# Triptycene-based three-dimensional covalent organic frameworks with stp topology of honeycomb structure

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## Supporting Information

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# 1. Supporting Methods

## 1.1 General materials and methods

Unless otherwise specified, all reactions were performed in dried glassware under an ambient atmosphere. All other reagents were purchased commercially and used without further purification. Organic solvents including ethanol, dichloromethane (DCM), petroleum ether, and tetrahydrofuran (THF) were purchased from Adamas; 1,2-Dichlorobenzene, n-butanol, and 1,4-dioxane were purchased from Alfa Aesar. Monomer C is commercial avalible.

$^{1}H$ and $^{13}C$ NMR spectra were performed on 400 MHz spectrometers (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature. High-resolution solid-state NMR spectra were recorded on Agilent NMR Spectrometer (60054-ASC) using a standard CP pulse sequence probe with 4 mm (outside diameter) zirconia rotors. Mass spectra were recorded with Waters GCT high-resolution mass spectrometer.

Transmission electron microscope (TEM) was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV.

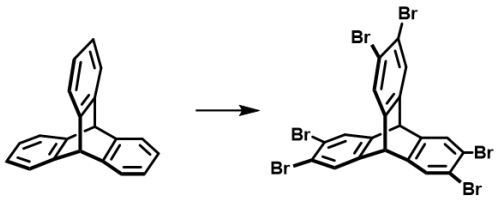
TGA was carried out on an American TA-Q20 in a nitrogen atmosphere using a 10 °C/min ramp without equilibration delay.

Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical Empyrean X-ray diffractometer with Cu Kα line focused radiation at 40 kV and 40 mA from 2θ = 1.5° up to 40° with 0.02° increment by Bragg-Brentano. The powdered sample was added to the glass and compacted for measurement.

$N_2$ adsorption isotherms were measured up to 1 bar at 77 K using a Micrometrics ASAP 2460 surface area analyzer. Before measurements, samples (ca. 50 mg) were degassed for over 12 h at 120 °C. UHP grade $N_2$ and He were used throughout the adsorption experiments. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to prevent contamination of the samples during the degassing

process and isotherm measurement.

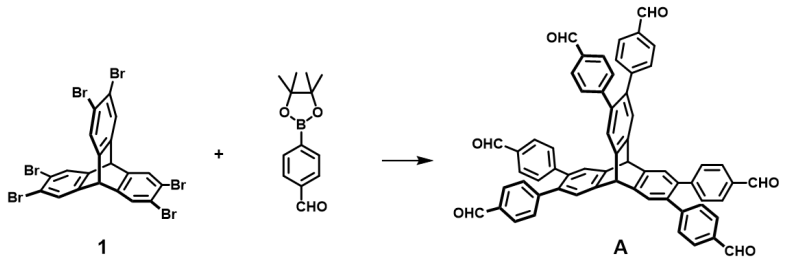
### 1.2 Synthesis procedure




1

**Synthesis of compound 1.**

Compound **1**was prepared according to the reference.[1] The iron powder (0.085 g, 1.52 mmol) was added to a solution of tryptone (3.00 g, 11.80 mmol) in chloroform (250 mL) at room temperature under vigorous stirring. After stirring for 15 min, 3.8 mL bromine (11.80 g, 73.84 mmol) in chloroform (20 mL) was added to the reaction mixture in one portion. After stirring under reflux for 3 h, the reaction was cooled to room temperature and the solvent was removed under vacuum. The brown solid was redissolved in chloroform (ca. 800 mL) and filtered through a pad of silica gel using additional chloroform (ca. 400 mL). The chloroform was then removed under vacuum and the obtained solid was recrystallized with acetone to give 3.86 g pure compound **1** (yield, 45.0%). $^1$H NMR (400 MHz, $CDCl_3$, δ): 7.62 (s, 6H), 5.23 (s, 2H).

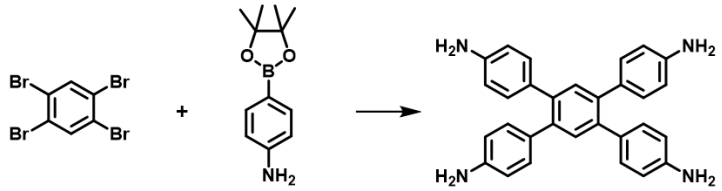



1 A

**Synthesis of monomer A.**

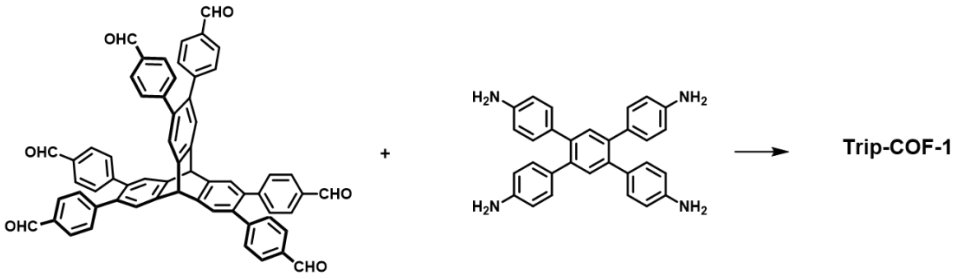
A mixture of compound **1** (1.00 g, 1.37 mmol), 4-formylbenzeneboronic acid pinacol ester (2.87g, 12.37 mmol), $Pd_2(dba)_3$ (128.2 mg, 0.14 mmol) and Xphos (133.5 mg, 0.28 mmol) in the mixed solvent containing tetrahydrofuran (100 mL) and 2.0 M $K_2CO_3$ (aq) (30 mL) was refluxed at 80 °C under nitrogen for 20 h. After cooling down to room temperature, the mixture was extracted with DCM. The organic phase was dried with

$MgSO_4$ and condensed under reduced pressure. The residue was purified by chromatography ($SiO_2$, 50% petroleum ether in dichloromethane) to give the product as a white solid powder (0.96 g, 79.6%). $^1$H NMR (400 MHz, $CDCl_3$, δ): 9.96 (s, 6H), 7.72 (d, *J* = 8.2 Hz, 12H), 7.63 (s, 6H), 7.24 (d, *J* = 8.2 Hz, 12H), 5.78 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$, δ):191.7, 147.0, 144.6, 137.1, 134.8, 130.5, 129.6, 126.3, 53.1. HRMS (MALDI) m/z: [$M^+$] calcd. for $C_{62}H_{38}O_6$ 878.2663; found 878.2661.




**Synthesis of monomer B.**

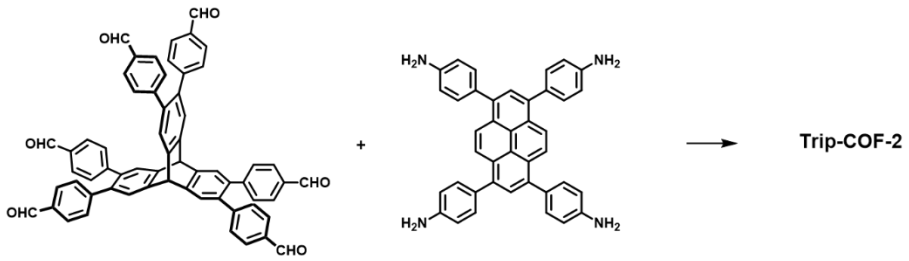
A mixture of 1,2,4,5-Tetrabromobenzene (1.00 g, 2.54 mmol), 4-aminophenylboronic acid pinacol ester (3.34 g, 15.24 mmol), $Pd_2(dba)_3$ (128.2 mg, 0.14 mmol) and Xphos (133.5 mg, 0.28 mmol) in the mixed solvent containing tetrahydrofuran (100 mL) and 2.0 M $K_2CO_3$ (aq) (30 mL) was refluxed at 80 °C under nitrogen for 20 h. After cooling down to room temperature, the mixture was extracted with ethyl acetate. The organic phase was dried with $MgSO_4$ and condensed under reduced pressure. The residue was purified by chromatography ($SiO_2$, 50% petroleum ether in ethyl acetate) to give the product as a grayish white solid powder (0.72 g, 63.9%). $^1$H NMR (400 MHz, DMSO-$d_6$, δ): 7.10 (s, 2H), 6.83 (d, *J* = 8.0 Hz, 8H), 6.43 (d, *J* = 8.0 Hz, 8H), 4.99 (s, 8H). $^{13}$C NMR (100 MHz, DMSO-$d_6$, δ): 147.5, 138.5, 132.4, 130.4, 129.3, 114.0. HRMS (EI) m/z: [$M^+$] calcd. for $C_{30}H_{26}N_4$ 442.2157; found 442.2154.




**Synthesis of Trip-COF 1**.

A Pyrex tube was charged with monomer **A** (30.0 mg, 0.034 mmol), **B** (22.7 mg, 0.051

mmol), 1,2-dichlorobenzene (1.8 ml), n-butanol (0.2 mL) and 6 M aqueous acetic acid (0.2 mL). After being degassed by freeze-pump-thaw technique for three times and sealed under vacuum, the tube was placed in an oven at 120 ℃ for 3 d. After cooling to room temperature, the resulting precipitate was filtered and washed by Soxhlet extractions with tetrahydrofuran and ethanol for 2 d, and then dried at 120 ℃ under vacuum for 12 h. **Trip-COF 1** was isolated as light yellow powder (42.7mg, yield 87.2%) insoluble in common organic solvents.




**Synthesis of Trip-COF 2**.

A Pyrex tube was charged with monomer **A** (25.0 mg, 0.028 mmol), **C** (24.2 mg, 0.043 mmol), 1,2-dichlorobenzene (1.8 ml), n-butanol (0.2 mL) and 6 M aqueous acetic acid (0.2 mL). After being degassed by freeze-pump-thaw technique for three times and sealed under vacuum, the tube was placed in an oven at 120 ℃ for 3 d. After cooling to room temperature, the resulting precipitate was filtered and washed by Soxhlet extractions with tetrahydrofuran and ethanol for 2 d, and then dried at 120 ℃ under vacuum for 12 h. **Trip-COF 2** was isolated as yellow powder (42.3 mg, yield 91.7%) insoluble in common organic solvents.

## 2. Supporting Figures and Legends

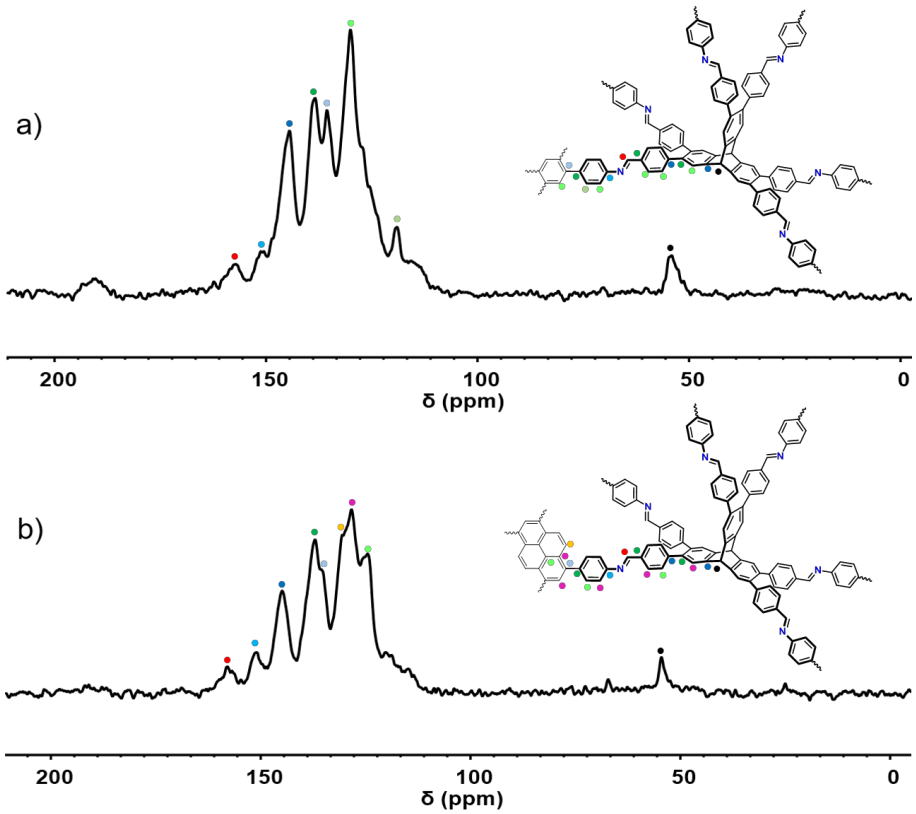



**Figure S1**. $^{13}C$ CP-MAS NMR spectra of **Trip-COF 1** (a) and **Trip-COF 2** (b).

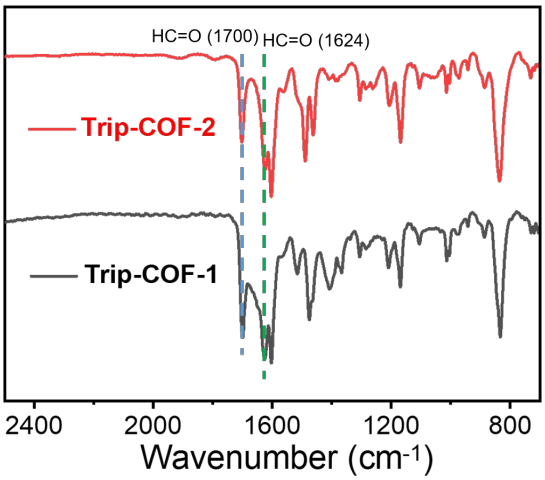



**Figure S2**. The FT-IR spectra of **Trip-COF 1, 2**.

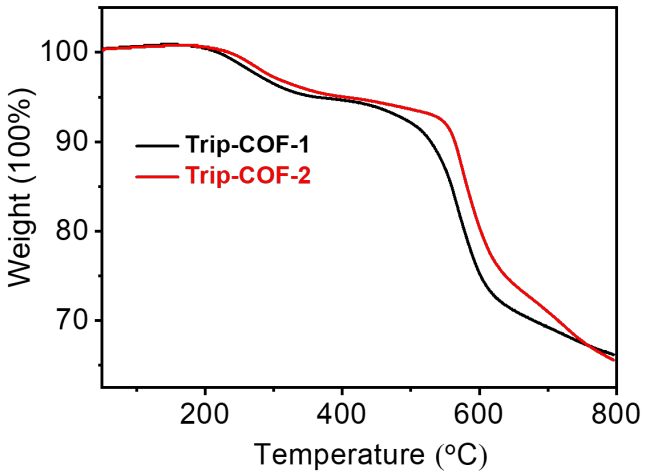



**Figure S3**. The thermogravimetric analysis profiles of **Trip-COF 1**, **2**.

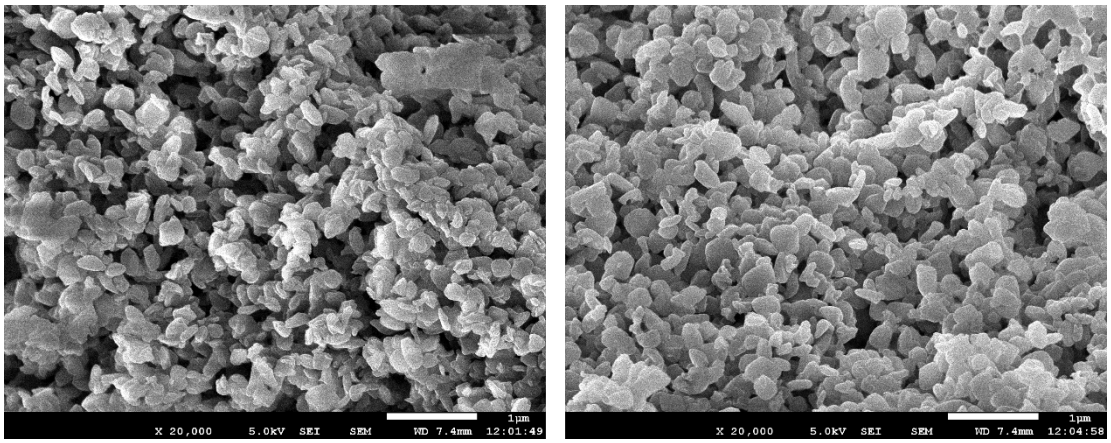



**Figure S4**. SEM images of **Trip-COF 1**.

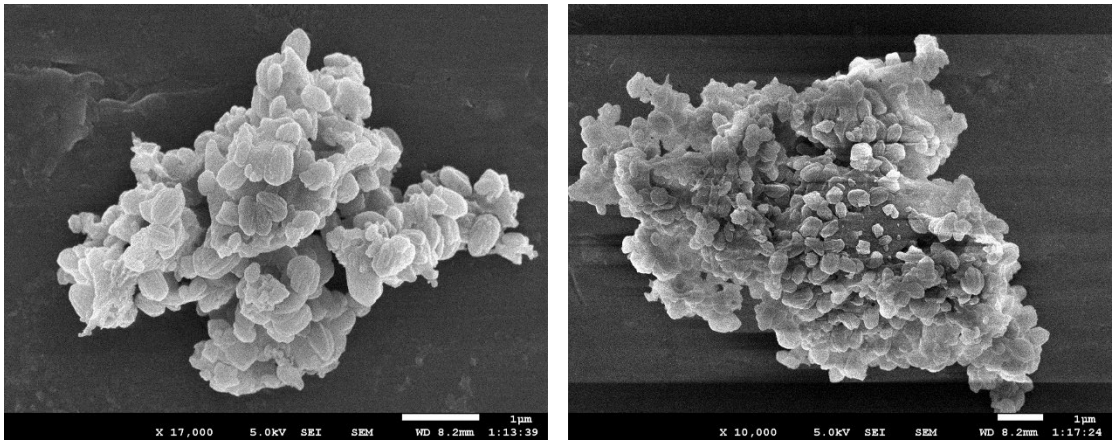



**Figure S5**. SEM images of **Trip-COF 2**.

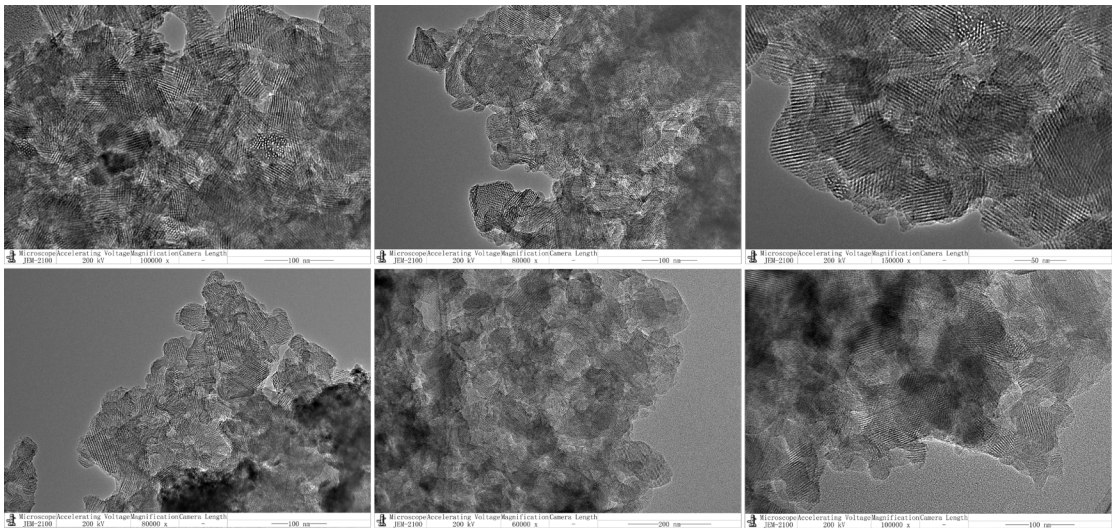


**Figure S6**. TEM images of **Trip-COF 1**.

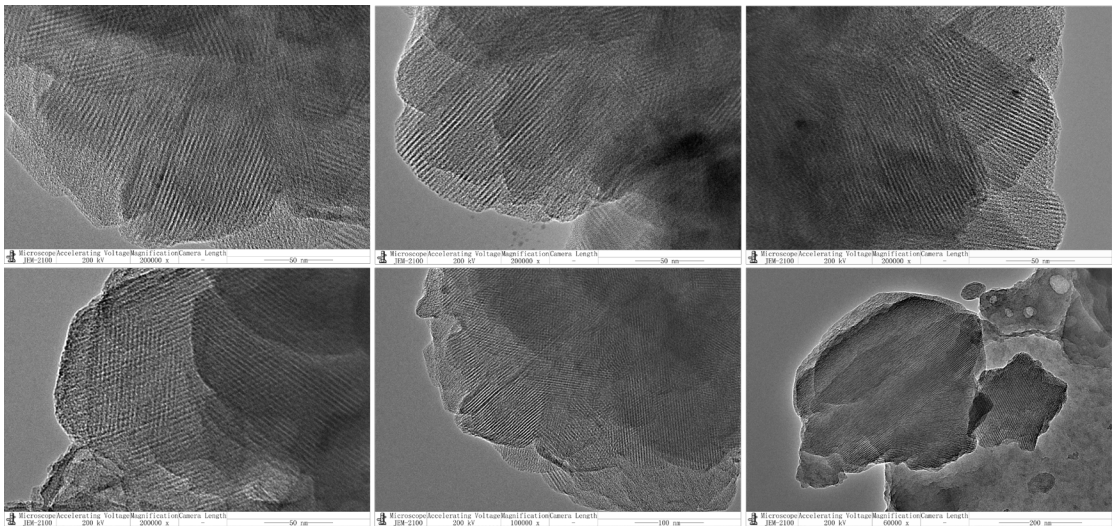


**Figure S7**. TEM images of **Trip-COF 2**.

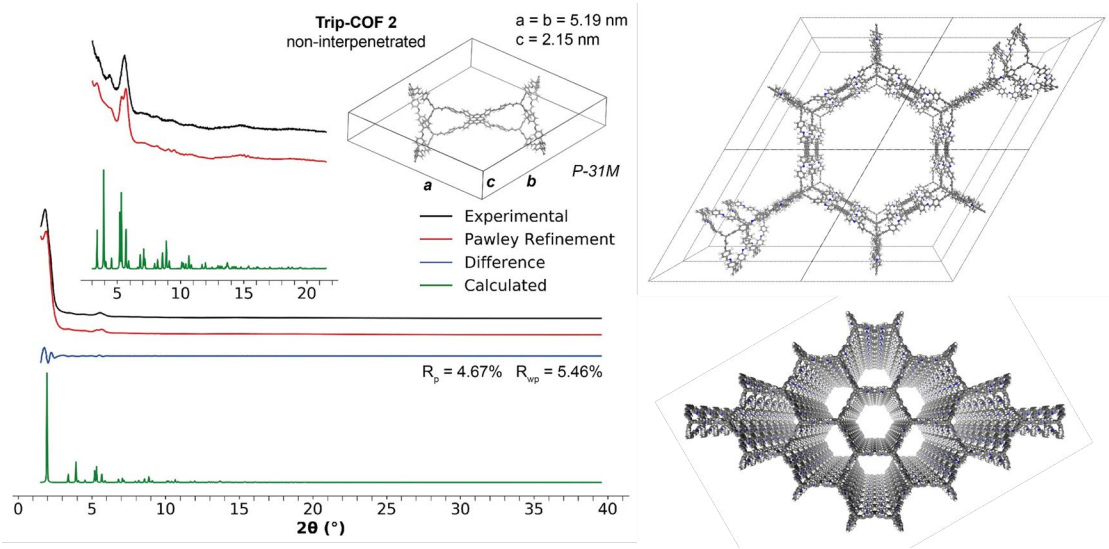



**Figure S8**. Indexed experimental (black), Pawley refined (red) PXRD patterns with their difference (blue), and the calculated pattern (green) from non-interpenetrated **Trip-COF 2**. Inset: zoomed view of detailed PXRD profile without the primary peak and optimized unit cell model. Structural representation of non-interpenetrated **Trip-COF 2**. Up: ball-and-stick images; down: space-filling model views perpendicular to 1D channels.

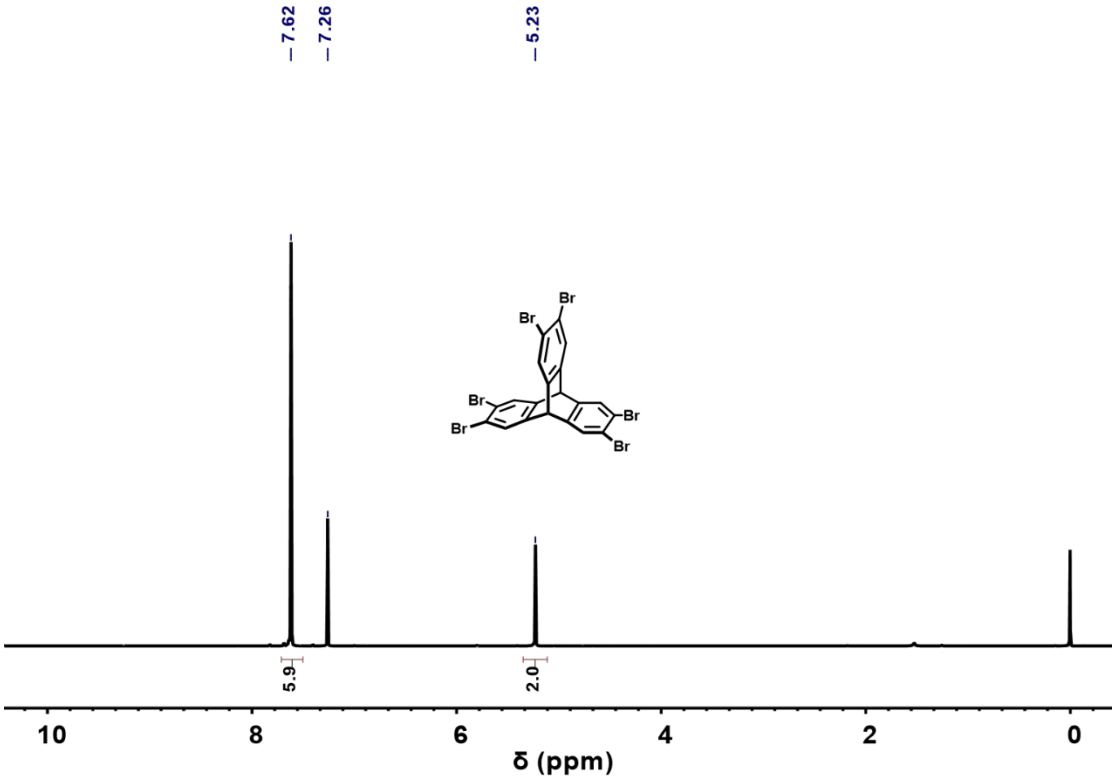



**Figure S9**. $^{1}$H NMR spectrum of compound **1**.

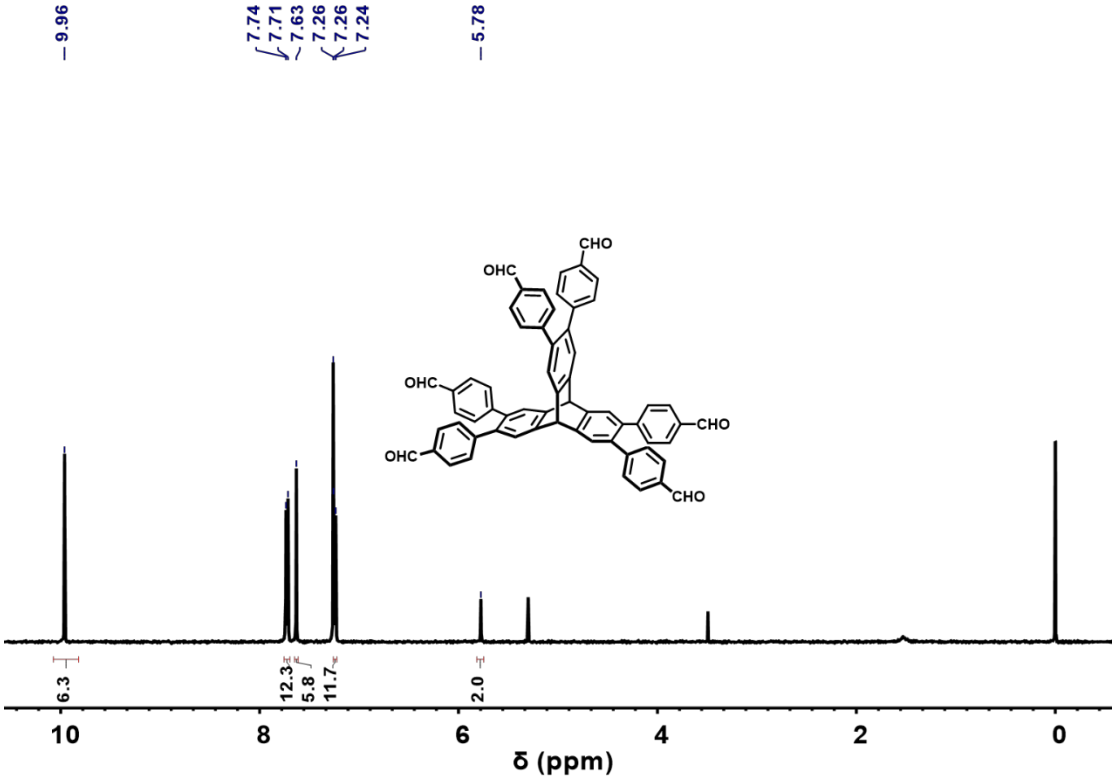



**Figure S10**. $^{1}$H NMR spectrum of monomer **A**.

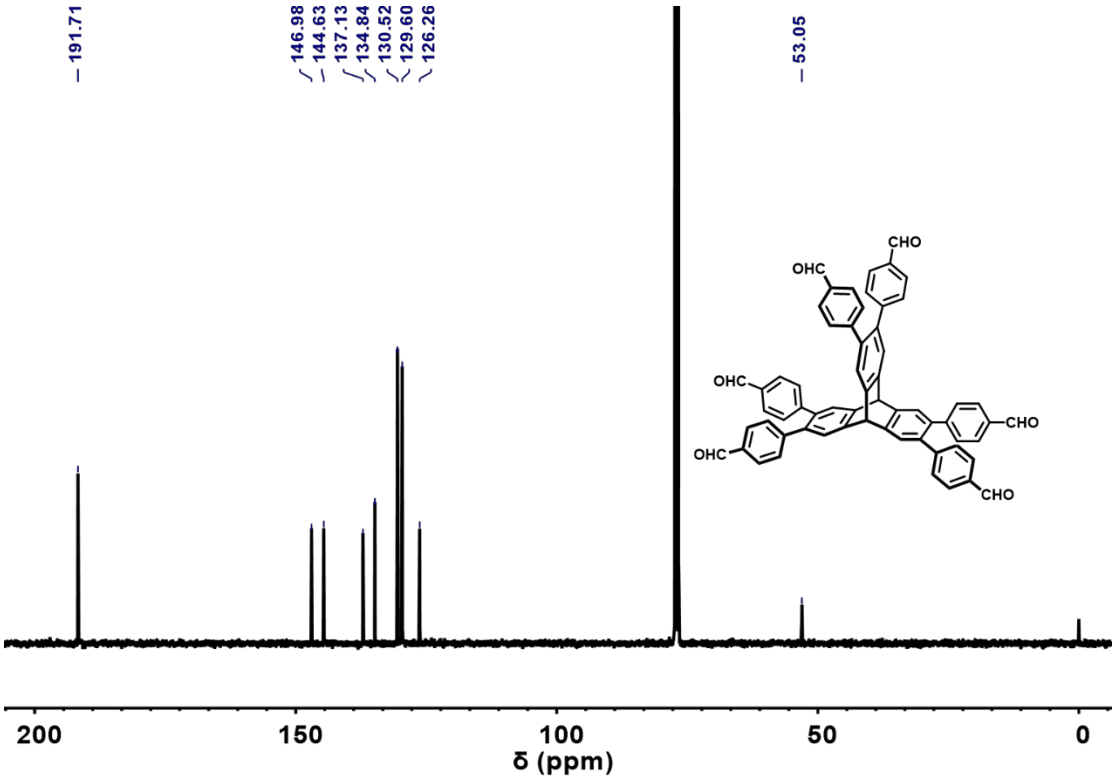



**Figure S11**. $^{13}$C NMR spectrum of monomer **A**.

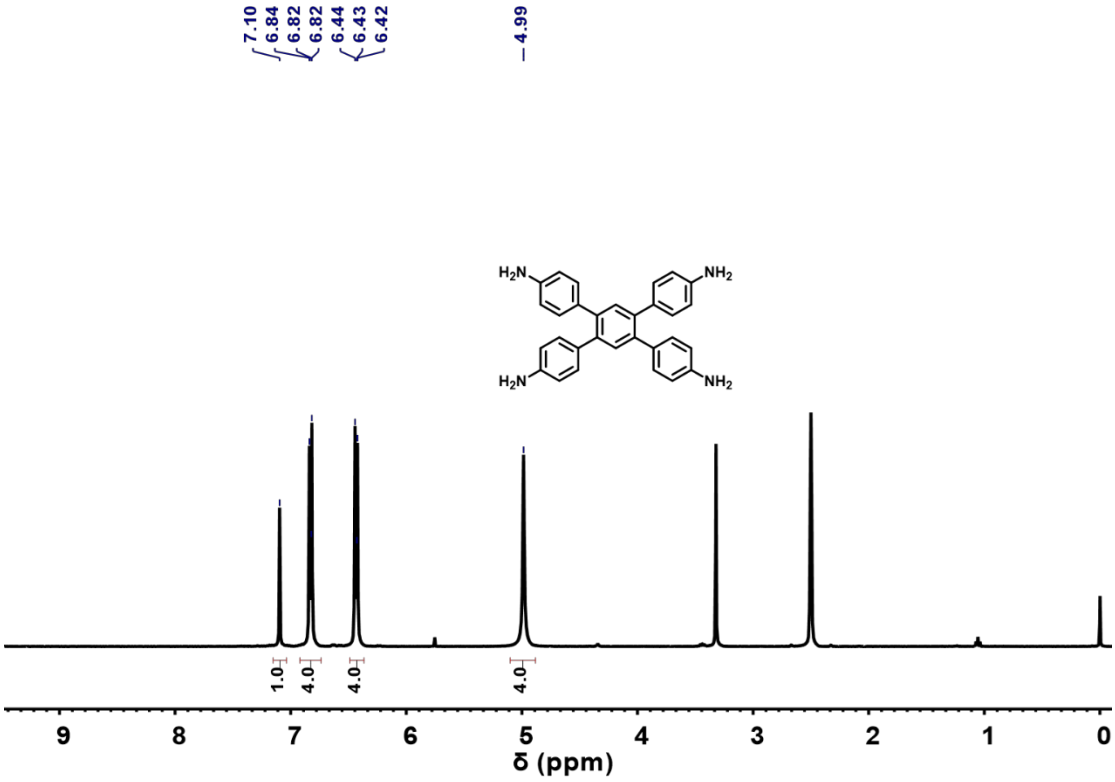



**Figure S12**. $^{1}$H NMR spectrum of monomer **B**.

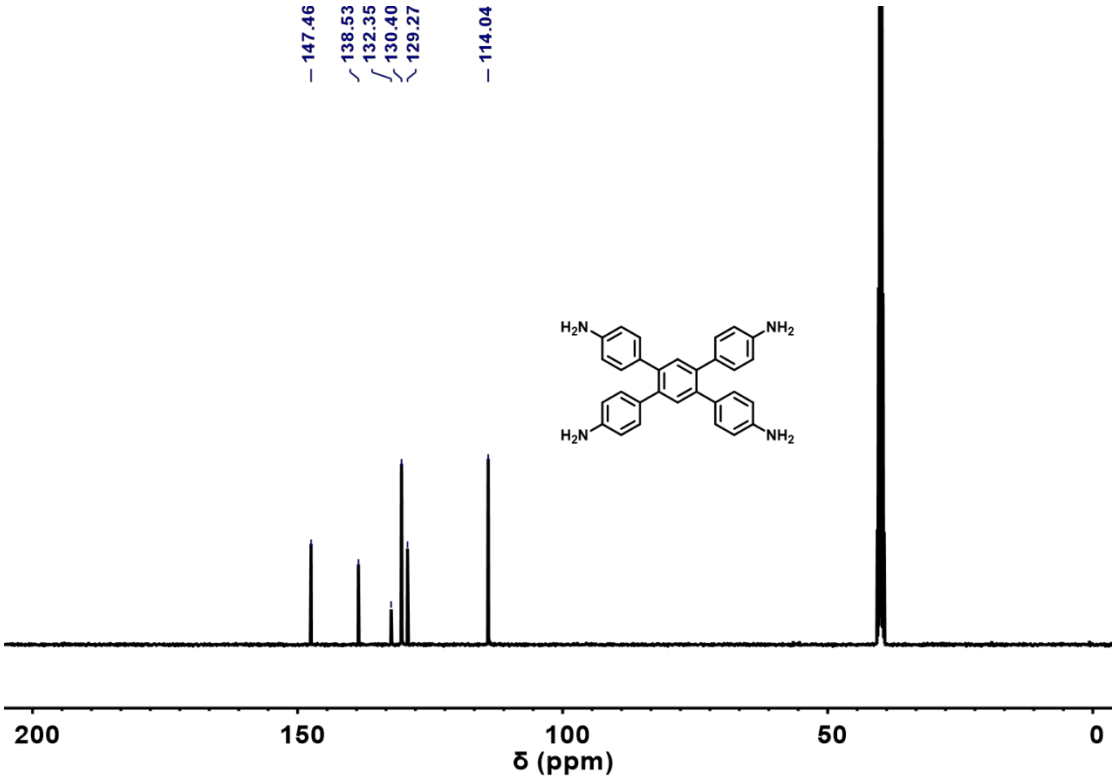



**Figure S13**. $^{13}$C NMR spectrum of monomer **B**.

## Reference

(1) Kissel, P.; Murray, D. J.; Wulftange, W. J.; Catalano, V. J.; King, B. T., A nanoporous two-dimensional polymer by single-crystal-to-single-crystal photopolymerization. *Nat. Chem.* **2014,** *6*, 774-778.