

Supporting Information

Palladium nanoparticles immobilized on COFs-modified honeycomb chitosan microcapsules as catalysts for Suzuki reaction and p-nitrophenol reduction

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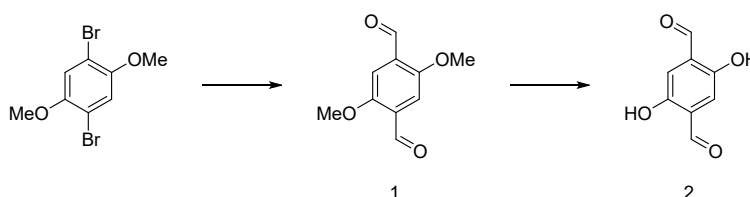
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1. Materials and Instruments.

All materials and solvents used were purchased from commercial channels without further treatment. Chitosan (>400 MPa·s, deacetylation degree of 85-95%), palladium chloride (PdCl₂), 2-methylimidazole, zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), 1,3,5-Tris(4-aminophenyl)benzene, acetonitrile were all purchased from Sinopharm Chemical Reagent. P-Nitrophenol, phenylboronic acid, iodobenzene, bromobenzene, chlorobenzene, and their derivatives were purchased from Innochem Scientific Co., Ltd. An Empyrean diffractometer collected the X-ray diffraction patterns (XRD) of the material.

Fourier transform infrared (FT-IR) spectra were tested with a PerkinElmer Spectrum One (B) spectrometer in the wavelength region of 4000-500 cm⁻¹. The transmission electron microscopic (TEM) images were obtained by JEM2100PLUS instruments. ICP-OES: Thermo Fisher iCAP PRO. The Scanning electron microscopy (SEM) images were recorded by scanning electron microscopy (SU8010). X-ray photoelectron spectroscopy (XPS) was used to probe the surface composition of samples using ESCALAB250. The thermogravimetric (TGA) analyses were carried out on Netzsch 209C from 45 to 700 °C at a heating rate of 20 °C/min in a nitrogen atmosphere. The surface area and porous structure were obtained at 77 K by N₂ adsorption-desorption isotherms with an Autosorb-iQC apparatus. ¹H NMR spectra were performed on a Bruker ARX 600 high-resolution NMR spectrometer.

2. Synthesis of 2, 5-dimethoxyterephthalaldehyde (1) and 2, 5-dihydroxyterephthalaldehyde (2)

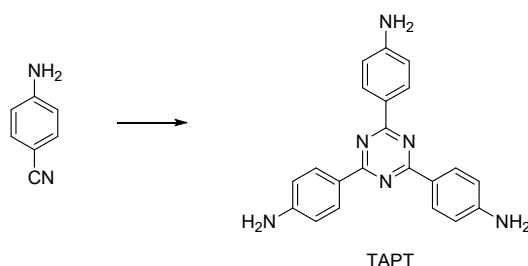


2, 5-dimethoxyterephthalaldehyde (DMTP) and 2, 5-dihydroxyterephthalaldehyde (DHTP) was synthesized according to report [22]. 2, 5-dimethoxyterephthalaldehyde (1). A solution of 1, 4-dibromo-2, 5-dimethoxybenzene (500 mg) in anhydrous tetrahydrofuran 8.5 mL was cooled to -78 °C and n-BuLi (1.6 M in hexane, 2.3 mL) was added dropwise. After 3 h, DMF, 0.6 mL was added and the mixture stirred for 1 hour at -78 °C warmed to room temperature and stirred for 1 h. The reaction was quenched with saturated NH₄Cl, THF was

eliminated under reduced pressure and the resulting solution extracted with DCM. The organic phase was dried over NaSO₄ and the solvent removed in vacuo. The crude product was purified by column chromatography (silica gel flash, petroleum ether /ethyl acetate 10:1) to afford a yellow solid. ¹H NMR (DMSO-d₆, 600 MHz) δ (ppm): 10.51 (s, 2H), 7.47 (s, 2H), 3.41 (s, 6H).

To a solution of 2, 5-dimethoxyterephthalaldehyde (900 mg) in DCM (20 mL) under N₂ atmosphere BBr₃ (1 M in CH₂Cl₂, 20 mL) was added dropwise at -78 °C. The solution was allowed to warm to room temperature and stirred overnight. H₂O (40 mL) was added to quench the reaction and the resulting mixture was extracted repeatedly with DCM. The organic phase was dried over NaSO₄, The crude product was purified by column chromatography (silica gel flash, petroleum ether /ethyl acetate 15:1). ¹H NMR (DMSO-d₆, 600 MHz) δ (ppm): 10.21 (s, 2H), 9.98 (s, 2H), 7.22 (s, 2H).

3. Synthesis of 1, 3, 5-tris-(4-aminophenyl)triazine (TAPT):



1, 3, 5-tris-(4-aminophenyl)triazine (TAPT), was synthesized according to report [23]. In a typical synthesis, 0.772 g (6.538 mmol) 4-aminobenzonitrile was taken in a round bottom flask at 0 °C. Then 2 mL (22.2 mmol) trifluoromethanesulfonic acid was added dropwise for 20 min maintaining the temperature at 0 °C. The resultant mixture was stirred for 24 h at room temperature in inert atmosphere. After that, 20 mL distilled water was added to the mixture and it was neutralized by adding 2 M NaOH solution until the pH reaches to 7. Initially, with increase in pH, the orange precipitate dissolves to give a bright orange solution, which upon further increase in pH gives a pale yellow precipitate. The resultant pale yellow product was filtered and washed several times with distilled water. ¹H NMR (DMSO-d₆, 600 MHz, ppm): δ 8.36 (d, J = 8.8 Hz, 6H), 6.70 (d, J = 8.4 Hz, 6H), 5.89(s,6H).

4. Synthesis of chitosan/ZIF-8 aerogel microspheres.

CS/ZIF-8 microspheres were prepared by impregnation-gelation-hydrothermal technique.

Typically, 0.6 g (2 mmol) of zinc nitrate hexahydrate was dissolved in 10 g of 2.0 wt% chitosan solution consisting of 2.0 g chitosan, 94.8 g deionized water, and 3.2 ml acetic acid (36 wt%). 2.0 g NaOH and 2.6 g 2-Methylimidazole (Hmim) were dissolved in 35.4 g deionized water, making the NaOH and Hmim contents of 5 wt% and 6.6 wt%, respectively. Then 8.2 g of the Zn²⁺-chitosan solution was added to 40 g of the mixture solution of NaOH and Hmim through a syringe. Microspheres were immediately formed. They were left at 80 °C for 12 hours. CS/ZIF-8 microspheres were obtained after filtrating, washing and freeze-drying.

5. Synthesis of chitosan/ZIF-8 aerogel microspheres.

10 g chitosan microspheres and 5 mL glutaraldehyde were added to 100 mL ethanol solution and stirred vigorously at 50 °C until the pores on the surface of CS/ZIF-8 microspheres were completely opened. After the reaction, the CS/ZIF-8 microspheres were filtered and washed with ethanol and water and vacuum dried at 60 °C.

6. Stabilization experiments of CS/ZIF-8@COFs in aqueous solutions

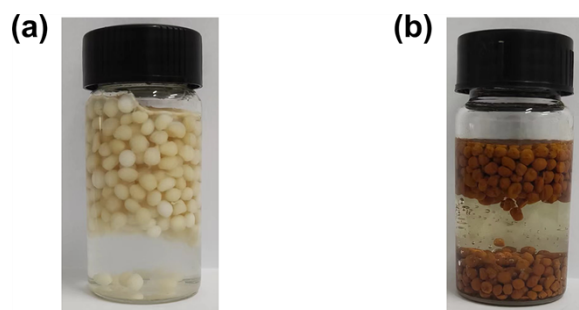


Figure S1. Photographs of CS/ZIF-8 and CS/ZIF-8@COFs immersed in aqueous solution for 48h.

7. Structural formula and SEM images of CS/ZIF-8, COFs, CS/ZIF-8@COF

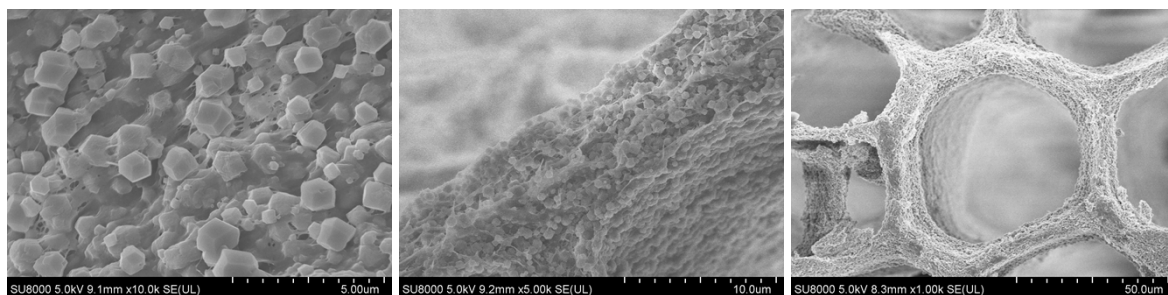


Figure S2 SEM images of CS/ZIF-8

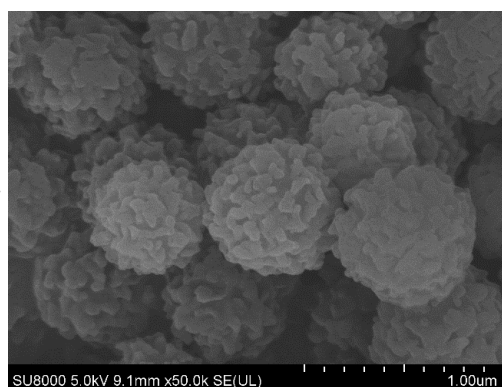
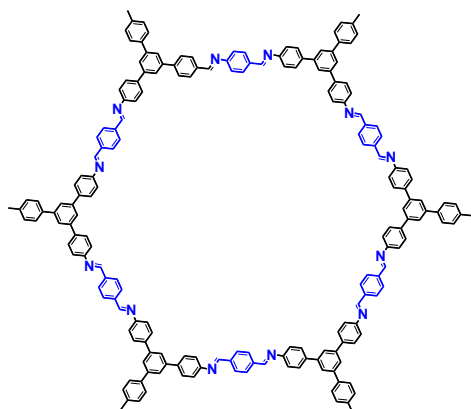


Figure S3 Structural formula and SEM image of COF_{a-1}

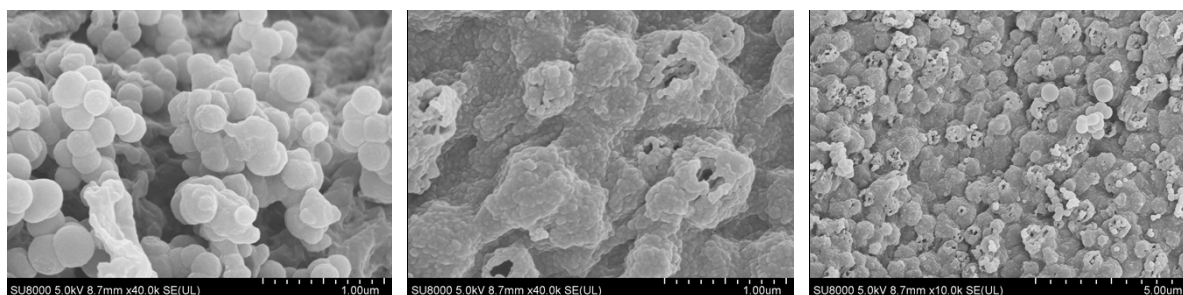


Figure S4 SEM images of CS/ZIF-8@COF_{a-1}

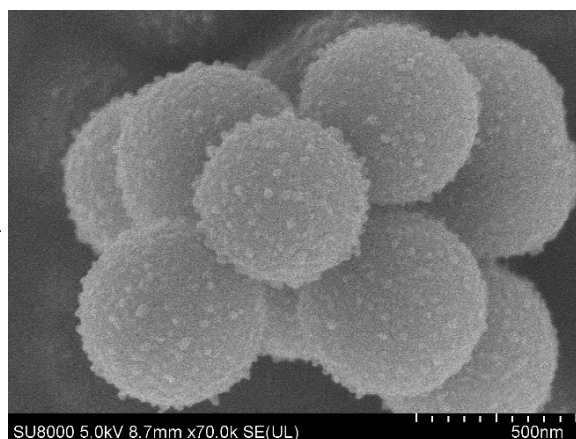
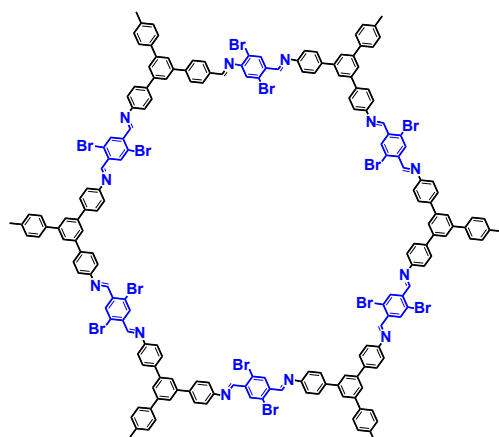


Figure S5 Structural formula and SEM image of COF_{a-2}

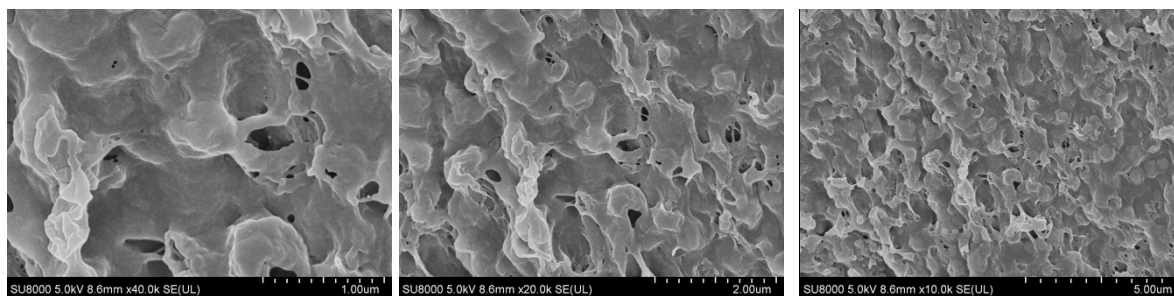


Figure S6 SEM images of CS/ZIF-8@COF_{a-2}

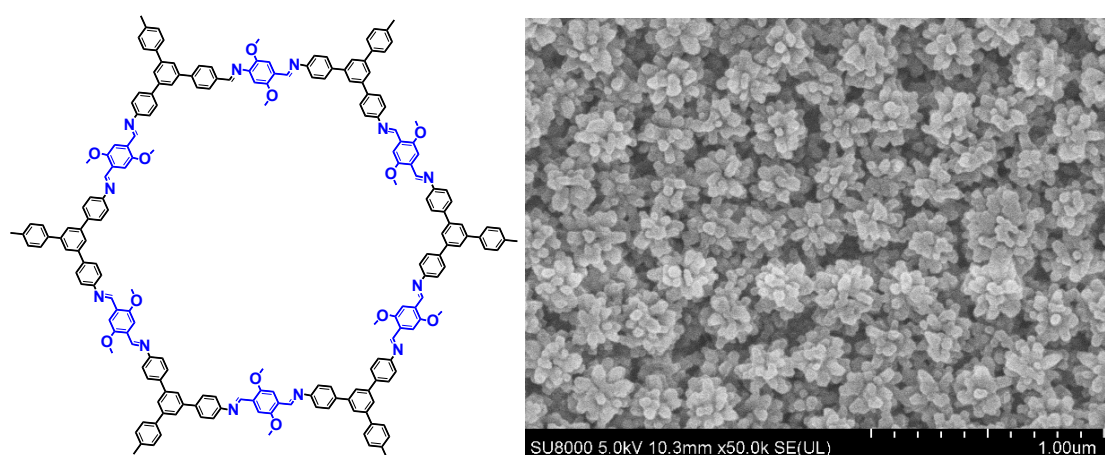


Figure S7 Structural formula and SEM image of COF_{a-3}

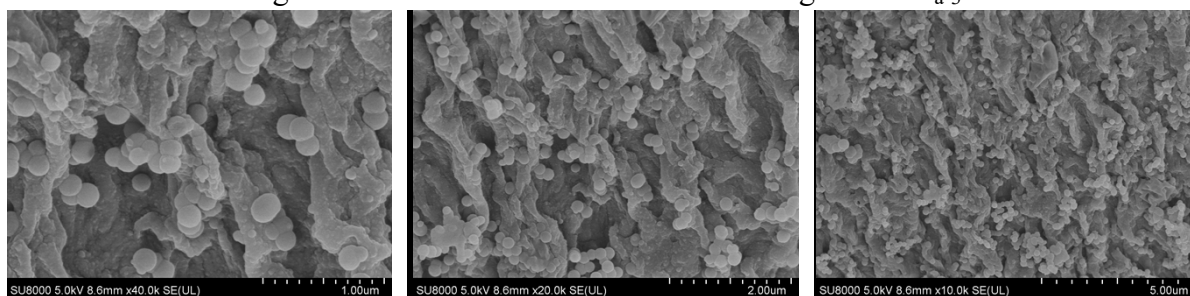


Figure S8 SEM images of CS/ZIF-8@COF_{a-3}

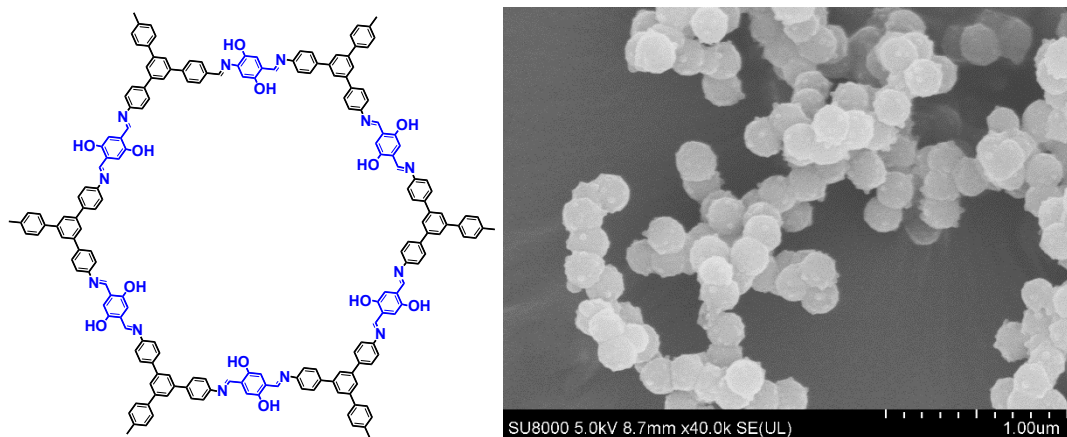


Figure S9 Structural formula and SEM image of COF_{a-4}

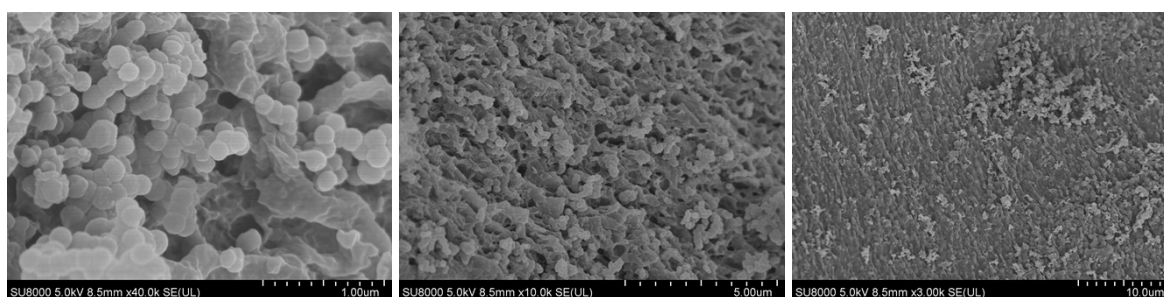


Figure S10 SEM images of CS/ZIF-8@COF_{a-4}

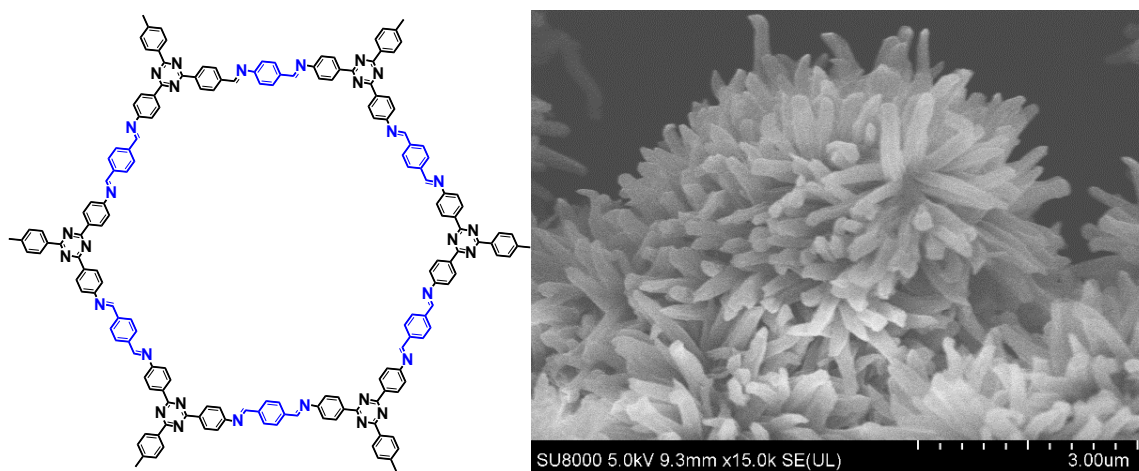


Figure S11 Structural formula and SEM image of COF_{b-1}

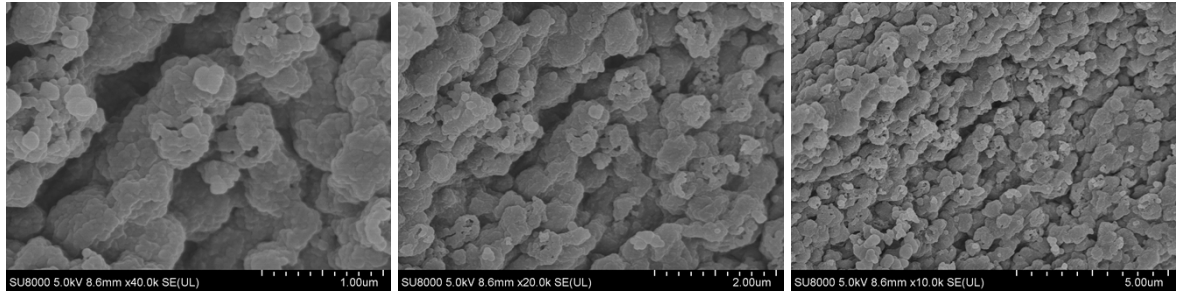


Figure S12 SEM images of CS/ZIF-8@COF_{b-1}

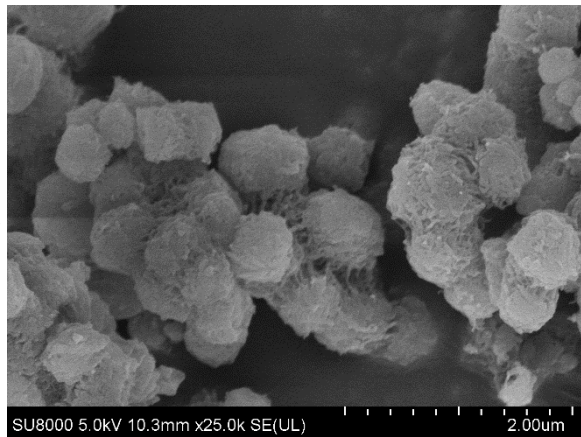
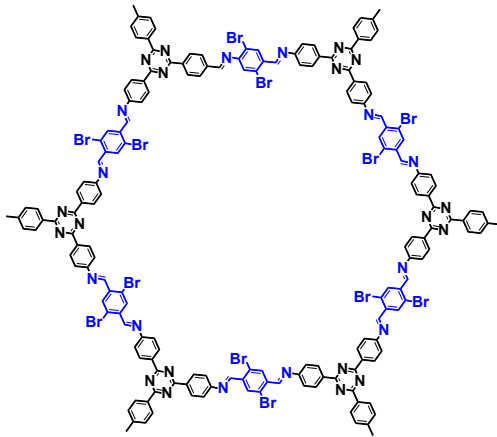


Figure S13 Structural formula and SEM image of COF_{b-2}

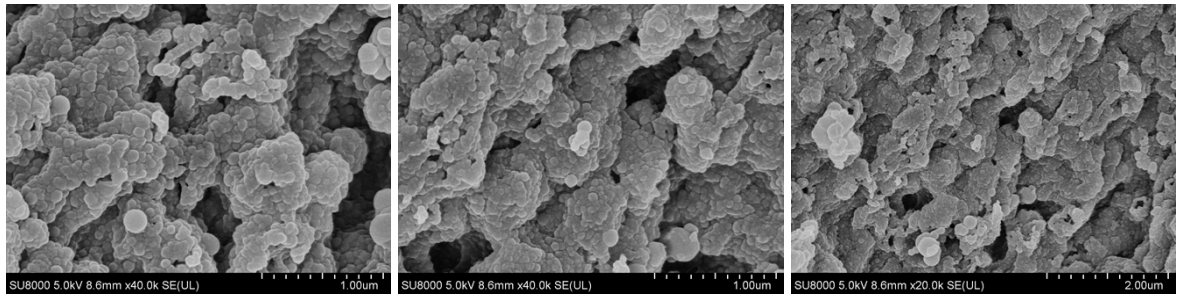


Figure S14 SEM images of CS/ZIF-8@COF_{b-2}

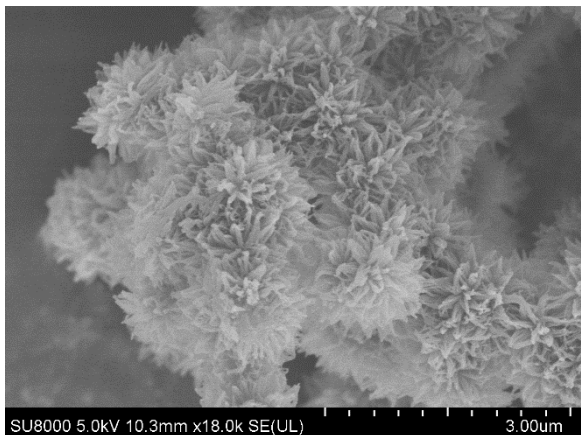
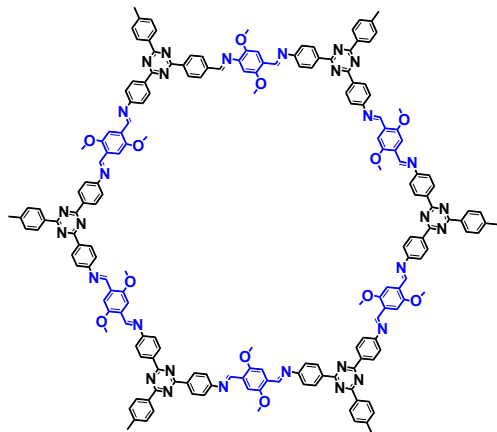


Figure S15 Structural formula and SEM image of COF_{b-3}

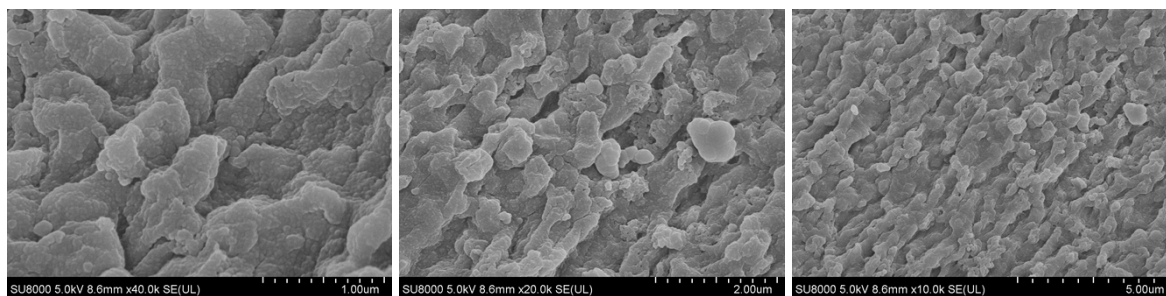


Figure S16 SEM images of CS/ZIF-8@COF_{b-3}

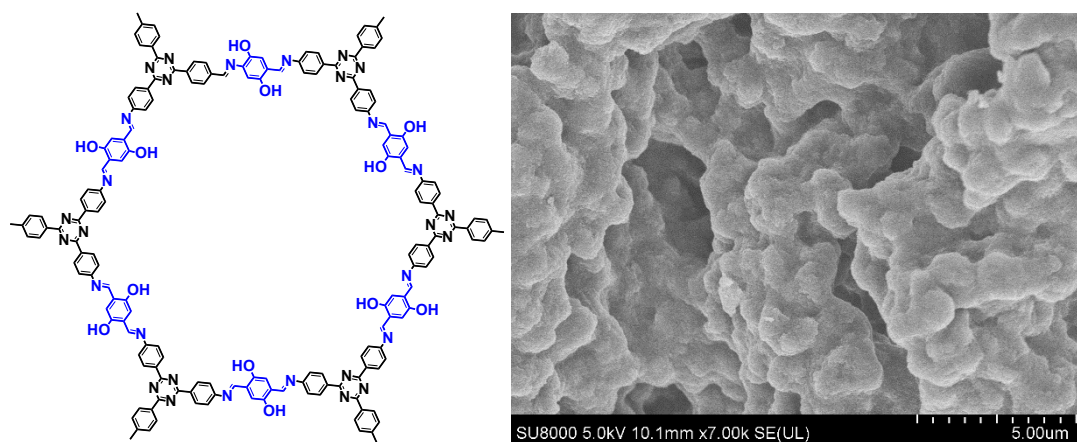


Figure S17 Structural formula and SEM image of COF_{b-4}

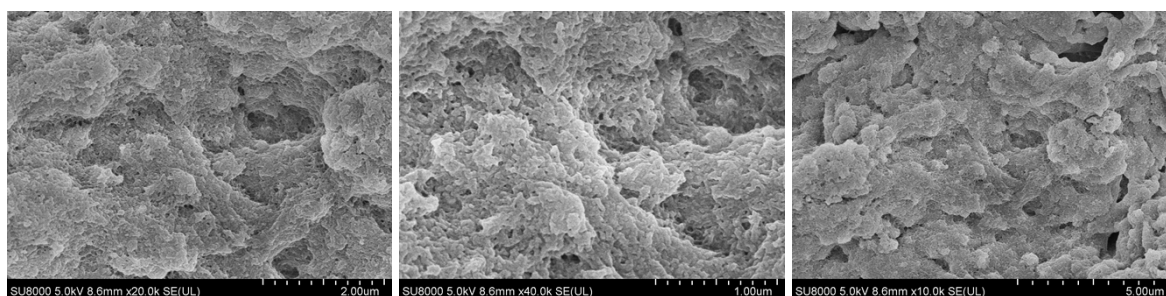


Figure S18 SEM images of CS/ZIF-8@COF_{b-4}

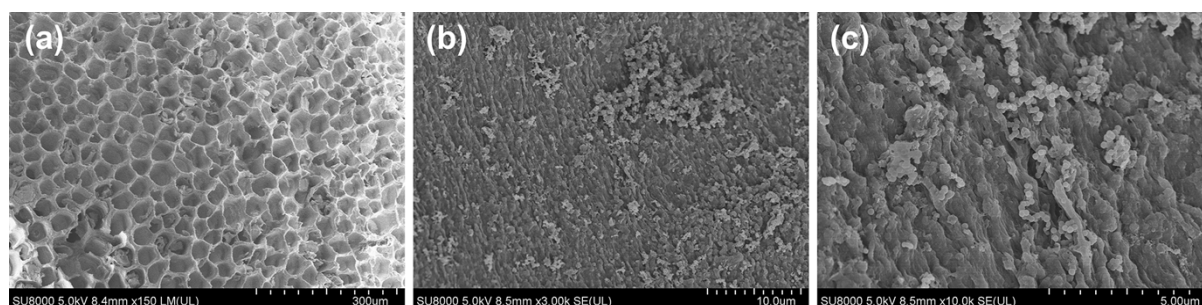


Figure S19. SEM images of catalyst CS/ZIF-8@COF_{a-4}@Pd after reaction

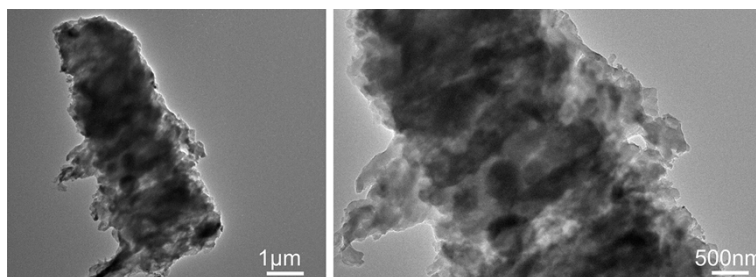


Figure S20 TEM images of CS/ZIF-8@COF_{a-4}@Pd

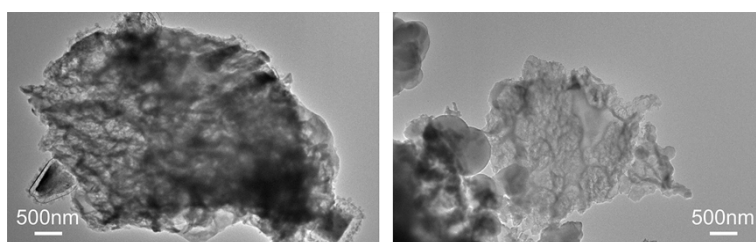


Figure S21 TEM images of CS/ZIF-8@COF_{a-4}@Pd after 5 cycles.

8. ¹H NMR spectra of Suzuki coupling reaction products.

