Supporting Information

One-Pot Mechanochemical Access to Quinoline-Linked Covalent Organic Frameworks

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Synthesis of COF Materials

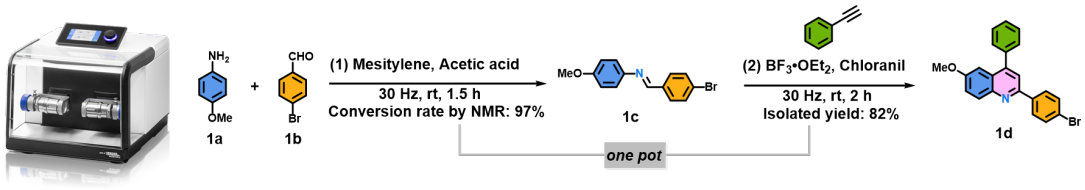

Fig. S1. Synthesis of Model Compound: 7 - Methoxy - 2 - (4 - bromophenyl) - 4 - phenylquinoline (**1d**).

Into a 10 mL stainless steel milling jar, 4-methoxyaniline (8.6 mg, 0.07 mmol, **1a**), 4-Bromobenzaldehyde (12.9 mg, 0.07 mmol, **1b**), mesitylene (40 μL), and glacial acetic acid (20 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. A small amount of **1c** was taken for NMR calibration, and the conversion rate was calculated to be 97%. After that, phenylacetylene (23 μL, 0.21 mmol), $BF_3 \cdot OEt_2$ (10.4 μL, 0.084 mmol), and chloranil (20.65 mg, 0.084 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. After completion of the reaction, the product was transferred to an eggplant-shaped flask using a small amount of dichloromethane and dried on a rotary evaporator. The concentrated residue was purified by silica gel flash column chromatography using petroleum ether (PE)/ethyl acetate (EA) (10:1, v/v) as the eluent, yielding 7-Methoxy-2-(4-bromophenyl)-4-phenylquinoline (**1d**) as a light gray product with a yield of 82%. ^{1}H NMR (400 MHz, Chloroform-*d*) of **1c**: δ 8.45 (s, 1H), 7.78 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.30 – 7.24 (m, 2H), 6.99 – 6.93 (m, 2H), 3.86 (s, 3H).; ^{1}H NMR (400 MHz, Chloroform-*d*) of **1d**: δ 8.13 (d, J = 9.0 Hz, 1H), 8.05 (d, J = 8.1 Hz, 2H), 7.73 (s, 1H), 7.63 (d, J = 8.1 Hz, 2H), 7.60 – 7.47 (m, 5H), 7.40 (d, J = 9.0 Hz, 1H), 7.18 (s, 1H), 3.80 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) of **1d**: δ 157.96, 153.23, 148.05, 144.78, 138.53, 138.49, 131.88, 131.49, 129.30, 128.81, 128.71, 128.71, 128.43, 126.77, 123.50, 122.06, 119.14, 103.68, 55.44.; HRMS (ESI) of **1d** ($C_{23}H_{16}BrN_2O^+$), *m/z* calculated for $[M + H]^+$: 415.0441, found 415.0404.

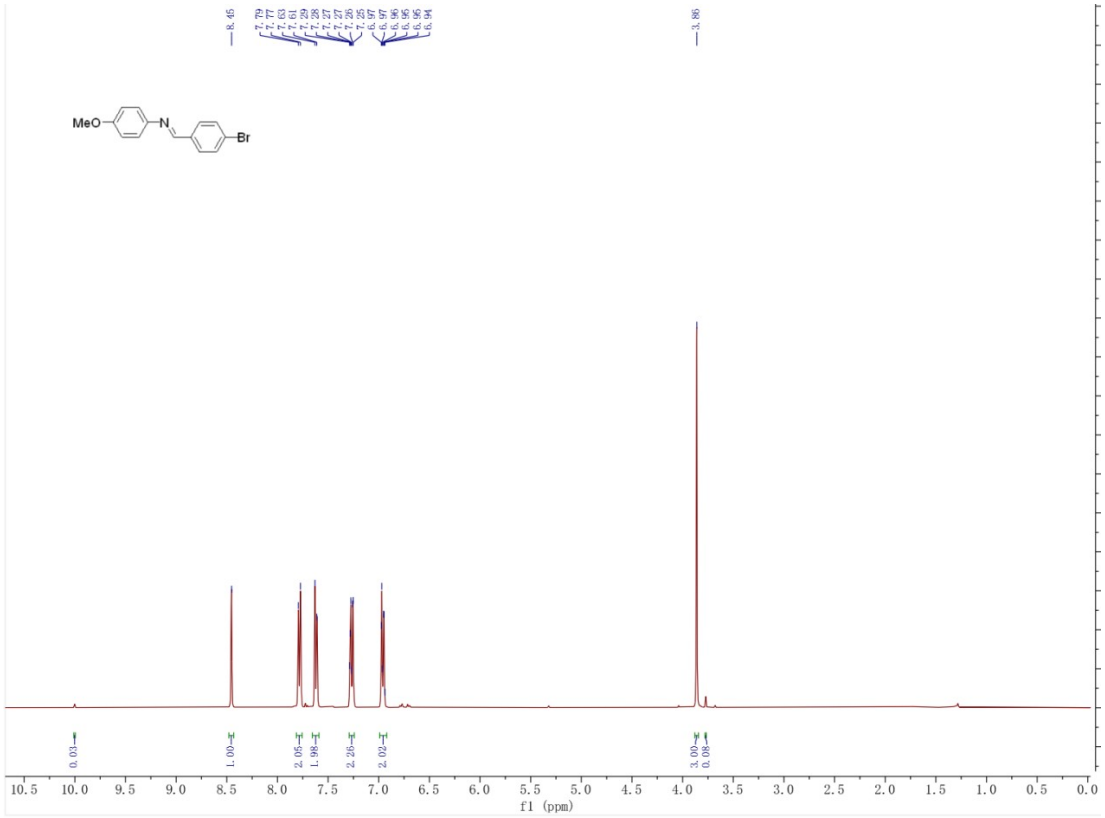

Fig. S2. [1]H NMR (400 MHz, Chloroform-*d*) of **1c**.

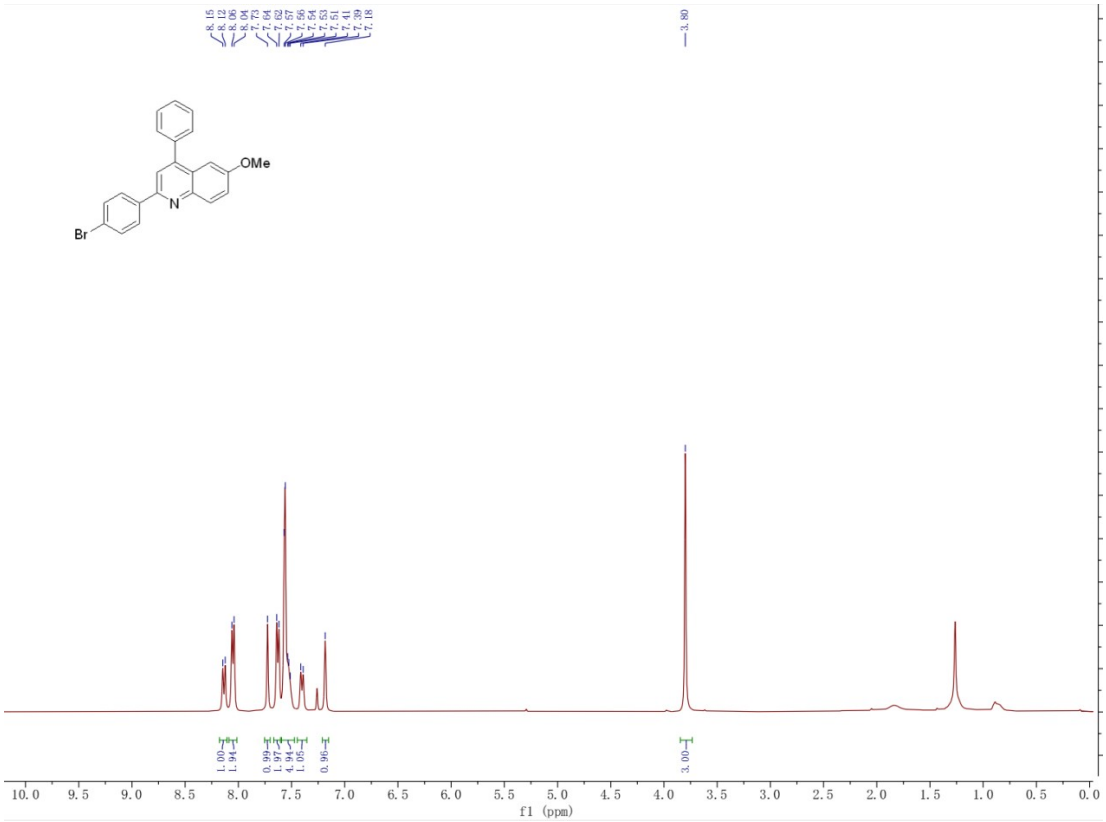

Fig. S3. [1]H NMR (400 MHz, Chloroform-*d*) of **1d**.

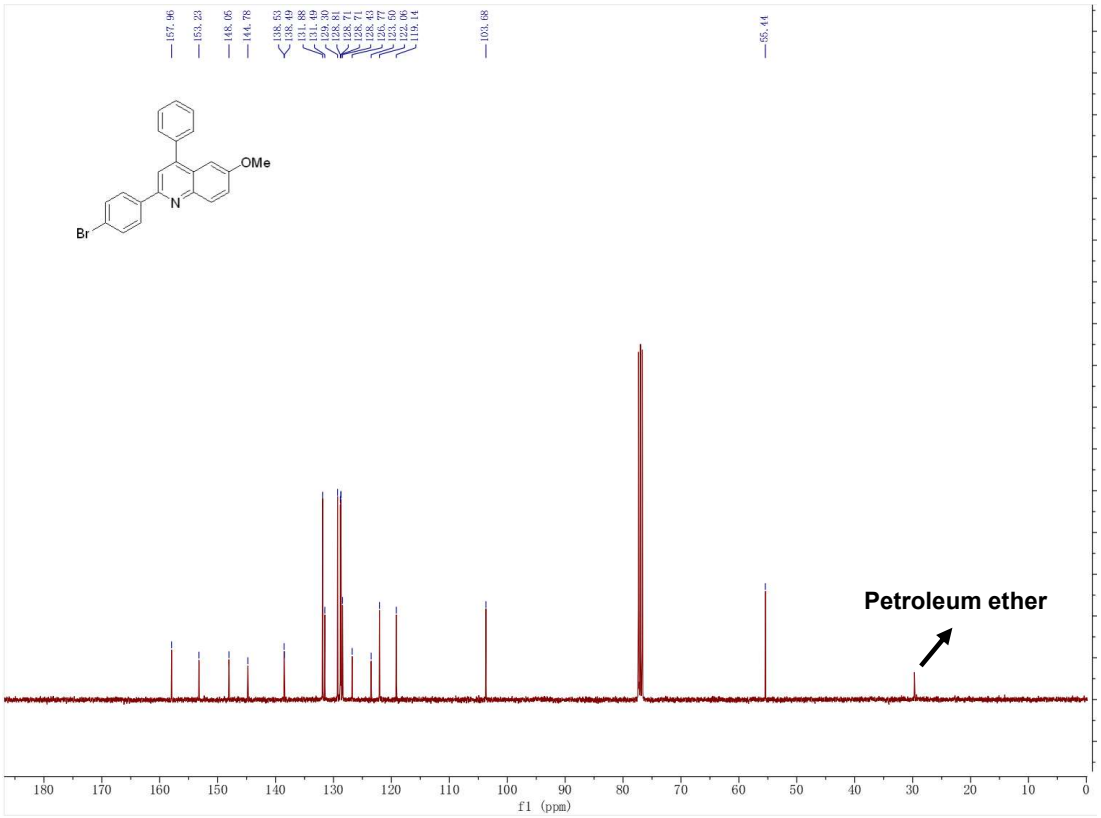

Fig. S4. ^{13}C NMR (101 MHz, $CDCl_3$) of **1d**.

The synthesis of imine-linked COFs:

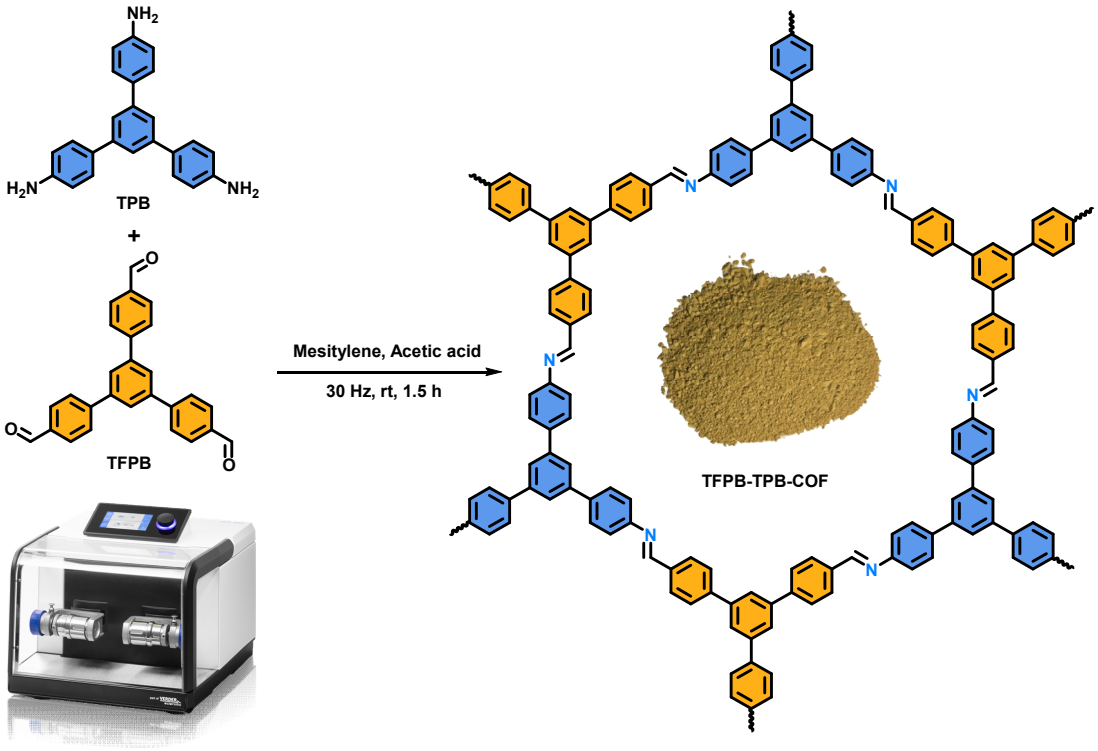

Fig. S5. Mechanochemical synthesis of TFPB-TPB-COF.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 1,3,5-tris(4-formylphenyl)benzene (TFPB) (109.3 mg, 0.28 mmol), mesitylene (160 µL), and glacial acetic acid (80 µL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 ℃ under a high vacuum overnight to produce TFPB-TPB-COF in an isolated yield of 98.3 % (189.2 mg).

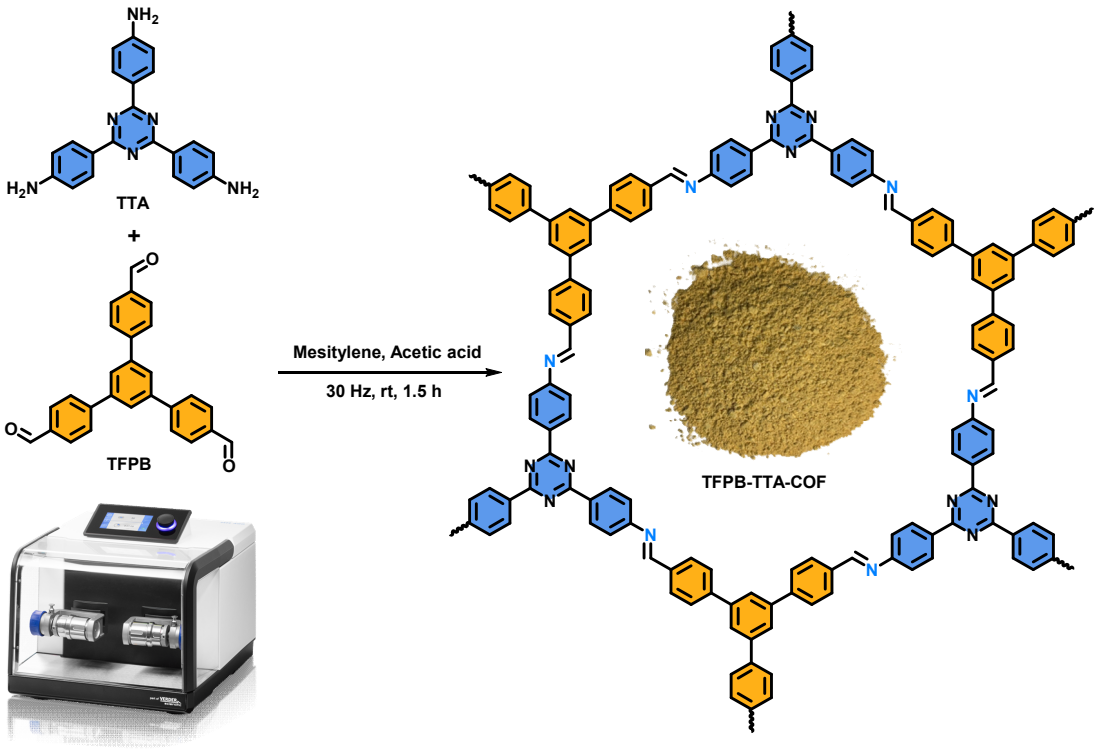

Fig. S6. Mechanochemical synthesis of TFPB-TTA-COF.

Into a 10 mL stainless steel milling jar, 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA) (99.2 mg, 0.28 mmol), 1,3,5-tris(4-formylphenyl)benzene (TFPB) (109.3 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TFPB-TTA-COF in an isolated yield of 89.7 % (172.6 mg).

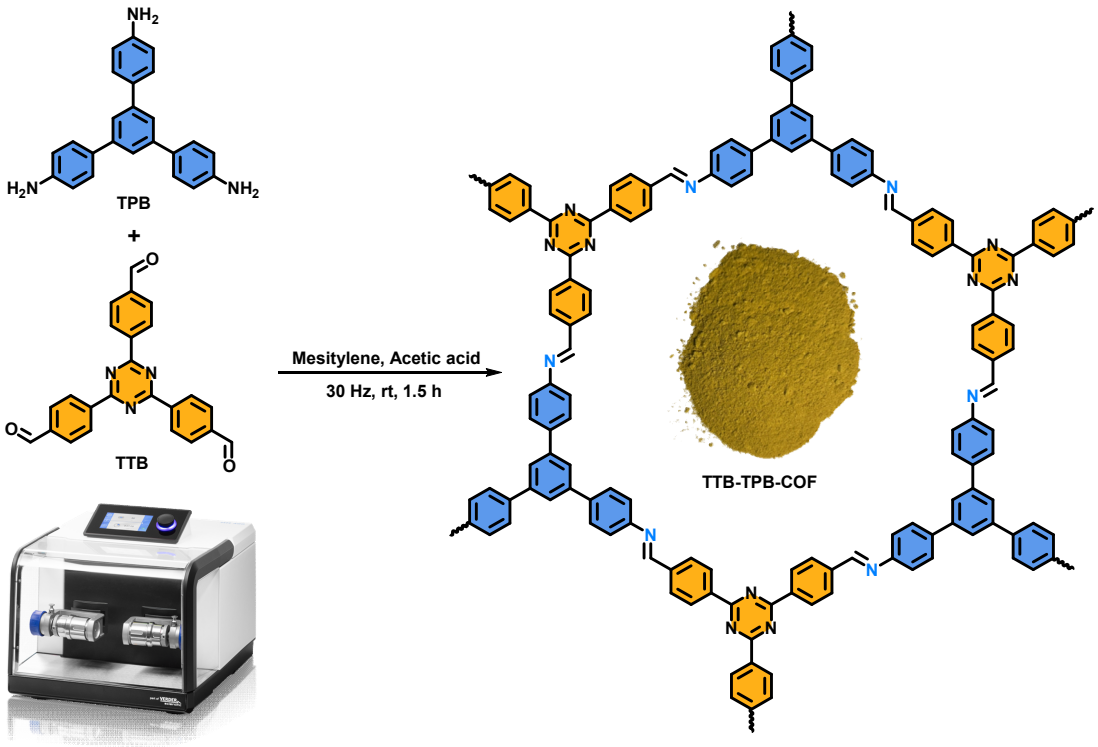

Fig. S7. Mechanochemical synthesis of TTB-TPB-COF.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 4,4',4"-(1,3,5-triazine-2,4,6-triyl) tribenzaldehyde (TTB) (110.1 mg, 0.28 mmol), mesitylene (160 µL), and glacial acetic acid (80 µL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TTB-TPB-COF in an isolated yield of 96.6 % (186.8 mg).

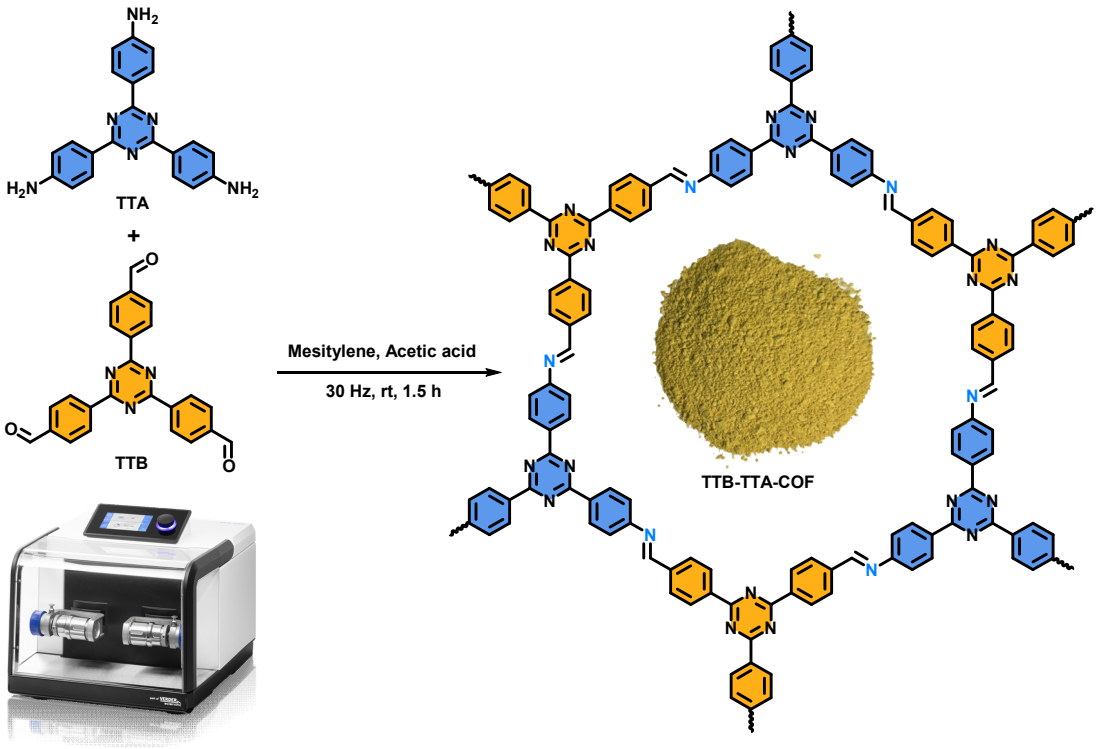

Fig. S8. Mechanochemical synthesis of TTB-TTA-COF.

Into a 10 mL stainless steel milling jar, 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA) (99.2 mg, 0.28 mmol), 4,4',4"-(1,3,5-triazine-2,4,6-triyl) tribenzaldehyde (TTB) (110.1 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TTB-TTA-COF in an isolated yield of 99% (191.5 mg).

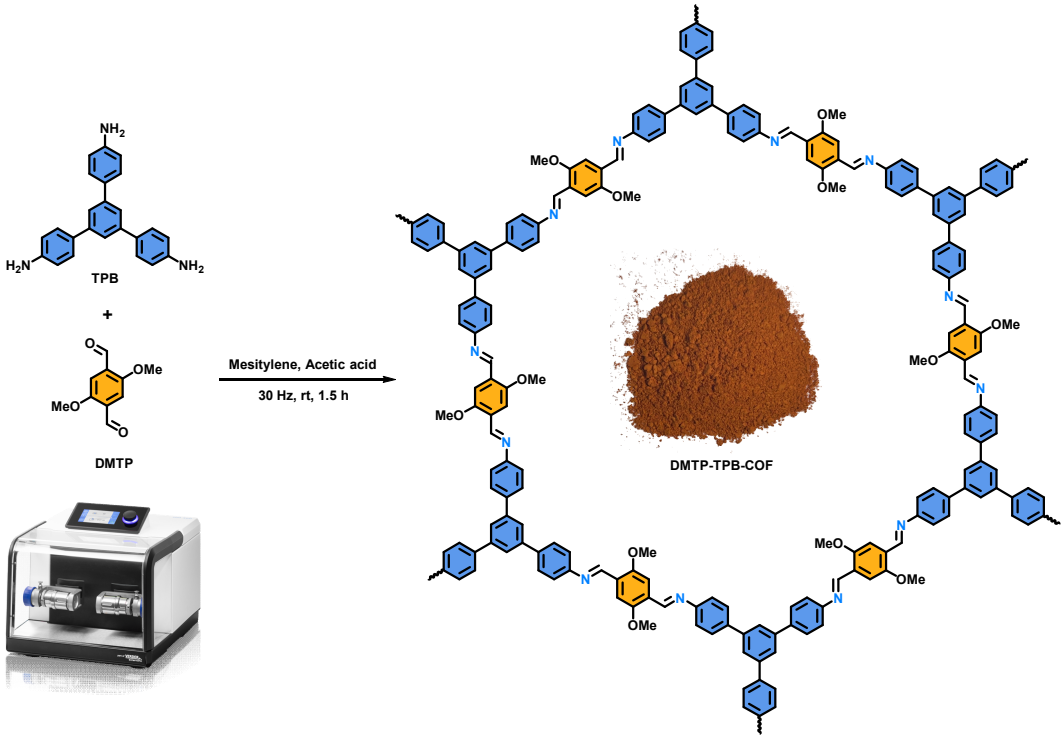

Fig. S9. Mechanochemical synthesis of DMTP-TPB-COF.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 2,5-dimethoxy terephthalaldehyde (DMTP) (81.6 mg, 0.42 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TPB-DMTP-COF in an isolated yield of 97.2 % (160.2 mg).

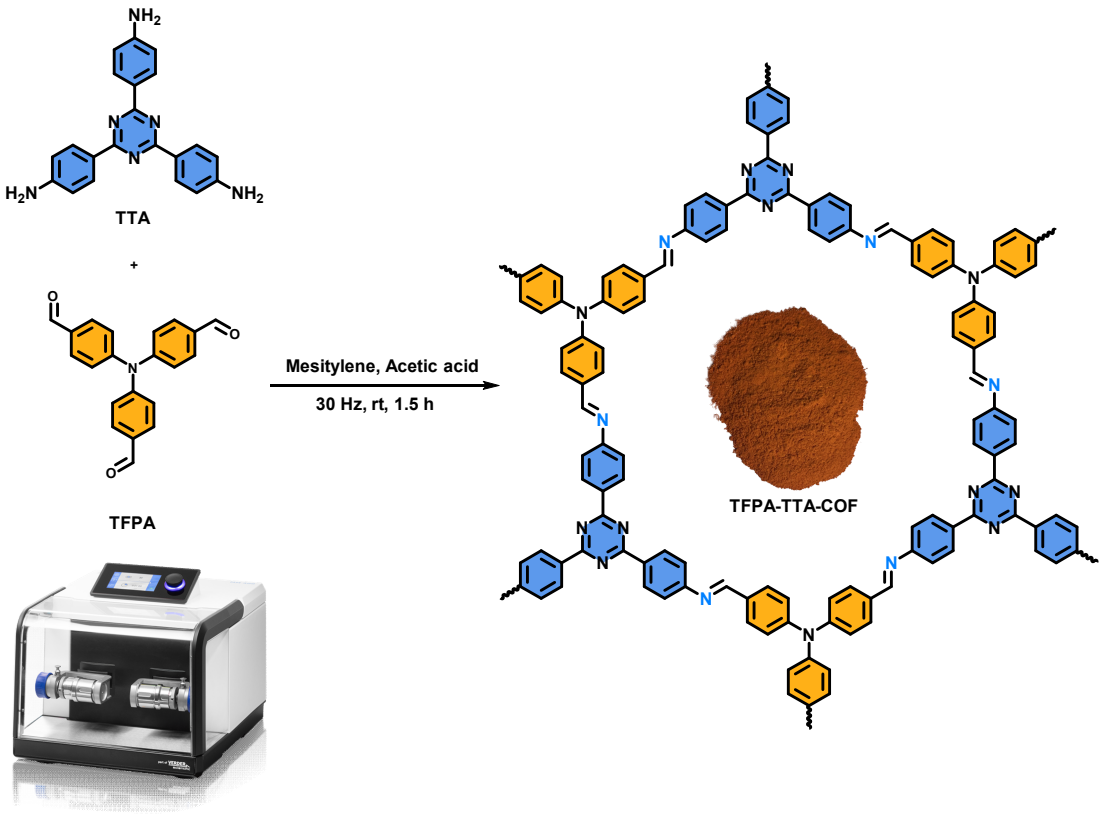

Fig. S10. Mechanochemical synthesis of TFPA-TTA-COF.

Into a 10 mL stainless steel milling jar, 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA) (99.2 mg, 0.28 mmol), tris (4-formylphenyl) amine (TFPA) (92.2 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 ℃ under a high vacuum overnight to produce TFPA-TTA-COF in an isolated yield of 99 % (173.8 mg).

The synthesis of quinoline-linked COFs:

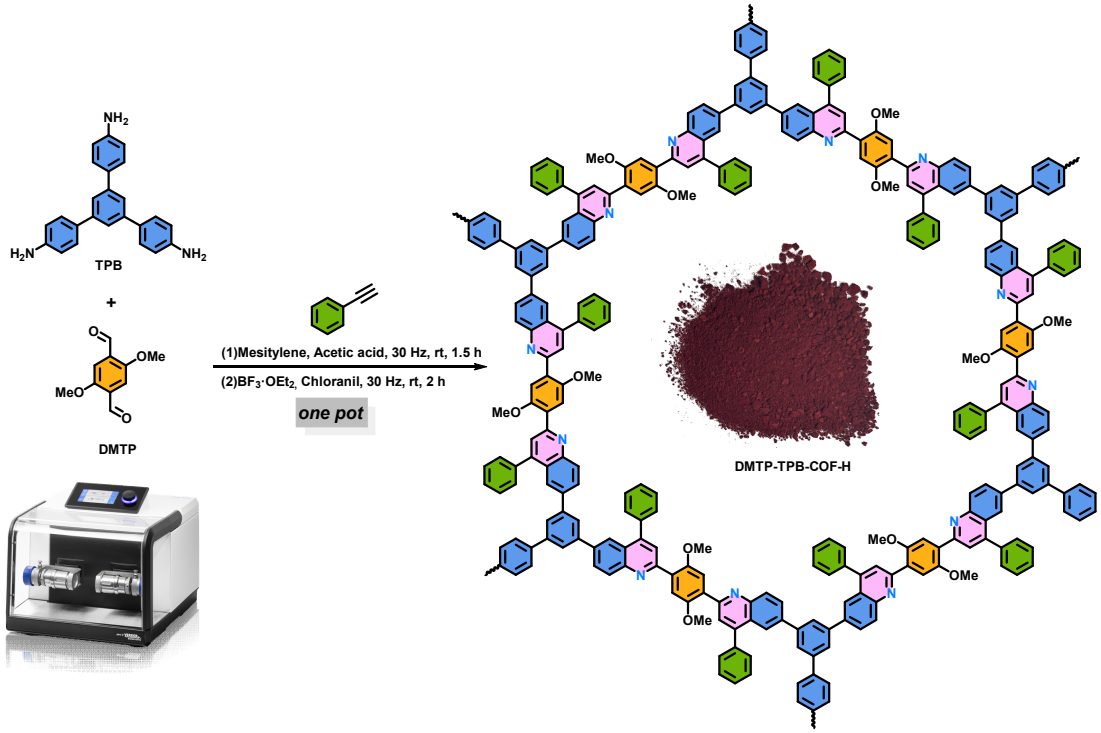

Fig. S11. Mechanochemical synthesis of DMTP-TPB-COF-H.

Into a 10 mL stainless steel milling jar, 1,3,5-tri (4-aminophenyl) benzene (TPB) (98.4 mg, 0.28 mmol), 2,5-dimethoxy terephthalaldehyde (DMTP) (81.6 mg, 0.42 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, phenylacetylene (92 μL, 0.84 mmol), $BF_3 \cdot OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 ℃ under a high vacuum overnight to produce TPB-DMTP-COF-H in an isolated yield of 78.9 % (196.4 mg).

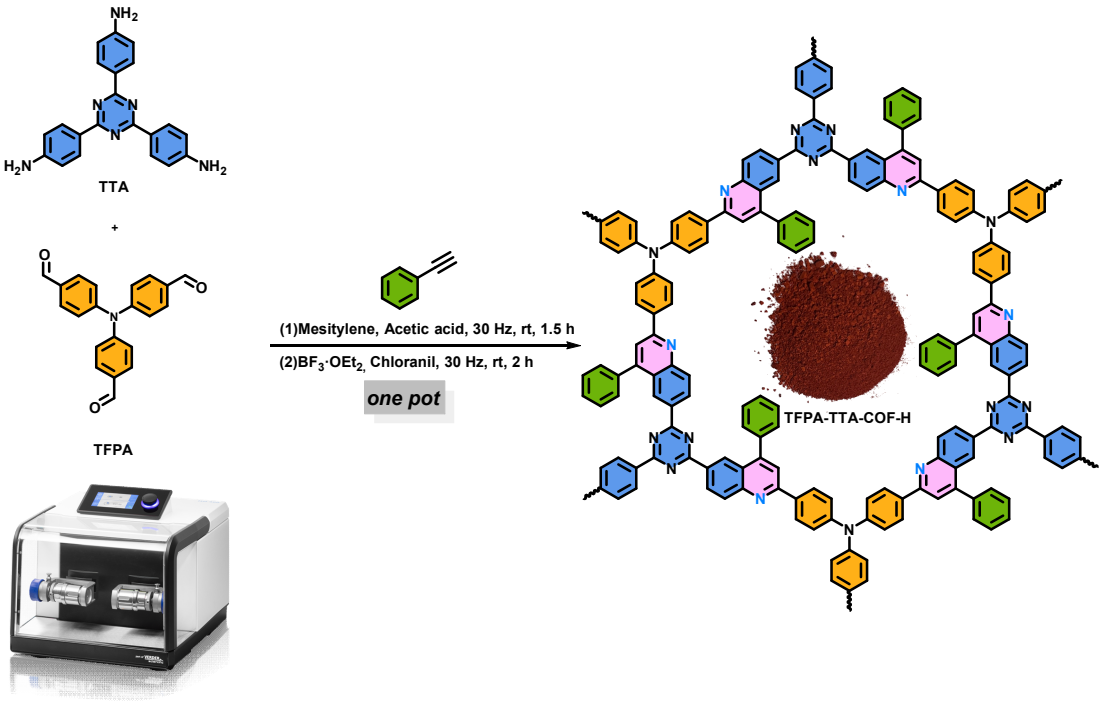

Fig. S12. Mechanochemical synthesis of TFPA-TTA-COF-H.

Into a 10 mL stainless steel milling jar, 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA) (99.2 mg, 0.28 mmol), tris (4-formylphenyl) amine (TFPA) (92.2 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, phenylacetylene (92 μL, 0.84 mmol), $BF_3{\cdot}OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 ℃ under a high vacuum overnight to produce TFPA-TTA-COF-H in an isolated yield of 68.6 % (178.1 mg).

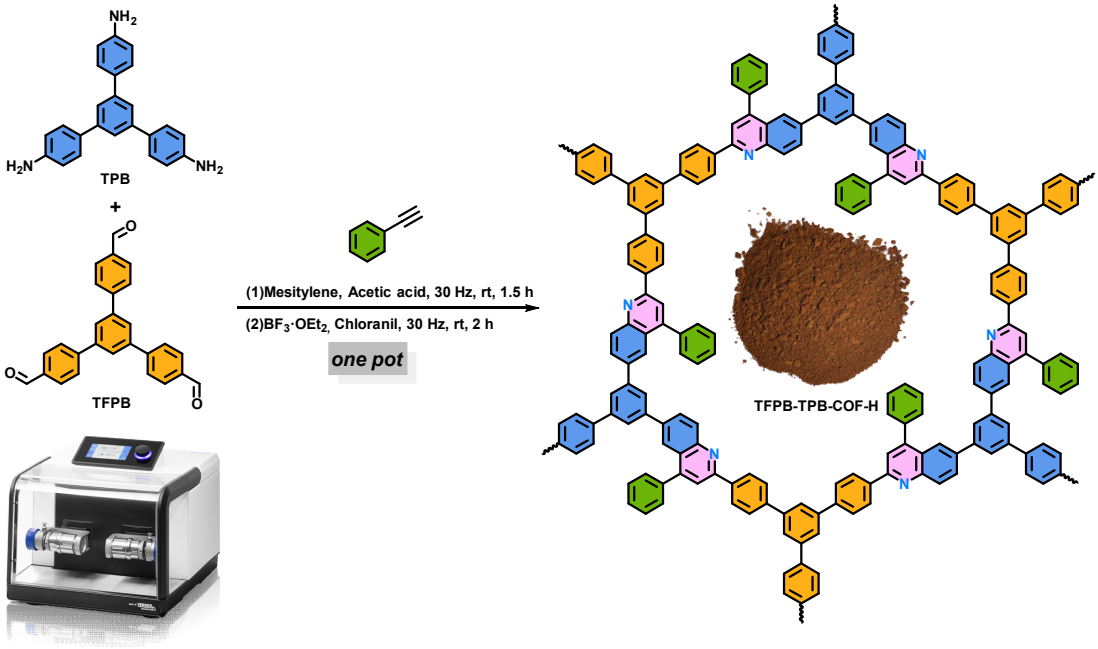

Fig. S13. Mechanochemical synthesis of TFPB-TPB-COF-H.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 1,3,5-tris(4-formylphenyl)benzene (TFPB) (109.3 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, phenylacetylene (92 μL, 0.84 mmol), $BF_3{\cdot}OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 ℃ under a high vacuum overnight to produce TFPB-TPB-COF-H in an isolated yield of 80.4 % (222.5 mg).

Into a 50 mL stainless steel milling jar, amine monomer (1.68 mmol), aldehyde monomer (1.68 mmol), mesitylene (960 μL), and glacial acetic acid (480 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, aryl alkyne monomer (5.04 mmol), $BF_3 \cdot OEt_2$ (264 μL, 2.01 mmol), and chloranil (495.6 mg, 2.01 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 ℃ under a high vacuum overnight to produce the target products.

Fig. S14. Gram-Scale Preparation of Quinoline-linked COFs.

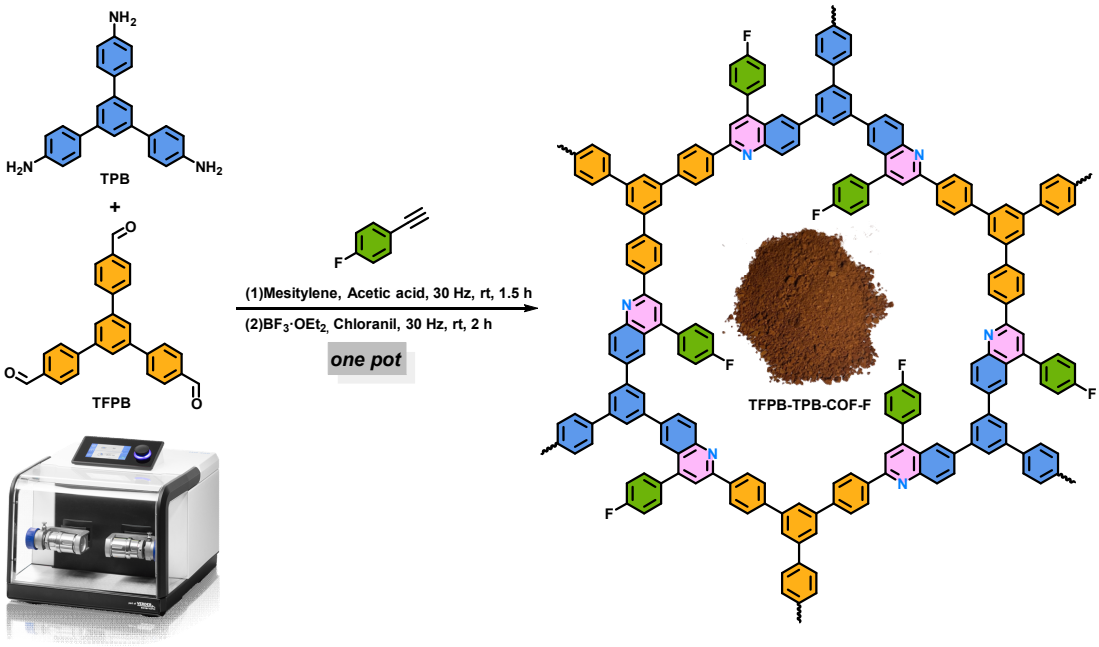

Fig. S15. Mechanochemical synthesis of TFPB-TPB-COF-F.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 1,3,5-tris(4-formylphenyl)benzene (TFPB) (109.3 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, 4-fluorophenylacetylene (96 μL, 0.84 mmol), $BF_3{\cdot}OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TFPB-TPB-COF-F in an isolated yield of 76.1 % (222.0 mg).

Solvothermal Preparation of TFPB-TPB-COF-F

To a 25 mL Pyrex glass tube, TFPB-TPB-COF-F (50 mg), styrene (75 μL), $BF_3 \cdot OEt_2$ (25 μL), chloranil (50 mg) and toluene (10 mL) were added. The glass tube was sonicated for 10 minutes, rapidly frozen at 77 K (in a liquid nitrogen bath), and degassed through three consecutive freeze-pump-thaw cycles. After reducing the internal pressure to 10^{-3} bar, the glass tube was flame-sealed and then placed in an oven preheated to 120 ℃ for a 72 h reaction. Upon the completion of the reaction, the sample was transferred to a Buchner funnel, washed sequentially with N,N-dimethylformamide (DMF) and acetone until the filtrate turned colorless. The solid product was transferred onto filter paper and purified by Soxhlet extraction using tetrahydrofuran as the extractant for 24 h. Finally, the wet powder was dried overnight at 110 ℃ under high vacuum conditions, affording the target product TFPB-TPB-COF-F (solvothermal) with a yield of 54.6 mg.

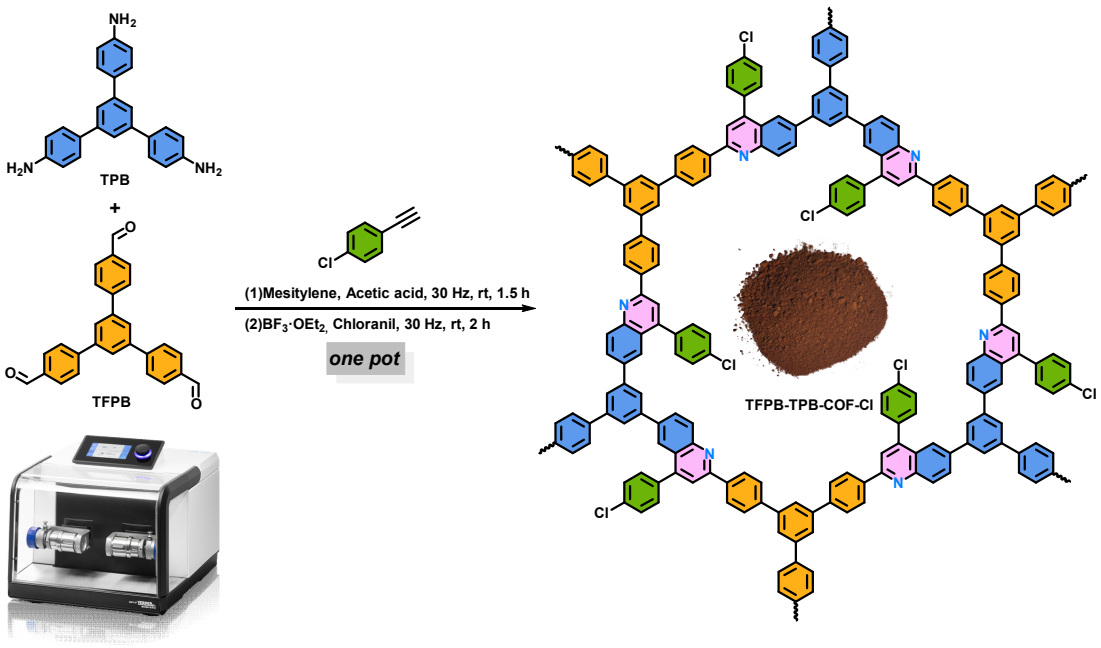

Fig. S16. Mechanochemical synthesis of TFPB-TPB-COF-Cl.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 1,3,5-tris(4-formylphenyl)benzene (TFPB) (109.3 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, 4-chlorophenylacetylene (114.7 mg, 0.84 mmol), $BF_3{\cdot}OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TFPB-TPB-COF-Cl in an isolated yield of 72.9 % (222.9 mg).

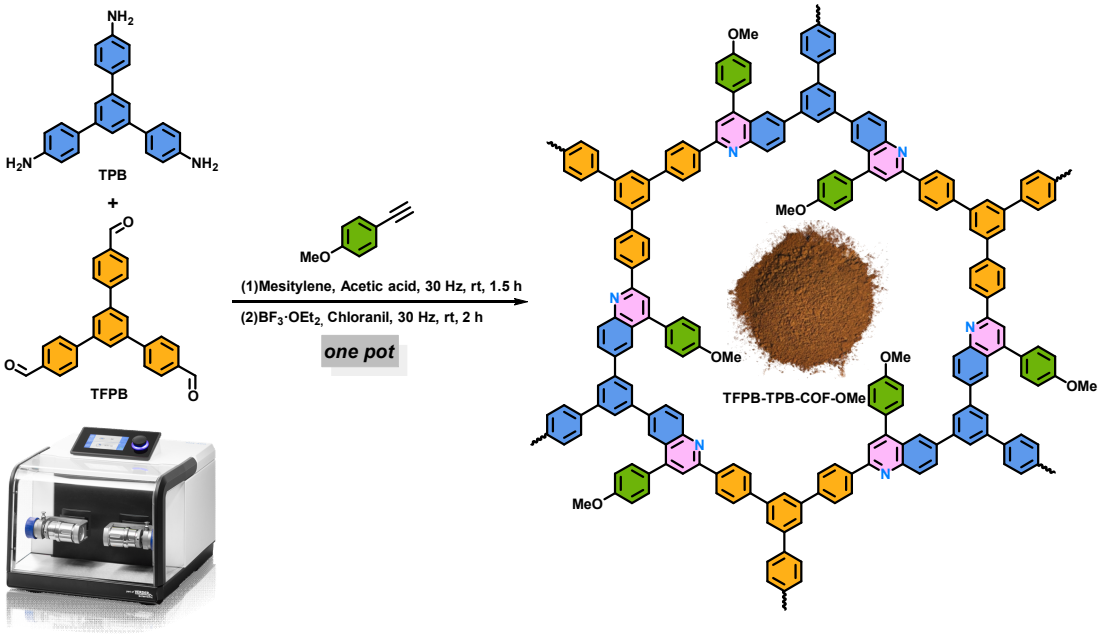

Fig. S17. Mechanochemical synthesis of TFPB-TPB-COF-OMe.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 1,3,5-tris(4-formylphenyl)benzene (TFPB) (109.3 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, 4-ethynylanisole (109 μL, 0.84 mmol), $BF_3{\cdot}OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TFPB-TPB-COF-OMe in an isolated yield of 89.7 % (270.8 mg).

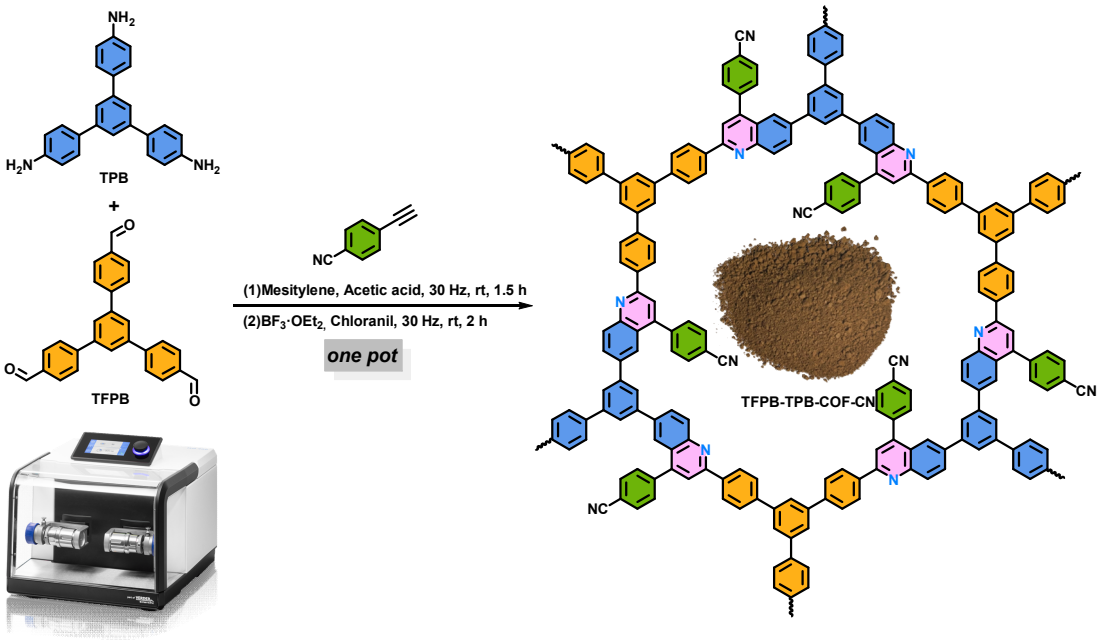

Fig. S18. Mechanochemical synthesis of TFPB-TPB-COF-CN.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 1,3,5-tris(4-formylphenyl)benzene (TFPB) (109.3 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, 4-cyanophenylacetylene (106.8 mg, 0.84 mmol), $BF_3{\cdot}OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 ℃ under a high vacuum overnight to produce TFPB-TPB-COF-CN in an isolated yield of 72.8% (216.8 mg).

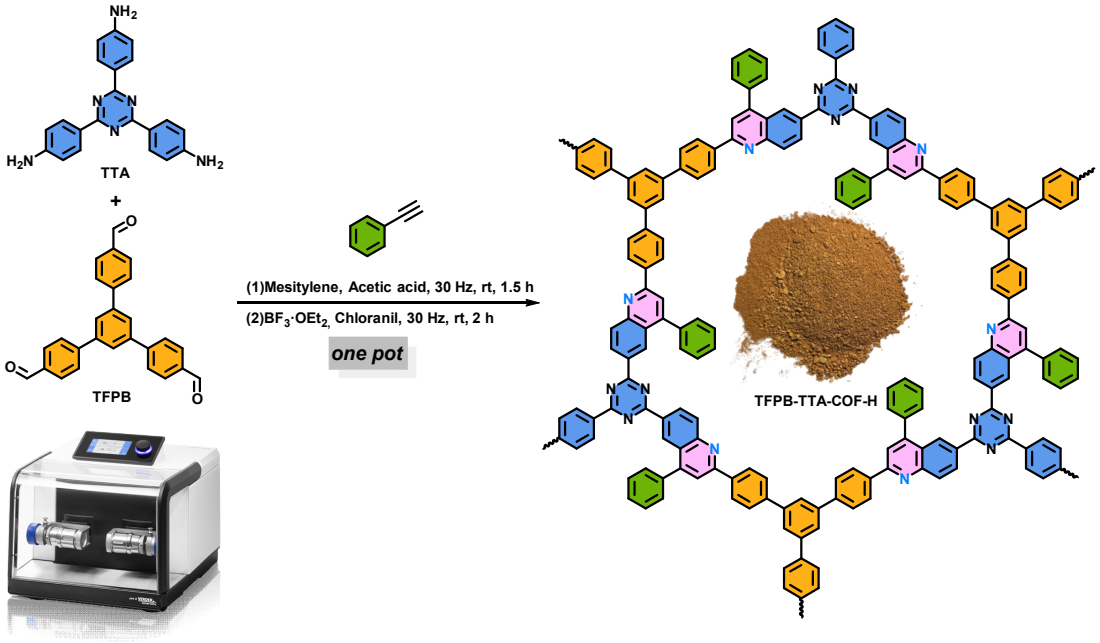

Fig. S19. Mechanochemical synthesis of TFPB-TTA-COF-H.

Into a 10 mL stainless steel milling jar, 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA) (99.2 mg, 0.28 mmol), 1,3,5-tris(4-formylphenyl)benzene (TFPB) (109.3 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, phenylacetylene (92 μL, 0.84 mmol), $BF_3 \cdot OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 ℃ under a high vacuum overnight to produce TFPB-TTA-COF-H in an isolated yield of 68.1 % (176.7 mg).

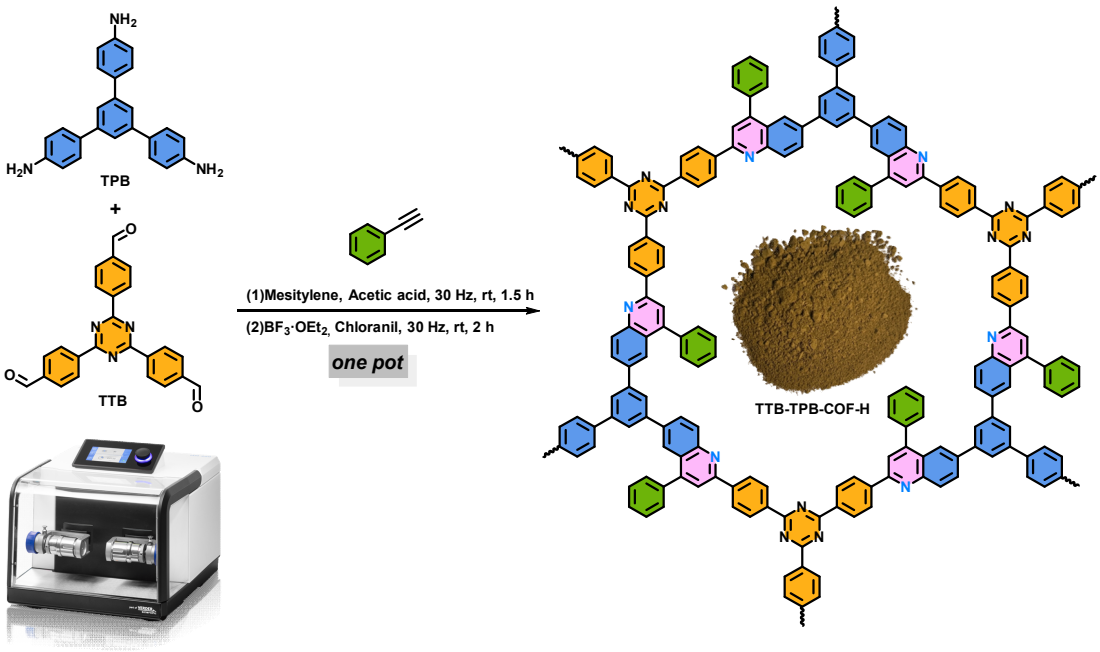

Fig. S20. Mechanochemical synthesis of TTB-TPB-COF-H.

Into a 10 mL stainless steel milling jar, 1,3,5-tri(4-aminophenyl)benzene (TPB) (98.4 mg, 0.28 mmol), 4,4',4"-(1,3,5-triazine-2,4,6-triyl) tribenzaldehyde (TTB) (110.1 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, phenylacetylene (92 μL, 0.84 mmol), $BF_3 \cdot OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TTB-TPB-COF-H in an isolated yield of 92.2 % (255.9 mg).

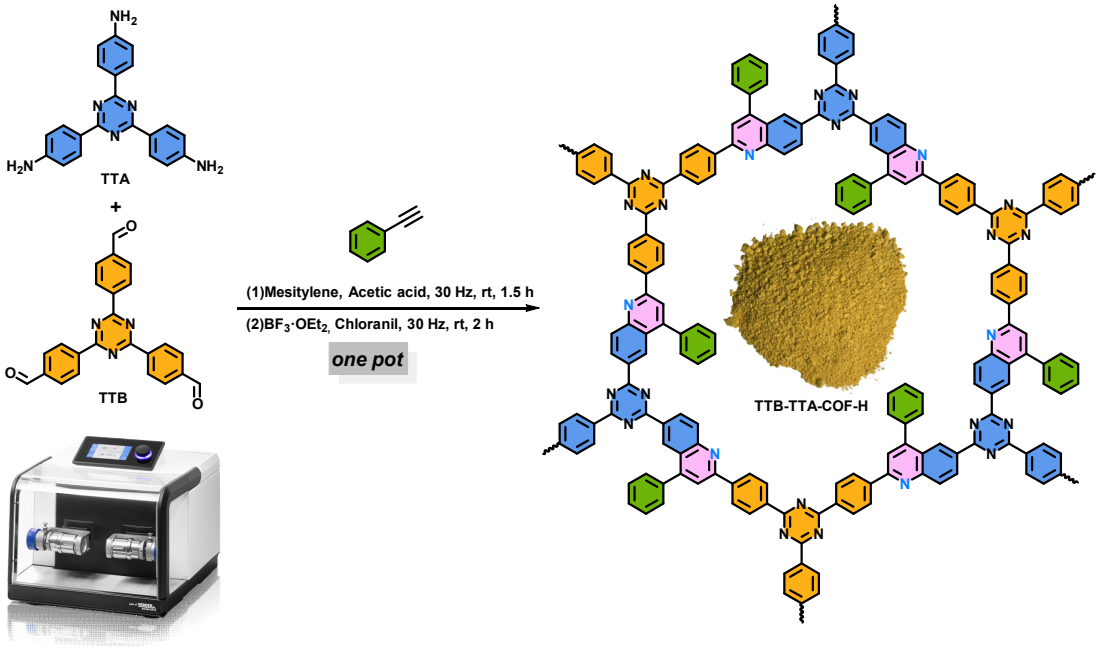

Fig. S21. Mechanochemical synthesis of TTB-TTA-COF-H.

Into a 10 mL stainless steel milling jar, 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA) (99.2 mg, 0.28 mmol), 4,4',4"-(1,3,5-triazine-2,4,6-triyl) tribenzaldehyde (TTB) (110.1 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, phenylacetylene (92 μL, 0.84 mmol), $BF_3 \cdot OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TTB-TTA-COF-H in an isolated yield of 90.5 % (251.3 mg).

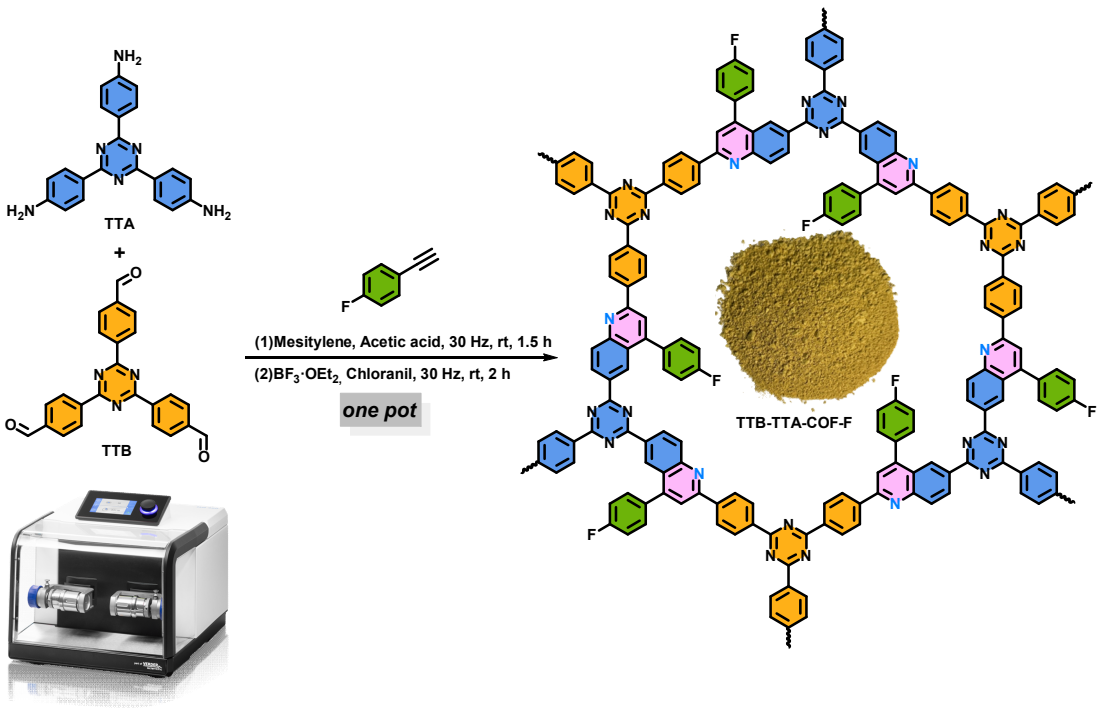

Fig. S22. Mechanochemical synthesis of TTB-TTA-COF-F.

Into a 10 mL stainless steel milling jar, 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA) (99.2 mg, 0.28 mmol), 4,4',4"-(1,3,5-triazine-2,4,6-triyl) tribenzaldehyde (TTB) (110.1 mg, 0.28 mmol), mesitylene (160 μL), and glacial acetic acid (80 μL) were added along with four 4 mm steel balls. The reaction mixture was milled in a Retsch MM 400 Mixer Mill at 30 Hz for 1.5 h at room temperature. After that, 4-fluorophenylacetylene (96 μL, 0.84 mmol), $BF_3{\cdot}OEt_2$ (41.5 μL, 0.34 mmol), and chloranil (82.6 mg, 0.34 mmol) were added to the stainless steel milling jar, and the mixture was further milled at 30 Hz for 2 h at room temperature. The solid in the stainless steel milling jar was removed, immersed in N,N-dimethylformamide (DMF) in a small glass vial, and ultrasonically dispersed for 2 min. The sample was transferred to a suction funnel, washed first with N,N-dimethylformamide (DMF) and then with acetone until the filtrate was colorless. It was transferred to filter paper and purified by Soxhlet extraction (using tetrahydrofuran) for 24 h. The wet powder was dried at 110 °C under a high vacuum overnight to produce TTB-TTA-COF-F in an isolated yield of 87.6 % (256.3 mg).

Characterizations of COF Materials

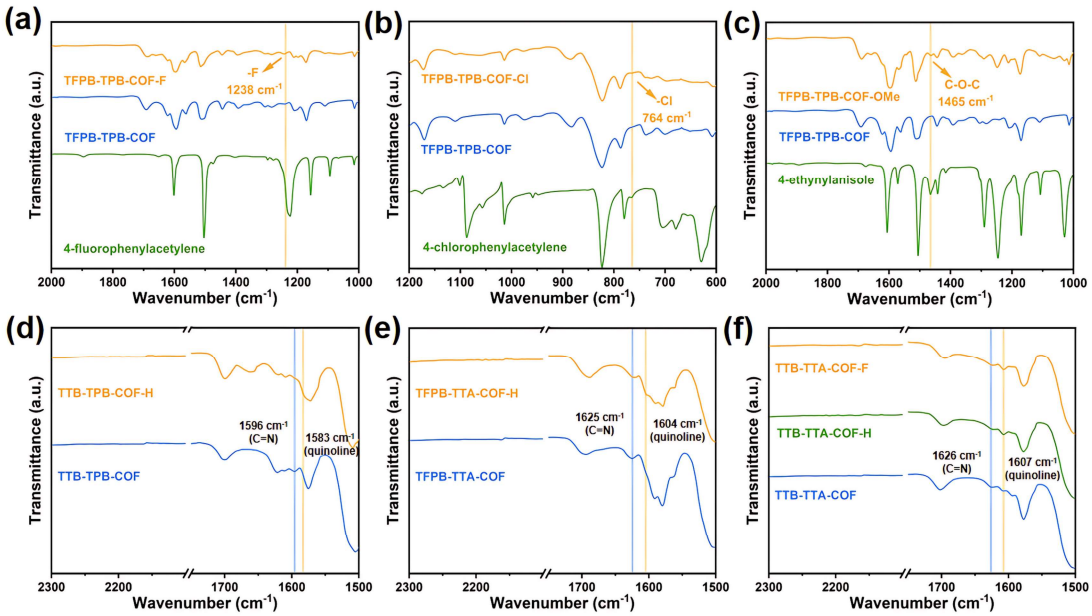

Fig. S23. FT-IR spectra of a) TTB-TPB-COF, b) TFPB-TTA-COF and c) TTB-TTA-COF and there corresponding monomers. FT-IR spectra of d) TTB-TPB-COF, e) TFPB-TTA-COF and f) TTB-TTA-COF before and after imine-to-quinoline conversion.

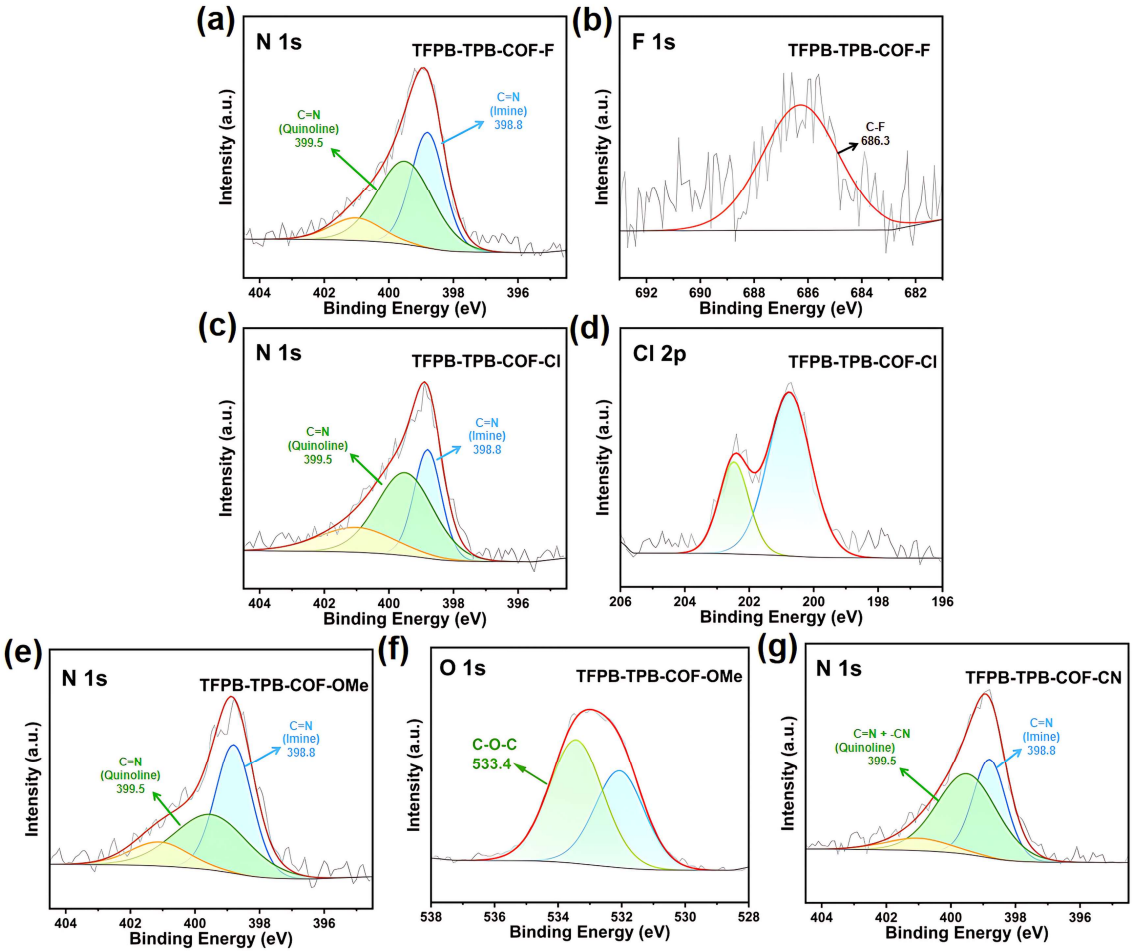

Fig. S24. High resolution N 1s XPS spectra of a) TFPB-TPB-COF-F, c) TFPB-TPB-COF-Cl, e) TFPB-TPB-COF-OMe, g) TFPB-TPB-COF-CN. F 1s XPS spectrum of b) TFPB-TPB-COF-F. Cl 2p deconvolution spectra of d) TFPB-TPB-COF-Cl. O 1s XPS spectrum of f) TFPB-TPB-COF-OMe.Note: The N1s peak centered at 401 eV is assigned to the unreacted -NH_2 at the defective edges of COF (yellow area).

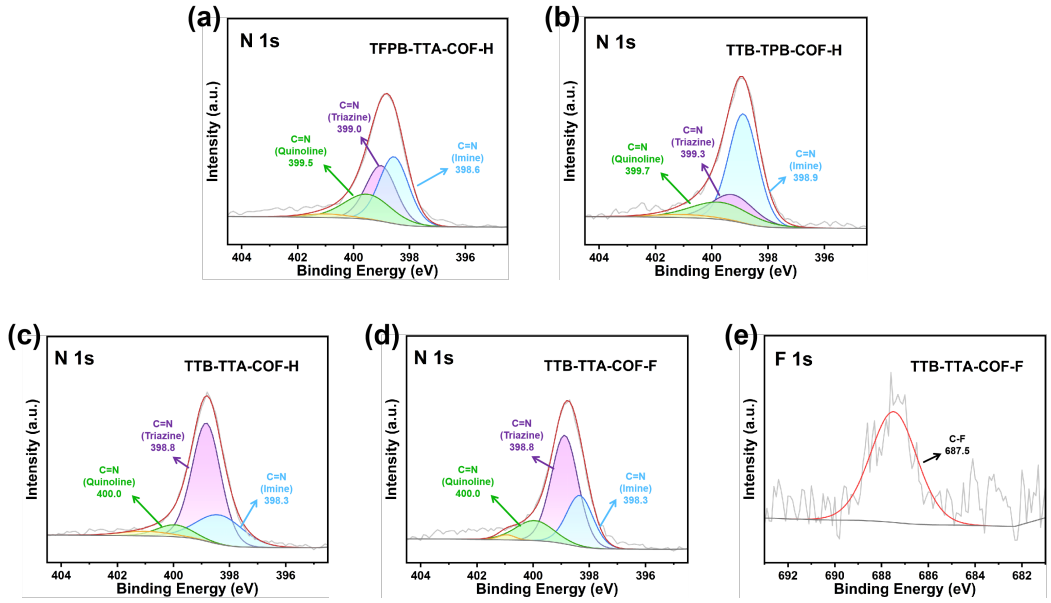

Fig. S25. The high resolution XPS N 1s deconvolution spectra of a) TFPB-TTA-COF-H, b) TTB-TPB-COF-H, c) TTB-TTA-COF-H and d) TTB-TTA-COF-F. F 1s XPS spectrum of e) TTB-TTA-COF-F containing pentafluoro benzene. Note: The N1s peak centered at 401 eV is assigned to the unreacted -NH_2 at the defective edges of COF.

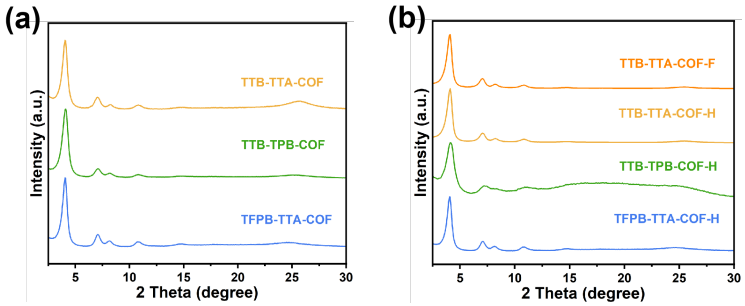

Fig. S26. a) PXRD patterns of TFPB-TTA-COF (blue), TTB-TPB-COF (green) and TTB-TTA-COF (yellow). b) PXRD patterns of TFPB-TTA-COF-H (blue), TTB-TPB-COF-H (green), TTB-TTA-COF-H (yellow) and TTB-TTA-COF-F (orange).

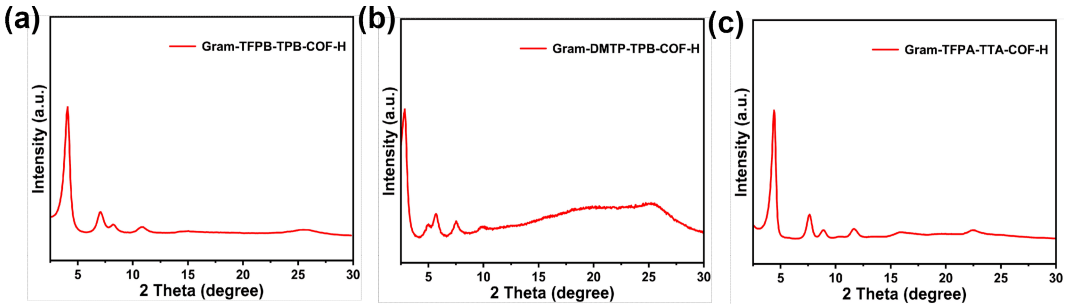

Fig. S27. PXRD patterns of a) Gram-TFPB-TPB-COF-H, b) Gram-DMTP-TPB-COF-H and c) Gram-TFPA-TTA-COF-H Prepared via Gram-Scale Synthesis.

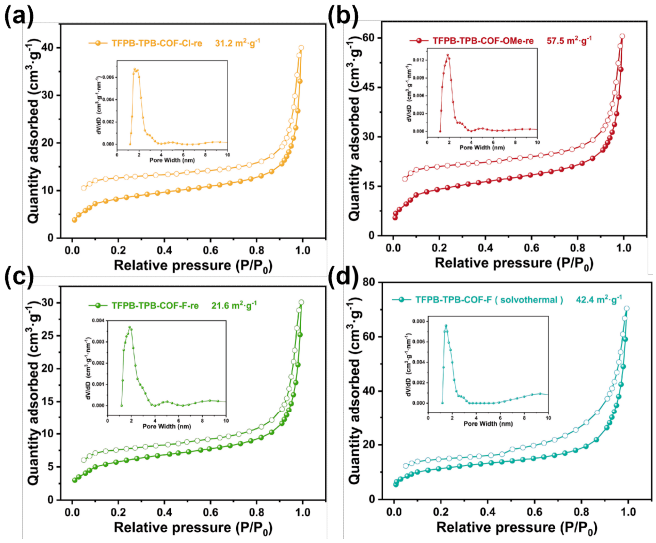

Fig. S28. N_2 adsorption–desorption isotherms and corresponding pore-size distributions of a) TFPB-TPB-COF-Cl-re, b) TFPB-TPB-COF-OMe-re, c) TFPB-TPB-COF-F-re and d) TFPB-TPB-COF-F (solvothermal).

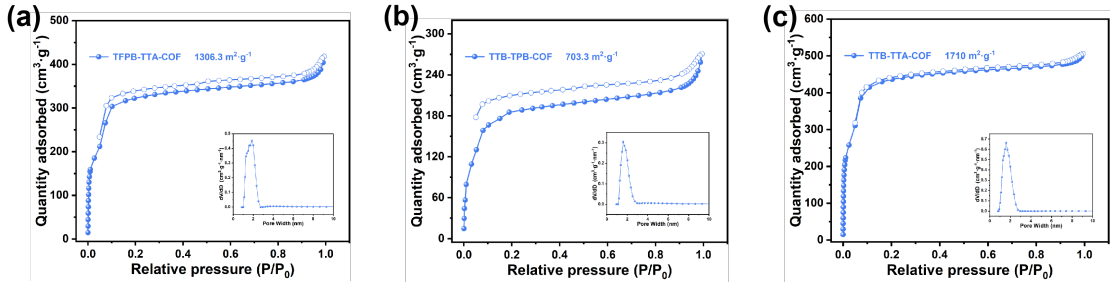

Fig. S29. N_2 adsorption–desorption isotherms and corresponding pore-size distributions of a) TFPB-TTA-COF, b) TTB-TPB-COF and c) TTB-TTA-COF.

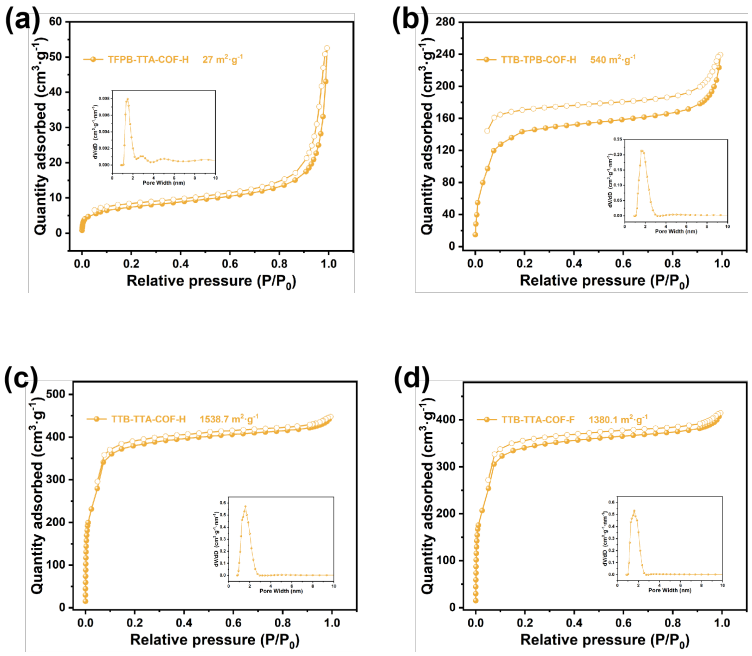

Fig. S30. N_2 adsorption–desorption isotherms and corresponding pore-size distributions of a) TFPB-TTA-COF-H, b) TTB-TPB-COF-H, c) TTB-TTA-COF-H and d) TTB-TTA-COF-F.

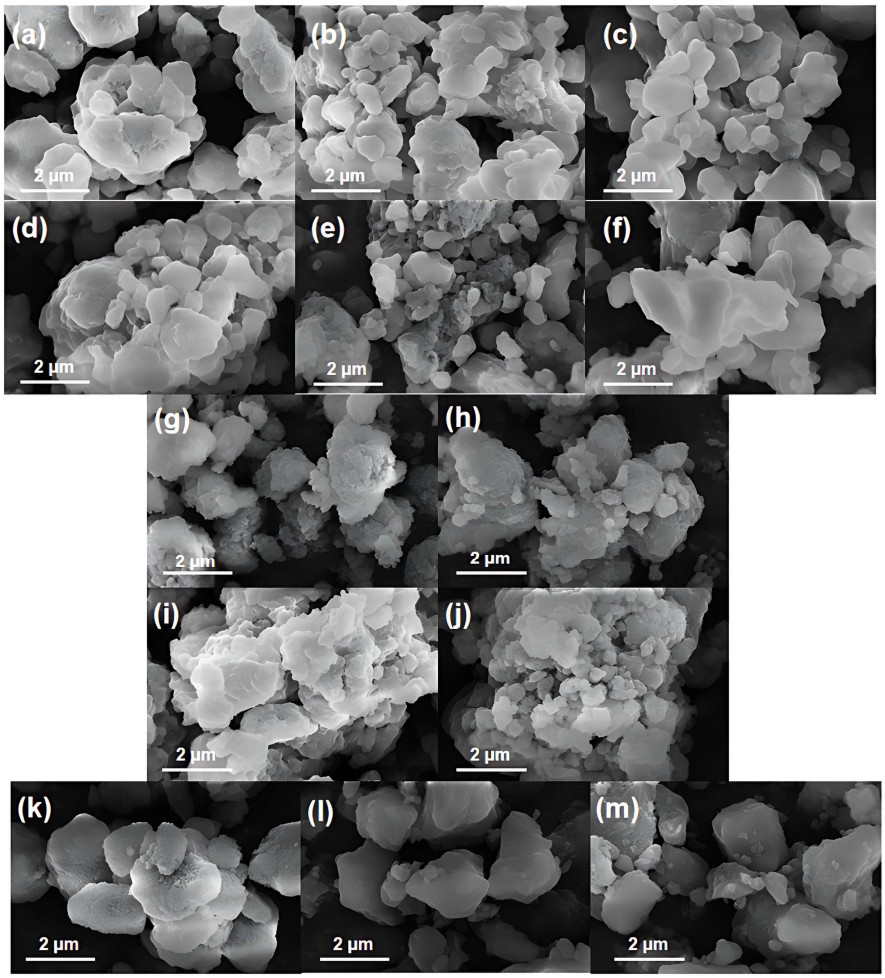

Fig. S31. SEM images of a) TFPB-TPB-COF, b) TFPB-TPB-COF-H, c) TFPB-TPB-COF-F, d) TFPB-TPB-COF-Cl, e) TFPB-TPB-COF-Ome, f) TFPB-TPB-COF-CN, g) TFPB-TTA-COF, h) TFPB-TTA-COF-H, i) TTB-TPB-COF, j) TTB-TPB-COF-H, k) TTB-TTA-COF, l) TTB-TTA-COF-H and m) TTB-TTA-COF-F.

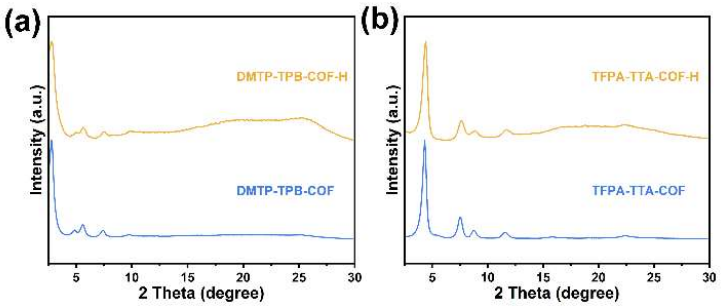

Fig. S32. a) PXRD patterns of DMTP-TPB-COF and DMTP-TPB-COF-H. b) PXRD patterns of TFPA-TTA-COF and TFPA-TTA-COF-H.

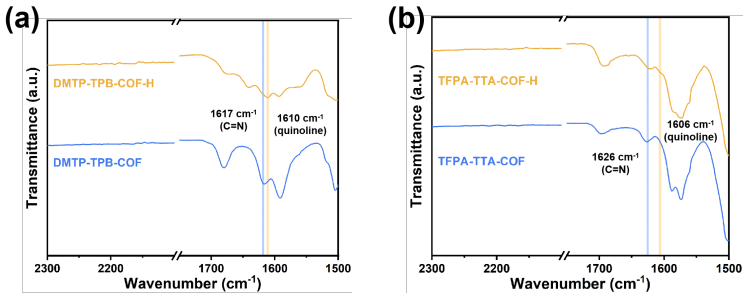

Fig. S33. FT-IR spectra of a) DMTP-TPB-COF, and c) TFPA-TTA-COF before and after imine-to-quinoline conversion.

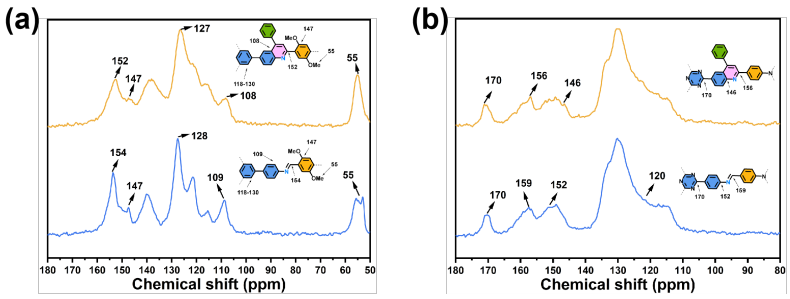

Fig. S34. The blue line represents the solid-state ^{13}C nuclear magnetic resonance (NMR) spectrum of DMTP-TPB-COF, and the yellow line represents the solid-state ^{13}C NMR spectrum of DMTP-TPB-COF-H. b) The blue line represents the solid-state ^{13}C NMR spectrum of TFPA-TTA-COF, and the yellow line represents the solid-state ^{13}C NMR spectrum of TFPA-TTA-COF-H.

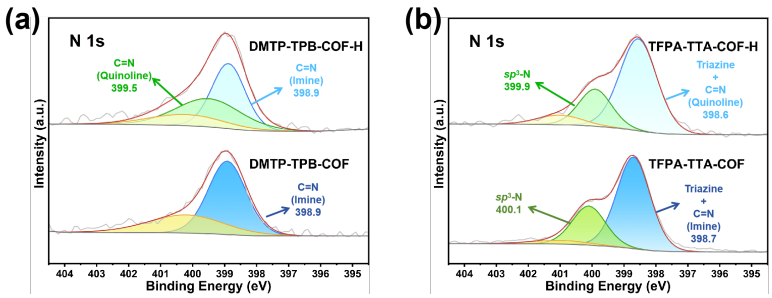

Fig. S35. The high resolution XPS N 1s deconvolution spectra of a) DMTP-TTA-COF and b) TFPA-TPB-COF before and after imine-to-quinoline conversion.

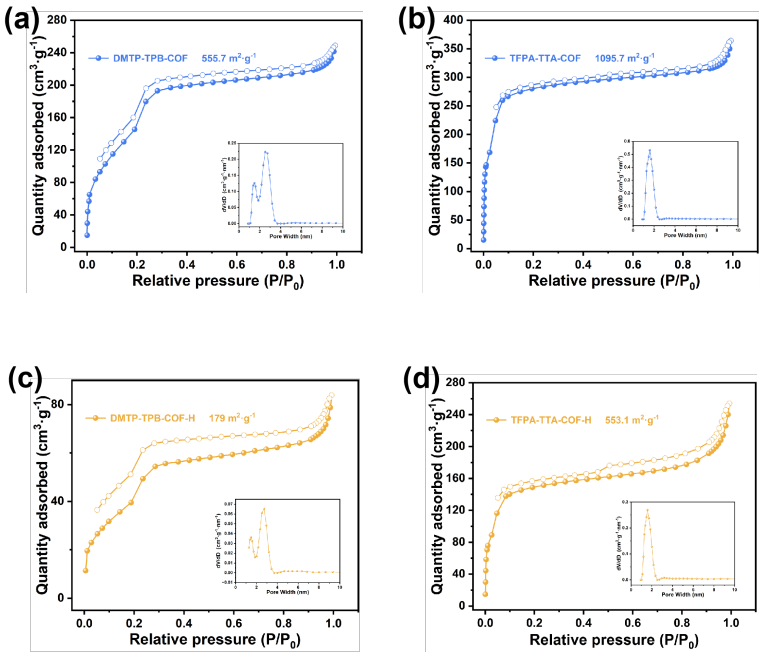

Fig. S36. N_2 adsorption–desorption isotherms and corresponding pore-size distributions of a) DMTP-TPB-COF, b) TFPA-TTA-COF, c) DMTP-TPB-COF-H and d) TFPA-TTA-COF-H.

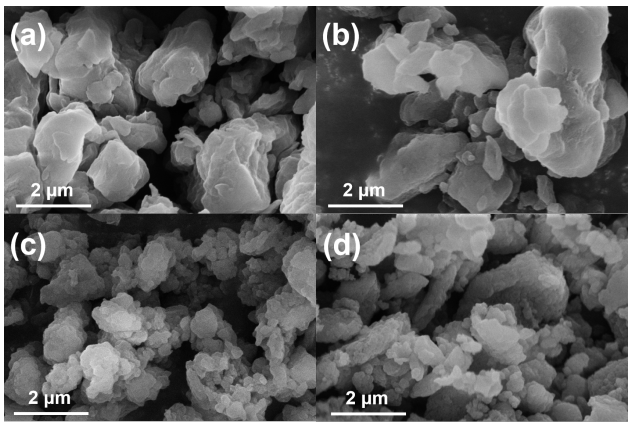

Fig. S37. SEM images of a) DMTP-TPB-COF, b) DMTP-TPB-COF-H, c) TFPA-TTA-COF and d) TFPA-TTA-COF-H.

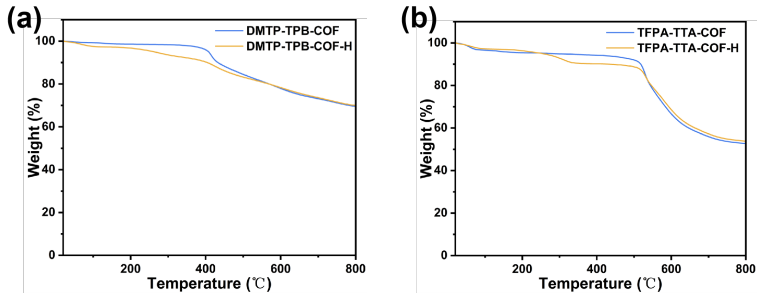

Fig. S38. TGA profiles of a) DMTP-TTA-COF and b) TFPA-TPB-COF before and after imine-to-quinoline conversion, tested under N_2 with rate 10 °C/min.

Chemical Stability Test

The as-synthesized TFPB-TPB-COF and TFPB-TPB-COF-H were separately placed in glass vials containing 5 mL of respective test media: both COFs were exposed to 12 M HCl, 12 M NaOH, 5 M $KMnO_4$ (in acetonitrile), and 5 M $NaBH_4$ (in THF); additionally, TFPB-TPB-COF-H was further tested in DMSO, ethanol, acetonitrile, and H_2O. A magnetic stir bar was added to each vial, and all mixtures were stirred for 72 h. Subsequently, the samples were transferred to a Buchner funnel, washed sequentially with distilled water and THF until the filtrate became colorless. The washed samples were dried overnight at 110 °C under high vacuum, followed by powder X-ray diffraction (PXRD) measurements.

One-Pot Mechanochemical vs Solvothermal Routes

Table S1. Summary and comparison of synthesis methods for five representative quinoline-linked COFs.

Quinoline-linked COFs	Solvent	Temp (℃)	Time (h)	Atmosphere	Crystallinity	Yield (%)	BET surface area (m^2/g)	Ref
TTB-TTA-COF-H	dioxane, mesitylene/toluene	120	72/48	vacuum/N_2	high	NR	709.1	38
	o-DCB, *n*-BuOH	120	72	N_2	high	76.3	921.5	18
	o-DCB, *n*-BuOH	120	72	vacuum/N_2	high	95	1739	17
	mesitylene	RT	3.5	air	high	90.5	1538.7	This work
TTB-TTA-COF-F	dioxane, mesitylene/DMF	120/110	72/72	vacuum/N_2	high	NR	1716.1	41
	mesitylene	RT	3.5	air	high	87.6	1380.1	This work
TTB-TPB-COF-H	o-DCB, *n*-BuOH	120	72	vacuum/N_2	high	73	1590	42
	mesitylene	RT	3.5	air	high	92.2	540	This work
DMTP-TPB-COF-H	o-DCB, *n*-BuOH	120	72	N_2	high	95	1305.4	16
	o-DCB,	120/110	72/72	vacuum/N_2	high	NR	955	15

	n-BuOH/toluene							
	o-DCB, *n*-BuOH/toluene	120/110	72/72	vacuum/N_2	high	NR	940	19
	mesitylene	RT	3.5	air	high	78.9	179	This work
TFPA-TTA -COF-H	dioxane, mesitylene	120	72	vacuum/N_2	high	78.2	1058.9	14
	dioxane, mesitylene	120	72	vacuum/N_2	high	89	1720	40
	mesitylene	RT	3.5	air	high	68.6	553.1	This work

Note: In the table, the expression logic of process parameters is as follows: For the stepwise process, the parameters are presented as "120 ℃/110 ℃" and "72 h/72 h", where the parameters before the "/" correspond to the first-step process conditions (120 ℃, 72 h), and those after the "/" correspond to the second-step process conditions (110 ℃, 72 h); for the one-pot process, the parameters are directly denoted as 120 ℃ and 72 h; RT: room-temperature; "NR": not reported in the literature.