

Electronic Supplementary Information

Bimetallic Docked Covalent Organic Frameworks with High Catalytic Performance towards Tandem Reaction

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Experimental Details

Reagents: All the bought reagents were used as received without further purification. 1,3,6,8-Tetrabromopyrene, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 4,4'-biphenyl dialdehyde, manganese(II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), palladium(II) acetate [$\text{Pd}(\text{OAc})_2$], and tetrakis(triphenylphosphine)palladium(0) were purchased from TCI Chemicals. 5,5'-Dimethyl-2,2'-dipyridyl, and tert-butoxy bis(dimethylamino)methane were purchased from Aldrich. Iodobenzene, styrene, isobutyraldehyde, mesitylene, dioxane, acetic acid, tetrahydrofuran, acetone, dichloromethane, methanol, ether, N,N-dimethylformamide, acetonitrile, potassium carbonate, and sodium periodate were purchased from Sinopharm Chemical Reagent Co..

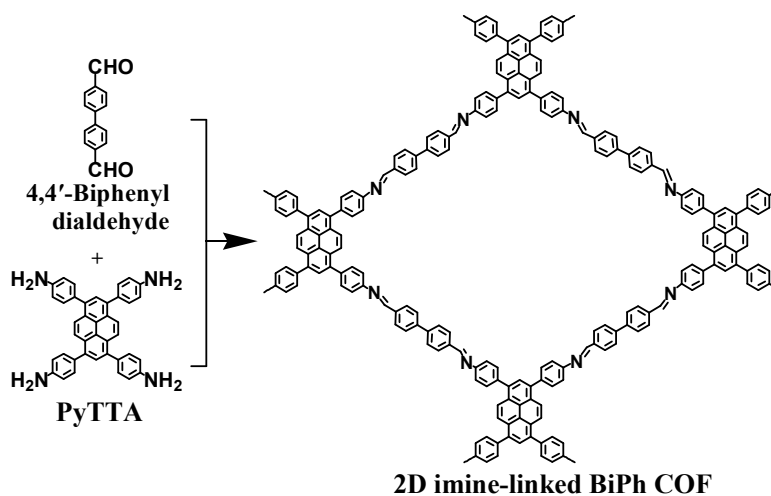
4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetraaniline (PyTTA),^{S1} and 2,2'-bipyridine-5,5'-dicarbaldehyde (2,2'-BPyDCA)^{S2} were prepared according to the reported literatures.

Synthesis of Py-2,2'-BPyPh COF. PyTTA (68 mg, 0.05 mmol) and 2,2'-BPyDCA (31 mg, 0.05 mmol) were placed in a glass ampule vessel (20 mL), followed by adding a solution of mesitylene/dioxane/3 M acetic acid (3/3/1 by volume; 3.5 mL). The mixture was sonicated for 5 min and then flash frozen in liquid nitrogen. The vessel was evacuated to an inner pressure of ~20 Pa, flame-sealed, and heated at 120 °C for 3 days. The resulting precipitate was washed sequentially with tetrahydrofuran (3 times) and acetone (3 times) to give an orange powder, which was dried at 120 °C under vacuum for 12 h to give the desired product in 82% yield. Elemental analysis (%) calcd. for $(\text{C}_{64}\text{H}_{38}\text{N}_8)_n$: C 83.7; H 4.1; N 12.2; Found: C 79.2; H 4.0; N 11.5.

Synthesis of Mn@Py-2,2'-BPyPh COF. Mn ions were incorporated into Py-2,2'-BPyPh COF using a simple solution infiltration method, and the resulting composites were nominated as Mn@Py-2,2'-BPyPh COF. In a typical procedure, Py-2,2'-BPyPh COF (100 mg, 0.11 mmol, calculated by the

framework repeating unit) was treated with a solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (172 mg, 0.87 mmol) in methanol (10 mL), and the resulting suspension was stirred at room temperature for 12 h. The precipitate was washed with excess methanol and deionized water to remove any dissociated $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and then dried at 120 °C under vacuum to give Mn@Py-2,2'-BPyPh COF. The Mn loading content was measured to be 0.8 wt% by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Synthesis of Mn/Pd@Py-2,2'-BPyPh COF. After Mn docking, $\text{Pd}(\text{OAc})_2$ were further introduced into Mn@Py-2,2'-BPyPh COF through another round of solution infiltration, and this final product was nominated as $\text{Mn/Pd@Py-2,2'-BPyPh}$ COF. Typically, Mn@Py-2,2'-BPyPh COF (100 mg) was treated with a solution of $\text{Pd}(\text{OAc})_2$ (137 mg) in dichloromethane (10 mL), and the resulting suspension was stirred at room temperature for 12 h. The precipitate was washed with excess dichloromethane to remove any dissociated $\text{Pd}(\text{OAc})_2$ and then dried at 120 °C under vacuum to give $\text{Mn/Pd@Py-2,2'-BPyPh}$ COF. The Mn and Pd loading content were measured to be 0.8 wt% and 9.3 wt%, respectively.



Synthesis of 2D imine-linked BiPh COF. 4,4'-Biphenyl dialdehyde (47 mg, 0.225 mmol) and PyTTA (85 mg, 0.15 mmol) placed in a glass ampule vessel (20 mL) were mixed with a solvent of mesitylene/dioxane/3 M acetic acid (1.5 mL/1.5 mL/0.5 mL) upon sonication treatment for 5 min. After flash frozen in liquid nitrogen, the bottle was evacuated to an inner pressure of ~20 Pa. Then the tube was flame-sealed and heated at 120 °C for 3 days. The precipitate was washed by tetrahydrofuran (3 times) and acetone (3 times). The powder was dried at 120 °C under vacuum for 12 h to give powder product in 85% yield, nominated as BiPh COF. Elemental analysis (%) calcd. for $(\text{C}_{68}\text{H}_{42}\text{N}_4)_n$: C 89.3; H 4.6; N 6.1. Found: C 86.2; H 4.4; N 6.0. This bipyridine free 2D

imine-linked COF product was poorly crystallized (Fig. S1). However, it was still synthesized to compare with the Py-2,2'-BPyPh COF for metal docking since the two COFs share similar structures.

Synthesis of Mn@BiPh COF. Mn ions were incorporated into BiPh COF using a simple solution infiltration method, and the resulting composites were nominated as Mn@BiPh COF. In a typical procedure, BiPh COF (70 mg, 0.08 mmol, calculated by the framework repeating unit) was treated with a solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (121 mg, 0.61 mmol) in methanol (10 mL), and the resulting suspension was stirred at room temperature for 12 h. The precipitate was washed with excess methanol and deionized water to remove any dissociated $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and then dried at 120 °C under vacuum to give Mn@BiPh COF. The Mn loading content was measured to be negligible.

Synthesis of Pd@BiPh COF. $\text{Pd}(\text{OAc})_2$ were incorporated into BiPh COF using a simple solution infiltration method, and the resulting composites were nominated as Pd@BiPh COF. Typically, Py-2,2'-BPyPh COF (70 mg) was treated with a solution of $\text{Pd}(\text{OAc})_2$ (96 mg) in dichloromethane (10 mL), and the resulting suspension was stirred at room temperature for 12 h. The precipitate was washed with excess dichloromethane to remove any dissociated $\text{Pd}(\text{OAc})_2$ and then dried at 120 °C under vacuum to give Pd@BiPh COF. The Pd loading content was measured to be 5.1 wt%.

Heck-epoxidation tandem reaction. For the Pd-catalyzed Heck reaction: iodobenzene (1.0 mmol), styrene (1.1 mmol), potassium carbonate (2.0 mmol), COF catalyst (10 mg), and acetonitrile (10 mL) were mixed and allowed to react at 353 K for 24 h under N_2 protection. For the subsequent Mn-catalyzed epoxidation reaction: after the Heck reaction, isobutyraldehyde (IBA) (3.0 mmol) was added into the organic phase to react at 298 K for another 12 h in the air. The product was isolated by flash column chromatography. NMR spectra of both trans-stilbene (the intermediate after the Heck reaction) and trans-stilbene oxide (the final product after the tandem reaction) can be found in Fig. S6–7.

Characterization: Elemental analysis was performed by organic elemental analyzer (vario MACRO cube, Elementar, Germany). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted by ICP-OES 7300DV (PerkinElmer). The sample was firstly calcinated at 1000 °C in the air for 12h to burn out organic moieties. The residue was dissolved by aqua regia

and then diluted by water for ICP-OES testing. Fourier transform infrared (FTIR) measurements were carried out on a Bruker spectrophotometer (Model TENSOR27) with powder pressed KBr pellets. Powder X-ray diffraction (PXRD) analysis was carried out on a Rigaku RINT D/Max 2500 powder diffraction system, using a Cu $K\alpha$ radiation ($\lambda = 1.5432 \text{ \AA}$). The nitrogen physisorption experiment was conducted at 77 K on a QUADRASORB SI gas sorption system (Quantachrome Instruments), which was degassed at 120 °C under vacuum before testing. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was evaluated by the nonlocal density function theory (NLDFT) method. Thermogravimetric analysis (TGA, STA449F3, NETZSCH, Germany) was performed from room temperature to above 750 °C at a heating rate of 10 °C min⁻¹ and a N₂ flow rate of 20 mL min⁻¹. X-ray photoelectron spectroscopy (XPS) was recorded by ESCALAB 250Xi equipped with Al $K\alpha$ radiation (1486.6 eV, 200 W) on sample powder pressed pellet. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded by a Bruker Advance III 400 MHz NMR spectrometer (Bruker BioSpin Corporation, Fällanden, Switzerland).

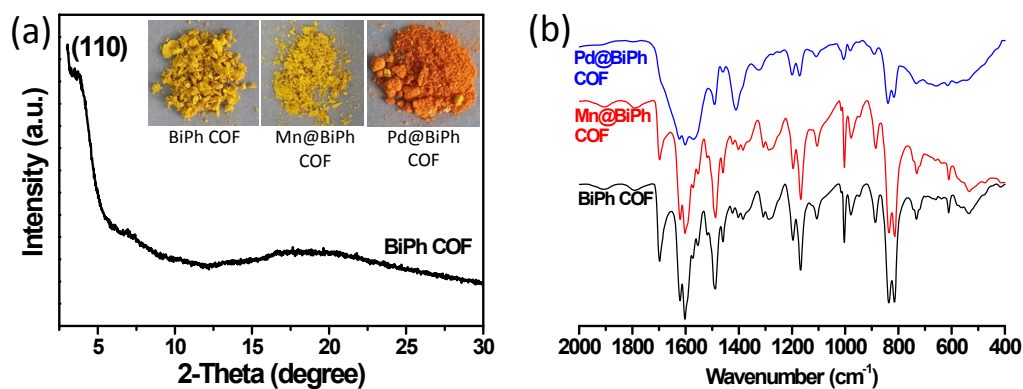


Fig. S1 (a) PXRD pattern of BiPh COF, insets were the appearances of the BiPh COFs before and after Mn/Pd docking; (b) FTIR spectra of the BiPh COFs before and after Mn/Pd docking.

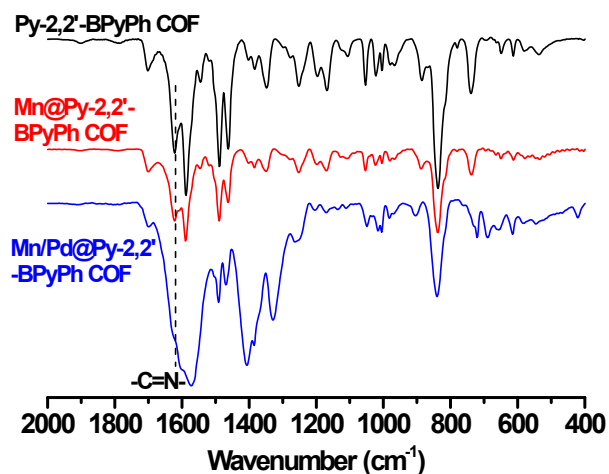


Fig. S2 FTIR spectra of the Py-2,2'-BPyPh COF, Mn@ Py-2,2'-BPyPh COF, and Mn/Pd@ Py-2,2'-BPyPh COF

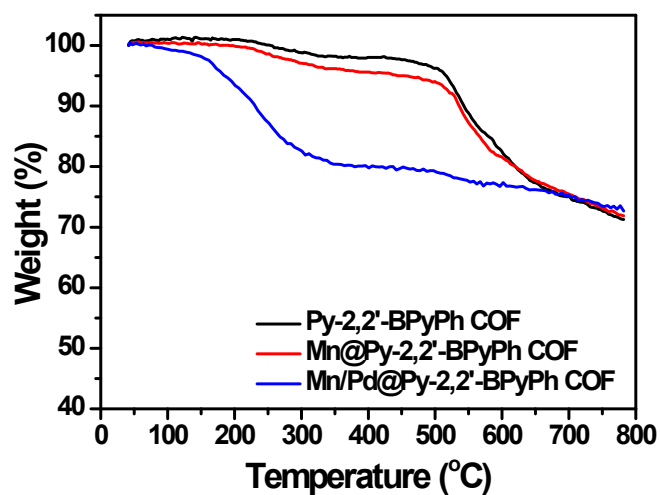


Fig. S3 TGA curves of the Py-2,2'-BPyPh COF, Mn@ Py-2,2'-BPyPh COF, and Mn/Pd@ Py-2,2'-BPyPh COF

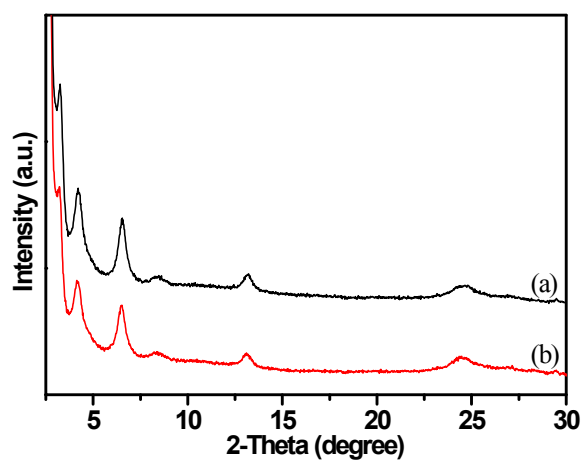


Fig. S4 PXRD patterns of (a) pristine Mn/Pd@Py-2,2'-BPyPh COF and (b) Recycled Mn/Pd@Py-2,2'-BPyPh COF after catalyzing the Heck-epoxidation tandem reaction.

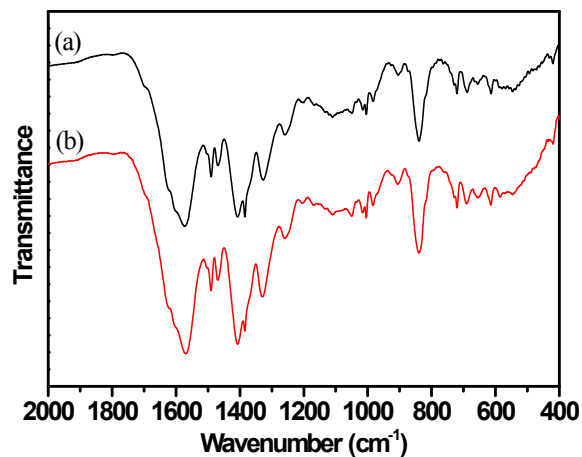
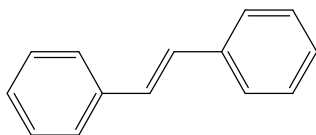
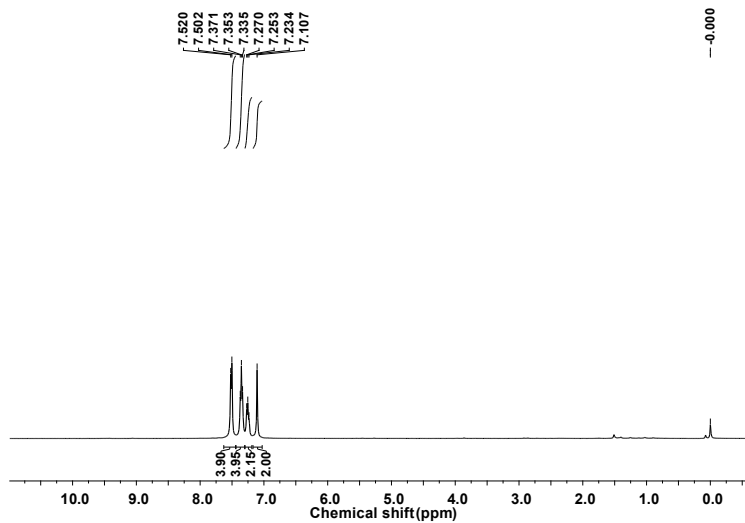


Fig. S5 FTIR patterns of (a) pristine Mn/Pd@Py-2,2'-BPyPh COF and (b) Recycled Mn/Pd@Py-2,2'-BPyPh COF after catalyzing the Heck-epoxidation tandem reaction.



^1H NMR (400 MHz, CDCl_3) δ = 7.51 (d, 4H), 7.35 (t, 4H), 7.25 (t, 2H), 7.11 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 137.4, 128.7, 127.7, 126.5. Isolated as white powder.



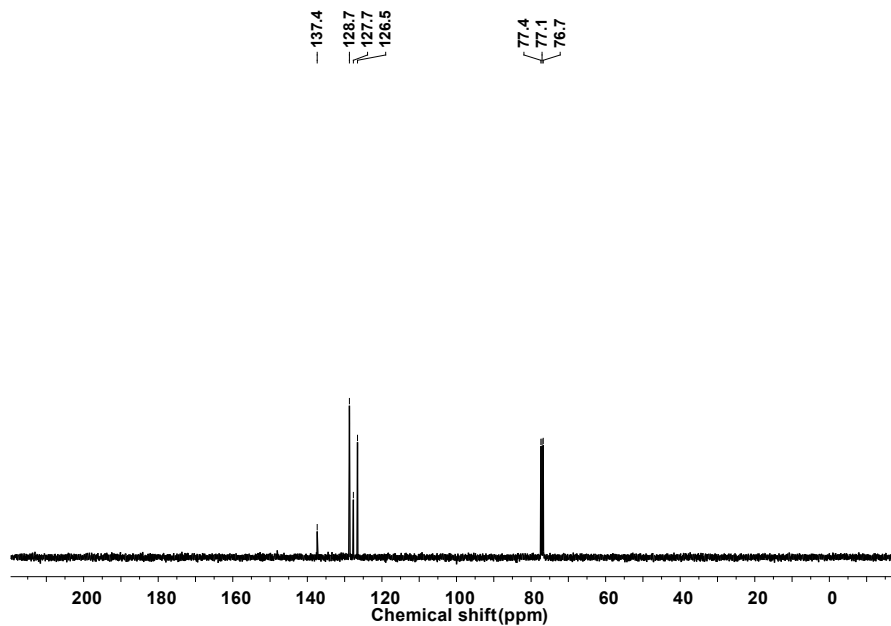
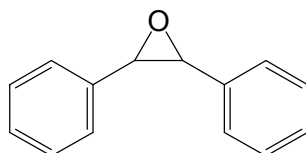
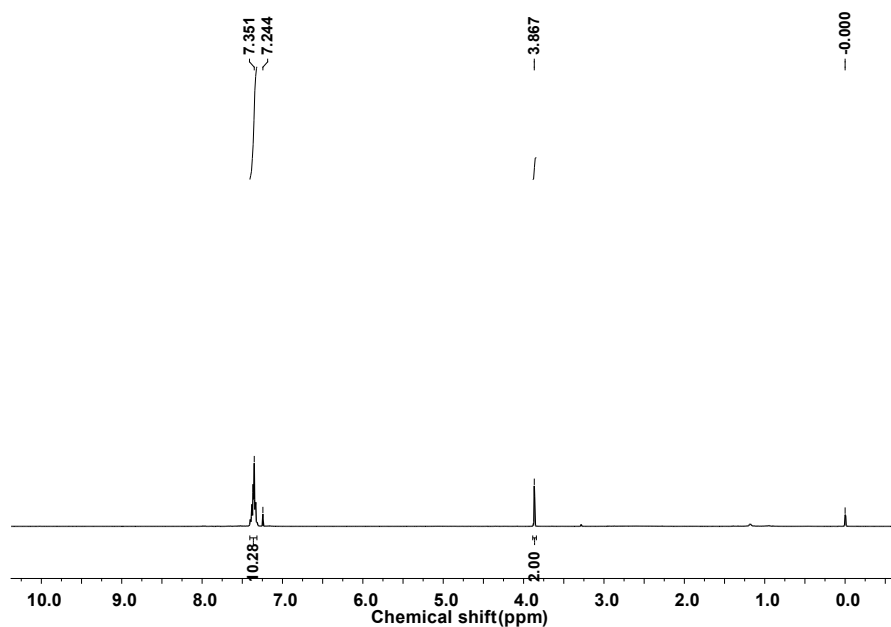


Fig. S6 Chemical structure, ^1H and ^{13}C NMR spectra of the Heck reaction product: trans-stilbene.



^1H NMR (400 MHz, CDCl_3) δ = 7.35 (m, 10H), 3.87 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 137.1, 128.6, 128.4, 125.5, 62.9. Isolated as pale yellow powder.



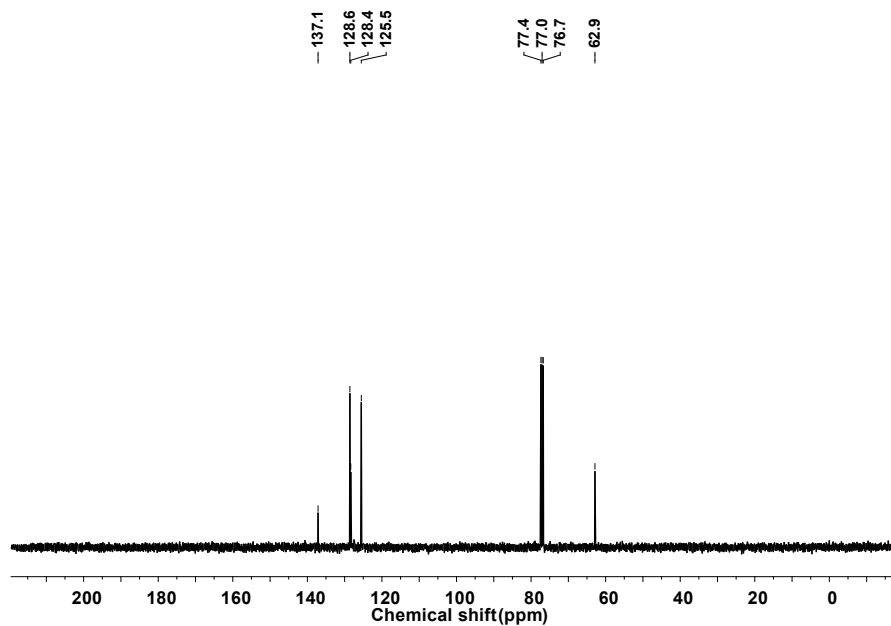


Fig. S7 Chemical structure, ^1H and ^{13}C NMR spectra of the tandem reaction product: trans-stilbene oxide.

References

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S2 J. Hodačová and M. Buděšínský, *Org. Lett.*, 2007, **9**, 5641.