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Supplementary Information

Polyoxometalates built-in conjugated microporous polymers for visible-light heterogeneous photocatalysis

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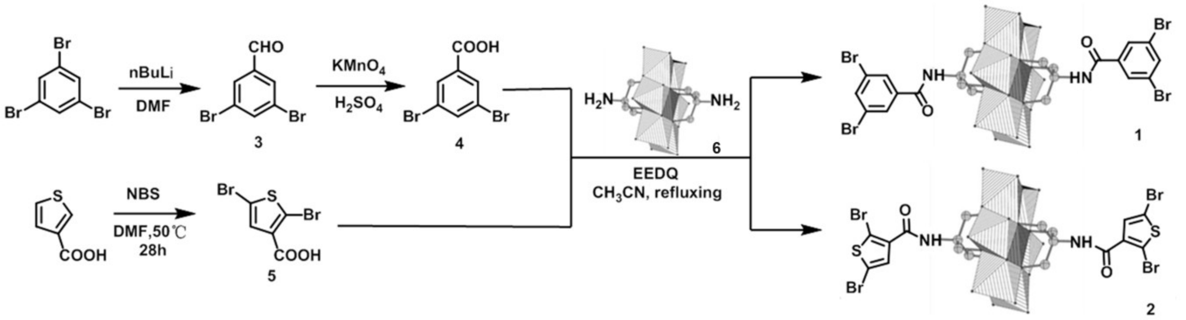
Section 1. Materials and Methods

1,3,5-tribromobenzene and thiophene-3-carboxylic acid were purchased from commercial sources. All chemicals were of analytical grade and were used without further purification except acetonitrile was dried by CaH_2.

The electrospray mass spectra (ESI-MS) of compounds **1** and **2** were recorded on a Bruker miorOTOF-QII in negative mode using acetonitrile as solvent. Single-crystal X-ray data for compound **1** was collected on a Rigaku SCX-mini diffractometer with graphite monochromatic Mo-Kα radiation (λ = 0.7173 Å) by ω scan mode. The thermal stabilities of the polyoxometalates (POMs) based CMPs were evaluated using thermogravimetric analysis (TGA) with a differential thermal analysis instrument (TA Instruments TGA Q50-1918 analyzer) over the temperature range from 20 to 800 °C under N_2 atmosphere with a heating rate of 10 °C min^{-1} using an empty Al_2O_3 crucible as the reference. Surface areas were measured by nitrogen adsorption and desorption at 77 K using a Bel Japan Inc. model BELSOPR-mini II analyzer and the samples were degassed at 150 ^oC for 3 h under vacuum (10^{-5} bar) before analysis. Pore size distribution was calculated from the adsorption branch with the nonlocal density functional theory (NLDFT). Powder X-ray diffraction (PXRD) were performed on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. Fourier transform infrared (FT-IR) spectra were recorded in transmission mode on a Bruker Alpha spectrometer using KBr pellets within the range 400–4000 cm^{-1}. ^{13}C cross-polarization magic angle spinning (CP/MAS) spectra were recorded with a 4 mm double resonance MAS probe and at a MAS rate of 10.0 kHz with a contact time of 2 ms (ramp 100) and a pulse delay of 3 s. High resolution imaging of the polymer morphologies was obtained using a Hitachi S-4800 cold field emission scanning electron microscope (FE-SEM). HRTEM was carried out on a JEOL JEM-2100F electron microscope with a LaB_6 filament operated at 200 kV. Elemental analysis (C, H, N) was analyzed on a Perkin-Elmer 240C elemental analyzer. The residual Pd content was determined by ICP-MS techniques using Agilent 7700X ICP-MS model. The samples were prepared by nitrohydrochloric acid digestion before measurement. The high photocatalytic activity of POM clusters based CMPs was demonstrated in degradation of rhodamine B and methylene blue under irradiation of 300W Xenon lamp (handled by a 450 nm optical filter to filtrate off the ultraviolet light).

Section 2. SyntheticProcedures



Scheme S1. Synthetic routes of compounds **1** and **2**.

3, 5-dibromobenzaldehyde (3) ^{S1}

1,3,5-tribromobenzene (3.0 g, 9.5 mmol) and anhydrous diethyl ether (50 mL) were added to a dried flask. n-BuLi (3.8 mL, 95 mmol) was added dropwise to the solution at -78 °C and stirred for 1 h. Then anhydrous DMF (1.5 mL, 19 mmol) was added and the solution was allowed to stirr at 0 °C overnight. The reaction was quenched with HCl (10%) until the solution was acidic. The mixture was partitioned between DCM and water, and the aqueous layer was washed twice with DCM (50 mL ×2), then the organic layers were combined and dried over anhydrous $MgSO_4$. The combined organic phase was then concentrated under reduced pressure and run through a silica flash column using hexane as eluent. Removal of the solvent under reduced pressure gave a colorless solid as product **3** (1.62 g, 64%). GC-MS: *m/z* $C_7H_4Br_2O$ Calc. 263.92, found 263.75. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.91 (s, 1H), 7.94 (s, 2H), 7.92(s, 1H).

3,5-dibromobenzoic acid (4)

Compound **3** (0.5 g, 1.9 mmol) and potassium permanganate (0.2 g, 1.25 mmol) were added into a 250 ml round-bottom flask and dissolved in water (150 mL), then a few drops of sulfuric acid were added. The mixture was stirred at 100 °C for 4 hours. The precipitate was removed by filtration, the filtrate was extracted with ethyl acetate and dried with anhydrous $MgSO_4$, The organic layer was concentrated under reduced pressure and run through a silica flash column using hexane as eluent to remove the unreacted raw material, and then using ethyl acetate as eluent to get the product. Removal of the solvent under reduced pressure gave a colorless solid (0.36 g, 68%). GC-MS: *m/z* $C_7H_4Br_2O_2$ Calc. 279.92, found 279.70; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.17(s, 2H), 7.91(s, 1H).

$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH(C_7H_3Br_2O)\}_2]$ (1)

3,5-dibromobenzoic acid (0.32 g, 1.14 mmol) and 2-ethoxy-l-(ethoxycarbonyl)-1,2-

dihydroquinoline (0.42 g , 1.71 mmol) (EEDQ) were dissolved in CH_3CN (80 mL) and the reaction mixture was kept at 82 ^{o}C for 40 min, then $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ (0.8 g, 0.43 mmol) was added to the solution and the mixture was further refluxed for 24 h. The solution was cooled to room temperature and the solvent was concentrated under vacuum. The residue was added ethyl acetate (20 mL) to collect a light orange solid (0.89 g, 87%). ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 64.65 (br, 12H, $–CH_2–$) 7.97 (s, Ar-4H), 7.95 (s, Ar-2H), 3.17 (t, N-CH_2, 24H), 1.58 (m, 24H), 1.31 (dd, 24H), 0.94 (t, 36H); ESI-MS (negative mode, MeCN): 1922.4 g mol^{-1}, $[M – 2Bu_4N + H]^-$; FT-IR (KBr pellet): ν (cm^{-1}) 3427 (w), 2961 (ν C-H, m), 2933 (ν C-H, m), 2874 (ν C-H, m), 1670 (ν C , s), 1554 (m), 1481 (s), 1381 (m), 1318 (m), 1275 (m), 1103 (w), 941 (ν Mo=O, vs), 920 (ν Mo=O, vs), 902 (ν Mo=O, vs), 739 (m), 667 (ν Mo-O-Mo, vs, br.), 566 (m).

2,5-dibromothiophene-3-carboxylic acid (5) [S2]

Thiophene-3-carboxylic acid (1.49 g, 11.7 mmol) and *N*-bromosuccinimide (NBS) (4.60 g, 25.8 mmol) were added to degassed DMF (24 mL). The flask was then wrapped with aluminum foil to shield the reaction mixture from light. The mixture was then stirred at 50 ^{o}C for 28 h under N_2. The mixture was allowed to cool to room temperature and poured into water (300 mL). The resulting precipitate was collected by filtration and washed with brine, dried over anhydrous $MgSO_4$, and then filtered to afford pure 2,5-dibromo-3-thenoic acid as a white solid (3.1 g, 92%).^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.44 (s, 1H).

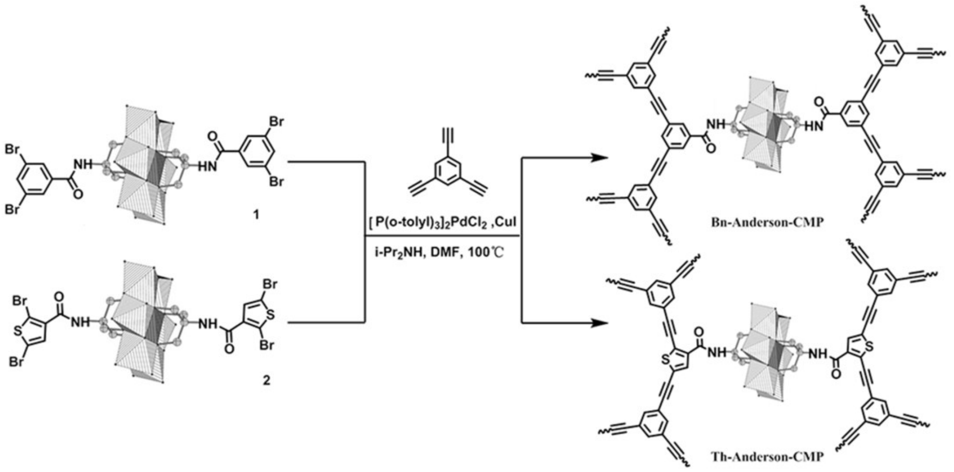
$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH(C_5Br_2HOS)\}_2]$ (2)

Compound **5** (0.32 g, 1.14 mmol) and 2-ethoxy-l-(ethoxycarbonyl)-1,2-dihydroquinoline (0.424 g, 1.71 mmol) (EEDQ) were dissolved in 80 mL acetonitrile and the reaction mixture was refluxed at 82 ^{o}C for 40 min, then $[N(C_4H_9)]_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ (0.8 g, 0.43 mmol) was added to the solution and the mixture was further refluxed for 24 h. The mixture was cooled to room temperature and the solvent was concentrated under vacuum. The concentrated solution was added ethyl acetate (20 mL) to collect a light orange solid (0.9 g, 88%). ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 64.45 (br, 12H, $–CH_2–$), 7.38 (s, Ar-2H), 3.17 (t, N-CH_2, 24H), 1.58 (m, 24H), 1.31 (dd, 24H), 0.94 (t, 36H); ESI-MS (negative mode, MeCN): 1935.4 g mol^{-1}, $[M - 2Bu_4N + H]^-$; FT-IR (KBr pellet): ν (cm^{-1}) 3446 (w), 2961 (ν C-H, m), 2873 (ν C-H, m), 1668 (ν C=O, s), 1541 (s), 1482 (s), 1416 (m), 1381 (m), 1313 (m), 1254 (w), 1151 (w), 1106 (m), 1026 (m), 941 (ν Mo=O, vs), 921 (ν Mo=O, vs), 900 (ν

Mo=O, vs), 667 (ν Mo-O-Mo, vs, br.), 566 (m).

$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ (6)

$[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ (4.0 g, 1.84 mmol), $Mn(acac)_3$ (0.75 g, 2.8 mmol) and Tris(hydroxymethyl)methyl aminomethane (0.78 g, 6.4 mmol) was dissolved in 100 mL anhydrous acetonitrile, the mixture was heated to reflux for 24 h under N_2. After cooling, the solid was separated by filtration and the solvent was concentrated under vacuum. Then the concentrated solution was exposed to ether vapor, a few hours later, a white precipitate appeared and was filtered off. The orange filtrate was again exposed to ether vapor. After two days, the resulted orange crystals were isolated by filtration, washed with a small amount of acetonitrile and ether, and dried under vacuum (3.55 g, 80%). FT-IR (KBr pellet): ν (cm^{-1}) 3288 (ν_{as}, NH, w), 2961 (ν CH, s), 2871 (ν CH, s), 1646 (w), 1477 (δ CH, s), 1381 (δ CH, m), 1034 (ν CO, s), 937 (ν Mo=O, s), 911 (ν Mo=O, s), 667 (ν Mo-O-Mo, vs), 563 (m), 462 (m), 413(m).



Scheme S2. Synthesis of **Bn-Anderson-CMP** and **Th-Anderson-CMP**.

Bn-Anderson-CMP:

$PdCl_2(PhCN)_2$ (5 mg, 0.013 mmol) and tri(o-tolyl)phosphine (8 mg, 0.026 mmol) were added to degassed DMF (5 mL). The solution was stirred for 5 minutes at room temperature. $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH(C_7H_3Br_2O)\}_2]$ (120 mg, 0.05 mmol), 1,3,5-triethynylbenzene (15 mg, 0.1 mmol) and CuI (3.6 mg, 0.013 mmol) were added. After diisopropylamine (2.5 mL) was added to the solution, the mixture was degassed by three freeze–pump–thaw cycles, purged with N_2, and stirred at 100 °C for 72 h. After the reaction mixture was cooled to room temperature, the precipitates were separated by centrifugation, washed with water, DCM, MeOH, The product was dried under vacuum to afford dark brown solid (60 mg, 53%). Elemental analysis (wt.%) calcd. For $\{C_{258}H_{396}N_{15}O_{78}Mn_3Mo_{18}\}_n$: C 45.25, H 5.83, N 3.07; found: C 53.11, H 4.32, N 2.49. The Pd residual content was determined to be 0.066% by ICP-MS techniques using Agilent 7700X ICP-MS model. Thus, the effect of the negligible Pd residue on photocatalytic performance could be ignored.

Th-Anderson-CMP:

$PdCl_2(PhCN)_2$ (5 mg, 0.013 mmol) and tri(o-tolyl)phosphine (8 mg, 0.026 mmol) were added to degassed DMF (5 mL). The solution was stirred for 5 minutes at room temperature. $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH(C_5HBr_2OS)\}_2]$ (120 mg, 0.05 mmol), 1,3,5-triethynylbenzene (15 mg, 0.1 mmol) and CuI (3.6 mg, 0.013 mmol) were added. After diisopropylamine (2.5 mL) was added to the solution, the mixture was degassed by three freeze–pump–thaw cycles, purged with N_2, and stirred at 100 ^{o}C for 72 h. After the reaction mixture was cooled to room temperature, the precipitates were separated by centrifugation, washed with water, DCM, MeOH, the product was dried under vacuum to afford dark brown solid (70 mg, 67%). Elemental analysis (wt%) calcd. For $\{C_{246}H_{384}N_{15}O_{78}S_6Mn_3Mo_{18}\}_n$: C 42.91, H 5.62, N 3.05; found: C 42.59, H 4.00, N 2.81. The Pd residual content was determined to be 0.103% by ICP-MS techniques using Agilent 7700X ICP-MS model. Thus, the effect of the negligible Pd residue on photocatalytic performance could be ignored.

Section 3. Solid State ^{13}C CP/MAS NMR Spectroscopy

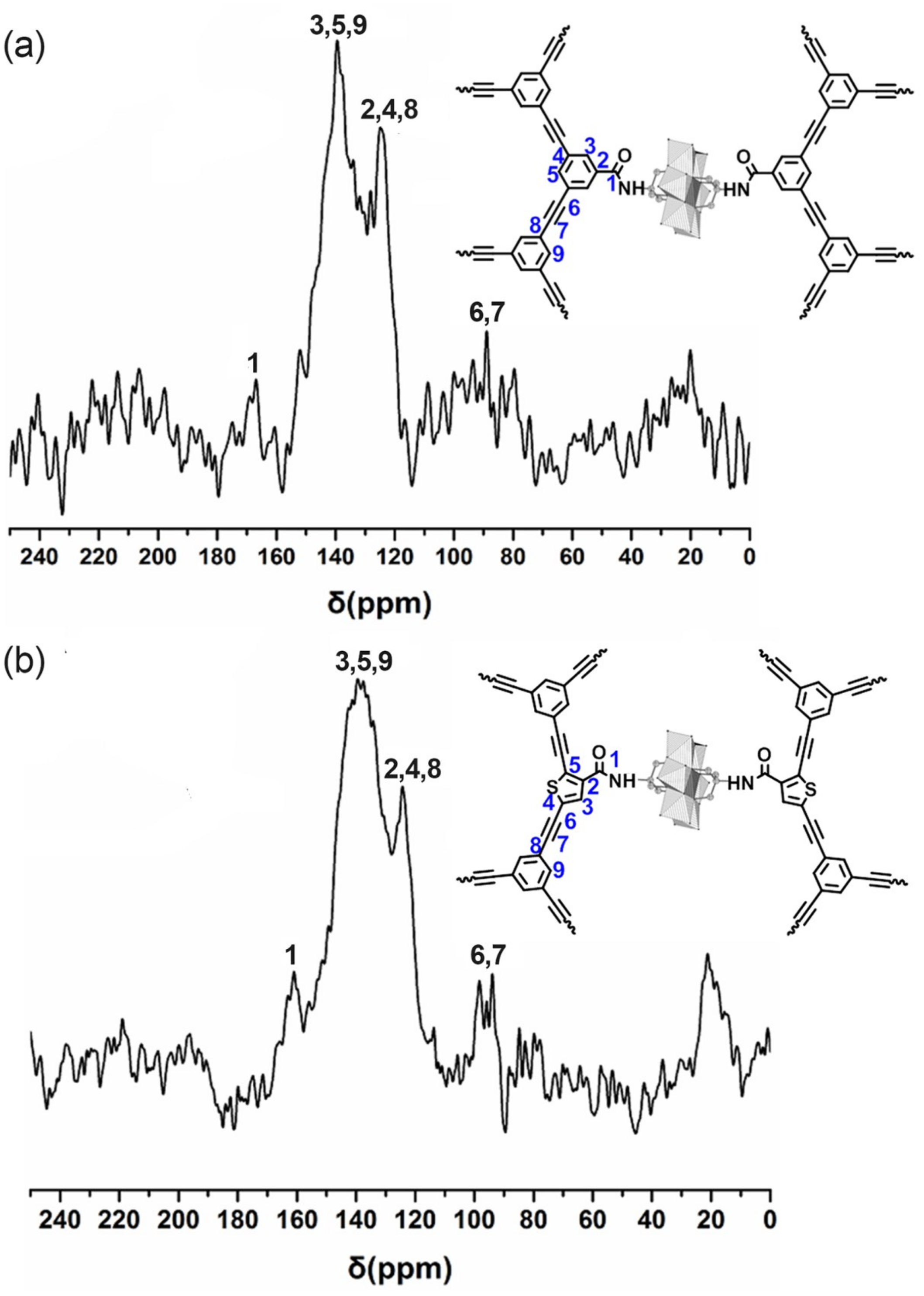


Figure S1. Solid state ^{13}C CP/MAS NMR spectra of (a) **Bn-Anderson-CMP** and (b) **Th-Anderson-CMP**.

Section 4. FT-IR Spectroscopy

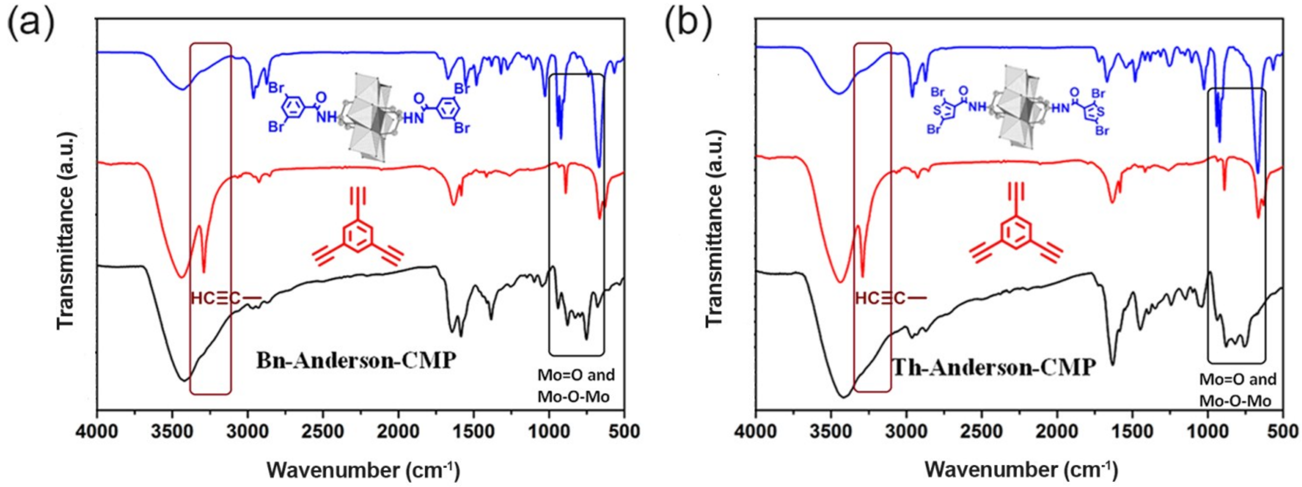


Fig. S2 FT-IR spectra of **Anderson-CMPs** (black line), 1,3,5-triethynylbenzene (red line), and the bifunctionalized Anderson POMs (blue line): (a) **Bn-Anderson-CMP**; (b) **Th-Anderson-CMP**.

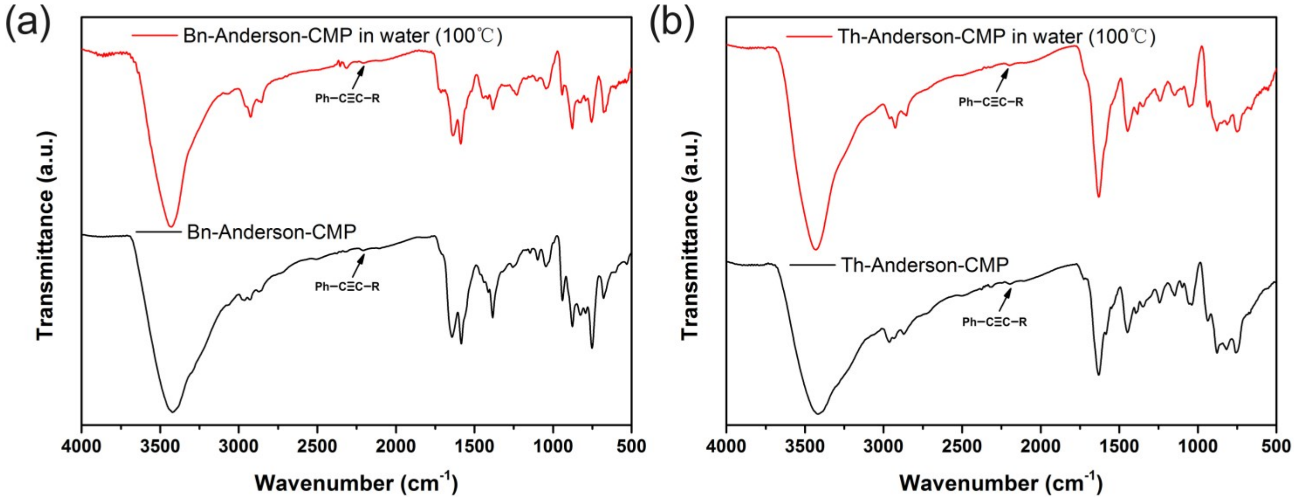


Fig. S3 FT-IR spectra comparison of POMs based CMPs before (black line) and after (red line) treatment with boiling water (100 ^{o}C) for 24 hours: (a) **Bn-Anderson-CMP**; (b) **Th-Anderson-CMP**.

Section 5. Thermogravimetric Analysis

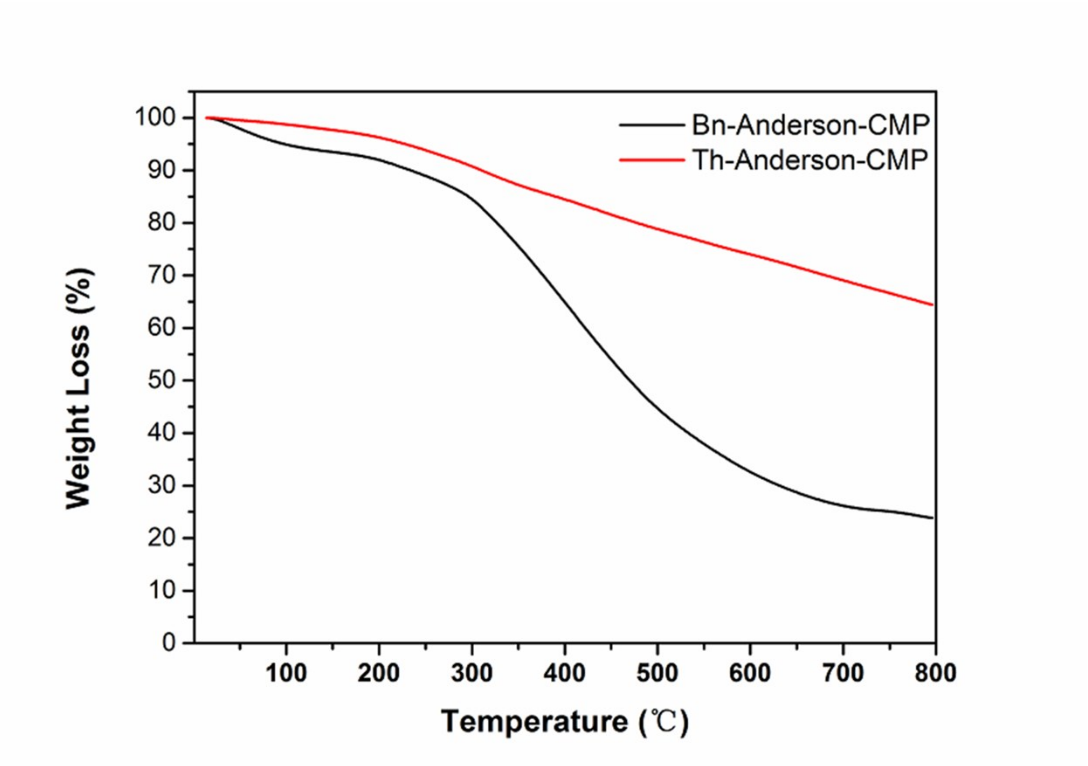


Figure S4. Thermogravimetric analysis for **Bn-Anderson-CMP** (black) and **Th-Anderson-CMP** (red), The slight weight loss under 100 °C is due to solvent release.

Section 6. PXRD Profiles

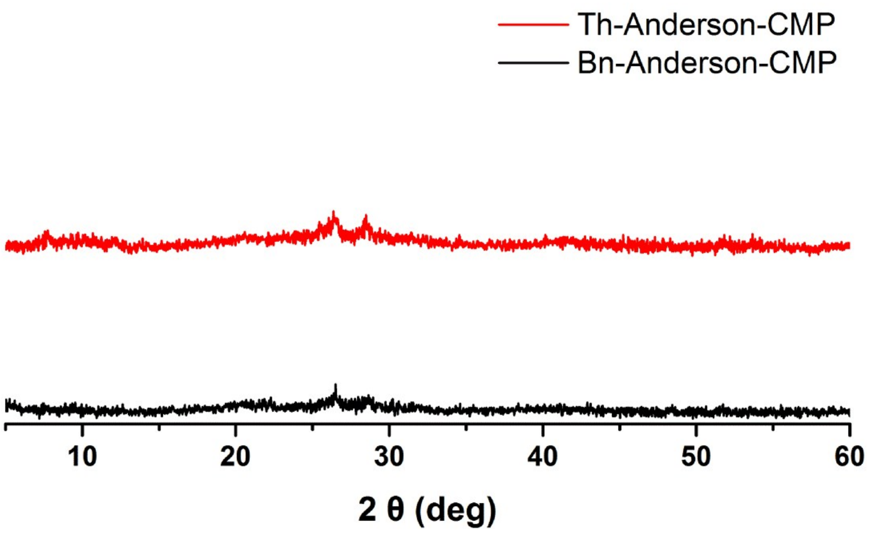


Figure S5. Powder X-ray diffraction profiles of POM clusters based CMPs (red line for **Th-Anderson-CMP**, black line for **Bn-Anderson-CMP**). No distinctive diffraction peaks were observable.

Section 7. UV/vis Absorption Spectroscopy

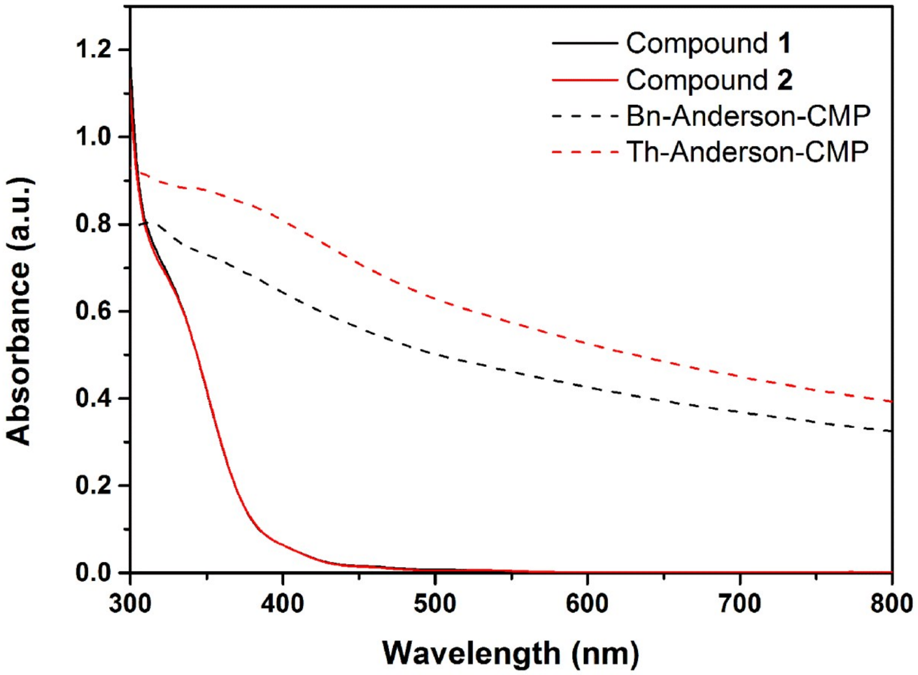


Figure S6. UV/vis absorption spectra of CMPs in acetonitrile dispersion and the solution of compounds **1-2** (1×10^{-5} M in acetonitrile).

Section 8. SEM & TEM images

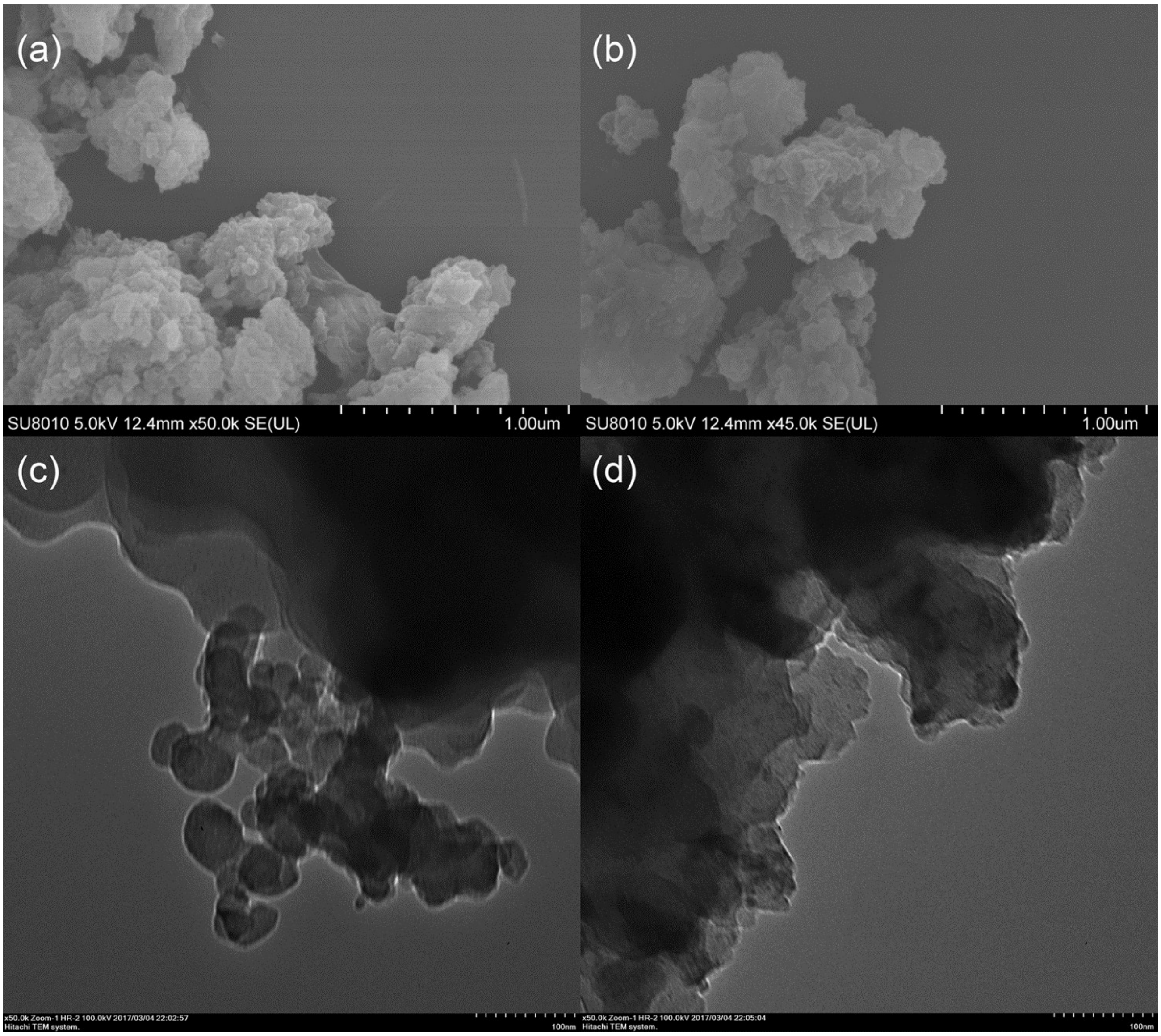


Figure S7. SEM images of (a) **Bn-Anderson-CMP**, (b) **Th-Anderson-CMP** and TEM images of (c) **Bn-Anderson-CMP**, (d) **Th-Anderson-CMP**.

Section 9. Photocatalysis Experiments

Experimental procedure of photodegradation of organic deys: Catalysts (40 mg) were dispersed into the solution of organic dyes (1×10^{-5} mg/L), then magnetically stirred for 30 min in the dark. After this, the mixture was allowed to expose to visible light ($\lambda > 450$nm) from a 300 W Xenon lamp at a distance of 5 cm between the liquid surface and the lamp. The solution was kept stirring during irradiation. At an interval of 10 min, 4 mL of the mixture was taken out of the beaker for analysis after centrifugation.

The radical scavenger experiments were performed using ammonium oxalate (0.142 g/L), *p*-benzoquinone (0.108 g/L), sodium azide (65 mg/mL) isopropanol (99%) (60 μL/mL) and Catalase (0.1 g/L), respectively. Other conditions remain unchanged.

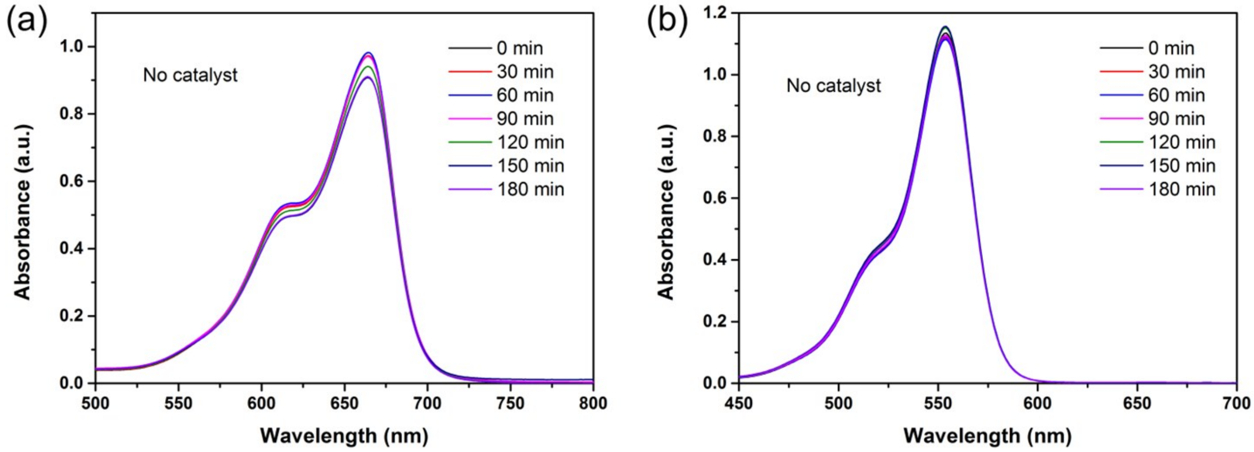


Figure S8. (a) UV-vis spectra of RhB (10 mg L^{-1}), (b) UV-vis spectrum of MB (10 mg L^{-1}) upon irradiation for 0.5-3 h under 300 W xenon lamp with 450 nm optical filter without catalyst.

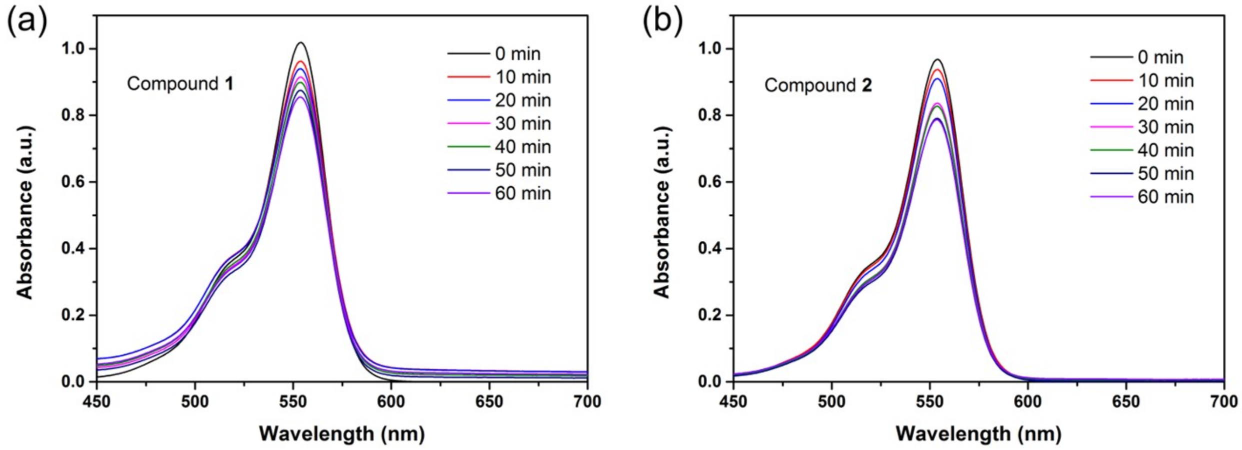


Figure S9. UV-vis spectra of RhB (10 mg L^{-1}) after different illumination time intervals in the presence of compound **1** (a) and compound **2** (b) (0.4 mg mL^{-1}) under 300 W xenon lamp with 450 nm optical filter.

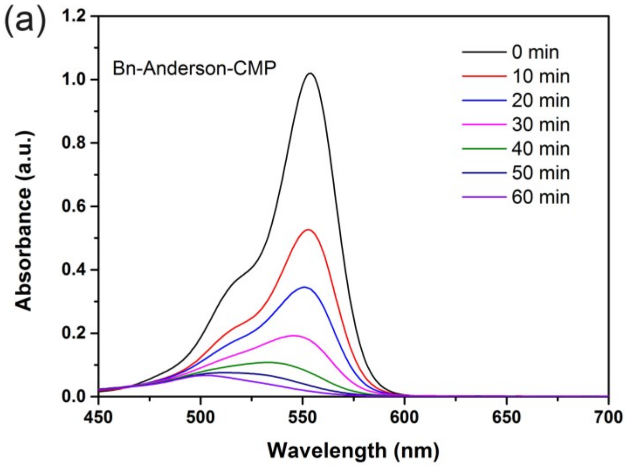


Figure S10. UV-vis spectra of rhodamine B (RhB) (10 mg L^{-1}) after different illumination time intervals in the presence of **Anderson-CMPs** (0.4 mg mL^{-1}): (a) for **Bn-Anderson-CMP** and (b) for **Th-Anderson-CMP** under 300 W xenon lamp with 450 nm optical filter.

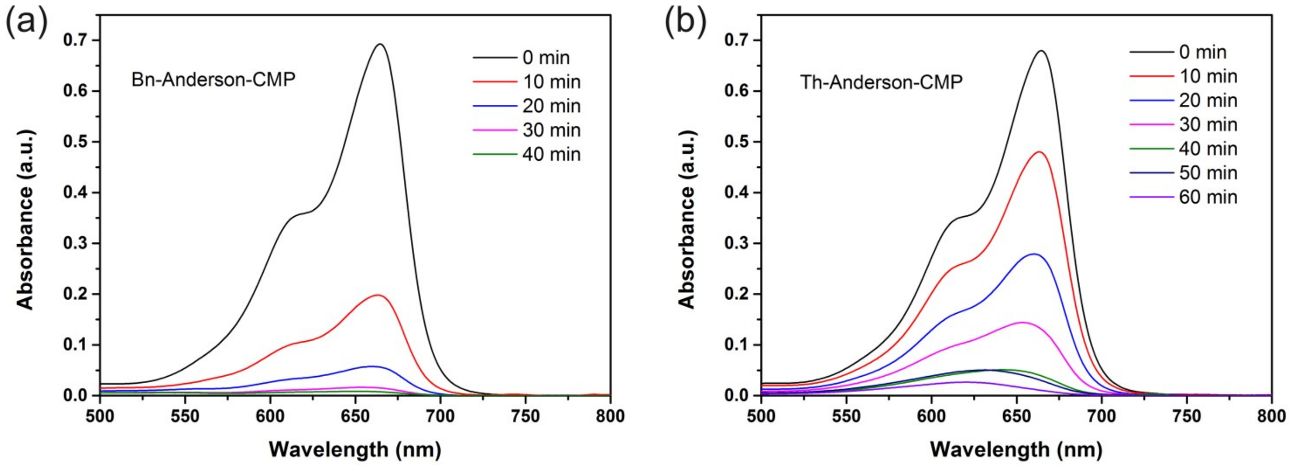


Figure S11. UV-vis spectra of methylene blue (MB) (10 mg L^{-1}) after different illumination time intervals in the presence of **Anderson-CMPs** (0.4 mg mL^{-1}): (a) for **Bn-Anderson-CMP** and (b) for **Th-Anderson-CMP** under 300 W xenon lamp with 450 nm optical filter.

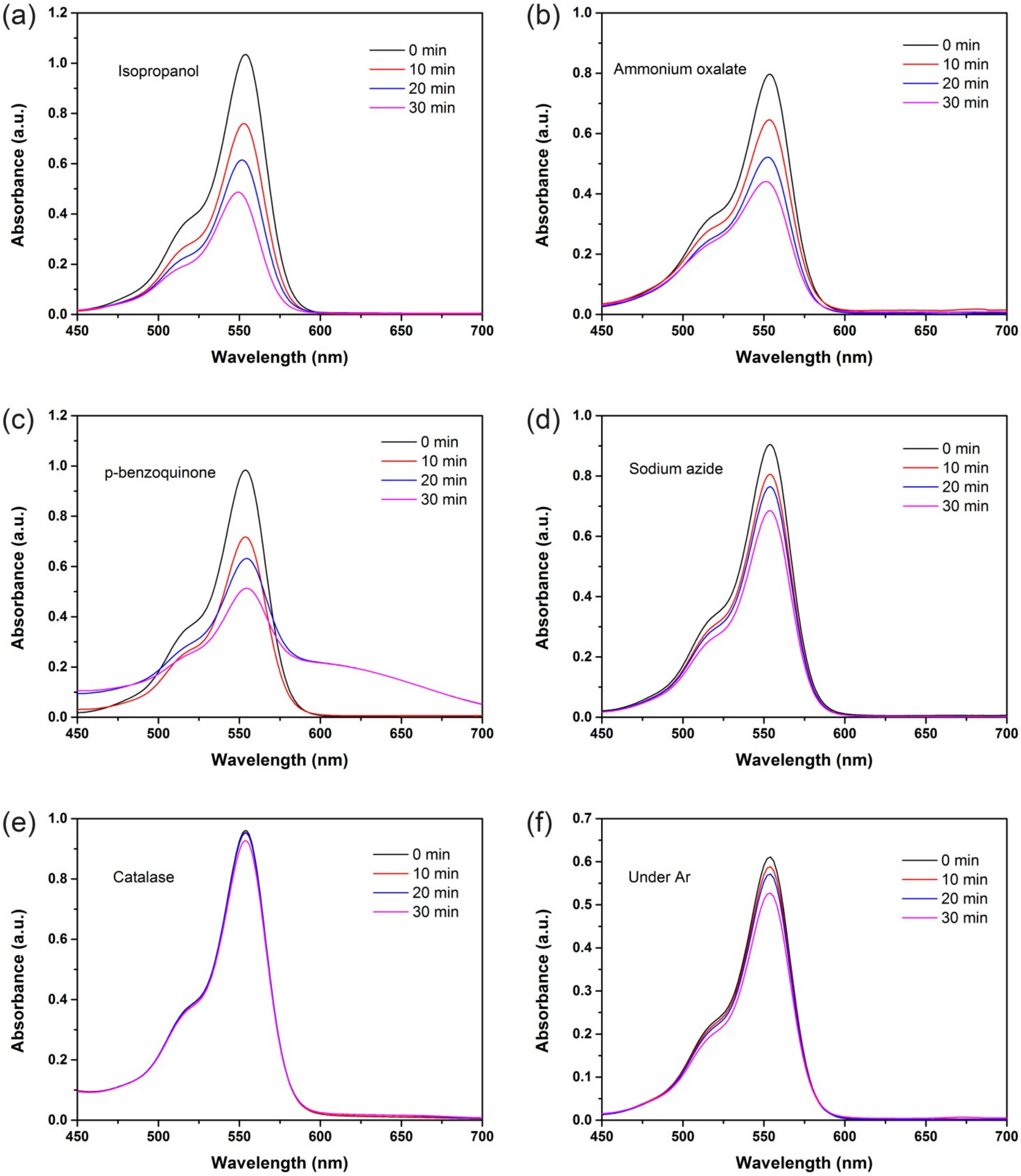


Figure S12. UV-vis spectra of RhB (10 mg L^{-1}) after irradiation for 30 min in the presence of **Anderson- CMPs** (0.4 mg mL^{-1}) with different kinds of scavengers: (a) for isopropanol (IP) (b) for ammonium oxalate (AO) (c) for p-benzoquinone (BQ) (d) for sodium azide (NaN_3) (e) for catalase (CAT) and (f) under Ar under 300 W xenon lamp with 450 nm optical filter.

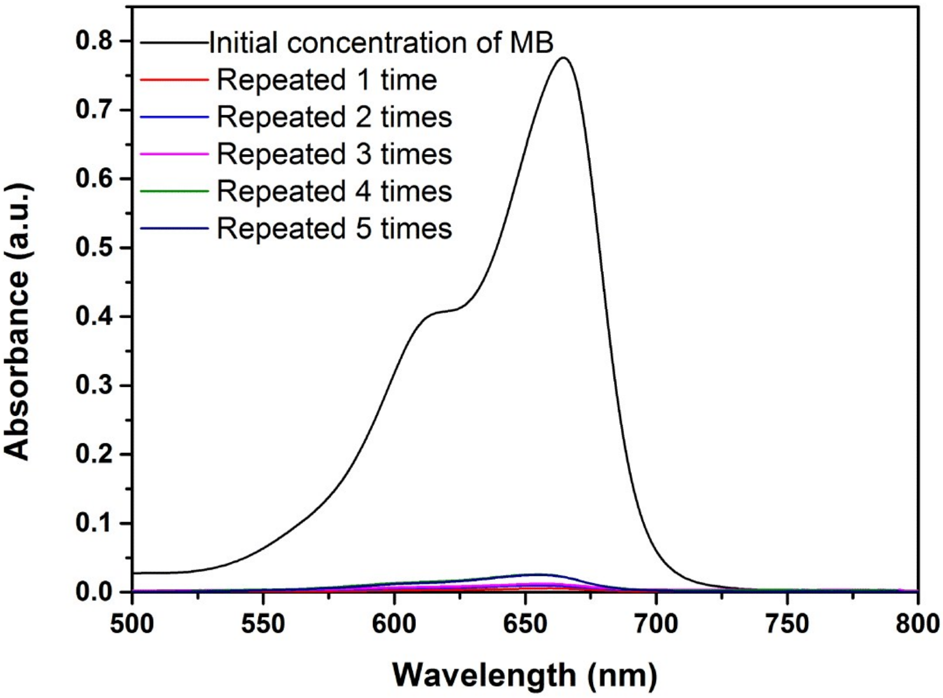


Figure S13. Recycling experiments of the photocatalytic degradation of mesitylene blue (MB) using **Bn-Anderson-CMP** in water under visible light (λ > 450 nm) irradiation.

Section 10. Comparison of the Photocatalytic Performance of Several Related Catalysts for Photodegradation of Rhodamine B

Table S1 The comparison of several kinds of catalyst.

Type and concentration of catalysts	**Concentration of RhB**	**Degradation rate**	**References**
Benzothiadiazole based CMPs (1mg/mL)	10mg/L	25 min over 80%	Ref. 21 in the manuscript
$\{Mn(salen)_2(H_2O)_2[AlMo_6(OH)_6O_{18}]\}[arg]\cdot16H_2O$ (2×10^{-5} mol / L about 0.4 mg/mL)	2×10^{-5} mol / L about 10mg/L	210 min over 80%	Ref. 8 (a) in the manuscript
$\{Mn(salen)_2(H_2O)_2[CrMo_6(OH)_6O_{18}]\}[arg]\cdot11H_2O$ (2×10^{-5} mol / L about 0.4 mg/mL）		210 min 0ver 80%	
TiO_2 (1 mg/mL)	2×10^{-5} mol / L about 10mg/L	180 min over 80%	Ref. 8 (b) in the manuscript
Bn-Anderson-CMP **(0.4 mg/mL)**	**10 mg/L**	**30 min over 80%**	**Our work**
Th-Anderson-CMP **(0.4 mg/mL)**		**40 min over 80%**	

Section 11. Crystal Data and Structure Refinement Parameters for Compound 1

Table S2. Crystal data and structure refinement details for **1**(CCDC deposition number: 1525924).

Formula	$C_{74}H_{134}Br_4MnMo_6N_7O_{26}$
Fw	2488.09
Crystal system	Monoclinic
Space group	C2/c
Temperature (K)	113.15
a (Å)	34.284(5)
b (Å)	14.7645(18)
c (Å)	24.392(4)
α (°)	90
β (°)	127.042(3)
γ (°)	90
V (Å^3)	9855(3)
Z	4
μ (mm^{-1})	2.555
Dc (g/cm^3)	1.677
R (int)	0.0593
GOF on F^2	1.091
R1[a] ［I>2σ(I)］	0.0625 (0929)
wR2[b] ［I>2σ(I)］	0.1579 (1800)

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2= [\Sigma[w(F_o^2-F_c^2)^2] /\Sigma w(F_o^2)^2]^{1/2}$.

Section 12. Ion Exchange Experiments of POM-CMPs

General process of cation exchange experiments:

POM clusters based CMPs (20 mg) were soaked in $CoCl_2$ acetone solution (0.1mol/L, 4 mL) for five days with the $CoCl_2$ solution being refreshed every day. Then the CMPs were isolated and washed with acetone five times and dried under vacuum for further analysis.

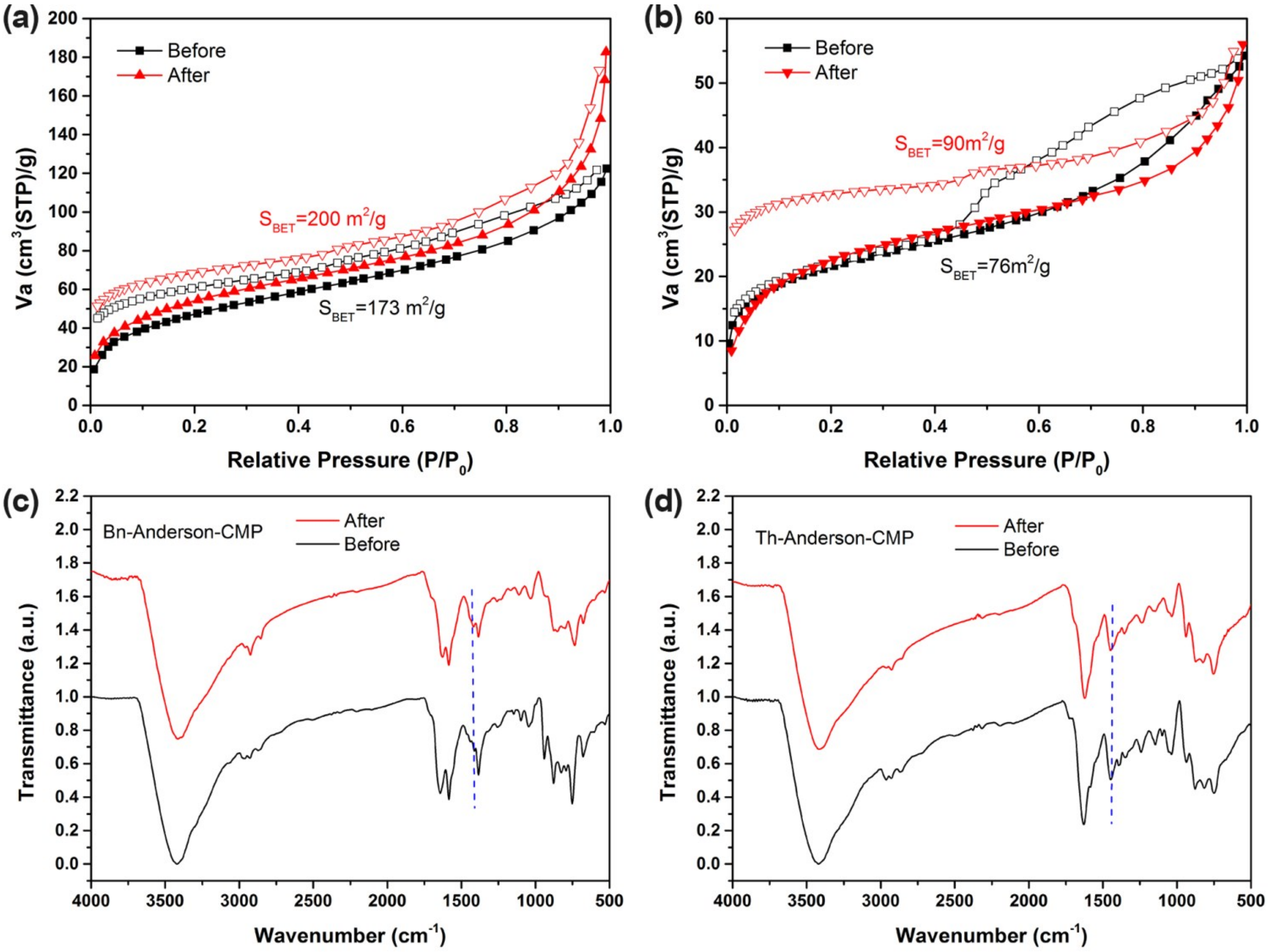


Fig. S14 Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K before (black line) and after (red line) Co^{2+}exchange for: (a) Bn-Anderson-CMP, (b) Th-Anderson-CMP. These results indicate that the exchange experiment using Co^{2+} to replace the bulky TBA cation was not efficient, only slightly increment of BET surface areas could be observed. A comparison of FT-IR spectra of (c) Bn-Anderson-CMP and (d) Th-Anderson-CMP before and after cation exchange experiment. The bands in the 1460-1380 cm^{-1} region (blue line) and 2900-2800 ascribed to the stretching vibrations of the TBA^+ cations did not disappear after exchanging, demonstrating the failure of cation exchange.

Section 13. Chemical Stabilities Studies of POM-CMPs

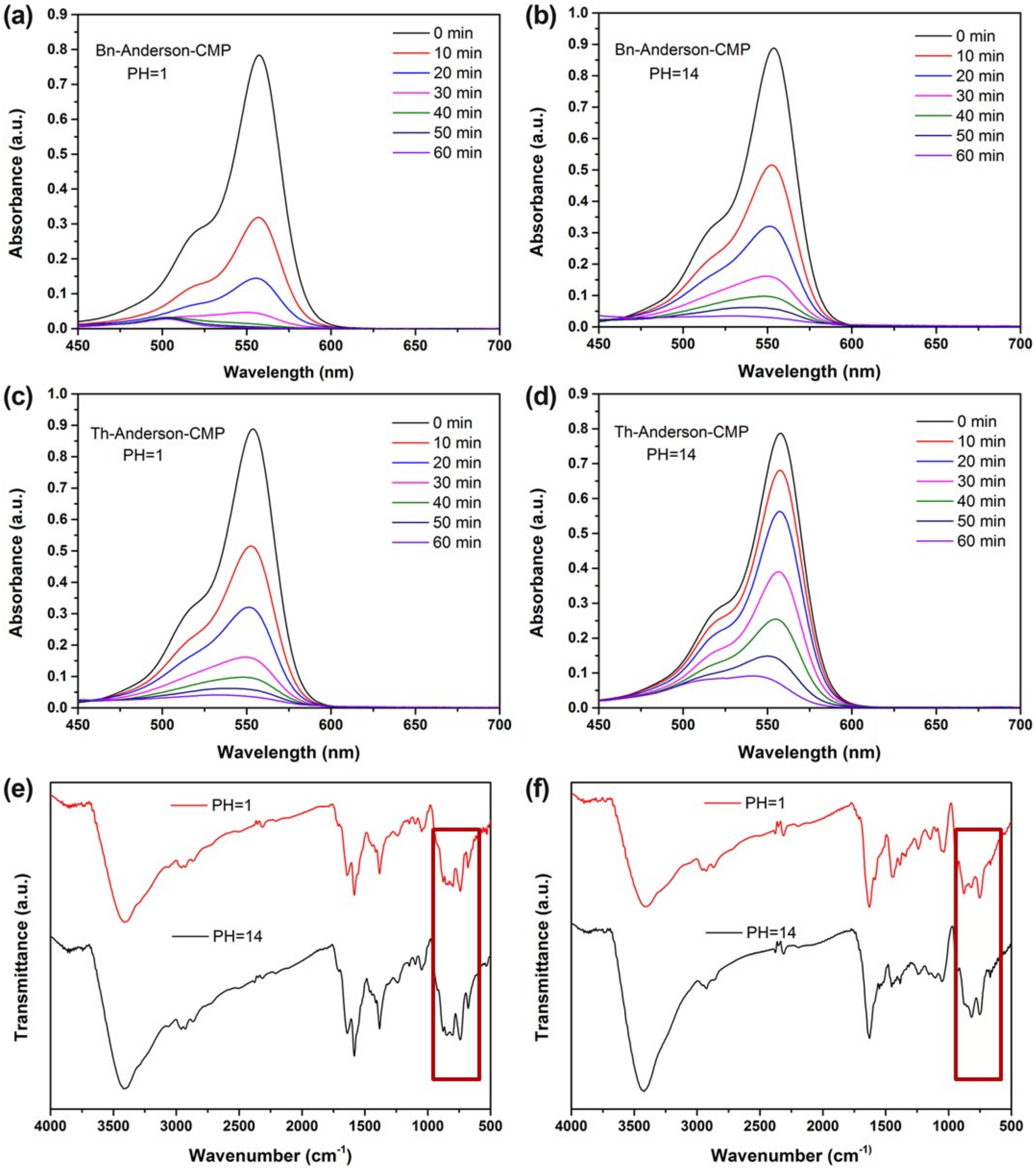


Fig. S15 (a) UV-vis spectra monitoring of rhodamine B (RhB) (10 mg L^{-1}) after different illumination time intervals in the presence of **Bn-Anderson-CMPs** (0.4 mg mL^{-1}) in 0.1 M HCl (pH = 1) aqueous solution and (b) 0.1 M NaOH (pH = 14) aqueous solution; (c) UV-vis spectra monitoring of rhodamine B (RhB) (10 mg L^{-1}) after different illumination time intervals in the presence of **Th-Anderson-CMPs** (0.4 mg mL^{-1}) in 0.1 M HCl (pH = 1) aqueous solution and (d) 0.1 M NaOH (pH = 14) aqueous solution; The photocatalytic degradation of RhB was nearly unchanged compared with that in neutral condition. (e) FT-IR spectra of POMs based CMPs after experiments of photocatalytic degradation of RhB in acidic (red line) and basic conditions (black line) for Bn-Anderson-CMP and (f) for Th-Anderson-CMP. POMs based CMPs show high chemical stability both in acidic and basic environment.

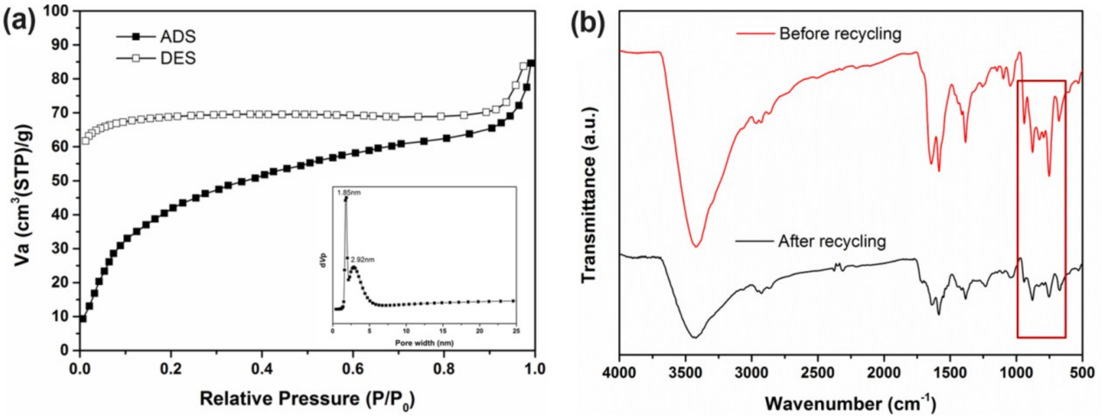


Fig. S16 (a) Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K and pore size distribution (inset) based on NLDFT calculation for **Bn-Anderson-CMP** after 5 times recycling experiments. The BET surface areas were calculated to be 195 m^2 g^{-1}, slightly lower compared with the as synthesized sample (218 m^2 g^{-1}); (b) FT-IR spectra comparison of Bn-Anderson-CMP before (red) and after (black) recycling experiments. The characteristic Mo=O (st) and Mo-O-Mo (st) stretching bands for POM active sites of in POM-CMP remain unchanged after recycling.

Section 14. Supporting References

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