Supporting Information

Dispersive 2D Triptycene-Based Crystalline Polymers: Influence of Regioisomerism on Crystallinity and Morphology

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X-ray single-crystal structures of triptycene-based molecules

Figure S1. X-Single-crystal structures of Triptycene-based molecules with C-H bonds pointing towards interlayer space.
**Figure S2.** Single-crystal structures of the triptycene-based molecules with CCDC number of 737428 and 1416311, wherein the distances between the hydrogen (C-H) atoms are within the sum of the van der Waals radii.
Preparation of monomers

Synthetic procedure for sr-TTN (s, r-2, 6, 14-trinitrotriptycene):\(^1\textsuperscript{2}\)

5 g triptycene (19.5 mmol) and 65 mL concentrated nitric acid (67 wt %, 0.98 mol) were added into a 500 mL eggplant-shaped flask and heated to 85 °C for 16 hours under the protection of nitrogen. Then after cooling to room temperature, the reaction solution was added to 2 L of pure water and the yellow solid precipitation appeared after vigorously stirring for 12 hours. Then the crude product was obtained by suction filtration of 6.72 g light yellow solid (yield, 88%). The crude product was purified through a silica gel column with eluent PE/EA=5/1, and finally 4.02 g (60%) light yellow powder of sr-TTN was collected. R\(_f\) = 0.38 (PE/EA = 5/1). Numbers (400 MHz, CDCl\(_3\), 298 K) \(\delta\) 8.33 (d, \(J = 10.5\) Hz, 3H), 8.04 (d, \(J = 5.9\) Hz, 3H), 7.61 (d, \(J = 5.2\) Hz, 3H), 5.81 (d, \(J = 5.2\) Hz, 1H), 5.80 (s, 1H), 5.80 (s, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\), 298 K) \(\delta\) 149.8, 146.7, 144.9, 125.2, 122.9, 119.4, 53.4, 53.2.

Figure S3. Synthesis of sr-TTN.

Figure S4. \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\), 298 K) of sr-TTN.
Synthetic procedure for ss-TTN (s,s-2,7,14-trinitrotriptycene):

5 g triptycene (19.5 mmol) and 200 mL concentrated nitric acid (67 wt %, 3.02 mol) were added into a 250 mL eggplant-shaped flask, and heated to 65 °C for 16 hours under the protection of nitrogen. Then after cooling to room temperature, the reaction solution was added to 2 L of pure water and the yellow solid precipitation appeared after vigorously stirring for 12 hours. Then the crude product was obtained by suction filtration to 6.54 g light yellow solid (yield, 85%). The crude product was purified through a silica gel column with eluent EA/PE = 3/1, and finally 2.57 g (33%) ss-TTN was collected. Rf = 0.27 (PE/EA = 3/1) 1H NMR (400 MHz, CDCl3, 298K) δ 8.34 (t, J = 11.1 Hz, 3H), 8.03 (dd, J = 8.2, 2.2 Hz, 3H), 7.61 (d, J = 8.2 Hz, 3H), 5.83 (s, 1H), 5.79 (s, 1H); 13C NMR (151 MHz, CDCl3, 298K) δ 148.8, 146.4, 144.8, 125.0, 122.6, 119.7, 53.5, 53.1.

Figure S5. 13C NMR spectrum (151 MHz, CDCl3, 298K) of sr-TTN.

Figure S6. Synthesis of ss-TTN.
Figure S7. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298K) of ss-TTN.

Figure S8. $^{13}$C NMR spectrum (151 MHz, CDCl$_3$, 298K) of ss-TTN.
Synthetic procedure for sr-TTA (s, r-2, 6, 14-triaminotiptycene):

200 mg of sr-TTN (0.5 mmol) and 12 equivalents of SnCl\textsubscript{2}.2H\textsubscript{2}O (1.36 g, 6 mmol) were added into a 50 mL eggplant-shaped flask, and then added 6 mL EtOH, 1.2 mL cHCl (12 mol/L, 14.4 mmol). Then, the solution was stirred and reacted at 100 °C under nitrogen protection for about 16 hours. After the reaction finished, the reaction was cooled and the pH value of the reaction solution was adjusted to weakly alkaline by saturated sodium bicarbonate solution, in air and then the reaction solution was extracted three times with ethyl acetate (100 mL*3), and finally, the organic phase is back-extracted once with saturated brine. After being treated with anhydrous Na\textsubscript{2}SO\textsubscript{4}, the solution was concentrated by a rotary evaporator. 115 mg (yield 91%) of triaminoterpene monomer crude product was obtained. After purification through silica gel chromatography with eluent EA/PE = 4/1, 94 mg (yield 74%) pure triaminoterpene monomer: ss-TTA is obtained (the third point in the silica column). R\textsubscript{f} =0.42 (EA/PE=5/1) \textsuperscript{1}\text{H} NMR (400 MHz, CDCl\textsubscript{3}, 298K) \text{δ} 7.05 (d, \textit{J} = 9.9 Hz, 3H), 6.70 (d, \textit{J} = 2.1 Hz, 3H), 6.23 (d, \textit{J} = 2.6 Hz, 3H), 5.03 (s, 1H), 5.00 (s, 1H), 3.48 (m, 6H); \textsuperscript{13}\text{C} NMR (151 MHz, CDCl\textsubscript{3}, 298K) \text{δ}147.1, 143.6, 136.2, 123.5, 111.4, 110.4, 53.6, 52.6.

**Figure S9.** Synthesis of sr-TTA.

**Figure S10** \textsuperscript{1}\text{H} NMR spectrum (400 MHz, CDCl\textsubscript{3}, 298K) of sr-TTA.
Synthetic procedure for ss-TTA (s, s-2, 7, 14-triaminotriptycene):

200 mg of ss-TTN (0.5 mmol) and 12 equivalents of SnCl₂·2H₂O (1.36 g, 6 mmol) were added into a 50 mL eggplant-shaped flask, and then added 6 mL EtOH, 1.2 mL cHCl (12 mol/L, 14.4 mmol). After stirring at 100 °C under nitrogen protection for about 16 hours, and monitored the reaction until it was completely complete by the TLC. Then, the reaction solution was cooled in air, and the pH value of the reaction solution was adjusted to weakly alkaline with saturated sodium bicarbonate solution, and then extracted three times with EA (100 mL*3), and finally, the organic phase is back-extracted once with saturated brine. After treatment with anhydrous sodium Na₂SO₄, the organic phase was concentrated by a rotatory evaporator and 105 mg (88% yield) crude product: ss-TTA, triaminopterene monomer. Then the crude product was purified through a silica gel column with EA/PE = 5/1, and finally, 78 mg (65% yield) pure triaminopterene monomer is obtained (the third point in the silica column). Rᵣ=0.28 (EA/PE=5/1). ¹H NMR (400 MHz, CDCl₃, 298K) δ7.04 (d, J = 7.8 Hz, 3H), 6.71 (d, J = 2.2 Hz, 3H), 6.24 (dd, J = 7.7, 2.1 Hz, 3H), 5.06 (s, 1H), 4.99 (s, 1H), 3.47 (m, 6H); ¹H NMR (400 MHz, DMSO-d₆, 298K) δ 6.91 (d, J = 7.5 Hz, 3H), 6.66 (s, 3H), 6.13 (d, J = 7.0 Hz, 3H), 4.95 (d, J = 7.1 Hz, 2H); ¹³C NMR (151 MHz, DMSO-d₆, 298K) δ 146.1, 143.7, 136.0, 122.8, 112.1, 111.6, 109.9, 53.6, 50.1.
Figure S12. Synthesis of ss-TTA

Figure S13. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298K) of ss-TTA.
Figure S14. $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$, 298K) of ss-TTA.

Figure S15. X-ray single-crystal structure of sr-TTA (CCDC: 1422762).

Figure S16. X-ray single-crystal structure of ss-TTA (CCDC: 1496656).
Figure S17. Comparisons between the $^1$H signals of –CH– in $^1$H NMR (400 MHz, CDCl$_3$, 298K) and $^{13}$C NMR spectrum (151 MHz, CDCl$_3$, 298K) for sr-TTN, ss-TTN, sr-TTA, and ss-TTA.

Synthetic procedure for TRIP-CP-1-Model:

300 mg of sr-TTA (1 mmol) and 6 equivalents of Salicylaldehyde (733 mg, 6 mmol) were added into a 50 mL eggplant-shaped flask, and then added 10 mL EtOH, 100 µL HOAc. After stirring at 80 °C under nitrogen protection for about 24 hours, and monitored the reaction until it was completely complete by the TLC. Then the reaction solution was cooled in air, and 90 mL MeOH was added to the reaction system. After standing for two hours, a large amount of light yellow precipitate was obtained, which was further filtered to obtain yellow solid particles. The yellow product was concentrated by a rotatory evaporator to give 417 mg (68% yield) orange product: TRIP-CP-1-Model. Then the orange product was purified through a silica gel column with PE/EA = 4/1. $^1$H NMR (400 MHz, Chloroform-d) δ 13.21 (s, 3H), 8.56 (s, 3H), 7.34 (d, $J = 9.4$ Hz, 12H), 7.08 – 6.83 (m, 9H), 5.51 (s, 2H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 162.4, 161.3, 146.1, 143.6, 133.1, 132.2, 124.5, 119.2, 117.5, 117.2, 54.0, 53.3. HRMS (ESI) m/z: [M] Calcd for C$_{41}$H$_{30}$N$_3$O$_3$ 612.2286; Found 612.2282
Figure S18. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298K) and $^{13}$C NMR spectrum (151 MHz, CDCl$_3$, 298K) of TRIP-CP-1-Model.
Synthetic procedure for TRIP-CP-2-Model:

300 mg of ss-TTA (1 mmol) and 6 equivalents of Salicylaldehyde (733 mg, 6 mmol) were added into a 50 mL eggplant-shaped flask, and then added 10 mL EtOH, 100 µL HOAc. After stirring at 80 °C under nitrogen protection for about 24 hours, and monitored the reaction until it was completely complete by the TLC. Then the reaction solution was cooled in air, and 90 mL MeOH was added to the reaction system. After standing for two hours, a large amount of light yellow precipitate was obtained, which was further filtered to obtain yellow solid particles. The yellow product was concentrated by a rotatory evaporator to give 443mg (72% yield) orange product: TRIP-CP-2-Model. Then the orange product was purified through the silica gel column with PE/EA=5/1. 1H NMR (400 MHz, Chloroform-d) δ 13.16 (s, 3H), 8.56 (s, 3H), 7.44 (d, J = 7.8 Hz, 3H), 7.41 – 7.30 (m, 7H), 7.34 (s, 3H), 7.02 – 6.87 (m, 8H), 5.51 (d, J = 9.2 Hz, 2H). 13C NMR (126 MHz, Chloroform-d) δ 6163.7, 161.4, 146.4, 143.8, 133.1, 132.3, 132.26, 126.7, 119.3, 118.6, 117.20, 117.0, 54.6, 53.1. HRMS (ESI) m/z: [M] Calcd for C41H30N3O3 612.2287; Found 612.2282.

Figure S19. 1H NMR spectrum (400 MHz, CDCl₃, 298K) of TRIP-CP-2-Model.
Figure S20. $^{13}$C NMR spectrum (151 MHz, CDCl$_3$, 298K) of TRIP-CP-2-Model.
Figure S21. Comparisons between the $^1$H signals of –CH– in $^1$H NMR (400 MHz, CDCl$_3$, 298K) and $^{13}$C NMR spectrum (151 MHz, CDCl$_3$, 298K) for TRIP-CP-1-Model and TRIP-CP-2-Model.
Preparation of TRIP-CPs and TBA-COFs

**Synthesis of TRIP-CP-1 in the interfacial reaction system:** 1.5 equivalent of 2,5-Dihydroxy-1,4-benzenedicarboxaldehyde (DHTA) (24.9 mg, 0.15 mmol) was added into a 250 mL round glass beaker, and then added 70 mL 1,2-dichlorobenzene, 30 mL Dichloromethane (DCM). After stirring at room temperature under nitrogen protection for about 30 minutes. Completely dissolve DHTA into a pale yellow solution. 40 mg Sc(OTf)3 (0.08 mmol) as Luis acid catalyst was dissolved into 100 mL of pure water, and then the aqueous phase system was slowly poured over the organic phase system. After that 30 mg of sr-TTA (0.1 mmol) dissolved in 10 mL DCM was slowly added to the interfacial reaction system for about 12 hours. The interface reaction proceeded for about 7 days. Finally, a dense yellow-brown organic film was observed at the interface. Then it was fixed onto the sand core by a bigger holder of the suction filter equipment. Finally, the product was washed several times with H2O, methanol (MeOH), tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) to remove the trapped guest molecules, and then further dried in vacuum. 14.8 mg TRIP-CP-1 product was obtained (37% yield).

**Synthesis of TRIP-CP-2 in the interfacial reaction system:** 1.5 equivalent of DHTA (24.9 mg, 0.15 mmol) was added into a 250 mL round glass beaker, and then added 50 mL 1,2-dichlorobenzene, 50 mL DCM. After stirring at room temperature under nitrogen protection for about 30 minutes. Completely dissolve DHTA into a pale yellow solution. 20 mg Sc(OTf)3 (0.04 mmol) and 20 µL TFA (0.2 mmol) as acid catalyst was dissolved into 100 mL of pure water, and then the aqueous phase system was slowly poured over the organic phase system. After that 30 mg of ss-TTA (0.1 mmol) dissolved in 10 mL DCM was slowly added in the interfacial reaction system about 12 hours. Finally, a yellow organic film was observed at the interface. The interface reaction was proceeded for about 7 days. Finally, the product was washed several times with H2O, MeOH, THF, and DMF to remove the trapped guest molecules, and then further dried in vacuum. 9.5 mg TRIP-CP-2 product was obtained (21% yield).

**Synthesis of TRIP-CP-3 in the interfacial reaction system:** 1 equivalent of 1,3,5-Triformylphloroglucinol (TFP) (21.0 mg, 0.10 mmol) was added into a 250 mL round glass beaker, and then added 100 mL Dichloromethane (DCM). After stirring at room temperature under nitrogen protection for about 30 minutes. Completely dissolve TFA into a pale colourless and transparent solution. 40 µL Trifluoroacetate (TFA) (5 mmol%) as acid catalyst was dissolved into 100 mL of pure water, then the aqueous phase system is slowly poured over the organic phase system. After that 30 mg of sr-TTA (0.1 mmol) dissolved in 10 mL DCM was slowly added to the interfacial reaction system about 12 hours. The interface reaction was proceeded for about 7 days. Finally, a dense yellow organic film was observed at the interface. Then it was fixed onto the sand core by a bigger holder of the suction filter equipment. Finally, the product was washed several times with H2O, MeOH, THF, and DMF to remove the trapped guest molecules. And then further dried in vacuum to give 43.2 mg TRIP-CP-3 (94% yield).

**Synthesis of TRIP-CP-4 in the interfacial reaction system:** 1 equivalent of TFP (21.0 mg, 0.10 mmol) was added into a 250 mL round glass beaker, and then added 100 mL DCM. After stirring at room temperature under nitrogen protection for about 30 minutes. Completely dissolve TFA into a pale colourless and transparent solution. 40 µL TFA (5 mmol%) as acid catalyst was dissolved into 100 mL of pure water, then the aqueous phase system is slowly poured over the organic phase system. After that 30 mg of ss-TTA (0.1 mmol) dissolved in 10 mL DCM was slowly added in the interfacial reaction system about 12 hours. The interface reaction was proceeded for about 7 days. Finally, a dense yellow organic film was observed at the interface. Then it was fixed onto the sand core by a bigger holder of the suction filter equipment. Finally, the product was washed several times with H2O, MeOH, THF, and DMF to remove the trapped guest molecules. And then it was further dried in vacuum to give 17.9 mg TRIP-CP-4 (39% yield).

**Synthesis of TBA-COF-5 in the interfacial reaction system:** 1.5 equivalent of DHTA (24.9 mg, 0.15 mmol) was added into a 250 mL round glass beaker, and then added 90 mL 1,2-dichlorobenzene, and 10 mL DMF. After stirring at room temperature under nitrogen protection for about 30 minutes. Completely dissolve DHTA into a pale yellow solution. 40 mg Sc(OTf)3 (0.08 mmol) as Luis acid catalyst was dissolved into 100 mL of pure water, then the aqueous phase system was slowly poured over the organic phase system. After that 35 mg of 1,3,5-tri(4-aminophenyl)benzene (TBA, 0.1 mmol) dissolved in 10 mL DCM was slowly added in the interfacial reaction system for about 12 hours. The interface reaction was proceeded for about 5 days. Finally, a dense brown organic film was observed at the
interface. Then it was fixed onto the sand core by a bigger holder of the suction filter equipment. Finally, the product was washed several times with H$_2$O, MeOH, THF, and DMF to remove the trapped guest molecules, and then further dried in vacuum. 22.5 mg TBA-COF-5 product was obtained (45% yield).

**Synthesis of TBA-COF-6 in the interfacial reaction system:** 1 equivalent of TFP (21.0 mg, 0.10 mmol) was added into a 250 mL round glass beaker, and then added 100 mL DCM. After stirring at room temperature under nitrogen protection for about 30 minutes. Completely dissolve TFA into a pale colourless and transparent solution. 40 uL TFA (5 mmol%) as acid catalyst was dissolved into 100 mL of pure water, then the aqueous phase system was slowly poured over the organic phase system. After that 35 mg of TBA (0.1 mmol) dissolved in 10 mL DCM was slowly added in the interfacial reaction system about 12 hours. The interface reaction was proceeded for about 7 days. Finally, a dense yellow organic film was observed at the interface. Then it was fixed onto the sand core by a bigger holder of the suction filter equipment. Finally, the product was washed several times with H$_2$O, MeOH, THF, and DMF to remove the trapped guest molecules. And then it was further dried in vacuum to give 48.4 mg TBA-COF-6 (88% yield).
Solid-state NMR spectra for TRIP-CPs

Figure S22. Solid-state $^{13}$C CP/MASS NMR spectra of TRIP-CP-1 and $^{13}$C liquid NMR of monomers.
**Figure S23.** Solid-state $^{13}$C CP/MASS NMR spectra of TRIP-CP-2 and $^{13}$C liquid NMR of monomers.
Figure S24. Solid-state $^{13}$C CP/MASS NMR spectra of TRIP-CP-3 and $^{13}$C liquid NMR of monomers.
Figure S25. Solid-state $^{13}$C CP/MASS NMR spectra of TRIP-CP-4 and $^{13}$C liquid NMR of monomers.
Figure S26. Solid-state $^{13}$C CP/MASS NMR spectra of TBA-COF-5 and $^{13}$C NMR liquid spectra of monomers.
Figure S27. Solid-state $^{13}$C CP/MASS NMR spectra of TBA-COF-6 and $^{13}$C liquid NMR spectra of monomers.
Figure S28. Solid-state $^{13}$C CP/MASS NMR spectra for keto-enol tautomerism Schiff COFs of TRIP-CP-3, TRIP-CP-4, and TBA-COF-6.
Simulated structures for TRIP-CPs$^{5,6}$

**Figure S29.** Eclipsed-AA stacking model cell of TRIP-CP-1.

**Figure S30.** AB-staggered stacking model cell of TRIP-CP-1.
Figure S31. Non-interpenetrated-staggered stacking model cell of TRIP-CP-1.

Figure S32. interpenetrated-staggered stacking model cell of TRIP-CP-1.
Figure S33. Different calculated stacking model cell of TRIP-CP-1.
Figure S34. Eclipsed-AA and AB-staggered stacking model cell of TRIP-CP-2.
Figure S35. Non-interpenetrated-staggered stacking model cell of TRIP-CP-2.

Figure S36. Non-interpenetrated-staggered stacking model cell of TRIP-CP-2.
Figure S37. Different calculated -stacking model cell of TRIP-CP-2.
Figure S38. Eclipsed-AA stacking model cell of TRIP-CP-3.

Figure S39. AB-staggered stacking model cell of TRIP-CP-3.
Figure S40. Eclipsed-AA stacking model cell of TRIP-CP-4.

Figure S41. AB-staggered stacking model cell of TRIP-CP-4.
Figure S42. Eclipsed-AA and AB-staggered stacking model cell of TBA-COF-5.
**Figure S43.** Eclipsed-AA and AB-staggered stacking model cell of TBA-COF-6.
Stability of TRIP-CPs

Figure S44. Crystal stability and Chemical stability test of TRIP-CP-1 after treatment in acid, base, and organic solvent for 24 hours.
Crystallinity and Pore Properties of TRIP-CPs and TBA-COFs

Figure S45. Powder X-ray diffraction (PXRD) patterns of TRIP-CP-3. Experimental patterns (red polka dots), refined patterns (black curves), the simulated patterns by Material Studio based on their simulated structures (blue curves).

Figure S46. Powder X-ray diffraction (PXRD) patterns of TRIP-CP-4. Experimental patterns (red polka dots), refined patterns (black curves), the simulated patterns by Material Studio based on their simulated structures (blue curves).
**Figure S47.** Powder X-ray diffraction (PXRD) patterns of **TBA-COF-5**. Experimental patterns (red polka dots), refined patterns (black curves), and error analysis (pink curve), the simulated patterns by Material Studio based on their simulated structures (blue curves).
Figure S48. PXRD patterns of TBA-COF-5 compared with different calculated-stacking model cell of TBA-COF-5.
Figure S49. Powder X-ray diffraction (PXRD) patterns of TBA-COF-6. Experimental patterns (red polka dots), refined patterns (black curves), and error analysis (pink curve), the simulated patterns by Material Studio based on their simulated structures (blue curves).
Figure S50. TEM and HR-TEM images of TBA-COF-6.
Figure S51. Characterization of the Porosity of TBA-COF-5 and TBA-COF-6. Nitrogen adsorption (filled dots) and desorption (unfilled dots) isotherms at 77 K. Pore size distribution curves obtained based on NLDFT calculation for TBA-COFs.
Figure S52. HR-TEM images of TRIP-CP-1 observed in different local positions corresponding to different facets.
Figure S53. HR-TEM images of TRIP-CP-1 corresponding to (001) facet (FFT image inset).
Figure S54. HR-TEM images of TRIP-CP-2 in different local positions.
Figure S55. TEM images of TRIP-CP-2.
Figure S56. TEM and HR-TEM images of TRIP-CP-3.
Figure S57. TEM and HR-TEM images of TRIP-CP-4.
Figure S58. TEM images of TRIP-CPs.
Figure S59. SEM images of TRIP-CP-1, TRIP-CP-2, TRIP-CP-3, and TRIP-CP-4 samples (4 hours).
Figure S60. SEM images of TRIP-CP-3 samples observed in different reaction time.
Figure S61. Energies for stacking the hexagonal building units of TRIP-CP-1, TRIP-CP-3, TBA-COF-5, and TBA-COF-6. Simulations were performed with Materials Studios using MS Forcite Plus module in insets.
Table S1. XPS peak table of TRIP-CP-1.

| TRIP-CP-1 | Start BE | Peak BE | End BE  | Height CPS | FWHM eV | Atomic % | Wt. % |
|-----------|----------|---------|---------|------------|---------|----------|-------|
| C 1s      | 298.28   | 284.76  | 279.48  | 151155.2   | 2.06    | 80.4     | 75.8  |
| N 1s      | 410.28   | 398.98  | 392.48  | 16542.46   | 1.65    | 4.8      | 5.3   |
| O 1s      | 545.28   | 532.52  | 525.48  | 60193.61   | 2.43    | 14.72    | 18.5  |

Table S2. The PDI of TRIP-CPs and TBA-COFs.

| Sample   | PDI (Size distribution by DLS) |
|----------|--------------------------------|
| TRIP-CP-1| 0.237                          |
| TRIP-CP-2| 0.347                          |
| TRIP-CP-3| 0.081                          |
| TRIP-CP-4| 0.203                          |
| TBA-COF-5| 0.418                          |
| TBA-COF-6| 0.715                          |

Table S3. Fractional atomic coordinates for the unit cell of TRIP-CP-1.

TRIP-CP-1 -AA

\[ a = 30.5957 \, \text{Å}, \ b = 30.2345 \, \text{Å}, \ c = 7.311 \, \text{Å}; \ \alpha = 90^\circ, \ \beta = 90^\circ, \ \gamma = 120^\circ \]

| Atoms | X      | Y      | Z      | Atoms | X      | Y      | Z      |
|-------|--------|--------|--------|-------|--------|--------|--------|
| C1    | 0.22306| -1.43931| 0.22411| C41   | 0.52435| -1.75858| 0.1375 |
| C2    | 0.26041| -1.38455| 0.18364| C42   | 0.53779| -1.7412 | -0.05599|
| C3    | 0.27481| -1.37356| -0.01407| C43   | 0.62042| -1.73019| -0.00307|
| C4    | 0.24997| -1.41911| -0.1484| C44   | 0.60694| -1.74726| 0.19101 |
| C5    | 0.24815| -1.46695| 0.14268| C45   | 0.64369| -1.73188| 0.33472 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C6 | 0.2622 | -1.4569 | -0.05576 | C46 | 0.69378 | -1.6986 | 0.28676 |
| C7 | 0.19384 | -1.44062 | -0.11195 | C47 | 0.70751 | -1.68136 | 0.09381 |
| C8 | 0.17938 | -1.45229 | 0.08559 | C48 | 0.67056 | -1.69792 | -0.05187 |
| C9 | 0.129 | -1.47346 | 0.13961 | C49 | 0.55029 | -1.84226 | -0.26545 |
| C10 | 0.09272 | -1.48234 | -0.00363 | C50 | 0.52898 | -1.89293 | -0.2214 |
| C11 | 0.10822 | -1.4672 | -0.1977 | C51 | 0.51279 | -1.91077 | -0.02993 |
| C12 | 0.15842 | -1.4466 | -0.25176 | C52 | 0.52015 | -1.87641 | 0.11866 |
| C13 | 0.30806 | -1.3245 | -0.07136 | C53 | 0.49019 | -1.75035 | 0.2402 |
| C14 | 0.32867 | -1.2863 | 0.0694 | C54 | 0.46945 | -1.72432 | 0.15039 |
| C15 | 0.31406 | -1.29809 | 0.26684 | C55 | 0.48299 | -1.70608 | -0.04162 |
| C16 | 0.27966 | -1.3469 | 0.32283 | C56 | 0.51767 | -1.71434 | -0.14482 |
| C17 | 0.25807 | -1.49919 | 0.24944 | N57 | 0.75903 | -1.65033 | 0.03874 |
| C18 | 0.28208 | -1.52184 | 0.15859 | N58 | 0.4917 | -1.95996 | 0.0169 |
| C19 | 0.29612 | -1.51263 | -0.03952 | C59 | 0.79452 | -1.61825 | 0.15067 |
| C20 | 0.28547 | -1.48042 | -0.14801 | C60 | 0.41582 | 0.85021 | 1.0522 |
| N21 | 0.0408 | -1.50501 | 0.05182 | C61 | 0.84764 | 1.40856 | 1.08618 |
| N22 | 0.31843 | -1.53849 | -0.13174 | C62 | 0.4134 | 0.86376 | 0.85674 |
| N23 | 0.36064 | -1.23887 | 0.00884 | C63 | 0.43218 | 0.91393 | 0.80976 |
| C24 | 0.39007 | -1.19902 | 0.12306 | C64 | 0.45632 | 0.95197 | 0.94868 |
| C25 | 0.36782 | -1.57995 | -0.11589 | C65 | 0.46266 | 0.93896 | 1.13935 |
| C26 | 0.33342 | -1.63179 | -0.13292 | C66 | 0.44246 | 0.88846 | 1.18846 |

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Table S4. Fractional atomic coordinates for the unit cell of TRIP-CP-2.

TRIP-CP-2 -AA

\[ a = 29.9781 \text{ Å}, \ b = 28.7337 \text{Å}, \ c = 7.3880 \text{ Å}; \ \alpha = 90^\circ, \ \beta = 90^\circ, \ \gamma = 120^\circ \]
|   |       |       |       |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|-------|-------|-------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |   C2  |   C3  |   C4  |   C5  |   C6  |   C7  |   C8  |   C9  |   C10 |   C11 |   C12 |   C13 |   C14 |   C15 |   C16 |   C17 |   C18 |   C19 |   C20 |   N21 | N22 |
|  | 1.68184 | 1.68376 | 1.71424 | 1.77024 | 1.76898 | 1.68991 | 1.69134 | 1.67054 | 1.64774 | 1.64547 | 1.66745 | 1.65825 | 1.62915 | 1.62503 | 1.64966 | 1.81817 | 1.86507 | 1.86415 | 1.81569 | 1.62274 | 1.91134 |
|  | -0.40346 | -0.40481 | -0.38019 | -0.40536 | -0.40787 | -0.32568 | -0.32299 | -0.27531 | -0.23003 | -0.23236 | -0.28058 | -0.42751 | -0.44792 | -0.44633 | -0.42595 | -0.42865 | -0.45434 | -0.45669 | -0.43304 | -0.18681 | -0.48038 |
|  | -0.5418 | -0.33966 | -0.25141 | -0.52571 | -0.33475 | -0.32867 | -0.51964 | -0.60675 | -0.50326 | -0.31215 | -0.22555 | -0.24494 | -0.33521 | -0.52688 | -0.64003 | -0.61772 | -0.51893 | -0.32757 | -0.23637 | -0.20138 | -0.22039 |
|  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|  | C42  | C43  | C44  | C45  | C46  | C47  | C48  | C49  | C50  | C51  | C52  | C53  | C54  | C55  | C56  | C57  | C58  | C59  | C60  | C61  | C62  |       |
|  | 2.43419 | 2.4341 | 2.45899 | 2.46131 | 2.43737 | 2.28112 | 2.23365 | 2.23362 | 2.28165 | 2.48251 | N51  | 2.5065 | 1.95648 | 2.14122 | 2.18601 | 2.50974 | 1.58851 | 1.95648 | 2.14122 | 2.43419 |       |
|  | -0.82631 | -0.67258 | -0.64768 | -0.64879 | -0.67244 | -0.67329 | -0.6511 | -0.65281 | -0.67762 | -0.92004 | C51  | -0.59831 | -0.46939 | -0.64107 | -0.63081 | -0.96638 | -0.14096 | -0.46939 | -0.64107 | -0.82631 |       |
|  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       | S55 |
|  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|     |   X      |   Y      |   Z      |   X      |   Y      |   Z      |
|-----|-----|-----|-----|-----|-----|-----|
| N23 |  1.60596 | -0.46961 | -0.23013 | C63 | -0.44591 | -0.55051 |
| C24 |  1.5721 | -0.48755 | -0.27962 | C64 | -0.47899 | -0.56978 |
| C25 |  2.00384 | -0.53389 | -0.15163 | C65 | -0.49722 | -0.5585 |
| C26 |  2.00203 | -0.51277 |  0.02161 | C66 | -0.48001 | -0.53062 |
| C27 |  2.05066 | -0.57623 | -0.20953 | O67 | -0.40016 | -0.50121 |
| C28 |  2.09538 | -0.5982  | -0.09763 | O68 | -0.5332  | -0.57378 |
| C29 |  2.09351 | -0.57718 |  0.0759  | C69 |  0.53179 | -1.01152 |
| C30 |  2.04667 | -0.53484 |  0.13372 | C70 |  0.57224 | -1.06053 |
| C31 |  2.3835  | -0.72271 |  0.53054 | C71 |  0.58955 | -1.10236 |
| C32 |  2.41199 | -0.69612 |  0.43976 | C72 |  0.56865 | -1.09663 |
| C33 |  2.4115  | -0.69732 |  0.24799 | C73 |  0.52893 | -1.04804 |
| C34 |  2.38367 | -0.7261  |  0.16899 | C74 |  0.51088 | -1.00607 |
| C35 |  2.32865 | -0.69731 |  0.44493 | O75 |  0.5974  | -1.06955 |
| C36 |  2.32884 | -0.69935 |  0.25319 | O76 |  0.50716 | -1.04193 |
| C37 |  2.41043 | -0.77902 |  0.26032 |
| C38 |  2.41017 | -0.77719 |  0.45204 |
| C39 |  2.43336 | -0.82264 |  0.55267 |
| C40 |  2.45722 | -0.8702  |  0.46241 |

**TRIP-CP-2-AB staggered stacking**

a=58.7514 Å, b= 57.4674 Å, c= 14.7759 Å; α = 90°, β = 90°, γ = 120°
| Atoms | X    | Y     | Z     | Atoms | X    | Y     | Z     |
|-------|------|-------|-------|-------|------|-------|-------|
| C1    | 0.31282 | 0.69346 | 0.35833 | C41   | 0.06365 | 1.13541 | 0.22881 |
| C2    | 0.29836 | 0.72924 | 0.34123 | C42   | 0.08661 | 1.08521 | 0.21697 |
| C3    | 0.29766 | 0.83029 | 0.34215 | C43   | 0.1633  | 1.07304 | 0.21729 |
| C4    | 0.31015 | 0.87468 | 0.35721 | C44   | 0.17574 | 1.11761 | 0.22981 |
| C5    | 0.29794 | 0.73764 | 0.38524 | C45   | 0.17521 | 1.21361 | 0.23098 |
| C6    | 0.29659 | 0.83308 | 0.38461 | C46   | 0.16345 | 1.26413 | 0.21893 |
| C7    | 0.33738 | 0.83629 | 0.34488 | C47   | 0.16315 | 1.269   | 0.14063 |
| C8    | 0.33881 | 0.74085 | 0.34559 | C48   | 0.17428 | 1.22049 | 0.1169  |
| C9    | 0.36264 | 0.6975  | 0.33506 | C49   | 0.17342 | 1.12463 | 0.11688 |
| C10   | 0.38519 | 0.74941 | 0.3235  | C50   | 0.16094 | 1.07796 | 0.14089 |
| C11   | 0.38395 | 0.84491 | 0.32234 | N51   | 0.03983 | 1.08583 | 0.2409  |
| C12   | 0.35986 | 0.88801 | 0.33347 | N52   | 0.18854 | 1.06602 | 0.23956 |
| C13   | 0.28614 | 0.87741 | 0.32948 | C53   | 0.2013  | 1.09967 | 0.06985 |
| C14   | 0.27578 | 0.83207 | 0.31507 | C54   | 0.24432 | 0.86194 | 0.47912 |
| C15   | 0.27647 | 0.73622 | 0.31316 | C55   | 0.20041 | 1.09424 | 0.25364 |
| C16   | 0.28684 | 0.67987 | 0.32538 | N56   | 0.18453 | 1.07205 | 0.09307 |
| C17   | 0.28657 | 0.69169 | 0.40922 | C57   | 0.01668 | 1.11847 | 0.25403 |
| C18   | 0.27385 | 0.74108 | 0.43267 | C58   | 0.42945 | 0.87403 | 0.29354 |
| C19   | 0.27251 | 0.83669 | 0.4322  | O59   | 0.26585 | 1.04031 | 0.47867 |
| C20   | 0.28412 | 0.88227 | 0.40796 | O60   | 0.17982 | 0.92069 | 0.07044 |

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|    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|
| N21 | 0.40665 | 0.90041 | 0.31084 | C61 | 0.24354 | 0.92132 | 0.27743 |
| N22 | 0.26068 | 0.89018 | 0.45581 | C62 | 0.23916 | 1.01362 | 0.28514 |
| N23 | 0.26488 | 0.88443 | 0.30345 | C63 | 0.2244 | 1.06784 | 0.27742 |
| C24 | 0.25583 | 0.85947 | 0.28656 | C64 | 0.21467 | 1.03477 | 0.26093 |
| C25 | 0.23365 | 0.9242 | 0.00201 | C65 | 0.22025 | 0.94443 | 0.25187 |
| C26 | 0.24411 | 1.01083 | 0.00129 | C66 | 0.2342 | 0.88868 | 0.26051 |
| C27 | 0.21243 | 0.89505 | 0.02529 | O67 | 0.2492 | 1.05467 | 0.30021 |
| C28 | 0.20129 | 0.95083 | 0.04766 | O68 | 0.21254 | 0.91074 | 0.2339 |
| C29 | 0.21169 | 1.03764 | 0.04689 | C69 | 0.49413 | 1.05686 | 0.26504 |
| C30 | 0.23292 | 1.06673 | 0.02362 | C70 | 0.46972 | 1.08444 | 0.28525 |
| C31 | 0.13843 | 1.26478 | 0.1918 | C71 | 0.44881 | 1.02492 | 0.29395 |
| C32 | 0.15164 | 1.21924 | 0.20615 | C72 | 0.45159 | 0.93716 | 0.28353 |
| C33 | 0.15099 | 1.12338 | 0.20591 | C73 | 0.47579 | 0.90931 | 0.26364 |
| C34 | 0.13663 | 1.08407 | 0.1919 | C74 | 0.49677 | 0.96901 | 0.25459 |
| C35 | 0.15111 | 1.22197 | 0.16439 | O75 | 0.46532 | 1.16864 | 0.29782 |
| C36 | 0.15004 | 1.12613 | 0.16448 | O76 | 0.47876 | 0.82264 | 0.25278 |
| C37 | 0.11024 | 1.12991 | 0.20518 |
| C38 | 0.11122 | 1.22575 | 0.20504 |
| C39 | 0.08857 | 1.27624 | 0.21654 |
| C40 | 0.06481 | 1.23132 | 0.22837 |

**Table S5.** Fractional atomic coordinates for the unit cell of TRIP-CP-3.
TRIP-CP-3- AA

\[ a = 14.5432 \, \text{Å}, \ b = 15.6056\, \text{Å}, \ c = 7.5158 \, \text{Å}; \ \alpha = 90^\circ, \ \beta = 90^\circ, \ \gamma = 120^\circ \]

| Atoms | X   | Y   | Z    |
|-------|-----|-----|------|
| C1    | 0.40716 | -0.20216 | -1.81238 |
| C2    | 0.47567 | -0.09374 | -1.76568 |
| C3    | 0.53853 | -0.06752 | -1.5909 |
| C4    | 0.52057 | -0.15428 | -1.46931 |
| C5    | 0.48129 | -0.24303 | -1.78005 |
| C6    | 0.54223 | -0.21738 | -1.60267 |
| C7    | 0.3981 | -0.21487 | -1.46426 |
| C8    | 0.34114 | -0.23783 | -1.64419 |
| C9    | 0.222 | -0.29923 | -1.65705 |
| C10   | 0.15744 | -0.34576 | -1.49016 |
| C11   | 0.21054 | -0.32196 | -1.30481 |
| C12   | 0.33269 | -0.25471 | -1.29156 |
| C13   | 0.61716 | 0.04129 | -1.54665 |
| C14   | 0.6344 | 0.12158 | -1.68395 |
| C15   | 0.56796 | 0.09253 | -1.85698 |
| C16   | 0.48381 | -0.0144 | -1.8923 |
| C17   | 0.49005 | -0.31125 | -1.916 |
| C18   | 0.55977 | -0.35596 | -1.87255 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C19  | 0.6236  | -0.32883| -1.69808|
| C20  | 0.61756 | -0.25754| -1.56272|
| N21  | 0.688   | -0.37793| -1.66736|
| C22  | 0.66178 | -0.46382| -1.7882 |
| C23  | 0.91847 | -0.50183| -1.77228|
| C24  | 0.84622 | -0.45836| -1.73111|
| C25  | 0.73452 | -0.50736| -1.81102|
| C26  | 0.69298 | -0.60266| -1.91792|
| C27  | 0.76394 | -0.64776| -1.94842|
| C28  | 0.88112 | -0.59089| -1.89645|
| O29  | 0.88481 | -0.36855| -1.61296|
| O30  | 0.95406 | -0.63019| -1.94376|
| O31  | 0.57994 | -0.65484| -1.98505|
| C32  | 0.71033 | -0.7562 | -1.99992|
| C33  | 1.02107 | -0.46433| -1.66824|
| N34  | 1.04371 | -0.41844| -1.5247 |

**Table S6.** Fractional atomic coordinates for the unit cell of TRIP-CP-4.

**TRIP-CP-4-AA**

\[a = 14.9565 \text{ Å}, \ b = 15.1043 \text{ Å}, \ c = 6.4467 \text{ Å}; \ \alpha = 90^\circ, \ \beta = 90^\circ, \ \gamma = 120^\circ\]

| Atoms | X   | Y   | Z   |
|-------|-----|-----|-----|
|       |     |     |     |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| C1 | 1.56241 | -0.28869 | -1.18658 |
| C2 | 1.32509 | -0.02276 | -0.72946 |
| C3 | 1.35721 | 0.08661 | -0.79792 |
| C4 | 1.34057 | 0.09634 | -1.01427 |
| C5 | 1.2972 | -0.00171 | -1.14404 |
| C6 | 1.38888 | -0.04858 | -0.87325 |
| C7 | 1.3688 | -0.04654 | -1.09125 |
| C8 | 1.19668 | -0.07491 | -1.02384 |
| C9 | 1.2146 | -0.0837 | -0.80673 |
| C10 | 1.13369 | -0.12945 | -0.66577 |
| C11 | 1.03482 | -0.17527 | -0.73804 |
| C12 | 1.01435 | -0.17624 | -0.9528 |
| C13 | 1.09496 | -0.12496 | -1.09752 |
| C14 | 1.36404 | 0.19004 | -1.0963 |
| C15 | 1.40907 | 0.27684 | -0.96784 |
| C16 | 1.42616 | 0.26732 | -0.75564 |
| C17 | 1.40331 | 0.1739 | -0.67096 |
| C18 | 1.47224 | -0.05921 | -0.8042 |
| C19 | 1.52808 | -0.0763 | -0.95465 |
| C20 | 1.49078 | -0.10148 | -1.16089 |
| C21 | 1.40825 | -0.08856 | -1.23085 |
|   |   |   |   |
|---|---|---|---|
| N22 | 1.53212 | -0.14954 | -1.29005 |
| C23 | 1.49956 | -0.25536 | -1.25933 |
| C24 | 1.51872 | -0.40076 | -1.15307 |
| C25 | 1.58089 | -0.44074 | -1.04965 |
| C26 | 1.68947 | -0.36656 | -0.99285 |
| C27 | 1.73972 | -0.25809 | -1.06079 |
| C28 | 1.67329 | -0.21758 | -1.13573 |
| O29 | 1.73903 | -0.3959  | -0.89024 |
| O30 | 1.71066 | -0.1254  | -1.1581  |
| O31 | 1.43016 | -0.46002 | -1.20973 |
| C32 | 1.54411 | -0.54092 | -1.00266 |
| N33 | 1.44395 | -0.62384 | -1.05734 |
| C34 | 1.84355 | -0.19668 | -1.05445 |
| N35 | 1.91096 | -0.2374  | -1.02606 |
Table S7. Fractional atomic coordinates for the unit cell of TBA-COF-5.

**TBA-COF-5-AA**

\[a = 37.0922 \text{ Å}, \ b = 38.0279 \text{ Å}, \ c = 3.5852 \text{ Å}; \ \alpha = 90^\circ, \ \beta = 90^\circ, \ \gamma = 120^\circ\]

| Atoms | X   | Y    | Z    | Atoms | X   | Y    | Z    |
|-------|-----|------|------|-------|-----|------|------|
| C1    | 2.475 | 0.93222 | 0.0764 | C43   | 2.69462 | 0.32748 | -0.00528 |
| C2    | 2.46118 | 0.8884 | 0.05209 | C44   | 2.67031 | 0.34606 | -0.05339 |
| C3    | 2.40454 | 0.81803 | 0.03273 | C45   | 2.62681 | 0.32279 | -0.09655 |
| C4    | 2.36308 | 0.79334 | 0.1405 | C46   | 2.6081 | 0.28023 | -0.10694 |
| C5    | 2.34445 | 0.75115 | 0.12846 | C47   | 2.63139 | 0.26094 | -0.04148 |
| C6    | 2.36676 | 0.73258 | -0.00045 | C48   | 2.67444 | 0.28494 | 0.01684 |
| C7    | 2.40834 | 0.75749 | -0.11407 | C49   | 2.60078 | 0.34269 | -0.11477 |
| C8    | 2.42713 | 0.7998 | -0.09706 | C50   | 2.61081 | 0.21581 | -0.02975 |
| C9    | 2.34652 | 0.68751 | -0.01771 | C51   | 2.57008 | 0.19228 | 0.10961 |
| C10   | 2.30392 | 0.66388 | -0.09979 | C52   | 2.55108 | 0.15 | 0.12763 |
| C11   | 2.2835 | 0.62128 | -0.09071 | C53   | 2.5726 | 0.13024 | 0.00816 |
| C12   | 2.3073 | 0.60239 | -0.02996 | C54   | 2.61303 | 0.15359 | -0.13108 |
| C13   | 2.35044 | 0.62535 | 0.03622 | C55   | 2.6319 | 0.1958 | -0.15269 |
| C14   | 2.36937 | 0.66789 | 0.05379 | C56   | 2.61715 | 0.38263 | -0.25011 |
| C15   | 2.37574 | 0.60501 | 0.07965 | C57   | 2.59383 | 0.40227 | -0.23331 |
| C16   | 2.23722 | 0.59682 | -0.12632 | C58   | 2.55322 | 0.38211 | -0.08709 |
| C17   | 2.35827 | 0.56563 | 0.23045 | C59   | 2.53603 | 0.34181 | 0.02886 |
| C18   | 2.38116 | 0.54558 | 0.24566 | C60   | 2.55959 | 0.32248 | 0.02125 |
| C19  | 2.42241 | 0.56467 | 0.11309 | N61  | 2.8734 | 0.42621 | -0.01715 |
| C20  | 2.44034 | 0.60431 | -0.02436 | N62  | 2.52854 | 0.40135 | -0.04912 |
| C21  | 2.41732 | 0.62418 | -0.04435 | C63  | 2.90085 | 0.41646 | -0.12026 |
| C22  | 2.21218 | 0.61234 | 0.00619 | O64  | 2.52679 | 0.55462 | 0.33988 |
| C23  | 2.16884 | 0.58889 | -0.00287 | O65  | 2.4527  | 0.39206 | -0.11933 |
| C24  | 2.14926 | 0.54893 | -0.14153 | N66  | 2.10485 | 0.52246 | -0.13638 |
| C25  | 2.17397 | 0.53349 | -0.27667 | N67  | 2.55541 | 0.08702 | 0.03028 |
| C26  | 2.21738 | 0.55714 | -0.27272 | C68  | 2.07703 | 0.532   | -0.04053 |
| N27  | 2.44724 | 0.54532 | 0.1116  | C69  | 2.51827 | 0.06022 | 0.13993 |
| C28  | 2.46332 | 0.49112 | 0.15481 | C70  | 0.44755 | 0.94741 | 1.02533 |
| C29  | 2.44586 | 0.45018 | 0.05325 | C71  | 0.46262 | 0.98927 | 1.05653 |
| C30  | 2.4709  | 0.43273 | -0.01014 | C72  | 0.50461 | 1.01645 | 1.13604 |
| C31  | 2.51448 | 0.45667 | 0.02946 | C73  | 0.53186 | 1.00010 | 1.19739 |
| C32  | 2.53193 | 0.49754 | 0.1335  | C74  | 0.51693 | 0.95938 | 1.15839 |
| C33  | 2.507   | 0.51476 | 0.20533 | C75  | 0.94577 | 0.44667 | 0.88527 |
| C34  | 2.54279 | 0.44019 | -0.02655 | C76  | 0.96191 | 0.48862 | 0.8177 |
| N35  | 2.4219  | 0.86124 | 0.05048 | C77  | 1.00459 | 0.51548 | 0.85765 |
| C36  | 2.43482 | 0.50759 | 0.18961 | C78  | 1.03215 | 0.50165 | 0.94879 |
| C37  | 2.76548 | 0.33633 | -0.1302 | C79  | 1.01602 | 0.45969 | 1.0158 |
| C38  | 2.8084 | 0.35972 | -0.13462 | C80  | 0.97334 | 0.43281 | 0.9753 |
| C39  | 2.829  | 0.39992 | -0.00171 | O81  | 1.04049 | 0.44355 | 1.14035 |

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Table S8. Fractional atomic coordinates for the unit cell of TBA-COF-6.

TBA-COF-6-AA

\[ a = 18.6367 \text{ Å}, \; b = 18.7945 \text{ Å}, \; c = 3.6088 \text{ Å}; \; \alpha = 90^\circ, \; \beta = 90^\circ, \; \gamma = 120^\circ \]

| Atoms | X     | Y     | Z     |
|-------|-------|-------|-------|
| N1    | 1.23511 | -0.93189 | 0.08543 |
| C2    | 1.28774 | -0.84426 | 0.07171 |
| C3    | 1.37078 | -0.80558 | 0.1874 |
| C4    | 1.42 | -0.72012 | 0.17403 |
| C5    | 1.38752 | -0.6714 | 0.04334 |
| C6    | 1.30408 | -0.71044 | -0.06838 |
| C7    | 1.25467 | -0.79583 | -0.05044 |
| C8    | 1.44052 | -0.58044 | 0.0243 |
| C9    | 1.5249 | -0.54442 | -0.06444 |
| C10   | 1.577 | -0.45869 | -0.06509 |
| C11   | 1.54169 | -0.4088 | -0.00207 |
| C12   | 1.45651 | -0.44342 | 0.07046 |
| C13   | 1.40723 | -0.5293 | 0.09536 |
| C14   | 1.6682 | -0.42186 | -0.12144 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C15 | 1.41842 | -0.39039 | 0.11015 |   |   |
| C16 | 1.70887 | -0.46424 | -0.00606 |   |   |
| C17 | 1.79443 | -0.42908 | -0.04565 |   |   |
| C18 | 1.84214 | -0.34985 | -0.19067 |   |   |
| C19 | 1.80208 | -0.30748 | -0.31165 |   |   |
| C20 | 1.71614 | -0.34326 | -0.2791 |   |   |
| C21 | 1.46313 | -0.31098 | 0.26273 |   |   |
| C22 | 1.42802 | -0.26049 | 0.28252 |   |   |
| C23 | 1.3472 | -0.2882 | 0.15481 |   |   |
| C24 | 1.30239 | -0.36747 | 0.00165 |   |   |
| C25 | 1.33753 | -0.4178 | -0.01982 |   |   |
| N26 | 1.31314 | -0.23436 | 0.17549 |   |   |
| N27 | 1.93036 | -0.31507 | -0.21739 |   |   |
| C28 | 0.98797 | -0.22832 | -0.19218 |   |   |
| C29 | 1.06904 | -0.19599 | -0.10352 |   |   |
| C30 | 1.10487 | -0.24624 | 0.0373 |   |   |
| C31 | 1.19614 | -0.21248 | 0.03799 |   |   |
| C32 | 1.24984 | -0.12424 | -0.05769 |   |   |
| C33 | 1.21481 | -0.06892 | -0.04994 |   |   |
| C34 | 1.12547 | -0.10583 | -0.13948 |   |   |
| C35 | 1.22641 | -0.26242 | 0.12761 |   |   |
|     |      |      |      |
|-----|------|------|------|
| C36 | 1.26497 | 0.01166 | 0.02596 |
| O37 | 1.32161 | -0.09737 | -0.15347 |
| O38 | 1.09935 | -0.0631 | -0.26845 |
| O39 | 1.05975 | -0.31383 | 0.17174 |
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