Supplementary Materials

Amorphous-to-Crystalline Transformation: A Mechanochemical Pathway to Imine-linked Covalent Organic Frameworks

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Materials and Methods

Chemicals

Glacial acetic acid, ethanol, 1,4-dioxane, *p*-phenylenediamine (PDA), *N, N*-dimethylformamide (DMF), *N, N*-dimethylacetamide (DMAc), mesitylene (98%), tris(4-formylphenyl) amine (97%), triethylamine, trifluoroacetic acid (TFA), dimethyl sulfoxide (DMSO), and methanol were purchased from Sigma Aldrich. 3,3′-dimethylbenzidine (BD-Me, 95%) was purchased from Acros Organics. 2,5-Dibromobenzene-1,4-dicarboxaldehyde (DBrTP, 97%), 1,3,5-tris(4-aminophenyl)benzene (TPB, 99.6%), 1,3,5-triformylbenzene (TFB), 4,4′,4″-(1,3,5,-triazine-2,4,6-triyl) trianiline (TTA), tetrakis(4-aminophenyl)methane, and 2,5-dimethoxybenze-1,4-dicarboxaldehyde (DMTP, 98%) were obtained from ChemScene. 4,4′,4″,4‴-(Pyrene-1,3,6,8-tetrayl)tetrebenzaldehyde (TFPPy), terephthaldehyde, 1,3,5-tris(4-formylphenyl)benzene, and 4,4′,4″,4‴-(ethene-1,1,2,2-tetrayl)tetraaniline (ETTA) were purchased from Ambeed. Tetrahydrofuran (THF) was purchased from Macro-Fine Chemicals. Acetone (99.8%) and dichloromethane were purchased from VWR Chemicals. 2,3,5,6-Tetrafluoroterephthalaldehyde was purchased from AA Blocks. Dimethyl sulfoxide (99+%) was purchased from Alfa Aesar. *p*-anisidine was purchased from ThermoScientific. 1,2-Dichlorobenzene and 4-bromoaniline were purchased from TCI America. Tris(4-aminophenyl) amine (97%) and acetonitrile were obtained from Fisher Chemicals. Deuterated chloroform was purchased from Cambridge Isotope Laboratories Inc. All chemicals were used without further purification.

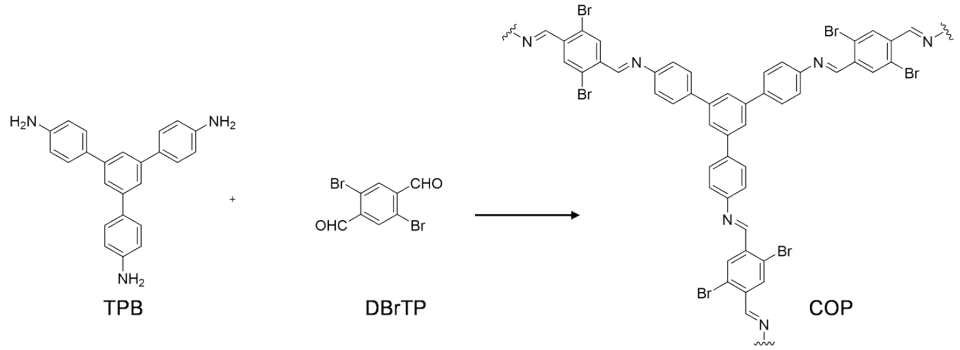
Instrumentation

Powder X-ray diffraction (PXRD) patterns were recorded using a Rigaku MiniFlex 600 Benchtop X-ray diffractometer with Cu Kα_1 radiation (λ = 1.5406 Å) operating at 40 kV and 15 mA. Nitrogen sorption isotherms were obtained at 77 K using a Micromeritics 3Flex gas sorption analyzer and Anton Paar Autosorb 6100 physisorption analyzer, with the COF samples activated under a dynamic vacuum at 120 °C overnight before measurement. ^{1}H NMR spectra were acquired on a Bruker Avance III 500 NMR spectrometer. Fourier transform infrared (FTIR) spectra were recorded using an Agilent Cary 630 FTIR spectrometer. Transmission electron microscopy (TEM) images were obtained from a JEM-2100 plus microscope at 200 kV. Thermogravimetric analysis

(TGA) was performed on a TA Instruments Q50 under N_2 from 30 to 600 °C. Solution ^{1}H NMR spectra were acquired on a Bruker Avance NEO 400 spectrometer.

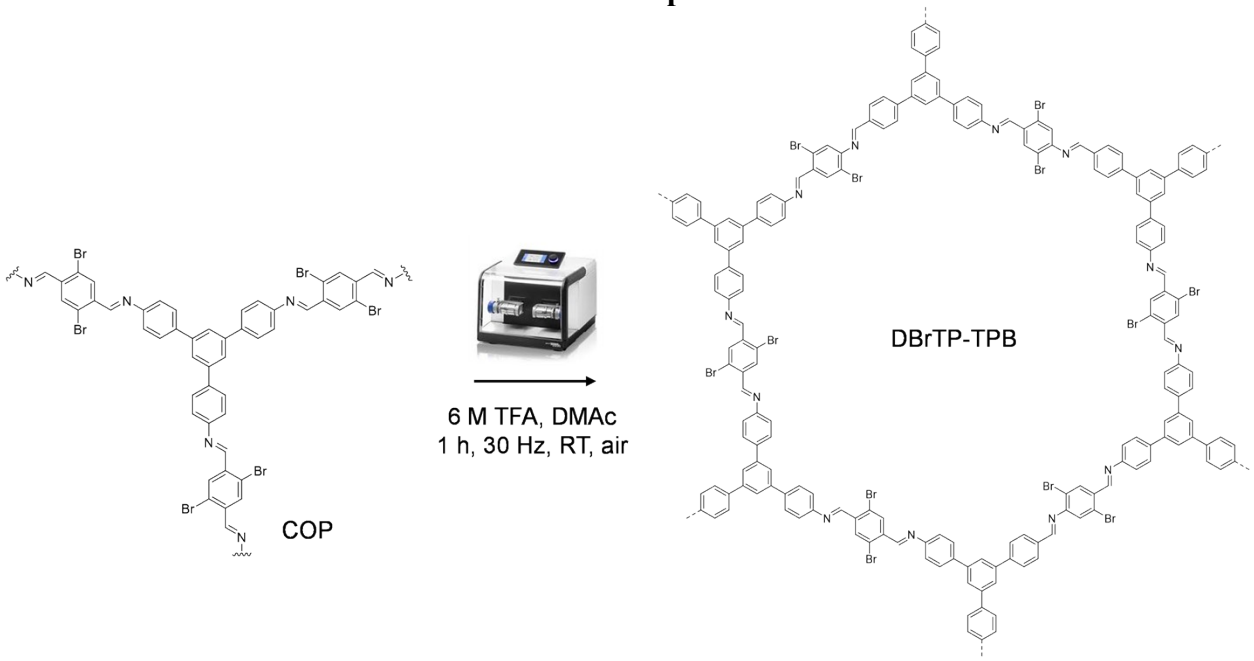
1. Synthetic procedures

1.1 A. Room-temperature synthesis of amorphous covalent organic polymer (COP)



2,5-Dibromobenzene-1,4-dicarboxaldehyde (DBrTP, 122.6 mg, 0.42 mmol) and 1,3,5-tris(4-aminophenyl)benzene (TPB, 98.4 mg, 0.28 mmol) were dissolved in dimethyl sulfoxide (DMSO, 5 mL) in a 20 mL scintillation vial. To this solution, 6 M aqueous acetic acid (700 µL) was added as a catalyst. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 92%.

1.1 B. Mechanochemical transformation of amorphous COP to DBrTP-TPB COF

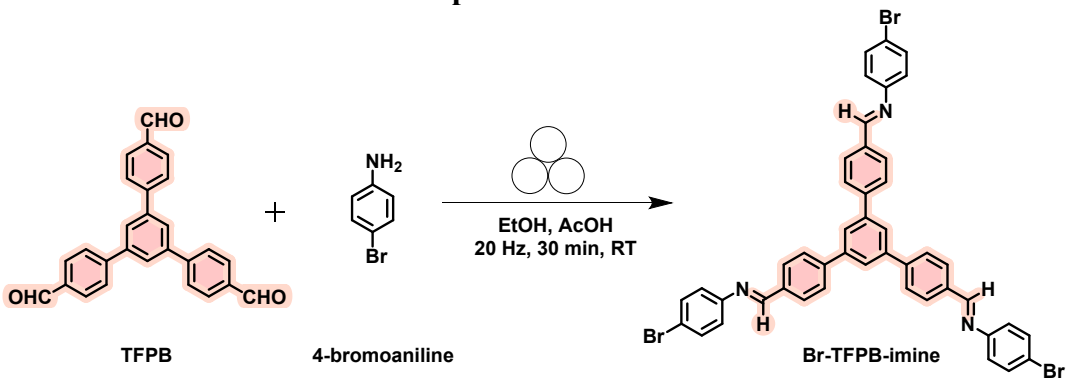


In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with 6 M trifluoroacetic acid (TFA, 15 µL), *N, N*-dimethylacetamide (DMAc, 20 µL), and a 5 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 30 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration, neutralized with

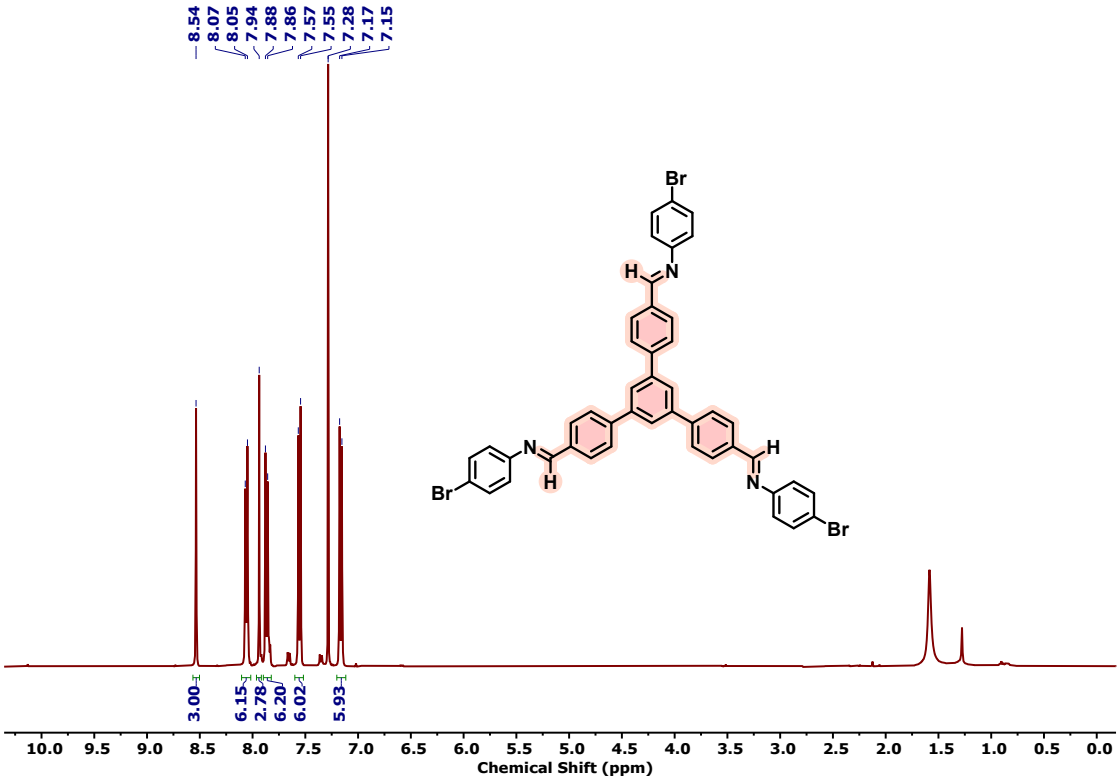
triethylamine, and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding DBrTP-TPB COF in 70% isolated yield.

1.1 C. Mechanochemistry-enabled scrambling reaction of molecular model compound

Synthesis of Br-TFPB-imine model compound:

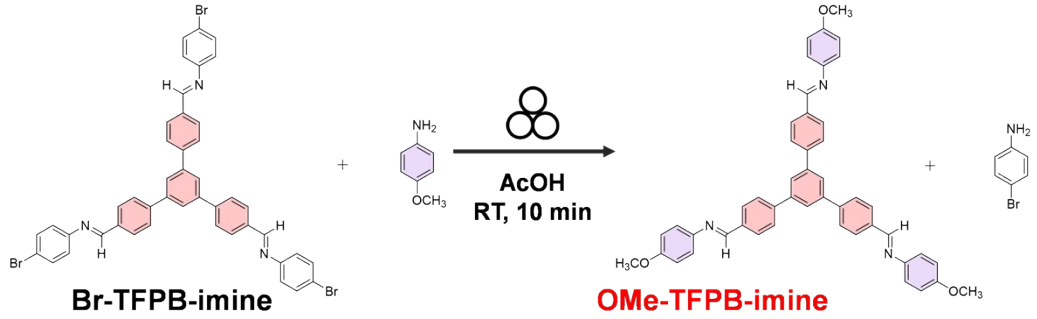


1,3,5-Tris(4-formylphenyl)benzene (TFPB, 100 mg, 0.25 mmol), 4-bromoaniline (172 mg, 1 mmol), ethanol (150 µL), and acetic acid (50 µL) were added in a 25 mL stainless steel jar along with a 7 mm ball. The jar was tightly sealed and subjected to ball milling at 20 Hz for 30 min in a Retsch MM 400 Mixer Mill. After milling, the mixture was collected, dissolved in chloroform and precipitated using methanol. The precipitated was filtered and washed with methanol yielding the off-white powder in 95 % isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 3H), 8.10 – 8.02 (m, 6H), 7.94 (s, 3H), 7.87 (d, J = 8.2 Hz, 6H), 7.60 – 7.52 (m, 6H), 7.20 – 7.12 (m, 6H).

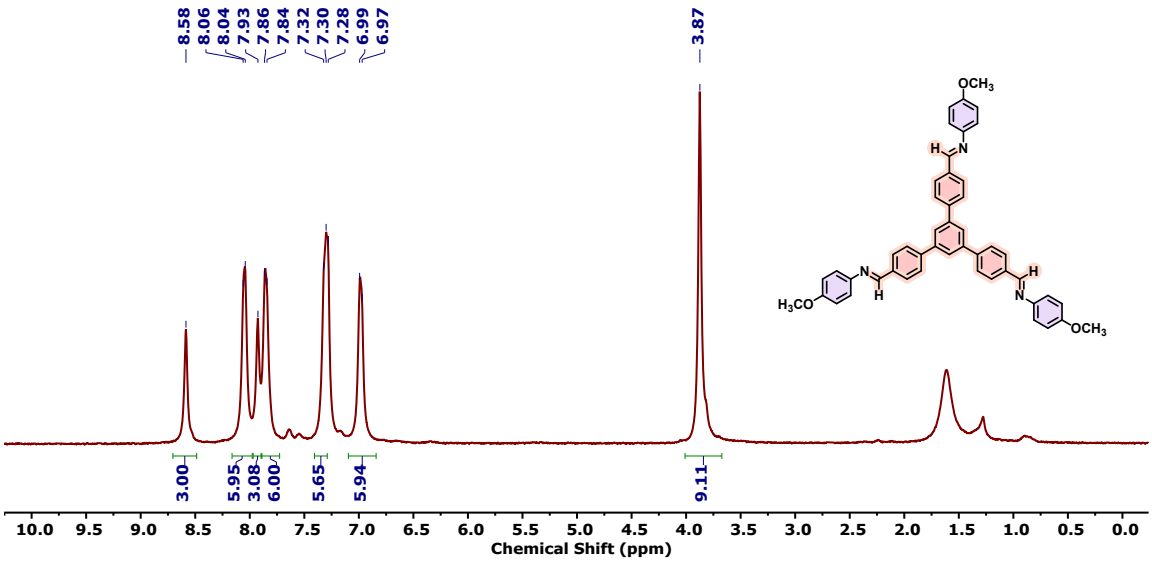


^{1}H NMR spectrum ($CDCl_3$) of Br-TFPB-imine model compound.

Mechanochemical scrambling reaction



A 25 mL stainless-steel milling jar was charged with Br-TFPB-imine (50 mg, 0.06 mmol), *p*-anisidine (29 mg, 0.24 mmol), ethanol (25 µL), acetic acid (50 µL), and a 7 mm stainless-steel ball. The mixture was milled at 20 Hz for 10 minutes. The resulting product was dissolved in chloroform and subsequently precipitated by the addition of methanol. The precipitate was filtered and washed with methanol, yielding OMe-TFPB-imine as an off-white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 3H), 8.05 (d, J = 7.7 Hz, 6H), 7.93 (s, 3H), 7.85 (d, J = 8.4 Hz, 6H), 7.31 (d, J = 8.4 Hz, 6H), 6.98 (d, J = 8.4 Hz, 6H), 3.87 (s, 9H).



^{1}H NMR spectrum ($CDCl_3$) of OMe-TFPB-imine model compound.

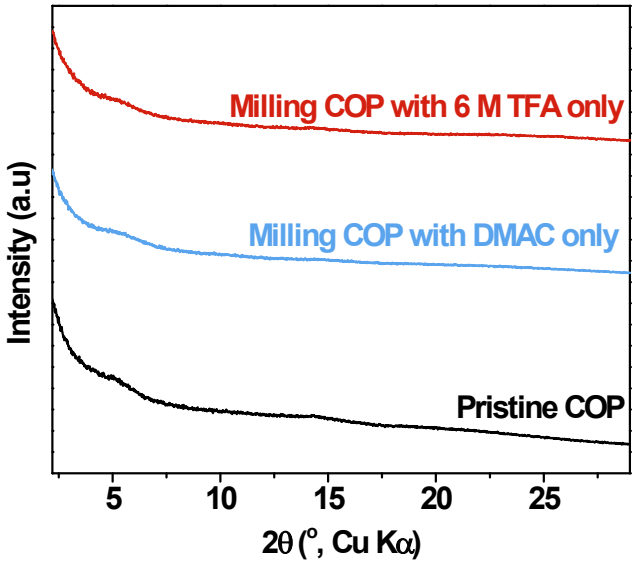


Figure S1. PXRD patterns of pristine DBrTP-TPB COP (black curve), the sample obtained by milling COP with DMAc only (no TFA, blue curve), and the sample obtained by milling COP with 6 M TFA only (no liquid additive, red curve).

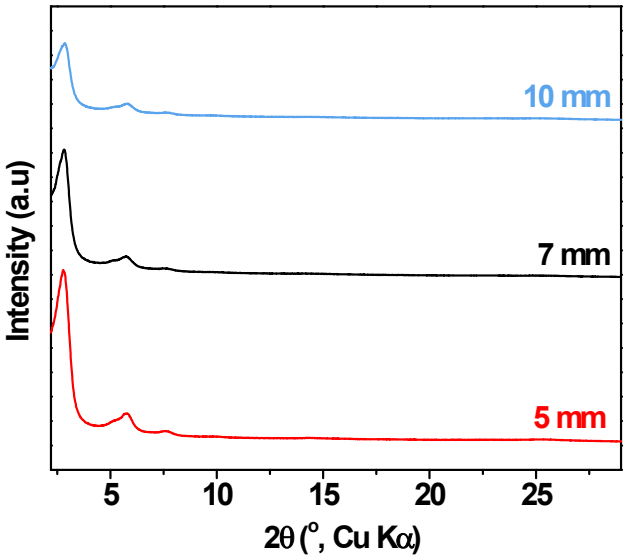


Figure S2. PXRD patterns of DBrTP-TPB COF using different balls at a frequency of 30 Hz with 6 M TFA as a catalyst.

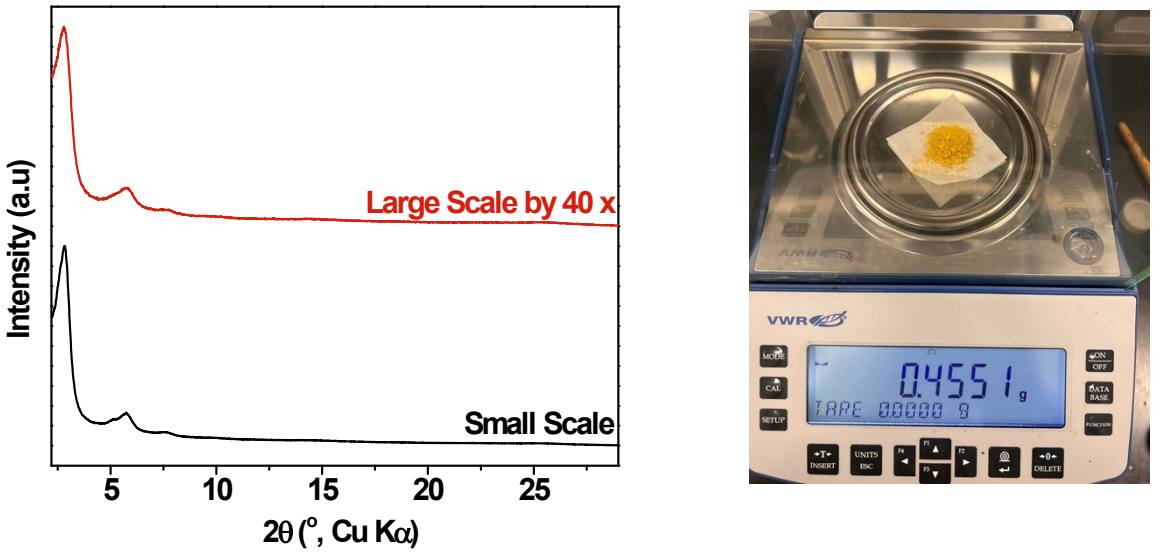


Figure S3. Scalable synthesis of DBrTP-TPB COF, which was made by ball milling COP for 1 hour using a 10-mm diameter stainless steel ball in the presence of 6 M TFA (94 μL) and DMAc (94 μL) as the liquid additive in a 25 mL stainless steel jar. Inset is the digital photo of the obtained COF (0.4551 g).

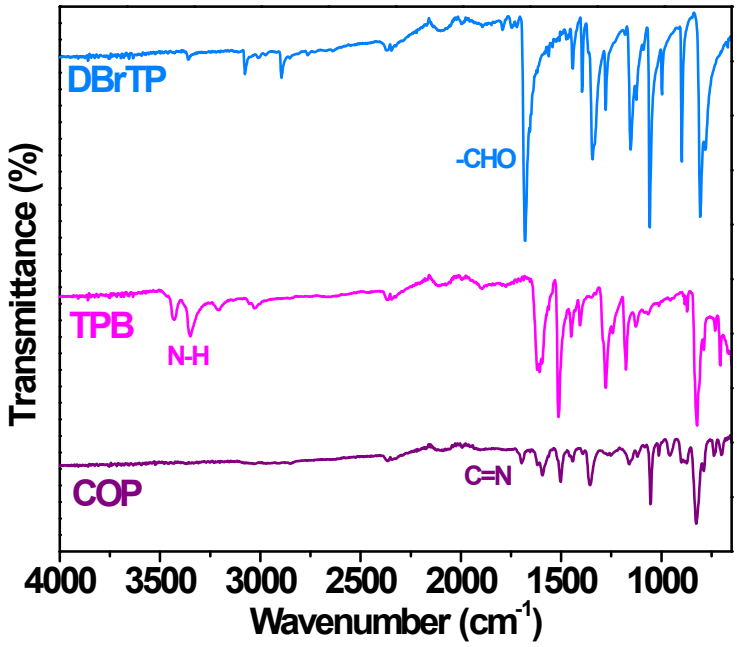


Figure S4. Stacked FTIR spectra of DBrTP (blue), TPB (pink), and COP precursor (purple).

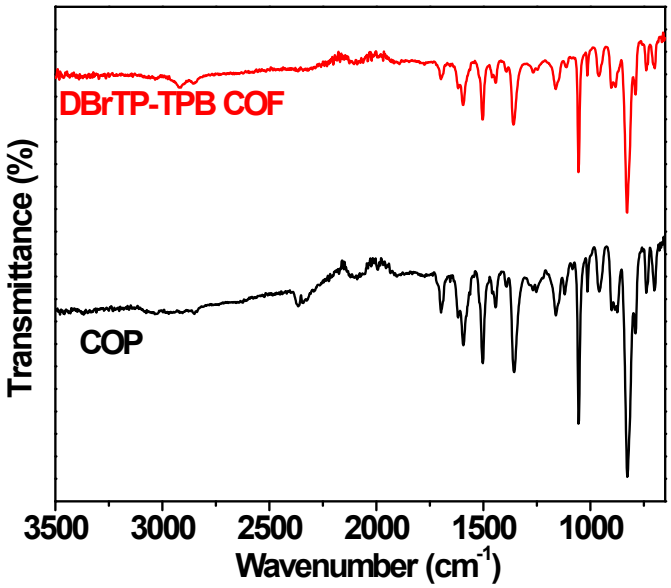


Figure S5. Stacked FTIR spectra of COP (black) and DBrTP-TPB COF (red).

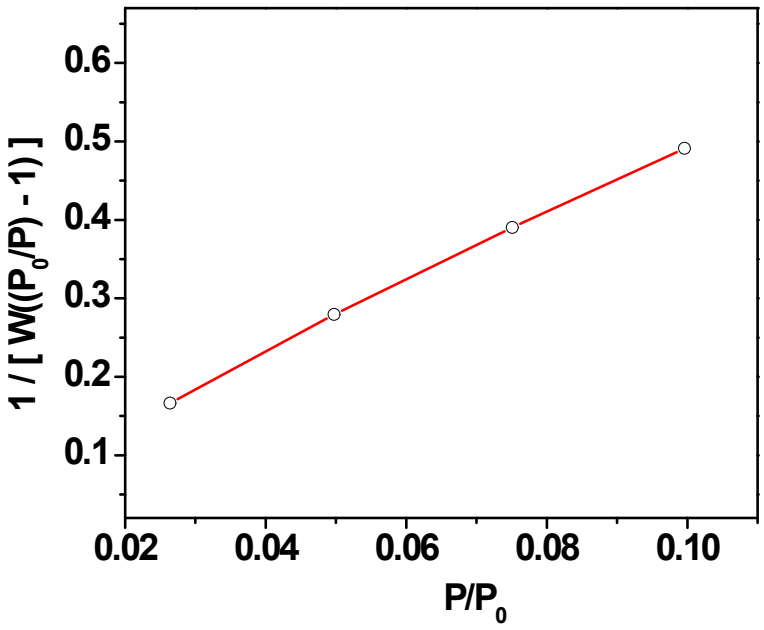


Figure S6. Multi-point BET plot derived from the N_2 sorption isotherm of DBrTP-TPB COF measured at 77 K. r = 0.99933.

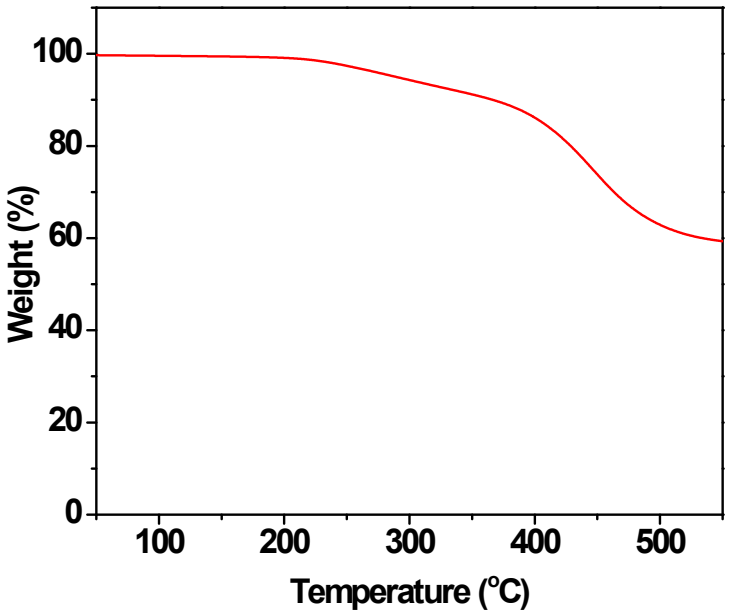


Figure S7. TGA profile of DBrTP-TPB COF measured under N_2.

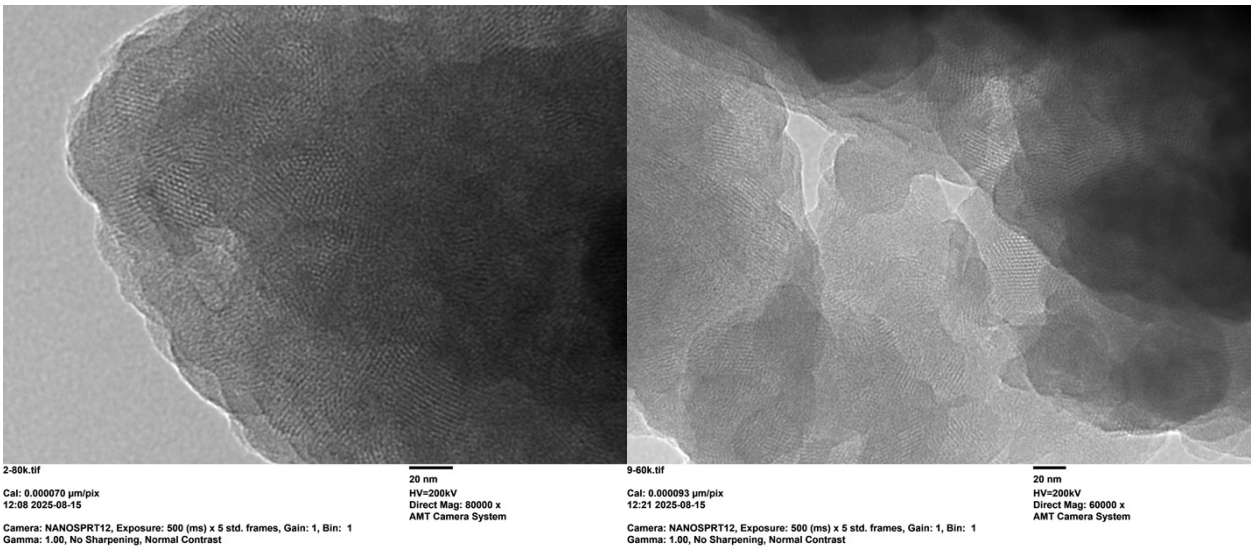
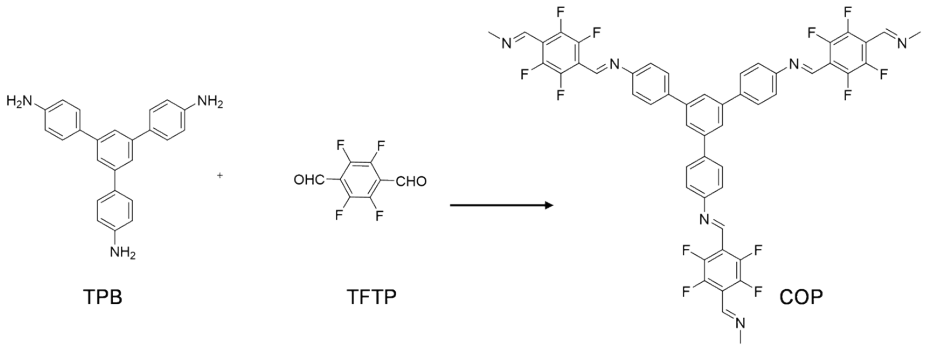


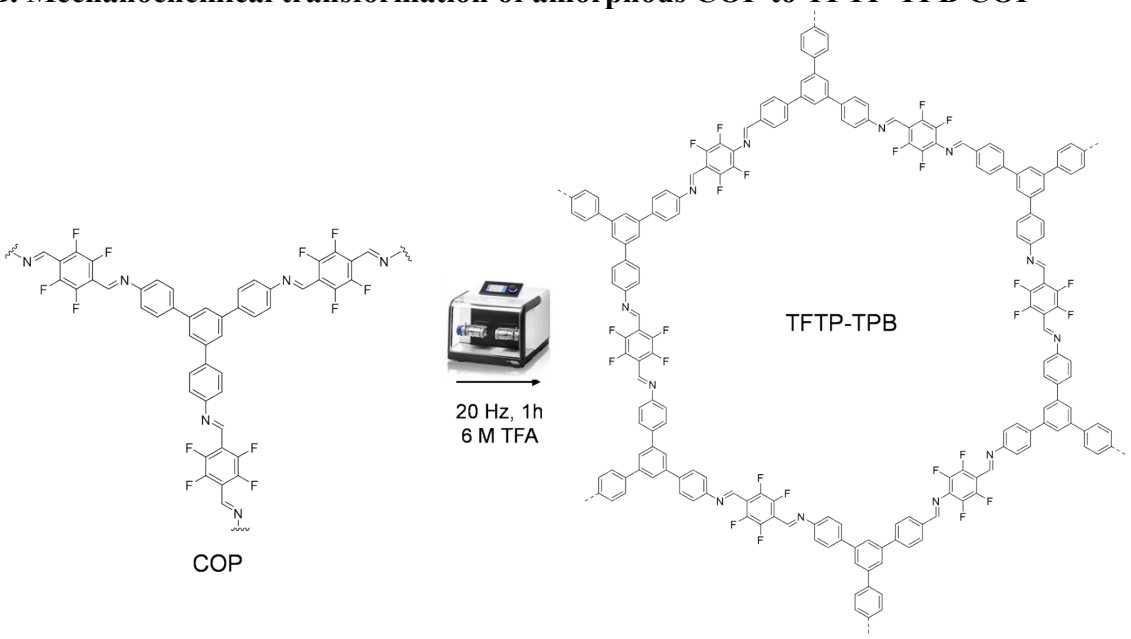
Figure S8. TEM images of DBrTP-TPB COF.

1.2 A. Room-temperature synthesis of amorphous COP from TFTP and TPB



2,3,5,6-Tetrafluoroterephthalaldehyde (TFTP, 0.6 mmol, 123 mg) and 1,3,5-tris(4-aminophenyl) benzene (TPB, 140 mg, 0.4 mmol) were dissolved in DMSO (5 mL) in a 20 mL scintillation vial. To this solution, 6 M aqueous acetic acid (1 mL) was added as a catalyst. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 91%.

1.2 B. Mechanochemical transformation of amorphous COP to TFTP-TPB COF



In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with 6 M TFA (20 μL), 1-butanol (20 μL), and a 7 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 20 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration, washed with tetraethylamine, and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding TFTP-TPB COF as a crystalline solid in 87% isolated yield.

Table S1. Condition screening for TFTP-TPB via mechanochemical transformation of COP precursor.

Condition	Liquid Additive	Catalyst	Ball Size	Frequency	Time
1	DCB 20 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
2	Dioxane 20 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
3	Mesitylene 20 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
4	ACN 20 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
5	Mesitylene/Dioxane 10 μL/10 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
6	DCB/BuOH 20 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
7	DMAc 20 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
8	DMF 20 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
9	BuOH 20 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
10	BuOH 15 μL	6 M TFA 15 μL	7 mm	20 Hz	1 h
11	BuOH 20 μL	6 M TFA 20 μL	7 mm	20 Hz	1 h
Condition: 40 mg of COP in a 5 ml stainless steel jar, one milling ball, 6 M TFA, milled for 1 h.					

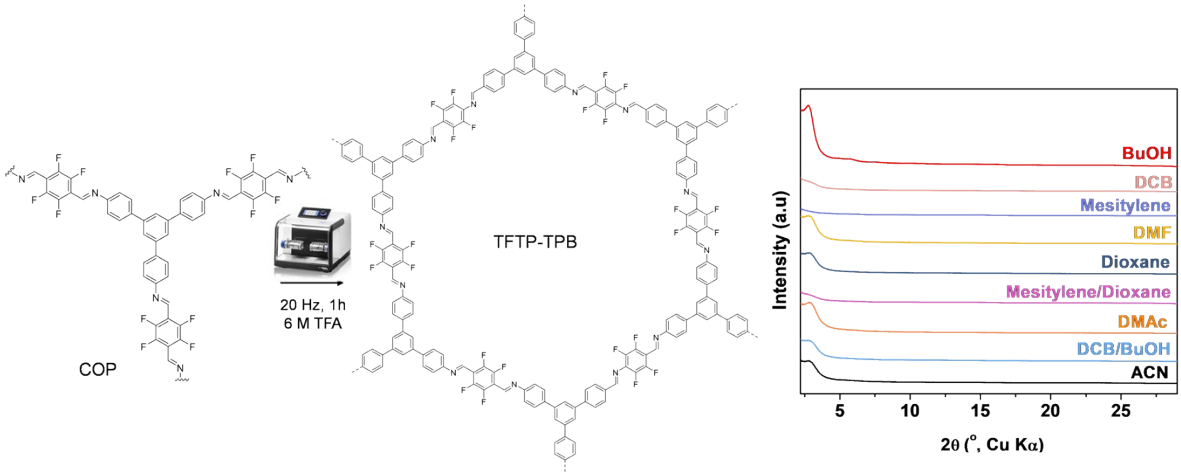
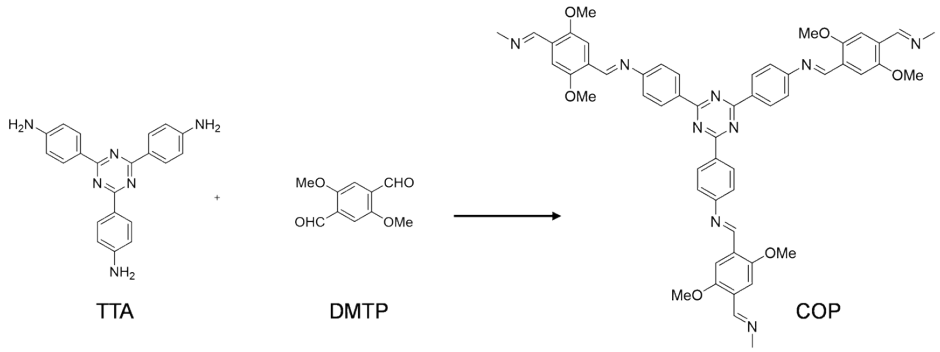


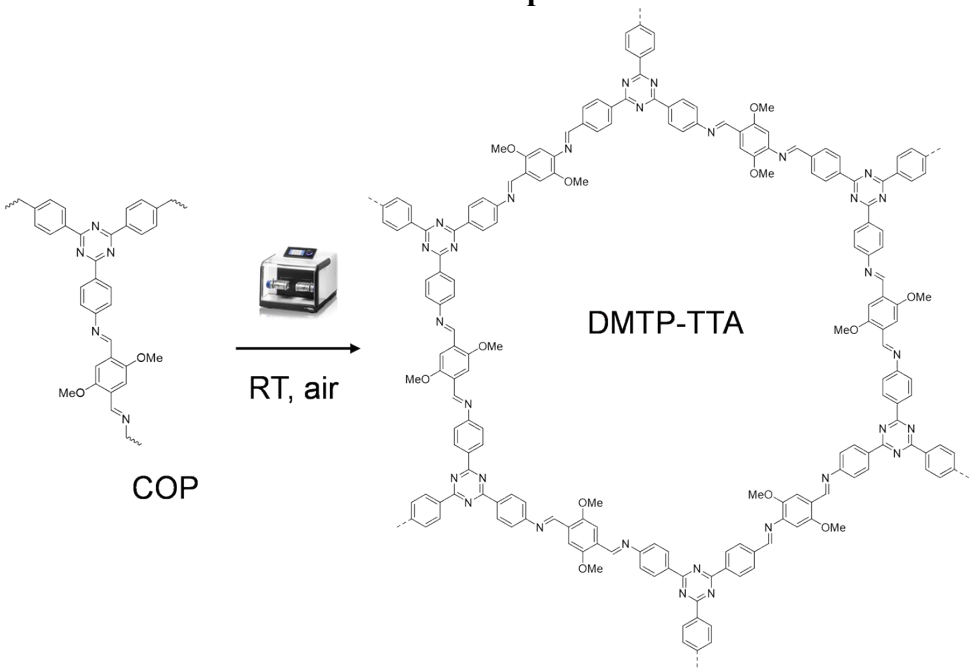
Figure S9. PXRD patterns of TFTP-TPB COF obtained via mechanochemical transformation of amorphous COP using various liquid additives.

1.3 A. Room-temperature synthesis of amorphous COP from DMTP and TTA



2,5-Dimethoxybenze-1,4-dicarboxaldehyde (DMTP, 0.42 mmol, 142 mg) and 4,4′,4″-(1,3,5,-triazine-2,4,6-triyl) trianiline (TTA, 0.28 mg, 173 mg) were dissolved in DMSO (5 mL) in a 20 mL scintillation vial. To this solution, 6 M aqueous acetic acid (0.7 mL) was added as a catalyst. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 91%.

1.3 B. Mechanochemical transformation of amorphous COP to DMTP-TTA COF



In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with 6 M TFA (15 μL), DMF (20 μL), and a 7 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 30 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration, neutralized with triethylamine, and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding DMTP-TTA COF as a crystalline solid in 85% isolated yield.

Table S2. Condition screening for DMTP-TTA via mechanochemical transformation of COP precursor.

Condition	Liquid Additive	Catalyst	Ball Size	Frequency	Time
1	BuOH 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
2	DCB 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
3	Dioxane 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
4	Mesitylene 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
5	Acetonitrile 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
6	DMF 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
7	DMAc 20 µL each	6 M TFA 15 µL	7 mm	30 Hz	1 h
8	DCB/BuOH 10 µL/10 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
9	Mesitylene/Dioxane 10 µL/10 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
Condition: 40 mg of COP in a 5 ml stainless steel jar, 6 M TFA 15 µL, milled at 30 Hz for 1 h.					

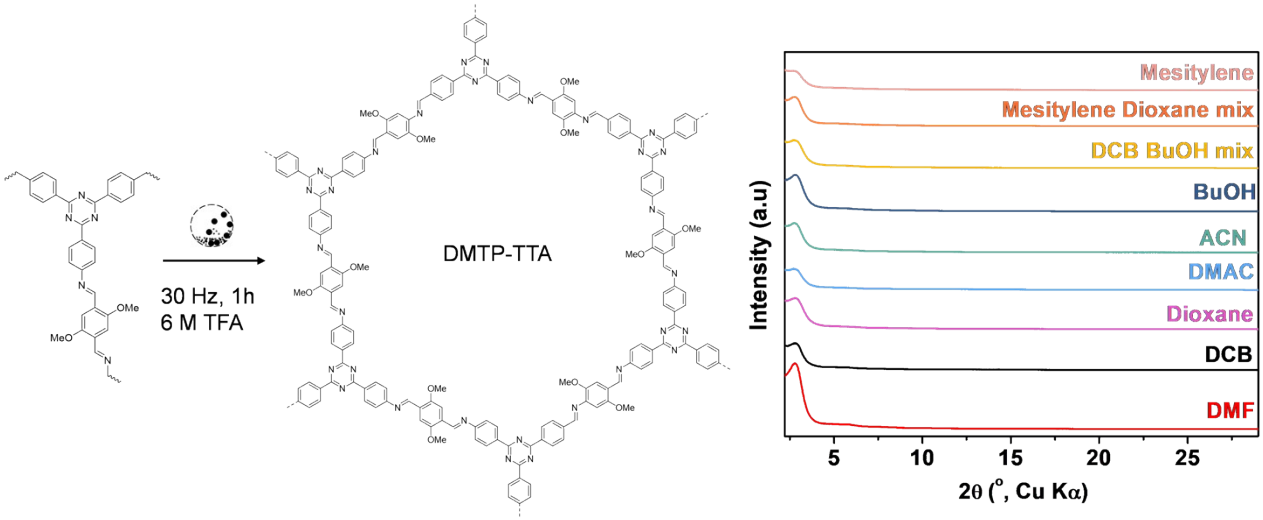
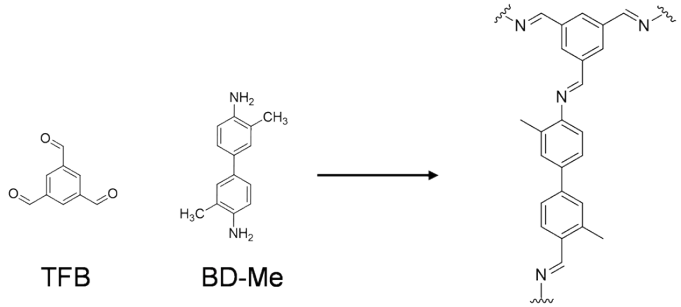


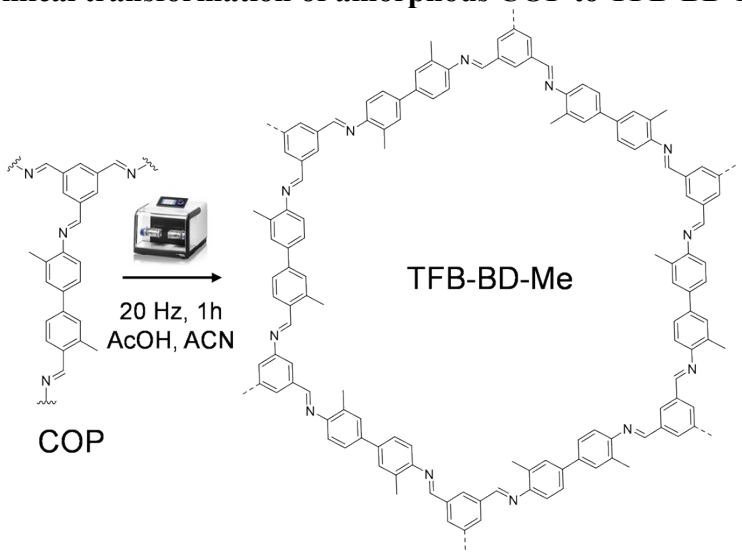
Figure S10. PXRD patterns of DMTP-TTA obtained via mechanochemical transformation of amorphous COP using various liquid additives.

1.4 A. Room-temperature synthesis of COP from TFB and BD-Me



1,3,5-Triformylbenzene (TFB, 79.1 mg, 0.49 mmol) and 3,3′-dimethylbenzidine (BD-Me, 156 mg, 0.74 mmol) were dissolved in 1,4-dioxane (5 mL) in a 20 mL scintillation vial. To this solution, 12 M aqueous acetic acid (1 mL) was added. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 90%.

1.4 B. Mechanochemical transformation of amorphous COP to TFB-BD-Me COF



In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with glacial acetic acid (15 μL), acetonitrile (20 μL), and a 7 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 20 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding TFB-BD-Me COF as a crystalline solid in 85% isolated yield.

Table S3. Condition screening for TFB-BD-Me via mechanochemical transformation of COP precursor.

Condition	Liquid Additive	Catalyst	Ball Size	Frequency	Time
1	Mesitylene 20 µL	glacial AcOH 15 µL	7 mm	20 Hz	1 h
2	MeOH 20 µL	glacial AcOH 15 µL	7 mm	20 Hz	1 h
3	EtOH 20 µL	glacial AcOH 15 µL	7 mm	20 Hz	1 h
4	Dioxane 20 µL	glacial AcOH 15 µL	7 mm	20 Hz	1 h
5	BuOH 20 µL	glacial AcOH 15 µL	7 mm	20 Hz	1 h
6	ACN 20 µL	glacial AcOH 15 µL	7 mm	20 Hz	1 h
7	DCB/BuOH 10 µL/10 µL	glacial AcOH 15 µL	7 mm	20 Hz	1 h
Condition: 40 mg of COP in a 5 ml stainless steel jar, glacial acetic acid 15 µL, milled at 20 Hz for 1 h.					

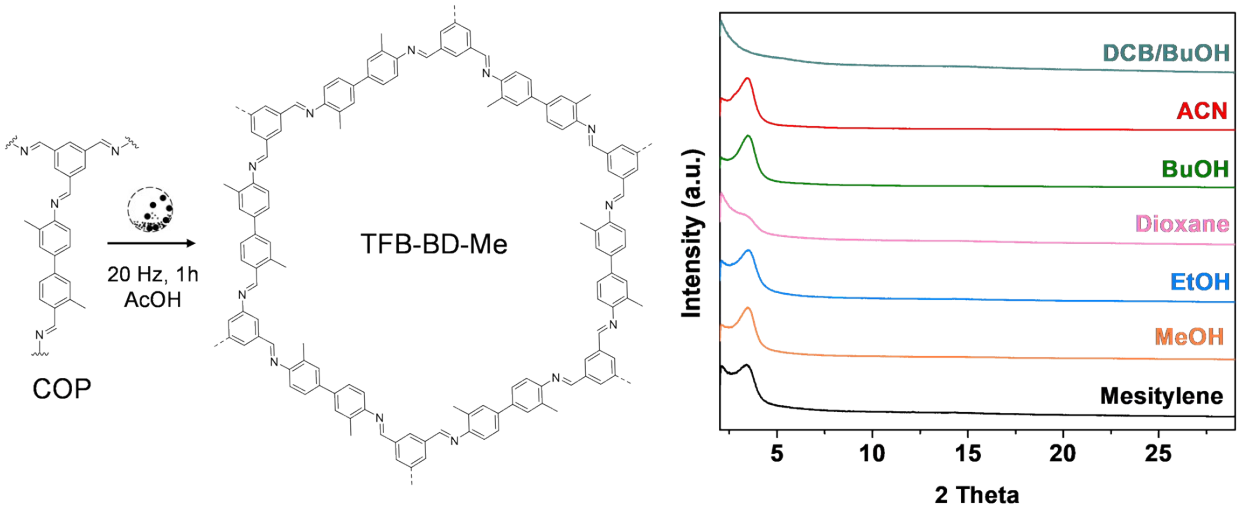
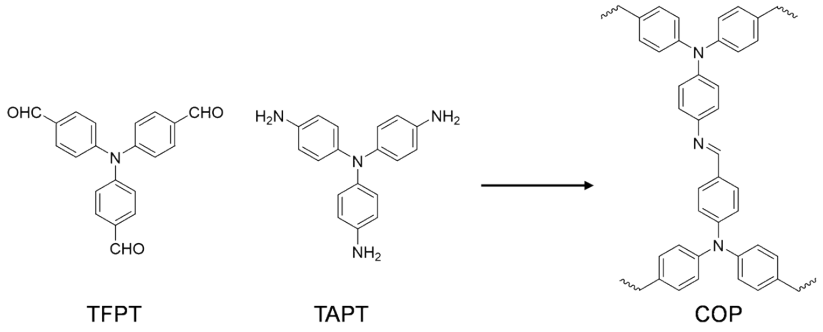


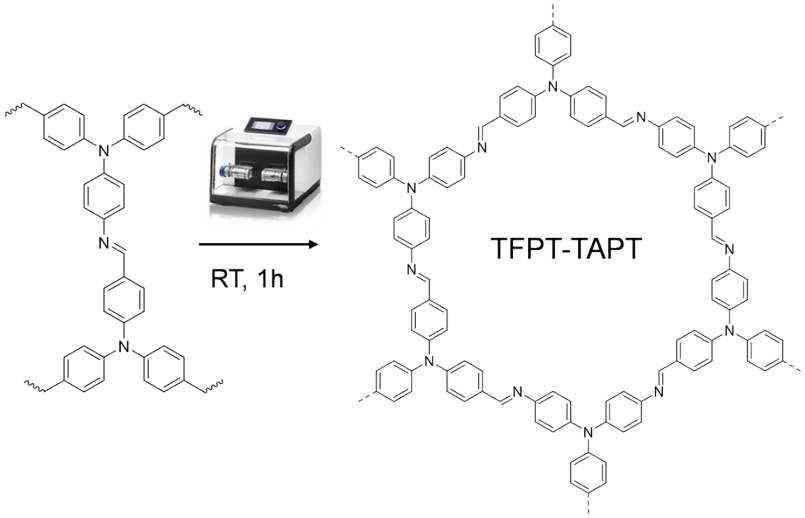
Figure S11. PXRD patterns of TFB-BD-Me COF obtained via mechanochemical transformation of amorphous COP using various liquid additives.

1.5 A. Room-temperature synthesis of amorphous COP from TFPT and TAPT



Tris(4-formylphenyl) amine (TFPT, 0.49 mmol, 161 mg) and tris(4-aminophenyl) amine (TAPT, 0.49 mmol, 142 mg) were dissolved in DMSO (5 mL) in a 20 mL scintillation vial. To this solution, 12 M aqueous acetic acid (1 mL) was added as a catalyst. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 94%.

1.5 B. Mechanochemical transformation of amorphous COP to TFPT-TAPT COF



In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with 6 M TFA (10 µL), mesitylene (20 µL), and a 7 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 30 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration, neutralized with triethylamine, and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding TFPT-TAPT COF as a crystalline solid in 90% isolated yield.

Table S4. Condition screening for TFPT-TAPT via mechanochemical transformation of COP precursor.

Condition	Liquid Additive	Catalyst	Ball Size	Frequency	Time
1	BuOH 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
2	DCB 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
3	Dioxane 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
4	Mesitylene 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
5	Acetonitrile 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
6	DMF 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
7	DMAc 20 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
8	DCB/BuOH 10 µL/10 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
9	Mesitylene/Dioxane 10 µL/10 µL	6 M TFA 15 µL	7 mm	30 Hz	1 h
Condition: 40 mg of COP in a 5 ml stainless steel jar, 6 M TFA 15 µL, milled at 30 Hz for 1 h.					

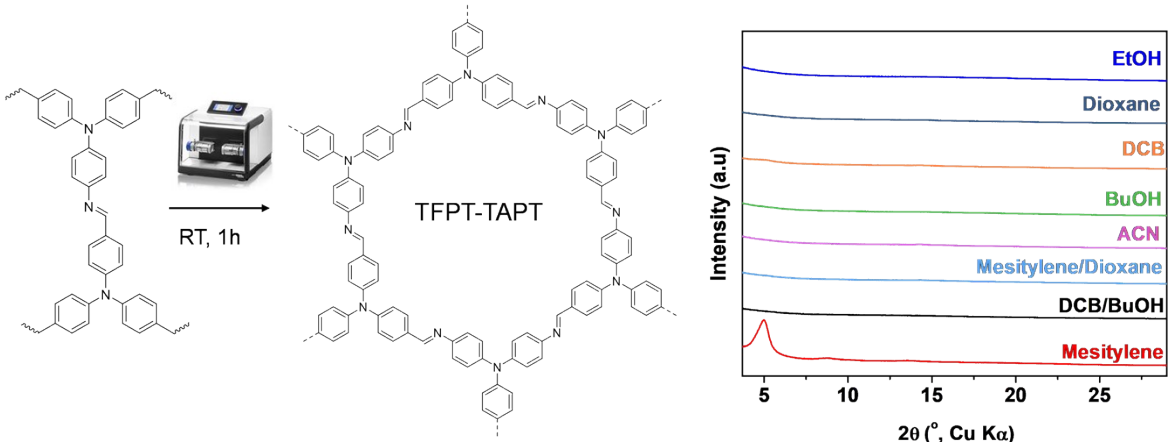
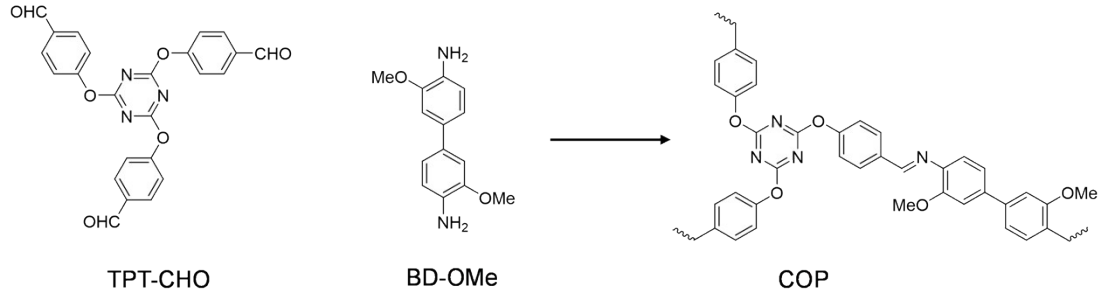


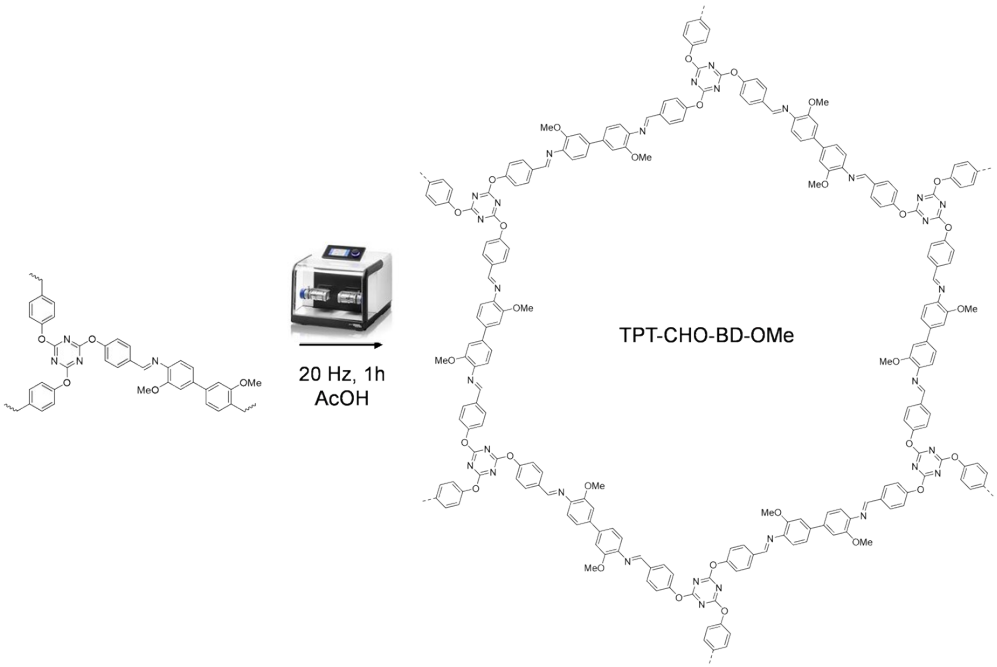
Figure S12. PXRD patterns of TFPT-TAPT obtained via mechanochemical transformation of amorphous COP using various liquid additives.

1.6 A. Room-temperature synthesis of amorphous COP from TPT-CHO and BD-OMe



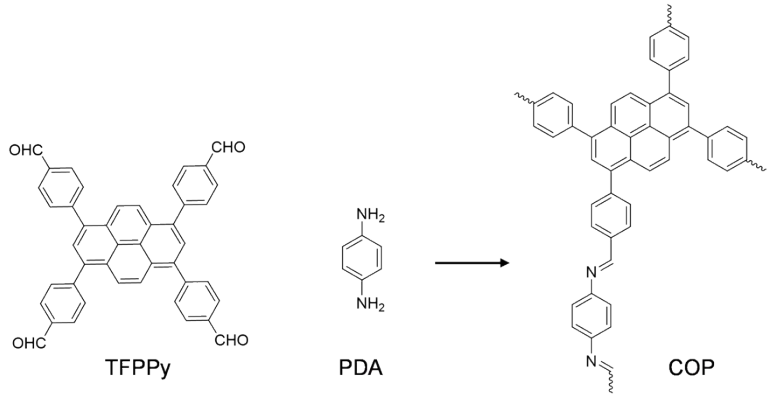
2,4,6-Tris(4-formylphenoxy)-1,3,5-triazine (TPT-CHO, 0.6 mmol, 265 mg) and 3,3′-dimethoxy-[1,1′-biphenyl]-4,4′-diamine (BD-OMe, 0.9 mmol, 219.6 mg) were dissolved in 1,4-dioxane (5 mL) in a 20 mL scintillation vial. To this solution, 6 M aqueous acetic acid (1 mL) was added. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 91%.

1.6 B. Mechanochemical transformation of amorphous COP to TPT-CHO-BD-OMe COF



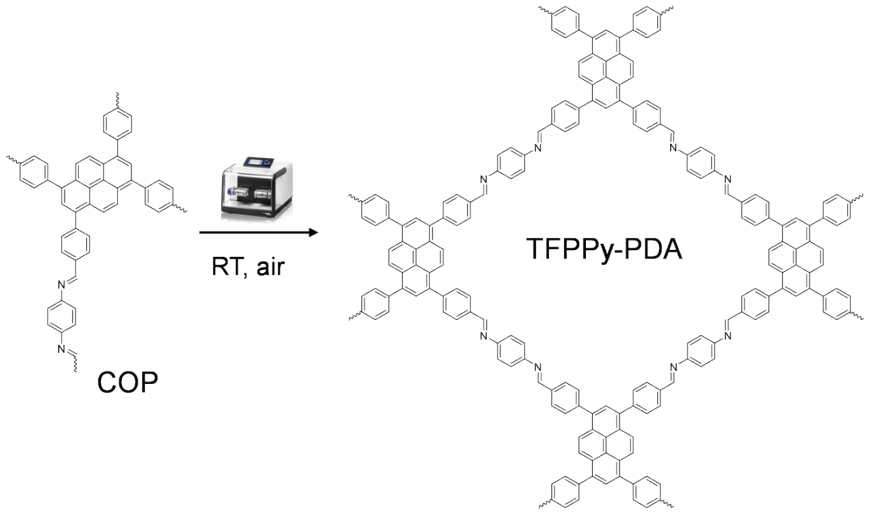
In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with glacial acetic acid (10 μL), mesitylene/ACN (10 μL/10 μL), and a 5 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 20 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding TPT-CHO-BD-OMe COF as a crystalline solid in 88% isolated yield.

1.7 A. Room-temperature synthesis of amorphous COP from TFPPy and PDA



4,4′,4″,4‴-(Pyrene-1,3,6,8-tetrayl)tetrebenzaldehyde (TFPPy, 0.448 mmol, 267 mg) and *p*-phenylenediamine (PDA, 0.896 mmol, 96.9 mg) were dissolved in DMSO (12 mL) in a 20 mL scintillation vial. To this solution, 6 M aqueous acetic acid (1.12 mL) was added as a catalyst. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 89%.

1.7 B. Mechanochemical transformation of amorphous COP to TFPPy-PDA COF



In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with 6 M TFA (15 µL), 1,4-dioxane (20 µL), and a 5 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 30 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration, neutralized with triethylamine, and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding TFPPy-PDA COF as a crystalline solid in 89% isolated yield.

Table S5. Condition screening for TFPPy-PDA via mechanochemical transformation of COP precursor.

Condition	Liquid Additive	Catalyst	Ball Size	Frequency	Time
1	BuOH 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
2	DCB 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
3	Dioxane 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
4	Mesitylene 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
5	Acetonitrile 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
6	DMF 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
7	DMAc 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
8	DCB/BuOH 10 µL/10 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
9	Mesitylene/Dioxane 10 µL/10 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
Condition: 40 mg of COP in a 5 ml stainless steel jar, 6 M TFA 15 µL, milled at 30 Hz for 1 h.					

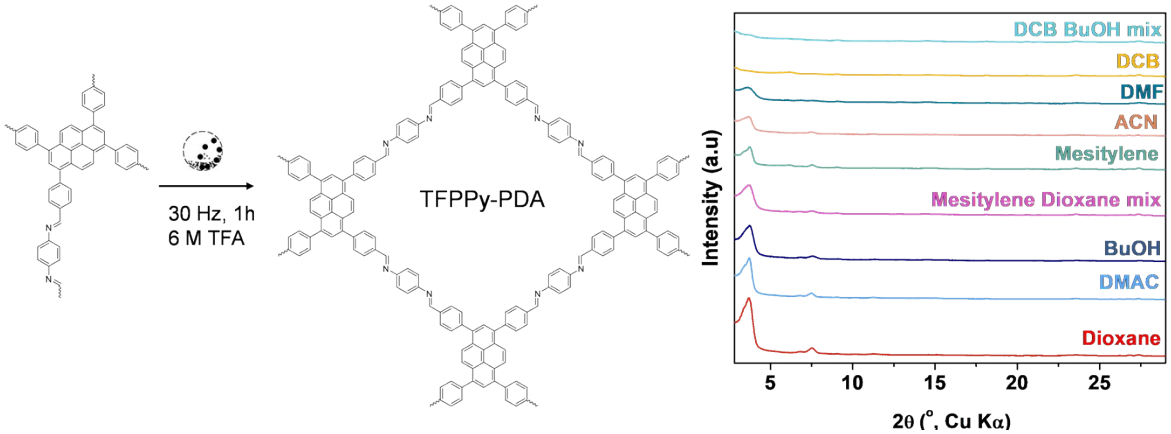
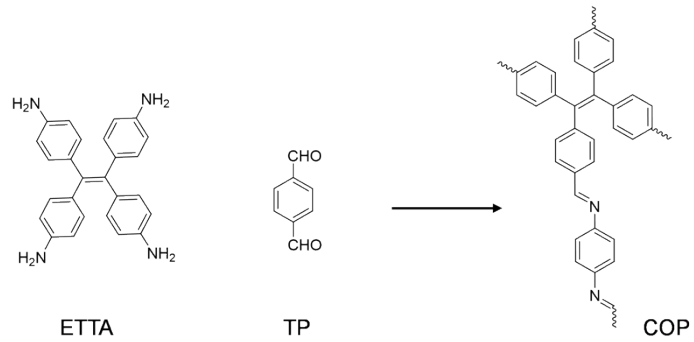


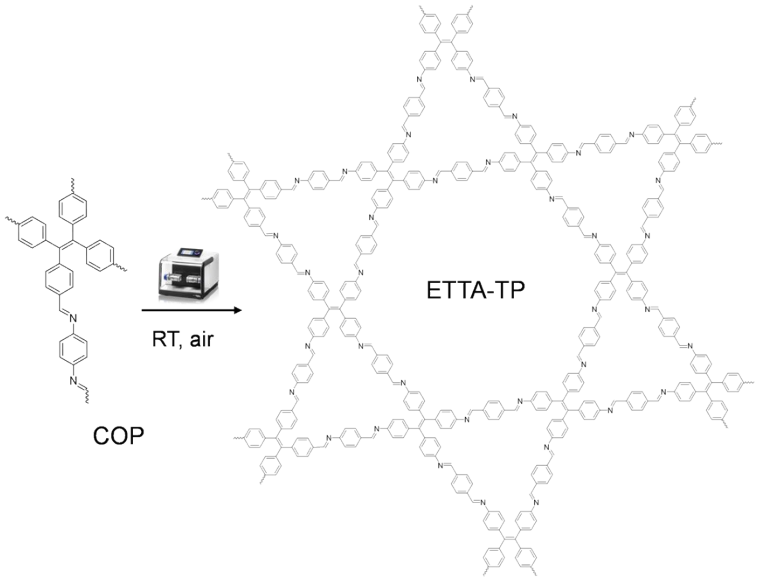
Figure S13. PXRD patterns of TFPPy-PDA obtained via mechanochemical transformation of amorphous COP using various liquid additives.

1.8 A. Room-temperature synthesis of amorphous COP from ETTA and TP



4,4′,4″,4‴-(Ethene-1,1,2,2-tetrayl)tetraaniline (ETTA, 0.35 mmol, 142 mg) and terephaldehyde (TP, 0.70 mmol, 173 mg) were dissolved in DMSO (5 mL) in a 20 mL scintillation vial. To this solution, 6 M aqueous acetic acid (0.875 mL) was added as a catalyst. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 93%.

1.8 B. Mechanochemical transformation of amorphous COP to ETTA-TP COF



In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with 6 M TFA (15 µL), DMAc (20 µL), and a 7 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 20 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration, neutralized with triethylamine, and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding ETTA-TP COF as a crystalline solid in 90% isolated yield.

Table S6. Condition screening for ETTA-TP via mechanochemical transformation of COP precursor.

Condition	Liquid Additive	Catalyst	Ball Size	Frequency	Time
1	BuOH 20 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
2	DCB 20 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
3	Dioxane 20 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
4	Mesitylene 20 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
5	Acetonitrile 20 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
6	DMF 20 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
7	DMAc 20 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
8	DCB/BuOH 10 μL/10 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
9	Mesitylene/Dioxane 10 μL/10 μL	6 M TFA 15 μL	7 mm	30 Hz	1 h
Condition: 40 mg of COP in 5 ml stainless steel jar, 6 M TFA 15 μL, milled at 30 Hz for 1 h.					

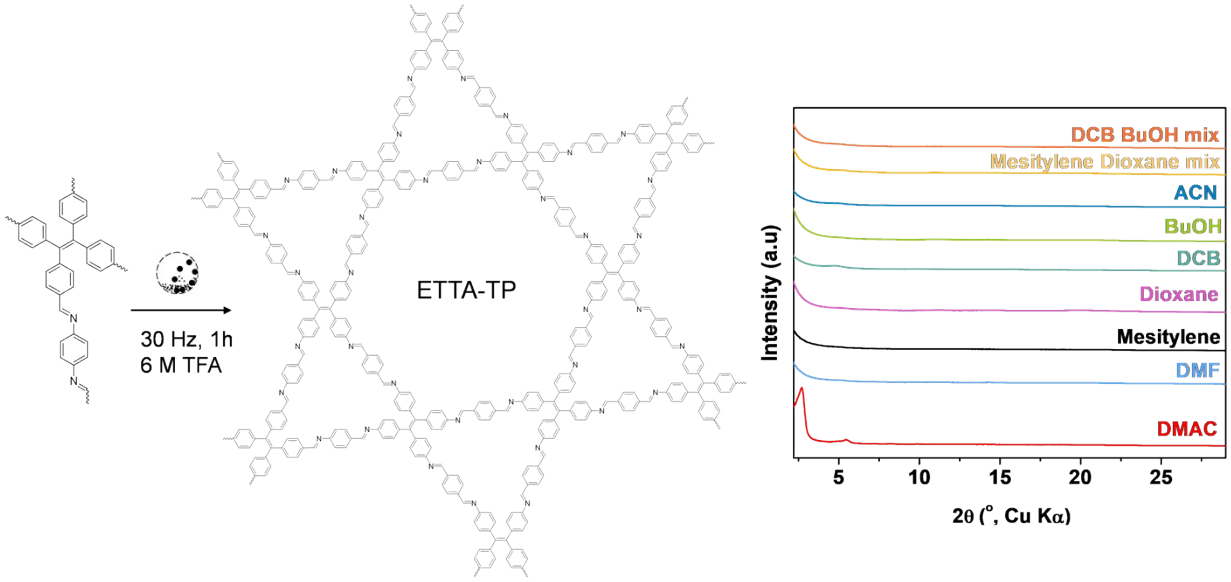
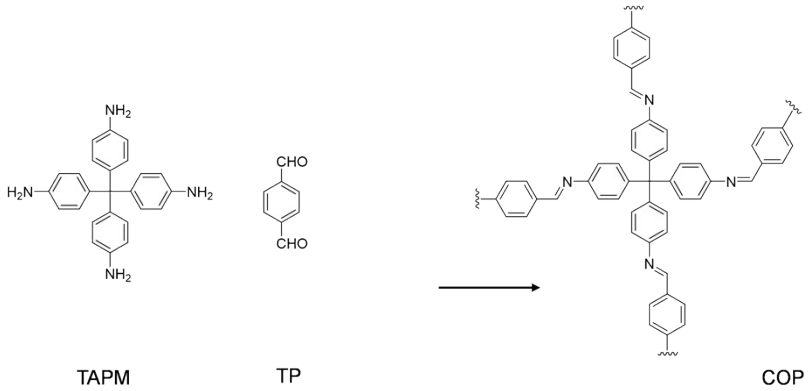


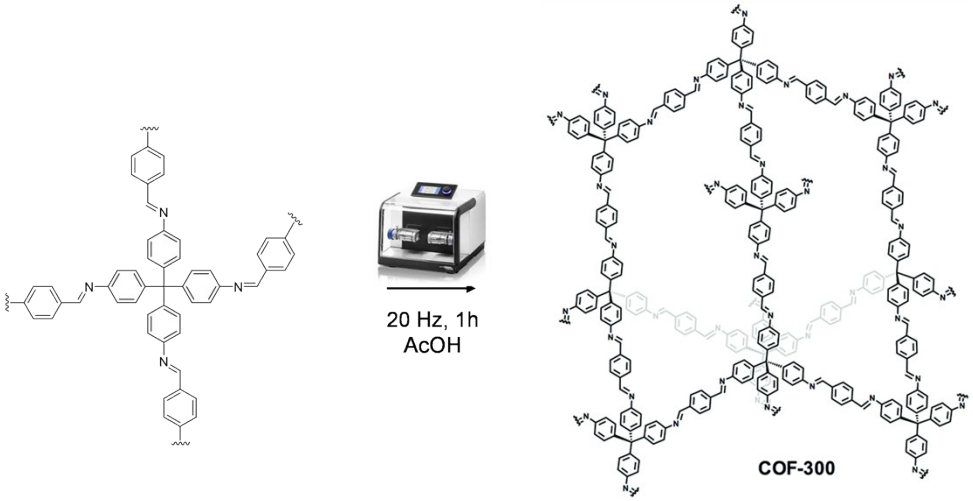
Figure S14. PXRD patterns of ETTA-TP obtained via mechanochemical transformation of amorphous COP using various liquid additives.

1.9 A. Room-temperature synthesis of amorphous COP from TAPM and TP



Terephthaldehyde (TP, 0.49 mmol, 161 mg) and tetrakis(4-aminophenyl)methane (TAPM, 0.49 mmol, 142 mg) were dissolved in 1,4-dioxane (5 mL) in a 20 mL scintillation vial. To this solution, 6 M aqueous acetic acid (1 mL) was added as a catalyst. The reaction mixture was left undisturbed at room temperature for 24 hours. The resulting solid was collected by vacuum filtration, followed by Soxhlet extraction with THF for 24 hours. The final product was dried under vacuum at 120 °C overnight, yielding the amorphous COP in an isolated yield of 94%.

1.9 B. Mechanochemical transformation of amorphous COP to COF-300



In a 5 mL stainless steel jar, amorphous COP (40 mg) was combined with glacial acetic acid (15 µL), DCB/BuOH (10 µL/10 µL), and a 7 mm stainless steel ball. The jar was tightly sealed and subjected to ball milling at 20 Hz for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration and purified via Soxhlet extraction with THF for 24 hours. The final powder was dried under vacuum at 120 °C overnight, yielding COF-300 as a crystalline solid in 90% isolated yield.

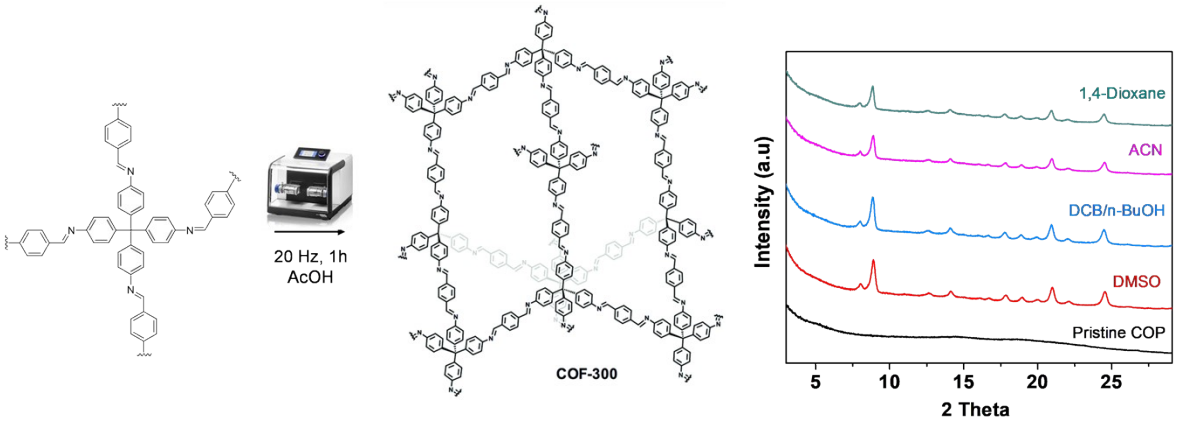
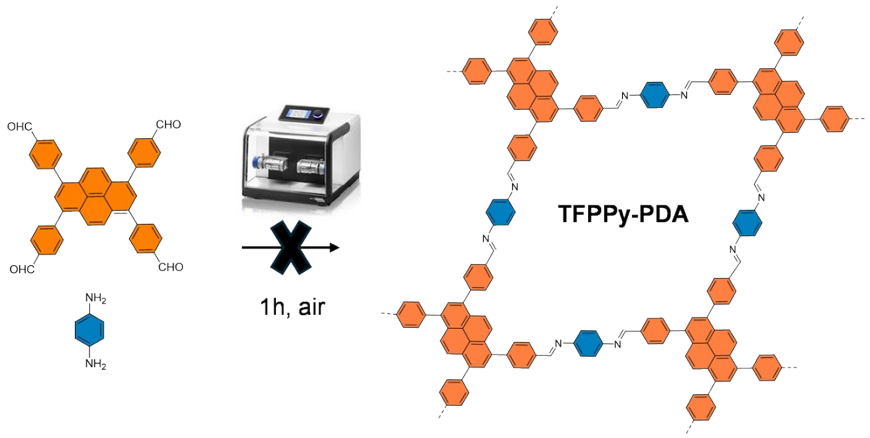


Figure S15. PXRD patterns of COF-300 obtained via mechanochemical transformation of amorphous COP using various liquid additives.

1.10 *De novo* mechanosynthesis of TFPPy-PDA



In a 5 mL stainless steel jar, 4,4′,4″,4‴-(pyrene-1,3,6,8-tetrayl)tetrebenzaldehyde (TFPPy, 0.05 mmol, 30.9 mg) and *p*-phenylenediamine (PDA, 0.1 mmol, 10.8 mg) were combined with acid, liquid additive, and a 5 mm stainless steel ball. The jar was sealed and subjected to ball milling for 1 hour in a Retsch MM 400 Mixer Mill. After milling, the solid product was collected by vacuum filtration, neutralized with triethylamine, dried under vacuum, and subjected to PXRD analysis.

Table S7. Condition screening for TFPPy-PDA via *de novo* mechanosynthesis.

Condition	Liquid Additive	Catalyst	Ball Size	Frequency	Time
1	DCB/BuOH 10 μL/10 μL	Glacial AcOH 15 μL	5 mm	20 Hz	1 h
2	Mesitylene/Dioxane 10 μL/10 μL	Glacial AcOH 15 μL	5 mm	20 Hz	1 h
3	Mesitylene 20 μL	Glacial AcOH 15 μL	5 mm	20 Hz	1 h
4	Dioxane 20 μL	Glacial AcOH 15 μL	5 mm	20 Hz	1 h
5	Acetonitrile 20 μL	Glacial AcOH 15 μL	5 mm	20 Hz	1 h
6	DMAc 20 μL	Glacial AcOH 15 μL	5 mm	20 Hz	1 h
7	BuOH 20 μL	Glacial AcOH 15 μL	5 mm	20 Hz	1 h
8	PhCN 20 μL	Glacial AcOH 15 μL	5 mm	20 Hz	1 h
9	Mesitylene 20 μL	6 M TFA 15 μL	5 mm	20 Hz	1 h
10	Dioxane 20 μL	6 M TFA 15 μL	5 mm	20 Hz	1 h

11	DMAc 20 µL	6 M TFA 15 µL	5 mm	20 Hz	1 h
12	BuOH 20 µL	6 M TFA 15 µL	5 mm	20 Hz	1 h
13	Dioxane 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
14	DMAc 20 µL	6 M TFA 15 µL	5 mm	30 Hz	1 h
15	Dioxane 20 µL	9 M TFA 15 µL	5 mm	30 Hz	1 h
16	DMAc 20 µL	9 M TFA 15 µL	5 mm	30 Hz	1 h
17	Dioxane 20 µL	TFA 15 µL	5 mm	30 Hz	1 h
18	DMAc 20 µL	TFA 15 µL	5 mm	30 Hz	1 h
19[a]	DCB/BuOH 10 µL/10 µL	Glacial AcOH 15 µL	10 mm ZrO_2 ball	30 Hz	1 h
20[a]	Mesitylene/Dioxane 10 µL/10 µL	Glacial AcOH 15 µL	10 mm ZrO_2 ball	30 Hz	1 h
21	Dioxane 30 µL	9 M TFA 15 µL	5 mm	30 Hz	1 h
22	DMAc 30 µL	9 M TFA 15 µL	5 mm	30 Hz	1 h
Condition: TFPPy (0.05 mmol, 30.9 mg) and PDA (0.1 mmol, 10.8 mg), milled in a 5 mL stainless steel jar for 1 h. [a] 25 mL ZrO_2 jar					

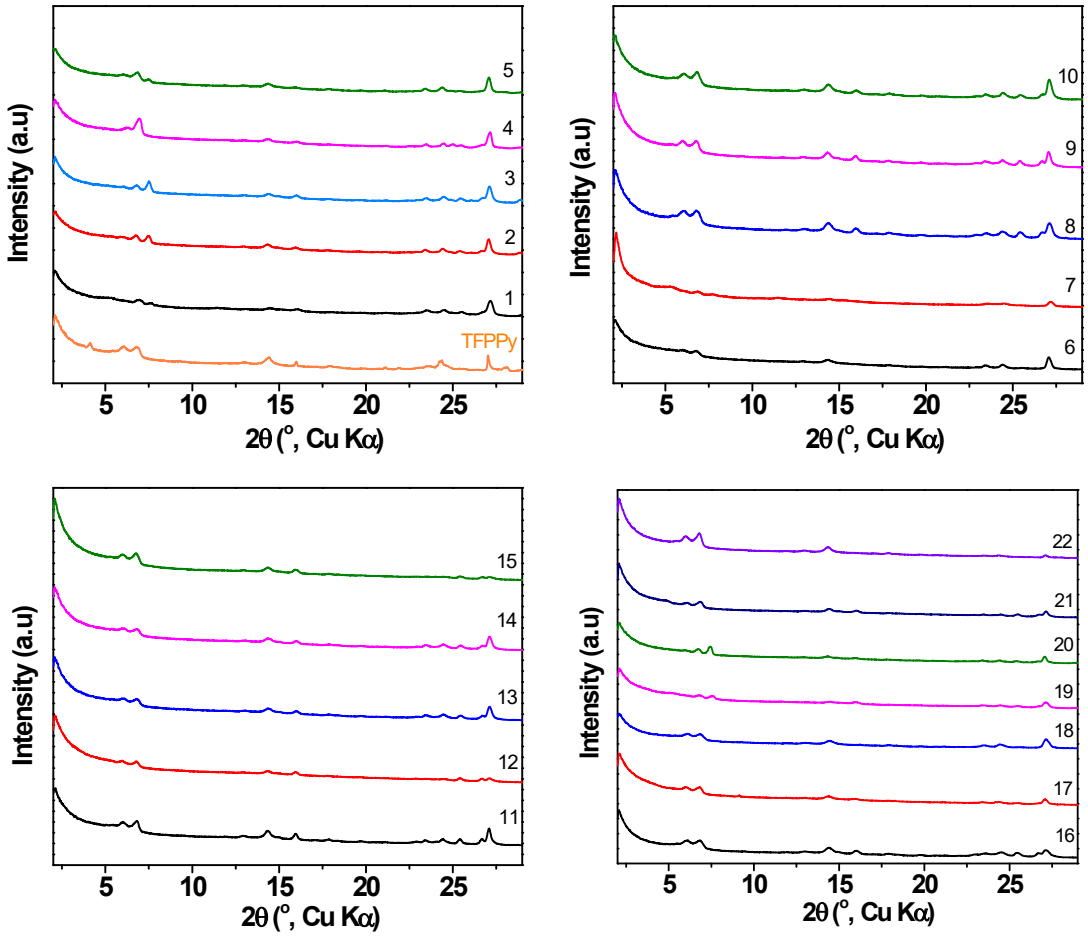


Figure S16. Condition screening for the mechanosynthesis of TFPPy-PDA using different liquid additives, acid catalyst, milling frequency, and milling materials (stainless steel vs ZrO_2).