Electronic Supplementary Information (ESI) for

Supramolecular organic networks assembled from quadruple hydrogen-bonding motifs

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Experimental

Instrumental characterization

Infrared (IR) spectra were recorded in KBr pellets using a Spectrum One Fourier transform infrared (FTIR) spectrometer (Perkin–Elmer Instruments Co. Ltd., USA). Thermal gravimetric analysis (TGA) was performed on a Pyris Diamond thermogravimetric/differential thermal analyzer by heating the samples to 800 °C at 10 °C min^{-1} in the atmosphere of nitrogen. Mass spectrum was performed on a Microflex LRT MALDI-TOF mass spectrometer (Bruker, Germany). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX400 NMR spectrometer, with tetramethylsilane as an internal reference. Nitrogen adsorption–desorption and carbon dioxide sorption experimentations were performed by using a TriStar II 3020 accelerated surface area and porosity analyzer (Micromeritics, USA). Before measurement, the samples were degassed *in vacuo* at 120 °C for more than 12 h. A sample of *ca.* 100 mg was used for the gas sorption measurements. The gas sorption experiments were performed at least two times. A liquid nitrogen, dry ice–acetone, and ice-water baths were utilized to control the temperature at 77, 196, and 273 K, respectively. Specific surface area was calculated from nitrogen adsorption data by BET analysis in the relative pressure (P/P_0) range from 0.05 to 0.20, whereas pore size distribution (PSD) profile was estimated through Density Functional Theory (DFT) methods. Total pore volume was calculated from nitrogen adsorption–desorption isotherms at $P/P_0 = 0.97$. The specific surface area and micropore volume was also calculated from carbon dioxide adsorption isotherms at

273 K by using the Dubinin–Astakhov equation based on micropore filling theory, whereas PSD profile was estimated through the Horvath–Kawazoe (HK) method. Elemental analysis was performed on a Flash EA 1112 Elemental Analyzer (Thermo Scientific, Italy).

Materials

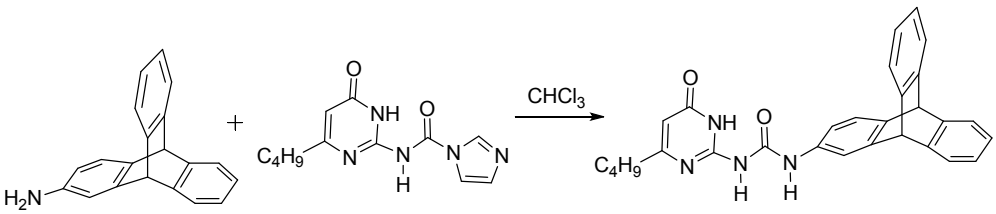
Concentrated nitric acid, hydrazine hydrate, ethanol, and chloroform were purchased from Beijing Chemical Reagent Company. Guanidine carbonate salt, 1,1'-carbonyldiimidazole, and palladium on carbon (5–10 % Pd) were purchased from Aldrich. 2,6,14-Triaminotriptycene, blocked 6-*n*-butyl-substituted isocytosine isocyanate, and 2-amiontriptycene were synthesized according to the reported procedures in References S1, S2 and S3, respectively. Ethanol was purified by refluxing with magnesium powder and trace iodine and then distilling in nitrogen atmosphere. Chloroform was purified by stirring with calcium hydride overnight and distilling in nitrogen atmosphere. Ethyl acetate, petroleum ether, dichloromethane, acetone, and other chemical reagents were used as received. All of the reactions were operated using standard Schlenk line technique.

Synthesis of HOP-1

Blocked 6-*n*-butyl-substituted isocytosine isocyanate (147 mg, 0.56 mmol) and 2,6,14-triaminotriptycene (50 mg, 0.17 mmol) were dissolved in 20 mL of chloroform and this solution was stirred for 12 h under nitrogen atmosphere at 60 °C. The solution

was reduced to about 10 mL by evaporation in *vacuo*. This concentrated solution was slowly added to 20 mL of methanol under vigorous stirring, which resulted in a precipitate. The precipitate was filtered off and washed thoroughly with methanol. Then the resulted white solid was purified by Soxhlet extraction in tetrahydrofuran for 24 h followed by dry process in a vacuum oven at 60 °C for 24 h. The resulting off-white powder was obtained in an 80 % yield. Sample for ^{1}H NMR spectroscopy was prepared by dissolve the fresh synthesized **HOP-1** in DMSO at 5 mM to characterize TUPy. ^{1}H NMR (400 MHz, DMSO) δ (ppm) 11.32 (br. s., 3H, N*H*–C=N), 10.08 (br. s., 6H, Ar–N*H*–(C=O)N*H*–C=N), 7.68 (s, 3H, Ar–*H*), 7.46–7.21 (m, 3H, Ar–*H*), 7.13–6.93 (m, 3H, Ar–*H*), 5.82 (br. s., 3H, C=*CH*–(C=O)), 5.68–5.42 (d, *J*=12.6 Hz, 2H, Ar–C*H*–Ar), 2.44 (t, *J* = 7.4 Hz, 6H, CH_2–CH_2–CH_2–CH_3), 1.65–1.50 (m, 6H, CH_2–CH_2–CH_2–CH_3), 1.40–1.26 (sextet, 6H, CH_2–CH_2–CH_2–CH_3), 0.90 (t, *J* = 7.3 Hz, 9H, CH_2–CH_2–CH_2–CH_3). ^{13}C NMR (101 MHz, DMSO) δ (ppm) 163.05, 152.36, 146.85, 146.53, 140.89, 140.54, 135.49, 124.32, 124.13, 116.02, 104.22, 52.75, 52.05, 35.76, 29.86, 22.03, 14.12. MALDI-TOF-MS: calcd. for [M+Na] 901.4 (*m/z*), found 901.4. Elemental analysis: For $C_{47}H_{50}N_{12}O_6$， calculated: C, 64.22; H, 5.73; N, 19.12 %. Found: C; 63.72; H, 5.83; N, 18.90 %.

Synthesis of OUPy



Blocked 6-*n*-butyl-substituted isocytosine isocyanate (112 mg, 0.43 mmol) and 2-aminotriptycene (100 mg, 0.37 mmol) were dissolved in 20 mL of chloroform. Then, the formed solution was stirred for 12 h under nitrogen atmosphere at 60 °C. The mixture was added into 50 mL chloroform and washed with 20 mL of aqueous HCl solution (1.0 M), 20 mL saturated $NaHCO_3$ followed by 20 mL of brine and dried with Na_2SO_4. The organic layer was reduced to about 10 mL by evaporation in *vacuo*. The concentrated solution was slowly added to 20 mL of methanol under vigorous stirring, which resulted in a precipitate. The precipitate was filtered off, and washed thoroughly with methanol. The resulting white powder was obtained in 82 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.97 (s, 1H, N*H*–C=N), 11.97 (br s, 2H, Ar–N*H*–(C=O)N*H*–C=N), 7.73 (s, Ar–*H*, 1H), 7.34 (m, 5H, Ar–*H*), 6.98 (m, 4H, Ar–*H*), 5.86 (s, 1H, C=C*H*–(C=O)), 5.41 (d, J = 21.8 Hz, 2H, Ar–C*H*–Ar), 2.35 (m, 2H, CH_2–CH_2–CH_2–CH_3), 1.56 (m, 2H, CH_2–CH_2–CH_2–CH_3), 1.29 (m, 2H, CH_2–CH_2–CH_2–CH_3), 0.90 (t, J = 6.8 Hz, 3H, CH_2–CH_2–CH_2–CH_3). ^{1}H NMR (400 MHz, DMSO) δ (ppm) 11.33 (s, 1H, N*H*–C=N), 9.77 (br s, 2H, Ar–N*H*–(C=O)N*H*–C=N), 7.68 (s, Ar–*H*, 1H), 7.40 (m, 5H, Ar–*H*), 7.03 (m, 5H, Ar–*H*), 5.83 (s, 1H, C=C*H*–(C=O)), 5.61 (d, J = 11.1 Hz, 2H, Ar–C*H*–Ar), 2.44 (m, 2H, CH_2–CH_2–CH_2–CH_3), 1.58 (m, 2H, CH_2–CH_2–CH_2–CH_3), 1.39-1.27 (m, 2H, CH_2–CH_2–CH_2–CH_3), 0.90 (t, J = 7.2 Hz, 3H, CH_2–CH_2–CH_2–CH_3). ^{13}C NMR (101 MHz, DMSO) δ (ppm) 146.05, 145.32, 145.01, 140.37, 134.85, 124.93, 124.81, 123.71, 123.58, 123.40, 115.49, 115.36, 103.71, 52.57, 51.88, 35.37, 29.34, 21.50, 13.65. MALDI-TOF-MS: calcd. for [M+Na] 485.2 (*m/z*), found 485.3.

References

[S1] Zhang, C.; Chen, C.-F. Synthesis and structure of 2,6,14- and 2,7,14-trisubstituted triptycene derivatives. *J. Org. Chem*. **2006**, *71* (17), 6626–6629.

[S2] Keizer, H. M.; Sijbesma, R. P.; Meijer, E. W. The convenient synthesis of hydrogen-bonded ureidopyrimidinones. *Eur. J. Org. Chem.* **2004**, *2004* (12), 2553–2555.

[S3] Chong, H. J.; Maclachlan, M. J.; Robust non-interpenetrating coordination frameworks from new shape-persistent building blocks. *Inorg. Chem*. *2006*, 45 (4), 1442–1444.

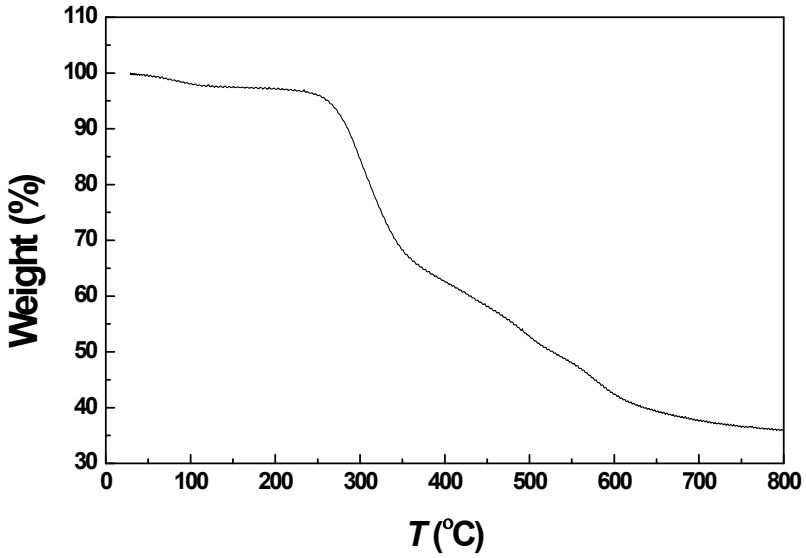


Fig. S1 TGA curve of **HOP-1**.

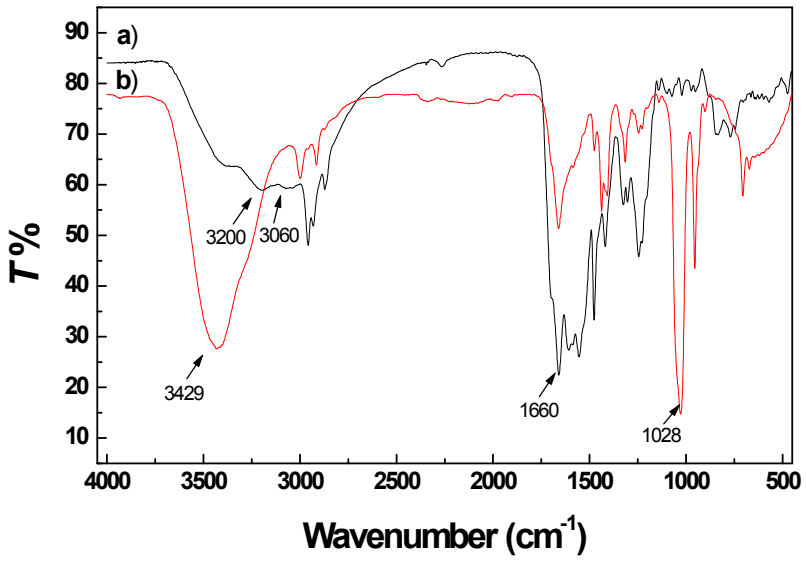


Fig. S2 FT-IR spectrum of **HOP-1** (a) and the TUPy-based organogel in DMSO (b).

(The peak around 1028 cm^{-1} is from DMSO.)

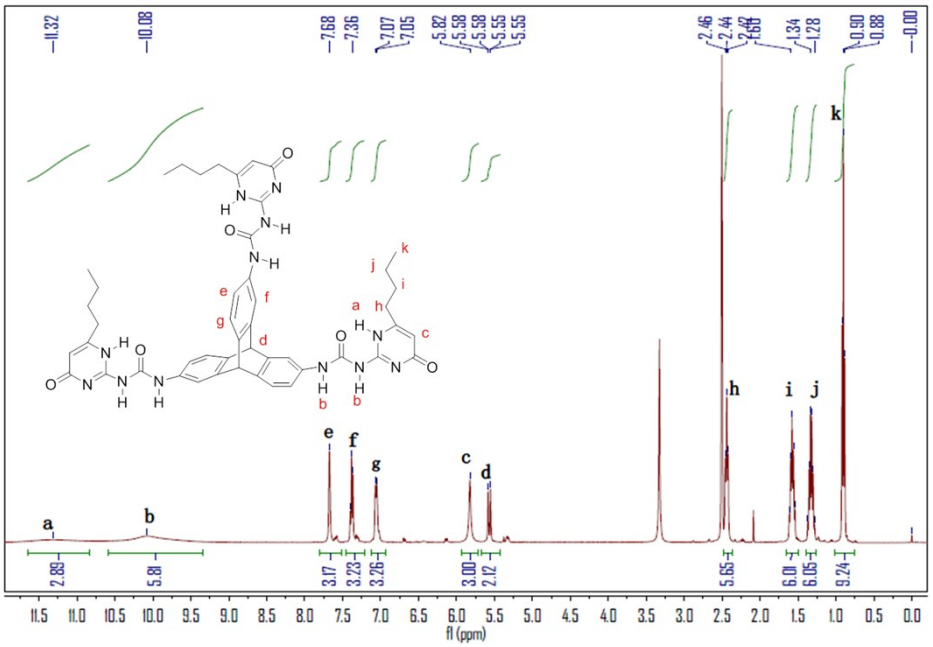


Fig. S3 ^{1}H NMR spectrum of TUPy.

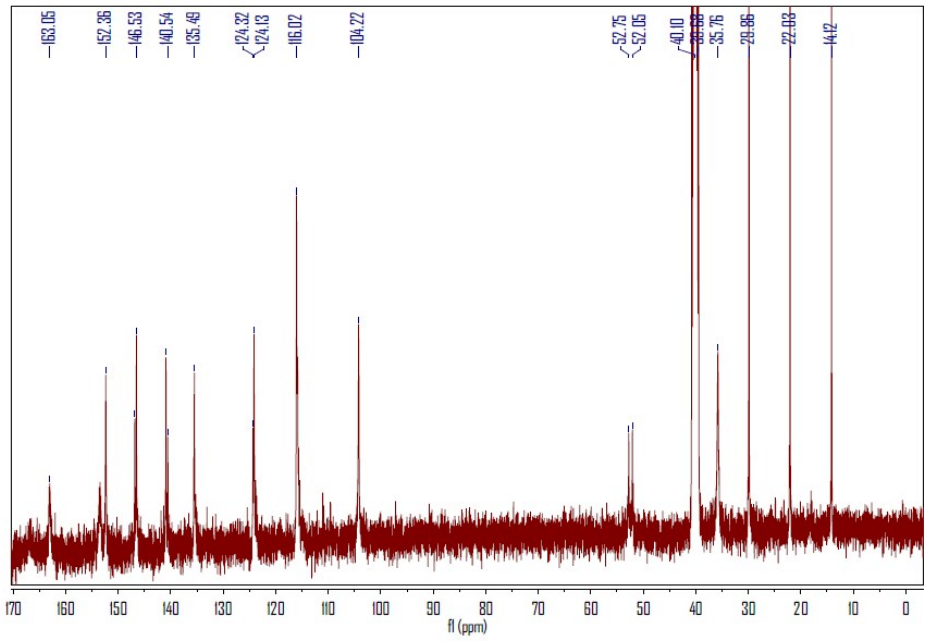


Fig. S4 ^{13}C NMR spectrum of TUPy.

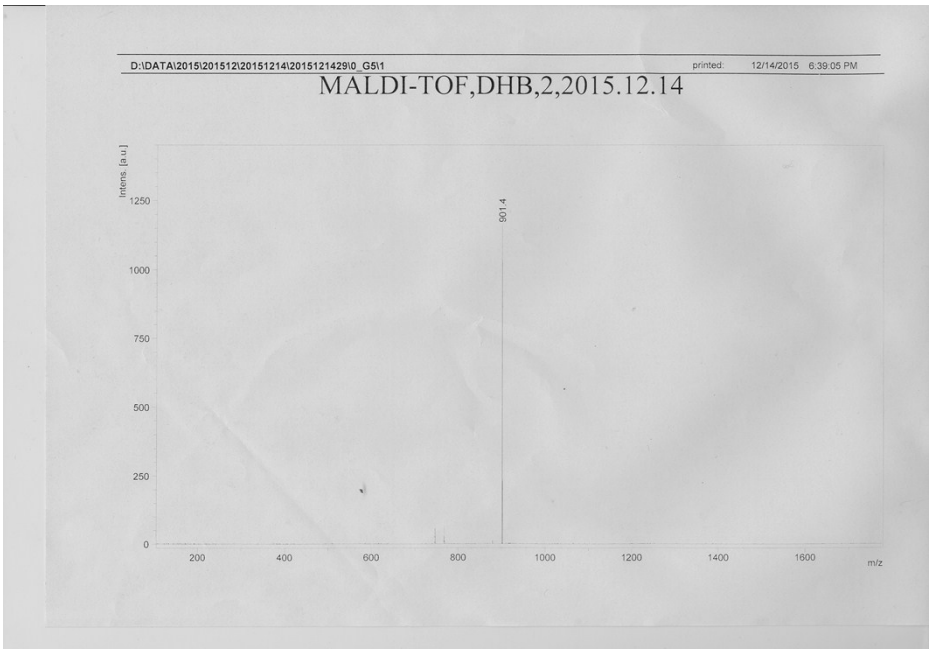


Fig. S5 MOLDI-TOF mass spectrum of TUPy.

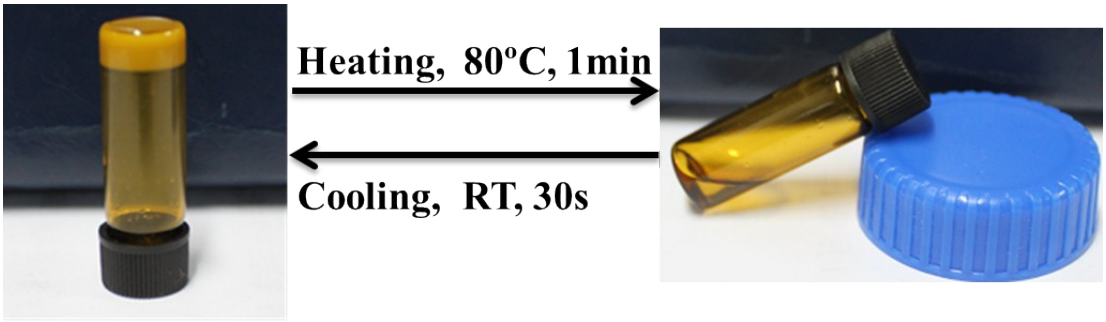


Fig. S6 Digital photographs of temperature induced reversible gel–sol transition of the TUPy-based organogel.

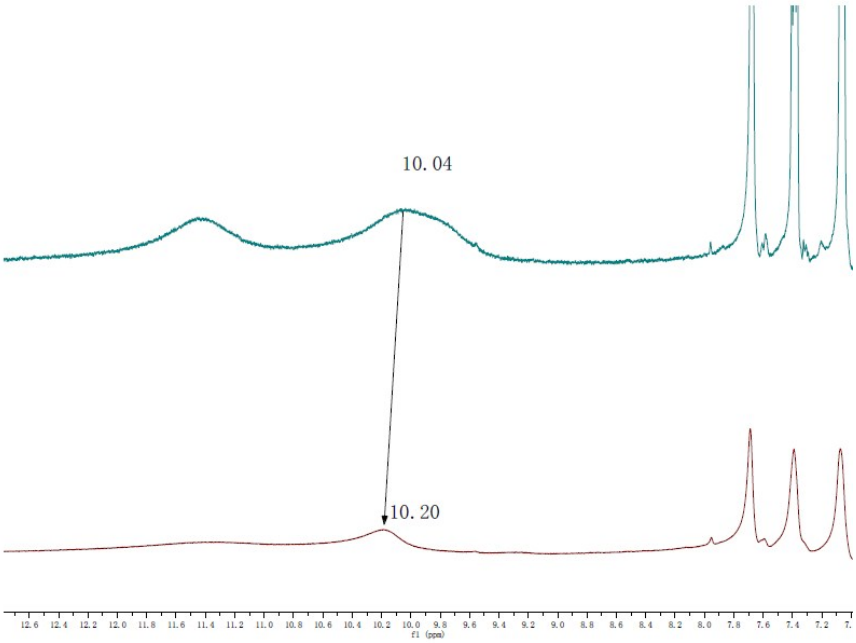


Fig. S7 Partial ^{1}H NMR spectra of TUPy at 5 mM (up) and at 80 mM (down).

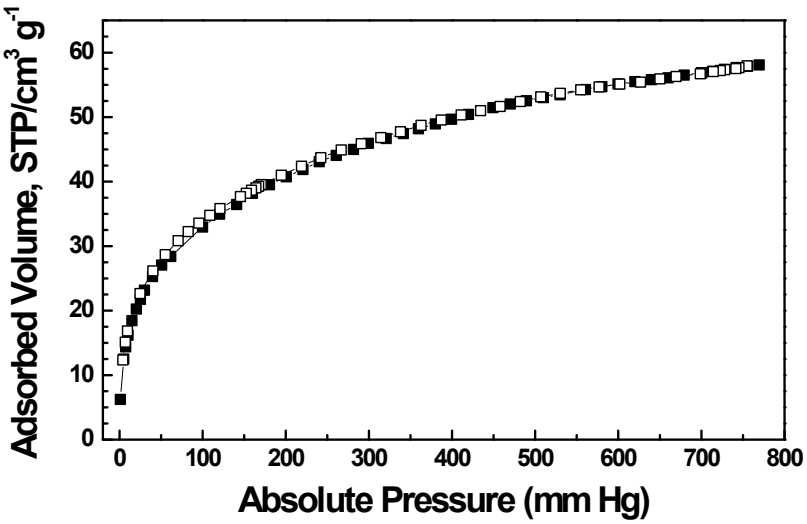


Fig. S8 Carbon dioxide sorption isotherms of the supramolecular network **HOP-1** at 196 K. (adsorption: solide, desorption: open).

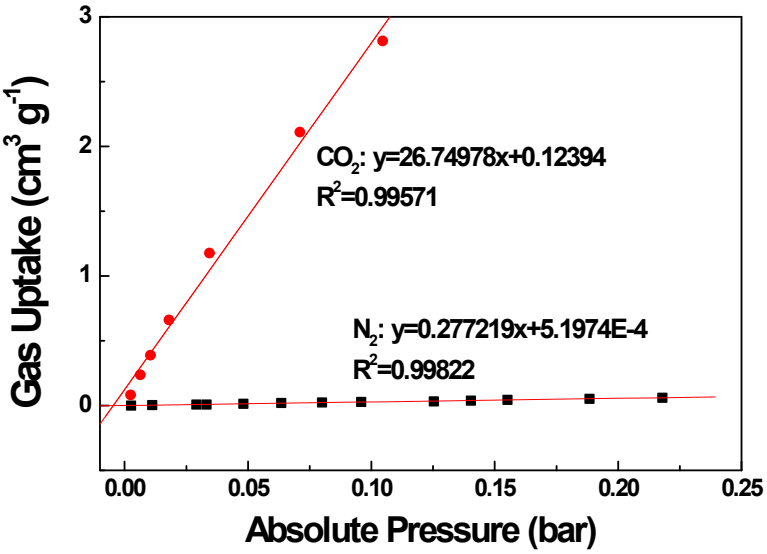
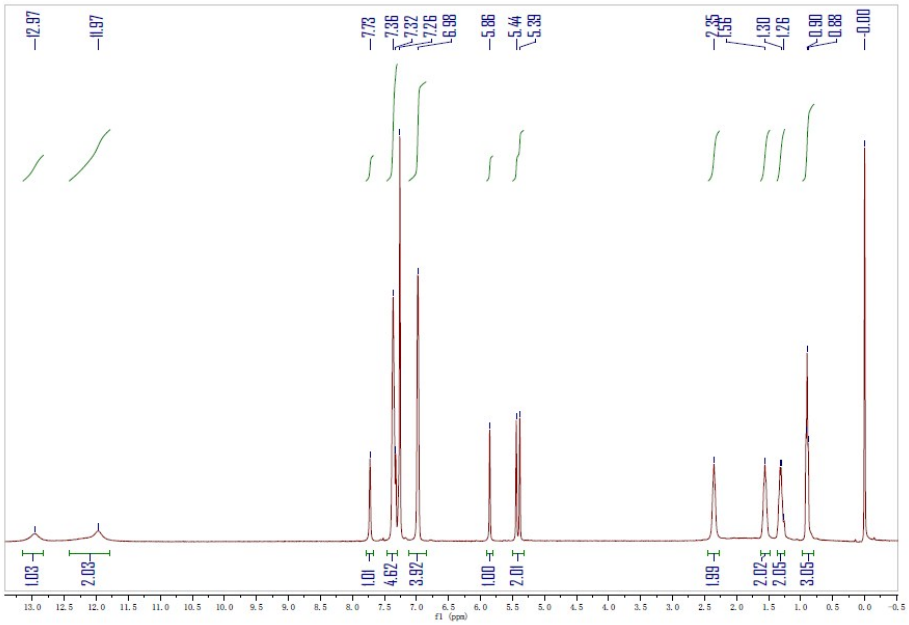
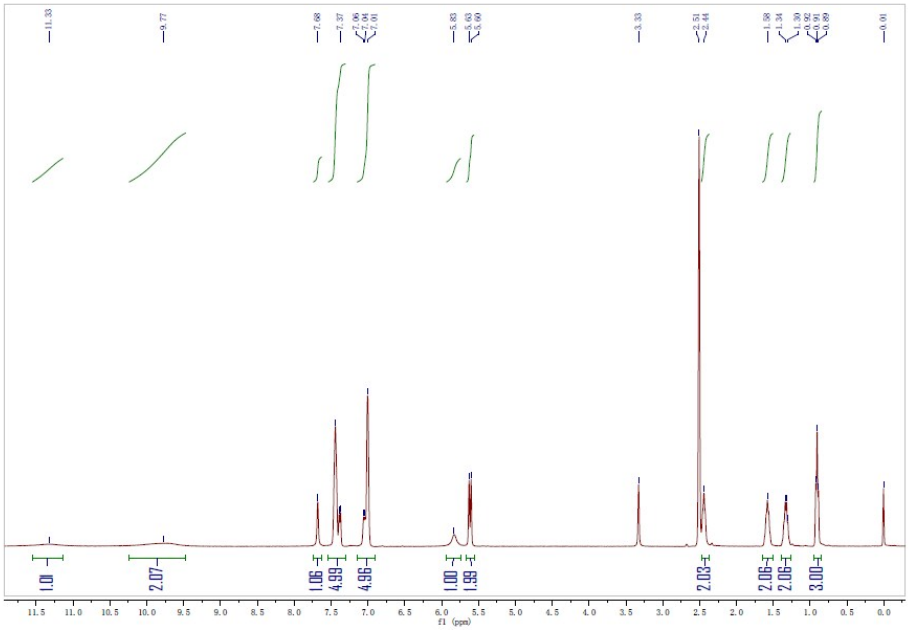


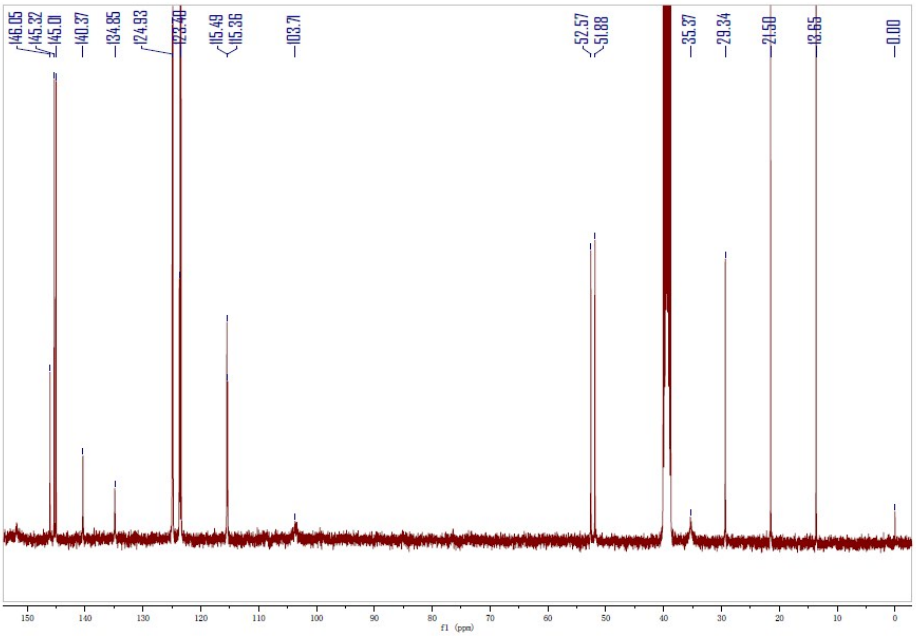
Fig. S9 Adsorption selectivity of carbon dioxide over nitrogen for **HOP-1** at 273 K based on initial slope calculations. Correlation coefficient R^2 of the linear fit is included.



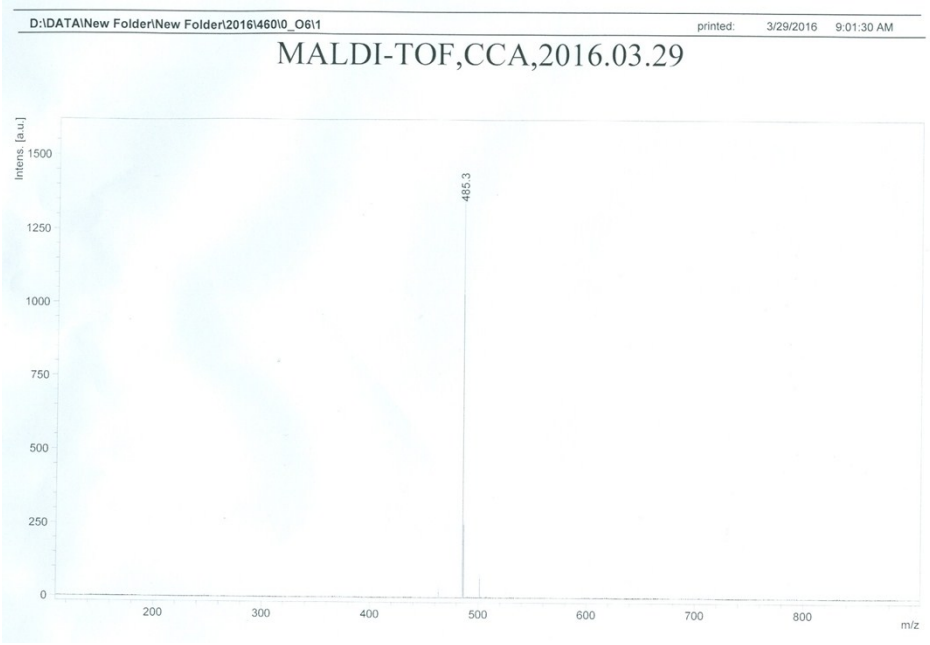
^{1}H NMR spectrum of OUPy in $CDCl_3$.



^{1}H NMR spectrum of OUPy in DMSO.



^{13}C NMR spectrum of OUPy in DMSO.



MALDI-TOF mass spectrum of OUPy.