Supporting Information

Continuous Photocatalytic C–C Coupling Achieved Using Palladium Anchored to a Covalent Organic Framework

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Materials and general methods

Power X-ray diffraction (PXRD) data were collected by a Smart X-ray diffractometer (Smart Lab 9 KW, Rigaku). Fourier transform infrared (FT-IR) spectroscopy was collected on a Frontier Mid-IR FTIF/STA6000-TL9000-Clarus SQ8 spectrometer with KBr as the diluents. The UV-vis diffuse reflectance spectra were detected on a spectrophotometer (Lambda 750 UV/vis/NIR). The steady-state photoluminescence (PL) spectrum was measured using F-4600 Fluorescence spectrophotometer (Hitachi). X-ray photoelectron spectroscopy (XPS) was detected with Al Kα as the excitation source on an ESCALAB 250 Xi spectrometer (Thermo). Nitrogen sorption measurements were conducted at 77 K using a multi-station specific surface micropore and vapor adsorption analyzer (BELSORPMas, Microtrac BEL, Japan). High resolution transmission electron microscope (HRTEM) images were characterized by a transmission electron microscope (FEI Talos F200X). Spherical aberration correction HRTEM images were conducted on FEI image Cs-corrected transmission electron microscope at an acceleration voltage of 200 kV (Themis Z). The metal content of each sample was quantified by an inductively coupled plasma mass spectrometer (ICP-MS, iCAP RQ, Germany). Electrochemical measurements were performed on a CHI 760E electrochemical workstation. The brand of Xe lamp used in the photocatalytic experiments was China Education Au-light and the model of Xe lamp was CEL-HXF300. The yield of biphenyl was analyzed by gas chromatograph of GC9720Plus FULI INSTRUMENTS.

Synthesis of Ace-COF.

The synthesis of Ace-COF was conducted in a 10 mL Schelk tube under an inert atmosphere. Initially, the tube was purged with argon gas to expel air. Subsequently, 35.4 mg of 4-(2,6-diisopropylphenyl)-1,3,5-triazine, 27.3 mg of quinone, 0.5 mL of 1,4-dioxane, 0.5 mL of acetonitrile and 0.1 mL of 6 M acetic acid were mixed into the reaction tube. The mixture was then subjected to three cycles of freeze-pump-thaw degassing using liquid nitrogen at 77 K to ensure the removal of dissolved gases. Upon heating up to room temperature, the tube was vacuum-sealed and transferred to an oven. The mixture was heated to 120 °C for 72 h. After cooling down to room temperature, the solid product was obtained via centrifugation. The supernatant was discarded and the resulting solid was treated with anhydrous methanol for 72 h. Fresh methanol was replaced every 24 h to ensure thorough cleaning. Subsequently, the product was subjected to centrifugation once more and washed three times in succession with acetone and tetrahydrofuran (THF) to eliminate any residual solvents and impurities. Finally, the product was dried overnight under vacuum at 120

°C to yield red-brown powder of Ace-COF.

Synthesis of Pd-Ace-COF.

In a 50 mL round-bottom flask, 20 mg of $PdCl_2$ was dissolved in 10 mL of acetonitrile, maintaining at 65 °C in an oil bath. Once $PdCl_2$ was completely dissolved, 30 mg of Ace-COF powder was introduced into the heated solution. The mixture was then stirred continuously for 12 h to promote the anchoring of Pd onto the Ace-COF framework. After cooling to room temperature, the resultant suspension was filtered using a fritted funnel to isolate the solid product. This product was subsequently washed three times with anhydrous acetonitrile to eliminate any unreacted $PdCl_2$. The filtered solid was subsequently transferred to a vacuum drying chamber and dried at 60 °C overnight to obtain the desired product, Pd-Ace-COF, as a red-brown powder.

Fourier transform infrared spectroscopy (FT-IR)

Experiments were performed on a Frontier Mid-IR FTIF/STA6000-TL9000-Clarus SQ8 spectrometer with KBr as the diluents. Before conducting the experiments, KBr was carefully ground to fine with a clean agate mortar and then dried at 120 °C for 24 h. The detailed steps were as follows: (1) KBr was pressed into tablet and the tablet was put into the sample rack in the sample compartment of the spectrometer and the reference background spectrum was collected. (2) The mixture of sample (1.0 mg) and KBr was fully ground and then pressed into tablets. The tablets were put into the sample rack in the sample compartment of the spectrometer and tested. The scanning range is 400-4000 cm^{-1}. (3) Each sample was scanned three times to ensure accurate results.

The steady-state photoluminescence (PL) spectroscopy

Experiments were performed on an F-4600 Fluorescence spectrophotometer (Hitachi). Sample (15.0 mg) was tiled into a round quartz cell for measurement upon excitation with 450 nm or 750 nm. Each sample was scanned three times to ensure accurate results.

X-ray photoelectron spectroscopy (XPS)

It was detected with Al Kα as the excitation source on an ESCALAB 250 Xi spectrometer (Thermo). The sample (10.0 mg) was adhered to a double-sided adhesive tape (1 × 1 cm) and then securely fastened onto the sample stage with a smooth surface for accurate signal transmission and measurement. Further, the sample prepared was placed into the vacuum chamber of the XPS instrument. Air was removed to establish a stable vacuum environment to exclude the interference from oxygen and other gases on the sample surface.

Electrochemical measurements

Preparation of working electrode.

The FTO glassy substrates were subjected to a sequential sonication process using deionized water, ethanol and acetone. Afterward, they were vacuum-dried at 60 °C for 12 h. The sample (2.0 mg) was dispersed in 10 μL Nafion and 1 mL ethanol to obtain a suspension, which was then subjected to ultrasonication for 60 min. 50 μL of the suspension was uniformly coated onto the FTO glassy (area of 1 cm^2) and then dried at an ambient temperature.

Photocurrent measurements.

Photocurrent measurements of COFs were performed in 0.5 M Na_2SO_4 electrolyte (pH = 6.8) at room temperature. CHI760E electrochemical workstation was employed to conduct photocurrent measurements in a standard three electrode cell comprising a working electrode, reference electrode (Ag/AgCl) and counter electrode (platinum plate). The working electrode was irradiated with a 300 W Xe lamp for 20 s to obtain the photocurrent, followed by a 20 s interval without exposure to measure the dark current. The initial potential was 0.6 V and the sensitivity (A/V) was 10^{-7}. The photocurrent response can be used to characterize the photogenerated electron transfer efficiency.

Mott-Schottky measurements.

The Mott-Schottky measurements of COFs were conducted using the CHI760E electrochemical workstation in a conventional three-electrode cell. The measurements were performed in 0.5 M Na_2SO_4 electrolyte with a pH of 6.8 at room temperature. The test was measured at frequencies of 1000, 1500 and 2000 Hz, respectively.

Electrochemical impedance spectroscopy (EIS) measurements.

EIS measurements were conducted in a conventional three electrode cell using a 0.5 M Na_2SO_4 electrolyte (pH = 6.8) at room temperature. The measurements spanned a frequency range of 0.05 to 50,000 Hz with an amplitude of 0.01 V.

Photocatalytic C-C cross-coupling reaction.

2 mg of the synthesized Pd-Ace-COF catalyst was introduced into a 15 mL clear quartz tube. Next, 0.1 mmol of iodobenzene, 0.12 mmol of phenylboronic acid and 0.2 mmol of potassium carbonate were dissolved into 5 mL of ethanol in the tube. The reaction mixture underwent

sonication to ensure uniform mixing of the reactants. The mixture was purged with argon gas for 15 min to fully eliminate the oxygen. The reaction was irradiated with a 300 W xenon lamp, equipped with a cutoff filter (> 400 nm). The light intensity was maintained at 100 mW/cm². The reaction was conducted under ambient condition for 6 h, resulting in the formation of biphenyl with a yield of 100%. Upon completion of the reaction, the catalyst was recovered by centrifugation, allowing for its potential reuse in subsequent reactions.

Continuous Photocatalytic C-C coupling Reaction.

20 mg of Pd-Ace-COF photocatalyst was dispersed in ethanol and subsequently coated onto a non-woven fabric surface. 1.2 mmol of iodobenzene, 1 mmol of phenylboronic acid and 1 mmol of potassium carbonate (K_2CO_3) were dissolved into 50 mL of ethanol in a three-neck flask. The mixture was subsequently introduced into the reactor at a controlled flow rate via a peristaltic pump. The reactor, equipped with a transparent tubular flat passage, facilitated the formation of stable alcohol phase segments, which were subsequently irradiated with a xenon lamp for 24 h. The continuous flow system enabled the production and collection of biphenyls in a product reservoir under visible light irradiation.

Recycle experiments.

To assess the recyclability of the photocatalyst, the Pd-Ace-COF catalyst underwent centrifugation after each 4 h illumination cycle. Subsequently, a rigorous washing procedure was performed, consisting of three sequential rinses with deionized water followed by three rinses with ethanol to eliminate any adsorbed reactants or products. After thoroughly cleaning the catalyst, the Pyrex reactor was refilled with fresh phenylboronic acid and iodobenzene. The solution was then irradiated using a 300 W xenon lamp with a UV cutoff filter (> 400 nm) at 298 K to initiate the catalytic reaction cycle.

Electron paramagnetic resonance (EPR) analysis.

We further performed EPR experiments under the reaction conditions involving iodobenzene, phenylboronic acid, ethanol, and K_2CO_3, as in Fig. S12. During EPR detection of the reaction system, we observed that the EPR spectrum curves remained nearly linear and no significant EPR signals were detected in the absence of iodobenzene and phenylboronic acid reagents. This indicates that there is no obvious detectable free radical generation under these conditions. However, when iodobenzene was added to the system, the EPR spectrum exhibited characteristic multi-peak signals, indicating the formation of free radicals after the addition reaction between iodobenzene and the spin trapping agent DMPO. This provided a strong evidence for a free radical reaction process initiated by a redox reaction within the system.

Reaction mechanism.

Under visible light irradiation, Pd-Ace-COF efficiently captures light energy, and Ace-COF transitions to an excited state (Ace-COF*). Subsequently, electrons within the framework are transferred to the Pd center to produce the reduced Pd. Iodobenzene undergoes oxidative addition with the reduced Pd active sites to form the intermediate Ph- Pd-I. Meanwhile, photogenerated holes can oxidize phenylboronic acid, causing the breaking of C-B bond. The target product, biphenyl, is ultimately obtained through the processes of transmetallation and reductive elimination.

Summary of figures and tables

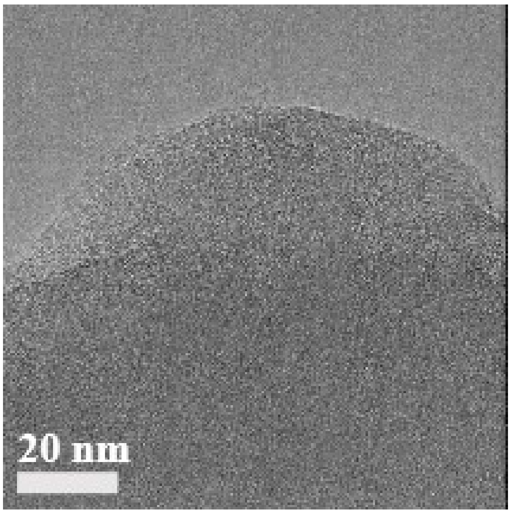


Fig. S1. HRTEM image of Pd-Ace-COF.

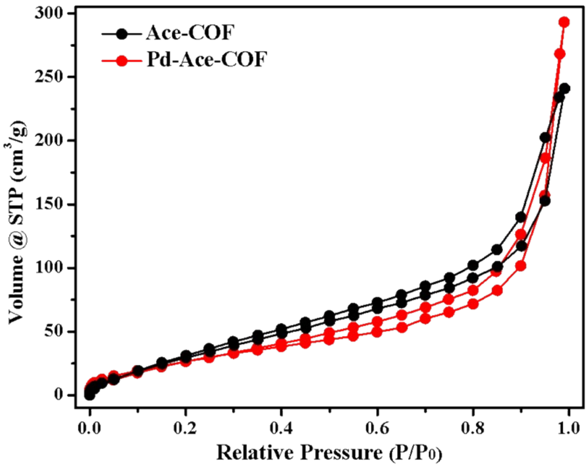


Fig. S2. N_2 adsorption−desorption isotherms of Ace-COF and Pd-Ace-COF.

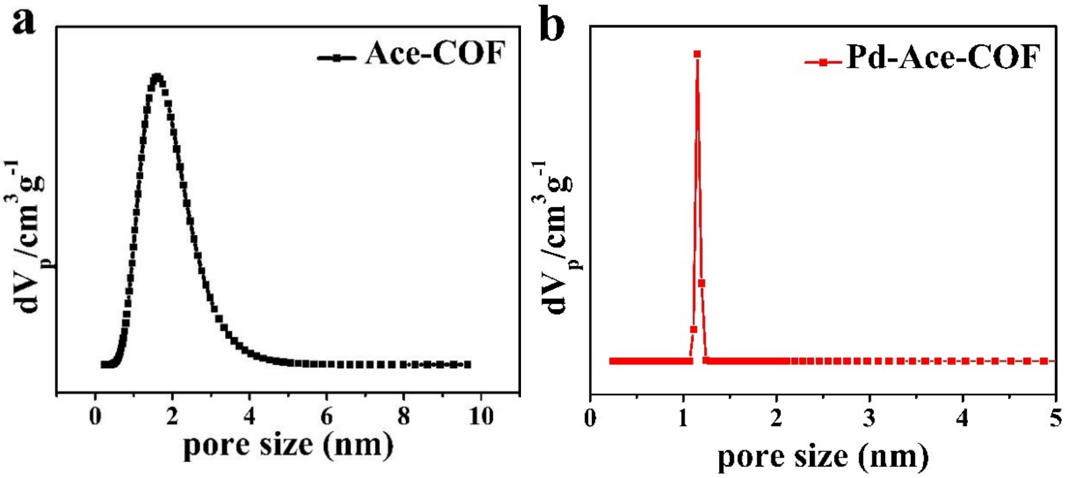


Fig. S3. Pore size distribution profile (inset) of (a) Ace-COF and (b) Pd-Ace-COF.

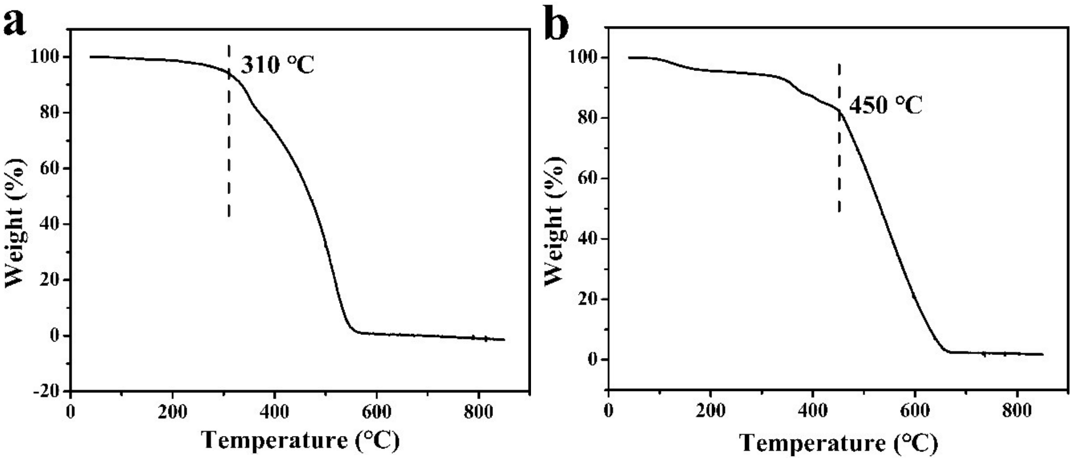


Fig. S4. TGA of (a) Ace-COF and (b) Pd-Ace-COF.

Table S1. Comparison chart of cell parameters and refinement details

	a	b	c	α	β	γ	Rp	Rwp
The work	28.7668 Å	28.7668 Å	3.5734 Å	90°	90°	120°	5.52%	7.21%

Table S1 presents a comparison of cell parameters (including lattice constants a, b, c and inter - axial angles α, β, γ) and refinement details (Rp and Rwp factors)

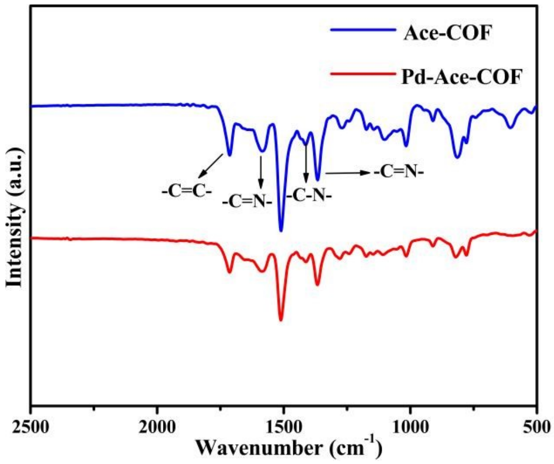


Fig. S5. FT-IR spectra of Pd-Ace-COF and Ace-COF.

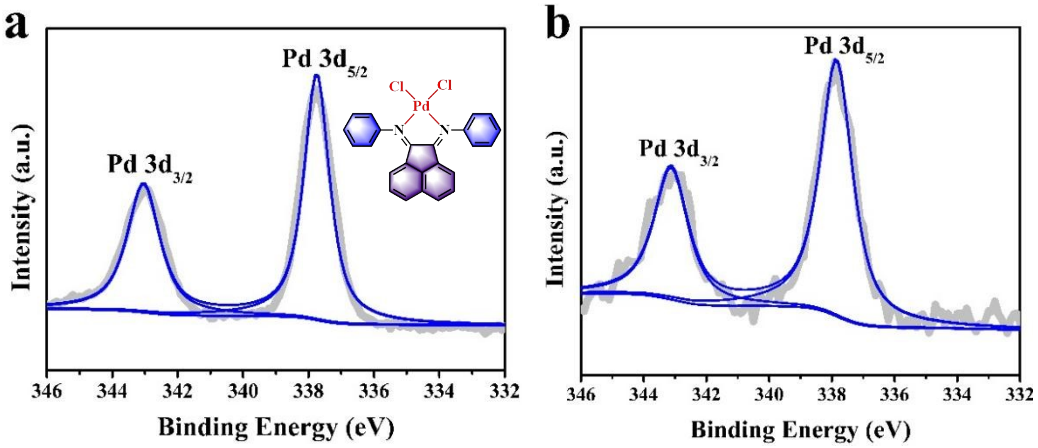


Fig. S6. XPS spectra of (a) Pd-1 and (b) Pd-Ace-COF.

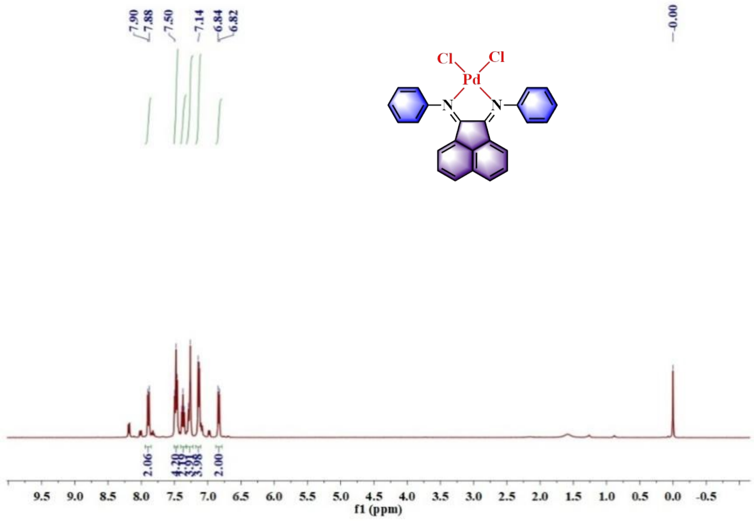


Fig. S7. ^{1}H NMR spectrum of Pd-1.

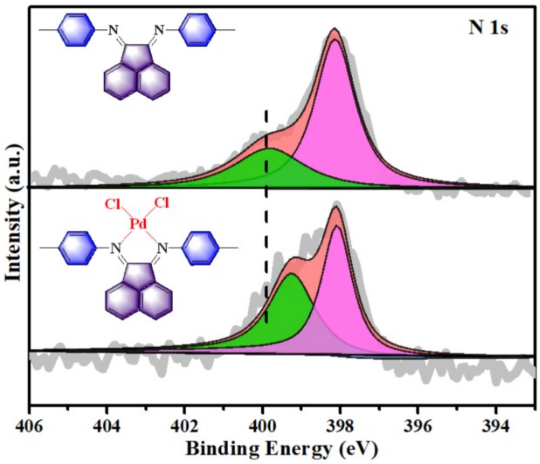


Fig. S8. N 1s XPS spectra of Ace-COF and Pd-Ace-COF.

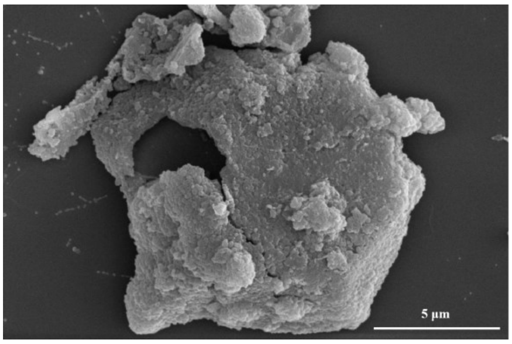


Fig. S9. SEM image of Pd-Ace-COF.

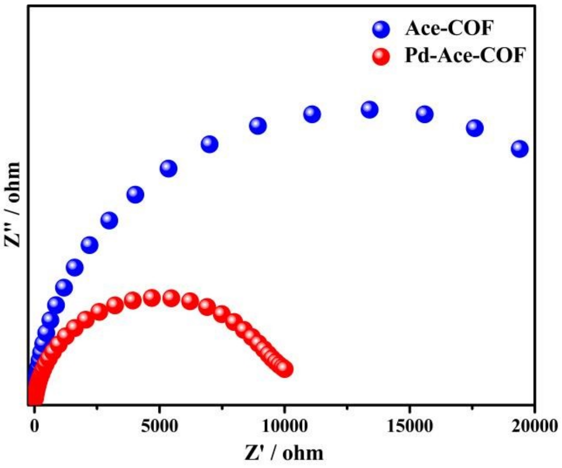
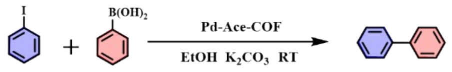


Fig. S10. EIS spectra of Ace-COF and Pd-Ace-COF.

Table S2. Control experiments of Pd-Ace-COF catalyzed suzuki coupling reaction.



1a 2a 3a

Entry	Variation from the standard conditions	Yield (%)
1	Normal condition	99
2	Dark	Trace
3	Ace-COF	Trace
4	No K_2CO_3	Trace
5	DMPO	Trace
6	Triethylamine	Trace
7	Physical mixture of $PdCl_2$ and COF	Trace
8	Pd NP-Ace-COF	58
9	Chlorobenzene	80
10	Bromobenzene	99

Reaction conditions: Pd-Ace-COF (2 mg), 1a (0.12 mmol), 2a (0.1 mmol), K_2CO_3 (0.1 mmol), CH_3CH_2OH (5 mL), 6 h (Chlorobenzene: 48 h; Bromobenzene: 24 h). Yields of biphenyl are determined by gas chromatography.

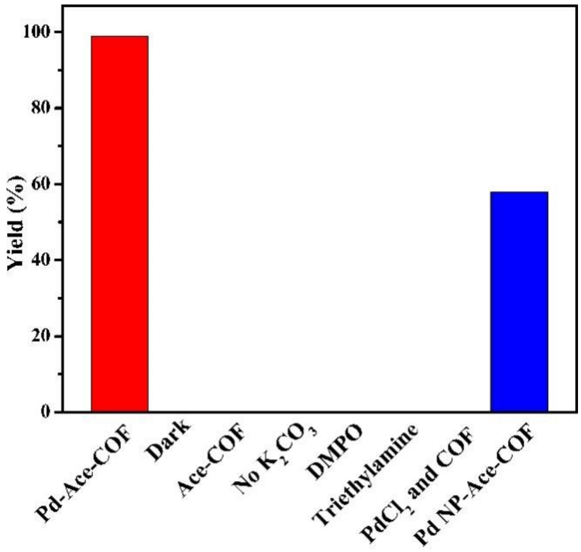


Fig. S11. Control experiments with single-atom Pd photocatalyst for suzuki C-C coupling.

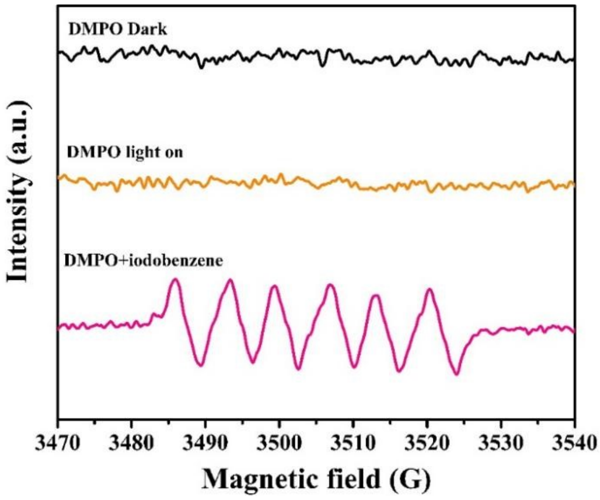
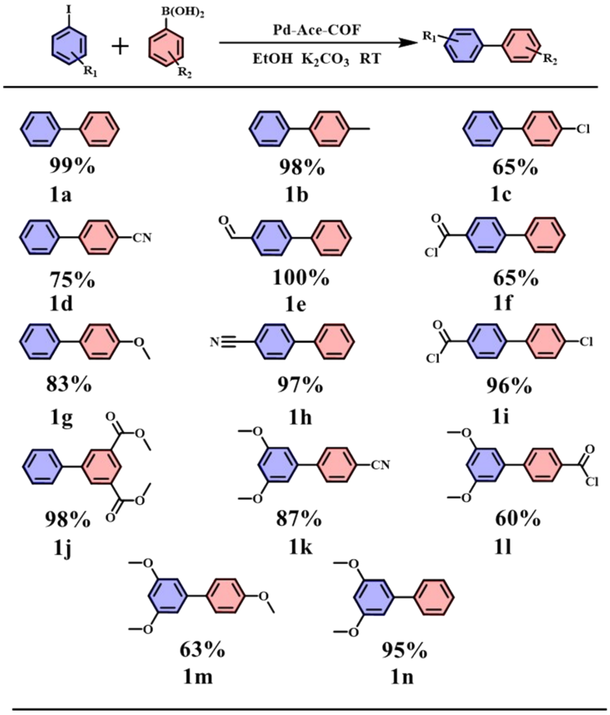


Fig. S12. Series of EPR spectra for reaction mixtures with consecutive addition of reagents.

Table S3. Substrate scope of Pd-Ace-COF catalyzed suzuki-miyaura cross-coupling reaction between iodophenyl derivatives and phenylboronic acid derivatives.



Reaction condition: 2 mg Pd-Ace-COF, 0.12 mmol iodophenyl derivatives, 0.1 mmol phenylboronic acid derivatives, 0.1 mmol K_2CO_3, 5 mL alcohol, 300 W xenon lamp, 6 h.

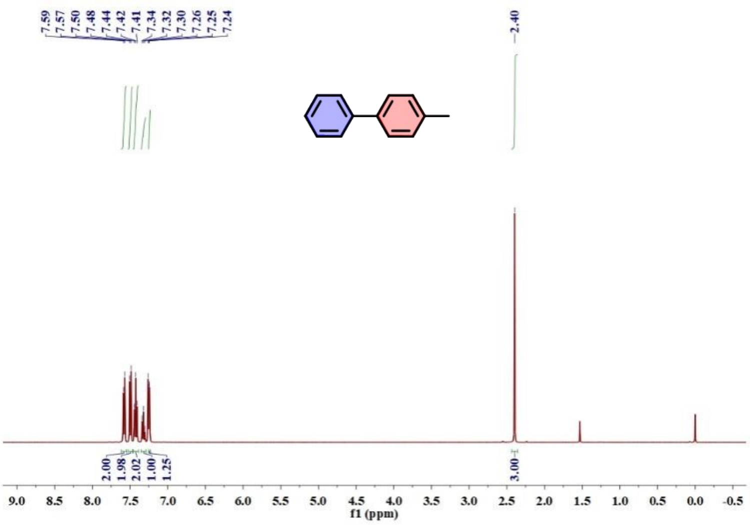


Fig. S13. ^{1}H NMR spectrum of 1b.

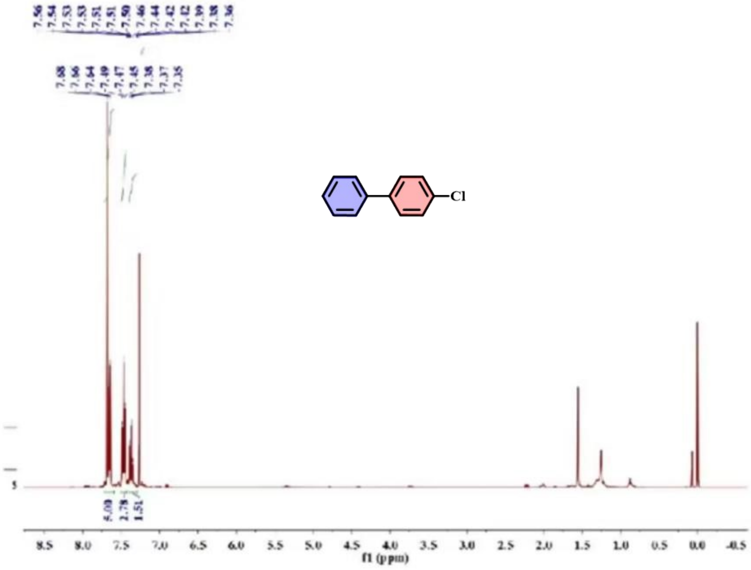


Fig. S14. ^{1}H NMR spectrum of 1c.

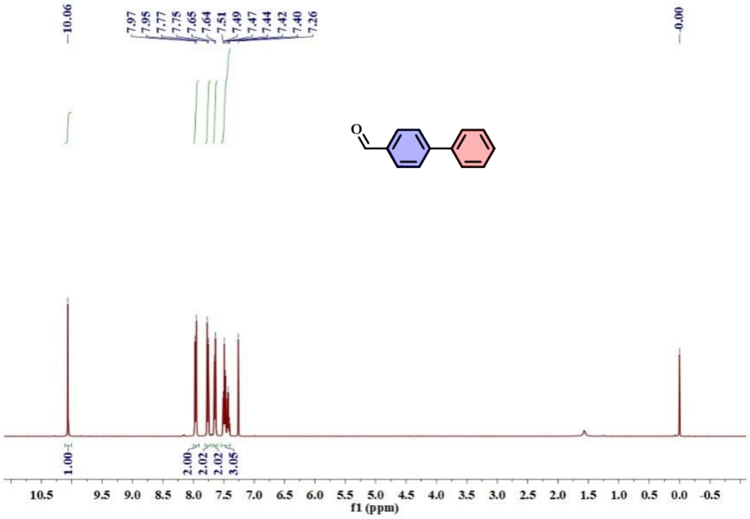


Fig. S15. ^{1}H NMR spectrum of 1e.

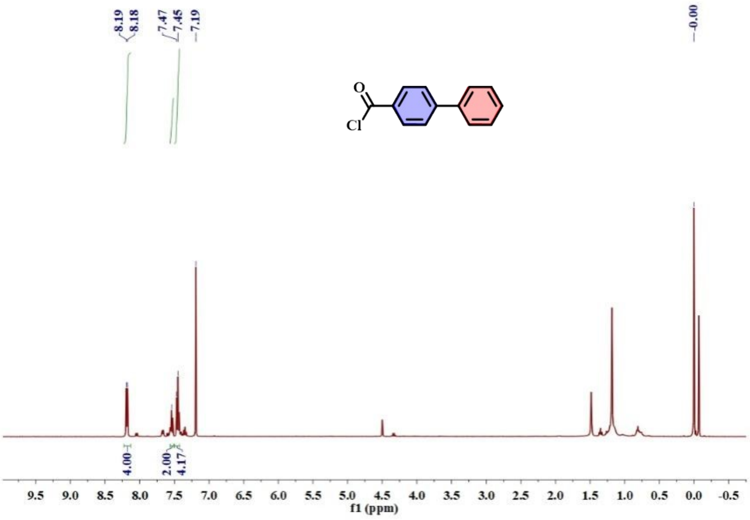


Fig. S16. ^{1}H NMR spectrum of 1f.

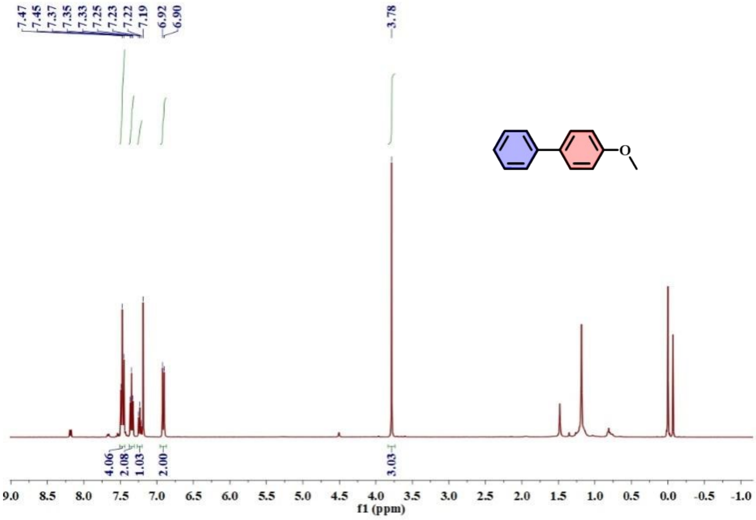


Fig. S17. ^{1}H NMR spectrum of 1g.

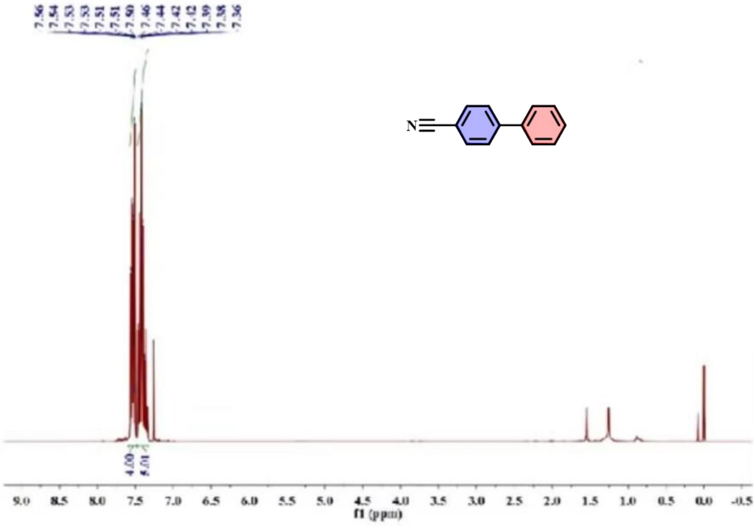


Fig. S18. ^1H NMR spectrum of 1h.

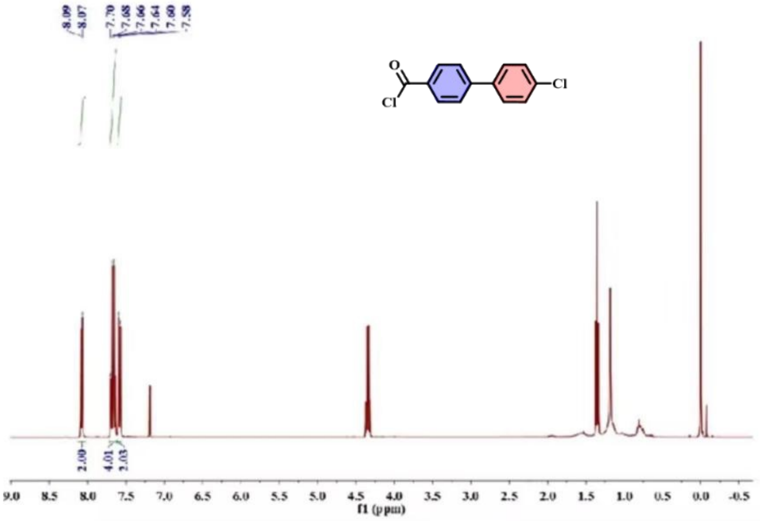


Fig. S19. ^1H NMR spectrum of 1i.

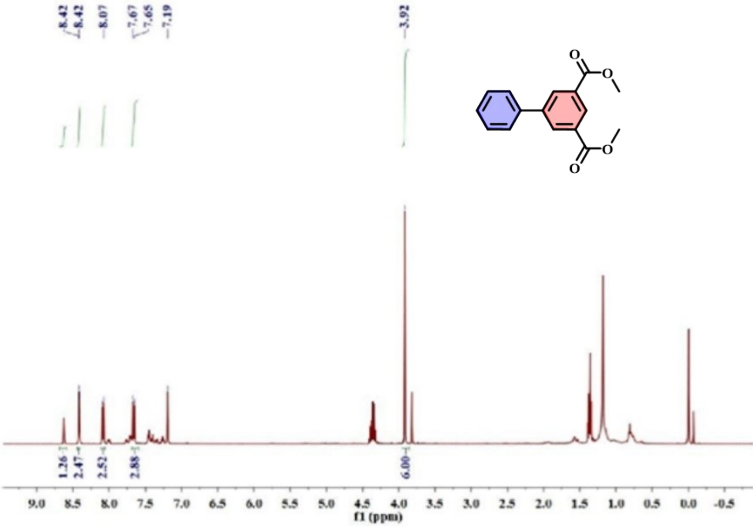


Fig. S20. ^{1}H NMR spectrum of 1j.

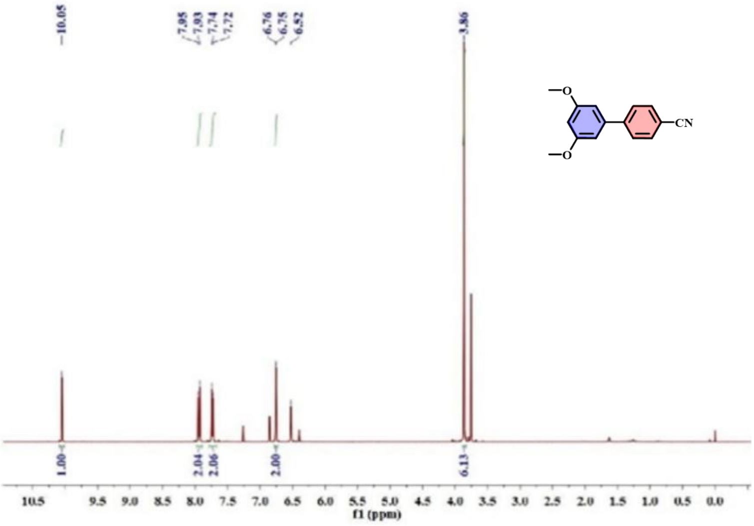


Fig. S21. ^{1}H NMR spectrum of 1k.

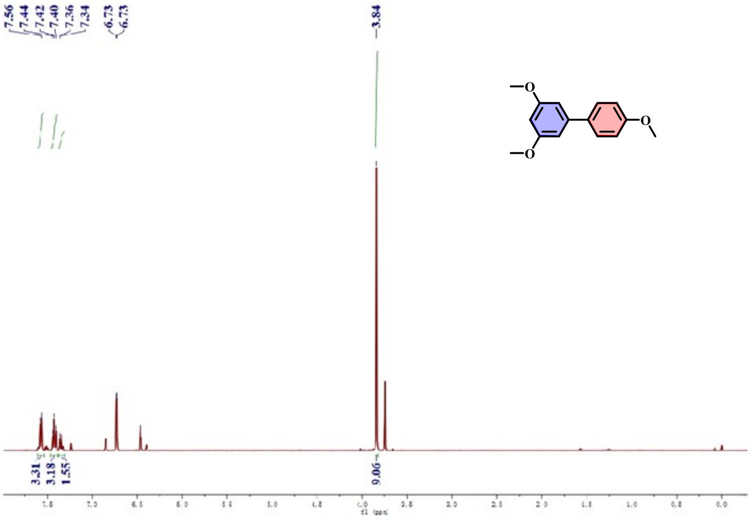


Fig. S22. ^{1}H NMR spectrum of 1m.

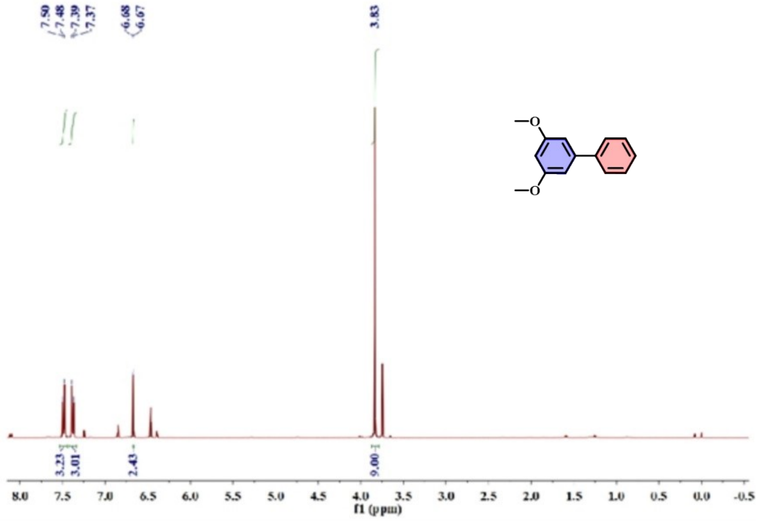


Fig. S23. ^{1}H NMR spectrum of 1n.

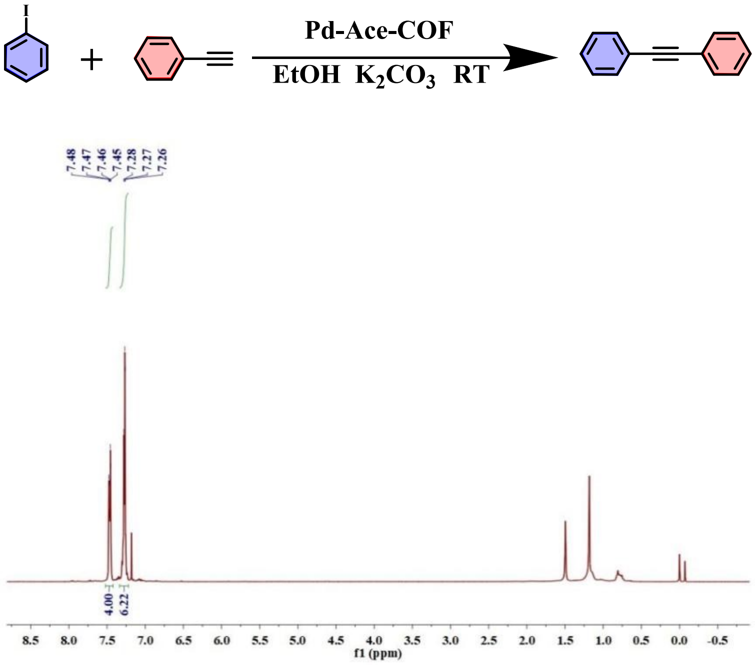


Fig. S24. ^{1}H NMR spectrum of 1,2-diphenylethyne.
Reaction condition: Under an Ar atmosphere, 0.12 mmol iodo-benzene, 0.1 mmol phenylacetylene, 2 mg Pd-Ace-COF, 0.1 mmol K_2CO_3, 5 mL alcohol.

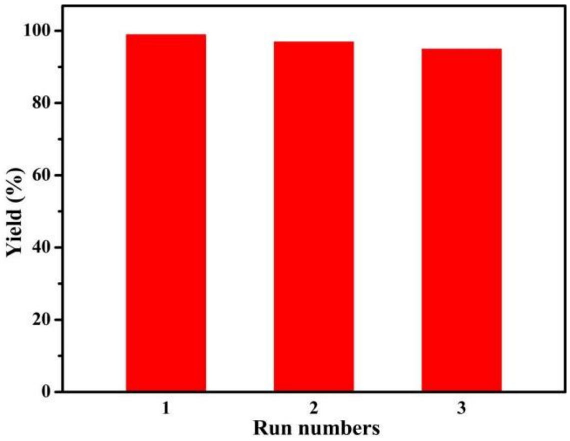


Fig. S25. Recyclability experiments. Reaction conditions: A mixture of 5 mL of alcohol, 0.12 mmol of iodo-benzene, 0.1 mmol of phenylboronic acid and 0.1 mmol of K_2CO_3 were added in 2 mg of Pd-Ace-COF reaction system. The reaction was irradiated with a 300 W xenon lamp at room temperature (298 K).

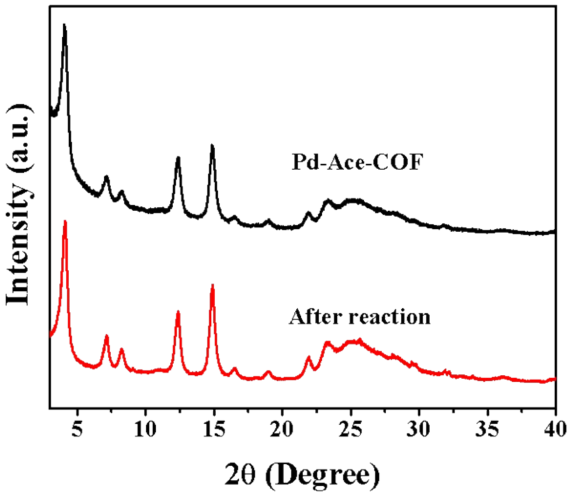


Fig. S26. Experimental PXRD patterns of Pd-Ace-COF and after the reaction.

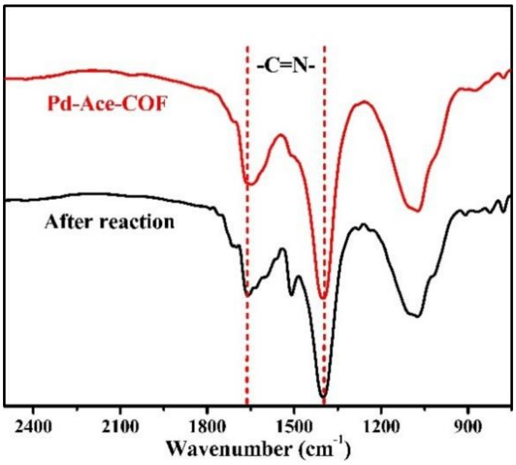


Fig. S27. FT-IR spectrum of Pd-Ace-COF and after the reaction.

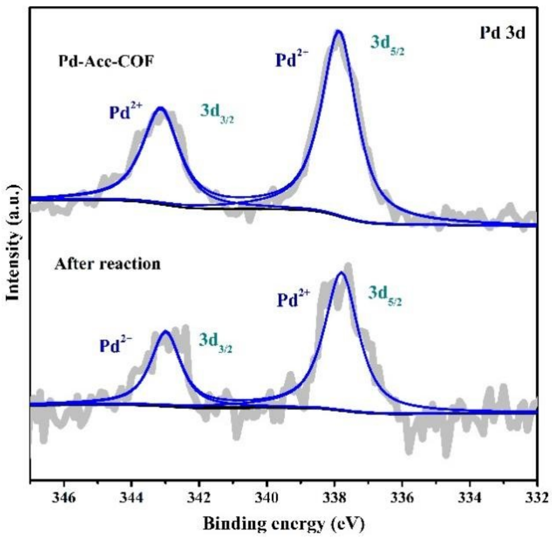


Fig. S28. XPS spectrum after reaction.

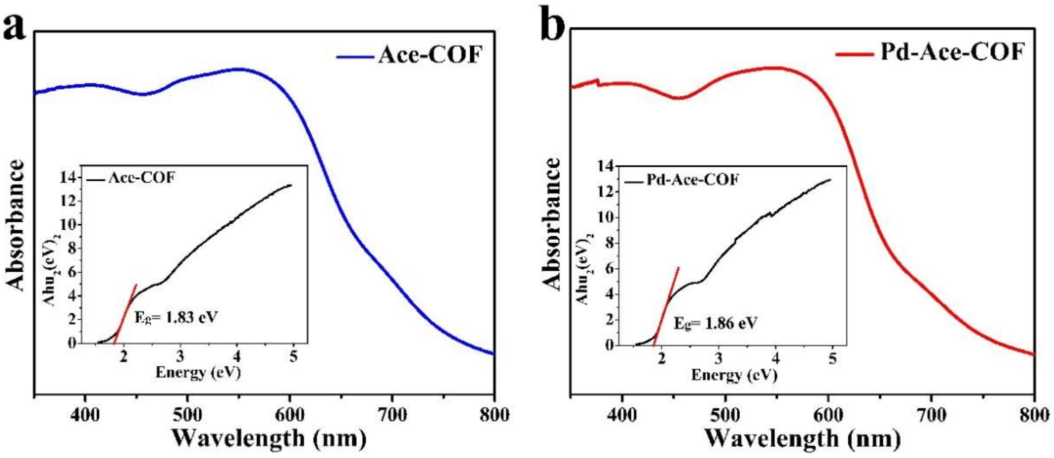


Fig. S29. UV-vis DRS spectra and Tauc plot of (a) Ace-COF and (b) Pd-Ace-COF.

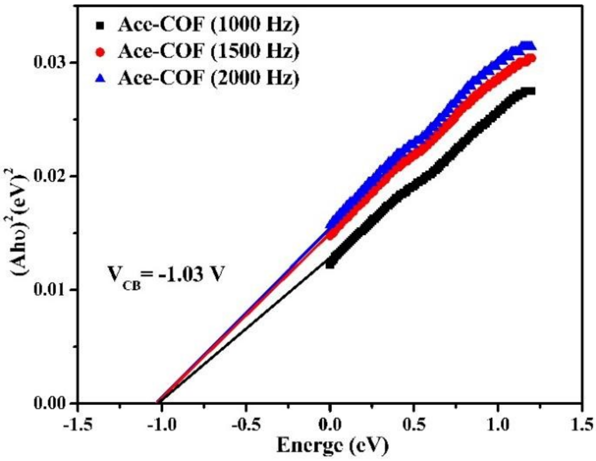


Fig. S30. Mott-Schottky plots of Ace-COF.

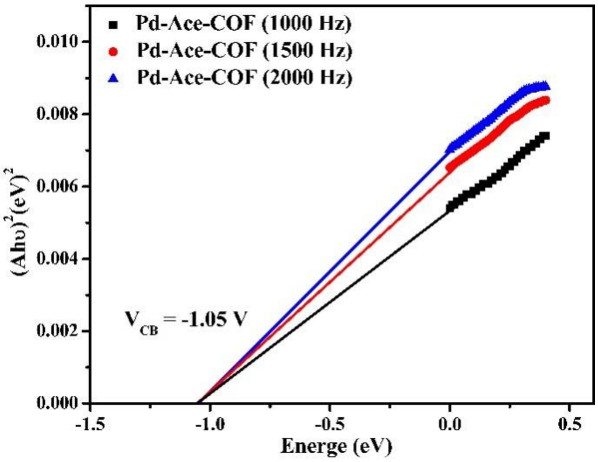


Fig. S31. Mott-Schottky plots of Pd-Ace-COF.

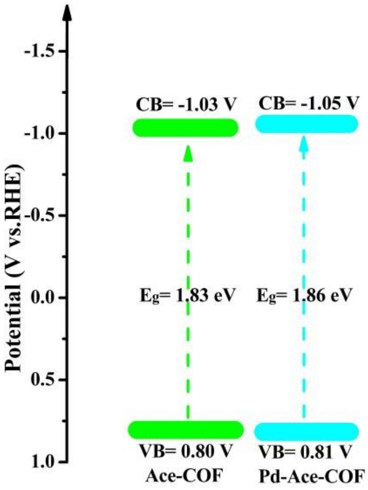


Fig. S32. Energy band of Ace-COF and Pd-Ac-COF.

In Pd-Ace-COF, Pd sites are catalytic centers and Ace-COF is the center of light absorption and electron/hole transfer. After introducing Pd, the fluorescence of Ace-COF was significantly quenched, indicating an electron transfer from Ace-COF to Pd for C-C coupling reaction. Therefore, despite the similar band positions between Pd-Ace-COF and Ace-COF, Ace-COF hard to drive C-C coupling reaction due to the lack of catalytic center.

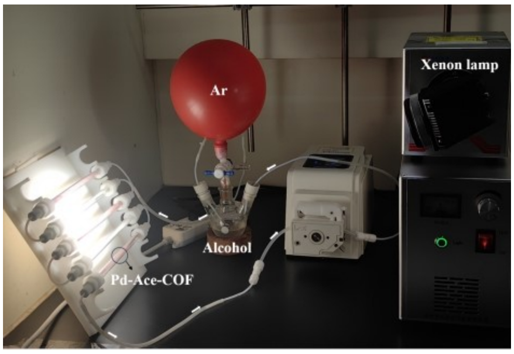


Fig. S33. Photograph of the mobile phase system.