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Electronic Supplementary Information

Robust porous organic polymers as efficiently heterogeneous organo-photocatalysts for aerobic oxidation reactions

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1. Materials and Synthesis

Materials. The 9-Fluorenone, Carbazole, Thioanisole and its derivatives were obtained from Aladdin. Copper iodide, 1,10-phenanthroline, 2,2'-bipyridine and others were obtained from Sinopharm Chemical Reagent. Benzylamine, Thioanisole and its derivatives were obtained from Energy Chemical. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Formaldehyde dimethyl acetal (FDA), anhydrous $FeCl_3$, 1,2-dichloroethane (DCE), and deuterated solvents for NMR measurement were obtained from Aladdin.

Synthesis of 2,7-di(carbazol-9-yl)-fluoren-9-one (CF).[1] 2,7-Dibromo-9-fluorenonet (2.0 g, 5.9 mmol), carbazole (2.37 g, 14.2 mmol), K_2CO_3 (4.9 g, 35.5 mmol), CuI (2.7 g, 14.2 mmol), 2,2'-bipyridine (5.0 mg, 0.032 mmol), 1,10-phenanthroline (5.0 mg, 0.028 mmol) and 1,2-dichlorobenzene (5.0 mL) were added to a 50 mL round-bottom flask under N_2. And then the mixture was heated in Silicone bath at 180 ^oC for 48 h. After the solution cooled to room temperature, the mixture was dissolved in CH_2Cl_2 (40 mL), the solute was filtered and obtained a red-brown solution, the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (petroleum ether/dichloromethane, 6:1) to obtain target compound CF (3.7 g, 72%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.17 (d, J = 8.0 Hz, 4H), 7.97 (s, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.45-7.47 (m, 8H), 7.32-7.36 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.1, 142.7, 140.7, 139.3, 136.6, 133.3, 126.6, 124.0, 123.4, 122.1, 120.8, 110.0 ppm.

Synthesis of CF-CMP. The monomer CF (150 mg, 0.26 mmol) was dispersed in anhydrous chloroform (20 mL), and then transferred dropwise to a suspension of ferric chloride (675 mg, 4.1 mmol) in anhydrous chloroform (15 mL). The mixture was stirred for 3 days under nitrogen at 60 ^oC, and then 50 mL of methanol was added to the reaction mixture. The resulting mixture was kept stirring for another hour and the precipitate was collected by filtration. After being washed with methanol, the

obtained solid was stirred vigorously in hydrochloric acid solution for 1 h. The suspension was then filtered and washed with water and methanol, and then extracted using a Soxhlet extractor with methanol and THF for 24 h. The target product was dried at 120 ^{o}C under vacuum for 24 h to give a yellow powder (yield: 96%). Elemental analysis (%) calcd.: C 87.04, H 4.34, N 5.49; found: C 84.63, H 4.11, N 5.39; IR (KBr): 3043, 2923, 1725, 1605, 1470, 1440, 1317, 1265, 1223, 1188, 1109, 1076, 872, 800, 787, 701, 667, 652, 582 and 505 cm^{-1}. The surface area (SA_{BET}) of CF-CMP (CF:$FeCl_3$:FDA = 1:4:4) is 1067 m^2/g.

2. Nitrogen Sorption Isotherms

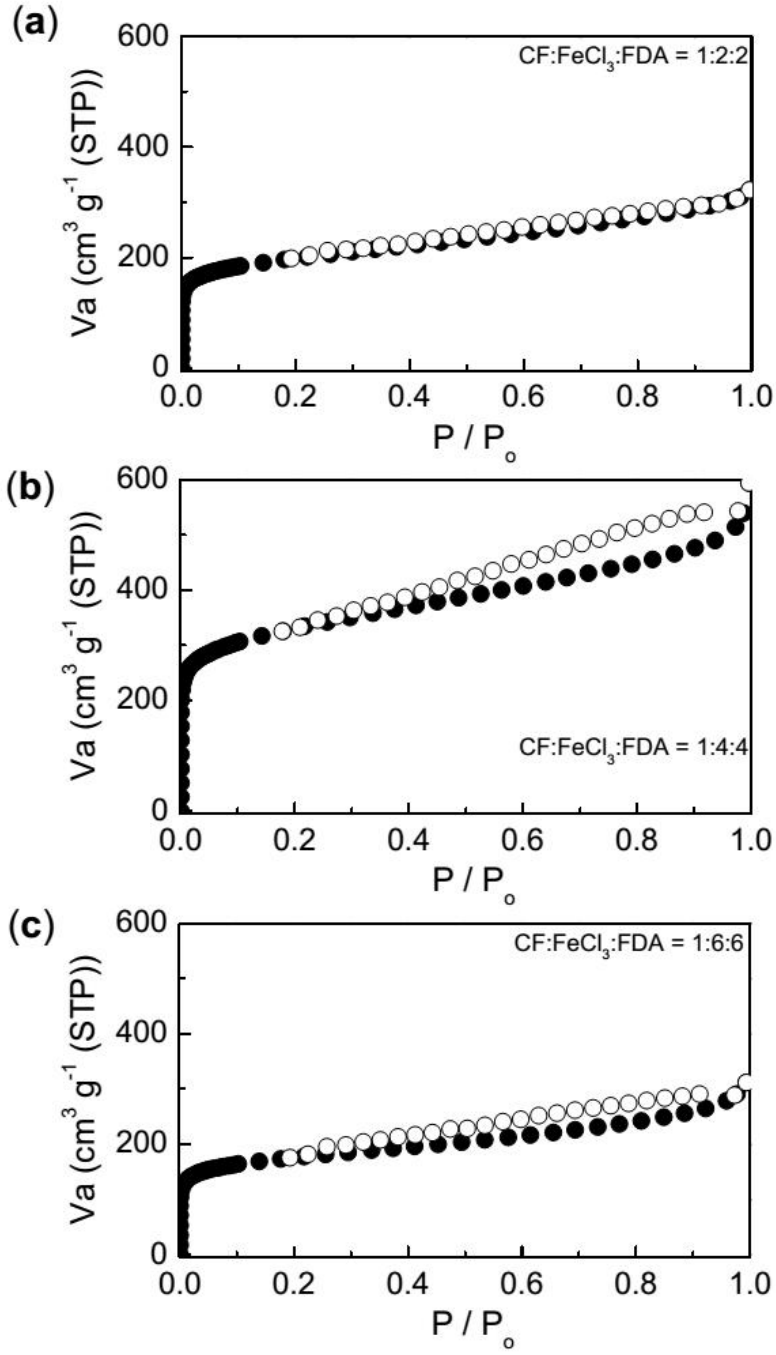


Figure S1. Nitrogen sorption isotherms of CF-HCPs at 77 K: (a) CF-HCP-1, CF:$FeCl_3$:FDA = 1:2:2, SA_{BET} = 735 m^2 g^{-1}, Pore volume = 0.499 cm^3 g^{-1} (b) CF-HCP-2, CF:$FeCl_3$:FDA = 1:4:4, SA_{BET} = 1217 m^2 g^{-1}, Pore volume = 0.919 cm^3 g^{-1} (c) CF-HCP-3, CF:$FeCl_3$:FDA = 1:6:6, SA_{BET} = 654 m^2 g^{-1}, Pore volume = 0.483 cm^3 g^{-1}.

3. NMR Spectra

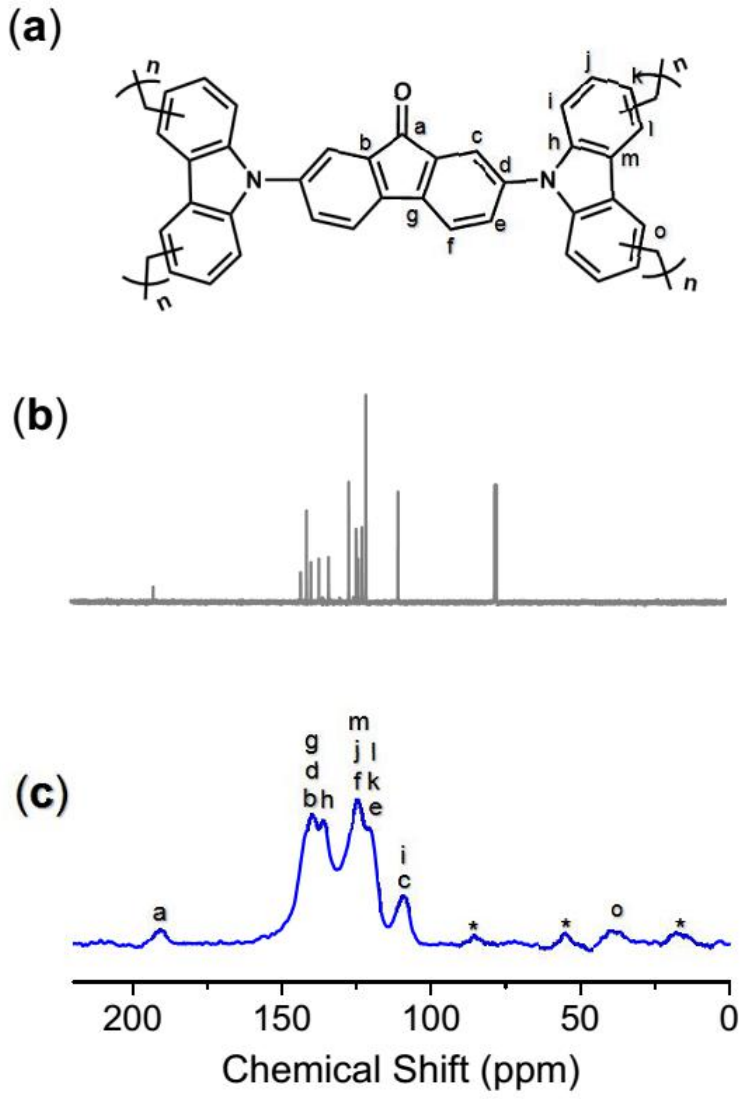


Figure S2. (a) The structure of CF-HCP. (b) ^{13}C NMR spectrum of monomer CF in $CDCl_3$. (c) Solid state ^{13}C CP MAS NMR spectra of the CF-HCP. Signals with * symbols are side peaks.

4. PXRD Curve

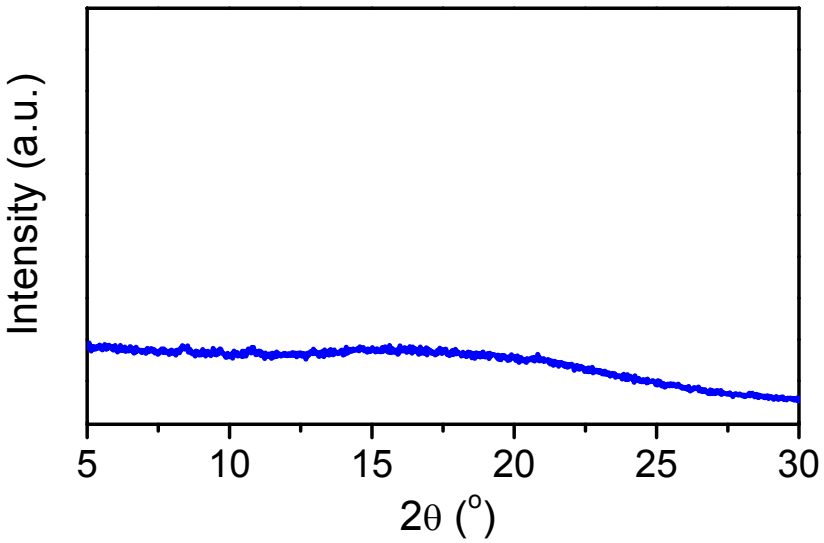


Figure S3. PXRD pattern of CF-HCP.

5. Lifetime Curve

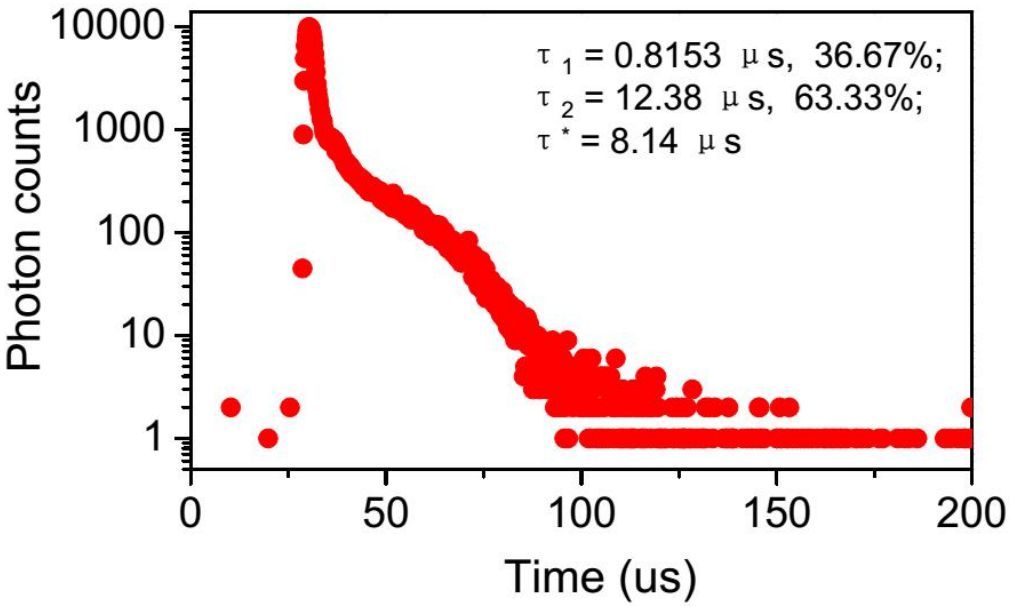


Figure S4. Luminescence lifetime for CF-HCP in the solid state under nitrogen atmosphere [The lifetime curve of CF-HCP can be fitted well with a double exponential function. The fitting luminescence lifetimes τ_1 and τ_2 are 0.8153 μs (36.67%) and 12.38 μs (63.33%), the pre-exponential factors A_1 and A_2 are 9011.718 and 1024.311, and the calculated average lifetime (τ^*) is 8.14 μs].

6. CV Curve

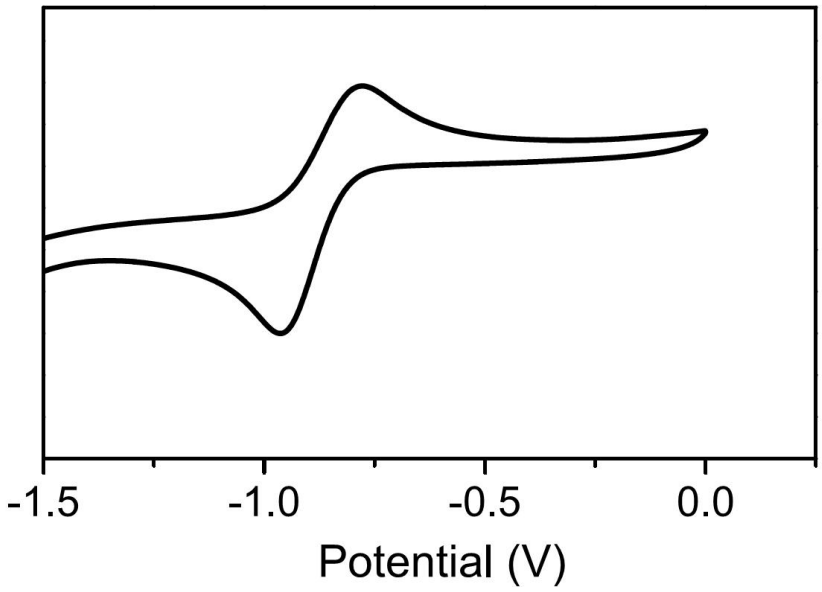


Figure S5. Cyclic voltammograms of CF-HCP.

7. TGA Curve

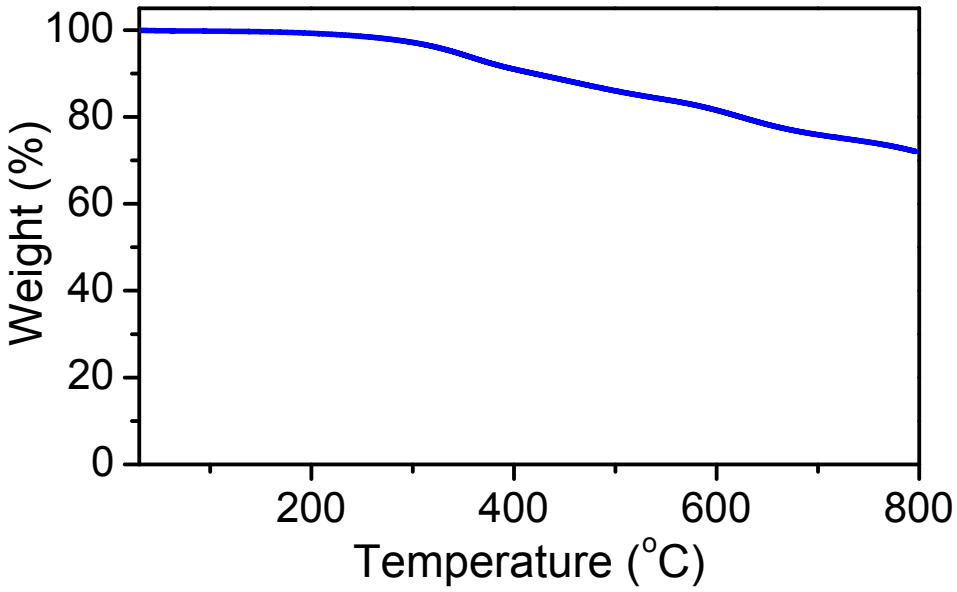


Figure S6. TGA curve of CF-HCP.

8. Nitrogen Sorption Isotherms

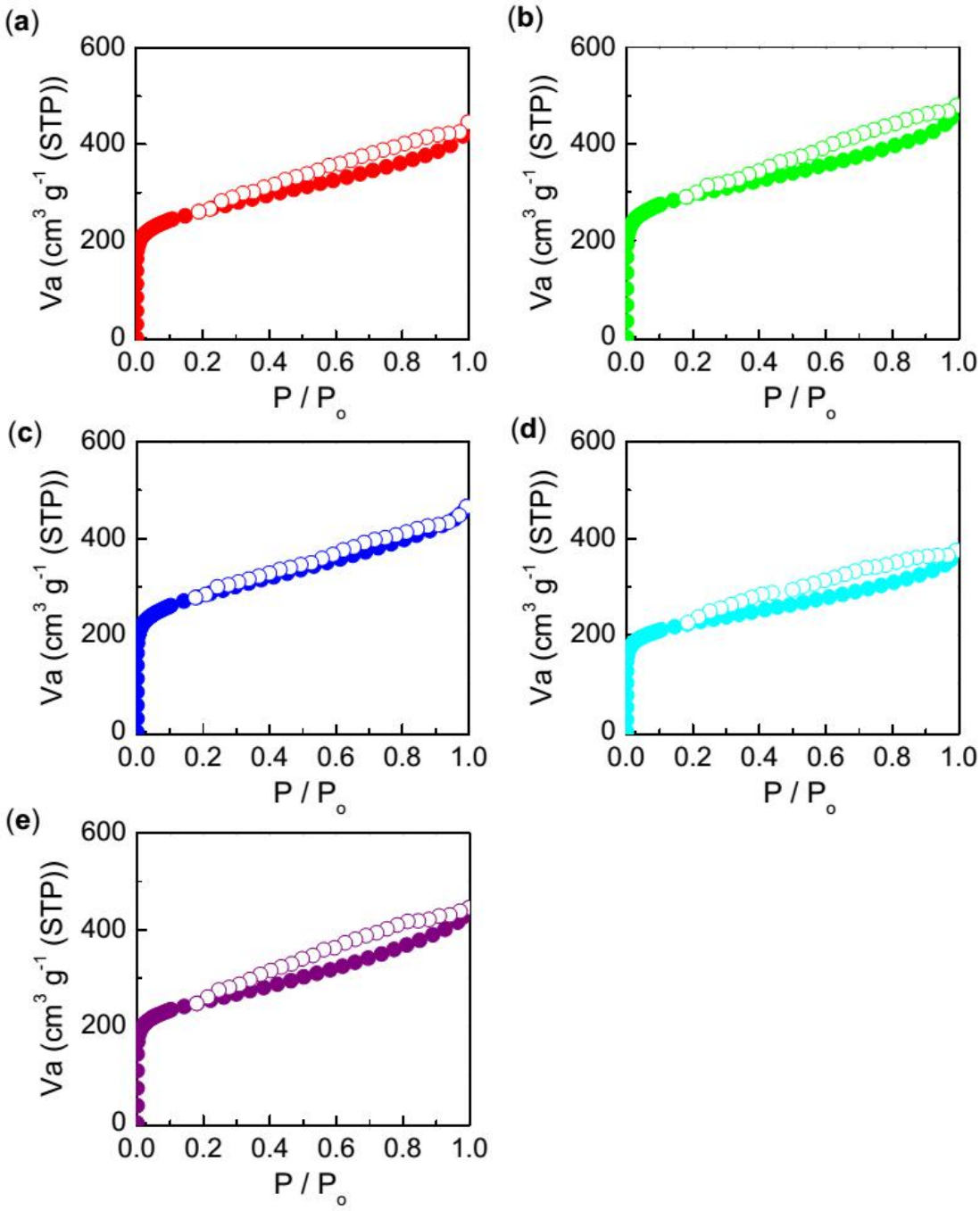


Figure S7. N_2 adsorption (●) and desorption (○) isotherm profiles of CF-HCP upon 24 h treatment in different conditions. (a) in HCl 1N, SA_{BET} = 969 m^2 g^{-1}, Pore Volume = 0.690 cm^3 g^{-1}; (b) in NaOH 1N, SA_{BET} = 1091 m^2 g^{-1}, Pore Volume = 0.742 cm^3 g^{-1}; (c) in DMSO, SA_{BET} = 835 m^2 g^{-1}, Pore Volume = 0.58 cm^3 g^{-1}; (d) in DMF, SA_{BET} = 1037 m^2 g^{-1}, Pore Volume = 0.721 cm^3 g^{-1}; (d) in CH_3CN under 520 nm 100W LED lamp, SA_{BET} = 932 m^2 g^{-1}, Pore Volume = 0.69 cm^3 g^{-1}.

9. IR Spectra

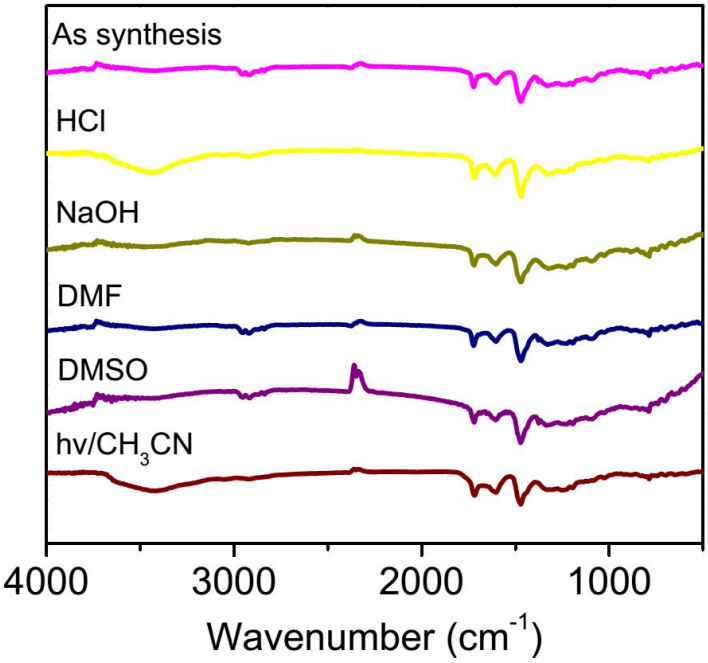


Figure S8. FT-IR spectra of the CF-HCP upon 24 h treatment in different conditions.

10. EPR spectra

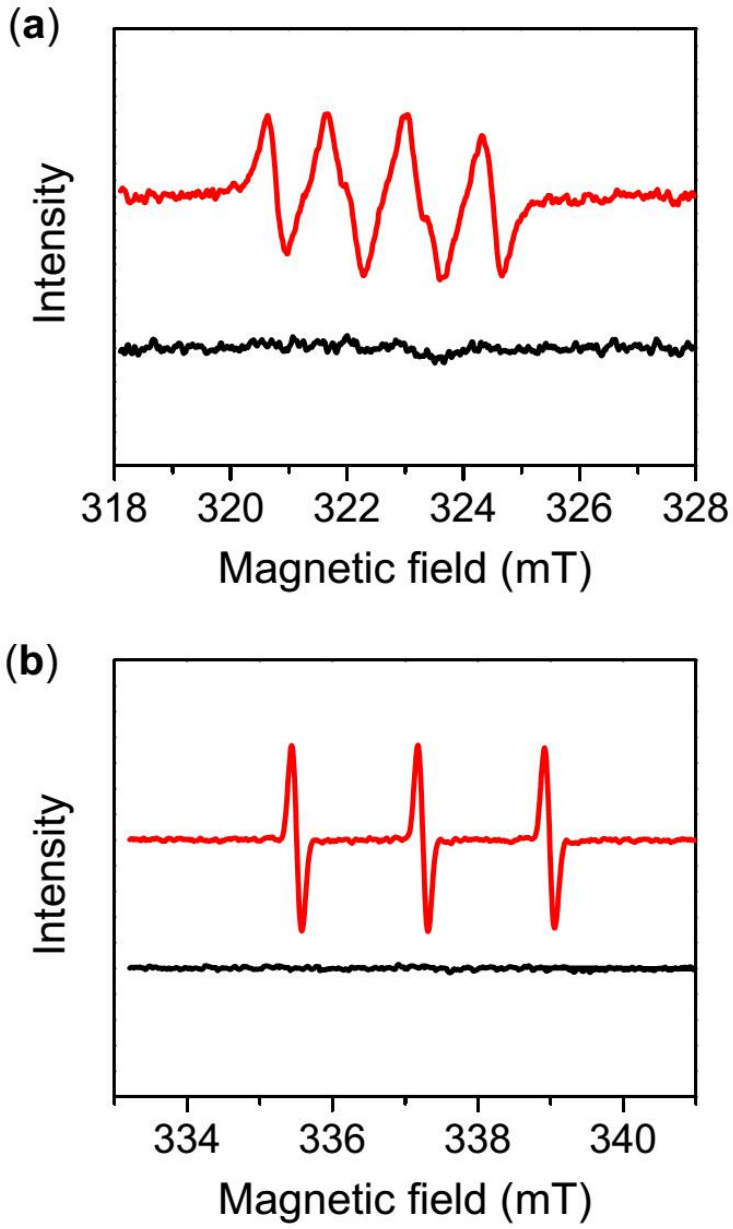


Figure S9. (a) EPR spectra of a solution in air-saturated MeOH of CF-HCP (1.0 mg mL^{-1}) in the presence of DMPO (0.1 M) in a dark environment (*black line*) and upon light irradiation (*red line*); (b) EPR spectra of a solution in air-saturated water of CF-HCP (1.0 mg mL^{-1}) in the presence of TEMP (0.1 M) in a dark environment (*black line*) and upon light irradiation (*red line*).

11. Comparative Data

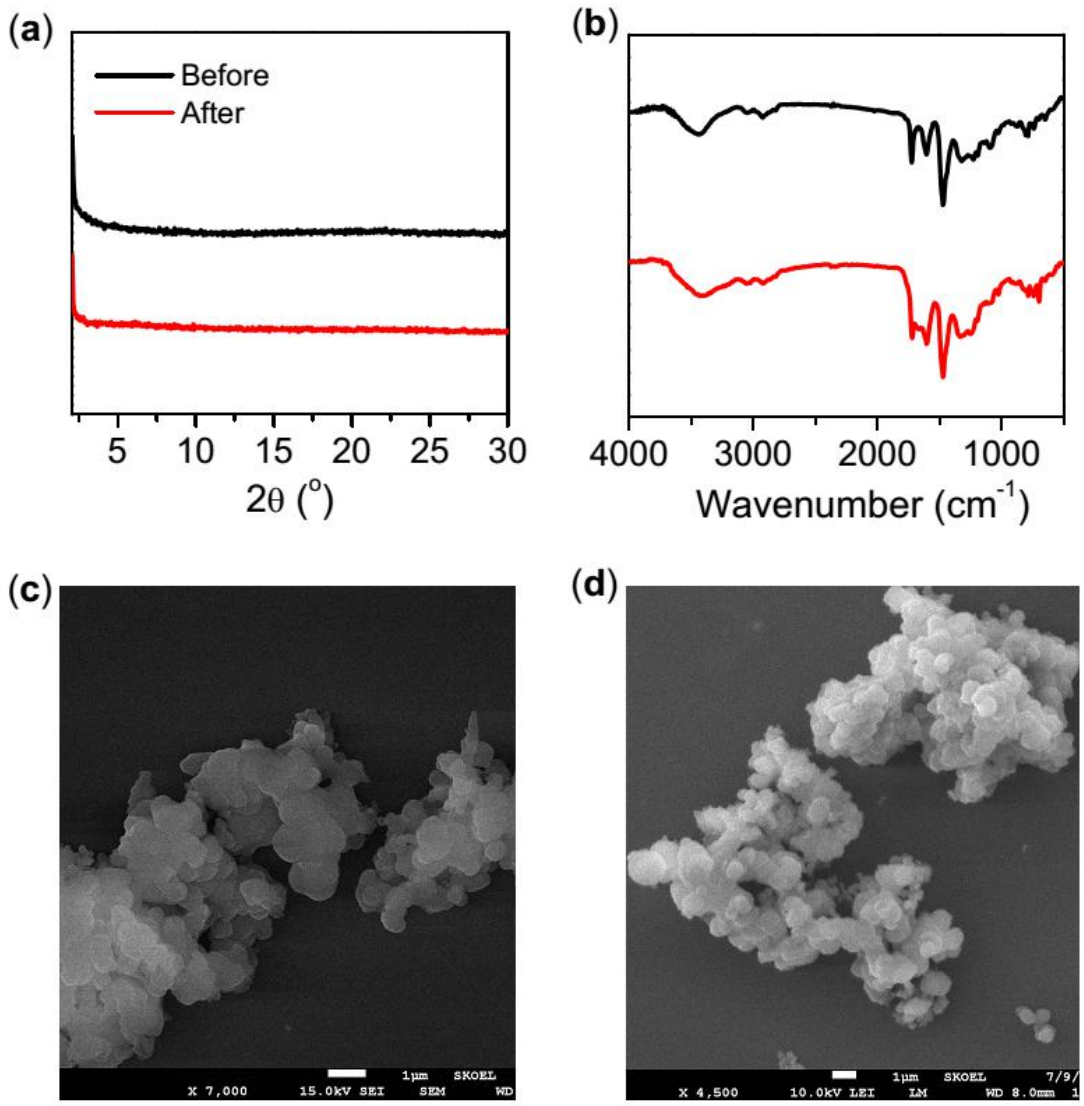


Figure S10. (a) FT-IR spectra of CF-HCP before (black line)and after the fifth run (red line); (b) PXRD curves of CF-HCP before (black line)and after the fifth run (red line); (c) The SEM image of CF-HCP; (d) The SEM image of CF-HCP after the fifth run.

12. Experimental Data of CF-CMP

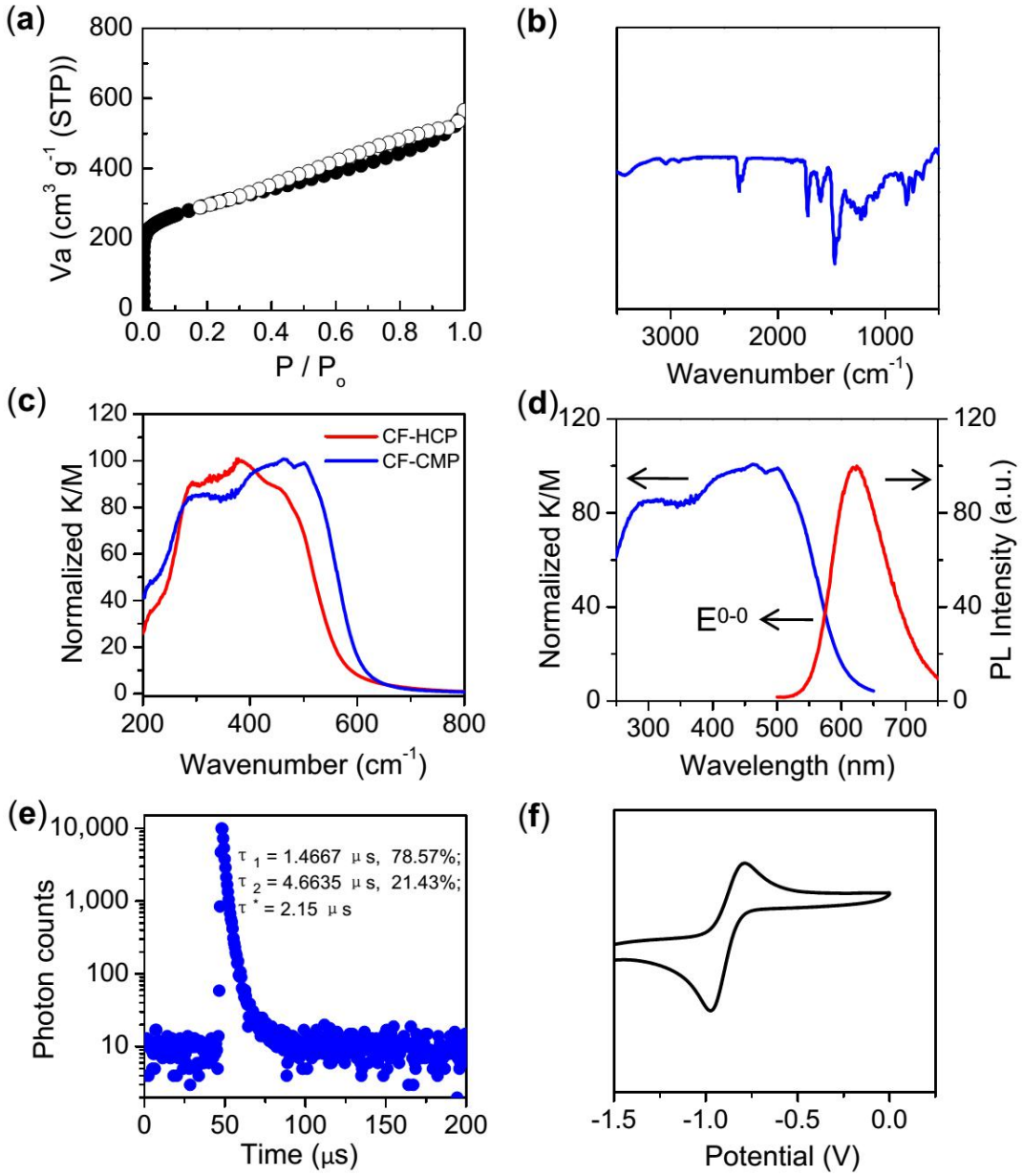
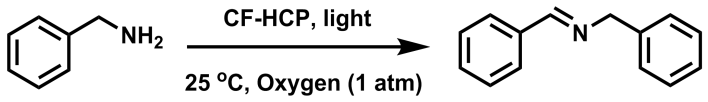


Figure S11. (a) Nitrogen adsorption-desorption isotherm (filled circles: adsorption; open circles: desorption) of CF-CMP at 77 K (SA_{BET} = 1067 m^2 g^{-1}, V = 0.88 cm^3 g^{-1}), (b) FT-IR spectra of CF-CMP, (c) Normalized UV-vis spectra of CF-HCP (red line) and CF-CMP (blue line), (d) Normalized UV-vis (blue line) and emission (red line) spectra of CF-CMP in the solid state, (e) Luminescence lifetime for CF-CMP in the solid state under nitrogen atmosphere (Lifetime: 2.15 μs), (f) Cyclic voltammograms of CF-CMP.

13. Catalytic Data

Table S1. The oxidative coupling of benzylamine using CF-HCP as photocatalyst[a]



Entry	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	Toluene	25	6	25
2	Methanol	25	6	7
3	DMF	25	6	18
4	DMSO	25	6	28
5	CH_3CN	25	6	91
6[c]	CH_3CN	25	6	86
7[d]	CH_3CN	25	6	90
8[e]	CH_3CN	25	12	42
9[f]	CH_3CN	25	12	30

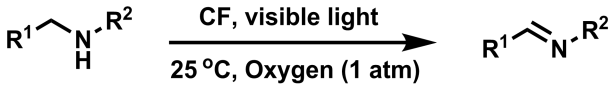
[a]CF-HCP (5.0 mg), Solvent (2.0 mL), benzylamine (0.2 mmol), green LED lamp (520 nm, 30 W). [b]Determined by ^{1}H-NMR spectroscopic analysis. [c]CF-HCP recovered from entry 5 was used. [d]CF-HCP recovered from entry 6 was used. [e]Blue LED lamp (380 nm, 10 W). [f]White LED lamp (15 W).

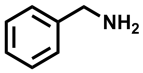
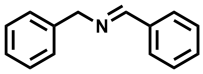
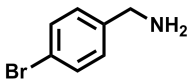
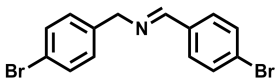
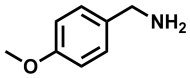
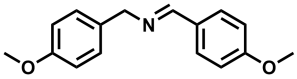
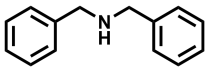
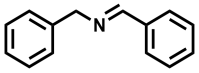
Table S2. The electrochemical properties of CF-HCP and CF-CMP.

Sample	$E^{0\text{-}0}$ [a]	CB (V Vs SCE) [b]	VB (V Vs SCE) [c]
CF-HCP	2.25	-0.87	1.38
CF-CMP	2.15	-0.88	1.27

[a]$E^{0\text{-}0}$ was estimated from the normalized UV-vis absorption and emission spectra of polymers in the solid state; [b]CB (V Vs SCE) was determined by the reduction peaks of CV profile; [c]VB (V Vs SCE) was determined by $E^{0\text{-}0}$ and CB.

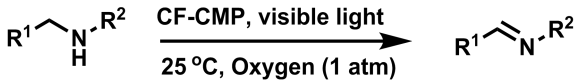
Table S3. The oxidative coupling of benzylamine using monomer CF as photocatalyst[a]

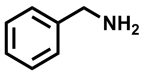
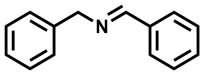
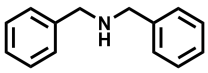
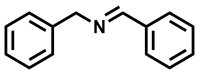
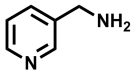
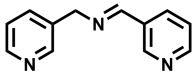


Entry	Substrate	Product	Yield (%)[b]
1			99
2			91
3			98
4			45, 98.0[c]

[a]Reaction conditions: CF (5.0 mg), substrate (0.2 mmol), CH_3CN (2.0 mL), green LED lamp (520 nm, 30 W), 6 h. [b]Determined by ^{1}H-NMR spectroscopic analysis. [c]20 h.

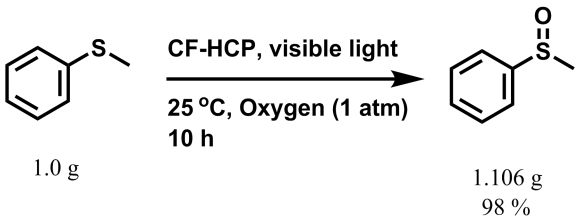
Table S4. The oxidative coupling of amines using monomer CF-CMP as photocatalyst[a]



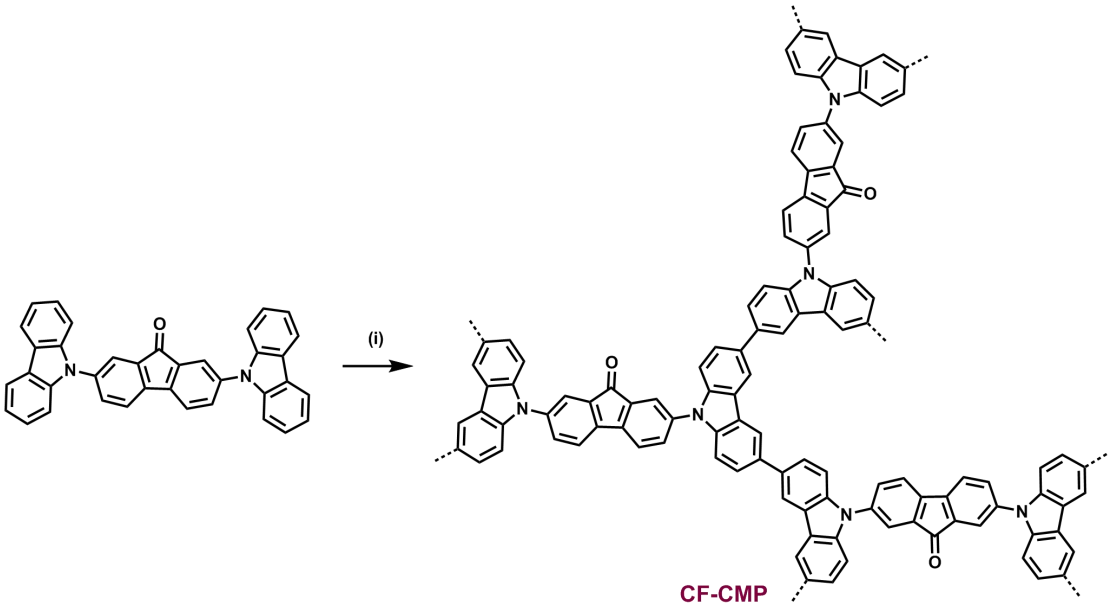
Entry	Substrate	Product	Yield (%)[b]
1			64.5
2			31.3
3			48.1

[a]Reaction conditions: CF-CMP (5.0 mg), substrate (0.2 mmol), CH_3CN (2.0 mL), green LED lamp (520 nm, 30 W), 6 h. [b]Determined by ^{1}H-NMR spectroscopic analysis.

Scheme S1. Large-scale catalytic oxidation using CF-HCP as a heterogeneous photocatalyst.



Scheme S2. Synthetic procedure to carbazole-fluorenone based conjugated mictoporous polymer CF-CMP (i) $FeCl_3/CHCl_3$.



14. Reference

[1] Z. D. Liu, Y. Z. Chang, C. J. Ou, J. Y. Lin, L. H. Xie, C. R. Yin, M. D. Yi, Y. Qian, N. E. Shi and W. Huang, *Polym. Chem.,* 2011, **2**, 2179.