Supporting Information

Modular Total Synthesis in Reticular Chemistry

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Materials and Instrumentation

All reagents and solvents were commercially available and used as received.

N_2 sorption isotherms. Gas sorption measurements were conducted using a Micromeritics ASAP 2020 system. Prior to gas sorption measurements, about 50-100 mg samples were washed thoroughly with fresh DMF and exchanged by chloroform for 3 times, during which the solvent was decanted and freshly replenished three times every day. The solvent was then removed under vacuum at 85 ^{o}C for 12 h, yielding porous material.

Powder X-ray diffraction (PXRD). PXRD was carried out with a Bruker D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at 40 kV and 40 mA.

^{1}H NMR spectroscopy. Nuclear magnetic resonance (NMR) data were collected on an Inova 500 spectrometer.

Scanning electron microscopy (SEM). Images and analyses of SEM/EDX were taken by FEI Quanta 600 FE-SEM. The Quanta 600 FEG is a field emission scanning electron microscope capable of generating and collecting high-resolution and low-vacuum images. It is equipped with a motorized x-y-z-tilt-rotate stage, providing the following movements: x = y = 150 mm (motorized); z = 65 mm (motorized); Tilt +70 degrees to –5 degrees (motorized); Source: Field emission gun assembly with Schottky emitter source. Voltage: 200 V to 30 kV. Beam Current: >100 nA.

Synthesis and Charactization

Crystallization of single-crystalline COF-303. COF-303 was synthesized on the basis of a previous report.[1] A vial was charged with tetrakis(4-formylphenyl)methane (TFM, 10.8 mg, 0.025 mmol), aniline (0.12 mL, 52 equiv.), and 0.25 mL of 1,4-dioxane, then 0.1 mL of aqueous acetic acid (6 M) was added to the solution. Phenylenediamine (PDA, 5.4 mg, 0.05 mmol) dissolved in 1,4-dioxane (0.25 mL) was then added. Then the mixture was allowed to further stand at ambient temperature. The single crystals of COF-303 then slowly crystallized out at ambient temperature and the crystal size reached ~15 μm in 15 days.

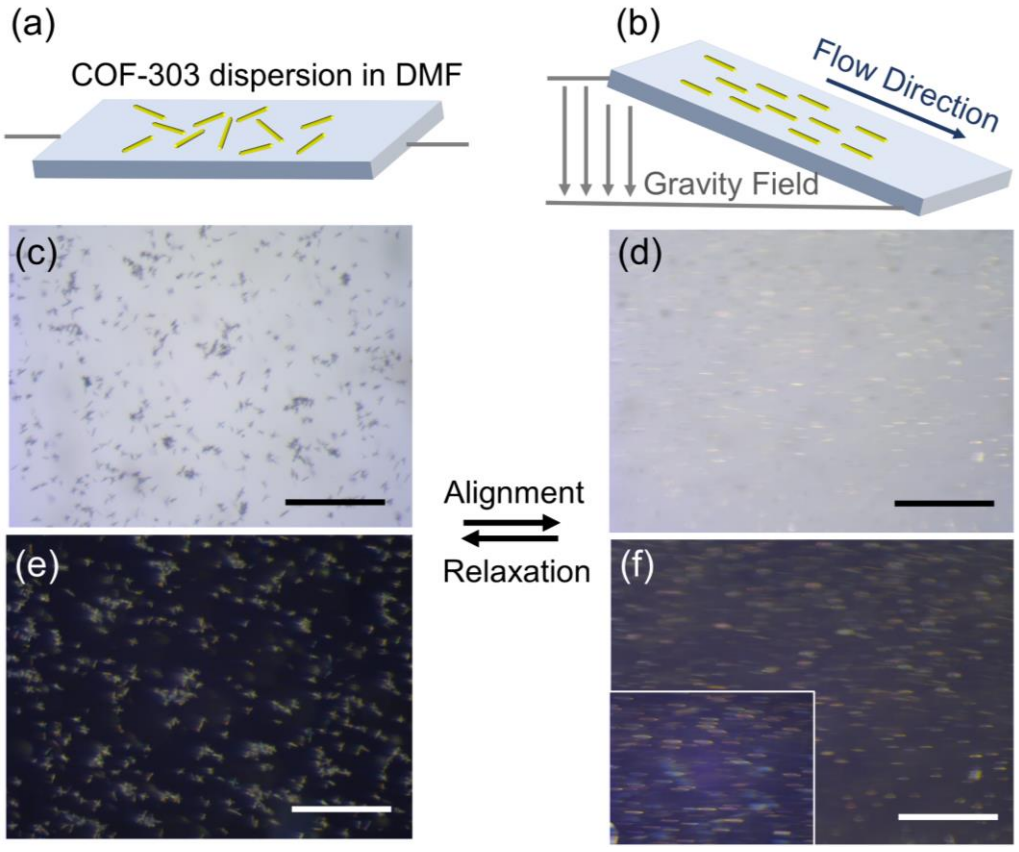

Figure S1. Gravitational field alignment of COF microrods. (a-b) Illustration of the reversible alignment and relaxation of COF-303 microrods in a DMF flow when exposed to a gravitational field. (c, e) Optical image and the corresponding polarized optical images of COF-303 microrods dispersed in a DMF solution. (d, f) Optical image and the corresponding polarized optical images of well-aligned COF-303 microrods in a DMF flow when the sample was inclined. Scale bar is 100 μm in (c-f).

Stability test of single-crystalline COF-303. About 5 mg COF-303 crystals were immersed into various solvent environments for 24 h, including organic solvents and aqueous solutions with varying pH values.

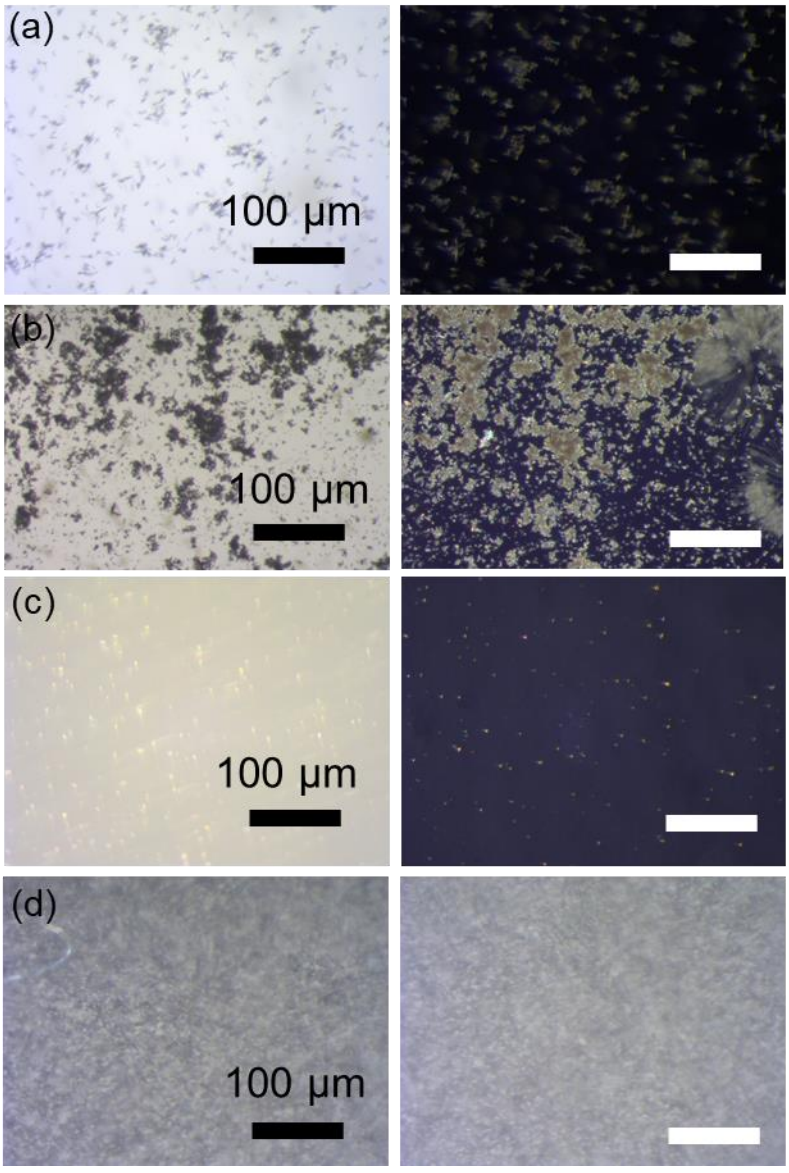

Figure S2. Optical images showing stability of COF-303 in various solvent environments for 24 h: (a) DMF; (b) pH = 7 aqueous solution; (c) pH = 1 aqueous solution; (d) UiO-67 precursor solutions. The COF-303 constructed from covalent bonds was robust enough to maintain the structural integrity under these harsh conditions.

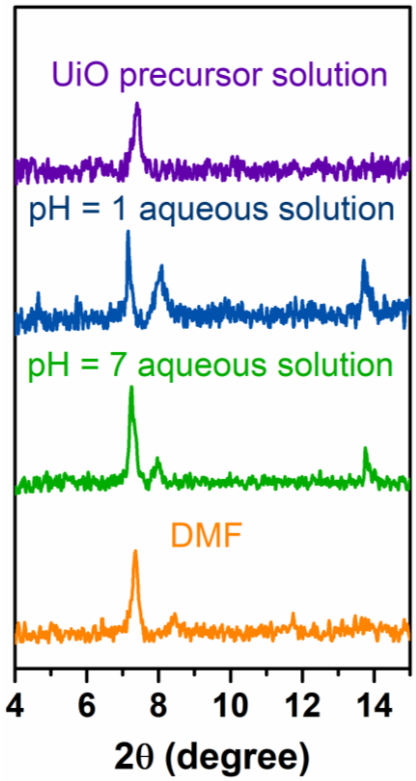

Figure S3. PXRD patterns showing high stability of COF-303 in various solvent environments for 24 h: DMF; pH = 7 aqueous solution; pH = 1 aqueous solution; and UiO-67 precursor solutions.

Synthesis of MOF-5. MOF-5 was synthesized on the basis of previous reports with slight modifications.[2] $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg), BDC (8.8 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h to generate the cubic crystals of MOF-5. The crystals of MOF-5 were collected by centrifugation and washed with fresh DMF for 3 times. Synthesis of MOF-5 under 100 ºC also generates similar cubic crystals.

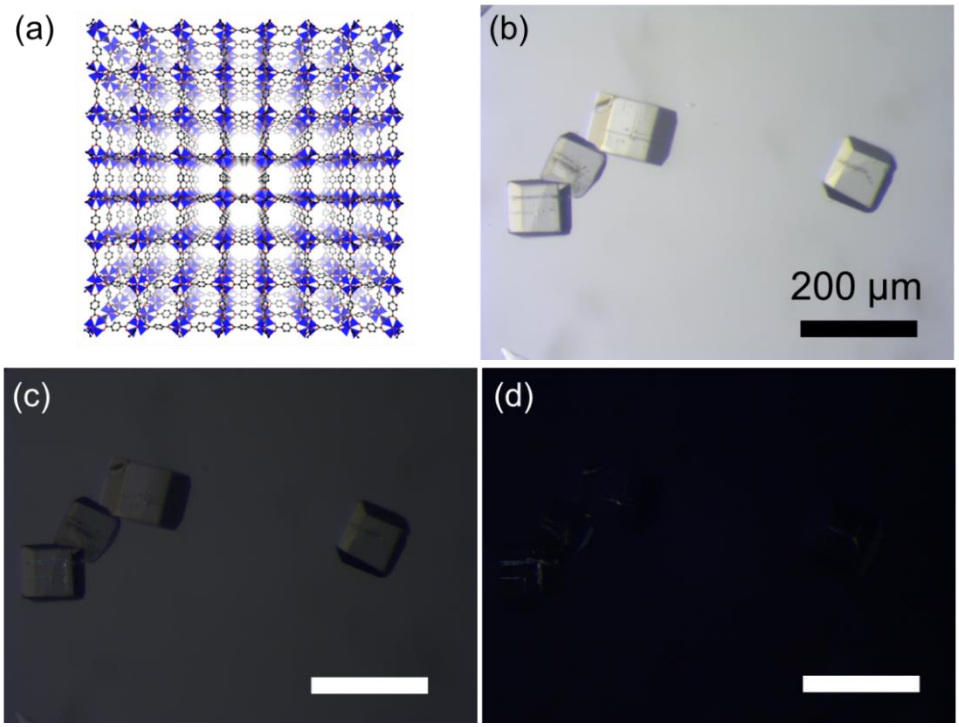

Figure S4. (a) The structure, (b) optical image and (c-d) the corresponding polarized optical images of MOF-5 crystals.

Synthesis of COF-303@MOF-5. COF-303 (1, 3 or 5 mg, respectively), H_2BDC (8.8 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h to generate the crystals of COF-303@MOF-5. The crystals were collected by centrifugation and washed with fresh DMF for 3 times. Various amounts of COF-303 can be immobilized into MOF-5 by tuning the initial amount during modular synthesis.

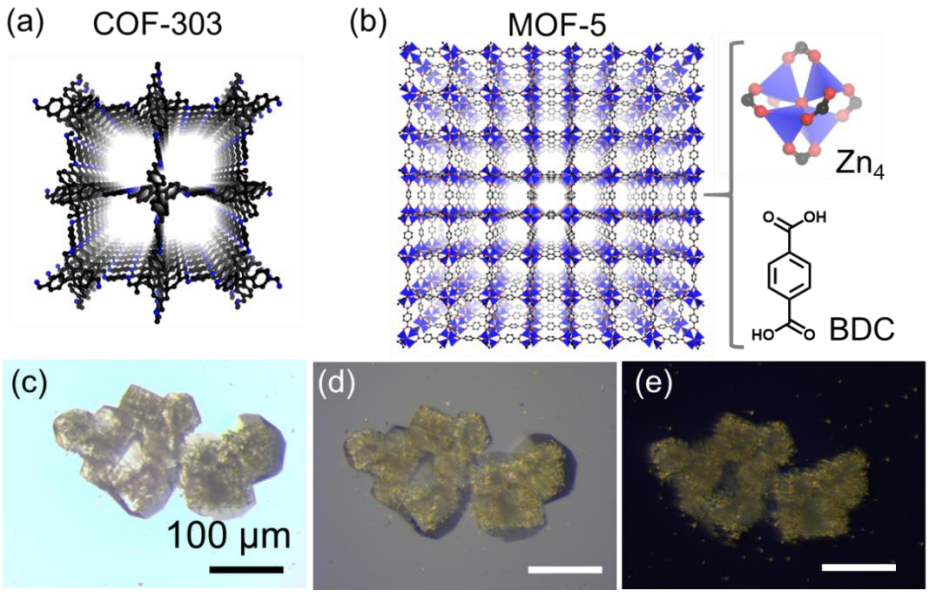

Figure S5. (a) The structure of COF-303 and (b) MOF-5, (c-e) optical images and the corresponding polarized optical images of COF-303@MOF-5 crystals.

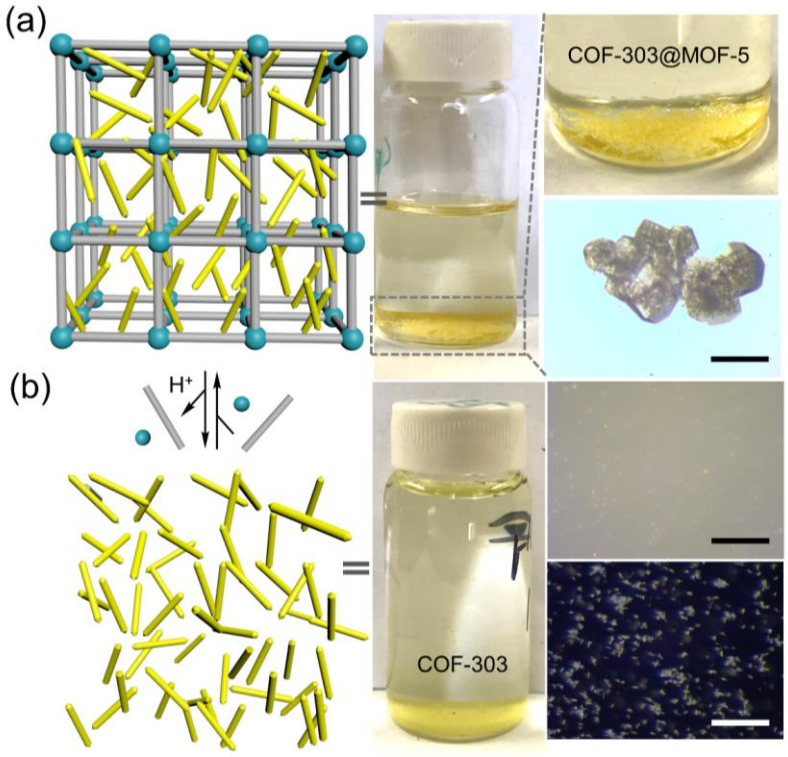

Figure S6. Optical image and the corresponding polarized optical images of COF-303@MOF-5 crystals (a) before and (b) after acid treatment. Scale bar is 100 μm.

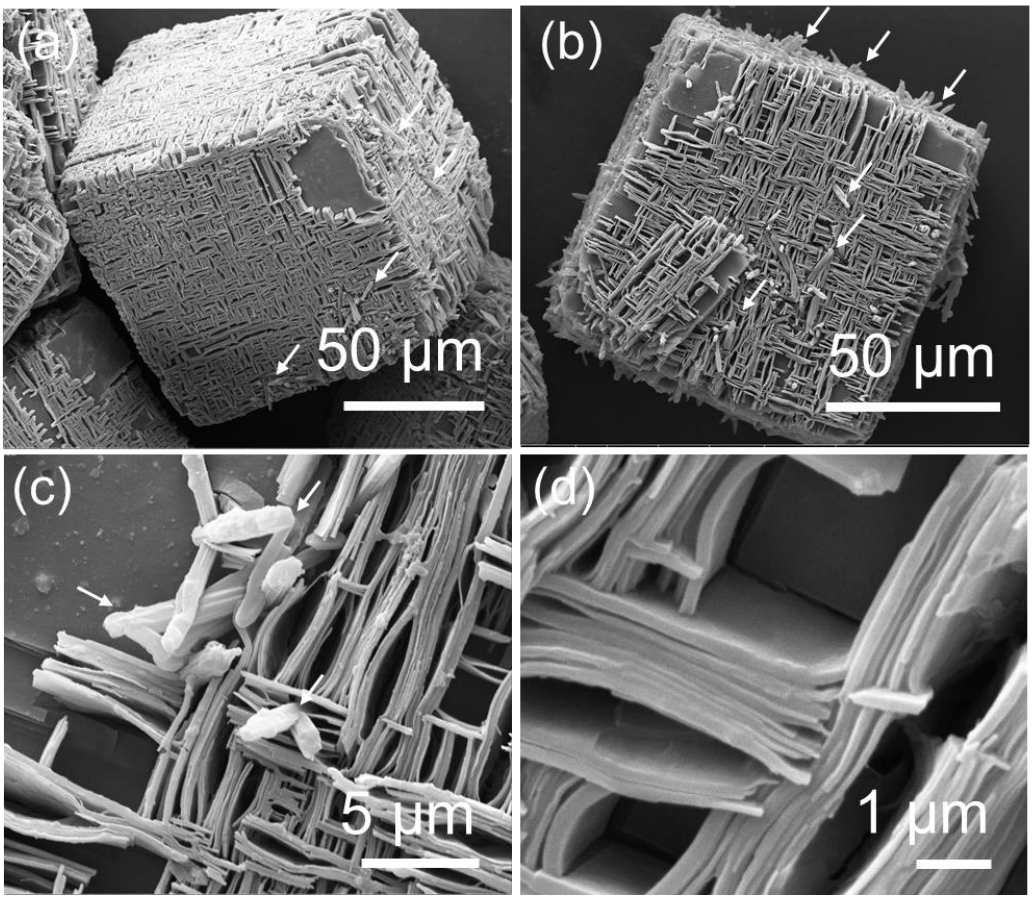

Figure S7. SEM images of the hierarchical COF-303@MOF-5 crystals: (a-b) the crystal of COF-303@MOF-5; (c-d) lamellar surface structures of COF-303@MOF-5. The white arrows indicate the positions of COF-303 microrods.

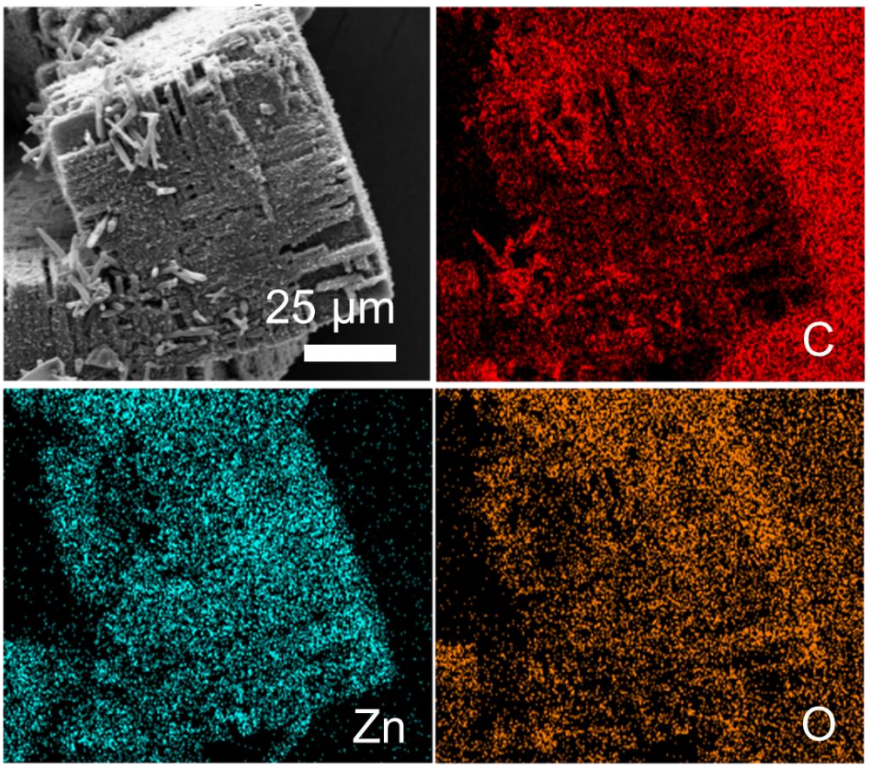

Figure S8. SEM images and EDS element mapping of COF-303@MOF-5 surfaces.

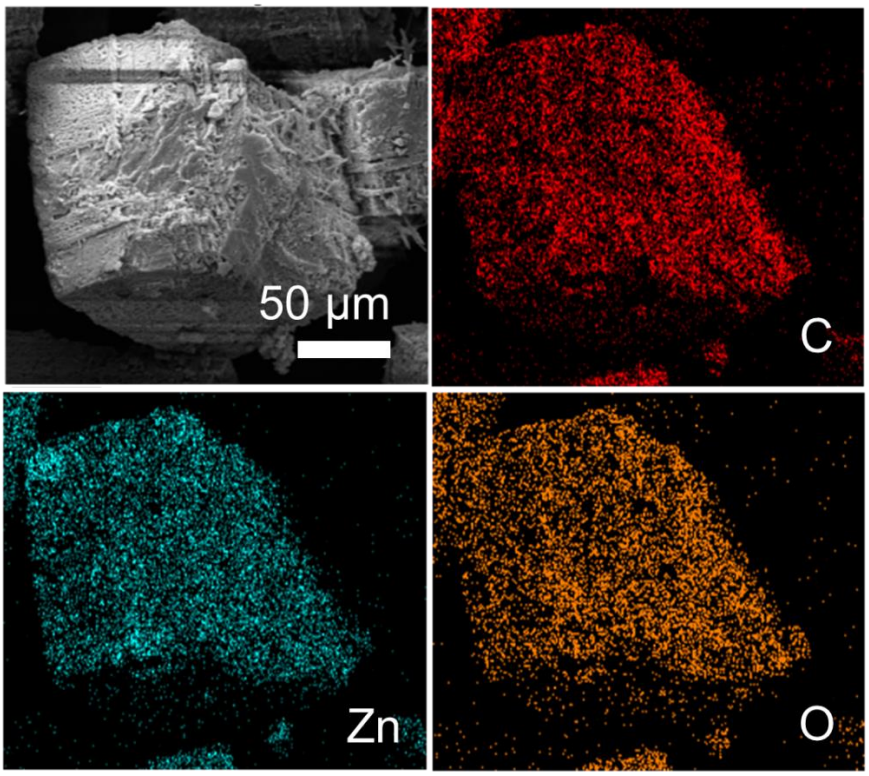

Figure S9. SEM images and EDS element mapping of a cracked COF-303@MOF-5 crystal showing the internal hierarchical structure.

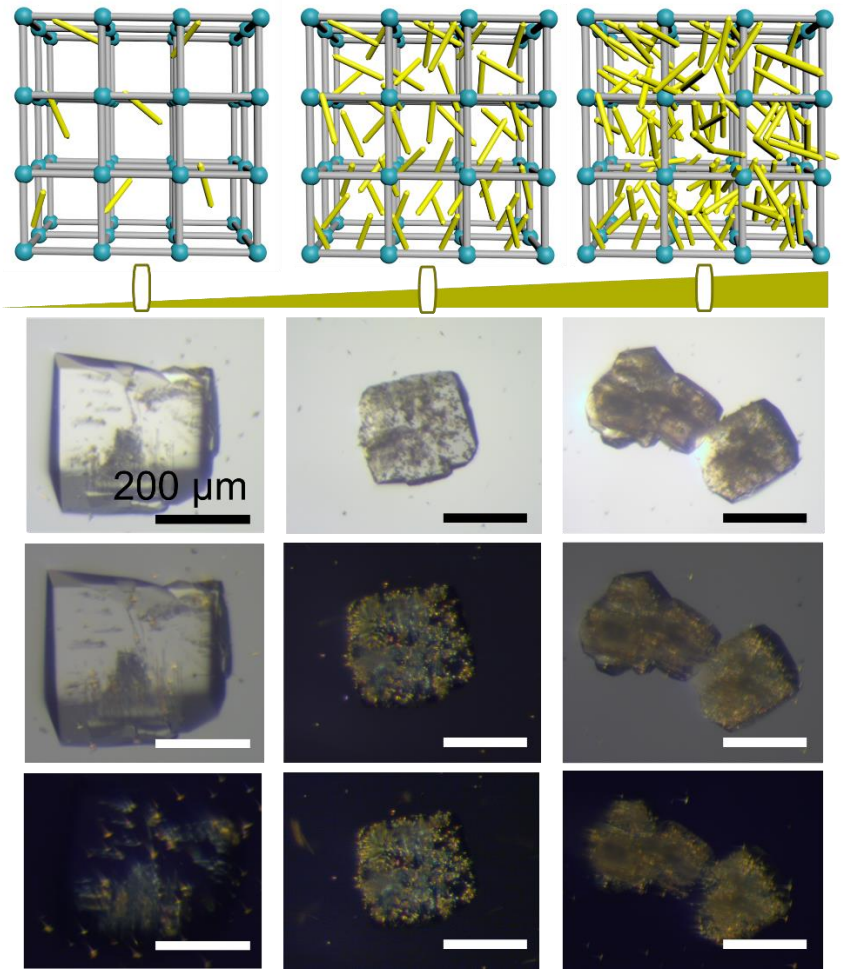

Figure S10. Various amounts of COF-303 can be immobilized into MOF-5 through modular synthesis. The corresponding polarized optical images placed in between crossed polarizers are also provided to visualize the apportion of COF microrods.

Table S1. Porosity parameter of COF-303@MOF-5, COF-303 and MOF-5.

Compounds	S_{BET}[a] (m^2g^{-1})	V_t[b] (cm^3g^{-1})	N_2 uptake (cm^3g^{-1})
COF-303@MOF-5	2682	1.033	667.6
COF-303	1487	0.648	418.8
MOF-5	3418	1.344	868.8

S_{BET}[a]: Brunauer-Emmett-Teller (BET) specific surface area; V_t[b]: total specific pore volume determined by using the adsorption branch of the N_2 isotherm at $P/P_0 = 0.95$.

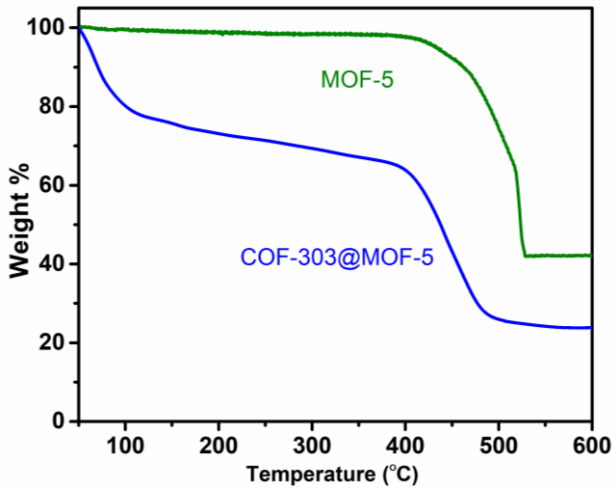

Figure S11. Thermogravimetric analysis (TGA) of MOF-5 and COF-303@MOF-5.

Synthesis of Janus COF-303@MOF-5. Before the addition of MOF-5 precursor, the COF-303 microrods (3 mg) were placed with 2 mL DEF in a Pyrex vial and centrifuged for ten minutes. H_2BDC (8.8 mg) and $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg) were subsequently added into the mixture. The mixture was heated in an 85 ºC oven for 24 h to generate the Janus crystals of COF-303@MOF-5. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

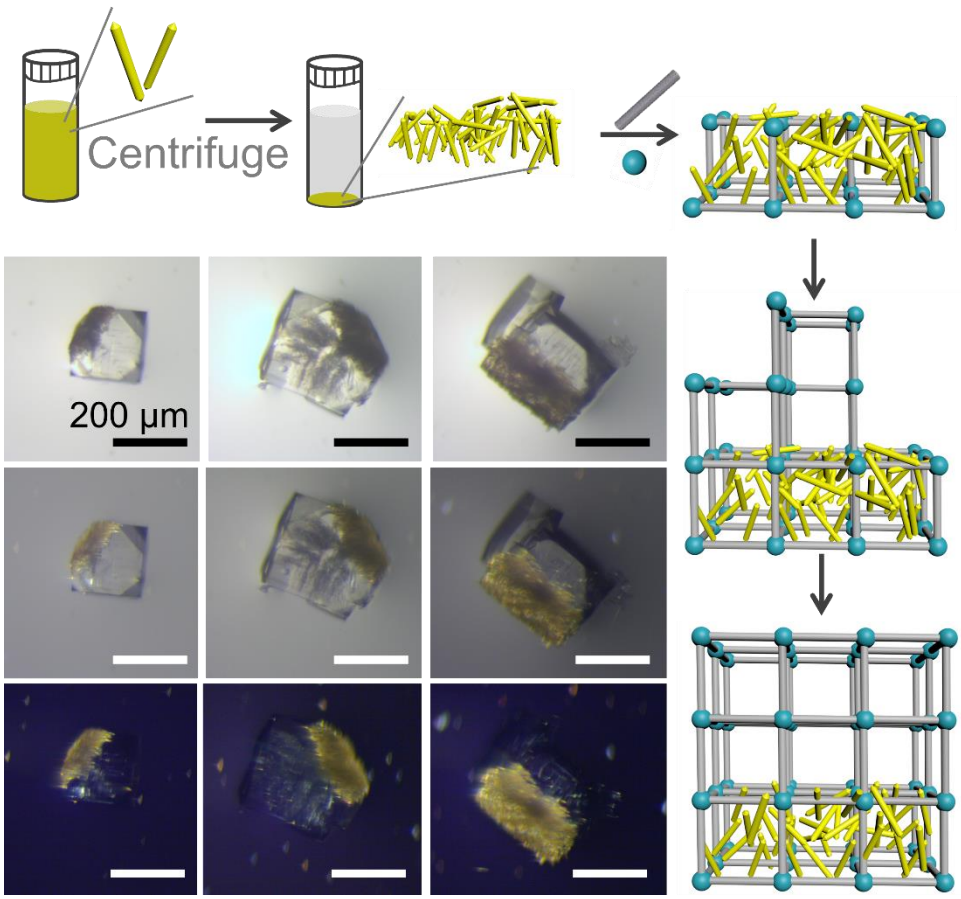

Figure S12. Models and optical images showing the preparation of Janus COF-303@MOF-5 crystals. The corresponding polarized optical images placed in between crossed polarizers are also provided to visualize the apportionment of COF microrods.

Synthesis of MOF-5-Br. MOF-5-Br was synthesized according to the literature with slight modification.[3] $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg), H_2BDC-Br (10 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in a 100 ºC oven for 24 h to generate the cubic crystals of MOF-5-Br. The crystals of MOF-5-Br were collected by centrifugation and washed with fresh DMF for 3 times.

Synthesis of COF-303@MOF-5-Br. COF-303 (5 mg), H_2BDC-Br (10 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h to generate the crystals of COF-303@MOF-5-Br. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

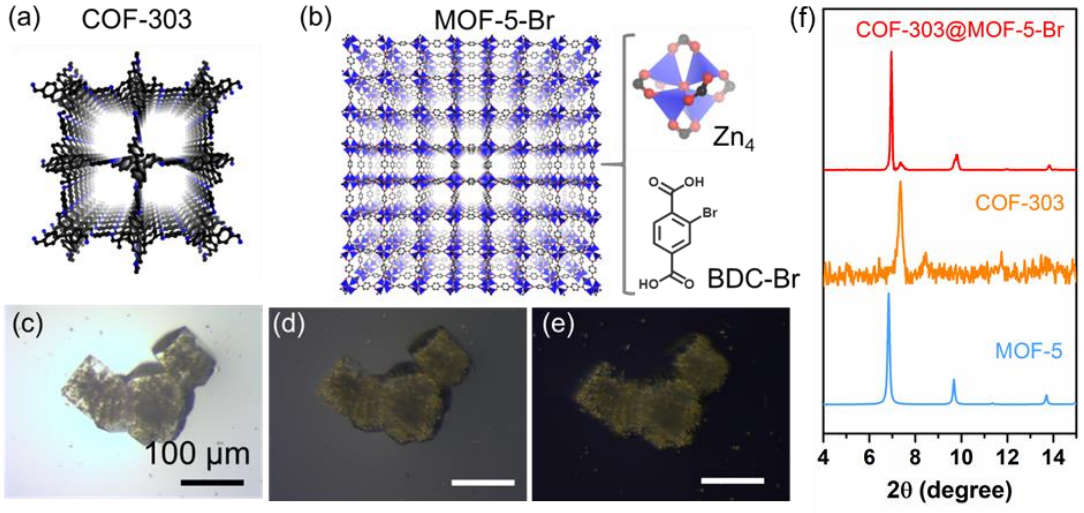

Figure S13. (a) The structure of COF-303 and (b) MOF-5-Br, (c-e) optical images and the corresponding polarized optical images, and (f) PXRD patterns of COF-303@MOF-5-Br crystals.

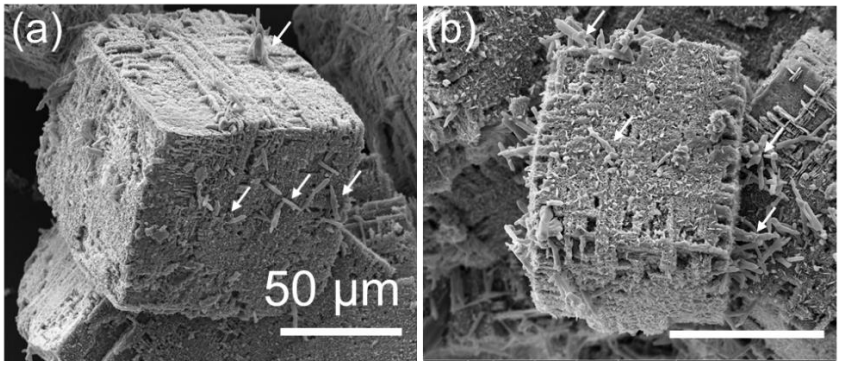

Figure S14. SEM images of COF-303@MOF-5-Br. The white arrows indicate the positions of COF-303 microrods.

Synthesis of MOF-5-1,4-NDC. MOF-5-1,4-NDC was synthesized according to the literature with slight modification.[3] $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg), 1,4-H_2NDC (12 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in a 100 ºC oven for 24 h to generate the cubic crystals of MOF-5-1,4-NDC. The crystals of MOF-5-1,4-NDC were collected by centrifugation and washed with fresh DMF for 3 times.

Synthesis of COF-303@MOF-5-NDC. COF-303 (5 mg), 1,4-H_2NDC (12 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h to generate the crystals of COF-303@MOF-5-NDC. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

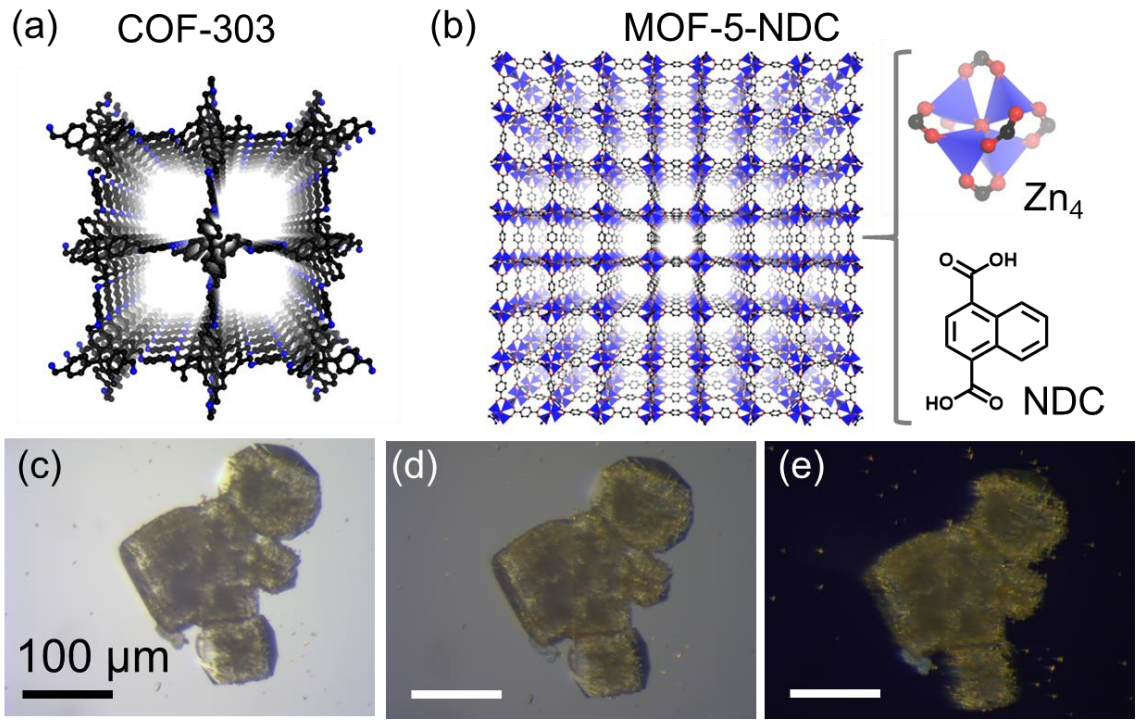

Figure S15. (a) The structure of COF-303 and (b) MOF-5-NDC, (c-e) optical images and the corresponding polarized optical images of COF-303@MOF-5-NDC crystals.

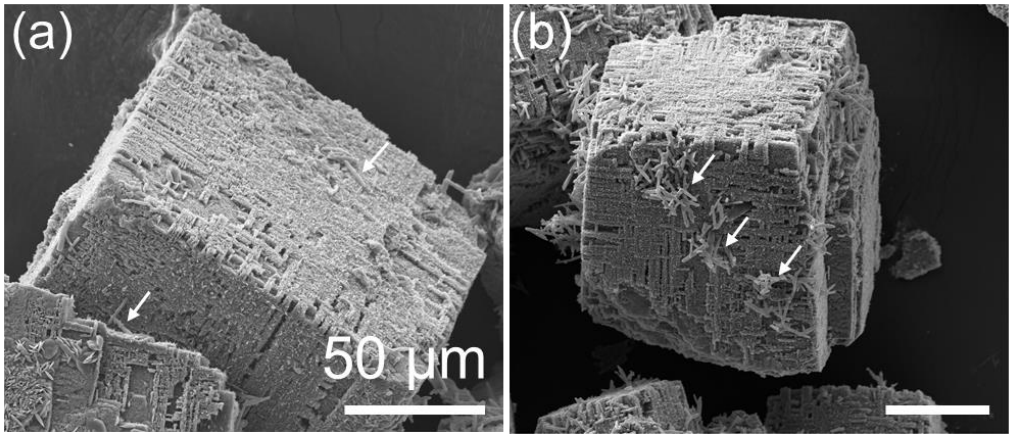

Figure S16. SEM images of COF-303@MOF-5-NDC. The white arrows indicate the positions of COF-303 microrods.

Synthesis of MOF-5-BPDC. MOF-5-BPDC was synthesized according to the literature with slight modification.[2] $Zn(NO_3)_2 \cdot 6H_2O$ (31 mg), H_2BPDC (5 mg) and DEF (16 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h to generate the cubic crystals of MOF-5-BPDC. The crystals of MOF-5-BPDC were collected by centrifugation and washed with fresh DMF for 3 times.

Synthesis of COF-303@MOF-5-BPDC. COF-303 (2 mg), H_2BPDC (5 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (31 mg) and DEF (16 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h to generate the crystals of COF-303@MOF-5-BPDC. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

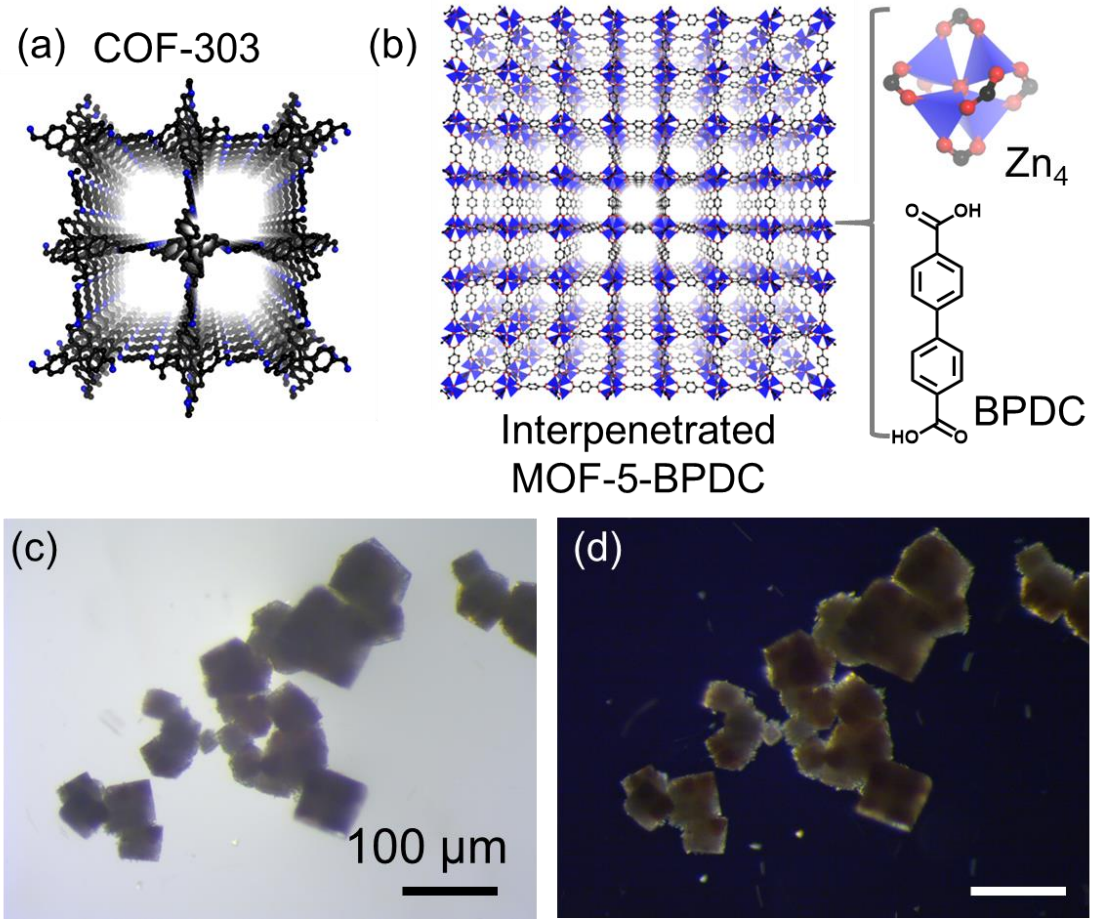

Figure S17. (a) The structure of COF-303 and (b) interpenetrated MOF-5-BPDC, (c-d) optical image and the corresponding polarized optical image of COF-303@ interpenetrated MOF-5-BPDC crystals.

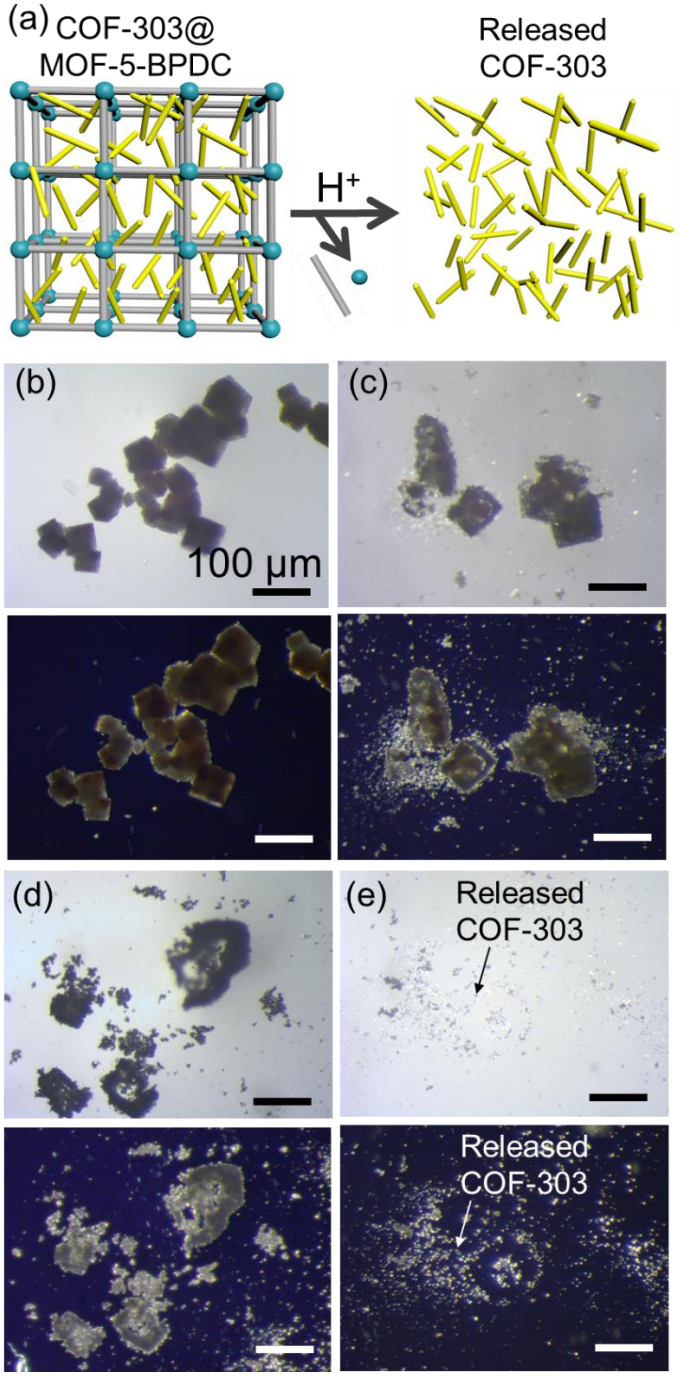

Figure S18. (a) Illustration of the decomposition of COF-303@MOF-5-BPDC under the treatment of HCl/DMF (1/5 v/v) solution; (b-e) Microscopic images of stepwise decomposition of COF-303@MOF-5-BPDC crystals under the treatment of HCl solution. (b) Before the addition of HCl solution, the COF-303@MOF-5-BPDC crystals displayed a multi-core-shell state; (c-e) after the acid addition, the MOF-5-BPDC crystals quickly dissolved from outside to inside, and released more acid-stable COF-303 crystals.

Synthesis of MOF-177. MOF-177 was synthesized according to the literature with slight modification.[4] $Zn(NO_3)_2 \cdot 6H_2O$ (20 mg), H_3BTB (5 mg) and DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in a 100 ºC oven for 24 h to generate the crystals of MOF-177. The crystals of MOF-177 were collected by centrifugation and washed with fresh DMF for 3 times.

Synthesis of COF-303@MOF-177. COF-303 (2 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (20 mg), H_3BTB (5 mg) and DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in a 100 ºC oven for 24 h to generate the crystals of COF-303@MOF-177. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

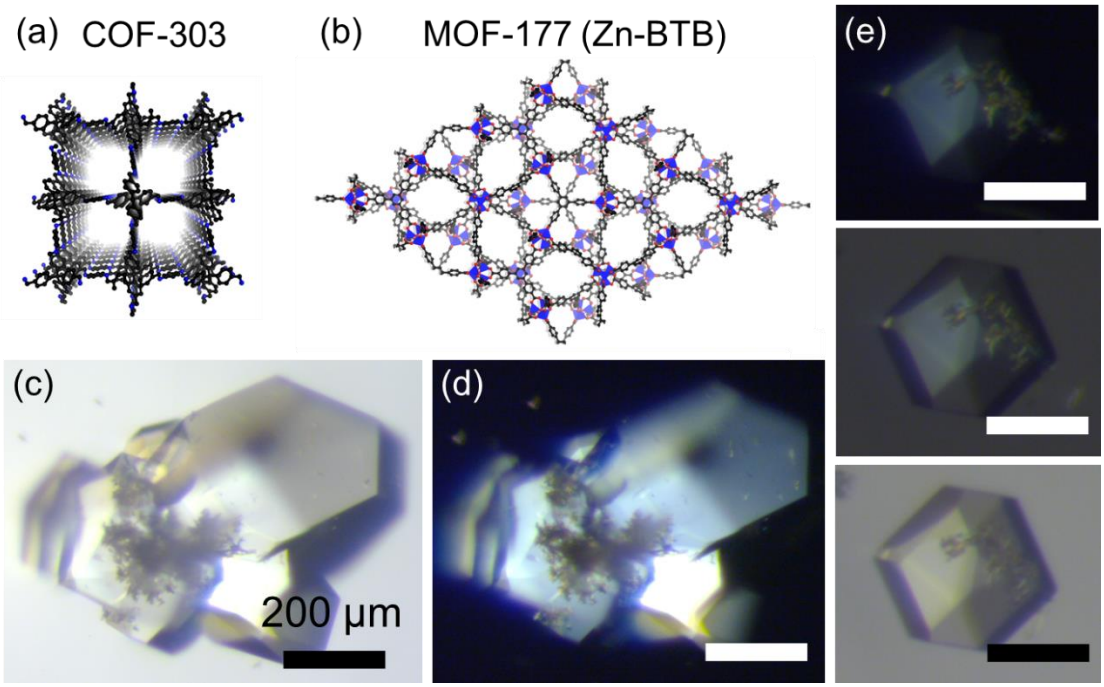

Figure S19. (a) The structure of COF-303 and (b) MOF-177, (c-e) optical image and the corresponding polarized optical image of COF-303@MOF-177 crystals.

Synthesis of ZIF-8. ZIF-8 was synthesized according to the literature with slight modification.[5] $Zn(NO_3)_2 \cdot 4H_2O$ (0.210 g, 0.803 mmol) and 2-methylimidazole (H-MeIM) (0.060 g, 0.731 mmol) were dissolved in 18 mL DMF in a 20 mL vial. The vial was then capped and placed in a 120 ºC oven for 48 h to yield polyhedral crystals. The crystals were then washed with fresh DMF for 3 times.

Synthesis of COF-303@ZIF-8. COF-303 (5 mg), 2-methylimidazole (H-mIM, 18 mg), $Zn(NO_3)_2 \cdot 4H_2O$ (63 mg) and DMF (5.4 mL) were charged in a Pyrex vial. The mixture was heated in a 120 ºC oven for 48 h to generate the crystals of COF-303@ZIF-8. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

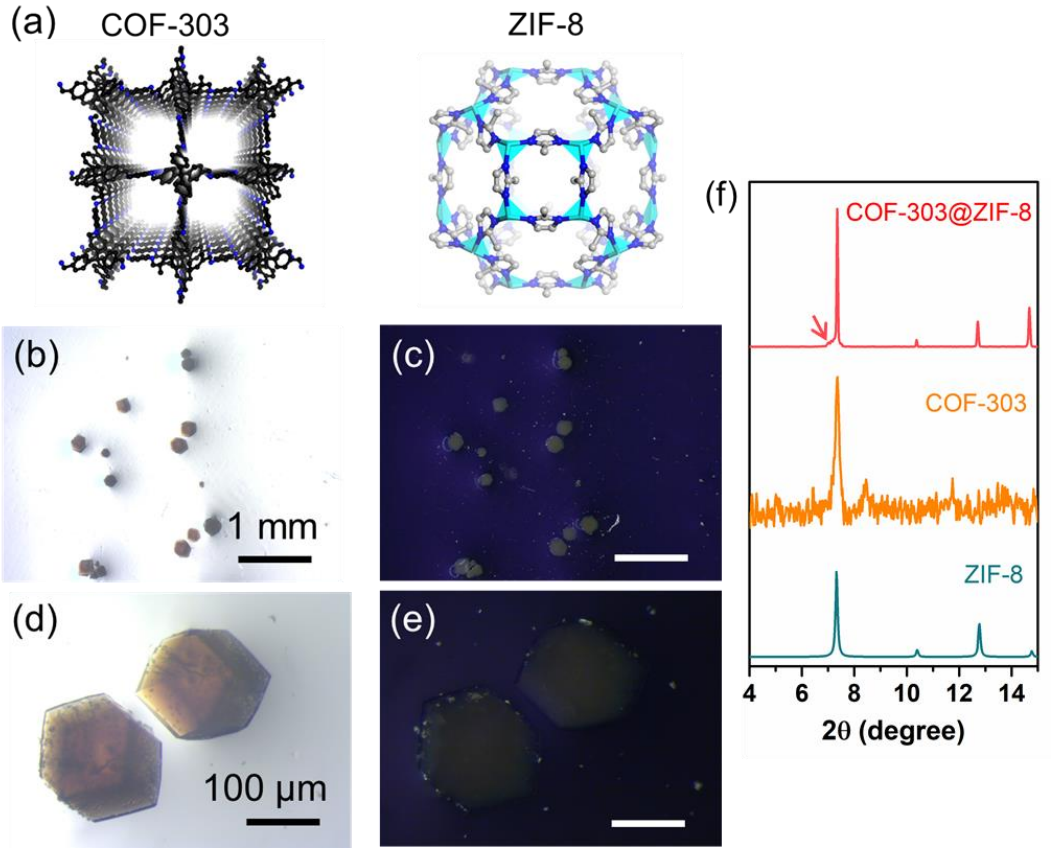

Figure S20. (a) The structure of COF-303 and ZIF-8, (b-e) optical image and the corresponding polarized optical image and (f) PXRD patterns of COF-303@ZIF-8 crystals.

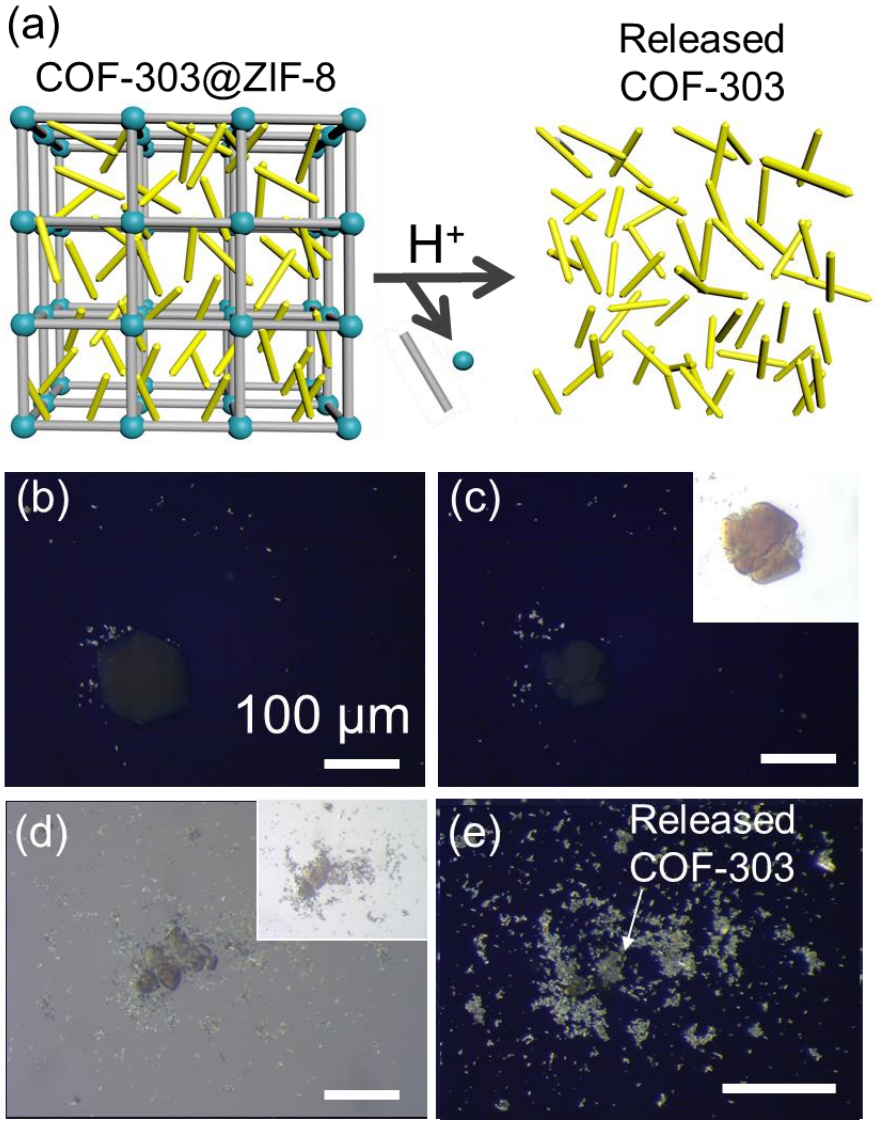

Figure S21. (a) Illustration of the decomposition of COF-303@ZIF-8 under the treatment of HCl/DMF (1/5 v/v) solution; (b-e) Microscopic images of stepwise decomposition of COF-303@ZIF-8 crystals under the treatment of HCl solution. (b) Before the addition of HCl solution, the COF-303@ZIF-8 crystals displayed a multi-core-shell state; (c-e) after the acid addition, the ZIF-8 crystals quickly dissolved from outside to inside, and released more acid-stable COF-303 crystals.

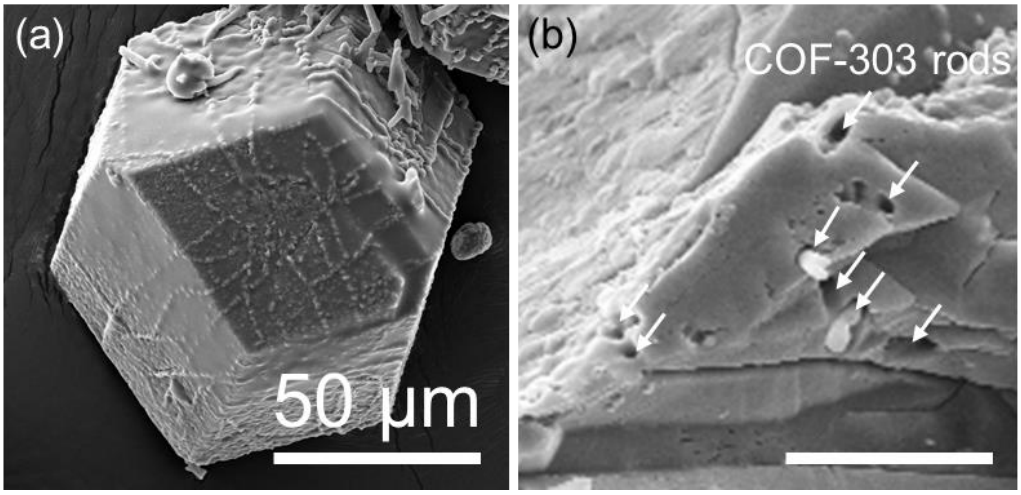

Figure S22. (a) SEM analysis of COF-303@ZIF-8, and (b) its internal structure with COF-303 microrods immobilized inside ZIF-8 crystals.

Synthesis of UiO-67. UiO-67 single crystals were synthesized according to the literature with slight modification.[6] $ZrCl_4$ (100 mg), BPDC (100 mg), TFA (2.0 mL) and DMF (15 mL) were charged in a Pyrex vial. The mixture was heated in 120 ºC oven for 5 days. After cooling down to room temperature, the resulting single crystals UiO-67 was separated by centrifugation and washed several times with DMF.

Synthesis of COF-303@UiO-67. COF-303 (3 mg), $ZrCl_4$ (10 mg), BPDC (10 mg), TFA (0.2 mL) and DMF (1.5 mL) were charged in a Pyrex vial. The mixture was heated in 120 ºC oven for 5 days. After cooling down to room temperature, the resulting COF-303@UiO-67 crystals were separated by centrifugation and washed several times with DMF.

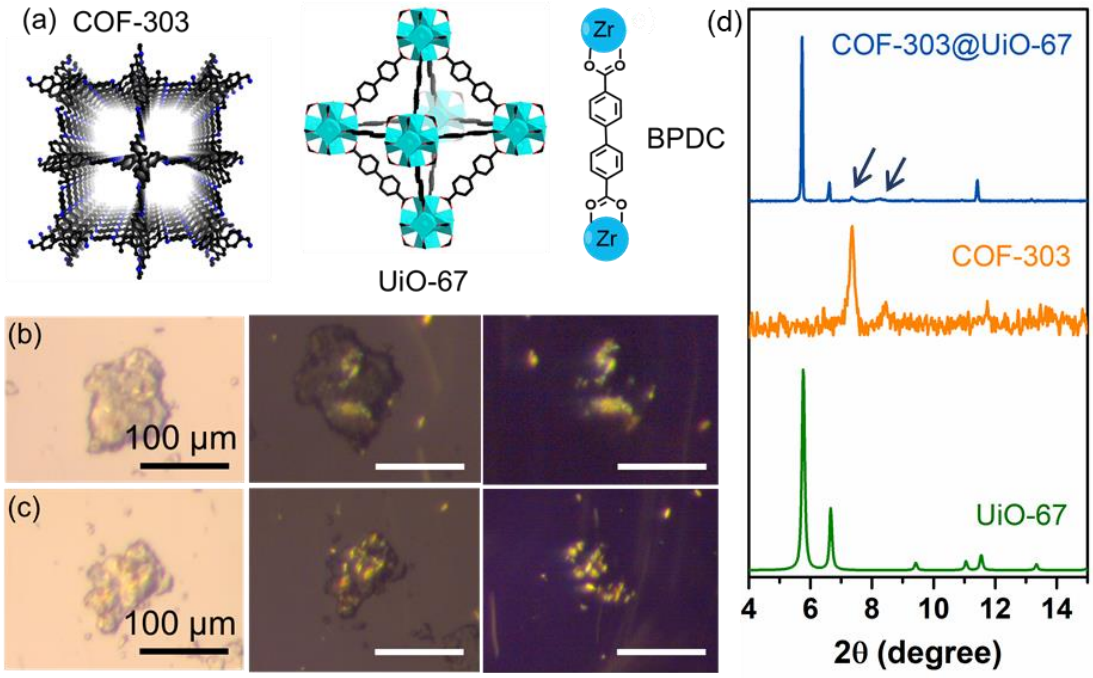

Figure S23. (a) The structure of COF-303 and UiO-67, (b-c) optical image and the corresponding polarized optical image and (d) PXRD patterns of COF-303@UiO-67 crystals.

Synthesis of PCN-160. PCN-160 single crystals were synthesized according to the literature with slight modification.[7] $ZrCl_4$ (100 mg), AZDC (100 mg), TFA (2.0 mL) and DMF (15 mL) were charged in a Pyrex vial. The mixture was heated in 120 ºC oven for 5 days. After cooling down to room temperature, the resulting single crystals PCN-160 was separated by centrifugation and washed several times with DMF.

Synthesis of COF-303@PCN-160. COF-303 (3 mg), $ZrCl_4$ (10 mg), AZDC (10 mg), TFA (0.2 mL) and DMF (1.5 mL) were charged in a Pyrex vial. The mixture was heated in 120 ºC oven for 5 days. After cooling down to room temperature, the resulting COF-303@PCN-160 crystals were separated by centrifugation and washed several times with DMF.

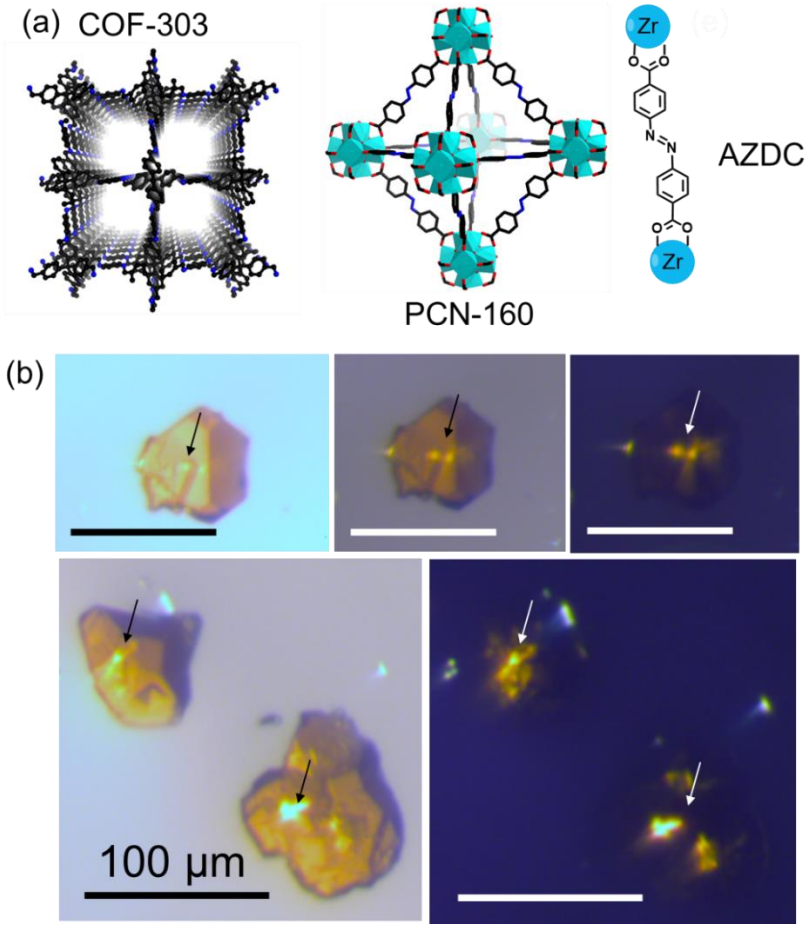

Figure S24. (a) The structure of COF-303 and PCN-160, (b) optical image and the corresponding polarized optical image of COF-303@PCN-160 crystals.

Crystallization of COF-300. Single-crystalline COF-300 was synthesized on the basis of a previous report.[1] A vial was charged with 12.0 mg terephthaldehyde (BDA), 0.12 mL aniline and 0.5 mL of 1,4-dioxane, then 0.2 mL of 6 M aqueous acetic acid was added to the solution. 20.0 mg Tetrakis(4-aminophenyl)methane (TAM) dissolved in 0.5 mL 1,4-dioxane was then added. Then the mixture was allowed to further stand at ambient temperature for 15 days.

Synthesis of COF-300@MOF-5. COF-300 (3 mg), H_2BDC (8.8 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg) and DEF (2 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h to generate the crystals of COF-300@MOF-5. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

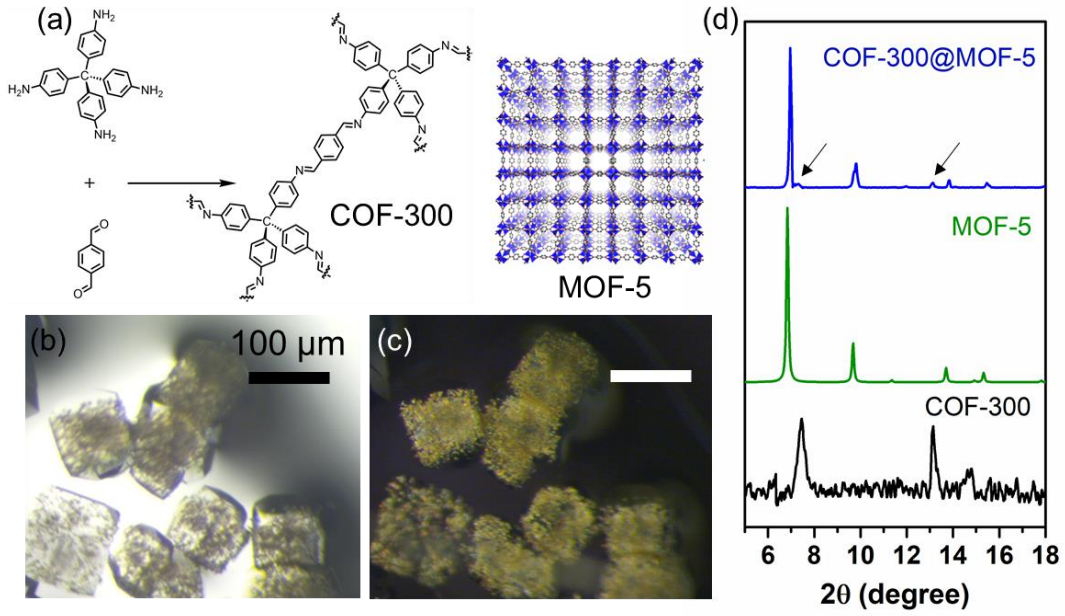

Figure S25. (a) The structure of COF-300 and MOF-5, (b-c) optical image and the corresponding polarized optical image of COF-300@MOF-5 crystals, and (d) PXRD patterns of COF-300@MOF-5.

Synthesis of Zn-AzTPDC. The ligands AzTPDC/CL4 and the MOF Zn-AzTPDC were prepared based on previous reports.[8] AzTPDC (28 mg, 0.065 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (57 mg, 0.19 mmol) were dissolved in 5 mL of N,N-diethylformamide (DEF) in a screw top vial. The vial was kept standing at 80 °C for 3 days. The solution was decanted, and yellow cubic crystals were repeatedly washed with DMF.

Synthesis of COF-303@Zn-AzTPDC. COF-303 (5 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (57 mg), AzTPDC (28 mg) and DEF (5.0 mL) were charged in a Pyrex vial. The mixture was heated in an 80 ºC oven for 3 days to generate the crystals of COF-303@Zn-AzTPDC. The solution was decanted, and the crystals were repeatedly washed with DMF.

Polymerization of hierarchical COF@polyMOF (COF-303@Zn-AzTPDC-CL4). The polymerization was conducted on the basis of previous reports with slight modifications.[8] COF-303@Zn-AzTPDC was immersed in 5 mL of 0.1 M CL4 solution (DMF) in a screw top vial, and 250 μL of saturated CuBr solution (DMF) was added to the mixture. The vial was kept standing at 80 °C for 3 days. The supernatant was decanted, and the cubic crystals, COF-303@Zn-AzTPDC-CL4, were repeatedly washed with DMF.

Synthesis of hierarchical COF@polymer (COF-303@poly-AzTPDC-CL4). The hydrolysis was conducted on the basis of previous reports with slight modifications.[8] COF-303@Zn-AzTPDC-CL4 was immersed in a mixed solvent of HCl/DMF (1:5, v/v) in a screw top vial. The vial was kept standing at room temperature for 3 h. The supernatant was decanted, and cubic crystals were repeatedly washed with DMF.

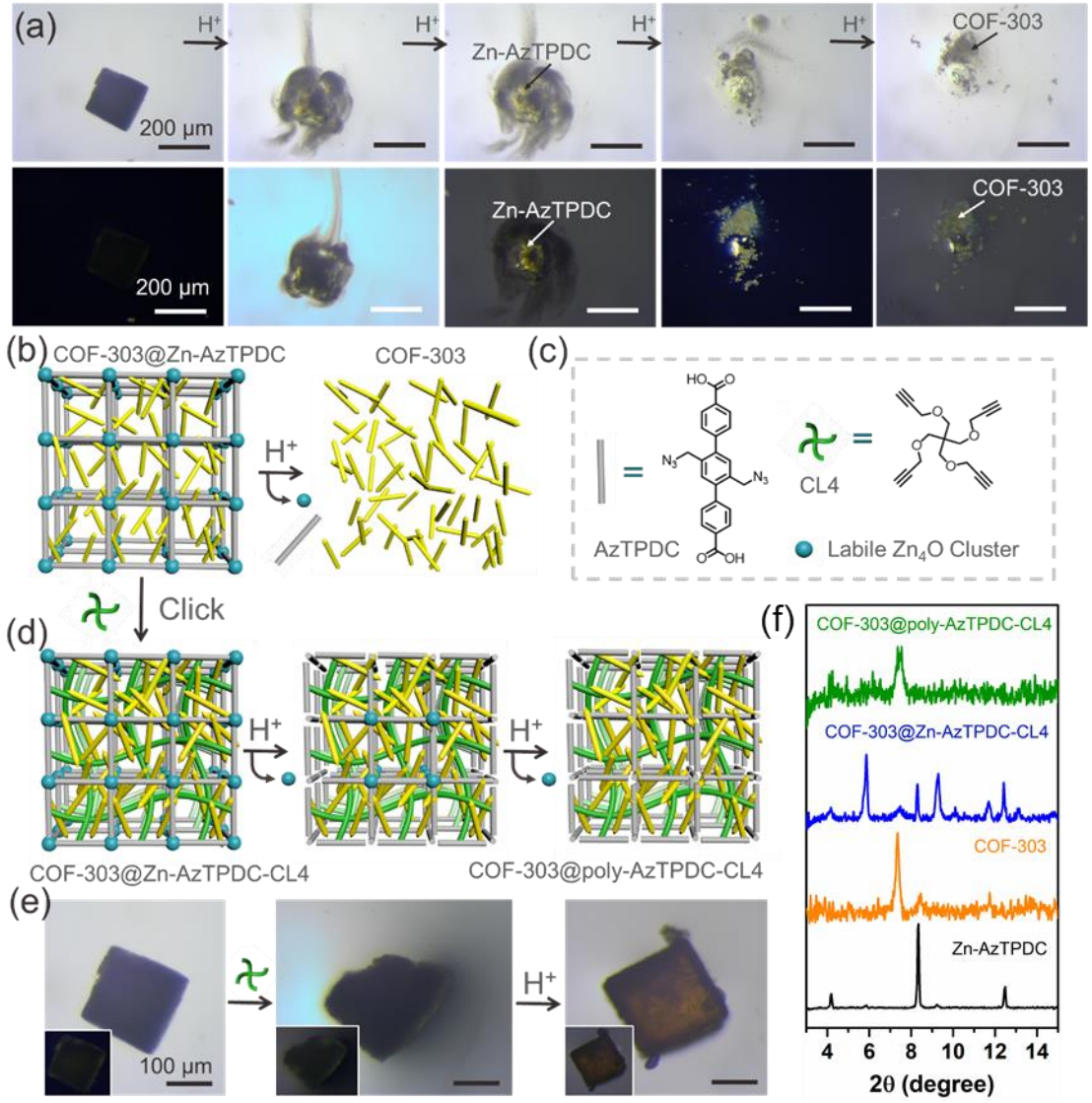

Figure S26. (a) Optical images and corresponding polarized optical images of COF-303@Zn-AzTPDC crystals treated with HCl/DMF (1/5, v/v), which shown fast decomposition of Zn-AzTPDC when in the absence of polymerization, while stable COF-303 survived after acid treatment. (b) Illustration of the decomposition of Zn-AzTPDC and preservation of COF-303 under acid treatment of COF-303@Zn-AzTPDC. (c) Basic building blocks AzTPDC, CL4 and labile Zn_4O clusters in ZnAzTPDC. (d) Illustration of the Zn_4O cluster removal in COF-303@Zn-AzTPDC. (e) Optical images and corresponding polarized optical images of COF-303@Zn-AzTPDC, COF-303@Zn-AzTPDC-CL4 and COF-303@poly-AzTPDC-CL4 crystals. (f) PXRD patterns of COF-303@Zn-AzTPDC-CL4 and COF-303@poly-AzTPDC-CL4.

Synthesis of COF-303@PCN-160. COF-303 (3 mg), $ZrCl_4$ (10 mg), AZDC (10 mg), TFA (0.2 mL) and DMF (1.5 mL) were charged in a Pyrex vial. The mixture was heated in 120 ºC oven for 5 days. After cooling down to room temperature, the resulting COF-303@PCN-160 crystals were separated by centrifugation and washed several times with DMF.

Synthesis of (COF-303@PCN-160)@MOF-5. COF-303@PCN-160 (5 mg), H_2BDC (8.8 mg), DEF (1 mL) were charged in a Pyrex vial. The mixture was heated in an 85 ºC oven for 24 h. $Zn(NO_3)_2 \cdot 6H_2O$ (41.6 mg) and DEF (1 mL) were further added into the vial. The mixture was heated in an 85 ºC oven for 24 h to generate the crystals of (COF-303@PCN-160)@MOF-5. The crystals were collected by centrifugation and washed with fresh DMF for 3 times.

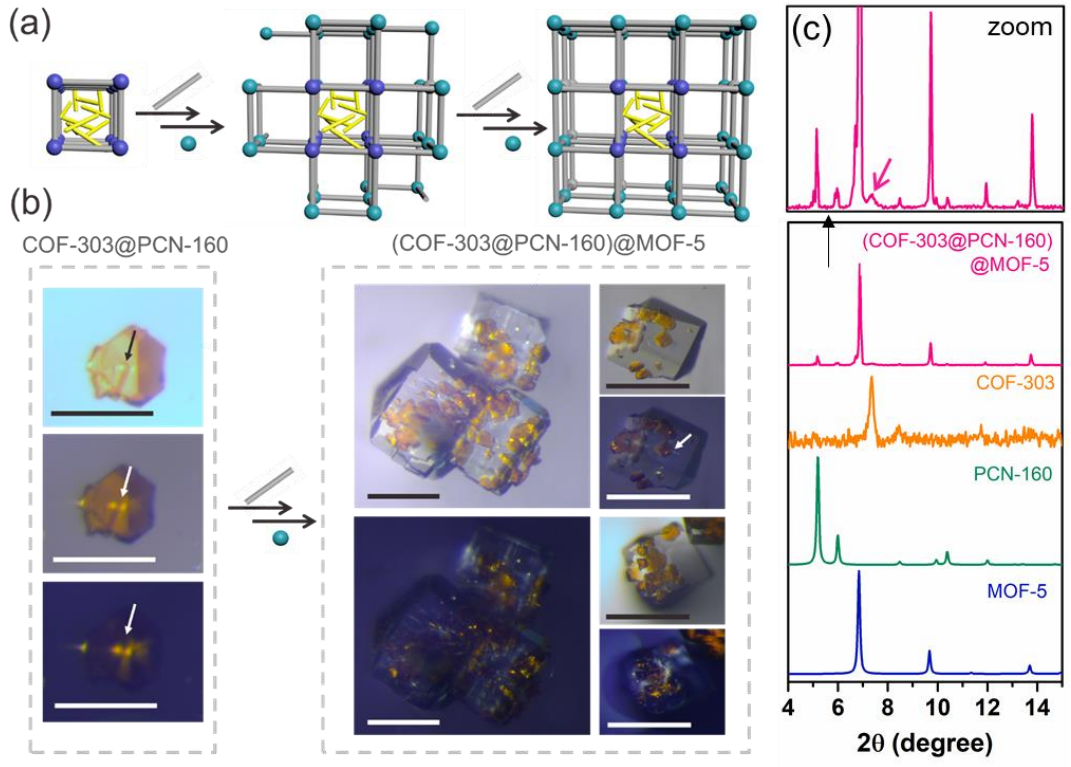

Figure S27. (a) Scheme illustration of the stepwise evolution from COF-303@PCN-160 to (COF-303@PCN-160)@MOF-5. (b) Optical images and corresponding polarized optical images of COF-303@PCN-160 and (COF-303@PCN-160)@MOF-5. (c) PXRD pattern of (COF-303@PCN-160)@MOF-5 and its components. Scale bar is 100 μm.

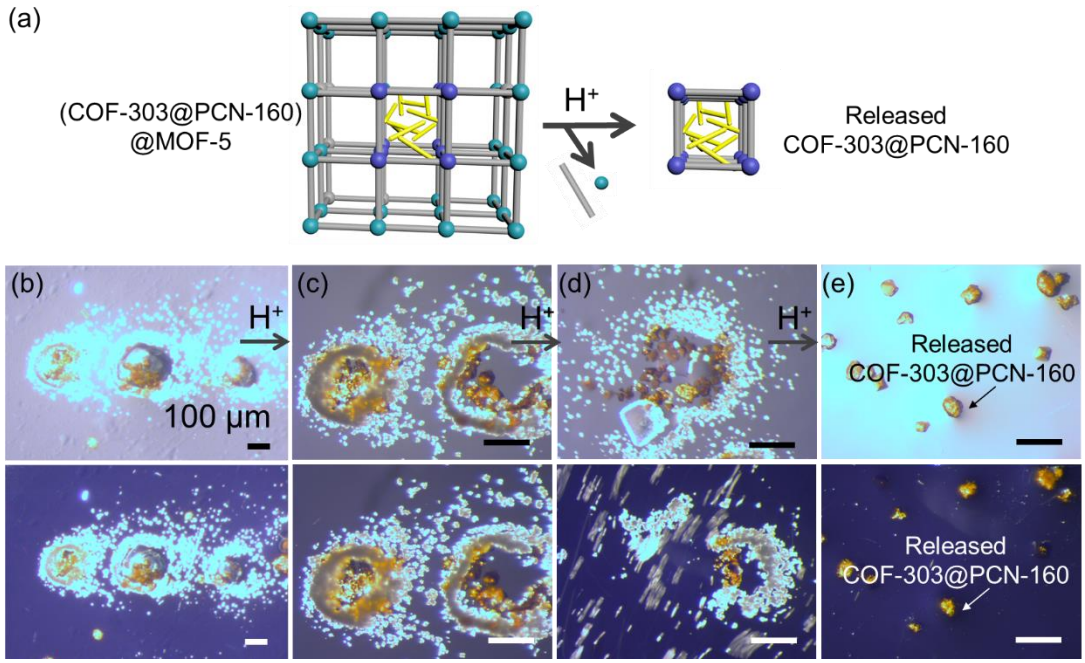

Figure S28. (a) Illustration of the decomposition of (COF-303@PCN-160)@MOF-5 under the treatment of HCl/DMF (1/5 v/v) solution; (b-e) Microscopic images of stepwise decomposition of (COF-303@PCN-160)@MOF-5 crystals under the treatment of HCl solution. Before the addition of HCl solution, the (COF-303@PCN-160)@MOF-5 crystals displayed a multi-core-shell state; after the acid addition, the core-shell COF-303@PCN-160 crystals were released and the shell MOF-5 quickly dissolved.

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