Electronic Supplementary Information (ESI)

Hydrothermal generation, structural versatility and properties of metal(II)-organic architectures driven by a pyridine-tricarboxylic acid

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*†Electronic Supplementary Information (ESI) available: synthesis and analytical data for **2**−**12**, structural parameters (Tables S1 and S2), additional structural representations (Figs. S1–S5), coordination modes of H_2cpia^-, $Hcpia^{2-}$, or $cpia^{3-}$ in other compounds (Scheme S1), emission data (Table S3), PXRD patterns (Fig. S6 and S13), diffuse reflectance spectra (Fig. S7), absorption spectra of the MB solutions in catalytic tests including kinetic data (Figs. S8–S11), and catalyst recycling experiments (Fig. S12). CCDC-1876103–1876114.*

Synthesis and analytical data for 2–12

Synthesis of [M(Hcpia)(phen)(H_2O)$_2$] (M = Co, 2; Ni, 3; Zn, 4). A mixture of $MCl_2 \cdot xH_2O$ (x = 6 for **2**; x = 6 for **3** and x = 0 for **4**, 0.2 mmol), H_3cpia (57.4 mg, 0.2 mmol), phen (40.0 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 120 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Crystals of **2**–**4** were isolated manually, and washed with distilled water. Yield: 65% for **2**, 50% for **3**, 55% for **4** (based on H_3cpia). Anal. Calcd for $C_{26}H_{19}CoN_3O_8$ (**2**): C 55.73, H 3.42, N 7.50%. Found: C 55.61, H 3.40, N 7.53%. IR (KBr, cm^{-1}): 3335 w, 3049 w, 1691 m, 1592 s, 1516 w, 1475 w, 1428 w, 1376 m, 1352 w, 1271 m, 1230 w, 1137 w, 1097 w, 1038 w, 1009 w, 921 w, 875 w, 846 m, 787 w, 723 m, 699 w, 682 w, 664 w, 636w. Calcd for $C_{26}H_{19}NiN_3O_8$ (**3**): C 55.75, H 3.42, N 7.50%. Found: C 55.63, H 3.41, N 7.55%. IR (KBr, cm^{-1}): 3324 w, 3061 w, 1685 m, 1586 s, 1516 w, 1487 w, 1428 w, 1399 m, 1376 w, 1352 w, 1271 m, 1236 w, 1137 w, 1091 w, 1038 w, 1009 w, 927 w, 852 m, 793 w, 776 w, 723 m, 700 w, 676 w, 648 w. Calcd for $C_{26}H_{19}ZnN_3O_8$ (**4**): C 55.09, H 3.38, N 7.41%. Found: C 55.21, H 3.36, N 7.45%. IR (KBr, cm^{-1}): 3405 w, 3160 w, 1685 m, 1586 s, 1516 w, 1487 w, 1428 w, 1394 s, 1358 w, 1277 m, 1230 w, 1142 w, 1097 w, 1038 w, 1009 w, 921 w, 875 w, 846 m, 811 w, 770 w, 723 m, 705 w, 682 w, 642 w.

Synthesis of [Zn(Hcpia)(2,2′-bipy)(H_2O)$_2$]$_5$·4H_2O (5). A mixture of $ZnCl_2$ (27.3 mg, 0.20 mmol), H_3cpia (57.4 mg, 0.20 mmol), 2,2′-bipy (31.2 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 120 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Colourless block-shaped crystals of **5** were isolated manually, washed with distilled water and dried (yield 55% based on H_3cpia). Anal. Calcd for $C_{120}H_{103}Zn_5N_{15}O_{44}$: C, 51.73; H, 3.73; N, 7.54. Found: C, 51.59; H, 3.75; N, 7.57%. IR (KBr, cm^{-1}): 3434 w, 3112 w, 1714 m, 1602 m, 1546 m, 1474 w, 1434 w, 1413 s, 1388 w, 1337 m, 1311 w, 1275 w, 1235 m, 1153 w, 1117 w, 1097 w, 1046 w, 1016 w, 934 w, 912 w, 882 w, 837 w, 806 w, 776 m, 730 w, 694 w, 654 w.

Synthesis of [Zn_2(μ-Hcpia)$_2$(2,2′-bipy)$_2$] (6). Synthesis of **6** was similar to **5** except using 160 °C

instead of 120 °C. Colorless block-shaped crystals of **6** were isolated manually, washed with distilled water and dried (yield 61% based on H_3cpia). Anal. Calcd for $C_{24}H_{15}ZnN_3O_6$: C, 56.88; H, 2.98; N, 8.29. Found: C, 56.71; H, 3.00; N, 8.34%. IR (KBr, cm^{-1}): 1711 w, 1655 s, 1599 s, 1565 m, 1470 w, 1437 w, 1386 w, 1342 m, 1276 w, 1231 m, 1153 w, 1114 w, 1097 w, 1041 w, 1013 w, 963 w, 914 w, 886 w, 830 w, 806 w, 763 m, 728 w, 695 w, 657 w.

Synthesis of [M(μ-Hcpia)(phen)(H_2O)]$_n$ (M = Co, 7; Cd, 8). A mixture of $CoCl_2·6H_2O$ /$CdCl_2·H_2O$ (0.20 mmol), H_3cpia (57.4 mg, 0.20 mmol), phen (40.0 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Pink (**7**) or colorless (**8**) block-shaped crystals of **7** and **8** were isolated manually, washed with distilled water and dried (yield 60% for **7**; 55% for **8** based on H_3cpia). Anal. Calcd for $C_{26}H_{17}CoN_3O_7$ (**7**): C, 57.58; H, 3.16; N, 7.75. Found: C, 57.41; H, 3.13; N, 7.70%. IR for **7** (KBr, cm^{-1}): 3434 w, 3189 w, 1644 s, 1597 s, 1540 w, 1510 w, 1428 w, 1388 s, 1341 w, 1230 w, 1160 w, 1142 w, 1038 w, 1021 w, 944 w, 858 m, 840 w, 811 w, 787 w, 729 w, 711 w, 670 w. Anal. Calcd for $C_{26}H_{17}CdN_3O_7$ (**8**): C, 52.41; H, 2.88; N, 7.05. Found: C, 52.57; H, 2.89; N, 7.09%. IR for **8** (KBr, cm^{-1}): 3434 w, 3331 w, 3127 w, 1694 w, 1607 m, 1592 w, 1541 w, 1449 w, 1383 s, 1296 w, 1240 w, 1158 w, 1082 w, 1041 w, 1010 w, 898 w, 842 m, 776 w, 724 w, 684 w, 659 w.

Synthesis of {[Pb(μ-Hcpia)]·2H_2O}$_n$ (9). A mixture of $PbCl_2$ (55.6 mg, 0.20 mmol), H_3cpia (57.4 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Colourless block-shaped crystals of **9** were isolated manually, washed with distilled water and dried (yield 58% based on H_3cpia). Anal. Calcd for $C_{14}H_{11}PbNO_8$: C, 31.82; H, 2.10; N, 2.65. Found: C, 31.71; H, 2.12; N, 2.62%. IR (KBr, cm^{-1}): 3440 w, 1674 w, 1586 m, 1568 m, 1540 s, 1499 w, 1376 s, 1301 w, 1242 w, 1160 w, 1131 w, 1068 w, 1038 w, 1009 w, 933 w, 875 w, 846 w, 816 m, 787 w, 770 w, 688 w, 658 w.

Synthesis of {[Cd_4(μ$_3$-cpia)$_2$$Cl_2$(phen)$_6$($H_2O$)$_2$]·10$H_2O$}$_n$ (10). A mixture of $CdCl_2·H_2O$ (60.3 mg,

0.30 mmol), H_3cpia (57.4 mg, 0.20 mmol), phen (60.0 mg, 0.30 mmol), NaOH (24.0 mg, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Colourless block-shaped crystals of **10** were isolated manually, washed with distilled water and dried (yield 41% based on H_3cpia). Anal. Calcd for $C_{100}H_{84}Cl_2Cd_4N_{14}O_{24}$: C, 50.33; H, 3.55; N, 8.22. Found: C, 50.48; H, 3.53; N, 8.27%. IR (KBr, cm^{-1}): 3440 w, 3061 w, 1609 m, 1592 s, 1552 s, 1422 m, 1394 m, 1358 w, 1306 w, 1248 w, 1166 w, 1131 w, 1097 w, 1044 w, 1015 w, 921 w, 846 w, 822 w, 770 w, 729 w, 706 w, 670 w.

Synthesis of $\{[Zn_3(\mu_3\text{-cpia})_2(phen)_3]\cdot 10H_2O\}_n$ (11). A mixture of $ZnCl_2$ (40.9 mg, 0.3 mmol), H_3cpia (57.4 mg, 0.20 mmol), phen (60.0 mg, 0.30 mmol), NaOH (24.0 mg, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Colourless block-shaped crystals of **11** were isolated manually, washed with distilled water and dried (yield 55% based on H_3cpia). Anal. Calcd for $C_{64}H_{56}Zn_3N_8O_{22}$: C, 51.75; H, 3.80; N, 7.54. Found: C, 51.65; H, 3.77; N, 7.59%. IR (KBr, cm^{-1}): 3438 m, 3331 w, 3056 w, 1638 m, 1607 s, 1561 w, 1515 w, 1449 w, 1429 m, 1368 s, 1250 w, 1168 w, 1138 w, 1102 w, 1046 w, 1016 w, 924 w, 842 m, 786 w, 724 m, 669 w.

Synthesis of $\{[Zn_4(\mu_4\text{-cpia})_2(\mu\text{-OH})_2(\mu\text{-4,4′-bipy})_2]\cdot 4,4′\text{-bipy}\cdot 2H_2O\}_n$ (12). A mixture of $ZnCl_2$ (40.9 mg, 0.3 mmol), H_3cpia (57.4 mg, 0.20 mmol), 4,4′-bipy (46.8 mg, 0.30 mmol), NaOH (28.0 mg, 0.70 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Colourless block-shaped crystals of **12** were isolated manually, washed with distilled water and dried (yield 52% based on H_3cpia). Anal. Calcd for $C_{58}H_{42}Zn_4N_8O_{16}$: C, 50.90; H, 3.09; N, 8.19. Found: C, 51.05; H, 3.07; N, 8.25%. IR (KBr, cm^{-1}): 3487 w, 3044 w, 1633 s, 1609 s, 1574 w, 1540 w, 1487 w, 1423 w, 1393 w, 1364 s, 1260 w, 1225 w, 1160 w, 1131 w, 1073 w, 1044 w, 1009 w, 875 w, 851 w, 817 m, 776 w, 717 w, 676 w, 642 w.

Table S1. Selected bond lengths [Å] and angles [°] for compounds **1**–**12**.[a]

1					
Mn(1)-O(2)	2.149(2)	Mn(1)-O(2)#1	2.149(2)	Mn(1)-O(7)	2.154(2)
Mn(1)-O(7)#1	2.154(2)	Mn(1)-N(1)	2.262(3)	Mn(1)-N(1)#1	2.262(3)
O(2)-Mn(1)-O(2)#1	170.66(13)	O(2)#1-Mn(1)-O(7)	93.96(9)	O(2)-Mn(1)-O(7)	92.79(9)
O(7)-Mn(1)-O(7)#1	87.36(15)	O(2)-Mn(1)-N(1)	74.75(8)	O(2)-Mn(1)-N(1)#1	98.94(9)
O(7)-Mn(1)-N(1)#1	88.97(10)	O(7)-Mn(1)-N(1)	166.74(9)	N(1)-Mn(1)-N(1)#1	97.32(13)
2					
Co(1)-O(2)	2.108(2)	Co(1)-O(7)	2.158(2)	Co(1)-O(8)	2.065(2)
Co(1)-N(1)	2.134(2)	Co(1)-N(2)	2.155(2)	Co(1)-N(3)	2.102(2)
O(8)-Co(1)-N(3)	98.40(8)	O(8)-Co(1)-O(2)	172.71(8)	N(3)-Co(1)-O(2)	86.68(8)
O(8)-Co(1)-N(1)	98.11(8)	N(3)-Co(1)-N(1)	162.66(8)	O(2)-Co(1)-N(1)	77.39(7)
O(8)-Co(1)-N(2)	86.17(8)	N(3)-Co(1)-N(2)	77.77(9)	O(2)-Co(1)-N(2)	100.08(8)
N(1)-Co(1)-N(2)	98.11(8)	O(8)-Co(1)-O(7)	87.18(7)	N(3)-Co(1)-O(7)	91.16(8)
O(2)-Co(1)-O(7)	N(3)-Co(1)-O(7)	N(1)-Co(1)-O(7)	94.91(8)	N(2)-Co(1)-O(7)	166.10(8)
3					
Ni(1)-O(2)	2.067(2)	Ni(1)-O(7)	2.114(2)	Ni(1)-O(8)	2.060 (2)
Ni(1)-N(1)	2.085(2)	Ni(1)-N(2)	2.067(2)	Ni(1)-N(3)	2.099(2)
O(8)-Ni(1)-O(2)	172.98(7)	O(8)-Ni(1)-N(2)	98.41(8)	O(2)-Ni(1)-N(2)	86.97(7)
O(8)-Ni(1)-N(1)	95.74(7)	O(2)-Ni(1)-N(1)	79.25(7)	N(2)-Ni(1)-N(1)	165.31(8)
O(8)-Ni(1)-N(3)	86.11(8)	O(2)-Ni(1)-N(3)	99.36(8)	N(2)-Ni(1)-N(3)	79.58(8)
N(1)-Ni(1)-N(3)	97.54(8)	O(8)-Ni(1)-O(7)	87.40(7)	O(2)-Ni(1)-O(7)	88.09(7)
N(2)-Ni(1)-O(7)	90.07(8)	N(1)-Ni(1)-O(7)	94.49(7)	N(3)-Ni(1)-O(7)	166.84(7)
4					
Zn(1)-O(2)	2.147(2)	Zn(1)-O(7)	2.169(2)	Zn(1)-O(8)	2.082(2)
Zn(1)-N(1)	2.125(2)	Zn(1)-N(2)	2.120(2)	Zn(1)-N(3)	2.188(2)
O(8)-Zn(1)-N(2)	99.77(9)	O(8)-Zn(1)-N(1)	97.46(8)	N(2)-Zn(1)-N(1)	161.83(9)
O(8)-Zn(1)-O(2)	70.96(8)	N(2)-Zn(1)-O(2)	86.40(8)	N(1)-Zn(1)-O(2)	77.20(8)
O(8)-Zn(1)-O(7)	86.45(8)	N(2)-Zn(1)-O(7)	90.21(9)	N(1)-Zn(1)-O(7)	96.60(8)
O(2)-Zn(1)-O(7)	86.93(8)	O(8)-Zn(1)-N(3)	86.74(9)	N(2)-Zn(1)-N(3)	77.11(9)
N(1)-Zn(1)-N(3)	98.22(9)	O(2)-Zn(1)-N(3)	101.15(9)	O(7)-Zn(1)-N(3)	164.37(8)
5					
Zn(1)-O(1)	2.137(5)	Zn(1)-O(7)	2.145(5)	Zn(1)-O(8)	2.094(5)
Zn(1)-N(1)	2.116(6)	Zn(1)-N(2)	2.077(7)	Zn(1)-N(3)	2.135(8)
O(8)-Zn(1)-N(2)	98.7(3)	N(2)-Zn(1)-N(1)	160.0(3)	O(8)-Zn(1)-N(1)	100.2(2)
N(3)-Zn(1)-N(2)	77.4(3)	N(3)-Zn(1)-O(8)	86.4(2)	N(1)-Zn(1)-N(3)	97.8(3)
N(2)-Zn(1)-O(1)	85.0(3)	O(1)-Zn(1)-O(8)	173.9(2)	N(1)-Zn(1)-O(1)	76.7(2)
N(3)-Zn(1)-O(1)	99.3(2)	O(7)-Zn(1)-N(2)	90.9(3)	O(8)-Zn(1)-O(7)	87.5(2)
N(1)-Zn(1)-O(7)	96.0(2)	O(7)-Zn(1)-N(3)	165.7(3)	O(7)-Zn(1)-O(1)	87.5(2)
6					
Zn(1)-O(2)	2.085(3)	Zn(1)-O(3)#1	2.558(3)	Zn(1)-O(4)#1	2.018(3)
Zn(1)-N(1)	2.130(3)	Zn(1)-N(2)	2.091(3)	Zn(1)-N(3)	2.143(3)
O(4)#1-Zn(1)-N(2)	151.81(13)	N(2)-Zn(1)-N(1)	103.27(12)	O(4)#1-Zn(1)-N(1)	102.94(12)
N(3)-Zn(1)-N(2)	76.99(13)	N(3)-Zn(1)-O(4)#1	90.90(12)	N(1)-Zn(1)-N(3)	94.24(13)
N(2)-Zn(1)-O(2)	99.44(12)	O(2)-Zn(1)-O(4)#1	95.77(11)	N(1)-Zn(1)-O(2)	78.50(11)
N(3)-Zn(1)-O(2)	171.06(12)	O(3)#1-Zn(1)-N(2)	100.65(11)	O(4)#1-Zn(1)-O(3)#1	55.91(12)
N(1)-Zn(1)-O(3)#1	154.44(13)	O(3)#1-Zn(1)-N(3)	99.83(12)	O(3)#1-Zn(1)-O(2)	88.83(11)
7					
Co(1)-O(2)	2.086(2)	Co(1)-O(5)#1	2.037(2)	Co(1)-O(7)	2.060(2)

Co(1)-N(1)	2.160(2)	Co(1)-N(2)	2.161(3)	Co(1)-N(3)	2.167(3)
O(5)#1-Co(1)-O(7)	90.62(9)	O(5)#1-Co(1)-O(2)	102.98(8)	O(2)-Co(1)-O(7)	93.37(8)
O(5)#1-Co(1)-N(1)	86.62(9)	O(7)-Co(1)-N(1)	169.87(8)	O(2)-Co(1)-N(1)	77.79(8)
O(5)#1-Co(1)-N(2)	91.21(9)	O(7)-Co(1)-N(2)	101.38(8)	O(2)-Co(1)-N(2)	159.43(9)
N(1)-Co(1)-N(2)	88.43(9)	O(5)#1-Co(1)-N(3)	167.47(10)	O(7)-Co(1)-N(3)	90.91(9)
O(2)-Co(1)-N(3)	89.35(9)	N(1)-Co(1)-N(3)	93.89(10)	N(2)-Co(1)-N(3)	76.30(10)
8					
Cd(1)-O(1)	2.201(2)	Cd(1)-O(6)#1	2.310(2)	Cd(1)-O(7)	2.244(2)
Cd(1)-N(1)#1	2.379(3)	Cd(1)-N(2)	2.381(3)	Cd(1)-N(3)	2.347(3)
O(1)-Cd(1)-O(7)	91.28(9)	O(1)-Cd(1)-O(6)#1	107.10(9)	O(7)-Cd(1)-O(6)#1	90.62(8)
O(1)-Cd(1)-N(3)	161.41(10)	O(7)-Cd(1)-N(3)	89.86(9)	O(6)#1-Cd(1)-N(3)	91.43(10)
O(1)-Cd(1)-N(1)#1	89.67(10)	O(7)-Cd(1)-N(1)#1	161.55(9)	O(6)#1-Cd(1)-N(1)#1	71.52(9)
N(3)-Cd(1)-N(1)#1	95.07(10)	O(1)-Cd(1)-N(2)	91.22(10)	O(7)-Cd(1)-N(2)	111.39(9)
O(6)#1-Cd(1)-N(2)	151.25(9)	N(3)-Cd(1)-N(2)	71.14(10)	N(2)-Cd(1)-N(1)#1	87.01(9)
9					
Pb(1)-O(1)	2.370(4)	Pb(1)-O(1)#2	2.758(5)	Pb(1)-O(3)#1	2.541(4)
Pb(1)-O(4)#1	2.527(4)	Pb(1)-N(1)	2.534(5)	Pb(1)-O(6)#3	3.035(4)
O(1)-Pb(1)-O(4)#1	95.35(15)	O(1)-Pb(1)-N(1)	67.20(15)	N(1)-Pb(1)-O(4)#1	78.85(15)
O(1)-Pb(1)-O(3)#1	74.46(14)	O(4)#1-Pb(1)-O(3)#1	51.39(14)	N(1)-Pb(1)-O(3)#1	112.29(16)
O(1)-Pb(1)-O(1)#2	66.72(18)	O(4)#1-Pb(1)-O(1)#2	133.76(13)	N(1)-Pb(1)-O(1)#2	124.81(14)
O(3)#1-Pb(1)-O(1)#2	82.40(14)	O(6)#3-Pb(1)-O(1)	142.12(13)	O(6)#3-Pb(1)-O(1)#2	94.82(14)
O(6)#3-Pb(1)-O(3)#1	70.34(14)	O(6)#3-Pb(1)-O(4)#1	73.33(13)	O(6)#3-Pb(1)-N(1)	140.35(15)
Pb(1)-O(1)-Pb(1)#2	113.28(18)				
10					
Cd(1)-O(1)	2.299(3)	Cd(1)-O(3)#1	2.257(3)	Cd(1)-O(7)	2.309(3)
Cd(1)-N(1)	2.334(4)	Cd(1)-N(2)	2.323(4)	Cd(1)-N(3)	2.375(4)
Cd(2)-O(5)	2.276(4)	Cd(2)-Cl(1)	2.505(2)	Cd(2)-N(4)	2.367(5)
Cd(2)-N(5)	2.377(5)	Cd(2)-N(6)	2.444(5)	Cd(2)-N(7)	2.401(5)
O(3)#1-Cd(1)-O(1)	156.62(13)	O(3)#1-Cd(1)-O(7)	86.79(12)	O(1)-Cd(1)-O(7)	86.50(12)
O(3)#1-Cd(1)-N(2)	93.92(14)	O(1)-Cd(1)-N(2)	109.02(14)	O(7)-Cd(1)-N(2)	95.70(14)
O(3)#1-Cd(1)-N(1)	88.36(14)	O(1)-Cd(1)-N(1)	71.54(13)	O(7)-Cd(1)-N(1)	103.54(13)
N(2)-Cd(1)-N(1)	160.73(15)	O(3)#1-Cd(1)-N(3)	101.53(14)	O(1)-Cd(1)-N(3)	90.44(14)
O(7)-Cd(1)-N(3)	164.70(14)	N(2)-Cd(1)-N(3)	71.14(16)	N(1)-Cd(1)-N(3)	89.64(15)
O(5)-Cd(2)-N(4)	86.47(17)	O(5)-Cd(2)-N(5)	117.08(17)	N(4)-Cd(2)-N(5)	70.6(2)
O(5)-Cd(2)-N(7)	82.86(17)	N(4)-Cd(2)-N(7)	96.53(18)	N(5)-Cd(2)-N(7)	154.43(17)
O(5)-Cd(2)-N(6)	150.36(16)	N(4)-Cd(2)-N(6)	87.96(16)	N(5)-Cd(2)-N(6)	88.17(16)
N(7)-Cd(2)-N(6)	68.90(16)	O(5)-Cd(2)-Cl(1)	96.66(12)	N(4)-Cd(2)-Cl(1)	164.08(14)
N(5)-Cd(2)-Cl(1)	94.23(15)	N(7)-Cd(2)-Cl(1)	99.35(12)	N(6)-Cd(2)-Cl(1)	96.62(12)
11					
Zn(1)-O(1)	2.475(4)	Zn(1)-O(1)#1	2.475(4)	Zn(1)-O(2)	1.994(3)
Zn(1)-O(2)#1	1.994(3)	Zn(1)-N(2)	2.083(4)	Zn(1)-N(2)#1	2.083(4)
Zn(2)-O(3)#2	2.426(5)	Zn(2)-O(4)#2	2.060(4)	Zn(2)-O(5)	2.083(3)
Zn(2)-N(1)	2.088(4)	Zn(2)-N(3)	2.078(4)	Zn(2)-N(4)	2.175(4)
O(2)-Zn(1)-O(2)#1	124.0(2)	O(2)-Zn(1)-N(2)#1	112.81(15)	O(2)-Zn(1)-N(2)	109.35(16)
N(2)-Zn(1)-N(2)#1	80.0(2)	O(2)-Zn(1)-O(1)	57.49(13)	O(2)#1-Zn(1)-O(1)	91.71(14)
N(2)#1-Zn(1)-O(1)	157.47(15)	N(2)-Zn(1)-O(1)	84.58(15)	O(1)-Zn(1)-O(1)#1	114.5(2)
O(4)#2-Zn(2)-N(3)	103.16(17)	O(4)#2-Zn(2)-O(5)	92.04(15)	N(3)-Zn(2)-O(5)	98.39(15)
O(4)#2-Zn(2)-N(1)	147.23(17)	N(3)-Zn(2)-N(1)	109.24(15)	O(5)-Zn(2)-N(1)	78.75(14)
O(4)#2-Zn(2)-N(4)	94.40(16)	N(3)-Zn(2)-N(4)	78.55(17)	O(5)-Zn(2)-N(4)	173.36(15)
N(1)-Zn(2)-N(4)	96.61(15)	O(4)#2-Zn(2)-O(3)#2	55.89(17)	N(3)-Zn(2)-O(3)#2	157.20(16)

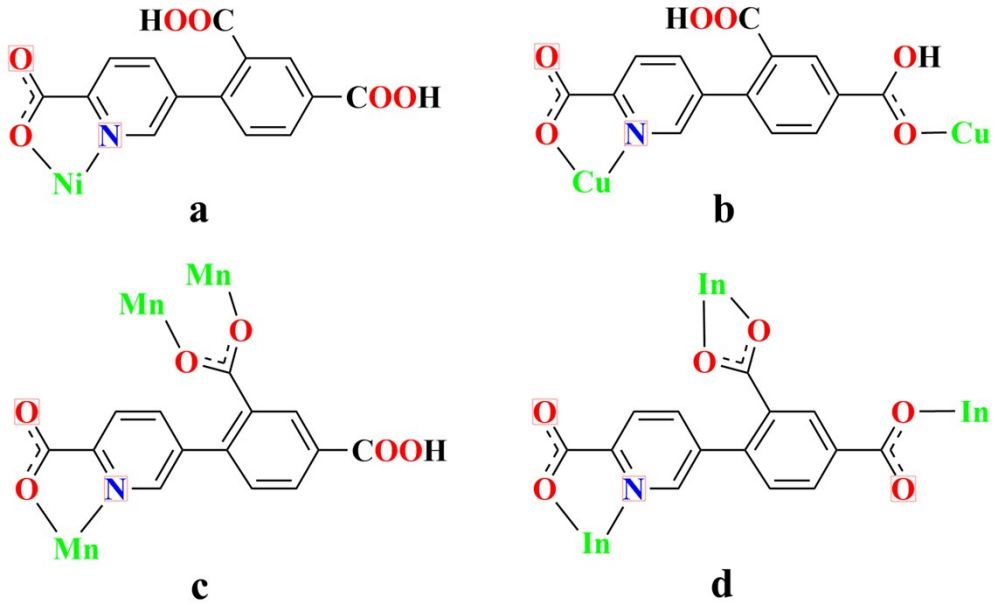
O(5)-Zn(2)-O(3)#2	91.81(17)	N(1)-Zn(2)-O(3)#2	92.68(16)	N(4)-Zn(2)-O(3)#2	93.15(18)
12					
Zn(1)-O(2)	1.973(3)	Zn(1)-O(3)#1	1.950(3)	Zn(1)-O(4)#1	2.763(3)
Zn(1)-O(13)	1.913(4)	Zn(1)-N(4)	2.069(4)	Zn(2)-O(1)	2.177(3)
Zn(2)-O(5)#2	2.105(3)	Zn(2)-O(13)	1.920(4)	Zn(2)-N(1)#2	2.069(4)
Zn(2)-N(6)	2.062(4)	Zn(3)-O(7)	1.968(3)	Zn(3)-O(9)#3	2.737(3)
Zn(3)-O(10)#3	1.934(3)	Zn(3)-O(14)	1.921(3)	Zn(3)-N(5)	2.072(4)
Zn(4)-O(8)	2.162(3)	Zn(4)-O(12)#4	2.103(3)	Zn(4)-O(14)	1.915(3)
Zn(4)-N(2)#4	2.063(4)	Zn(4)-N(3)	2.061(4)		
O(13)-Zn(1)-O(3)#1	122.57(14)	O(13)-Zn(1)-O(2)	112.64(15)	O(3)#1-Zn(1)-O(2)	104.21(13)
O(13)-Zn(1)-N(4)	104.15(16)	O(3)#1-Zn(1)-N(4)	110.84(15)	O(2)-Zn(1)-N(4)	100.33(14)
O(4)#1-Zn(1)-O(2)	155.89(13)	O(4)#1-Zn(1)-O(3)#1	51.95(13)	O(4)#1-Zn(1)-O(13)	87.13(13)
O(4)#1-Zn(1)-N(4)	87.27(13)	O(13)-Zn(2)-N(6)	111.24(16)	O(13)-Zn(2)-N(1)#2	133.43(15)
N(6)-Zn(2)-N(1)#2	115.28(14)	O(13)-Zn(2)-O(5)#2	98.53(14)	N(6)-Zn(2)-O(5)#2	95.66(14)
N(1)#2-Zn(2)-O(5)#2	79.14(13)	O(13)-Zn(2)-O(1)	91.05(14)	N(6)-Zn(2)-O(1)	89.66(13)
N(1)#2-Zn(2)-O(1)	87.36(12)	O(1)-Zn(2)-O(5)#2	166.50(12)	O(14)-Zn(3)-O(10)#3	121.78(13)
O(14)-Zn(3)-O(7)	110.66(14)	O(7)-Zn(3)-O(10)#3	106.17(14)	O(14)-Zn(3)-N(5)	105.08(15)
N(5)-Zn(3)-O(10)#3	109.97(15)	N(5)-Zn(3)-O(7)	101.34(14)	O(10)#3-Zn(3)-O(9)#3	51.94(13)
O(7)-Zn(3)-O(9)#3	157.35(14)	O(14)-Zn(3)-O(9)#3	81.74(14)	N(5)-Zn(3)-O(9)#3	93.11(14)
O(14)-Zn(4)-N(3)	111.09(15)	O(14)-Zn(4)-N(2)#4	135.61(15)	N(3)-Zn(4)-N(2)#4	113.30(15)
O(14)-Zn(4)-O(12)#4	98.17(14)	N(3)-Zn(4)-O(12)#4	92.98(15)	N(2)#4-Zn(4)-O(12)#4	79.50(14)
O(14)-Zn(4)-O(8)	92.25(14)	N(3)-Zn(4)-O(8)	90.03(14)	N(2)#4-Zn(4)-O(8)	87.96(13)
O(12)#4-Zn(4)-O(8)	167.29(13)	Zn(1)-O(13)-Zn(2)	117.84(17)	Zn(3)-O(14)-Zn(4)	116.72(16)

[a] Symmetry transformations used to generate equivalent atoms: #1 *x*, –*y*+1/2, –*z*+1/2 for **1** ; #1 –*x*+2, –*y*, –*z*+1 for **6**; #1 –*x*+1, *y*+1/2, –*z*+1/2 for **7**; #1 –*x*, *y*+1/2, –*z*+1/2 for **8**; #1 –*x*+1, –*y*+2, –*z*+1; #2 –*x*+2, –*y*+3, –*z*+1; #3 *x*+1, *y*+1, *z*+1 for **9**; #1 –*x*+2, –*y*+2, –*z*+1 for **10**; #1 –*x*+1, *y*, –*z*+1/2; #2 –*x*+2, –*y*, –*z* for **11**; #1 *x*, *y*+1, *z*; #2 –*x*, –*y*+1, –*z*+1; #3 *x*, *y*–1, *z*; #4 –*x*+1, –*y*+3, –*z* for **12**.

Table S2. Hydrogen bonds in crystal packing [Å, °] of **1**–**12**.

Complexes	D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(4)-H(4)···O(3)	0.811	1.853	2.618	156.97	-*x*+1/2, -*y*, *z*
	O(5)-H(5)···O(2)	0.768	1.896	2.649	166.44	*x*+1/2, *y*-1/2, *z*
	O(7)-H(1W)···O(6)	0.751	2.035	2.734	154.99	*x*-1/2, *y*+1/2, *z*
	O(7)-H(2W)···O(1)	0.768	1.938	2.695	168.64	-*x*+1/2, *y*, *z*-1/2
2	O(5)-H(1)···O(1)	0.820	1.792	2.602	169.41	*x*+1, *y*, *z*+1
	O(7)-H(1W)···O(4)	0.813	1.970	2.729	155.28	*x*-1, *y*, *z*
	O(7)-H(2W)···O(1)	0.811	1.945	2.750	172.49	-*x*+1, -*y*+1, -*z*+1
	O(8)-H(3W)···O(3)	0.944	1.688	2.631	178.38	-*x*+2, -*y*+2, -*z*+2
	O(8)-H(4W)···O(4)	0.847	1.865	2.703	170.22	*x*-1, *y*, *z*
3	O(5)-H(1)···O(1)	0.820	1.783	2.594	169.52	*x*+1, *y*, *z*+1
	O(7)-H(1W)···O(4)	0.872	1.877	2.733	167.08	*x*-1, *y*, *z*
	O(7)-H(2W)···O(1)	0.871	1.918	2.742	157.06	-*x*+1, -*y*+1, -*z*+1
	O(8)-H(3W)···O(3)	0.850	1.790	2.640	179.48	-*x*+2, -*y*+2, -*z*+2
	O(8)-H(4W)···O(4)	0.850	1.853	2.703	179.34	*x*-1, *y*, *z*
4	O(5)-H(1)···O(1)	0.820	1.793	2.603	168.80	*x*-1, *y*, *z*-1
	O(7)-H(1W)···O(1)	0.879	1.871	2.749	176.21	-*x*+2, -*y*+1, -*z*+1
	O(7)-H(2W)···O(3)	0.877	1.901	2.722	155.25	*x*+1, *y*, *z*
	O(8)-H(3W)···O(4)	0.854	2.122	2.650	119.61	-*x*+1, -*y*, -*z*
	O(8)-H(4W)···O(3)	0.854	2.141	2.712	123.91	*x*+1, *y*, *z*
5	O(6)-H(6)···O(2)	0.820	1.836	2.625	161.23	*x*-1, *y*, *z*
	O(7)-H(1W)···O(26)	0.820	2.084	2.883	164.77	
	O(7)-H(2W)···O(11)	0.850	1.872	2.722	179.65	
	O(8)-H(3W)···O(3)	0.820	1.861	2.665	166.21	-*x*+1, -*y*+1, -*z*+1
	O(8)-H(4W)···O(11)	0.850	1.873	2.723	179.89	
6	O(6)-H(1)···O(1)	0.820	1.776	2.584	168.06	*x*-1, *y*, *z*-1
7	O(3)-H(1)···O(1)	0.820	1.748	2.566	174.89	-*x*+2, *y*-1/2, -*z*+1/2
	O(7)-H(1W)···O(2)	0.876	2.041	2.818	147.39	-*x*+2, -*y*+2, -*z*+1
	O(7)-H(2W)···O(6)	0.875	1.761	2.615	164.82	*x*+1, -*y*+3/2, *z*+1/2
8	O(3)-H(3)···O(5)	0.820	1.743	2.556	170.97	-*x*-1, *y*+1/2, -*z*+1/2
	O(7)-H(1W)···O(2)	0.847	1.801	2.642	171.79	-*x*+1, -*y*+1, -*z*
	O(7)-H(2W)···O(6)	0.829	2.006	2.810	163.59	*x*+1, -*y*+1/2, *z*-1/2
9	O(5)-H(5)···O(7)	0.820	1.796	2.604	168.54	-*x*, -*y*, -*z*
	O(7)-H(1W)···O(3)	0.850	1.873	2.723	179.91	
	O(7)-H(2W)···O(8)	0.850	1.904	2.754	179.79	-*x*+1, -*y*+1, -*z*+1
	O(8)-H(3W)···O(4)	0.850	1.915	2.765	179.64	-*x*+1, -*y*+2, -*z*+1
	O(8)-H(4W)···O(2)	0.850	1.852	2.702	179.85	*x*, *y*-1, *z*
10	O(7)-H(1W)···O(1)	0.85	1.850	2.700	179.57	-*x*+2, -*y*+1, -*z*+1
	O(7)-H(2W)···O(4)	0.850	1.830	2.680	179.53	-*x*+2, -*y*+2, -*z*+1
	O(8)-H(3W)···O(6)	0.850	1.966	2.816	179.02	
	O(9)-H(5W)···O(4)	0.850	1.968	2.818	178.74	*x*, *y*-1, *z*
	O(10)-H(7W)···O(2)	0.871	1.923	2.787	170.92	
	O(11)-H(9W)···O(12)	0.620	2.186	2.680	138.24	-*x*+1, -*y*+1, -*z*+1

	O(12)-H(11W)···O(10)	0.850	1.972	2.822	177.93	
11	O(7)-H(1W)···O(2)	0.850	1.968	2.818	179.38	
	O(7)-H(2W)···O(8)	1.005	1.789	2.710	150.65	*x*+1, *y*, *z*
	O(8)-H(3W)···O(7)	0.977	1.809	2.753	161.40	-*x*+1, *y*, -*z*+1/2
	O(8)-H(4W)···O(9)	0.850	2.126	2.976	178.89	-*x*+1/2, -*y*+1/2, -*z*+1
	O(9)-H(5W)···O(6)	0.850	1.907	2.757	179.07	*x*-1/2, *y*+1/2, *z*+1
12	O(15)-H(1W)···O(11)	0.850	1.997	2.847	179.10	-*x*, -*y*+2, -*z*
	O(15)-H(2W)···O(16)	0.850	2.003	2.853	178.64	
	O(16)-H(3w)···O(6)	0.850	1.957	2.807	179.26	-*x*+1, -*y*+1, -*z*+1
	O(16)-H(4W)···O(4)	0.850	2.113	2.963	179.13	



Scheme S1 Coordination modes of H_2cpia^-, $Hcpia^{2-}$, or $cpia^{3-}$ in other reported compounds.

Table S3. Emission wavelengths (nm) of compounds **4**–**6**, **8**–**12**, and H_3cpia.

Compound	**H_3cpia**	**4**	**5**	**6**	**8**
λ_{em}	371	366, 384	349, 370	371	367, 386
Compound	**9**	**10**	**11**	**12**	
λ_{em}	374	368, 385	377, 394	377	

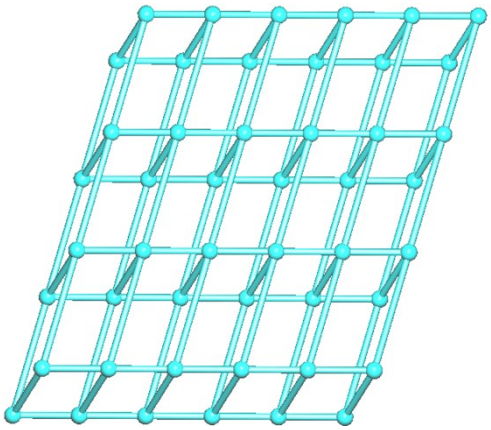


Fig. S1. Topological view of a simplified 2D H-bonded layer in **4** showing a uninodal 5-connected net with the **SnS** [SP 2-periodic net (4,4)Ia] topology and the ($4^8.6^2$) point symbol; view along the *b* axis; centroids of 5-connected [Zn(Hcpia)(2,2′-bipy)(H_2O)$_2$] nodes (cyan balls).

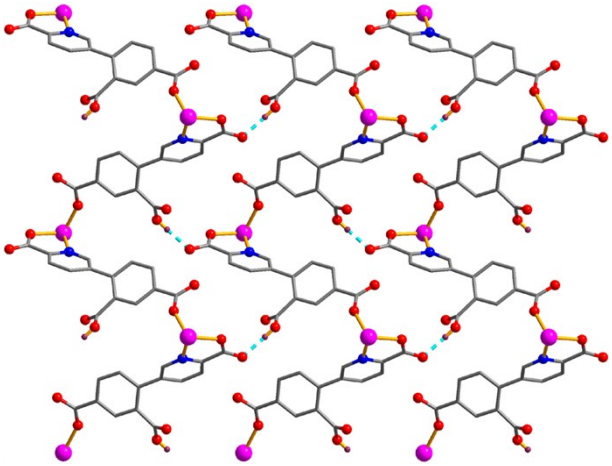


Fig. S2. 2D supramolecular network in **7** viewed along the *ab* plane (blue dashed lines represent the H-bonds).

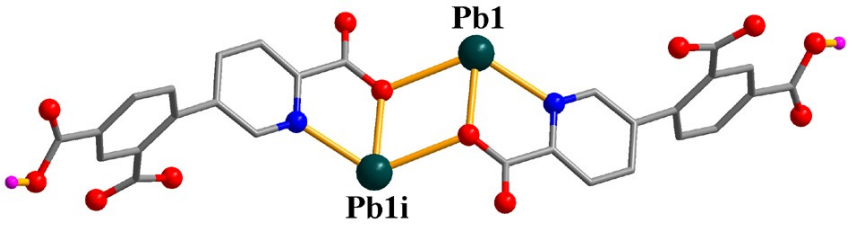


Fig. S3. Dimeric [Pb_2(μ_4-Hcpia)$_2$] unit in **9**. Symmetry code: i = –*x* + 2, –*y* + 3, –*z* + 1.

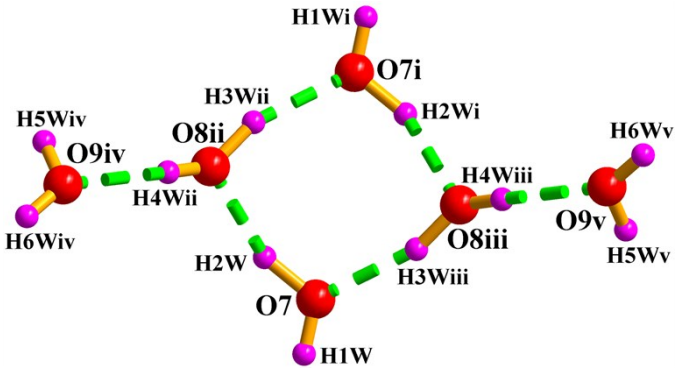


Fig. S4. Hexameric $(H_2O)_6$ cluster with a cyclic $(H_2O)_4$ core in **11**. Symmetry codes: i = $-x + 2$, y, $-z + 1/2$;. ii = $x + 1$, y, z; iii = $-x + 1$, y, $-z + 1/2$; iv = $-x + 3/2$, $-y + 1/2$, $-z + 1$; v = $x + 1/2$, $-y + 1/2$, $z - 1/2$.

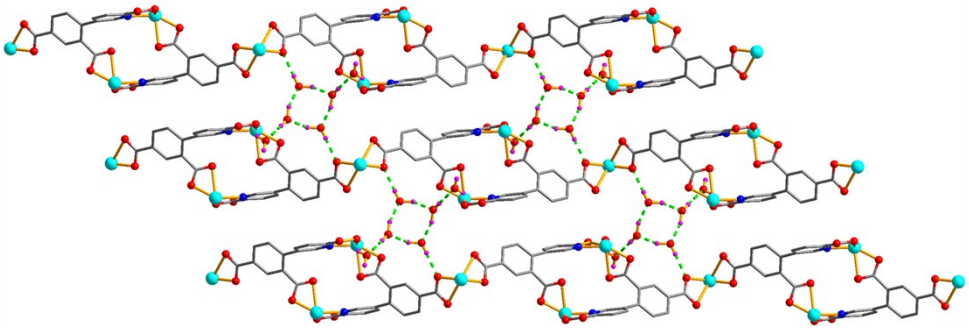
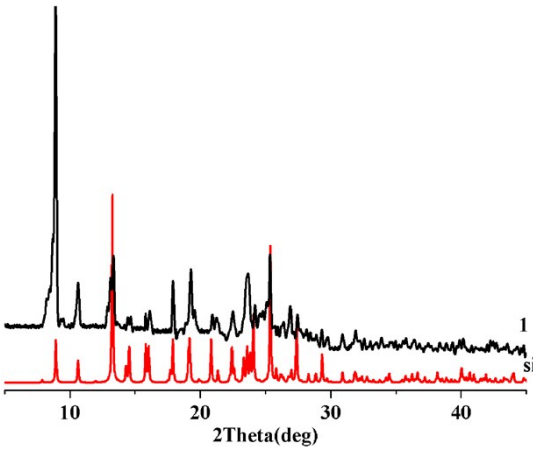
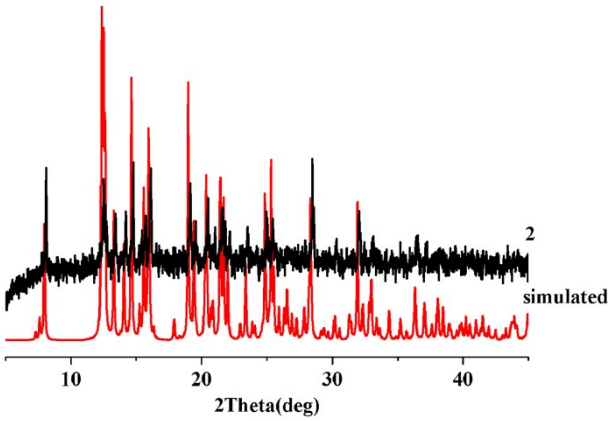
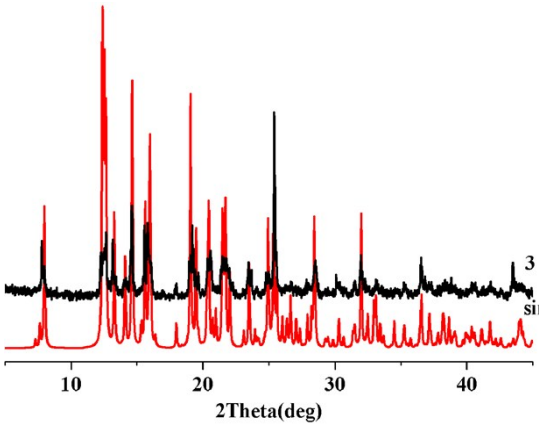
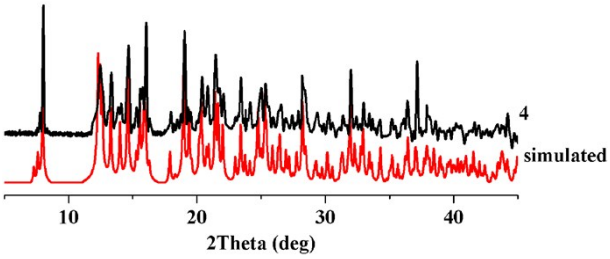


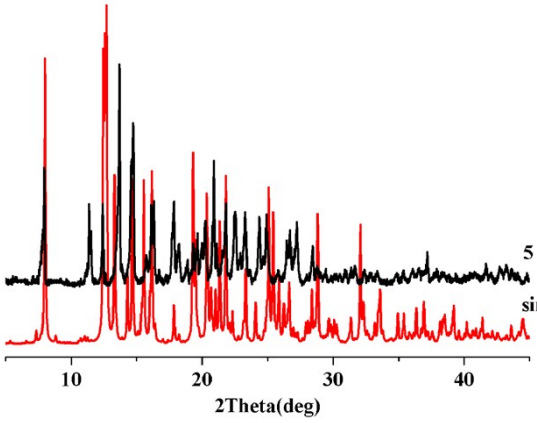
Fig. S5. The 2D H-bonded layer in **11** (view along the *b* axis, green dashed lines represent the H-bonds).

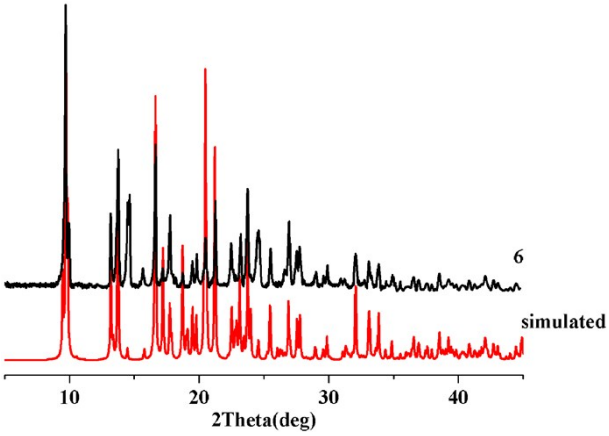

1
simulated
10
20
30
40
2Theta(deg)

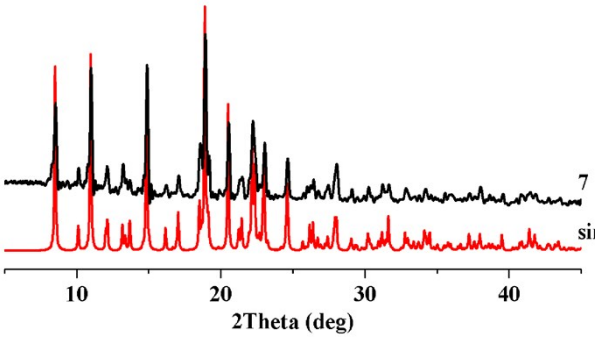

2
simulated
10
20
30
40
2Theta(deg)

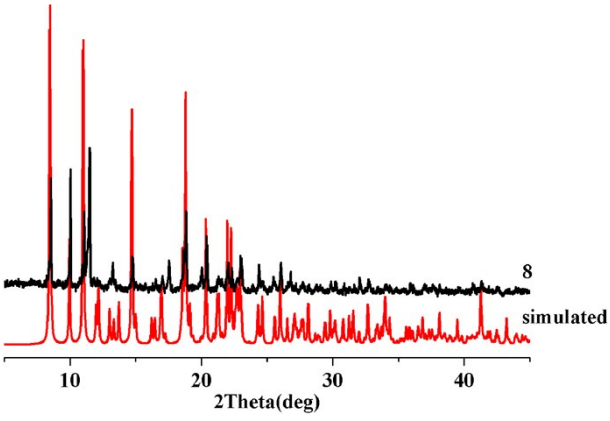

3
simulated
10
20
30
40
2Theta(deg)


4
simulated
10
20
30
40
2Theta (deg)


5
simulated
10
20
30
40
2Theta(deg)


6
simulated
10
20
30
40
2Theta(deg)


7
simulated
10
20
30
40
2Theta (deg)


8
simulated
10
20
30
40
2Theta(deg)

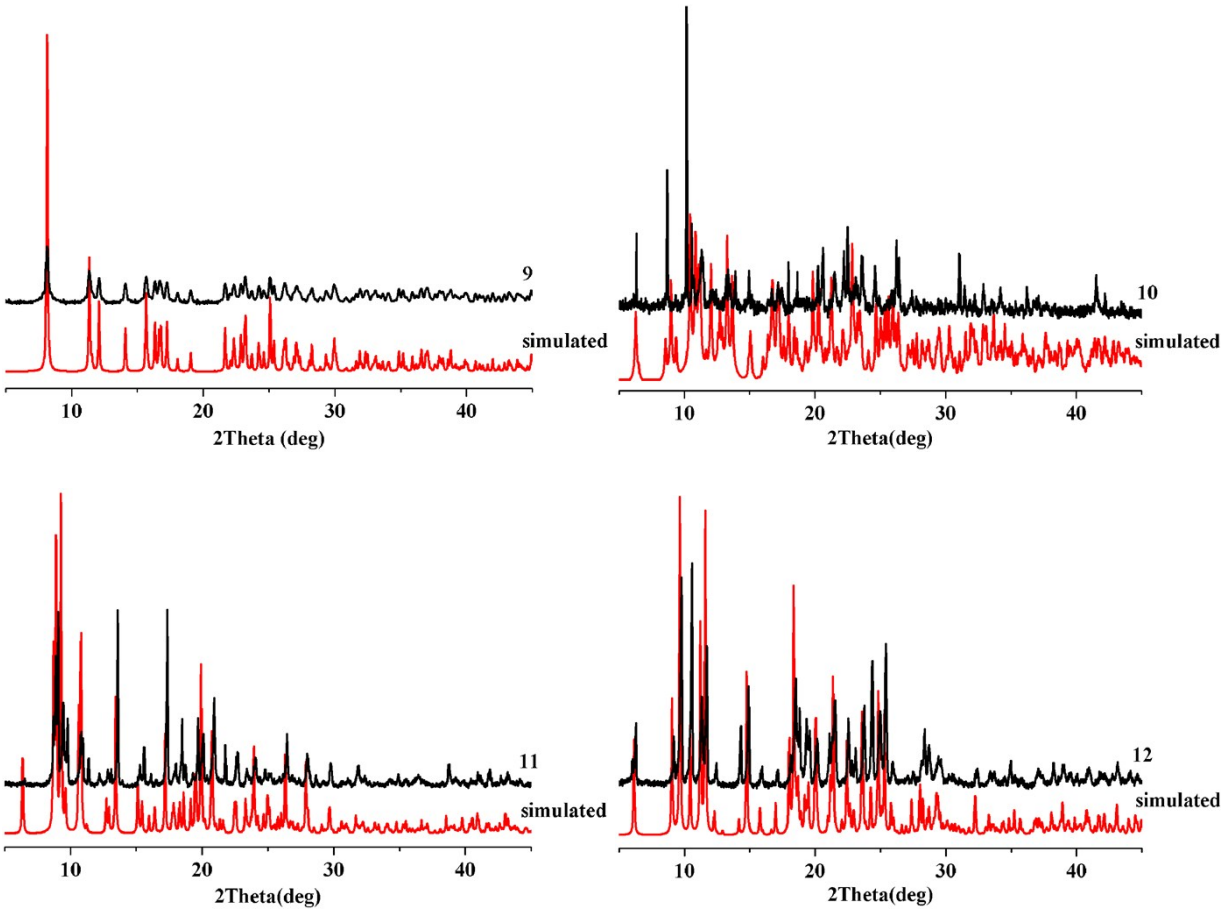
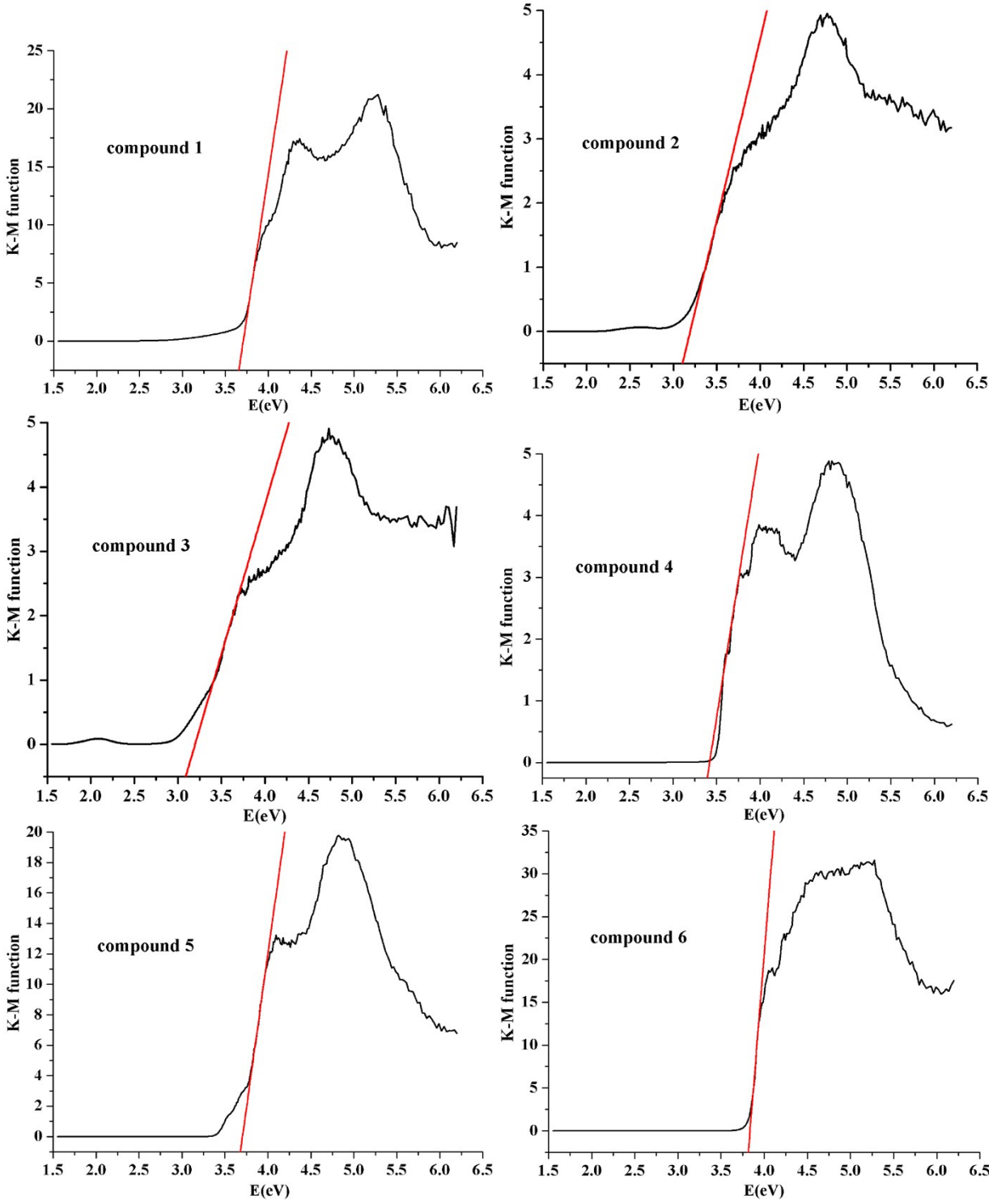


Fig. S6. PXRD patterns of compounds **1**–**12** at room temperature. Black patterns correspond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data.


compound 1
compound 2
compound 3
compound 4
compound 5
compound 6
K-M function
E(eV)

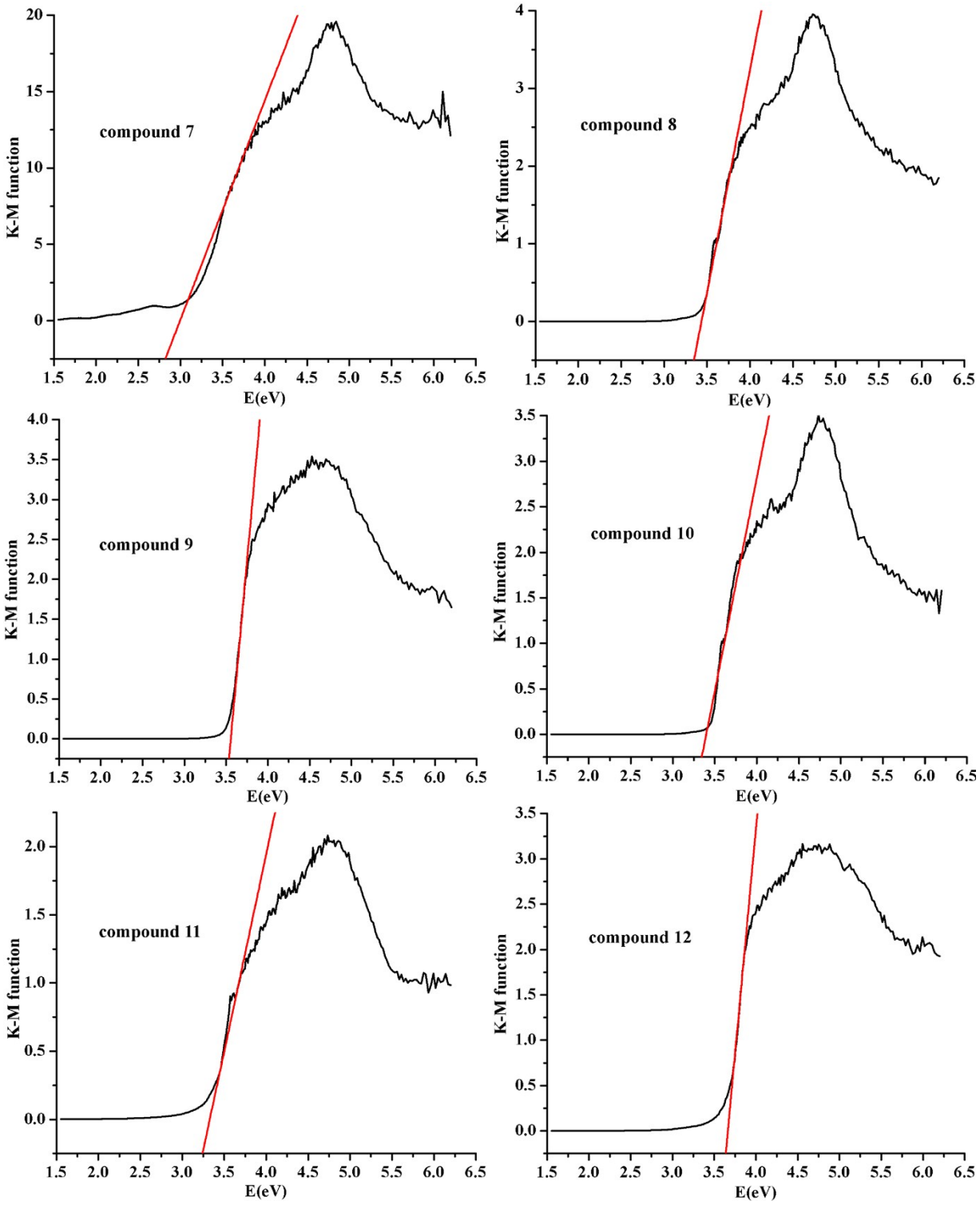


Fig. S7. Kubelka-Munk-transformed diffuse reflectance spectra of compounds **1**–**12**.

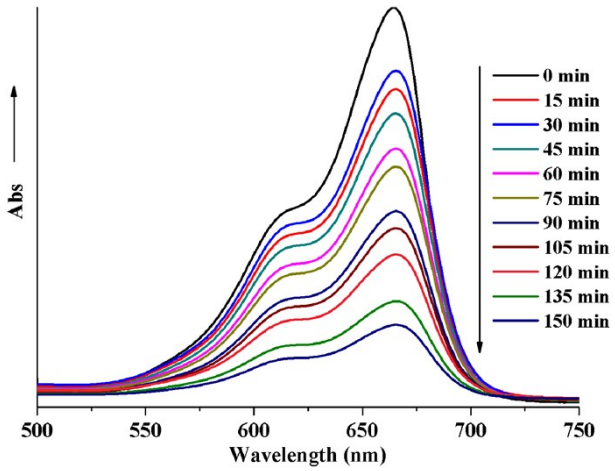


Fig. S8. Time-dependent UV-Vis spectra of the reaction mixtures in the course of the MB photodegradation catalyzed by **7**. Reaction conditions: catalyst (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

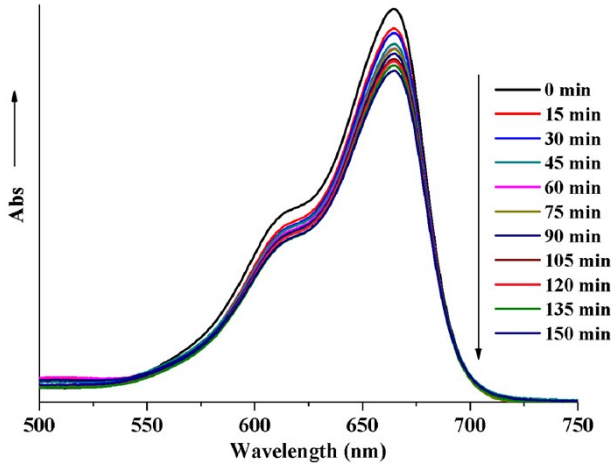


Fig. S9. Time-dependent UV-Vis spectra of the reaction mixtures in the course of the MB photodegradation catalyzed by H_3dbba (blank test). Reaction conditions: H_3cpia (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

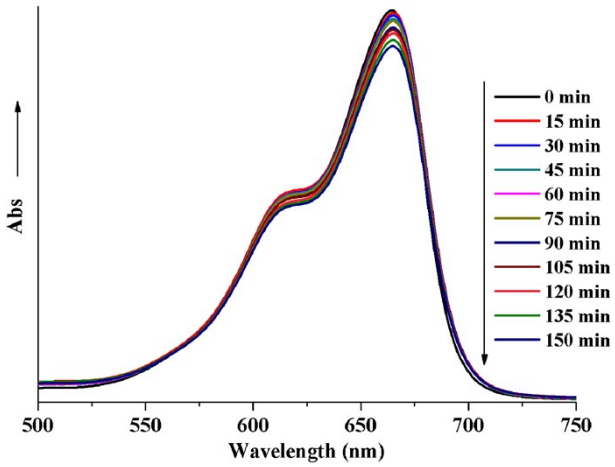


Fig. S10. Time-dependent UV-Vis spectra of the reaction mixtures in the course of the MB photodegradation catalyzed by phen (blank test). Reaction conditions: phen (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

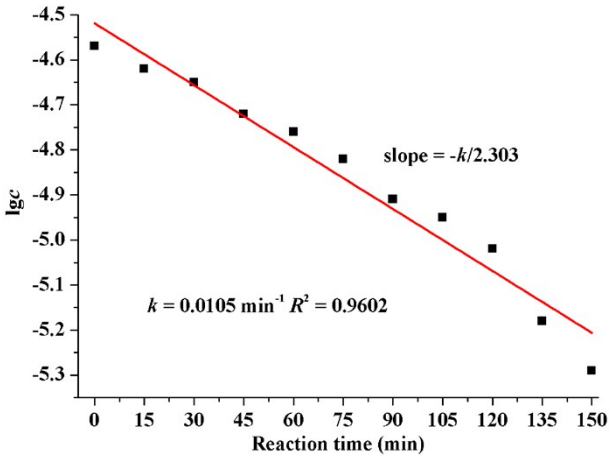


Fig. S11. Relationship between lg*c* and reaction time in the course of the MB photodegradation catalyzed by **7**. The red line corresponds to a linear fit. Reaction conditions: catalyst (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

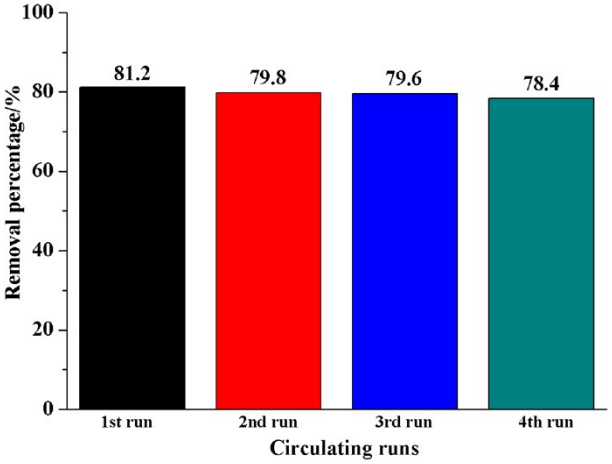


Fig. S12. Catalyst recycling experiments in the MB photodegradation (removal efficiency, %) under the UV light irradiation with catalyst **7**. Reaction conditions: catalyst (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

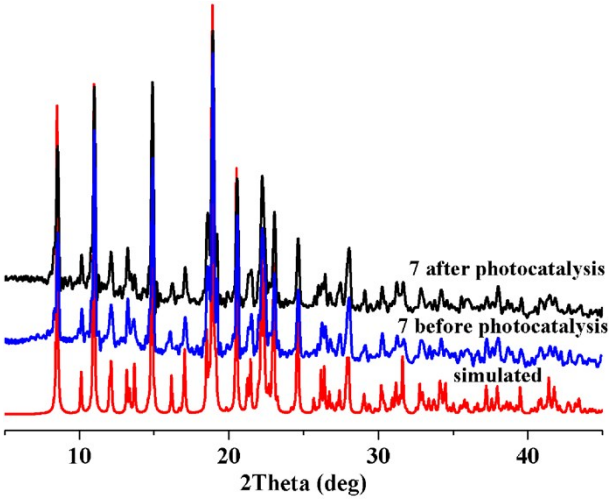


Fig. S13. PXRD patterns for **7**: simulated (red), before (blue) and after (black) photocatalysis.