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Supporting Information

Flexible Monomer based Covalent Organic Frameworks: Design, Structure and Functions

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1. Materials

All starting materials and solvents, unless otherwise noted, were obtained from the Sigma Aldrich and used without further purification. Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 spectrometer. Synchrotron powder X-ray diffraction (PXRD) was carried out with Bruker D8-Discover diffractometer equipped with a Mo sealed tube (λ = 0.72775 Å) on the beamline 17-BM at the Advanced Photon Source, Argonne National Laboratory. N_2 adsorption-desorption isotherms were measured using a Micrometritics ASAP 2020 system at 77K. Thermogravimetry analysis (TGA) was conducted on a TGA-50 (SHIMADZU) thermogravimetric analyzer from room temperature to 700 °C at a ramp rate of 2 °C/min in a flowing nitrogen atmosphere. Fourier transform infrared (FT-IR) measurements were performed on a SHIMADU IR Affinity-1 spectrometer.

2. The synthesis of ligand

2.1 The synthesis of 1,3,5-triformalbenzene

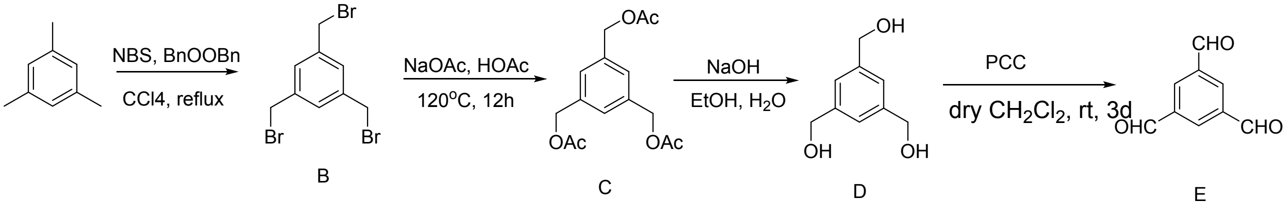

Figure S1. The synthetic procedure of 1,3,5-triformalbenzene.

Mesitylene (4.8 g, 40 mmol), N-bromosuccinimide (NBS, 17.8 g, 100 mmol), benzoyl peroxide (BnOOBn, 0.10 g) and CCl_4 (90 mL) were added to a 250 mL round-bottom flask. The mixture reacted under reflux for 12 h. The succinimide formed was removed through filtration and the solvent evaporated to give a white solid, 1,3,5-tris(bromomethyl)benzene.

1,3,5-tris(bromomethyl)benzene (10.33 g, 4 mmol), NaOAc (2.05 g, 25 mmol), and HOAc (45mL) was heated to 120^{o}C for 12h. This reaction was then cooled to room temperature. After water (90 mL) was added, the white solid was filtered off, washed with water and dried in air to give a white solid (C).

This white solid (C, 22.30 g, 6.1 mmol) and NaOH (1 g, 25 mmol) were dissolved in ethanol (25 mL). The mixture was refluxed for 5 h then cooled to room temperature. After adding water (25 mL), the yellow solid was filtered off, washed with water and dried in air to give 1,3,5-tris(hydroxymethyl)benzene (D).

To a stirring mixture of pyridinium chlorochromate (PCC, 5.6 g, 26 mmol) and celite (5 g) in CH_2Cl_2 (130 mL) was added solid 1,3,5-tris(hydroxymethyl)benzene (D, 1.1 g, 6.5 mmol). After 10 h, the reaction was diluted with ether (25 mL) and stirred for 30 min. The reaction mixture was then filtered through a bed of celite and the celite bed was further washed with CH_2Cl_2 (100mL). The combined filtrate was concentrated on a rotary evaporator to dryness and the crude product purified by flash chromatography (100% CH_2Cl_2) to afford 1,3,5-triformalbenzene as a white solid. ^{1}H-NMR (300MHz, $CDCl_3$): δ 8.64(aromatic H) and 10.20 (CHO) ppm.

2.2 The synthesis of 2,4,6-triformylphloroglucinol

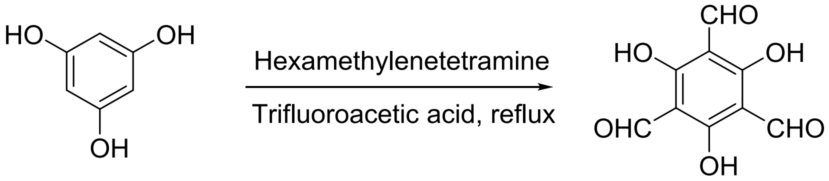

Figure S2. The synthetic procedure of 2,4,6-triformylphloroglucinol.

Hexamethylenetetramine (15.098g, 108 mmol) and phloroglucinol (6.014g, 49 mmol) were added to a 500mL round-bottom flask with a stir bar. Trifluoroacetic acid (TFA, 90mL) was added to the reflux setup under a nitrogen atmosphere. The reaction was heated to 100°C in an oil bath and stirred under reflux for 2.5h. After the reaction completed, 3M HCl (150mL) was added and heated again for 1.5h at 100°C. Once this had finished, the reaction was removed from the oil and cooled off to room temperature. Filtration took place through celite and filter paper, and the product in the flask was washed and extracted with dichloromethane and separated in a separatory funnel. To purify and obtain the triformylphloroglucinol, the solution was rotary evaporated to yield off-white, yellowish crystals. ^{1}H-NMR (300MHz, $CDCl_3$): δ 14.11 (OH) and 10.14 (CHO) ppm.

3. Synthesis of PPN-30 and PPN-31.

PPN-30: A Pyrex tube measuring o.d. × i.d. = 10 × 8 mm2 was charged with trans-1,4-cyclohexanediamine (10 mg, 0.0875 mmol) and 1,3,5-triformalbenzene (9.5 mg, 0.0583 mmol) in a solution of N,N-dimethylacetamide (1.5 mL) and 6 M acetic acid (25 μL). This mixture was then taken and flash frozen under liquid N_2 and degassed 3 times in a freeze-pump-thaw cycle. The tube was then sealed off under an acetylene torch and placed in a 120 ^{o}C oven for 3 days to afford a white precipitate which was isolated by filtration over a medium glass frit and washed with DMF (20.0 mL). The product was immersed in methanol (20.0 mL) overnight, during which the activation solvent was decanted and freshly replenished for four times. The solvent was removed under vacuum at room temperature to afford PPN-30 as a white powder (16.0 mg, 82%).

PPN-31: A Pyrex tube measuring o.d. × i.d. = 10 × 8 mm2 was charged with trans-1,4-cyclohexanediamine (10 mg, 0.0875 mmol) and 2,4,6-triformylphloroglucinol (12.5 mg, 0.0583 mmol) in a solution of N,N-dimethylacetamide (1.5 mL) and 6 M acetic acid (25 μL). This mixture was then taken and flash frozen under liquid N_2 and degassed 3 times in a freeze-pump-thaw cycle. The tube was then sealed off under an acetylene torch and placed in a 120 ^{o}C oven for 3 days to afford a red precipitate, which was isolated by filtration over a medium glass frit and washed with DMF (20.0 mL). The product was immersed in methanol (20.0 mL) overnight, during which the activation solvent was decanted and freshly replenished for four times. The solvent was removed under vacuum at room temperature to afford PPN-31 as a red powder (16.0 mg, 82%).

4. The synthetic condition optimization of PPN-30

The synthetic conditions were further optimized to achieve COFs with higher porosity. Firstly, we optimized the synthetic temperature while maintaining all the other synthetic conditions the same. From Figure S3, we can tell that with the increasing temperature from 120 °C to 150 °C, the porosity of PPN-30 did not increase. The N_2 uptake of PPN-30 was very similar for reaction temperature of 120 °C and 135 °C, with the one at 120 °C has a slightly advantage. However, increasing temperature from 135 °C to 150 °C, the porosity of PPN-30 decreased significantly. So we chose 120 °C as our reaction temperature.

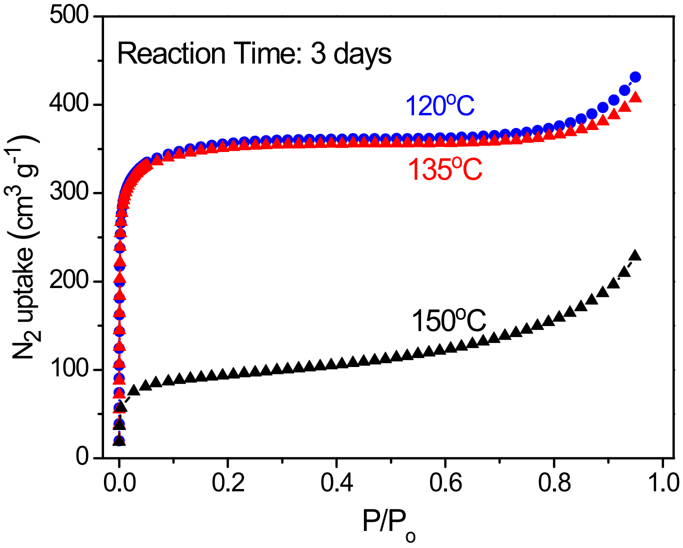

Figure S3. The optimization of reaction temperature for PPN-30.

Then we optimized the reaction time for PPN-30. From Figure S4, we can tell that the porosity of PPN-30 decreased as the increase of reaction time from 3 days to 5 days to 7 days. So we chose 3 days as our reaction time for PPN-30.

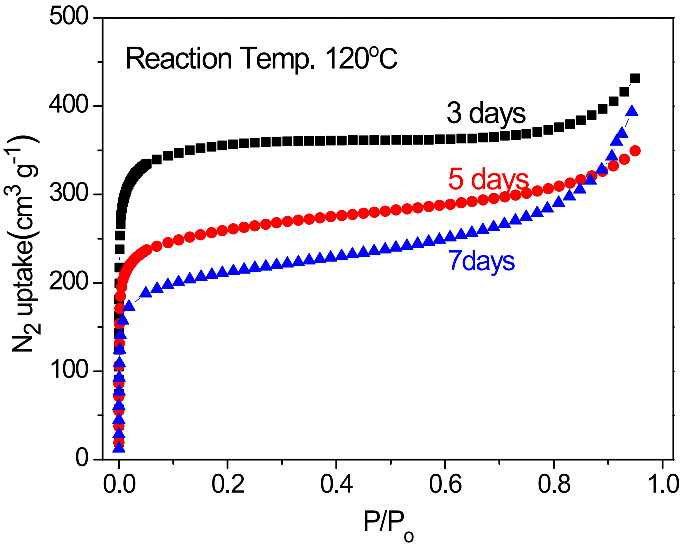

Figure S4. The optimization of reaction time for PPN-30.

5. The nitrogen uptake of PPN-31.

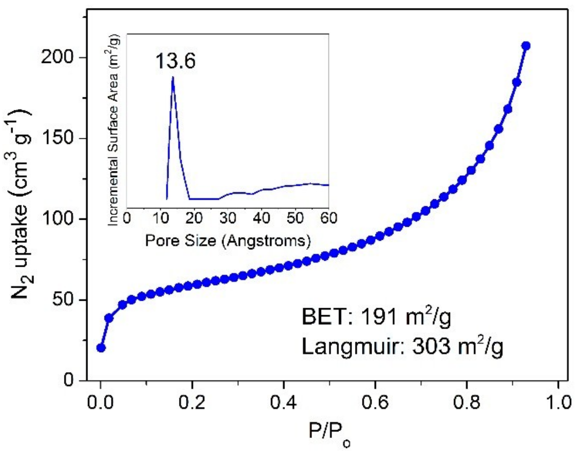

Figure S5. The N_2 uptake of PPN-31; the inset is the pore size distribution of PPN-31.

6. Thermal stability test of PPN-30

10.0 mg of fresh as-synthesized PPN-30 samples were heated on the TGA-50 (Shimadzu) thermogravimetric analyzer from room temperature to 700 °C at a rate of 2 °C min^{-1} under N_2 flow of 25 mL min^{-1}. Based upon the calculated composition, 50% weight loss is expected for solvent within the pores (30 - 70 °C) for the fresh sample. The observed decomposition temperature is around 330 °C for the fresh sample, suggesting the excellent thermal stability of PPN-30.

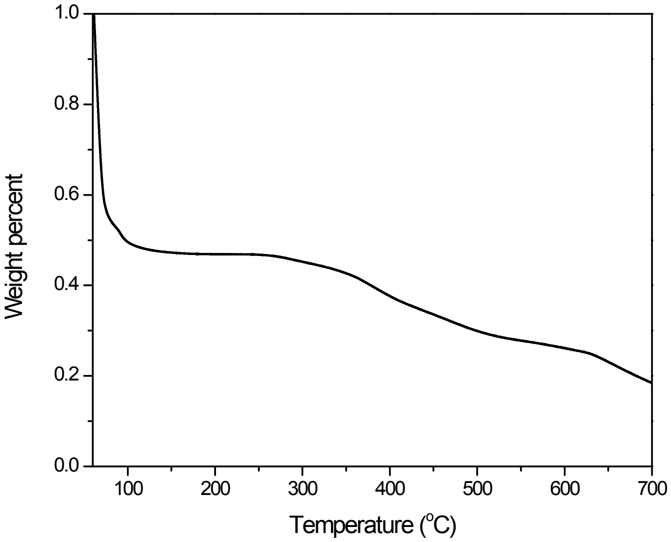

Figure S6. The thermal analysis of PPN-30.

7. The carbon capture property of PPN-30.

After we have successfully synthesized the flexible monomer based PPN-30, we went ahead and characterized it carbon capture property. Global warming has become one of the most pressing environmental concerns of our age and advanced porous materials have become very promising candidates to adsorb carbon dioxide, especially porous organic polymers. Due to its ordered crystalline nature, high porosity, as well as the high density of nitrogen atoms in the framework, PPN-30 shows very promising carbon capture property. At 273 K, the CO_2 uptake gets to 64.2 cm^3/g at 1 bar, which makes it very promising for gas storage applications.

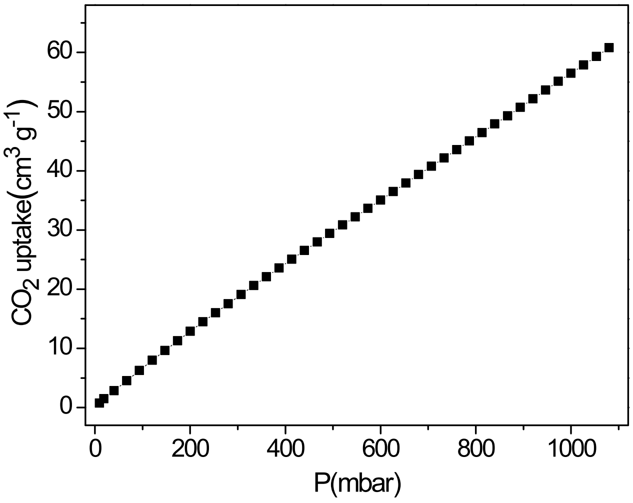

Figure S7. The carbon capture property of PPN-30 at 273 K.