

## Anderson polyoxometalate built-in covalent organic frameworks for enhancing catalytic performances

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### Experimental Section

#### Materials and physical measurements:

All materials and solvents were obtained from Energy Chemical Co. Ltd., TCI (Shanghai) Development Co., Ltd., MACKLIN, Aladdin, Tianjin Guangfu Fine Chemical Research Institute, and used without further purification.

Fourier-transform Infrared (FT-IR) spectra were recorded at the range of 400-4000 cm<sup>-1</sup> on a Bruker ALPHA spectrometer. Thermogravimetric analyzer (TGA) was performed on a DTG-60 instrument (SHIMADZU, Beijing, China) at a heating rate of 5 °C min<sup>-1</sup> from room temperature to 800 °C under nitrogen atmosphere with a flow rate of 100 mL min<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns of the samples were measured with a Cu-K $\alpha$  X-ray radiation source ( $\lambda = 0.154056$  nm) incident radiation by a Rigaku MiniFLEX 600 instrument operating at 40 kV voltage and 50 mA current. UV-vis absorption spectra were recorded on a Shimadzu Corporation UV-2600 220V CH spectrometer. The Xe lamp (300 W) with 410 nm optical filters were readjusted to the power density of 100 mW cm<sup>-2</sup> prior to the experimental process.

#### Synthesis:

$\text{NH}_2\text{-}\{\text{MnMo}_6\}\text{-NH}_2$  ( $[\text{N}(\text{C}_4\text{H}_9)_4]_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ ),  $\text{NH}_2\text{-}\{\text{CoMo}_6\}\text{-NH}_2$  ( $[\text{N}(\text{C}_4\text{H}_9)_4]_3[\text{CoMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ ),  $\text{NH}_2\text{-}\{\text{FeMo}_6\}\text{-NH}_2$  ( $[\text{N}(\text{C}_4\text{H}_9)_4]_3[\text{FeMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ ), and tetrakis(4-formylphenyl)silane (TFPS) were synthesized according to literatures.<sup>1-2</sup>

**Mn-Anderson-COF:** 1000 mg of  $\text{NH}_2\text{-}\{\text{MnMo}_6\}\text{-NH}_2$  and 119 mg of TFPS were dissolved in 15 mL of acetonitrile, and then added into a Teflon-lined autoclave. The Teflon-lined autoclave was placed in an oven at 80 °C for 3 days. The solid was thoroughly washed by acetonitrile and collected via centrifugation. The obtained solid was dried under vacuum to yield Mn-Anderson-COF (901 mg, 82% based on TFPS). Elemental Analysis: for  $\text{SiC}_{140}\text{H}_{260}\text{Mn}_2\text{Mo}_{12}\text{N}_{10}\text{O}_{48}$ : Calcd. Si 0.68%, C 40.60%, H 6.28%, N 3.38%, Mn 2.66%, Mo 27.84%, Found Si 0.67%, C 40.52%, H 6.19%, N 3.26%, Mn 2.54%, Mo 27.61%. IR (KBr,  $\text{cm}^{-1}$ ): 2960 ( $\nu_{\text{as}}$  NH s), 2933 ( $\nu$  CH s), 2873 ( $\nu$  CH s), 1643 ( $\nu$  C=N m), 1481 ( $\delta$  CH, s), 1382 ( $\delta$  CH, m), 1263 (s), 1157 (m), 1093 ( $\nu$  CO m), 1030 ( $\nu$  CO s), 941 ( $\nu$  Mo=O s), 920 ( $\nu$  Mo=O s), 903 ( $\nu$  Mo=O s), 819 (w), 736 (w), 667 ( $\nu$  Mo-O-Mo s), 563 (m), 522 (w), 486 (w), 411(w)  $\text{cm}^{-1}$ .

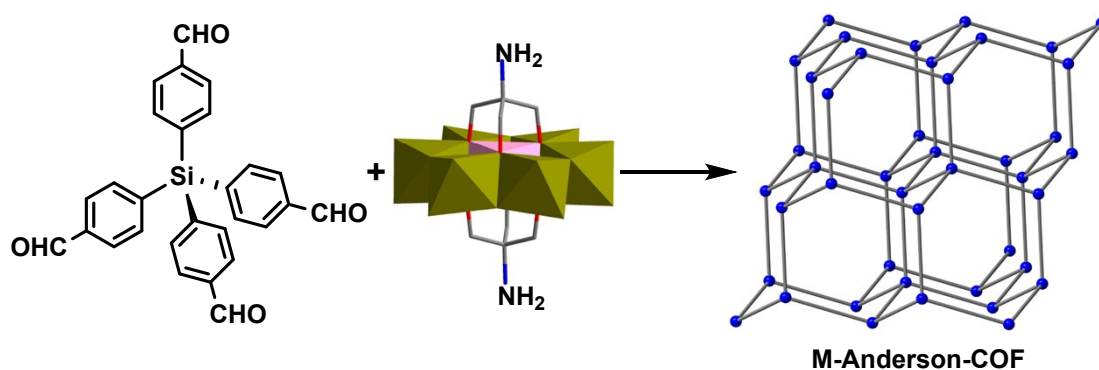
**Co-Anderson-COF:** A similar method as described above. The obtained solid was Co-Anderson-COF (878 mg, 80% based on TFPS). Elemental Analysis: for  $\text{SiC}_{140}\text{H}_{260}\text{Co}_2\text{Mo}_{12}\text{N}_{10}\text{O}_{48}$ : Calcd. Si 0.68%, C 40.52%, H 6.27%, N 3.38%, Co 2.85%, Mo 27.79%, Found Si 0.67%, C 40.46%, H 6.17%, N 3.25%, Co 2.77%, Mo 27.64%. IR (KBr,  $\text{cm}^{-1}$ ): 2962 ( $\nu_{\text{as}}$  NH s), 2937 ( $\nu$  CH s), 2875 ( $\nu$  CH s), 1643 ( $\nu$  C=N m), 1481 ( $\delta$  CH, s), 1383 ( $\delta$  CH, m), 1263 (s), 1157 (m), 1103 ( $\nu$  CO m), 1031 ( $\nu$  CO s), 939 ( $\nu$  Mo=O s), 921 ( $\nu$  Mo=O s), 904 ( $\nu$  Mo=O s), 819 (w), 741 (w), 667 ( $\nu$  Mo-O-Mo s), 570 (m), 523 (w), 487 (w), 434 (w)  $\text{cm}^{-1}$ .

**Fe-Anderson-COF:** A similar method as described above. The obtained solid was Fe-Anderson-COF (857 mg, 78% based on TFPS). Elemental Analysis: for  $\text{SiC}_{140}\text{H}_{260}\text{Fe}_2\text{Mo}_{12}\text{N}_{10}\text{O}_{48}$ : Calcd. Si 0.68%, C 40.58%, H 6.28%, N 3.38%, Fe 2.71%, Mo 27.83%, Found Si 0.67%, C 40.46%, H 6.17%, N 3.29%, Fe 2.66%, Mo 27.73%. IR (KBr,  $\text{cm}^{-1}$ ): 2962 ( $\nu_{\text{as}}$  NH s), 2937 ( $\nu$  CH s), 2875 ( $\nu$  CH s), 1643 ( $\nu$  C=N m), 1483

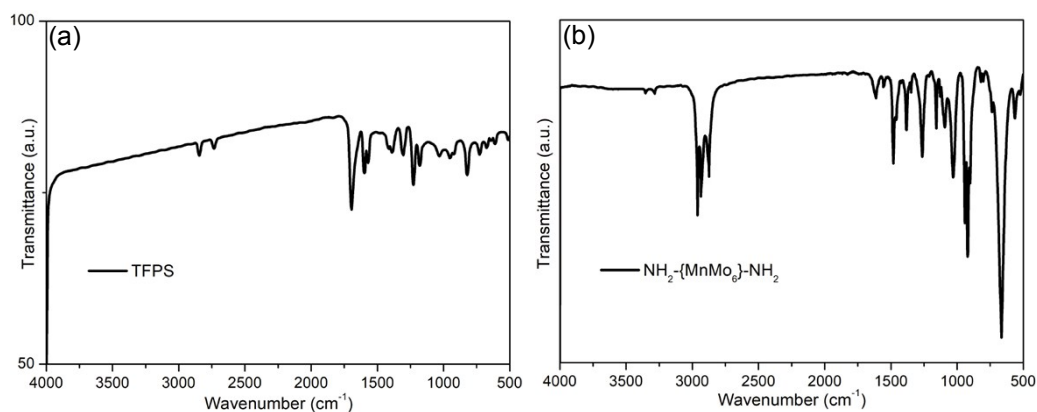
( $\delta$  CH, s), 1383 ( $\delta$  CH, m), 1263 (s), 1155 (m), 1089 (v CO m), 1029 (v CO s), 941 (v Mo=O s), 922 (v Mo=O s), 903 (v Mo=O s), 821 (w), 725 (w), 667 (v Mo-O-Mo s), 563 (m), 526 (w), 479 (w), 451 (w)  $\text{cm}^{-1}$ .

Ion exchange on Mn-Anderson-COF ( $\text{Li}^+$ ):

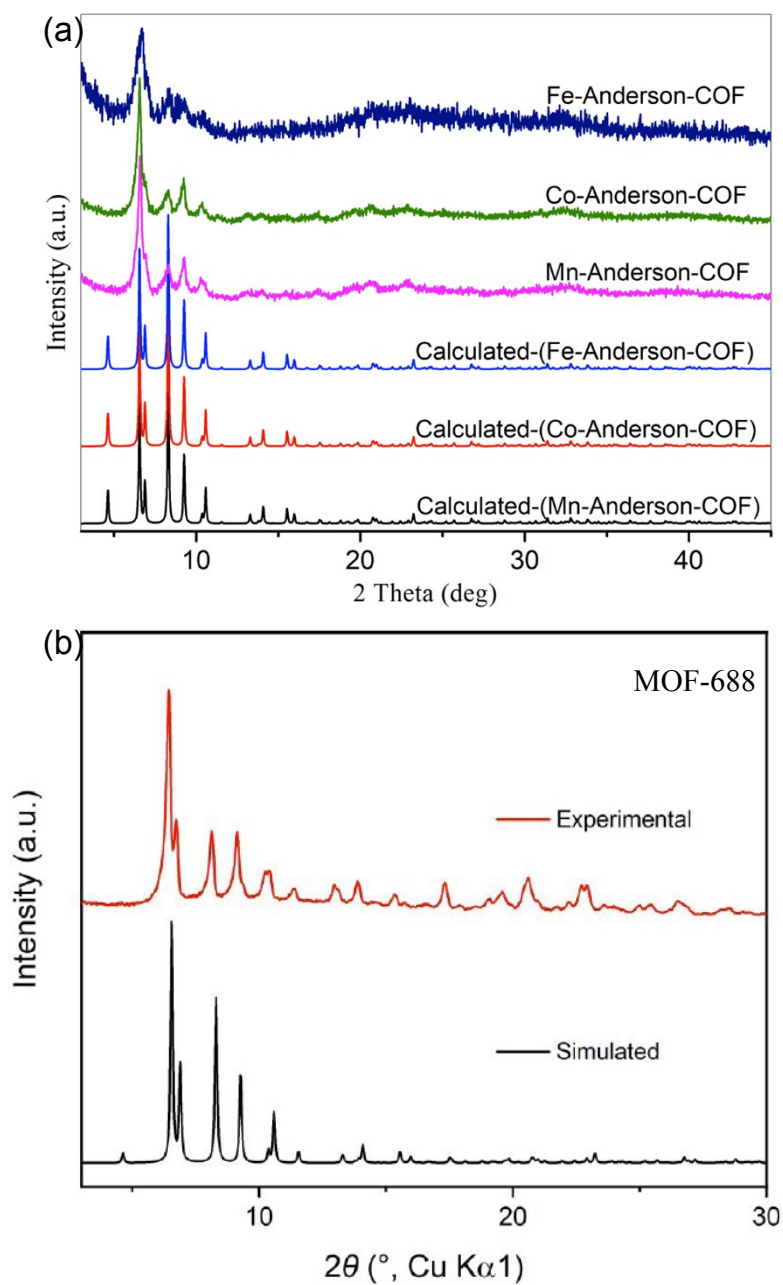
300 mg of Mn-Anderson-COF was immersed in 2 mL of 100 mg diethyl ether solution of LiOTf at room temperature. The solution was change two times per day over two weeks. The process was monitored by digestion IR. Upon  $\text{Li}^+$  exchange, the characteristic peaks of  $\text{TBA}^+$  decreased as indicated at 2962  $\text{cm}^{-1}$ , 2937  $\text{cm}^{-1}$  and 2875  $\text{cm}^{-1}$ .



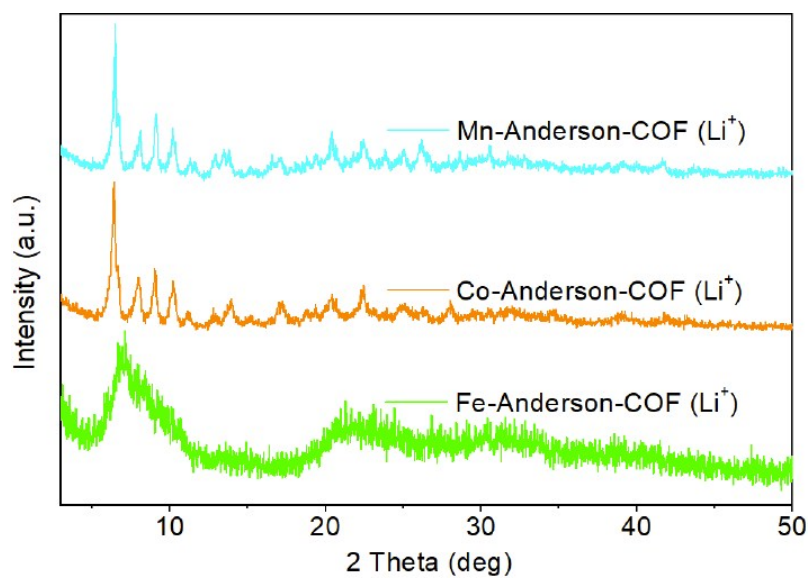
**Figure S1.** Designed synthesis of diamondoid network of **M-Anderson-COFs**.



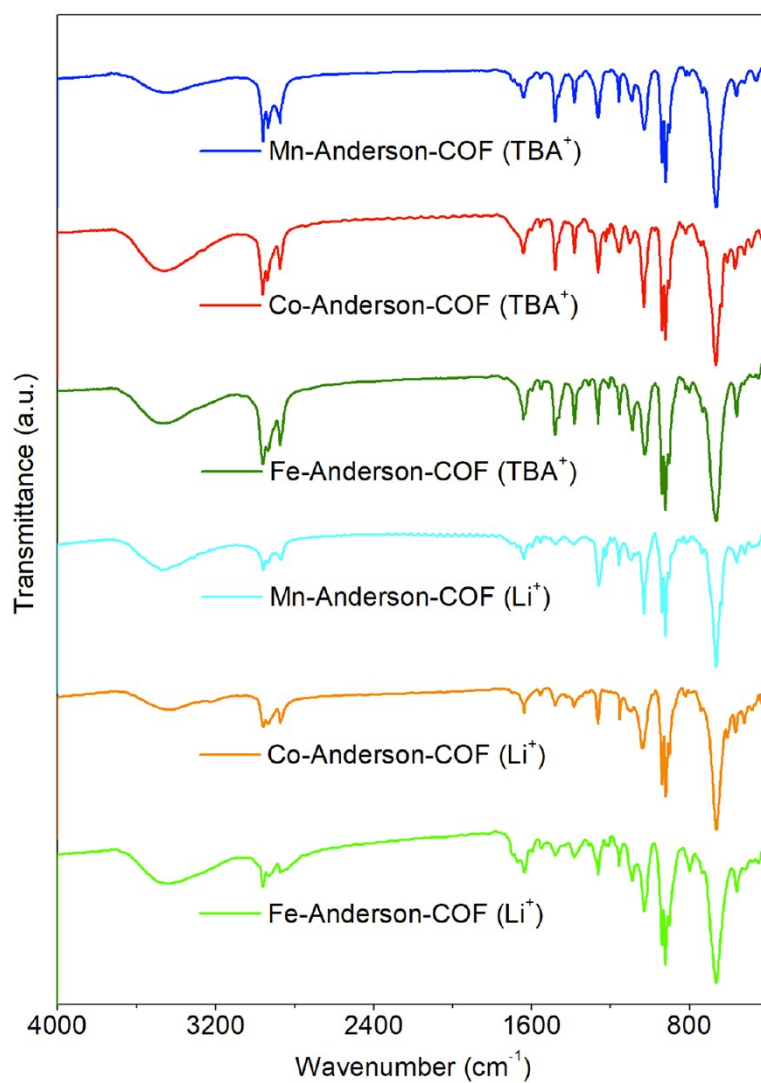
**Figure S2.** IR spectrums of TFPS and  $\text{NH}_2\text{-}\{\text{MnMo}_6\}\text{-NH}_2$ .



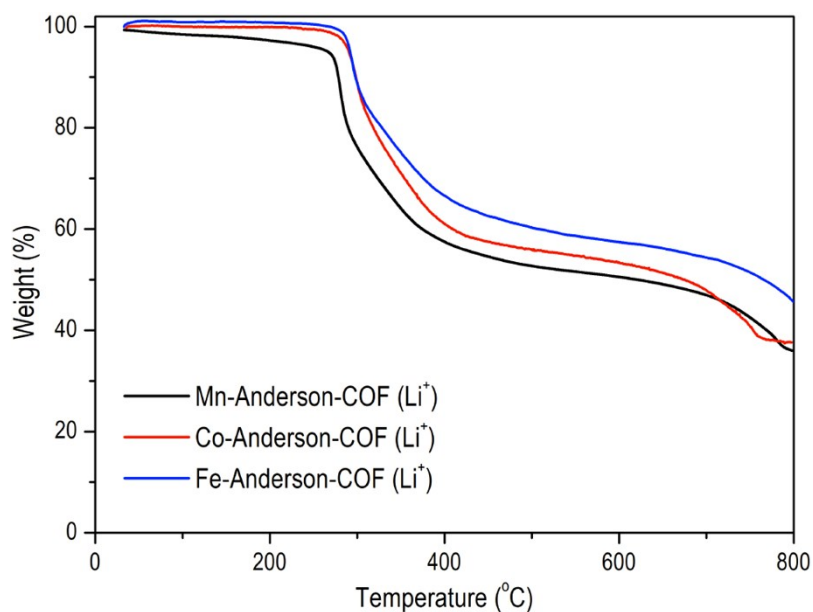
**Figure S3.** (a) Experimental and simulated PXRD patterns of **M-Anderson-COFs**; (b) Experimental and simulated PXRD patterns of MOF-688, adapted with permission from Ref. [24].



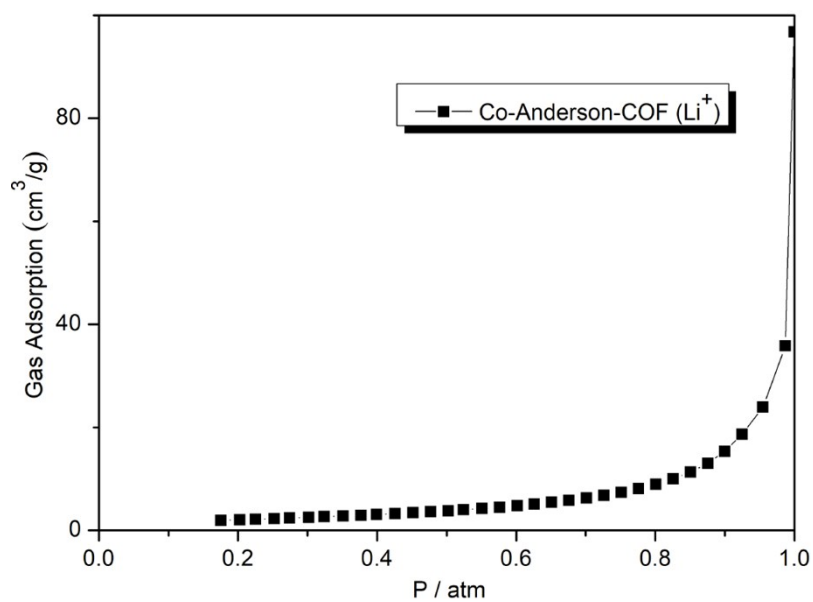
**Figure S4.** PXRD patterns of Li<sup>+</sup> exchanged M-Anderson-COFs.



**Figure S5.** IR spectra of different samples.



**Figure S6.** TGA of different samples.

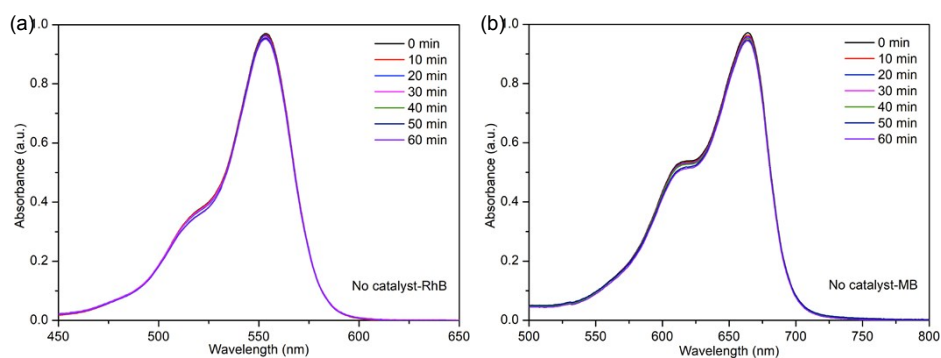


**Figure S7.** N<sub>2</sub> sorption curves (77 K) of Co-Anderson-COF (Li<sup>+</sup>).

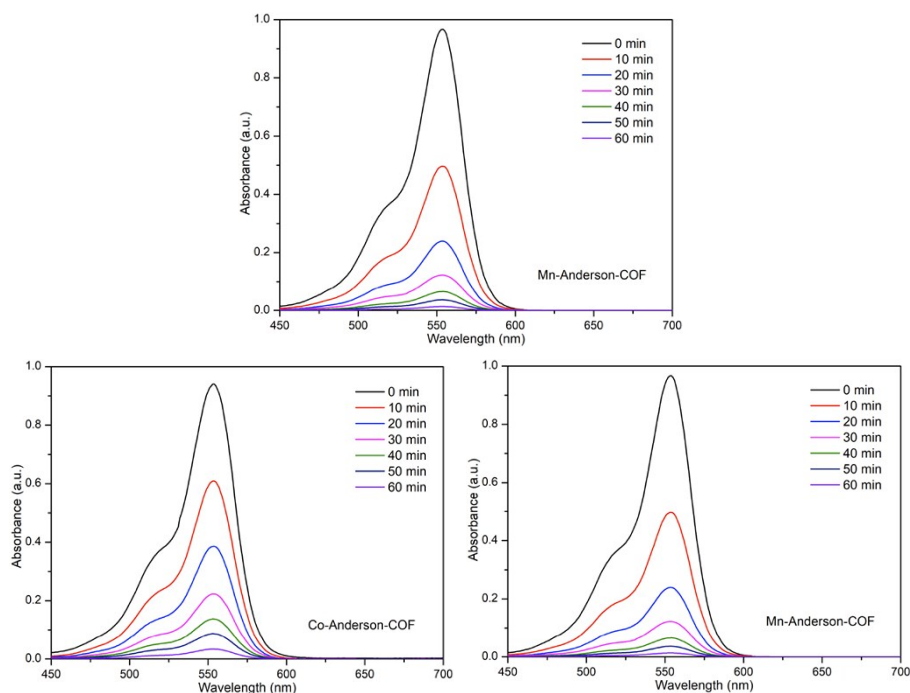
#### **Experimental procedure of photodegradation of organic dyes:**

Catalysts (10 mg) were dispersed into the solution (100 mL) of organic dyes (100 mg/L), then magnetically stirred for 30 min in the dark. After this, the mixture was allowed to expose to visible light ( $\lambda > 410$  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.

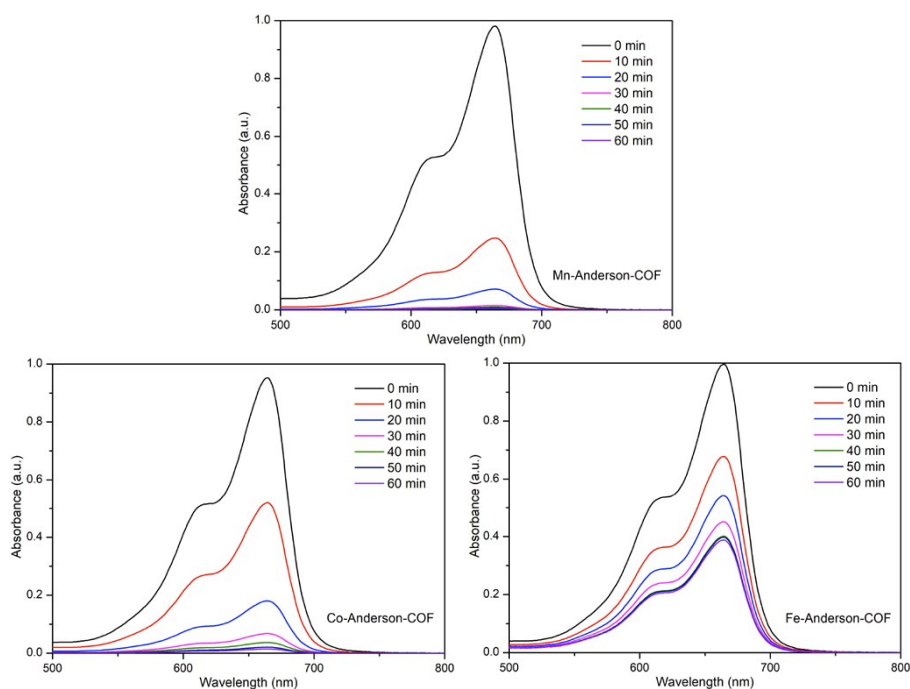
The radical scavenger experiments were performed using Isopropanol (IP, a scavenger of  $\cdot\text{OH}$ , 99% 60  $\mu\text{L}/\text{mL}$ ), Superoxide dismutase (SOD, a scavenger of  $\cdot\text{O}_2^-$ , 0.4 g/L), Ammonium Oxalate (AO, a scavenger of  $\text{h}^+$ , 3 mmol/L), L-Histidine (L-His, a scavenger of  $^1\text{O}_2$ , 3 mmol/L) and Catalase (CAT, a scavenger of  $\text{H}_2\text{O}_2$ , 0.3 g/L), respectively. Other conditions remain unchanged.



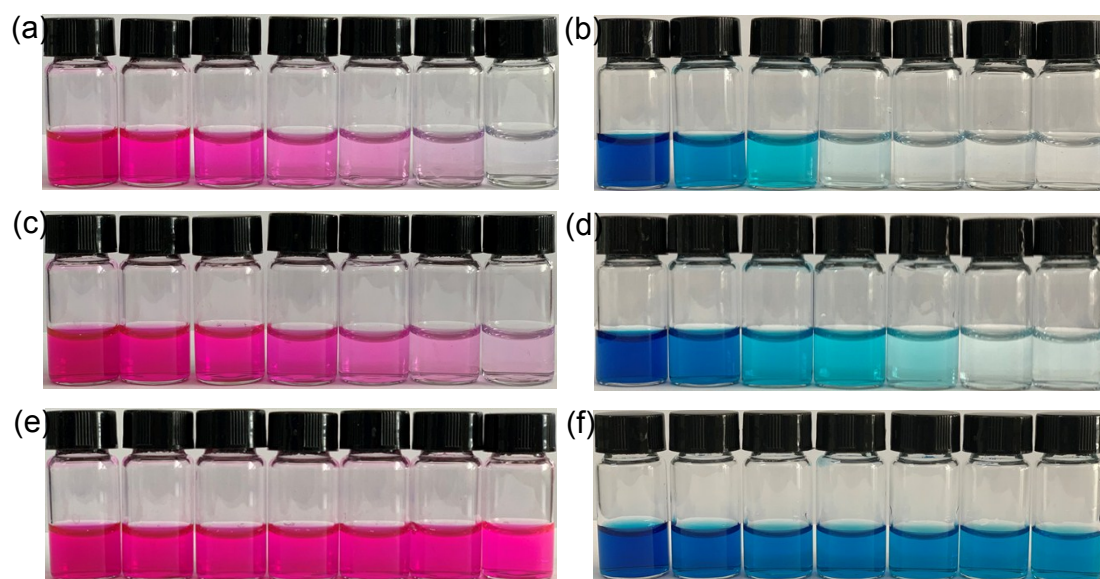
**Figure S8.** (a) UV-vis spectra of RhB (a) and MB (b) without catalyst.



**Figure S9.** UV-vis spectra of RhB (100 mg/L) after different illumination time intervals in the presence of **M-Anderson-COF** (0.1 mg/mL) under 300 W xenon lamp with 450 nm optical filter.

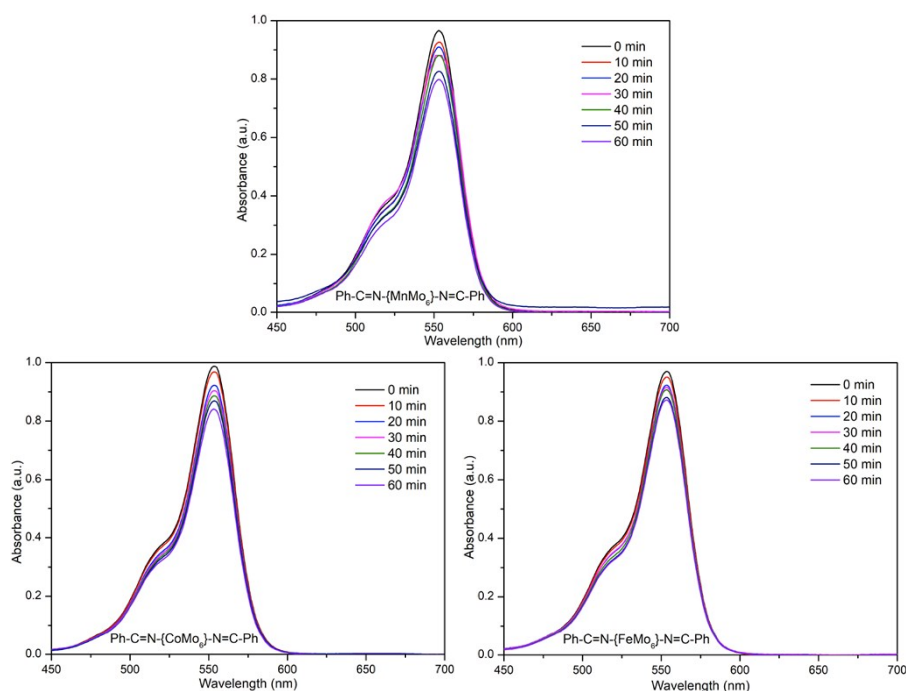


**Figure S10.** UV-vis spectra of MB (100 mg/L) after different illumination time intervals in the presence of **M-Anderson-COF** (0.1 mg/mL) under 300 W xenon lamp with 450 nm optical filter.

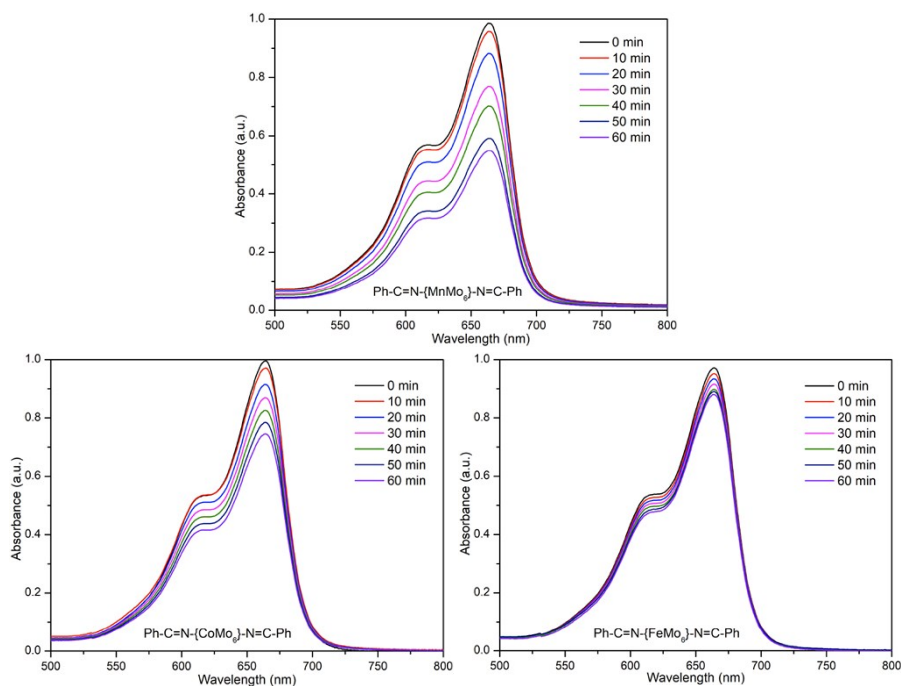


**Figure S11.** Photodegradation of RhB and MB using **M-Anderson-COF** catalysts in water. Concentration of **M-Anderson-COF**: 0.1 mg/mL, concentration of dye: 100 mg/L. The color change of dye when different **M-Anderson-COF** was used as catalyst [(a) dye = RhB, catalyst = **Mn-Anderson-COF**; (b) dye = MB, catalyst = **Mn-Anderson-COF**; (c) dye = RhB, catalyst = **Co-Anderson-COF**; (d) dye = MB, catalyst = **Co-Anderson-COF**; (e) dye = RhB, catalyst = **Fe-Anderson-COF**; (f) dye = MB, catalyst = **Fe-Anderson-COF**]. The sample interval is 10 min.

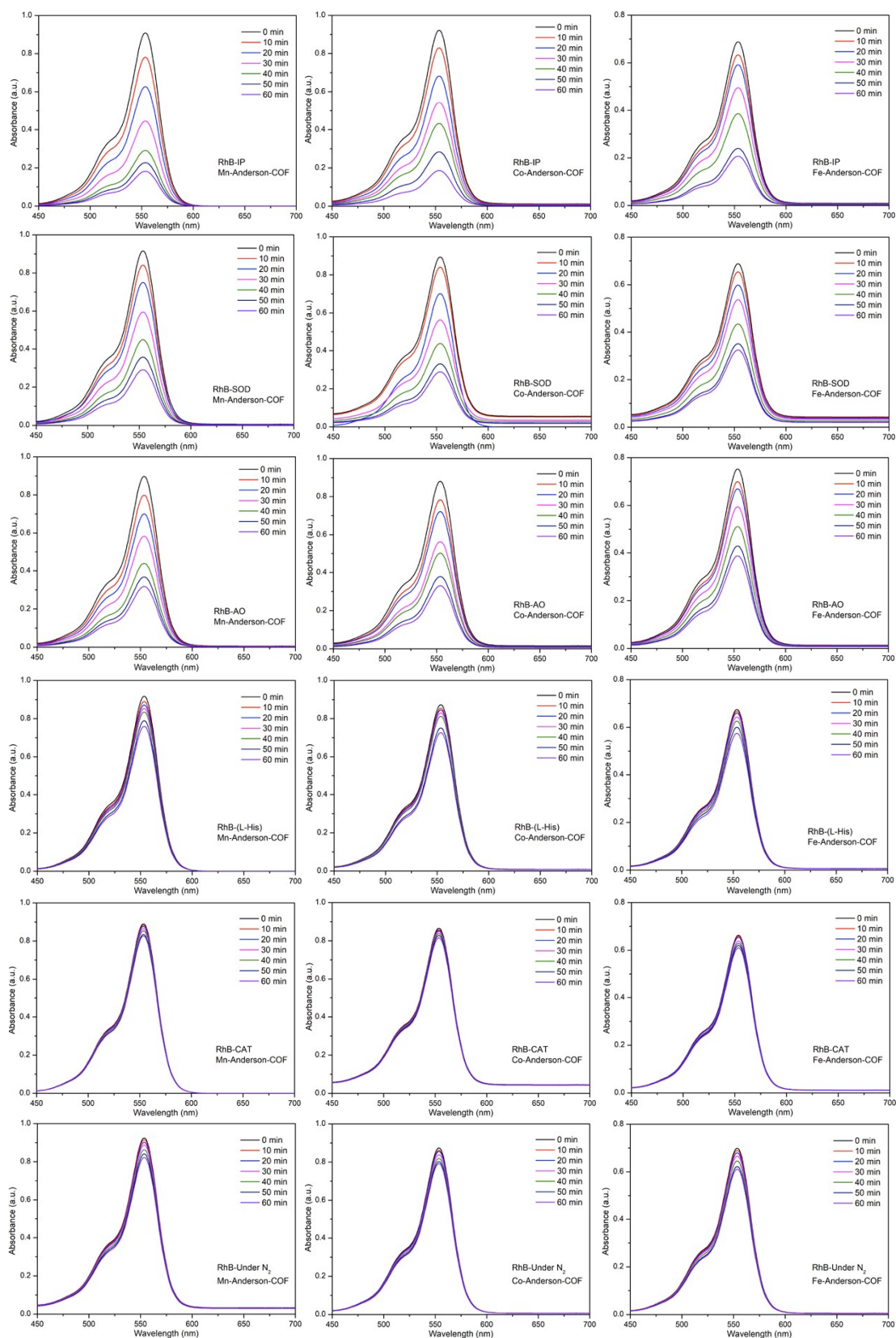




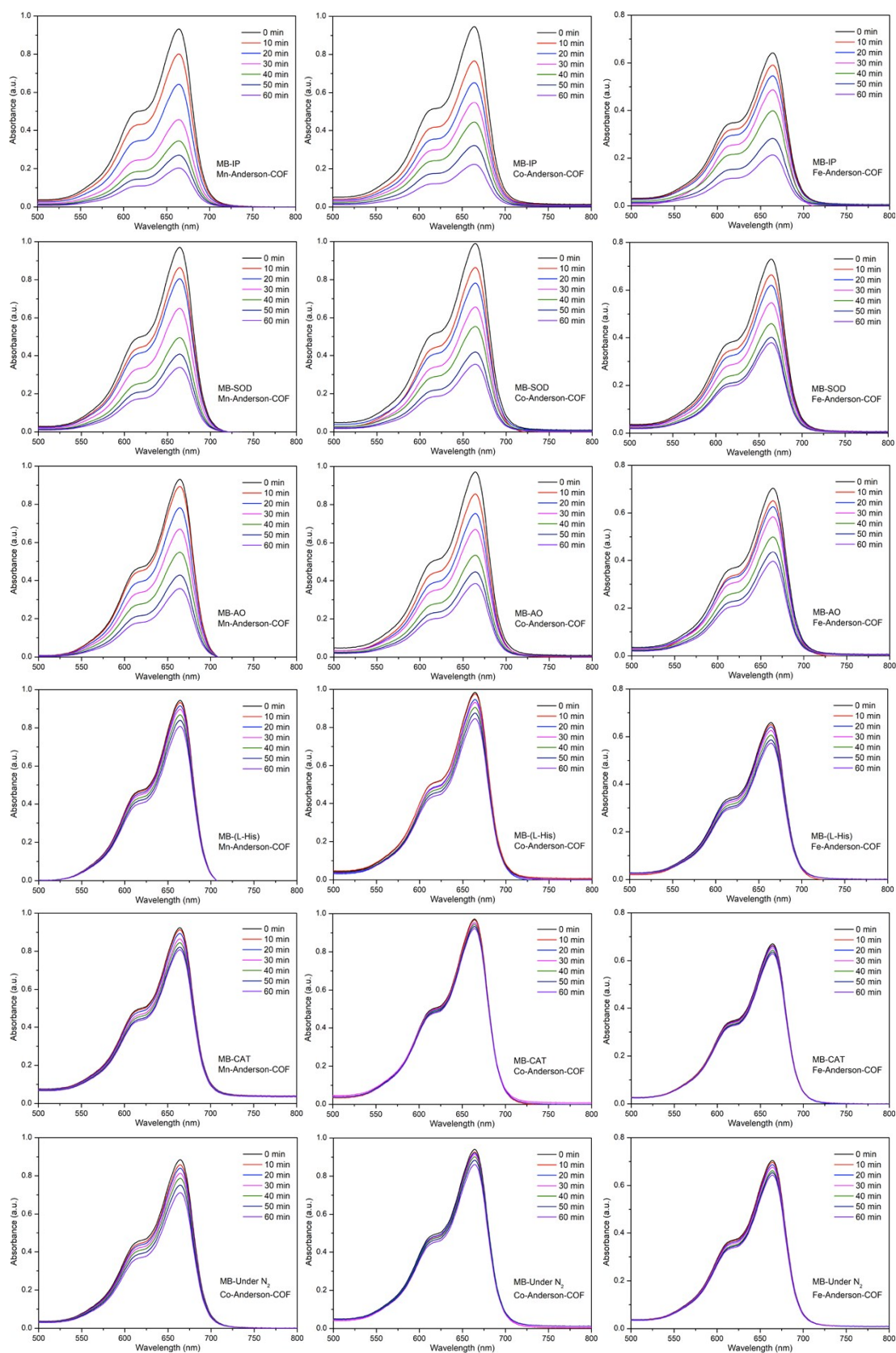
**Figure S12.** UV-vis spectra of RhB (100 mg/L) after different illumination time intervals in the presence of Ph-C=N-{MMo<sub>6</sub>}-N=C-Ph (0.1 mg/mL) under 300 W xenon lamp with 450 nm optical filter.



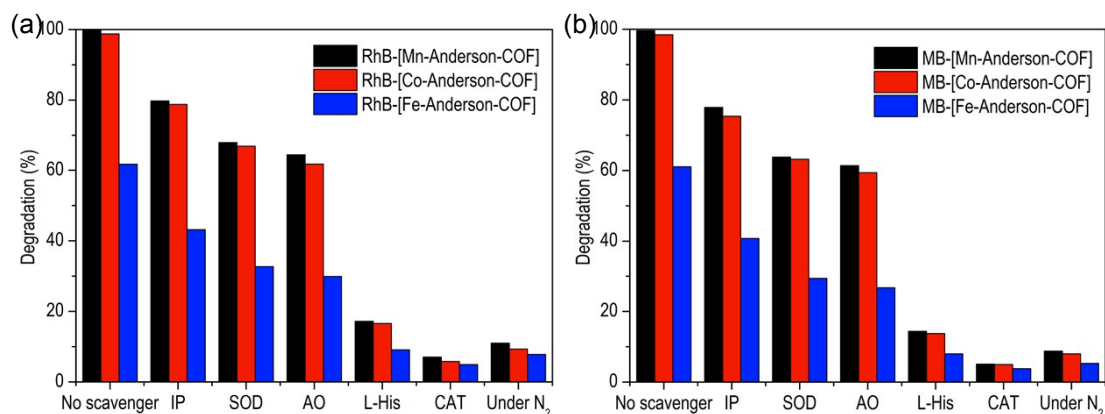
**Figure S13.** UV-vis spectra of MB (100 mg/L) after different illumination time intervals in the presence of Ph-C=N-{MMo<sub>6</sub>}-N=C-Ph (0.1 mg/mL) under 300 W xenon lamp with 450 nm optical filter.



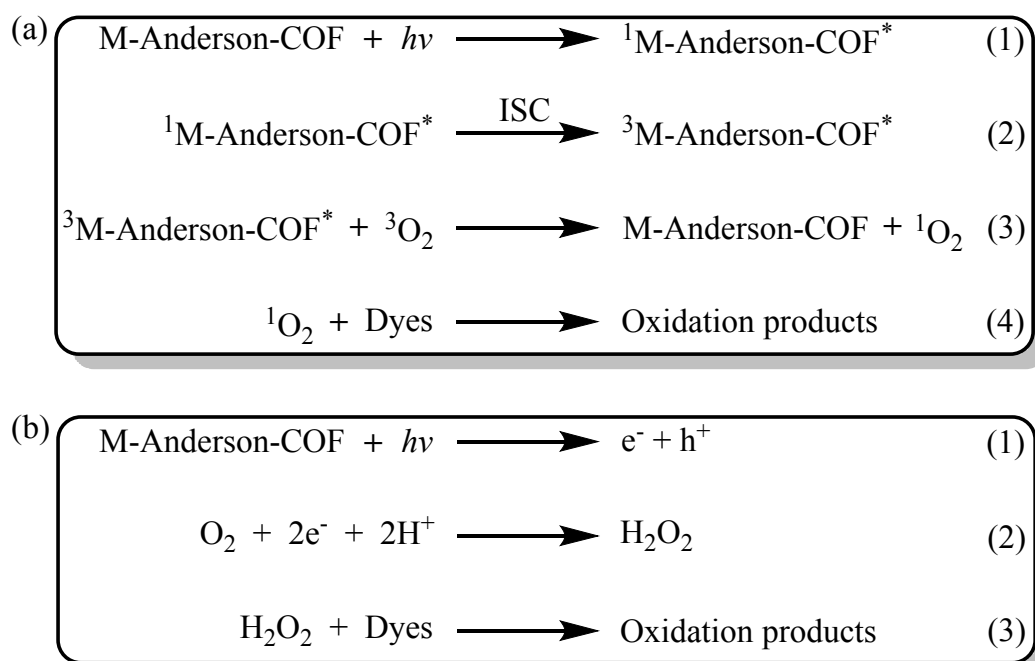
**Figure S14.** UV-vis spectra of RhB (100 mg/L) after different illumination time intervals in the presence of **M-Anderson-COF** (0.1 mg/mL) and different scavengers.



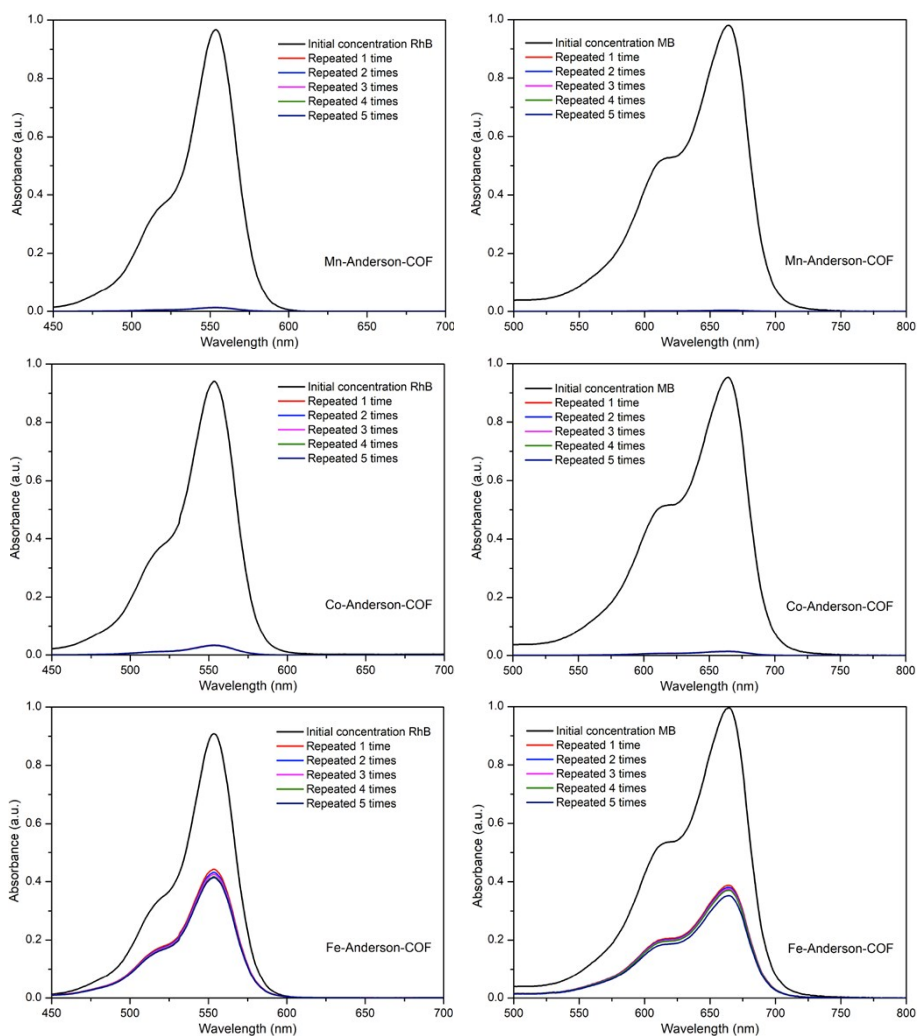
**Figure S15.** UV-vis spectra of MB (100 mg/L) after different illumination time intervals in the presence of **M-Anderson-COF** (0.1 mg/mL) and different scavengers.



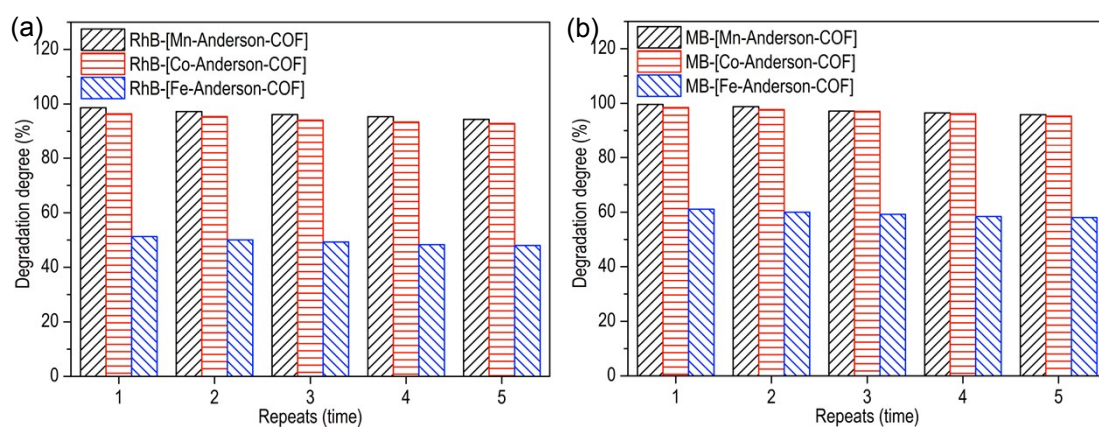
**Figure S16.** The effect of different scavengers, isopropanol (IP), superoxide dismutase (SOD), ammonium oxalate (AO), L-Histidine (L-His) and catalase (CAT), and the absence of oxygen (under N<sub>2</sub>) on the degradation of RhB (a) and MB (b) over **M-Anderson-COF** under 60 min of visible light irradiation.



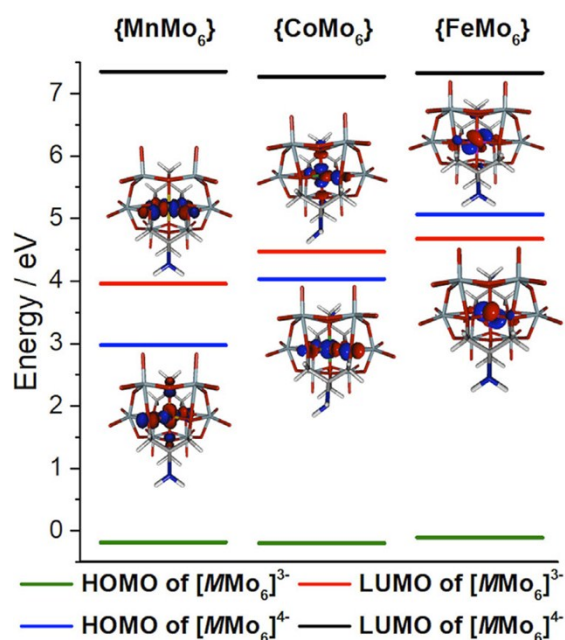
**Figure S17.** Proposed photodegradation reaction mechanism.



**Figure S18.** UV-vis spectra of RhB and MB in the presence of recycled **M-Anderson-COF** (0.1 mg/mL) in water under visible light irradiation.



**Figure S19.** Recycling experiments of the photocatalytic degradation of RhB (a) and MB (b) using **M-Anderson-COF** in water under visible light irradiation.



**Figure S20.** The HOMO–LUMO energy diagram of NH<sub>2</sub>-tris-functionalized Anderson anions {MMo<sub>6</sub>} (M=Mn<sup>3+</sup>, Co<sup>3+</sup>, Fe<sup>3+</sup>). Adapted with permission from Ref. [3].

**Table S1.** Summary of the performance of reported materials for the photodegradation of RhB.

Materials	Catalyst (g/L)	RhB (mg/L)	Irradiation source	Efficiency	Ref.
Mn-Anderson-COF	0.1	100	Visible light	98.6% (60 min)	This work
Co-Anderson-COF	0.1	100	Visible light	96.4% (60 min)	This work
Fe-Anderson-COF	0.1	100	Visible light	51.3% (60 min)	This work
Bn-Anderson-CMP	0.4	10	Visible light	~97% (60 min)	4
Th-Anderson-CMP				~94% (60 min)	
TiO <sub>2</sub>	1.0	10	Visible light	~95% (210 min)	5
Benzothiadiazole based CMPs	1.0	10	Visible light	~87% (30 min)	6
{Mn(salen) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [AlMo <sub>6</sub> (OH) <sub>6</sub> O <sub>18</sub> ]}[arg]•16H <sub>2</sub> O	0.4	10	Visible light	100% (300 min)	7
{Mn(salen) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [CrMo <sub>6</sub> (OH) <sub>6</sub> O <sub>18</sub> ]}[arg]•11H <sub>2</sub> O				99.6% (300 min)	

**Table S2.** Summary of the performance of reported materials for the photodegradation of MB.

Materials	Catalyst (g/L)	MB (mg/L)	Irradiation source	Efficiency	Ref.
Mn-Anderson-COF	0.1	100	Visible light	99.6% (60 min)	This work
Co-Anderson-COF	0.1	100	Visible light	98.4% (60 min)	This work
Fe-Anderson-COF	0.1	100	Visible light	61.1% (60 min)	This work
Fc-TEB-CMP	0.25	31.9	Visible light	87.8% (60 min)	8
			Solar light	92.9% (60 min)	
Bn-Anderson-CMP	0.4	10	Visible light	100% (40 min)	4
Th-Anderson-CMP				~97% (60 min)	
Ag <sub>3</sub> PO <sub>4</sub>	3.0	15.3	Visible light	100% (10 min)	9
PDINH	0.5	10	Visible light	50% (400 min)	10
[Ni <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (qa) <sub>2</sub> (4,4'-bpy) <sub>2</sub> U <sub>5</sub> O <sub>14</sub> (H <sub>2</sub> O) <sub>2</sub> (OAc) <sub>2</sub> ]	2.0	35.9	Visible light	80% (240 min)	11
Fe <sub>3</sub> O <sub>4</sub> @MIL-100(Fe)	0.1 (0.1 mL H <sub>2</sub> O <sub>2</sub> )	40	Visible light	99.8% (200 min)	12
NTU-9	0.5 (5 drops of 30% H <sub>2</sub> O <sub>2</sub> )	31.9	Visible light	100% (20 min)	13
MIL-53(Fe)	1.0 ((NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> )	127.6	Visible light	~40% (60 min)	14
ZnTCPc/UIO-66(NH <sub>2</sub> )	0.2	15	Visible light	~90% (120 min)	15
Cu(dm-bim)	30 (5 drops of 30% H <sub>2</sub> O <sub>2</sub> )	18.7	Visible light	96% (20 min)	16
[Cu <sup>II</sup> (salimcy)](Cu <sup>II</sup> ) <sub>2</sub>	0.6	12	Visible light	96% (20 min)	17
Fe <sub>3</sub> O <sub>4</sub> /FePc	1.0 (1 mL 9M H <sub>2</sub> O <sub>2</sub> )	10	Visible light	78% (120 min)	18
mesoporous BiVO <sub>4</sub>	1.0	10	Visible light	85% (180 min)	19
VC 1.0%	0.5	10	Visible light	~90% (120 min)	20
Fe-Ni/SiO <sub>2</sub>	0.85 (3mM)	30	Visible light	94.9%	21

				(60 min)	
	H <sub>2</sub> O <sub>2</sub> , pH=3.0)	20	Visible light	99.0% (60 min)	
		20	Solar light	99.8% (60 min)	
CuO/NX	0.1 (PH = 11)	5	Solar light	90% (160 min)	22
g-C <sub>3</sub> N <sub>4</sub> /Co <sub>3</sub> O <sub>4</sub>	0.5	3.19	Solar light	100% (90 min)	23

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