Supporting Information for **Polymer chemistry**

Rational skeletal rigidity of conjugated microporous polythiophenes for gas uptake

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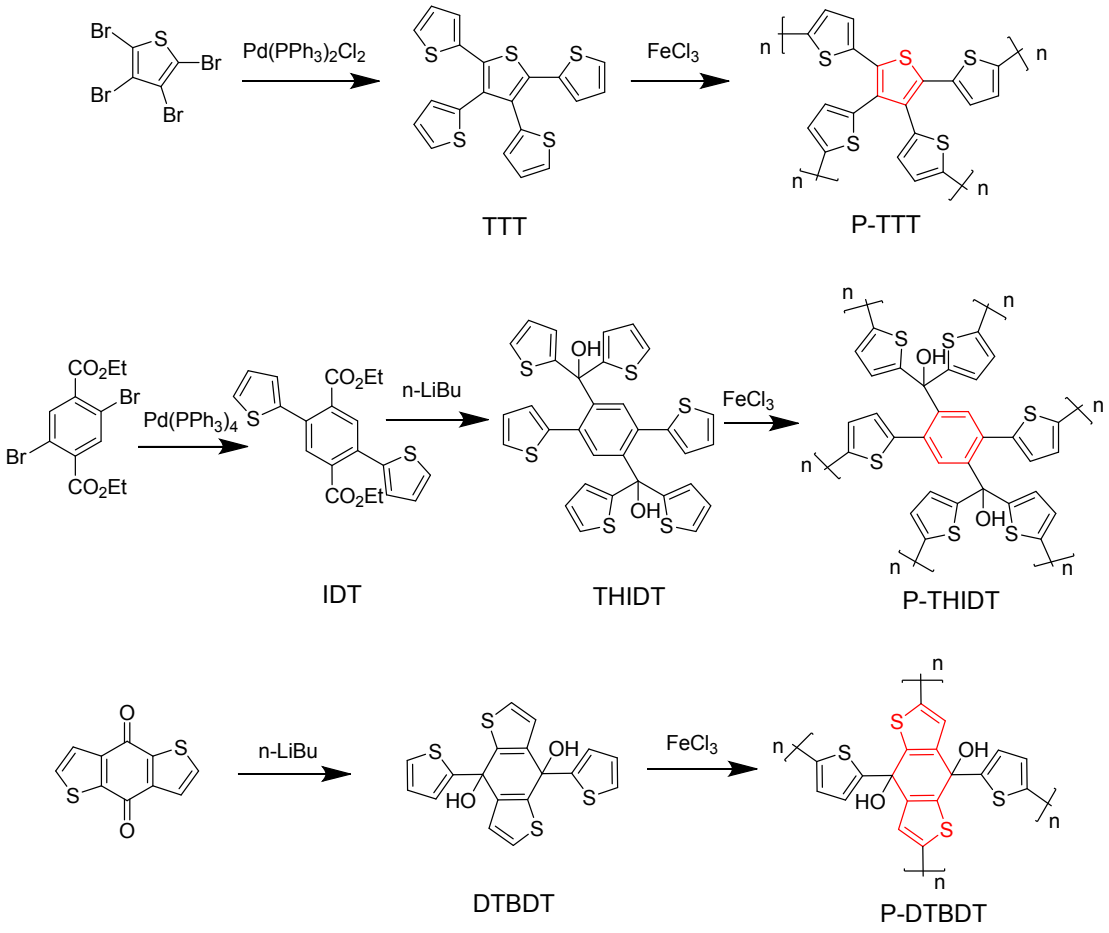
Experimental

All reagents and solvents were obtained from J&K, Aldrich and Acros Chemical Co. and were used as received unless otherwise specified. Anhydrous tetrahydrofuran (THF) and chloroform was distilled over sodium/benzophenone and calcium hydride under N_2 prior to use, respectively. The monomer TTT, THIDT and DTBDT were prepared by the Ullmann cross-coupling reactions catalyzed by palladium according the reported process.[1]



Scheme S1. Synthetic route towards the polythiophene networks of P-TTT, P-THIDT and P-DTBDT.

Synthesis of TTT 2, 3, 4, 5-tetrabromothiophene (1.0 g, 2.5 mmol) and 2-tris-butylstannyl-thiophene (5.0 g, 13.4 mmol) were dissolved in 20 mL anhydrous

toluene and deoxygenated with N_2 for 30 min, bis(triphenylphosphine)palladium (II) chloride ($Pd(PPh_3)_2Cl_2$) (175 mg) was then added under N_2. The mixture was stirred at reflux for 48 hour, then the solution was washed with a saturated solution of KCl in water, dried with Na_2SO_4 after extraction with CH_2Cl_2. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography using toluene/n-hexane as eluent given the target product (yield 46%). ^{1}H NMR ($CDCl_3$, 600 MHz), δ (ppm) 7.30 (d, 2 H), 7.19 (d, 2 H), 7.09 (d, 2 H), 6.96 (m, 4 H), 6.90 (d, 2 H). ^{13}C NMR ($CDCl_3$, 600 MHz), 135.66, 135.36, 133.32, 132.41, 129.38, 127.13, 126.93, 126.82, 126.41, 126.35.

Synthesis of IDT Ddiethyl 2, 5-dibromoterephthalate (1.43 g, 3.76 mmol), 2-(tributylstannyl)thiophene (3.7 g, 9.91 mmol) and dry toluene (30 mL) was added to a 100 mL double-neck flask. The mixture was purged with argon for 20 min to remove O_2, and then tetrakis(triphenylphosphine)palladium(0) (130 mg, 0.11 mmol) was added rapidly. After another flushing with argon for 15 min, the mixture was heated at reflux for 36 h. The reactant was cooled to room temperature and poured into saturated aqueous NH_4Cl (45 mL). The product was extracted with ethyl acetate (3 x 30 mL). The combined organic phases was washed with water and brine then dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica with hexanes/ethyl acetate as eluent to obtain 2, 5-dithien-2-ylterephthalic acid diethyl ester as pale yellow solid (1.02 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.81 (s, 2 H), 7.38 (d, 2

H), 7.10-7.07 (m, 4 H), 4.22 (m, 4 H), 1.15 (t, 6 H). ^{13}C NMR (600 MHz, $CDCl_3$, δ ppm): 167.71, 140.49, 134.07, 133.44, 131.87, 127.34, 126.97, 126.47, 61.66, 13.80.

Synthesis of THIDT n-BuLi (7.5 mL, 1.6 M in hexane) was added to a solution of IDT (1.00 g, 2.59 mmol) in anhydrous THF (30 mL) at -78 °C and stirred for 1.5 h, then 2-bromothiophene (2.00 g, 12.27 mmol) in anhydrous THF (10 mL) was added and stirred for another 1.5 h. After warm to the room temperature and the solvent was removed, the crude product was washed with hexane and methanol to afford a white powder. (1.55 g, 95%). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.34 (d, 2 H), 7.23 (d, 2 H), 7.12 (d, 2 H), 6.86 (t, 2 H), 6.74 (d, 2 H), 3.20 (s, 2 H). ^{13}C NMR (600 MHz, $CDCl_3$, δ ppm): 150.23, 144.51, 141.17, 127.39, 126.58, 125.23, 125.19, 124.85, 71.17.

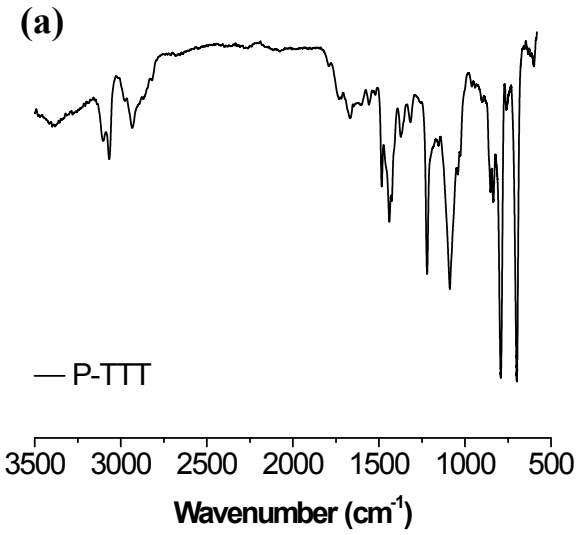
Synthesis of DTBDT To a solution of thiophene (1.00 g, 11.88 mmol) in anhydrous THF (30 mL) at -78 ° C was added n-BuLi (7.5 mL, 1.6 M in hexane), the mixture was kept at -78 ° C for 1.5 h and warmed to room temperature. Then benzo[1,2-b:4,5-b'] dithiophene-4, 8-dione (0.88 g, 4.00 mmol) was added, and the mixture stirred for 2 h at 55 °C. After cooling down to the room temperature, deionized water (30 mL) was added and stirred for another 30 min. The mixture was extracted with CH_2Cl_2 three times, and the combined organic phase was dried with Na_2SO_4. After removing the solvent, the crude product was purified by column chromatography on silica with hexanes/CH_2Cl_2 as eluent to obtain a white solid (0.78 g, 50%). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.34 (d, 2 H), 7.22 (d, 2 H), 7.12 (d, 2 H), 6.86 (t, 2 H), 6.74 (d, 2 H),

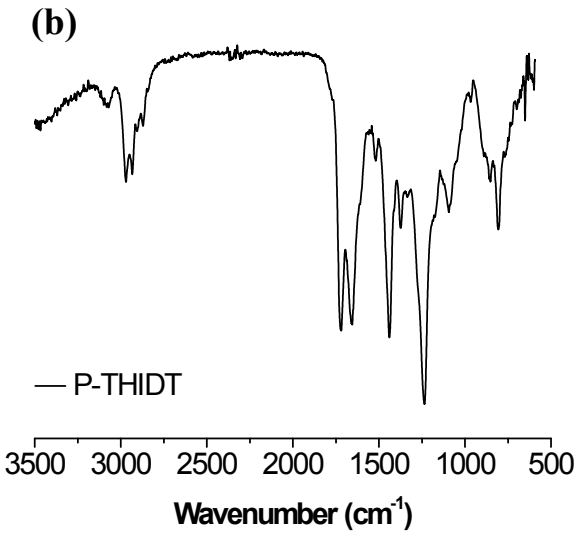
3.20(S, 2 H) ^{13}C NMR (600 MHz, $CDCl_3$, δ ppm): 150.23, 144.51, 141.17, 127.39, 126.58, 125.23, 125.19, 124.85, 71.17.

Synthesis of network P-DTBDT The solution of monomer DTBDT (200 mg, 0.51 mmol) dissolved in 30 mL of anhydrous chloroform was dropwise transferred to a suspension of ferric chloride (662 mg, 4.08 mmol) in 20 mL of anhydrous chloroform. The solution mixture was stirred for 24 h at room temperature under nitrogen protection, and then 100 mL of methanol was added to the above reaction mixture. The resulting precipitate was collected by filtration and washed with methanol and concentrated hydrochloric acid solution. After extracted in a Soxhlet extractor with methanol for 24 h, and then with tetrahydrofuran for another 24 h extraction, the desired polymer was collected (95% in yield) and dried in vacuum oven at 80 °C overnight. Anal. Calcd. for $C_{18}H_{12}O_2S_4$: C, 55.64; H, 3.11; Found: C 54.20, H 4.94.

P-TTT was synthesized follow the same procedure with P-DTBDT to give red powder, yield 90%. Anal. Calcd. for $C_{20}H_{12}S_5$: C, 58.21; H 2.93. Found: C 57.88, H 3.12.

P-THIDT was synthesized follow the same procedure with P-DTBDT to give dark red powder, yield 90%. Anal. Calcd. for $C_{32}H_{22}O_2S_6$: C, 60.92; H 3.51. Found: C 60.83, H 3.57.


(a)
— P-TTT
3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)


(b)
— P-THIDT
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Wavenumber (cm-1)

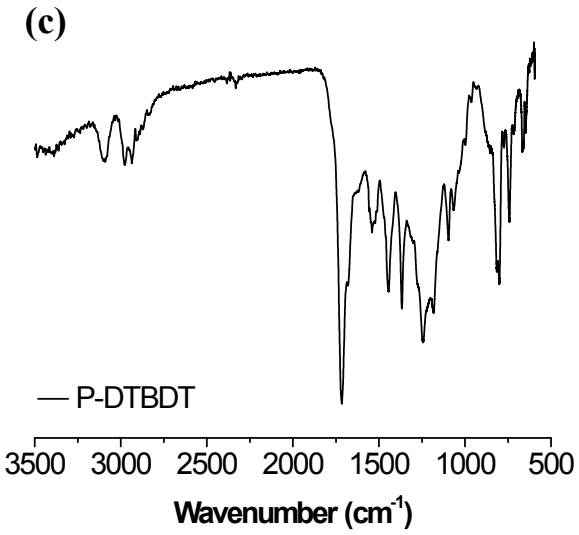

Fig. S1a-c FT-IR spectra of polythiophenes. (a)P-TTT, (B) P-THIDT, (C) P-DTBDT.

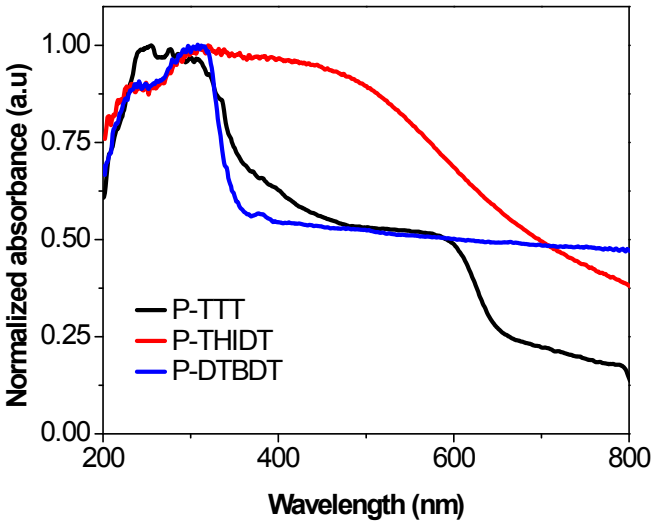

Fig. S2 UV spectra of polythiophenes.

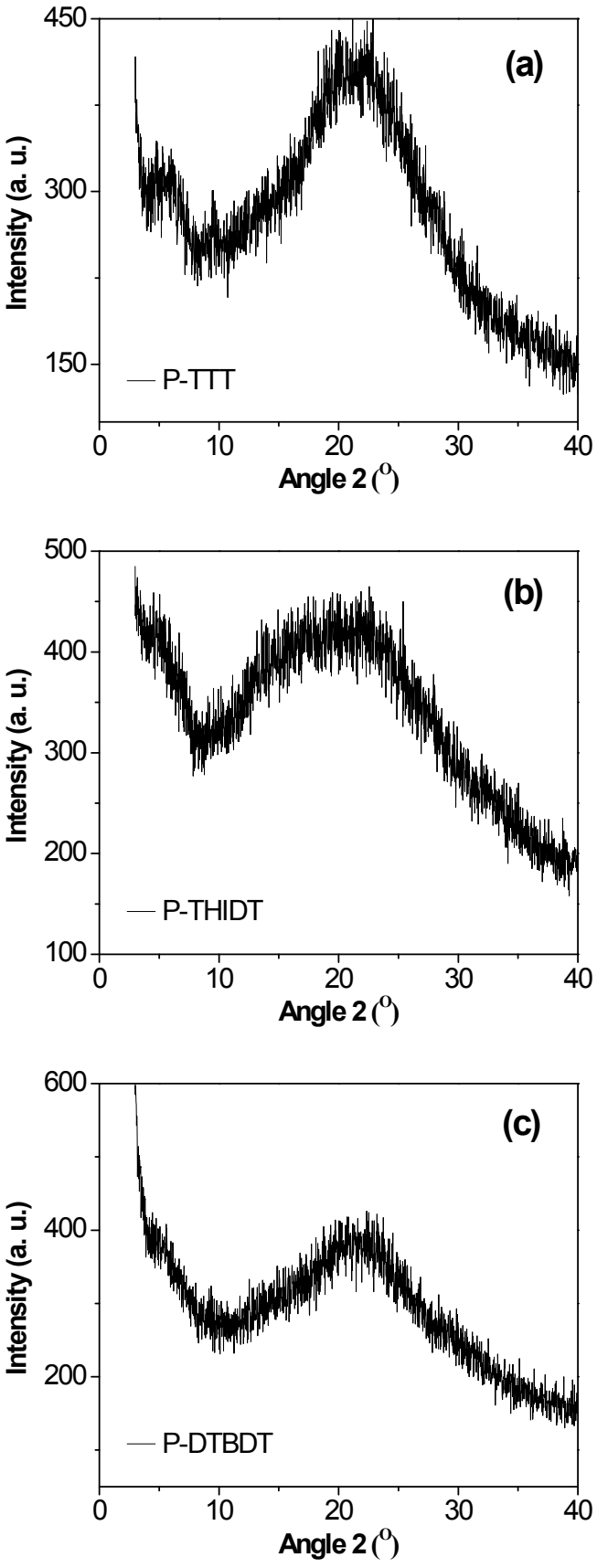

Fig. S3 Powder X ray diffraction (P-XRD) of the three polythiophenes.

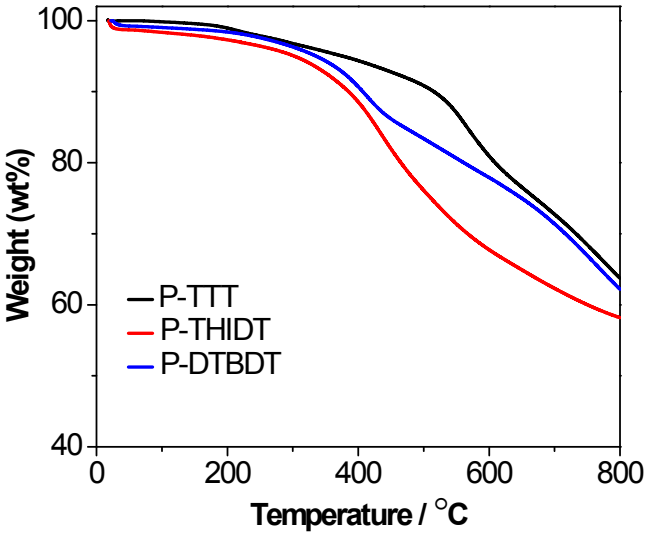

Fig. S4 TGA of polythiophenes networks.

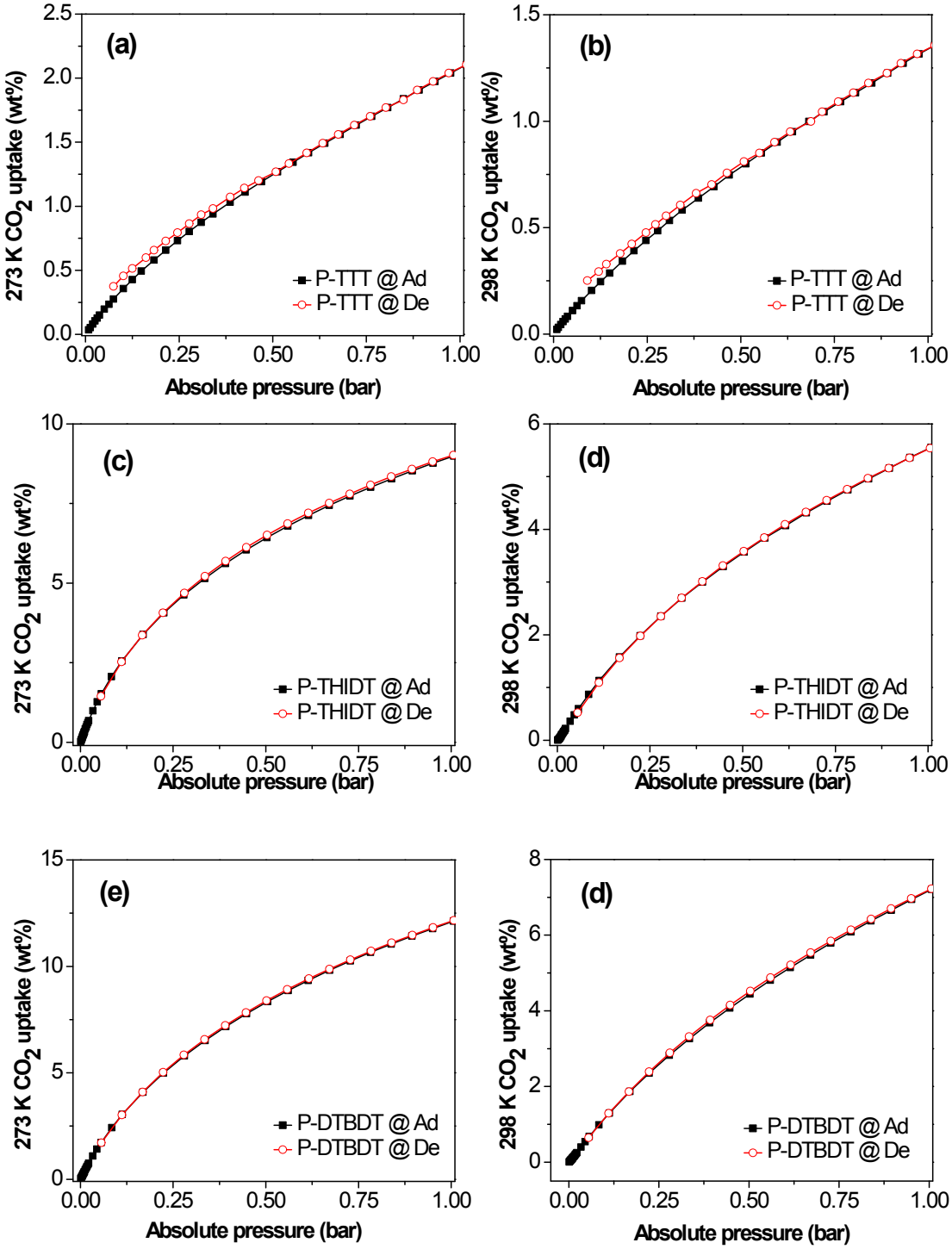

Fig. S5 CO_2 adsorption isotherms of polythiophene networks.

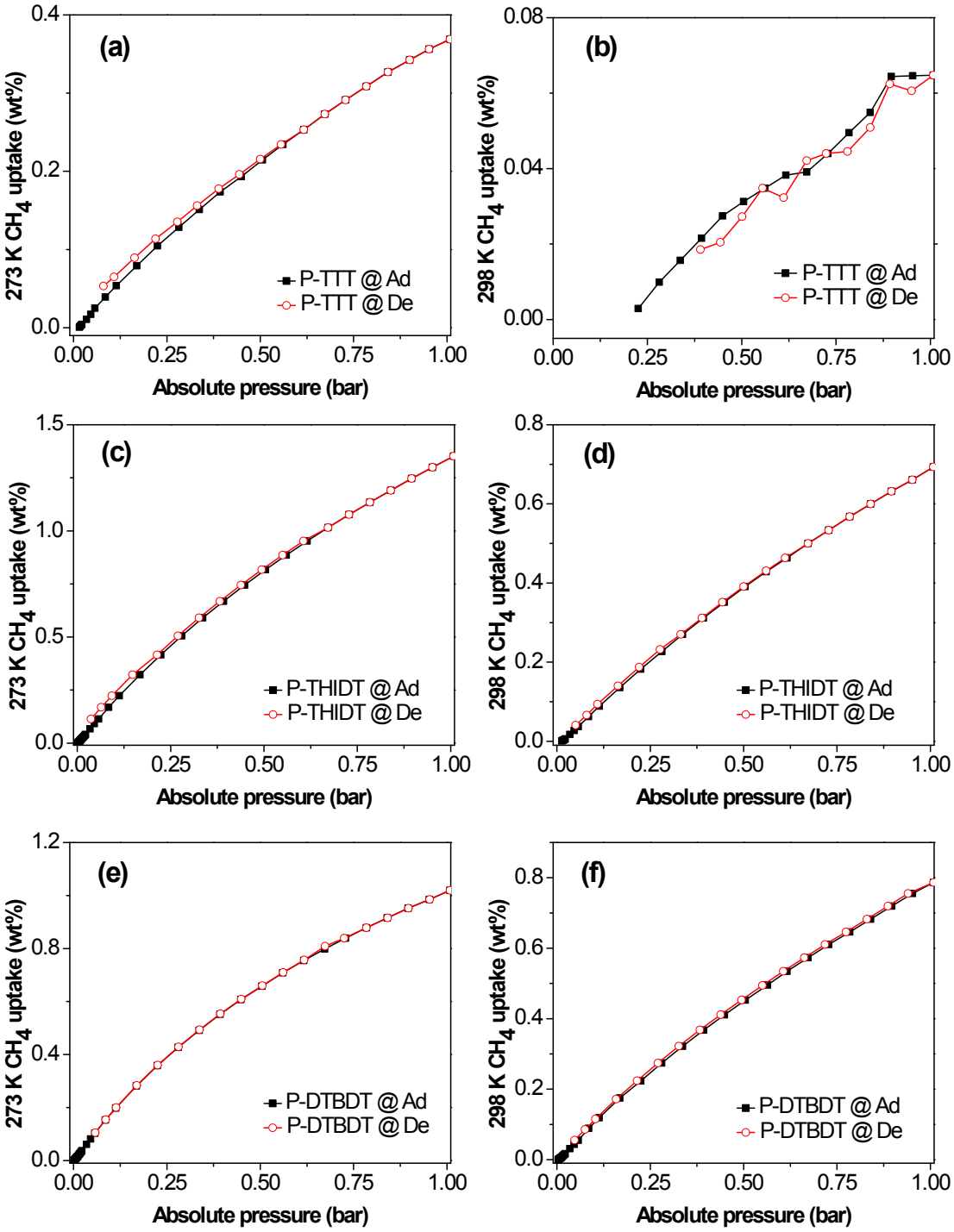

Fig. S6 CH_4 adsorption isotherms of polythiophene networks.

Reference

[1] J. P. Collman, M. Zhong, C. Zhong, S. Costanzo, *J. Org. Chem.,* 2001, **66,** 7892-7897.