# Synthesis, structure and photocatalytic properties of coordination polymers based on pyrazole carboxylic acid ligand

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**Supporting Information**

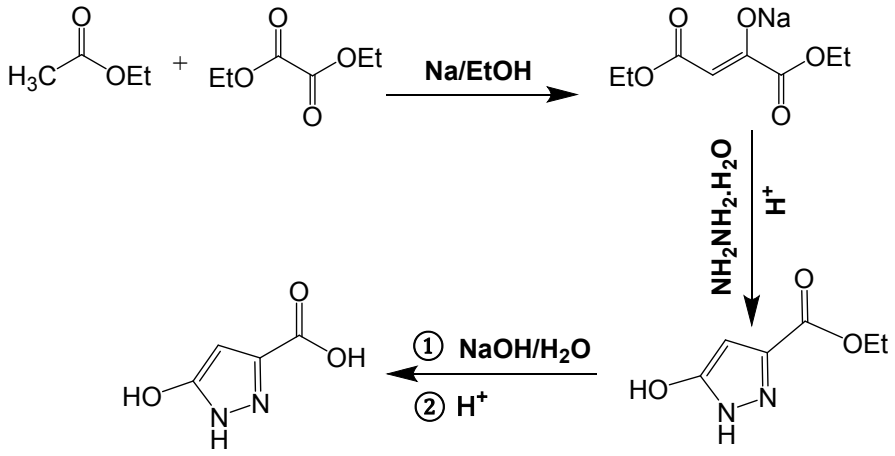
**Section S1** Preparation of 5-hydroxy-1H-pyrazole-3-carboxylic acid ($hpcH_3$) and LC-MS Analysis.

Diethyl oxalate (0.1 mol 14.61 g) and ethyl acetate (0.1 mol 8.81 g) were dropwise added in sodium ethoxide (19.5%, 42 ml) and stirred for 4 h in ice bath. The solution was then heated at 75 °C for 0.5 h and cooled to room temperature. After washing several times with ethanol and vacuum drying for 12 h, sodium-1,4-diethoxy-1,4-dioxobut-2-en-2-olate was obtained. Yield: 16.2 g (77.1%).

A stirred mixture of sodium-1,4-diethoxy-1,4-dioxobut-2-en-2-olate (0.07 mol, 14.7 g) and hydrazine hydrate (80%, 0.08 mol, 5.00 g) in 60 ml of deionized water and then concentrated HCl was added until pH 5~6. The reaction mixture was heated at 65 °C for 2 h. The resulting red brown solution stands in a refrigerator for 12 h. The yellow solid ethyl 5-hydroxy-1H-pyrazole-3-carboxylate was separated by filtering. Yield: 3.85 g (35.3%).

Ethyl 5-hydroxy-1H-pyrazole-3-carboxylate (3.8 mol, 0.6 g) was dissolved in a solution of 1M NaOH (15 mL) and heated at 100 °C for 1 h. The resulting solution was allowed to cool to room temperature. The yellow powder 5-hydroxy-1H-pyrazole-3-carboxylic acid ($hpcH_3$) was precipitated by dropwise addition of concentrated HCl (pH 2~3). Yield: 0.33 g (67.9%). m. p.: 258-260.3°C. $^1$H-NMR (300 MHz, DMSO-$d_6$, ppm): δ 12.79 (s, H); 5.88 (s, H); 10.03 (s, H). ESI–MS: m/z 127.0 ([M-H]). IR (KBr, $cm^{-1}$): 3249 (m), 3139 (w), 1693 (s), 1587 (m), 1506 (m), 1446 (m), 1224 (m), 1001 (m), 768 (m), 487 (m).

HPLC/MS experiments were carried out with HPLC 1260 liquid chromatograph (Agilent, USA) coupled to the Agilent 6460 triple quadrupole mass spectrometer. It was carried out using a two-way valve instead of a column. Eluent A was in water and eluent B was methanol (MeOH), and the mobile phase was delivered at a flow rate of 0.3 mL/min with a ratio of 90% MeOH; the injection volume was 2 µL. Mass spectra (in negative ionization mode) were acquired in total ion current (TIC) in the mass range 30−800 m/z, in Scan mode. The ESI parameters were set as the following: Fragmentor was 80 V; capillary voltage was 3.5 kV, source temperature was 350 °C; the gas ($N_2$) flow rate was 11 $L{\cdot}min^{-1}$, and nebulizer was 45 psi.




**Scheme S1** synthesis route of $hpcH_3$ ligand .

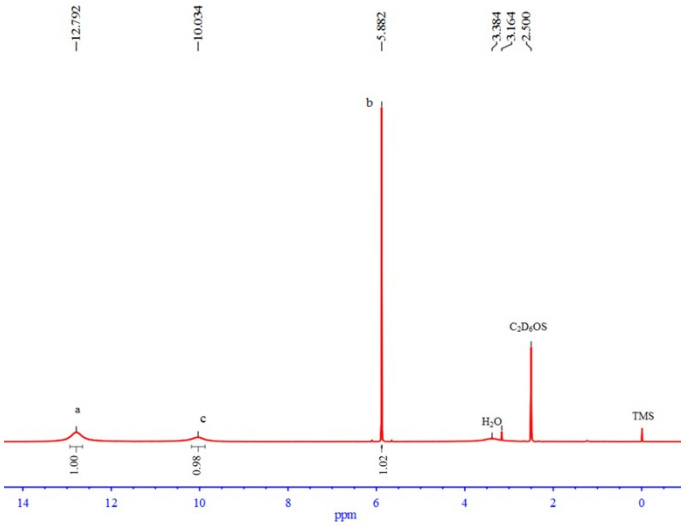



**Fig. S1** The $^{1}$H-NMR spectrum of $hpcH_3$.

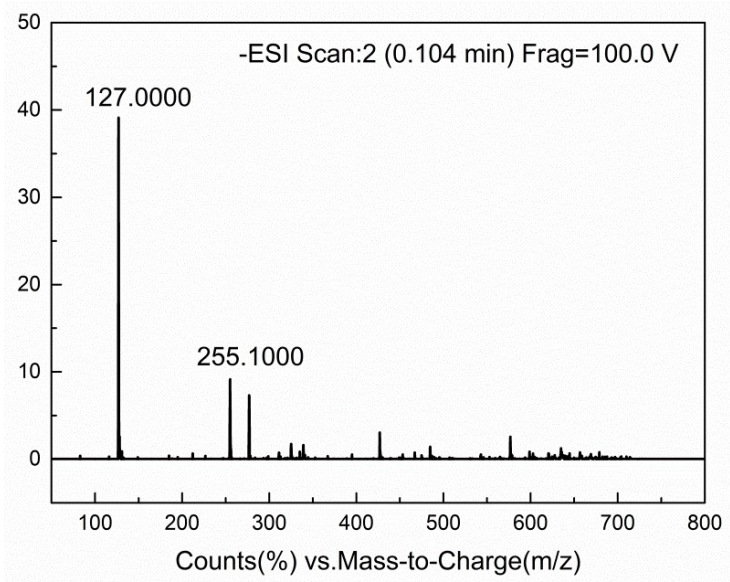



**Fig. S2** The MS spectrum of $hpcH_3$.(ESI, negative)

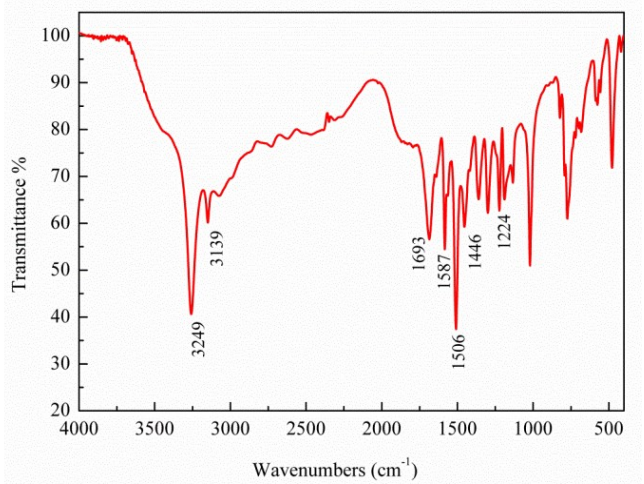



**Fig. S3** The FT-IR spectrum of $hpcH_3$.

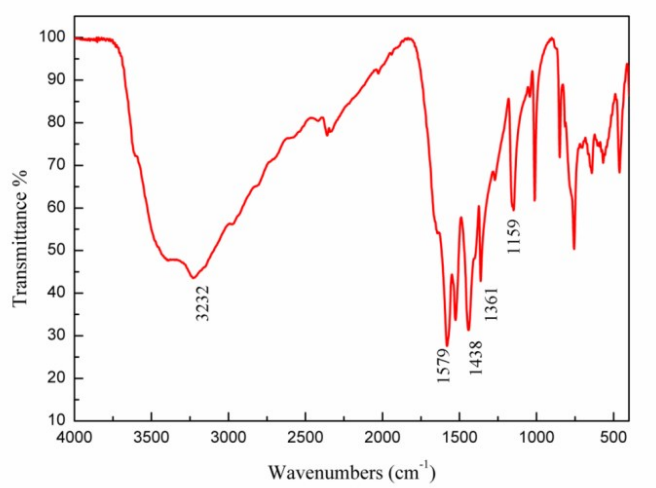



**Fig. S4** The FT-IR spectrum of compound **1**.

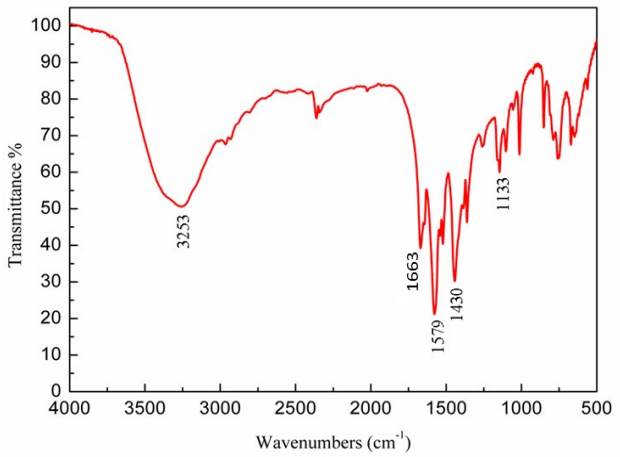



**Fig. S5** The FT-IR spectrum of compound **2**.

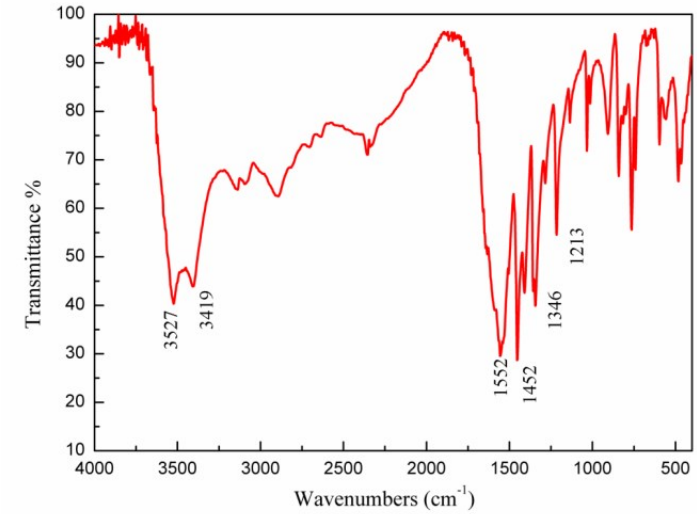



**Fig. S6** The FT-IR spectrum of compound **3**.

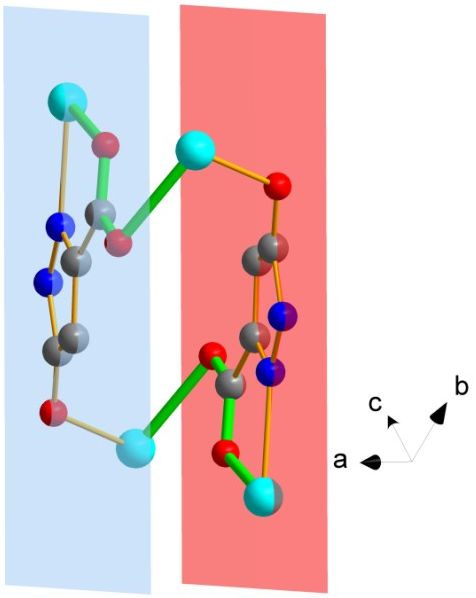



**Fig. S7** The tetrameric unit of **1**.

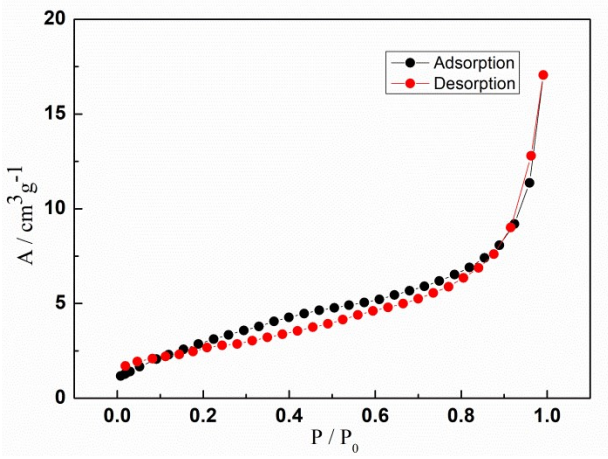



**Fig.S8** $N_2$ adsorption/desorption isotherm of **1** at 77 K.

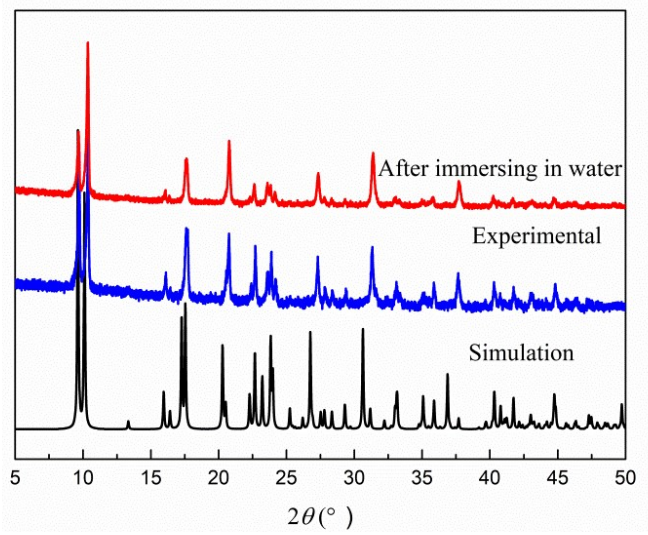



**Fig. S9** The PXRD spectra of compound **1**.

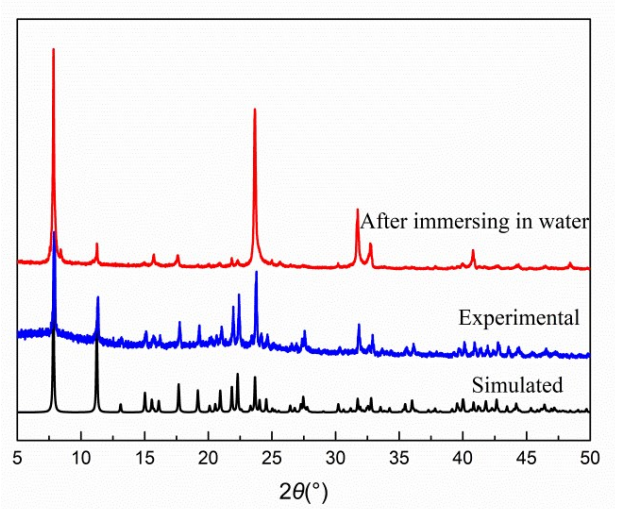



**Fig. S10** The PXRD spectra of compound **2**.

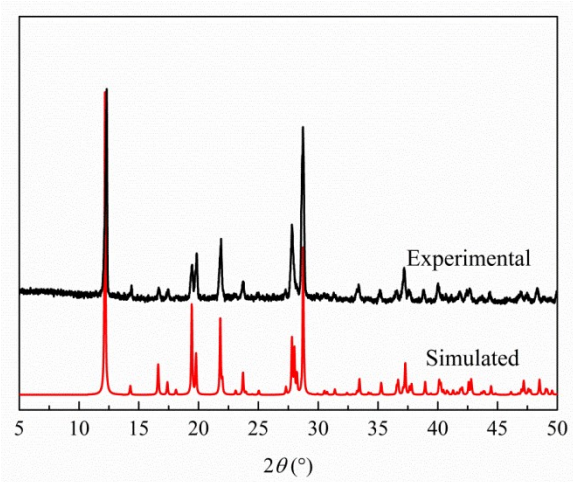



**Fig. S11** The PXRD spectra of compound **3**.

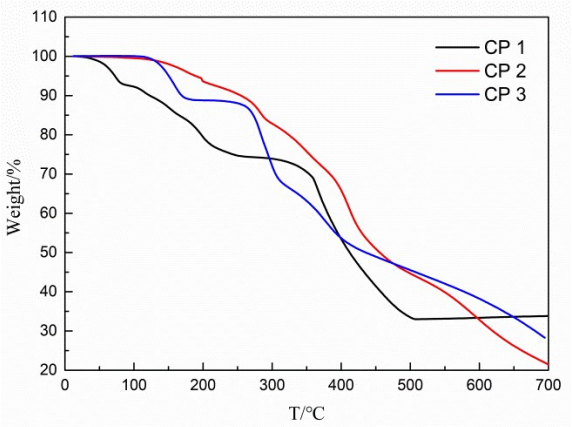



**Fig. S12** Thermal gravimetric analysis curves.

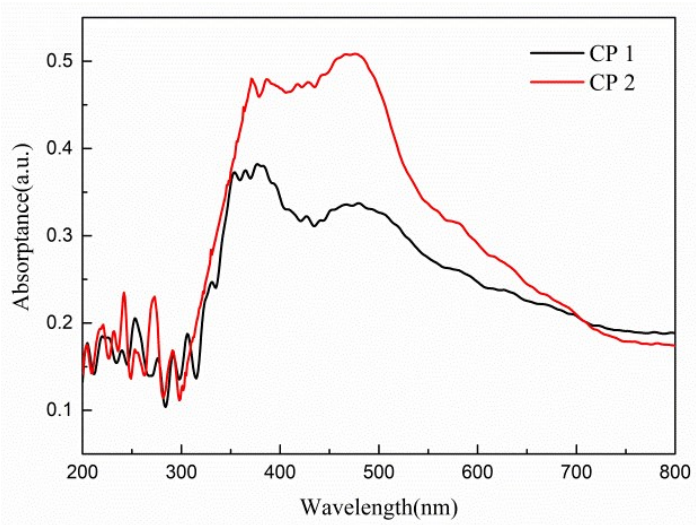



**Fig. S13** The solid state UV/vis absorption spectra of compounds **1** and **2**.

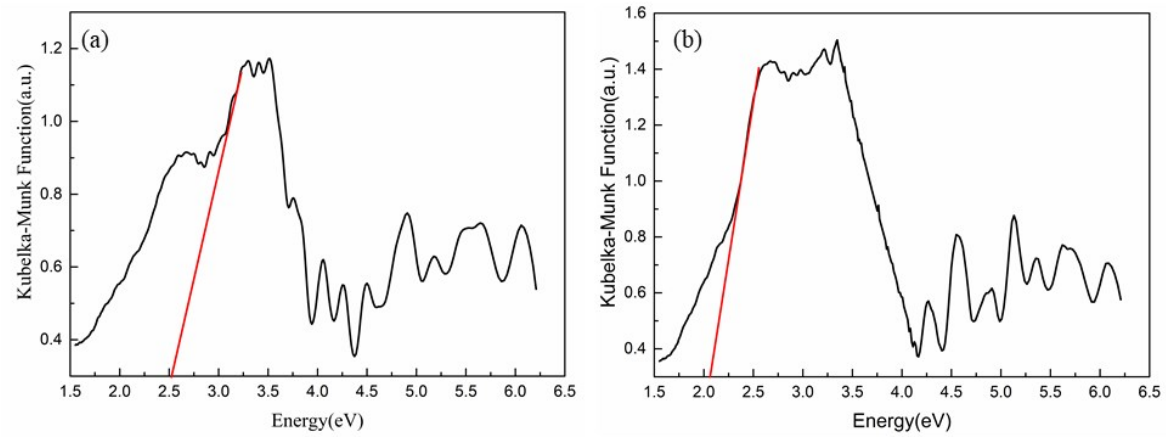



**Fig.S14** Kubelka-Munk-transformed diffuse reflectance spectrum of compounds **1**(a) and **2**(b).

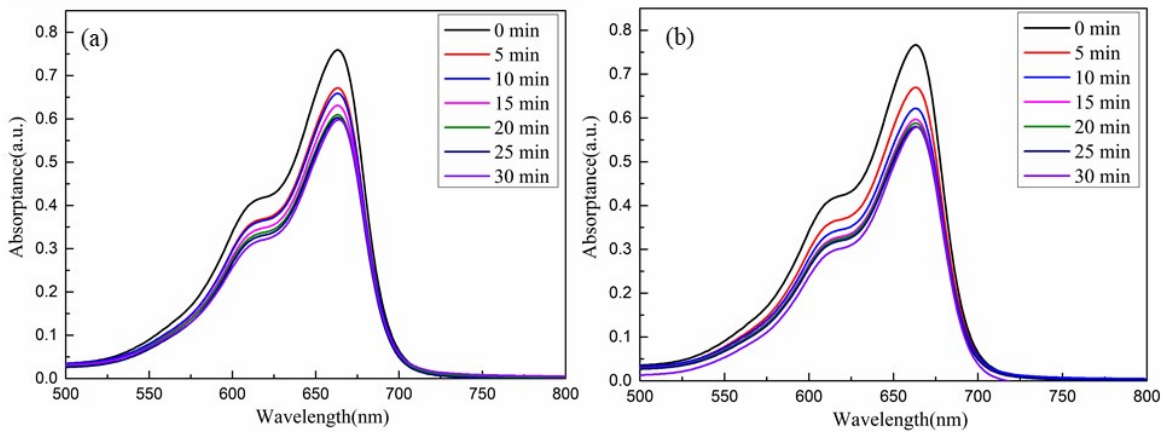



**Fig.15** Absorption spectra of the MB solution in the presence of compounds **1** (a) and **2**(b).

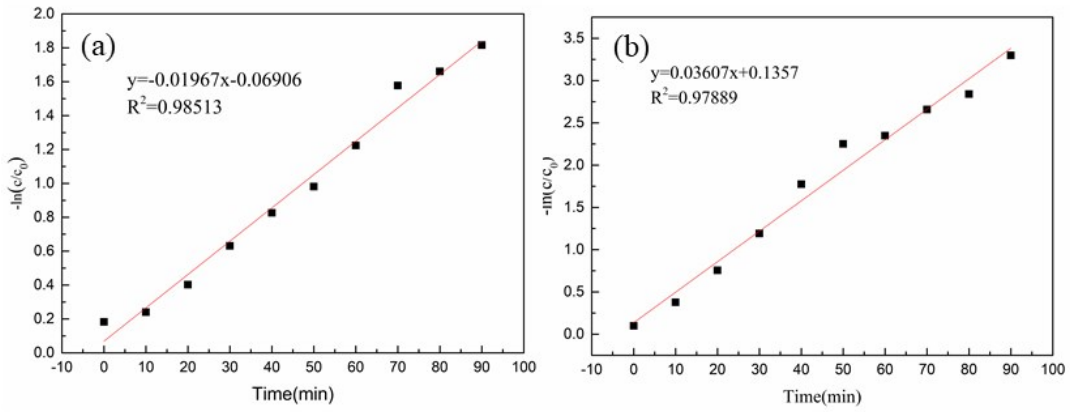



**Fig. S16** The degradation rate constants of MB in the presence of compounds **1** (a) and **2**(b).

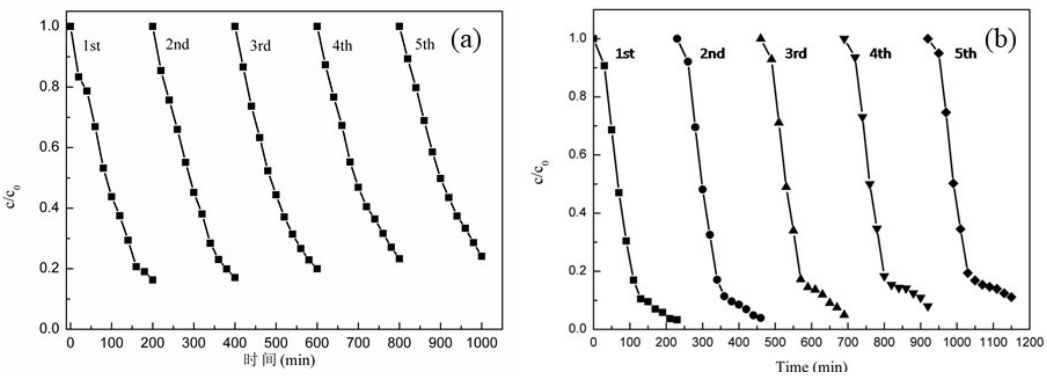



**Fig. S17** Cycling runs of the photocatalytic degradation of MB for compounds **1**(a) and **2** (b).

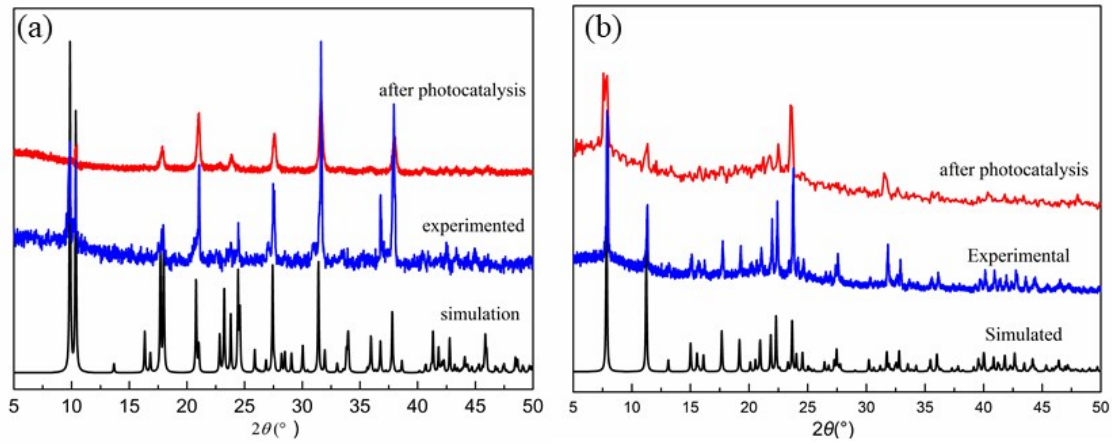



**Fig. S18** The PXRD of recycled compounds **1**(a) and **2** (b).

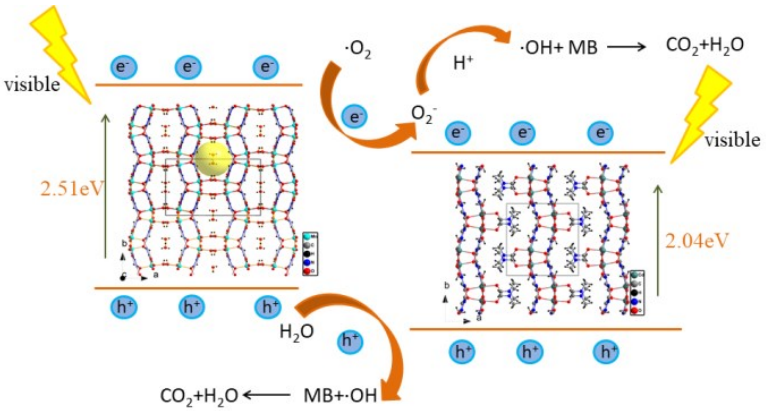



**Fig. S19** Schematic diagram of possible photocatalytic mechanisms.

**Table S1** Selected bond lengths and angles (Å/º) for **1**

| Compound | | [Mn(hpcH)($H_2O$)$_2$]·2$H_2O$ | |
|---|---|---|---|
| Mn1-O1 | 2.234(3) | O4-Mn1-N1 | 95.29(13) |
| Mn1-O1A | 2.641(2) | O2A-Mn1-O4 | 87.63(14) |
| Mn1-O4 | 2.214(3) | N1-Mn1-O1A | 160.74(9) |
| Mn1-O5 | 2.203(2) | O1A-Mn-O3C | 84.91(9) |
| Mn1-N1 | 2.263(3) | O3C-Mn1-O4 | 170.01(11) |
| Mn1-O2A | 2.309(2) | O5-Mn1-N1 | 86.19(10) |
| Mn1-O3C | 2.161(3) | O2A-Mn1-O5 | 126.92(9) |
| O1-Mn1-O4 | 88.48(12) | O3C-Mn1-O5 | 90.81(10) |
| O1-Mn1-O5 | 156.96(9) | O2A-Mn1-N1 | 146.86(10) |
| O1-Mn1-N1 | 72.83(9) | O4-Mn1-O1A | 85.49(12) |
| O1-Mn1-O2A | 74.26(9) | O3C-Mn1-N1 | 92.87 (10) |
| O1-Mn1-O3C | 99.44(10) | O2A-Mn1-O3C | 88.67(10) |
| O1-Mn1-O1A | 126.42(8) | O5-Mn1-O1A | 74.74(8) |
| O4-Mn1-O5 | 84.02(12) | O1A-Mn-O2A | 52.35(8) |

**Table S2** Selected bond lengths and angles (Å/º) for **2**

| Compound | | [Cd(hpcH)(DMF)($H_2O$)] | |
|---|---|---|---|
| Cd1-O1A | 2.3763(15) | O4-Cd1-O1A | 83.58(7) |
| Cd1-O2C | 2.4118(15) | N2A-Cd1-O1A | 70.45(5) |
| Cd1-O3 | 2.3019(15) | O5-Cd1-O2C | 129.83(5) |
| Cd1-O4 | 2.327(2) | O1C-Cd1-O2C | 52.47(5) |
| Cd1-O5 | 2.2750(15) | O3-Cd1-O4 | 173.11(6) |
| Cd1-N2A | 2.3338(16) | O3-Cd1-O2C | 86.69(5) |
| Cd1-O1C | 2.5456(15) | O4-Cd1-O2C | 86.42(6) |
| O5-Cd1-O3 | 94.77(6) | N2A-Cd1-O2C | 144.33(5) |
| O5-Cd1-O4 | 89.49(7) | O1A-Cd1-O2C | 74.18(5) |
| O5-Cd1-N2A | 85.83(5) | O5-Cd1-O1C | 77.87(5) |
| O3-Cd1-N2A | 91.70(5) | O3-Cd1-O1C | 83.05(5) |
| O4-Cd1-N2A | 94.01(7) | O4-Cd1-O1C | 92.59(7) |
| O5-Cd1-O1A | 154.65(5) | N2A-Cd1-O1C | 162.35(5) |
| O3-Cd1-O1A | 94.73(5) | O1A-Cd1-O1C | 126.65(5) |

**Table S3** Selected bond lengths and angles (Å/º) for **3**

| Complex | | $[Cu(hpcH_2)_2(H_2O)_2]$ | |
|---|---|---|---|
| Cu1-O1 | 1.978(2) | O1 -Cu1 –O1A | 180.00 |
| Cu1-O1A | 1.978(2) | O1 -Cu1 –N1A | 98.24(8) |
| Cu1-O4 | 2.559(2) | O1 -Cu1 –O4 | 90.90(7) |
| Cu1-O4A | 2.559(2) | O1 -Cu1 –O4A | 89.10(7) |
| Cu1-N1 | 1.951(2) | O4 -Cu1 –O4A | 180.00 |
| Cu1-N1A | 1.951(2) | O4 -Cu1 –N1A | 90.37(7) |
| N1-Cu1- N1A | 180.00 | O4 -Cu1 –O1A | 89.10(7) |
| N1-Cu1- O1 | 81.76(8) | O4A -Cu1 –N1A | 89.63(7) |
| N1-Cu1- O1A | 98.24(8) | O4A-Cu1 –O1A | 90.90(7) |
| N1-Cu1- O4 | 89.63(7) | O1A-Cu1 –N1A | 81.76(8) |
| N1-Cu1- O4A | 90.37(7) | | |

**Table S4** Hydrogen bonds for **1** lengths [Å] and angles [°].

| *D-H···A* | *D-H* | *H···A* | *D···A* | *D-H···A* |
|---|---|---|---|---|
| O4 –H4C···O4 | 0.85 | 2.58 | 2.862(5) | 101 |
| O4–H4A···O2 | 0.82 | 2.30 | 2.886(5) | 129 |
| O5–H5A···O2 | 0.82 | 2.00 | 2.812(3) | 171 |
| O5–H5A···O1 | 0.82 | 2.52 | 2.960(3) | 115 |
| O5–H5B···O3 | 0.88 | 1.91 | 2.743(3) | 159 |
| N2–H2···O3 | 0.96 | 2.06 | 3.000(4) | 167 |

**Table S5** Hydrogen bonds for **3** lengths [Å] and angles [°].

| *D-H···A* | *D-H* | *H···A* | *D···A* | *D-H···A* |
|---|---|---|---|---|
| N2–H2···O4 | 0.88 | 1.99 | 2.830(3) | 157 |
| O4–H4A···O3 | 0.87 | 2.11 | 2.966(4) | 135 |
| O4–H4B···O2 | 0.83 | 1.98 | 2.697(3) | 143 |
| O3–H3A···O2 | 0.82 | 1.79 | 2.592(3) | 167 |