Electronic Supplementary Information

Structural diversity of Zn(II) coordination polymers based on bis-imidazolyl ligands and 5-R-1,3-benzenedicarboxylate and their photocatalytic properties

Hong-Jian Cheng,[ab] Xiao-Yan Tang,[b] Rong-Xin Yuan[b] and Jian-Ping Lang*[a]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, Jiangsu, P. R. China

[b] School of Chemistry and Materials Engineering, Jiangsu Key Laboratory of Advanced Functional Materials, Changshu Insititute of Technology, Changshu, Jiangsu, 215500, P. R. China

Table of Contents

Preparation of ligands (nbimb, bimpa and bimcz)

Preparation of nbimb. A 10 mL deep porcelain crucible was filled with a mixture of 0.887 g (2.5 mmol) 2-nitro-4,4′-dibromo-bibenzene, 1.702 g (2.5 mmol) imidazole, 1.037 g (7.5 mmol) anhydrous potassium carbonate and 0.085 g (0.5 mmol) cuprous iodide. The reaction mixture was exposed to microwave irradiation at different temperatures and times. After cooling to room temperature, the residue was diluted with 10 mL H_2O. 0.073 g (0.25 mmol) ethylenediaminetetraacetic acid and 1 mL $NH_3 \cdot H_2O$ (28-29%) was added, and the resulting mixture was stirred at room temperature for 24 h. The resulting yellow precipitate was filtered and further purified by recrystallization in methanol to form yellow powder of nbimb. Yield: 0.439 g (53 %). m.p. 119.5-120.6 °C. Anal. Calcd for $C_{18}H_{13}N_5O_2$: C, 65.25; H, 3.95; N, 21.14; found: C, 65.24; H, 3.92; N, 21.84. IR (KBr, cm^{-1}): 3110 (m), 1644 (m), 1616 (m), 1513 (s), 1303 (s), 1247 (s), 1107 (s), 1057 (s), 822 (m), 739 (m), 656 (m). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ 8.313 (s, 1H), 7.856-7.731 (m, 9H), 7.11 (s, 2H).

Preparation of bimpa. bimpa was prepared as brown powder using a procedure similar to that adopted for nbimb using bis(4-bromophenyl)amine instead of 2-nitro-4,4'-dibromo-bibenzene. Yield: 0.58 g (77 %). m.p. 216.8-217.2 °C. Anal. Calcd for $C_{18}H_{15}N_5$: C, 71.74; H, 5.02; N, 23.24; found: C, 71.34; H, 5.42; N, 23.84. IR (KBr, cm^{-1}): 3219 (m), 3110 (m), 1601 (m), 1522 (s), 1394 (w), 1311 (m), 1056 (s), 827 (m), 741 (m), 624 (m). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ 8.54 (s, 1H), 8.16 (s, 2H), 7.66 (s, 2H), 7.51 (d, J = 8.4 Hz, 4H), 7.19 (d, J = 8.4 Hz, 4H), 7.11 (s, 2H).

Preparation of bimcz. bimcz was prepared as brown powder using a procedure similar to that adopted for nbimb using bis(4-bromophenyl)amine in place of 3,6-dibromocarbazole. Yield: 0.55 g (73 %). m.p. 273.5-274.3 °C. Anal. Calcd for $C_{18}H_{13}N_5$: C, 72.23; H, 4.38; N, 23.40; found: C, 72.54; H, 4.22; N, 23.10. IR (KBr, cm^{-1}): 3430 (w), 3115 (w), 1636 (m), 1587 (m), 1505 (s), 1326(m), 1229 (s), 1108 (m), 1054 (m), 913 (m), 804 (m), 733 (m), 657 (m). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ 11.636 (d, 1H), 8.652-8.467 (m, 4H), 7.829-7.658 (d, 8H).

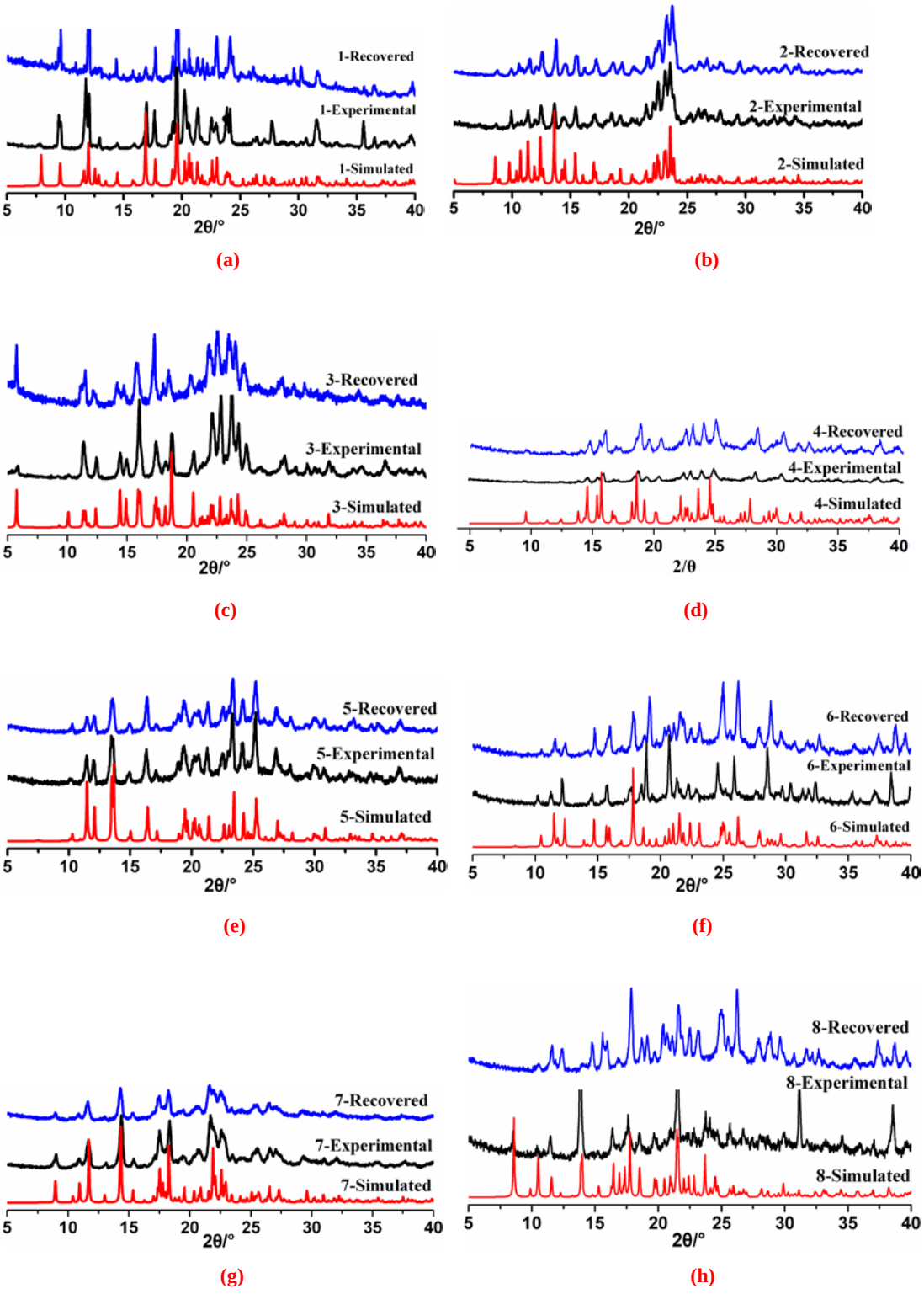
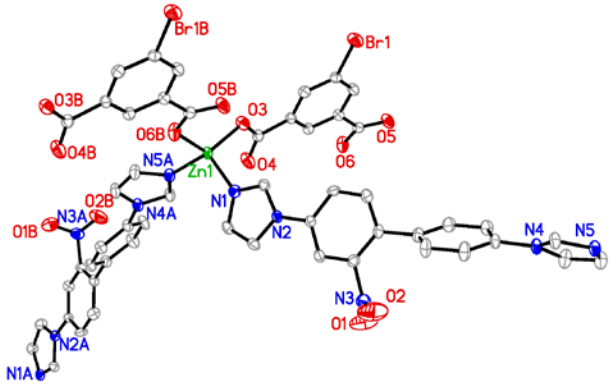
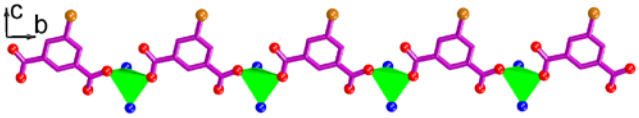


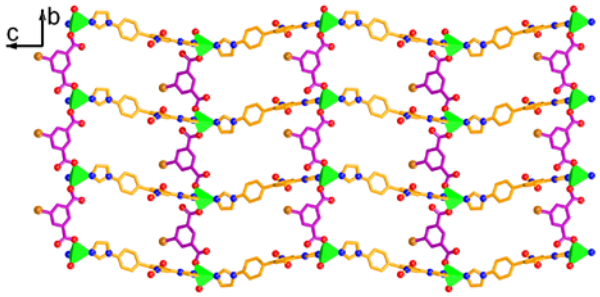
Fig. S1 PXRD patterns for **1-8**. (a-h) simulated (red), single-phase polycrystalline (black) and recovered (blue) samples of **1-8**.



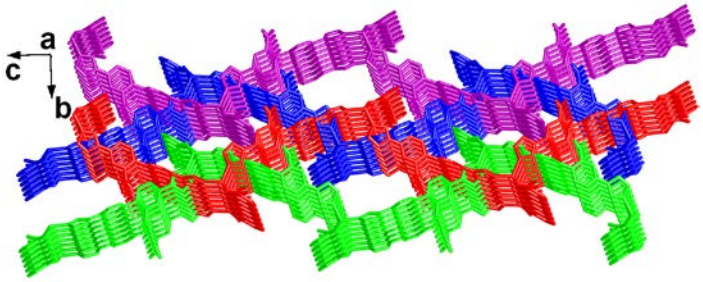
(a)



(b)

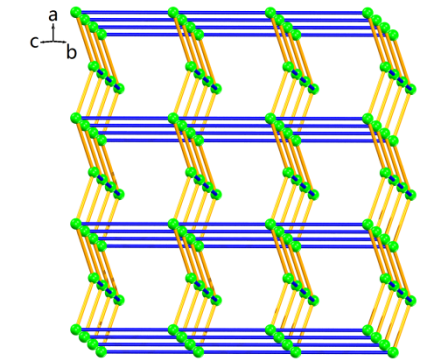


(c)

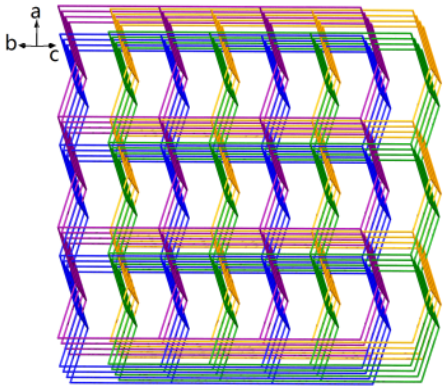


(d)

Fig. S2 (a) View of the coordination environment of Zn1 in **4** with a labelling scheme and 30 % thermal ellipsoids. All H atoms except the carboxylic H atoms have been omitted for clarity. Symmetry codes: (A) $-x + 1/2, -y + 1, z -1/2$; (B) $x, y + 1, z$. (b) View of a section of the 1D chain that is constructed by [Zn(5-Br-1,3-BDC)] units in **4** (extending along the *b* axis). (c) View of the 2D network (extending along the *bc* plane). Each green tetrahedron represents one Zn atom. The red and blue balls represent O and N atoms, respectively. (d) View of the parallel 2D → 3D polycatenation with alternative layers in **4** looking down the a axis. Each green tetrahedron represents one Zn atom. The red and blue balls represent O and N atoms, respectively.

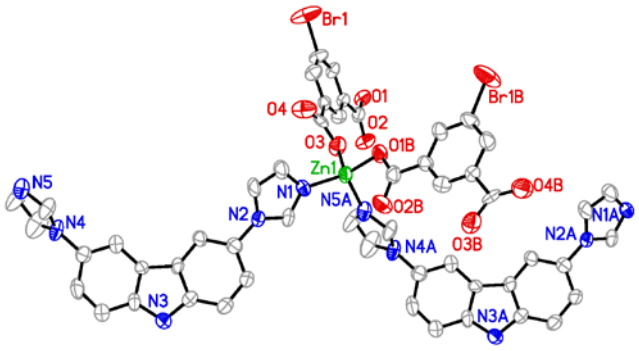


(a)

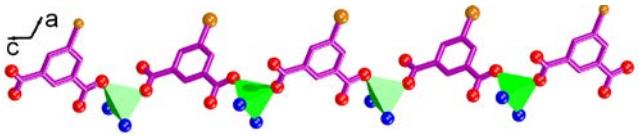


(b)

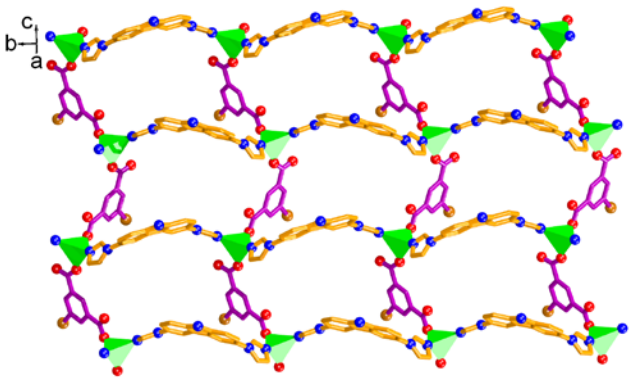
Fig. S3 (a) A schematic view of a ($6^5 \cdot 8$) topological net of **6**. The green balls represent 4-connecting Zn centres. Each pink line represents one bimba ligand. Each light orange line represents one 5-Br1,3-BDC ligand (e) View of 4-fold interpenetrating mode of **6** looking down the *b* axis.



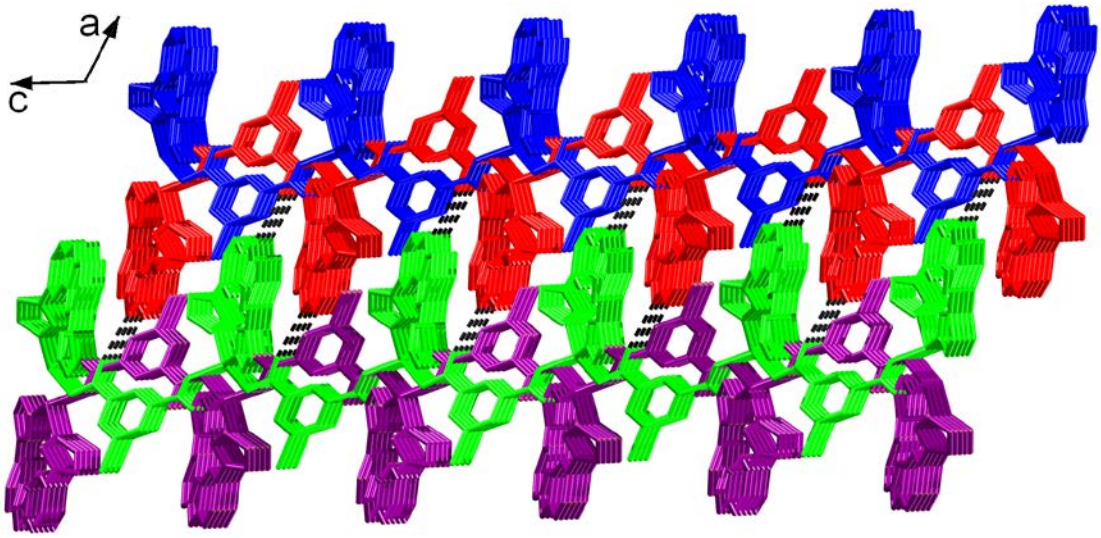
(**a**)



(b)



(c)



(d)

Fig. S4 (a) View of the coordination environment of Zn1 in **8** with a labelling scheme and 30 % thermal ellipsoids. All H atoms except the carboxylic H atoms have been omitted for clarity. Symmetry codes: (A) *x*, *y* – 1, *z*; (B) *x*, – *y* – 1/2, *z* + 1/2. (b) View of a section of the 1D chain that is constructed by [Zn(5-Br-1,3-BDC)] units in **8** (extending along the *b* axis). (c) View of the 2D network (extending along the *bc* plane). Each green tetrahedron represents one Zn atom. The red and blue balls represent O and N atoms, respectively. (d) View of the 3D polythreaded network of **8** looking down the b axis.

Table S1 Hydrogen-bonding interactions in **1**-**8**.

Interaction	D−H [Å]	H···A [Å]	D···A [Å]	Angle (D−H···A) [°]
Complex **1**				
O5-H5D···O3[a]	0.85	2.17	3.009(7)	169.3
O5-H5E···N3[b]	0.85	2.34	3.185(8)	175.6
N3-H3B···O1[c]	0.87	2.51	3.307(7)	153.4
N3-H3C···O5[d]	0.87	2.41	3.176(8)	147.4
C3-H3A···O2	0.94	2.47	3.049(6)	119.8
Symmetry codes: *a*, − *x* + 1, − *y* + 1, − *z* + 1; *b*, − *x* + 1, − *y* + 2, − *z* + 1; *c*, *x*, *y* + 1, *z*; *d*, *x* − 1, *y*, *z*; .				
Complex **2**				
N3A−H3AB···O6[a]	0.86	2.61	3.35(3)	144.7
N8−H8A··O4[b]	0.86	2.45	3.227(14)	151.2
C1−H1A···O3[c]	0.93	2.53	3.093(10)	119.6
C9−H9A···O9	0.93	2.42	3.350(14)	173.3
C18−H18A···O6[d]	0.93	2.38	3.049(12)	128.4
C19−H19A···O3[c]	0.93	2.52	3.048(10)	116.0
C20−H20A···O9[e]	0.93	2.65	3.356(14)	132.9
C30−H30A···O2[f]	0.93	2.53	3.453(10)	171.5
C34−H34A···O2[f]	0.93	2.51	3.402(12)	162.1
C35−H35A···O6	0.93	2.49	3.083(12)	121.6
Symmetry codes: *a*, − *x* + 1, − *y* + 1, − *z*; *b*, − *x*, − *y* + 1, − *z* + 1; *c*, *x*, − *y* + 3/2, *z* − 1/2; *d*, *x*, *y* + 1, *z* + 1; *e*, − *x*, *y* − 1/2, − *z* + 1/2; *f*, − *x*, − *y* + 1, − *z*.				
Complex **3**				
C1-H1A···O5[a]	0.85(6)	2.53	2.992(10)	110.8
C12-H12A···O6[b]	0.94	2.47	2.926(10)	110.2
C16-H16A···O6[c]	0.94	2.23	2.963(10)	133.9
Symmetry codes: *a*, *x* + 1, *y*, *z*; *b*, *x* + 1, − *y* + 1/2, *z* + 1/2; *c*, *x* + 1, − *y* + 3/2, *z* + 1/2.				
Complex **4**				
C18-H18A···O6[a]	0.93	2.46	2.951(5)	112.7

Symmetry codes: *a*, − *x* + 1/2, − *y*, *z* + 1/2.

Complex **5**

O5-H5B···O2[a]	0.88	2.18(5)	2.966(3)	148(4)
O5-H5C···O3[b]	0.86	2.06(5)	2.869(3)	156(4)
O6-H6B···O1	0.89	2.17(5)	3.047(4)	170(4)
O6-H6C···O5[c]	0.98	2.01(5)	2.832(4))	141(4)
N3-H3A···O3[d]	0.86	2.30	3.132(3)	163.0

Symmetry codes: *a*, − *x* + 1, *y* −1/2, − *z* + 3/2; *b*, − *x*, *y* − 1/2, − *z* + 3/2; *c*, *x* − 1, *y*, *z*; *d*, − *x* + 1, − *y* + 2, − *z* + 2.

Complex **6**

O5-H5B···O3	0.85	1.96	2.722(10)	149.1
O5-H5C···O6	0.85	2.23	2.857(12)	130.1
O6-H6B···O2	0.85	2.07	2.857(7)	158.3
N3-H3A···O2[a]	0.87	2.28	3.127(7)	165.7

Symmetry codes: *a*, *x*, *y*, *z* − 1.

Complex **7**

N3-H3A···O2[a]	0.87	2.02	2.793(2)	146.7
C3-H3B···O4[b]	0.94	2.56	3.393(2)	148.3
C5-H5B···O4[b]	0.94	2.42	3.111(2)	130.0
C17-H17A...O3[b]	0.94	2.46	3.321(1)	152.1
C8-H8A···O1[c]	0.94	2.60	3.388(2)	141.4

Symmetry codes: *a*, − *x* + 1, *y* − 1/2, − *z* − 1/2; *b*, − *x*, − *y* − 1, − *z* − 1; *c*, − *x*, − *y* − 1/2, − *z* − 1/2.

Complex **8**

N3−H3A···O2[a]	0.86	2.02	2.810(11)	152.8
C1−H1A···Br1[b]	0.93	3.09	3.967(11)	158.2
C3−H3B···O3[c]	0.93	2.56	3.442(12)	158.9
C8−H8A···O4[c]	0.93	2.43	3.224(13)	143.8
C16−H16A···O2[d]	0.93	2.65	3.223(14)	120.8

Symmetry codes: *a*, − *x*, − *y* + 1, − *z*; *b*, *x* − 1, *y*, *z* ; *c*, − *x* + 1, *y* + 1/2, − *z* + 1/2; *d*, *x*, − *y* + 3/2, *z* + 1/2.

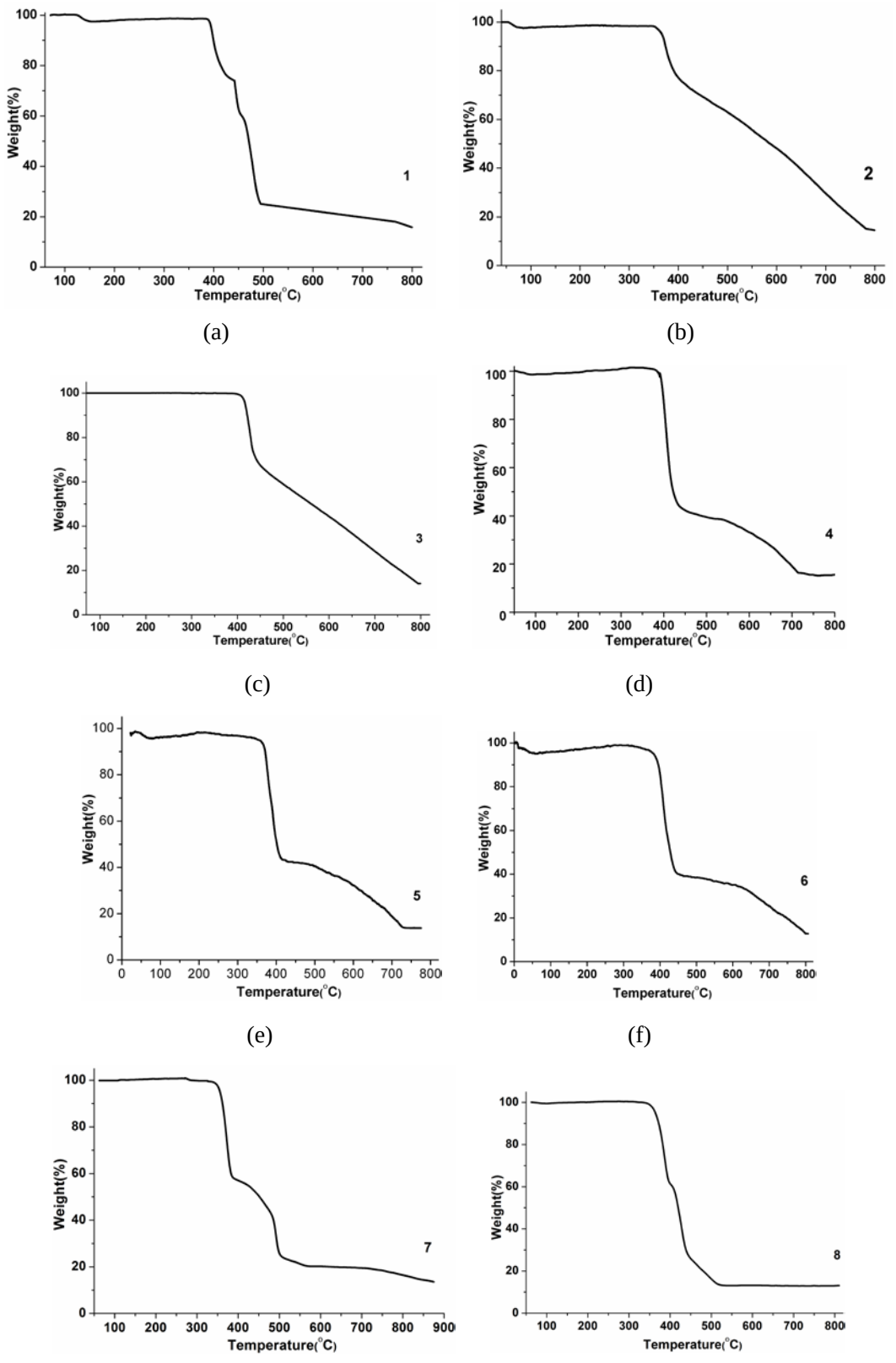


Fig. S5 The TGA curves for **1** (a), **2** (b); **3** (c); **4** (d); **5** (e); **6** (f); **7** (g); and **8** (h).

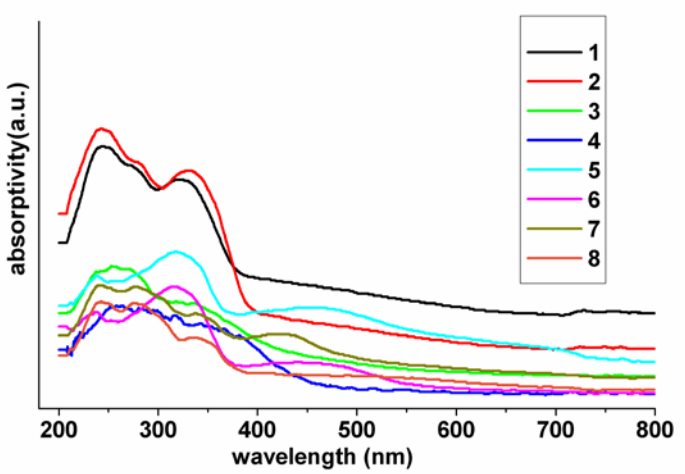
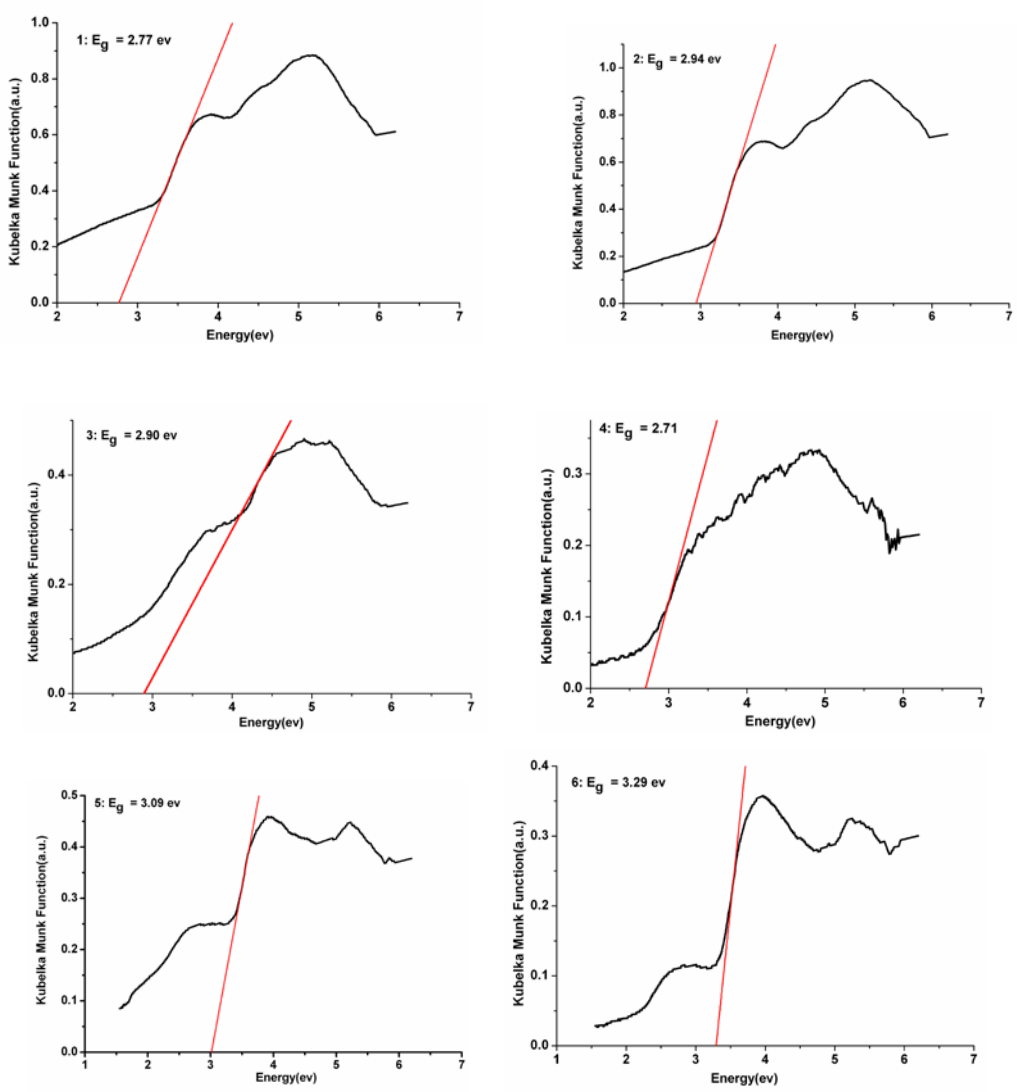


Fig. S6 The UV-vis absorption spectra for **1**–**8** in the solid state at room temperature.



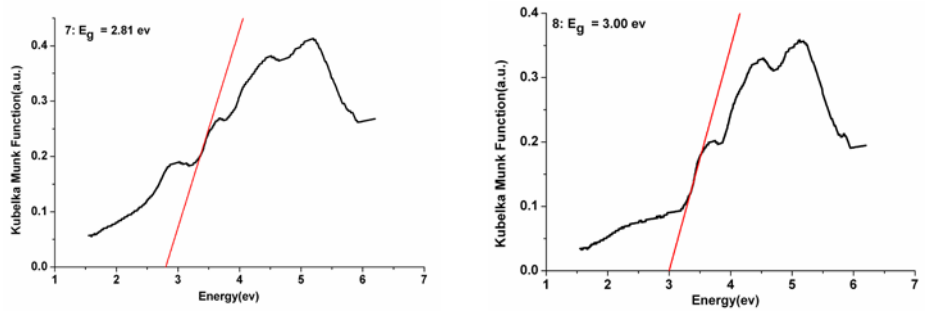


Fig. S7 Solid-state optical diffuse-reflection spectra of **1**-**8** derived from diffuse reflectance data at ambient temperature.

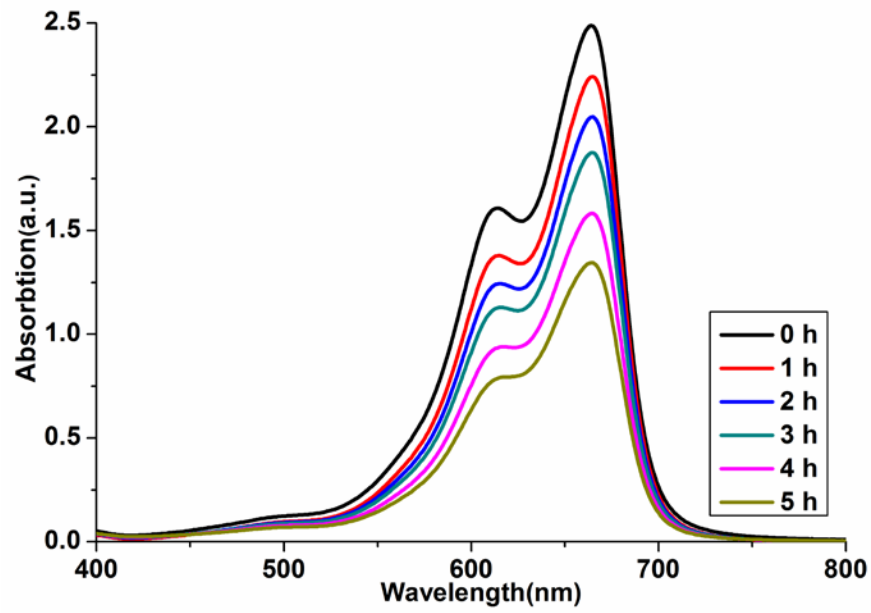
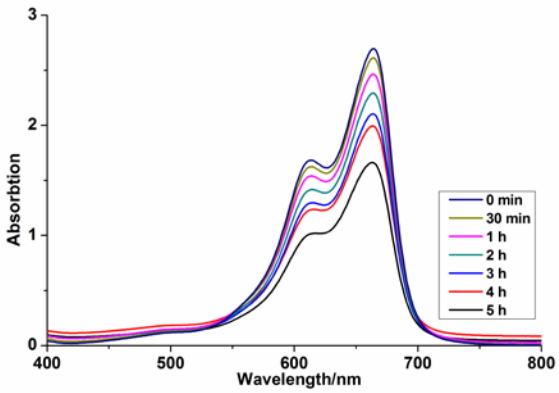
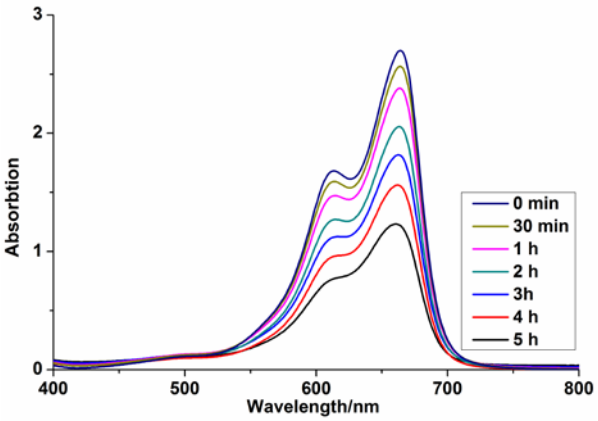


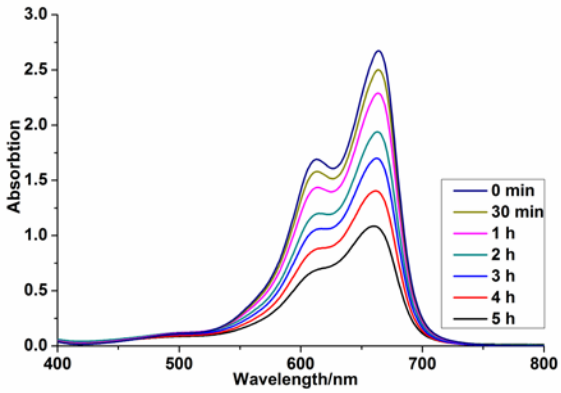
Fig. S8 UV-Vis absorption spectra of a MB (b) solution degraded without catalysts under UV irradiation at different time intervals.


Absorbtion
Wavelength/nm
0 min
30 min
1 h
2 h
3 h
4 h
5 h

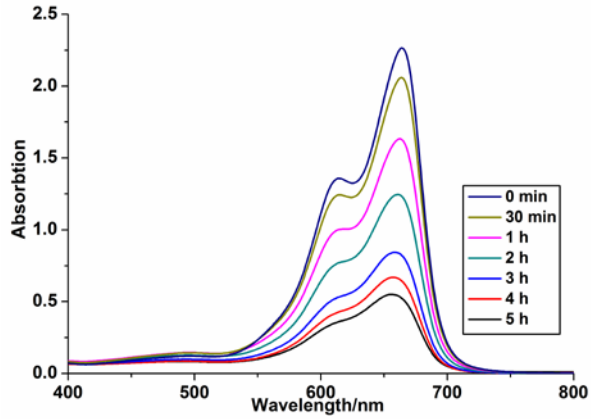
(a)


Absorbtion
Wavelength/nm
0 min
30 min
1 h
2 h
3h
4 h
5 h

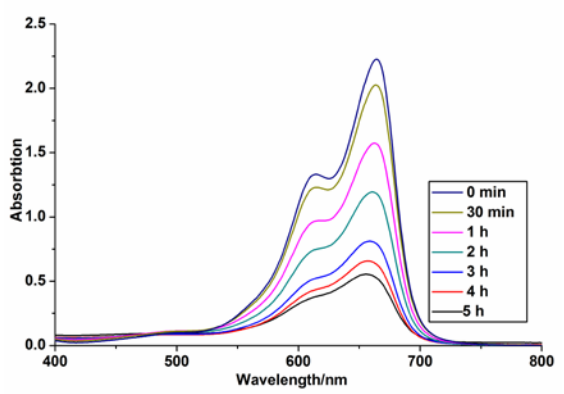
(b)


Absorbtion
Wavelength/nm
0 min
30 min
1 h
2 h
3 h
4 h
5 h

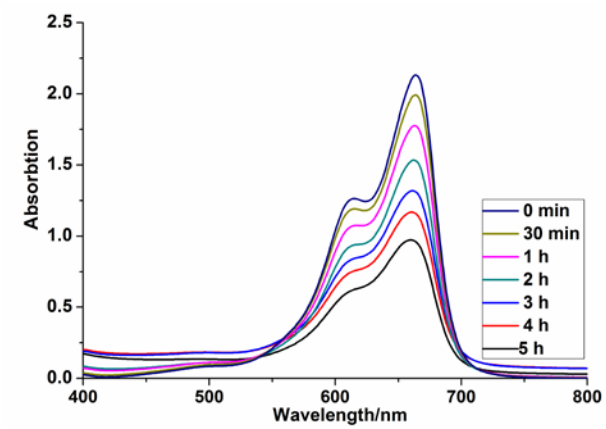
(c)


Absorbtion
Wavelength/nm
0 min
30 min
1 h
2 h
3 h
4 h
5 h

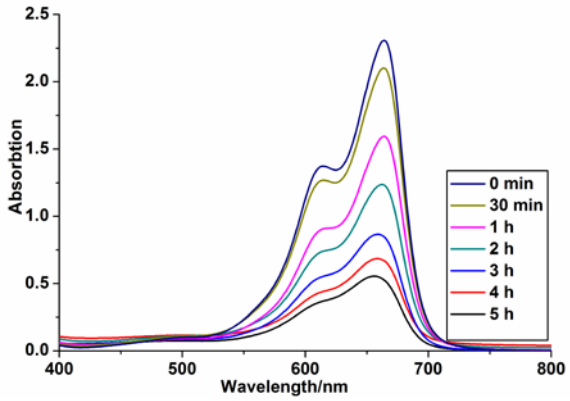
(d)



(e)



(f)



(g)

Fig. S9 UV-Vis absorption spectra of the MB solutions degraded by different photocatalysts under UV irradiation at different time intervals: (a) **1**; (b) **3**; (c) **4**; (d) **5**; (e) **6**; (f) **7** and (g) **8**.