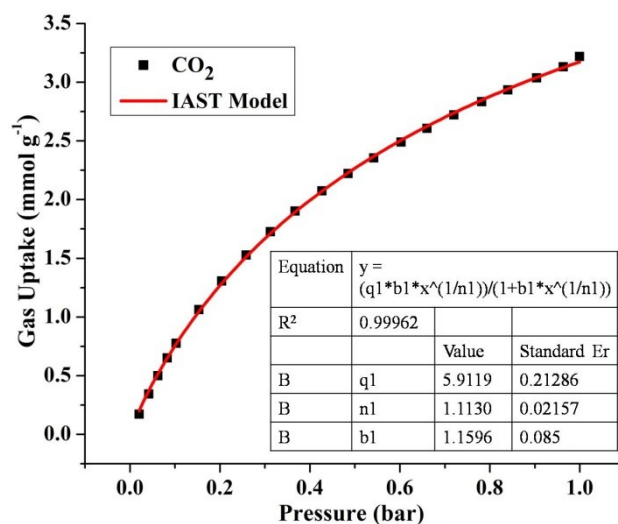


Fig. S22 CO₂ isotherm of NOP-34@7030 fitted by single-site Langmuir equation

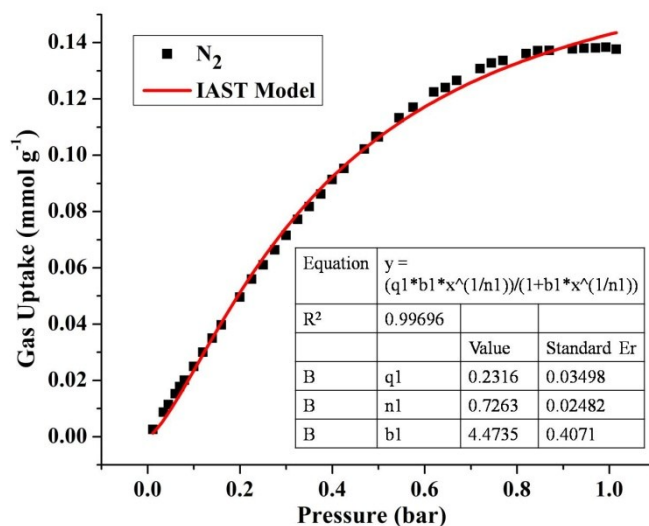


Fig. S23 N₂ isotherm of NOP-34@7030 fitted by single-site Langmuir equation

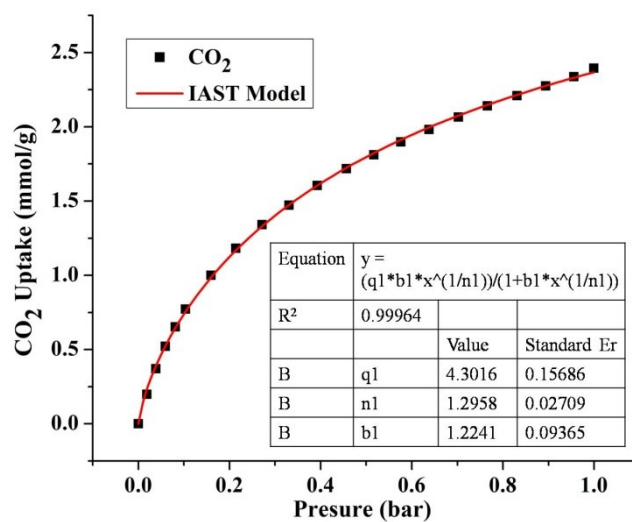


Fig. S24 CO₂ isotherm of NOP-34@5050 fitted by single-site Langmuir equation

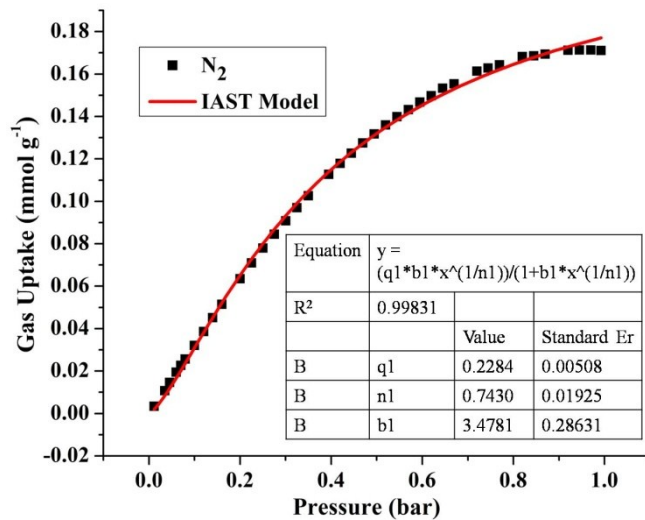


Fig. S25 N₂ isotherm of NOP-34@5050 fitted by single-site Langmuir equation

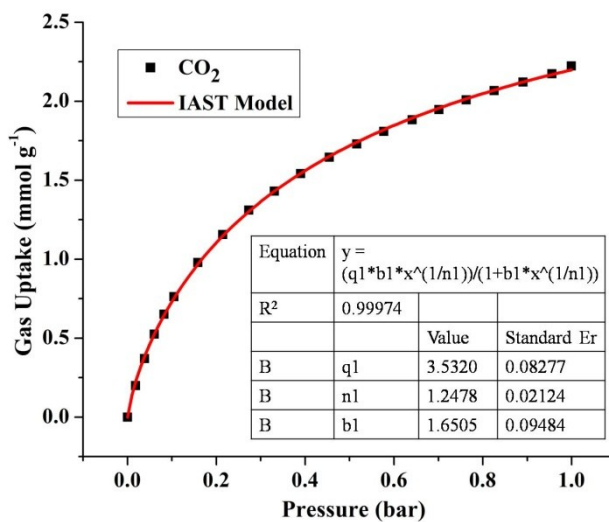


Fig. S26 CO₂ isotherm of NOP-34@3070 fitted by single-site Langmuir equation

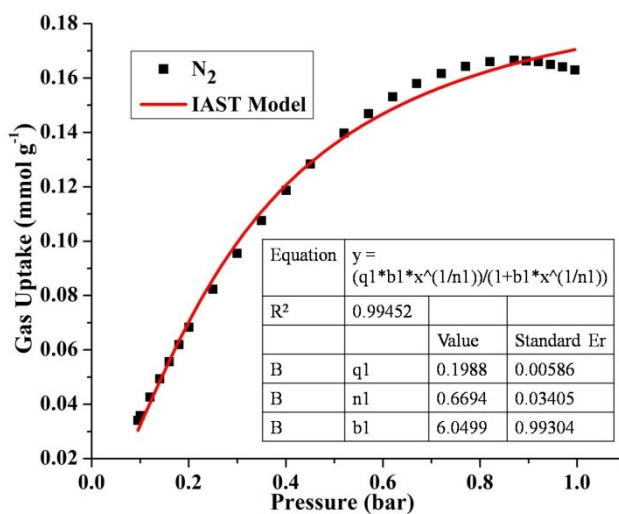


Fig. S27 N₂ isotherm of NOP-34@3070 fitted by single-site Langmuir equation

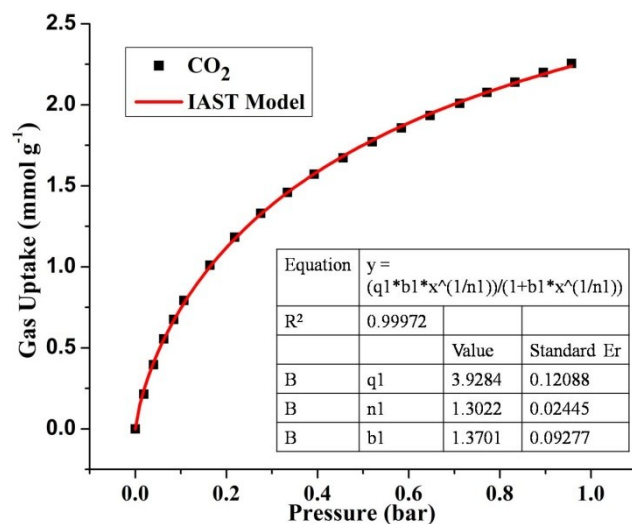


Fig. S28 CO₂ isotherm of NOP-34@0100 fitted by single-site Langmuir equation

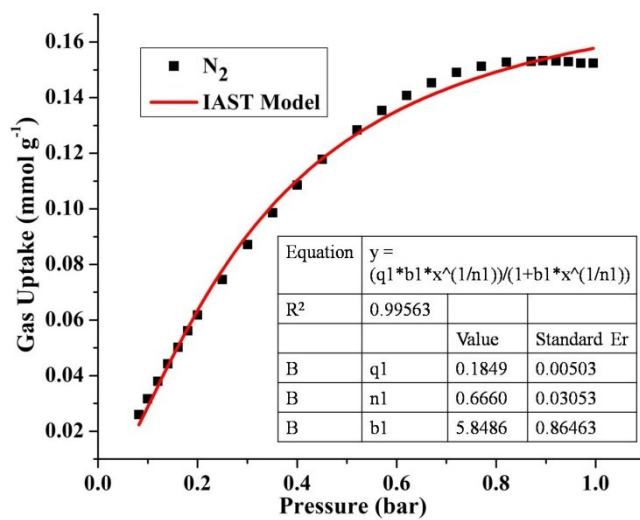


Fig. S29 N₂ isotherm of NOP-34@0100 fitted by single-site Langmuir equation

13 Gas adsorption selectivity study (CO₂/N₂, IAST, 298 K)

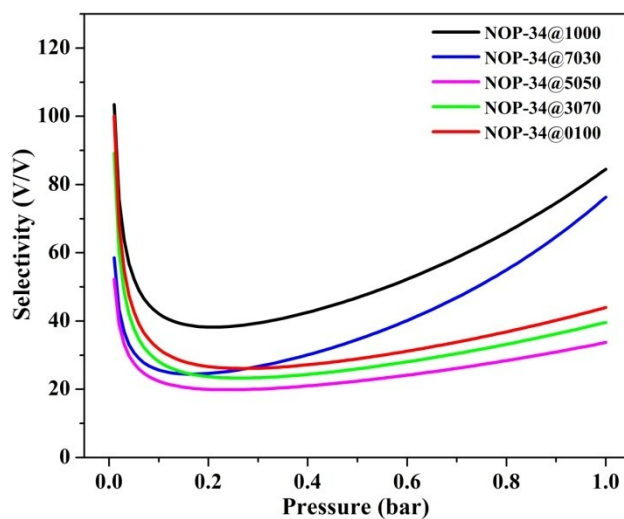


Fig. S30 CO₂/N₂ IAST selectivities (298 K) for NOP-34 series

14 References

- 1 C. Zhang, C. Chen, *J. Org. Chem.*, 2006, **71**, 6626-6629.
- 2 J. Fournier, T. Maris, and J. Wuest, *J. Org. Chem.*, 2004, **69**, 1762-1775.
- 3 Hyeun S., B. Han, *Bull. Korean Chem. Soc.*, 1995, **16**, 181.
- 4 J. Lu, J. Zhang, *J. Mater. Chem. A*, 2014, **2**, 13831-13834.
- 5 N. Tsui, A. Paraskos, L. Torun, T. Swager, and E. Thomas, *Macromolecules*, 2006, **39**, 3350-3358.