Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Dendrimer-Like Conjugated Microporous Polymers

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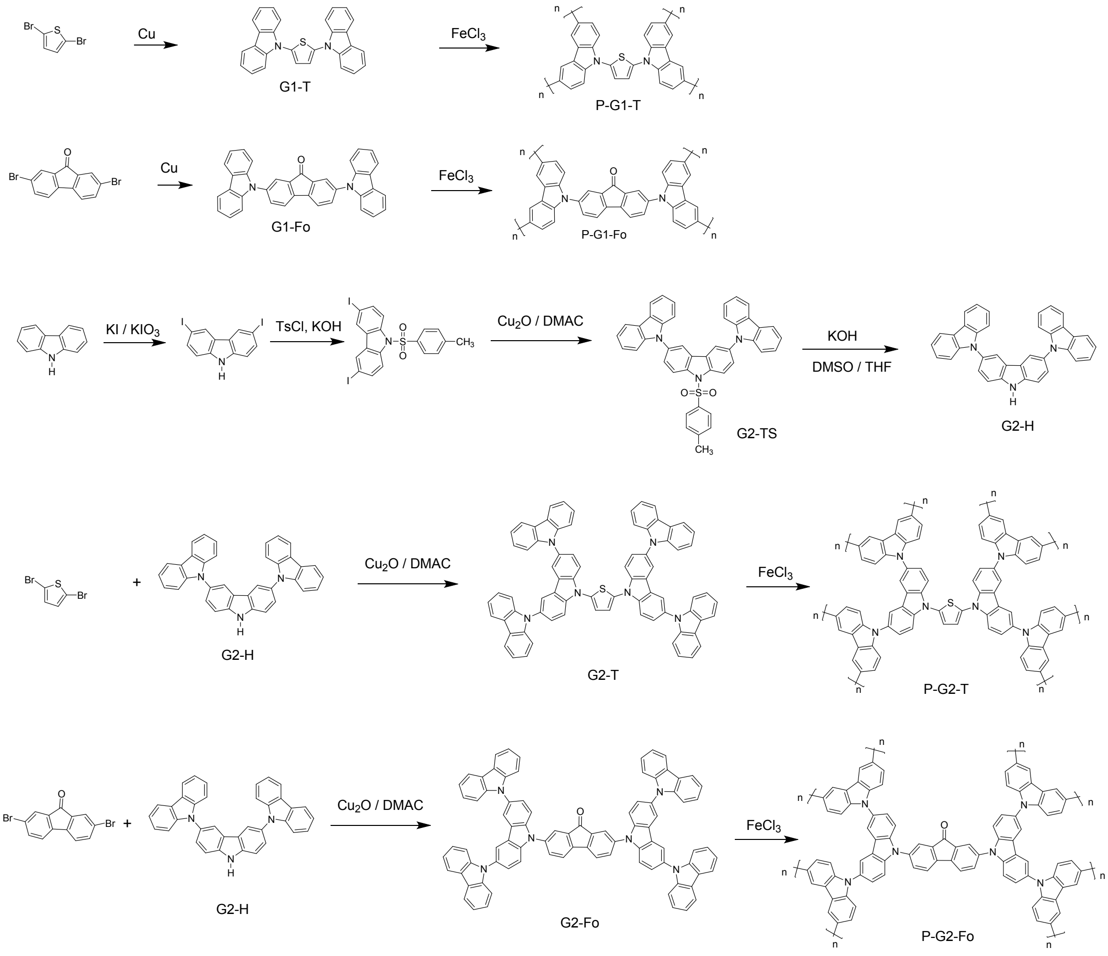
EXPERIMENTAL SECTION



Scheme S1. Synthetic routes toward the dendrimer-like conjugated microporous polymers.

Materials and synthesis

All chemical reagents were commercially available unless otherwise stated. Ferric chloride, copper, potassium iodide, potassium iodate, potassium hydroxide, Copper(I) oxide, p-toluenesulfonylchloride, carbazole, dimethylacetamide and 2, 7-dibromo-9-fluorenone were purchased from J&K, Aldrich and Acros Chemical Co. and were used as received. Anhydrous tetrahydrofuran (THF) and anhydrous 1, 2-dichlorobenzene were distilled over sodium/benzophenone and calcium hydride under

N_2 prior to use, respectively. 2, 5-dibromothiophene was prepared according to reported methods.

Synthesis of G1-T: A mixture of 2, 5-dibromothiophene (4.84 g, 20 mmol), carbazole (7.36 g, 44 mmol), K_2CO_3 (10.00 g, 72 mmol), Cu (2.80 g, 44 mmol), 2, 2'-bipyridine (5.00 mg) and 1, 10-phenanthroline (5.00 mg) was dissolved in dry and distilled 1, 2-dichlorobenzene (10 mL). The reaction mixture was kept out of light and stirred under nitrogen at 180 °C for 48 hours. After the solution was cooled to room tempreture, dichloromethane was added, and undissolved substance was filtered out. The residual organic liquid was washed thoroughly with water (4 x 20 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the crude product was recrystallized from ethyl acetate to yield the product as a white solid (4.98 g, 60 %). ^1H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.14 (d, 4H), 7.64 (d, 4H), 7.50 (t, 4H), 7.35(t, 4H), 7.30(s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm): 141.78, 136.56, 126.44, 123.88, 123.67, 120.94, 120.35, 110.19.

Synthesis of G1-Fo: 2,7-dibromofluoren-9-one (6.72 g, 20 mmol), carbazole (7.98 g, 48 mmol), K_2CO_3 (16.49 g, 119 mmol), Cu (3.05 g, 48 mmol), 2, 2'-bipyridine (5.00 mg) and 1, 10-phenanthroline (5.00 mg) were dissolved in dry and distilled 1, 2-dichlorobenzene (10 mL). The reaction mixture was kept out of light and stirred under nitrogen at 180 °C for 48 hours. After the solution was cooled to room tempreture, dichloromethane was added, and undissolved substance was filtered out. The residual organic liquid was washed thoroughly with water (4 x 20 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the crude product was recrystallized from ethyl acetate to yield the product as a yellow solid (5.70 g, 56 %). ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.16 (d, 4H), 7.96 (s, 2H), 7.84(d, 2H), 7.77 (d, 2H), 7.46 (m, 8H), 7.33 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm): 191.85, 142.40, 140.40, 138.96, 136.25, 133.04, 126.23, 123.72, 123.12, 121.85, 120.51, 109.72.

Synthesis of 3, 6-diiodo-9H-carbazole: A solution of 9 H-carbazole (10.00 g, 60 mmol), KI (13.00 g 78 mmol) and KIO_3 (12.84 g, 60 mmol) were dissolved ice acetic acid (130 mL) and deionized water (13 mL) under argon protection. The reaction solution, which was shielded from light with tin foil, was stirred at 80 °C for 48 h. The mixture was cooled to room temperature, then the precipitate was filtered off, subsequently washed with deionized water, saturated Na_2CO_3 solution and methanol in sequence to give compound 3, 6-diiodo-9H-carbazole as white solid. (16.30 g, 65 %). ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.32 (s, 2H), 7.68 (d, 2H), 7.21 (d, 2H), 3.50 (s, 1H).

Synthesis of 3, 6-diiodo-9-tosyl-9H-carbazole: A slurry of 3, 6-diiodocarbazole (10.00 g, 24 mmol), KOH (4.00 g, 71 mmol) in freshly distilled acetone (150 mL) was degassed, and then p-toluenensulfonylchloride was added slowly under nitrogen atmosphere. The mixture was heated to reflux for 1 h. Then the solution was cooled to room temperature, and the resulting slurry was extracted with dichloromethane and washed with water. The organic solvent was removed on a rotary evaporator and the residue was recrystallized in dichloromethane/n-hexane. This gave 12.65 g (92 %) of the desired product as a yellow powder. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.16 (d, 2H), 8.07 (d, 2H), 7.78 (d, 2H), 7.64 (d, 2H), 7.13 (d, 2H), 2.29(s, 3H); ^{13}C NMR

(150 MHz, $CDCl_3$), δ (ppm):145.48, 137.79, 136.54, 134.42, 129.90, 129.14, 127.16, 126.45, 116.96, 87.97, 21.56.

Synthesis of G2-TS: 3, 6-diiodo-9-tosyl-9H-carbazole (2.86 g, 5 mmol), carbazole (2.09 g, 12.5mmol) and Cu_2O (3.58 g, 25 mmol) were dissolved in dimethylacetamide (DMAc, 20 mL) in a two-necked round bottom flask under argon atmosphere in dark. The mixture was allowed to stir overnight at 180 °C for 24 h. After cooled to room temperature, the precipitate was filtered. Then the filter liquor was poured into deionized water and stirred for 20 minnutes. The filter cake was collected and the crude product was recrystallized in dichloromethane/methanol to give white powder (2.33 g, 72 %). ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.60 (d, 2H), 8.14 (d, 4H), 8.08 (s, 2H), 7.93 (d, 2H), 7.74 (d, 2H), 7.40-7.36 (m, 8H), 7.31-7.19 (m, 6H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm):145.59, 141.17, 137.68, 135.00, 133.99, 130.13, 127.20, 127.02, 126.78, 126.02, 123.38, 120.40, 120.08, 119.05, 116.38, 109.52, 21.70.

Synthesis of G2-H: G2-TS (1.96 g, 3.0 mmol) and KOH (336.63 mg, 6.0 mmol) were dissolved into the solvent of DMSO (20 mL), THF (40 mL), deionized water (10 mL). The mixture was vigorously stirred at 100 °C under nitrogen for 1 h. After cooling to room temperature, 10 % HCl (20 mL) and methanol (10 mL) were added to filter the precipitate, and the filter cake was washed with deionized water. The crude product was recrystallized in dichloromethane/methanol to give white powder (1.40 g, 95 %). ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.48 (s, 2H), 8.20 (s, 2H), 8.15 (d, 4H), 7.70 (d, 2H), 7.62 (d, 2H), 7.40-7.36 (m, 8H), 7.29-7.26 (m, 4H); ^{13}C NMR (150 MHz,

$CDCl_3$), δ (ppm):141.80, 139.27, 129.96, 126.24, 125.87, 124.10, 123.13, 120.28, 119.83, 119.66, 112.02, 109.71.

G2-T(Fo) was prepared from CuO-catalyzed coupling condensation reaction between G2-H and 2, 5-dibromothiophene (2, 7-dibromo-9-fluorenone), which is similar to the synthesis for G2-TS.

Four novel carbazole-based conjugated networks P-G1(G2)-T and P-G1(G2)-Fo were straightforward synthesized by $FeCl_3$ oxidative coupling from their corresponding monomers, respectively. A representative preparation for P-G1-T is given in details as follows.

P-G1-T: The solution of monomer G1-T (200 mg, 0.48 mmol) dissolved in 30 mL of anhydrous chloroform was dropwise transferred to a suspension of ferric chloride (778 mg, 4.8 mmol) in 20 mL of anhydrous chloroform. The mixture was stirred for 18 h at room temperature under nitrogen protection, and then 100 mL of methanol was added to the above reaction solution. The resulting precipitate was collected by filtration and washed with methanol and deionized water. The crude product was extracted in a soxhlet extractor with methanol for 48 h, and then the desired polymer was collected (black powder, 90 % in yield) and dried in vacuum oven at 80 °C overnight. $C_{28}H_{18}N_2S$: C, 81.13%; N, 6.76%; H, 4.38%; S, 7.74%. Found: C, 86.06%; N, 6.58%; H, 4.27%.

P-G2-T: The same procedure with P-G1-T network gave brownish powder, yield 99%. Calcd. $C_{76}H_{46}N_6S$: C, 84.89%; N, 7.82%; H, 4.31%; S, 2.98%. Found: C, 70.85%; N, 4.11%; H, 3.46%.P-G1-Fo (red powder, yield 93 %)

P-G1-Fo: The same procedure with **P-G1-T** network gave brownish powder, yield 94%. Calcd. $C_{37}H_{22}N_2O$: C, 87.04%; N, 5.49%; H, 4.34%; O, 3.13%. Found: C, 86.20%; N, 5.25%; H, 4.04%; O, 3.26%.

P-G2-Fo: The same procedure with **P-G1-T** network gave brownish powder, yield 94%. Calcd. $C_{85}H_{50}N_6O$: C, 87.16%; N, 7.17%; H, 4.30%; O, 1.37%. Found: C, 84.45%; N, 5.9%; H, 4.24%.

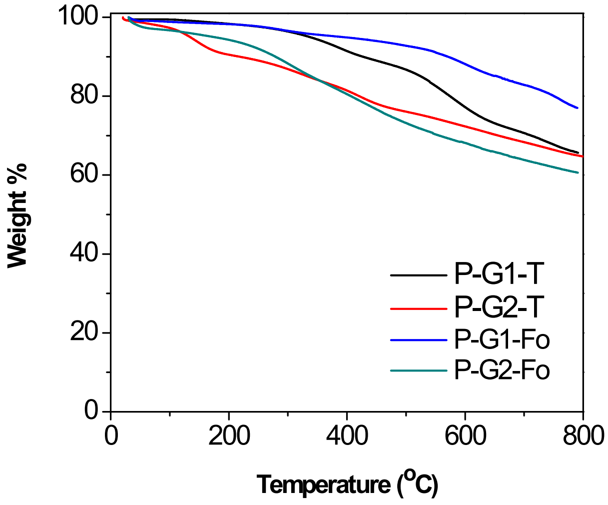


Figure S1. TGA of dendrimer-like conjugated microporous polymers.

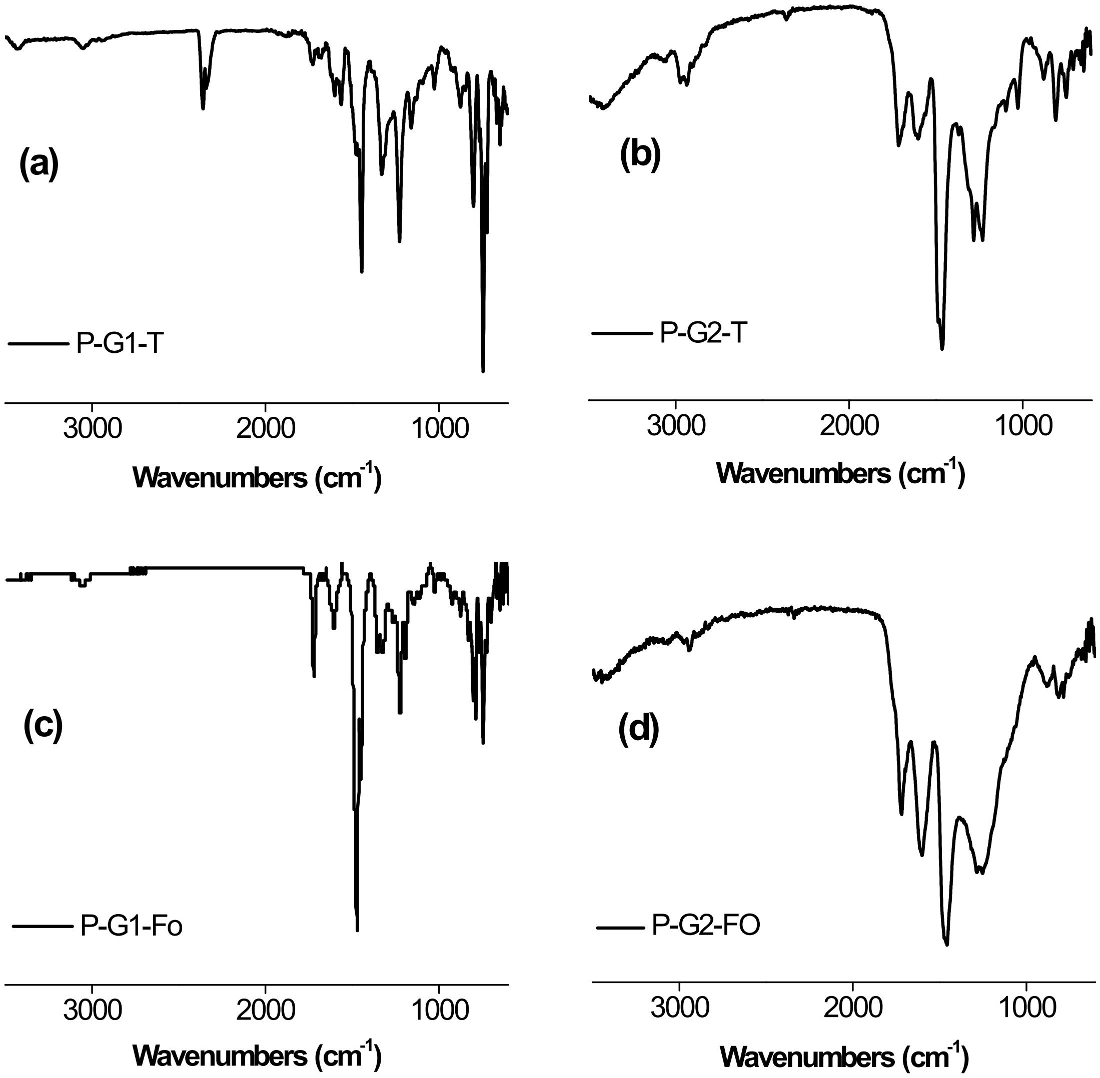


Figure S2. FT-IR spectra for the dendrimer-like conjugated microporous polymers collected in attenuated total reflection (ATR) mode.

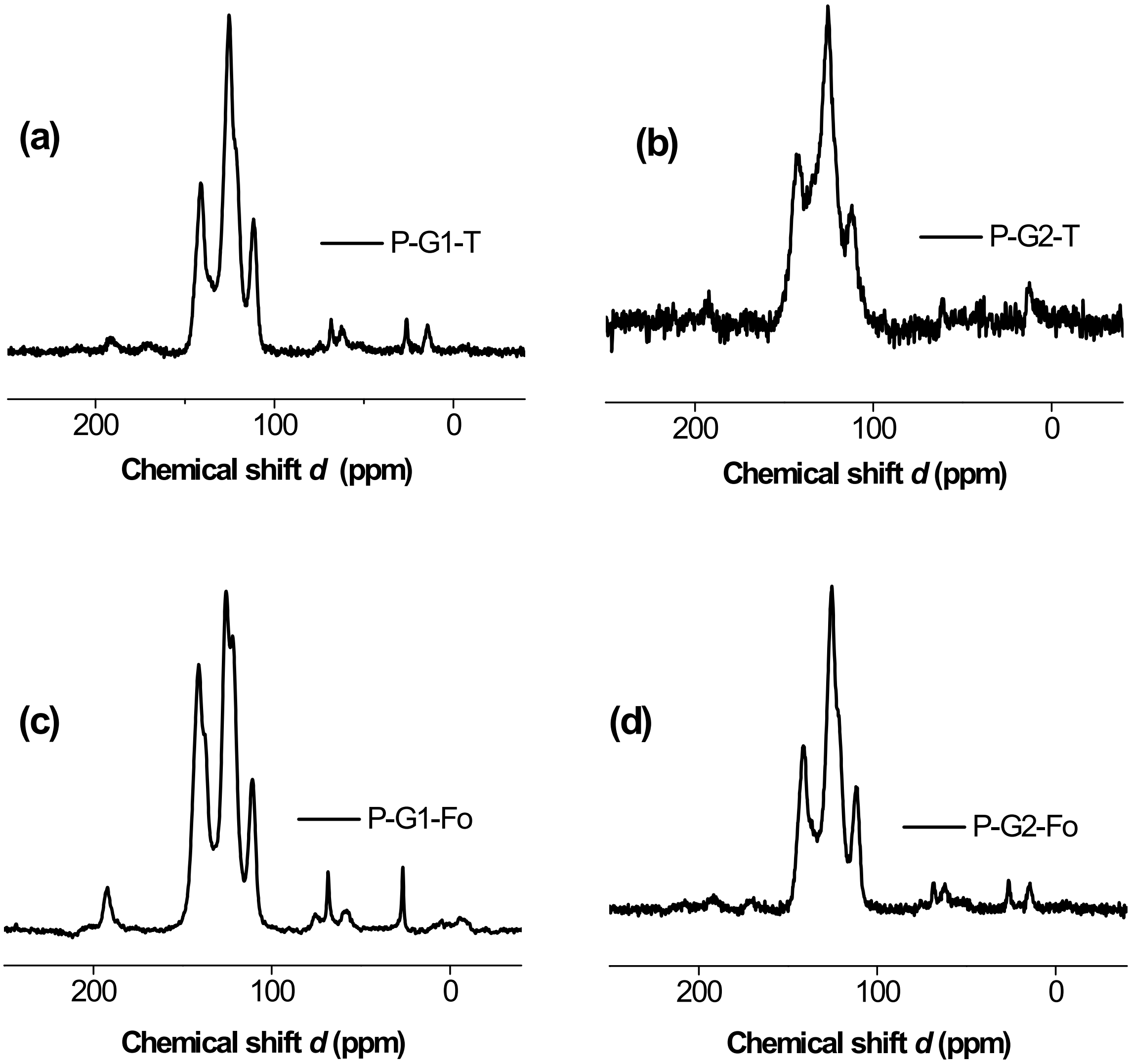


Figure S3. Solid state magic angle spinning ^{13}C CP/MAS NMR spectra of the dendrimer-like conjugated microporous polymers.

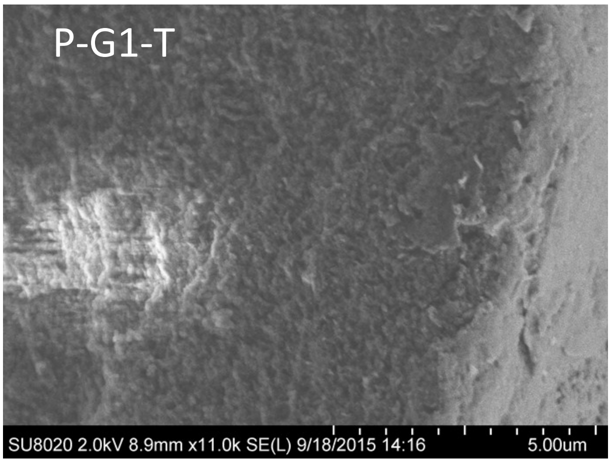


Figure S4. Field-emission scanning electron microscopy image of P-G1-T.

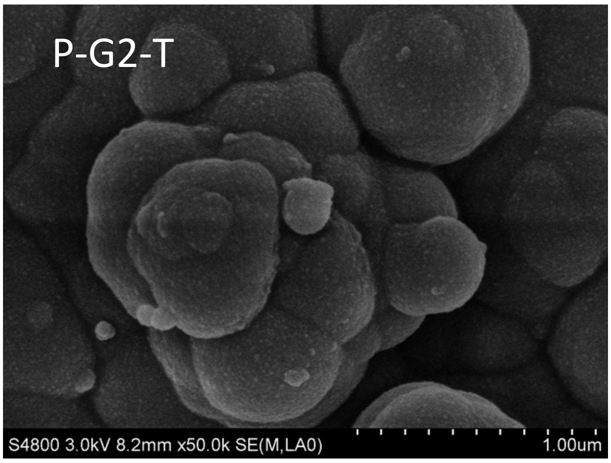


Figure S5. Field-emission scanning electron microscopy image of P-G2-T.

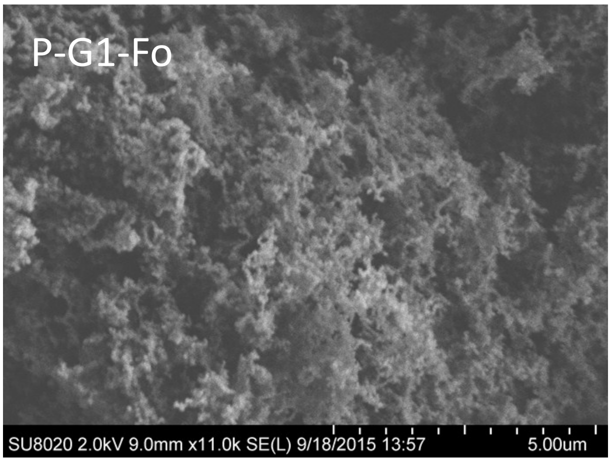


Figure S6. Field-emission scanning electron microscopy image of P-G1-Fo.

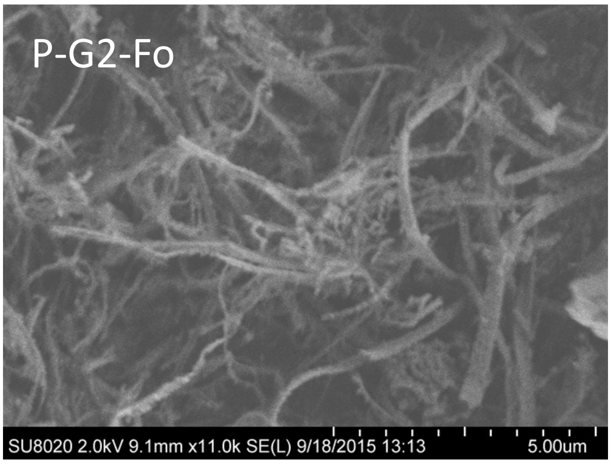


Figure S7. Field-emission scanning electron microscopy image of P-G2-Fo.

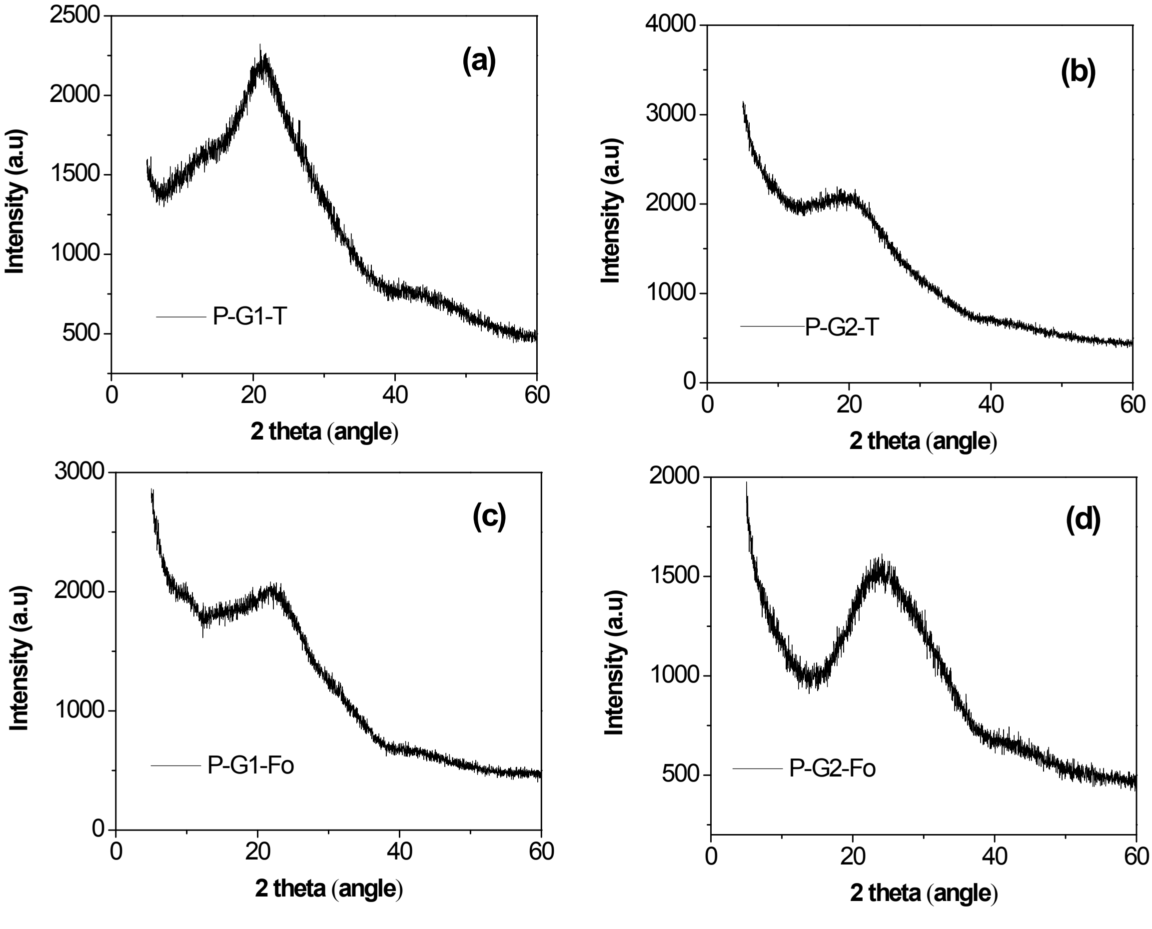


Figure S8. P-XRD spectra of the dendrimer-like conjugated microporous polymers.

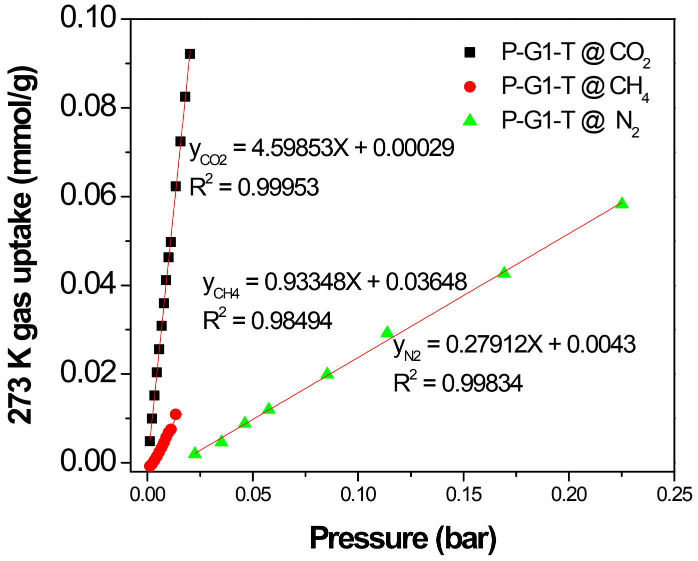


Figure S9. The selectivities of CO_2/CH_4 and CO_2/N_2 of P-G1-T at 273 K.

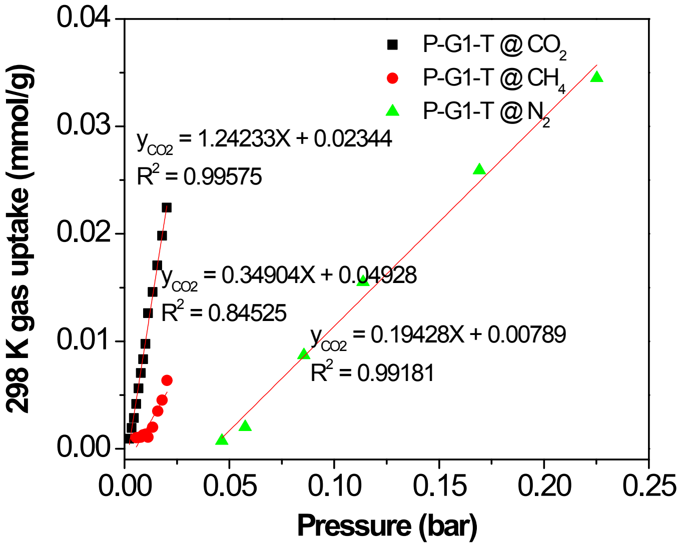


Figure S10. The selectivities of CO_2/CH_4 and CO_2/N_2 of P-G1-T at 298 K.

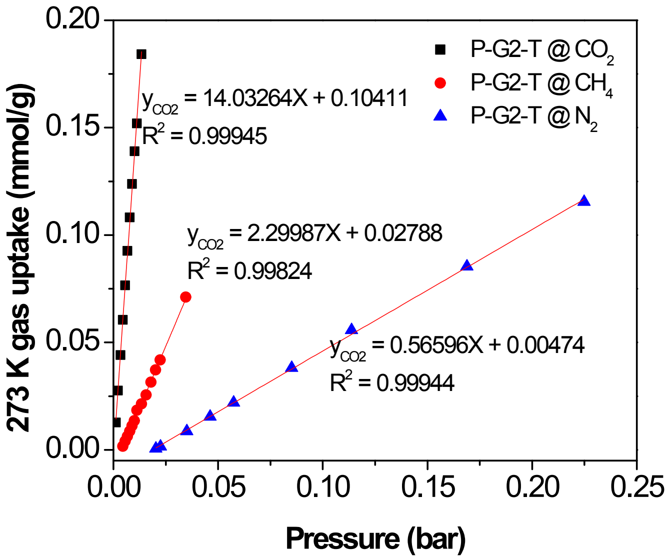


Figure S11. The selectivities of CO_2/CH_4 and CO_2/N_2 of P-G2-T at 273 K.

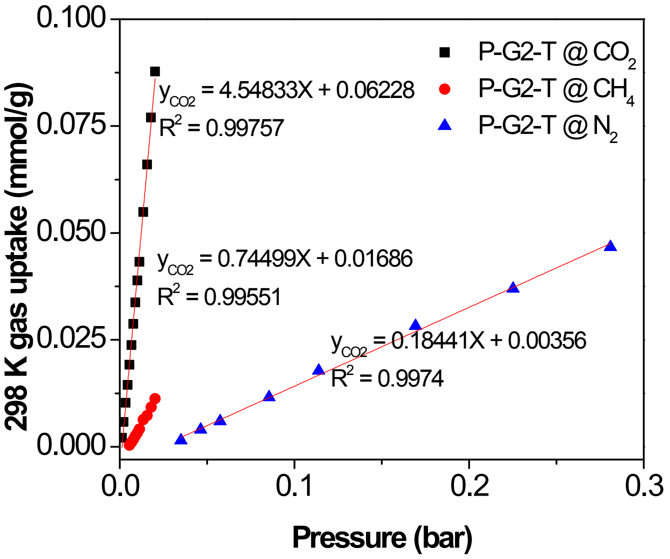


Figure S12. The selectivities of CO_2/CH_4 and CO_2/N_2 of P-G2-T at 298 K.

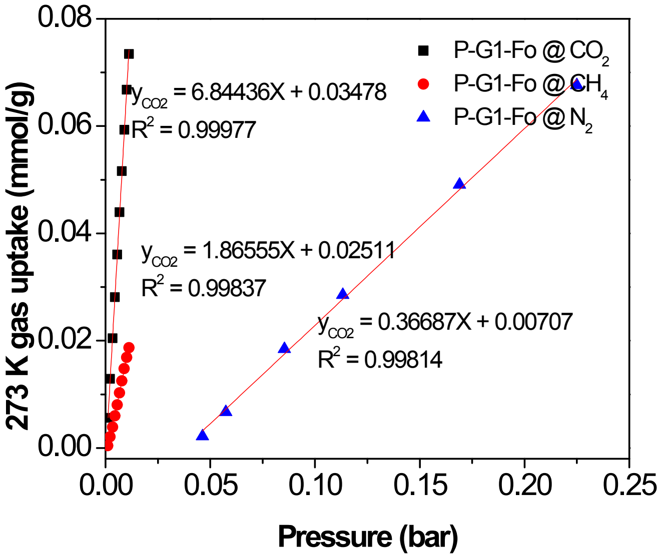


Figure S13. The selectivities of CO_2/CH_4 and CO_2/N_2 of P-G1-Fo at 273 K.

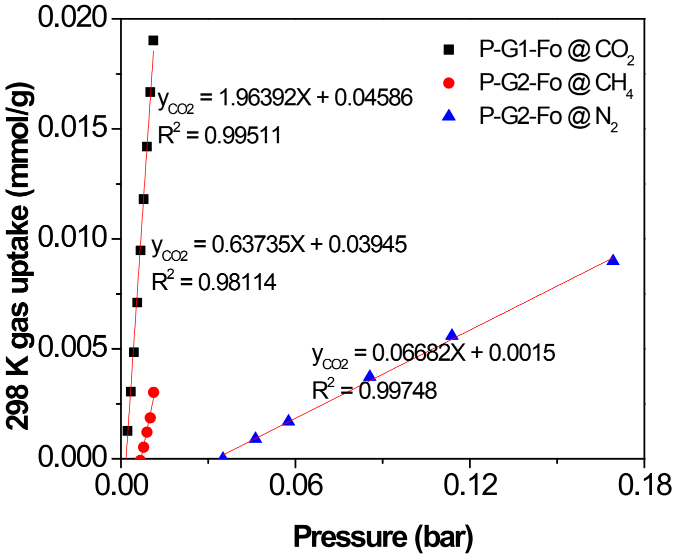


Figure S14. The selectivities of CO_2/CH_4 and CO_2/N_2 of P-G1-Fo at 298 K.

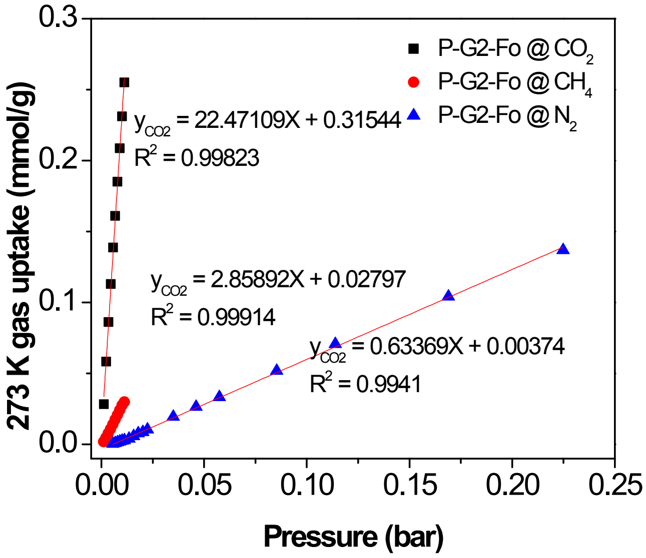


Figure S15. The selectivities of CO_2/CH_4 and CO_2/N_2 of P-G2-Fo at 273 K.

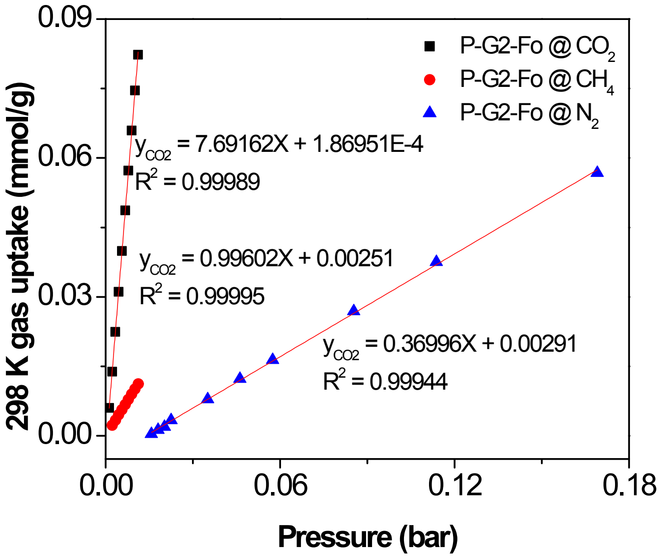


Figure S16. The selectivities of CO_2/CH_4 and CO_2/N_2 of P-G2-Fo at 298 K.