Supporting Information

Covalent Organic Framework-Supported Platinum Nanoparticles as Efficient Electrocatalysts for Water Reduction

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1. Materials and Instrument Information

Materials: Pyrrole (SAFC), *p*-nitrobenzaldehyde (Combi-Blocks, Inc), acetic anhydride (Sigma Aldrich), propionic acid (Alfa Aesar), $SnCl_2$ (Alfa Aesar), HCl (Fisher Scientific), 5,5'-dimethyl-2,2'-dipyridyl (TCI), N-bromosuccinimide (AK Scientific), benzoyl peroxide (Sigma Aldrich), hexamethylenetetramine (Sigma Aldrich), and 10 wt% of commercial platinum on carbon black (Sigma Aldrich) were purchased from the commercial providers and used without further purification. The free-base porphyrin **1** and the bipyridine-dialdehyde **2** were synthesized by following the previous literature reports.[1,2]

Instruments: ^1H NMR spectra were recorded on a Bruker Avance-III 300 NMR spectrometer. ^{13}C CP MAS solid state of NMR spectra were obtained with 4 mm revolution probe using the following parameters: 3 ms contact time, 2 sec relaxation time, 4096 number of scan, and 10 KHz spin rate. The UV-Vis absorption spectra were recorded on a Agilent 8453. Fourier transform infrared (FT-IR) spectra were measured with Agilent Technologies, Cary 630. The powder X-ray diffraction patterns (PXRD) were obtained on an X`Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å). Gas adsorption isotherms were measured by a Quantachrome Autosorb ASiQ automated gas sorption analyzer. The pore size distribution was calculated via NLDFT equilibrium method using Quantachrome AsiQwin program. Thermalgravimetric analysis was performed on a thermogravimetric/differential thermal analyzer. Transmission Electron Microscopy images were obtained on a FEI Tecnai T12, 120 kV TEM. HAADF STEM images were acquired by an aberration-corrected Titan Themis S/TEM at 300 keV. Inductively Coupled Plasma Mass Spectrometry was recorded on a Perkin Elmer Optima 7300DV. XPS was measured by PE-5800 X-ray photoelectron spectroscopy.

2. Preparation of working electrodes

A mixture of the catalyst (10 mg) and carbon black (10 mg) were sonicated for 30 min in of N,N-dimethylformamide (4.0 mL, DMF). Samples were then dried at room temperature (25 ± 0.1 °C) for 24 hours in a laminar flow hood. The resulting dry powders were then mixed with 5% nafion solution (700 μL per mg of powder mixture).[3] An aliquot of the resulting suspension (100 μL) was then drop casted on one side of carbon paper (Toray-50% wet-proofed) and dried for 48 hours at room temperature.

3. Controlled potential electrolysis

To investigate the hydrogen evolution capabilities of the catalysts, we conducted controlled potential electrolyses using a Pine Research (WaveDriver-200 series) potentiostat with a standard Pine Research electrochemical cell (AKCELL1) containing two chambers separated by a glass frit. The cathodic compartment contained catalysts coated-carbon paper as the working electrode (partly submerged in the electrolyte solution) and an Ag/AgCl reference electrode with ceramic porous frit (BASi-MW-2030). The anodic compartment had a large graphite electrode (OD= 0.250", L= 12"). The supporting electrolyte in both chambers contained 0.5 M $NaHCO_3$ dissolved in deionized water. Prior to the electrolysis, electrolytes were saturated with pure argon and the cell was sealed using gas tight rubber seals (Pine Research-14/20; 24/25).

4. Gas analysis

Gas samples were obtained directly from the headspace of the electrochemical cell using a 250 μL gas-tight syringe (Hamilton-1700 series) and immediately analyzed on an Agilent Technologies 7890 A gas chromatography system equipped with a thermal conductivity detector (TCD) and packed column. The oven temperature was a constant 60 °C. Injector and detector temperatures were stable at 150 °C and 250 °C, respectively. Argon gas was used as the carrier gas at a flow rate of 5 mL min^{-1}. 0.5 M H_2 molar concentrations were determined by fitting data to a five-point standard curve prepared for each gas using standard calibration gases.

5. FT-IR spectra of two monomers, COF-bpyTPP, and PtNPs@COF

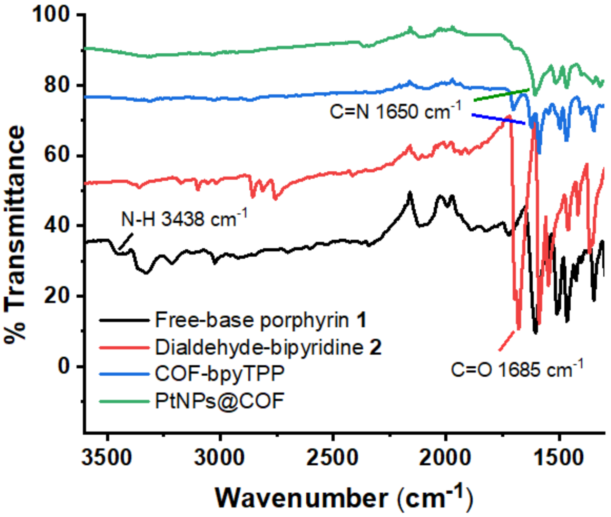

Fig. S1 FT-IR spectra of monomers **1** and **2**, COF-bpyTPP, and PtNPs@COF.

6. ^{13}C CP-MAS solid state NMR spectrum of COF-bpyTPP

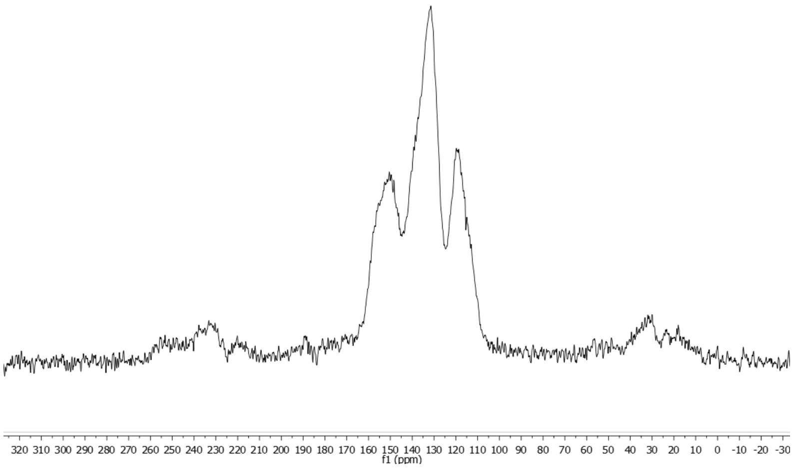

Fig. S2 Solid ^{13}C NMR spectrum of COF-bpyTPP.

7. PXRD analysis of COF-bpyTPP

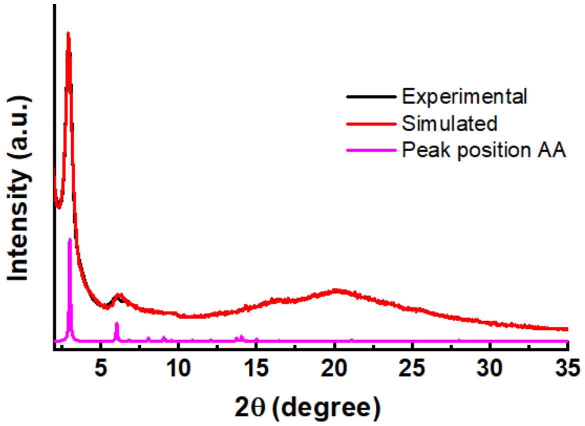

Fig. S3 PXRD patterns of COF-bpyTPP and simulation: Experimental diffraction patterns of COF-bpyTPP (black line) match well with the simulated values of the AA stacking mode (purple line) by the Materials Studio. Pawley refinements were performed on the optimized unit cell parameters (a = 29.93 Å and c = 12.55 Å), which led to good agreement factors ($R_p = 2.46\%$ and $R_{wp} = 3.29\%$).

8. Refined unit cell parameters and fractional atomic coordinates of COF-bpyTPP

Name	COF-bpyTPP		
Space group	*P4/m*		
***a* (Å)**	29.93		
***c* (Å)**	12.55		
Atom name	***x***	***y***	***z***
C1	0.26054	0.98632	0.25437
C2	0.23675	1.00595	0.33936
C3	0.19015	1.00865	0.33819
N4	0.45204	1.03713	0.36846
C5	0.16589	0.99279	0.25088
C6	0.1163	0.99555	0.24872
N7	0.30848	0.98232	0.25677
C8	0.19063	0.97273	0.16115
C9	0.23705	0.9696	0.16613
C10	0.45173	0.96225	0.30233
C11	0.47523	1.00001	0.3376
N12	0.04581	0.94866	0.24796
C13	0.09093	0.95281	0.24795
C14	0.11121	0.91128	0.24878

C15	0.03799	0.90403	0.24815
C16	0.0778	0.88044	0.24738
H17	0.25436	1.01902	0.40765
H18	0.17292	1.02355	0.40509
H19	0.38948	1.0688	0.39004
H20	0.17284	0.9597	0.09300
H21	0.25491	0.95427	0.10069
H22	0.32369	0.9615	0.20068
H23	0.38759	0.93392	0.27023
H24	0.14652	0.90372	0.25059
H25	0.08259	0.84462	0.24600
C26	0.4052	0.96342	0.29701
C27	0.38211	1.00217	0.3271
C28	0.40661	1.0387	0.36483
H29	0.46919	0.93245	0.27668
C30	0.33298	1.00559	0.32194
H31	0.46907	1.06521	0.39661

Table. S1 Refined unit cell parameters and fractional atomic coordinates of COF-bpyTPP.

9. Nitrogen adsorption-desorption isotherms of COF-bpyTPP

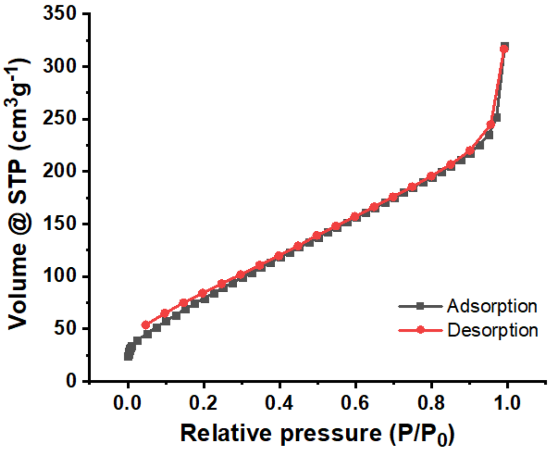

Fig. S4 Nitrogen adsorption-desorption isotherms of COF-bpyTPP at 77 K.

10. TGA graph of COF-bpyTPP

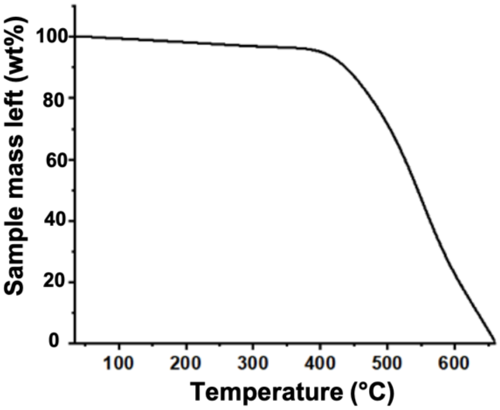

Fig. S5 TGA graph of COF-bpyTPP.

11. HAADF STEM of PtNPs@COF

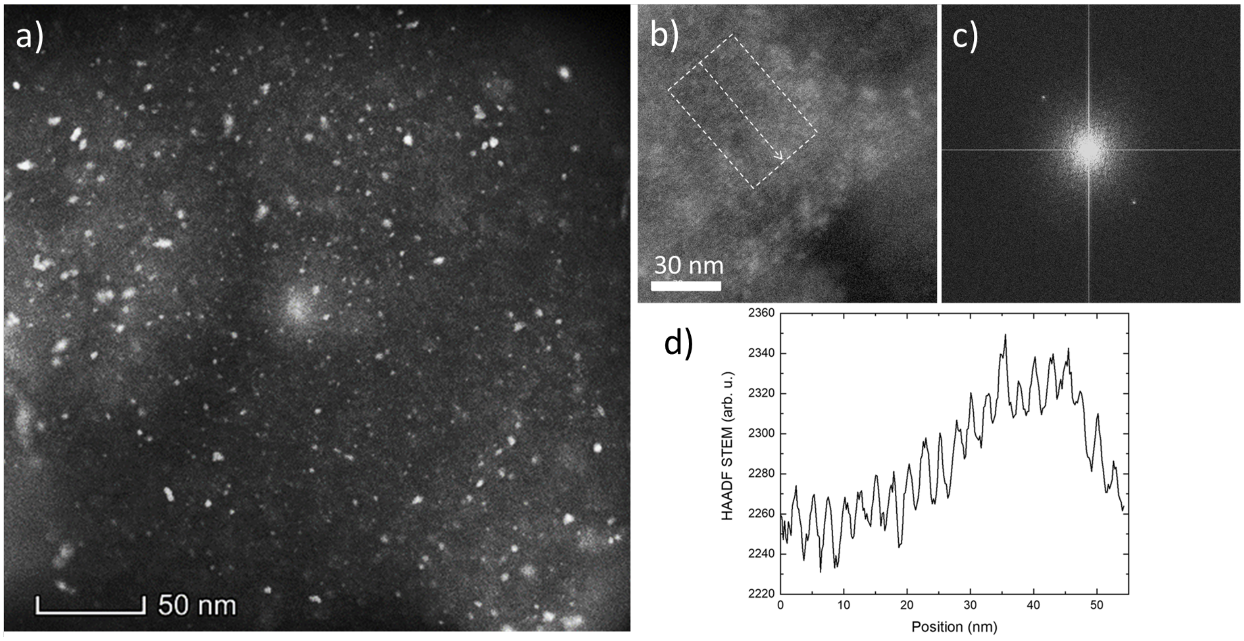

Fig. S6 HAADF STEM images of PtNPs@COF. a) A low magnification HAADF STEM image showing PtNPs as small as 1-2 nm distributed uniformly across the COF substrate. b) A HAADF STEM image taken at a higher magnification showing that small Pt nanoparticles follow the substrate periodicity, and c) its Fourier-transformed pattern (FFT) showing two distinct spots corresponding to a periodicity of 2.5 nm. d) A line profile from the region marked by a white dashed box in b) confirming the periodicity of the COF substrate.

12. TEM image of Pt NPs without any COF support

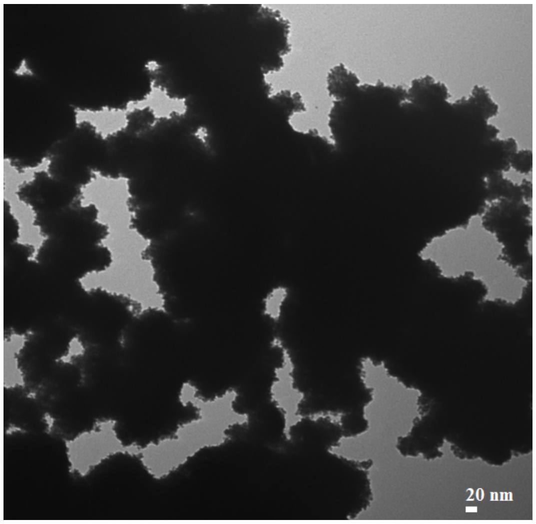

Fig. S7 The TEM image of PtNPs prepared in the absence of any COF materials.

13. ICP-MS analysis of PtNPs@COF

	PtNPs@COF
Concentration (ppb)	29.886
Mass of Pt (mg)	0.299
Mass of COF (mg)	4.904
% Pt	6.09

Table. S2 ICP-MS analysis results of PtNPs@COF.

14. XPS spectra of PtNPs@COF

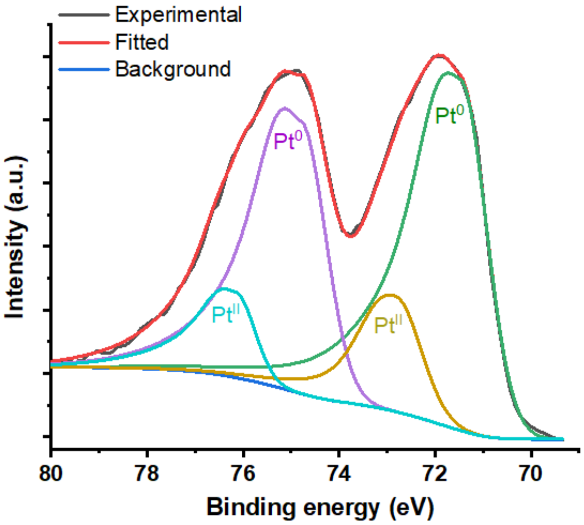

Fig. S8 XPS spectra of PtNPs@COF (black line): the two peaks with binding energy of 71.8 (green line) and 74.9 eV (purple line) correspond to 4f$_{7/2}$ and 4f$_{5/2}$ of Pt^0. None of peaks from Pt (II) was observed (yellow and blue line).

15. TEM image of PtNPs@COF after five runs of the reduction of 4NP

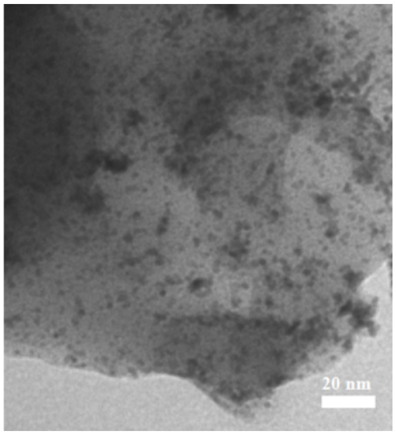

Fig. S9 TEM image of PtNPs@COF after five times of recycling and reuse in the reduction of 4NP.

16. TEM image of PtNPs@COF after electrolysis for 11 hour in alkaline electrolyte

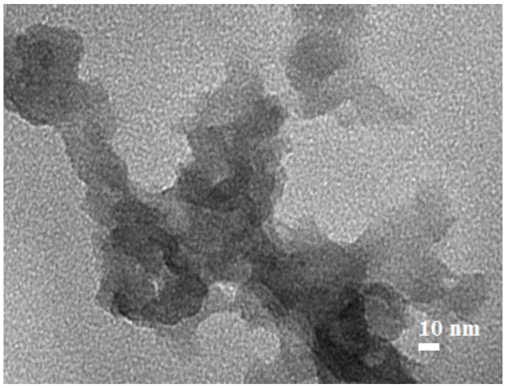

Fig. S10 TEM image of PtNPs@COF after 11 hours electrolysis in 0.5 M $NaHCO_3$ solution. A mixture of PtNPs@COF, carbon black, and nafion on the carbon paper was dissolved in methanol to prepare a sample of TEM.

17. TEM image of commercial Pt/C (10 wt% of Pt on carbon black)

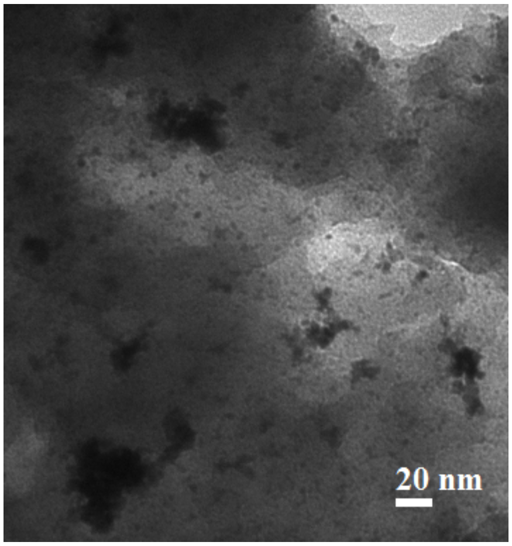

Fig. S11 TEM image of commercial Pt/C.

18. TEM image of higher loading PtNPs@COF-HL (11 wt%)

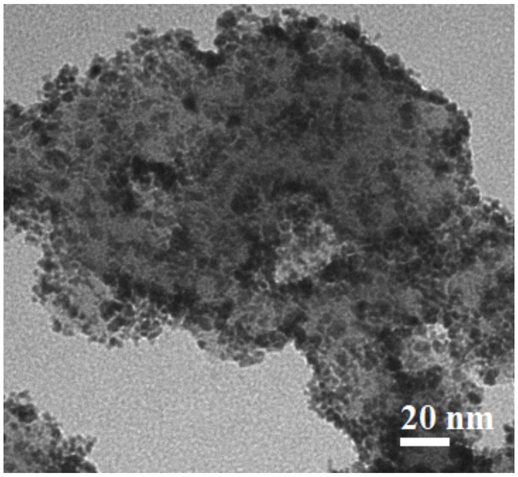

Fig. S12 For different Pt loading experiment, higher loading of Pt was prepared and characterized by TEM image.

19. ICP-MS analysis of different loading of PtNPs on COF

	PtNPs@COF-LL	PtNPs@COF-RL	PtNPs@COF-HL
Concentration (ppb)	6.831	11.591	15.795
Mass of Pt (mg)	0.03757	0.06375	0.08687
Mass of COF (mg)	0.9	1.0	0.8
% Pt	4.17	6.38	10.9

Table. S3 ICP-MS analysis results of different loading of PtNPs on COF.

References

S1. Bettelheim, A.; White, B. A.; Raybuck, S. A.; Muray, R. W. Electrochemical Polymerization of Amino-, Pyrrole-, and Hydroxy-Substituted Tetraphenylporphyrins. *Inorg. Chem.* **1987**, 26 (7), 1009-1017.

S2. Borozdina, Y. B.; Mostovich, E. A.; Cong, P. T.; Postulka, L.; Wolf, B.; Lang, M.; Baumgarten, M. Spin-dimer networks: engineering tools to adjust the magnetic interactions in biradicals. *J. Mater. Chem. C,* **2017**, 5, 9053.

S3. Shaoan, C.; Liu, H.; Logan, B. E. Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells. *Environmental science & technology* **2006**, 40 (1), 364-369.