Supplementary Material (ESI) for CrystEngComm
This journal is © The Royal Society of Chemistry

Substituent position-induced diverse architectures of polyoxovanadate-based hybrid materials constructed from linear trinuclear transition metal complex and hexanuclear $[V_6O_{18}]^{6-}$ cluster

Xiu-Li Wang,* Chun-Hua Gong, Ju-Wen Zhang, Li-Li Hou, Jian Luan, Guo-Cheng Liu

Department of Chemistry, Bohai University, Liaoning Province Silicon Materials Engineering Technology Research Centre, Jinzhou, 121000, P. R. China

Table S1 Selected bond distances (Å) and angles (°) for compounds **1**–**4**.

1			
Ni(1)–O(1)	2.053(4)	V(1)–O(1)	1.645(2)
Ni(1)–N(1)	2.0732(19)	V(1)–O(2)	1.795(2)
Ni(2)–N(2)	2.1204	V(1)–O(3)	1.620(4)
N(1)–Ni(1)–N(1)#2	92.10(15)	O(1)–V(1)–O(2)	112.16(11)
N(1)–Ni(1)–O(1)#1	90.12(12)	O(1)–V(1)–O(2)#3	110.62(13)
N(1)#1–Ni(1)–O(1)	177.48(12)	O(2)–V(1)–O(2)#3	110.76(6)
N(1)–Ni(1)–O(1)	89.01(12)	O(3)–V(1)–O(2)#3	108.46(19)
O(1)#1–Ni(1)–O(1)	88.72(8)	O(3)–V(1)–O(1)	107.91(19)
N(2)#4–Ni(2)–N(2)	180.00(18)	O(3)–V(1)–O(2)	106.75(18)
N(2)#5–Ni(2)–N(2)	90.16(7)		
N(2)–Ni(2)–N(2)#2	89.84(7)		
Symmetry codes: #1 $-x + y, -x, z$; #2 $-y, x - y, z$; #3 $x - y, x, -z - 1$; #4 $-x, -y, -z$; #5 $x - y, x, -z$.			
2			
Ni(1)–O(1)	2.069(3)	V(1)–O(1)	1.641(2)
Ni(1)–O(5)	2.056(2)	V(1)–O(2)	1.788(3)
Ni(1)–O(8)	2.029(3)	V(1)–O(3)	1.795(3)
Ni(1)–N(1)	2.062(3)	V(1)–O(4)	1.623(3)
Ni(1)–N(4)	2.058(3)	V(2)–O(5)	1.658(2)
Ni(1)–N(8)	2.052(3)	V(2)–O(6)	1.770(3)
Ni(2)–N(2)	2.106(3)	V(2)–O(7)	1.614(3)
Ni(2)–N(3)	2.104(3)	V(2)–O(2)#2	1.785(3)
Ni(2)–N(7)	2.115(3)	V(3)–O(8)	1.640(3)
		V(3)–O(9)	1.606(3)
		V(3)–O(3)#4	1.791(3)
		V(3)–O(6)#3	1.781(3)

* Corresponding author. Tel: +86-416-3400158 *E-mail address*: wangxiuli@bhu.edu.cn (X.-L. Wang)

O(8)–Ni(1)–N(8)	94.01(11)	O(4)–V(1)–O(1)	109.06(15)
O(8)–Ni(1)–O(5)	89.49(10)	O(4)–V(1)–O(2)	108.32(17)
N(8)–Ni(1)–O(5)	90.05(10)	O(1)–V(1)–O(2)	109.35(14)
O(8)–Ni(1)–N(4)	171.30(11)	O(4)–V(1)–O(3)	109.38(14)
N(8)–Ni(1)–N(4)	94.22(11)	O(1)–V(1)–O(3)	110.11(13)
O(5)–Ni(1)–N(4)	87.70(10)	O(2)–V(1)–O(3)	110.58(13)
O(8)–Ni(1)–N(1)	93.27(11)	O(7)–V(2)–O(5)	109.96(14)
N(8)–Ni(1)–N(1)	86.26(11)	O(7)–V(2)–O(6)	110.66(18)
O(5)–Ni(1)–N(1)	175.54(10)	O(5)–V(2)–O(6)	107.08(13)
N(4)–Ni(1)–N(1)	90.06(11)	O(7)–V(2)–O(2)#2	107.35(16)
O(8)–Ni(1)–O(1)	84.05(11)	O(5)–V(2)–O(2)#2	110.90(12)
N(8)–Ni(1)–O(1)	177.88(11)	O(6)–V(2)–O(2)#2	110.93(17)
O(5)–Ni(1)–O(1)	90.79(10)	O(9)–V(3)–O(8)	107.45(18)
N(4)–Ni(1)–O(1)	87.76(11)	O(9)–V(3)–O(6)#3	108.6(2)
N(1)–Ni(1)–O(1)	92.98(11)	O(8)–V(3)–O(6)#3	108.59(16)
N(3)–Ni(2)–N(3)#1	180	O(9)–V(3)–O(3)#4	110.49(17)
N(3)–Ni(2)–N(2)	90.44(11)	O(8)–V(3)–O(3)#4	110.10(13)
N(3)#1–Ni(2)–N(2)	89.56(11)	O(6)#3–V(3)–O(3)#4	111.52(14)
N(2)–Ni(2)–N(2)#1	179.999(1)		
N(3)–Ni(2)–N(7)	90.74(10)		
N(2)–Ni(2)–N(7)	88.96(11)		
N(3)–Ni(2)–N(7)#1	89.26(10)		
N(2)–Ni(2)–N(7)#1	91.04(11)		
N(7)–Ni(2)–N(7)#1	180		

Symmetry codes: #1 –*x*, –*y* + 1, –*z*; #2 –*x*, –*y* + 1, –*z* + 1; #3 –*x* + 1, –*y* + 1, –*z* + 1; #4 –*x* + 1, –*y* + 2, –*z* + 1.

3

Co(1)–O(1)	2.058(3)	V(1)–O(1)	1.660(3)
Co(1)–O(5)#1	2.063(3)	V(1)–O(2)	1.619(4)
Co(1)–O(9)#2	2.085(3)	V(1)–O(3)	1.773(3)
Co(1)–N(1)	2.120(4)	V(1)–O(8)#3	1.783(3)
Co(1)–N(5)	2.119(3)	V(2)–O(3)	1.775(3)
Co(1)–N(9)	2.122(3)	V(2)–O(4)	1.607(4)
Co(2)–N(2)	2.160(3)	V(2)–O(5)	1.640(3)
Co(2)–N(6)	2.147(3)	V(2)–O(6)	1.795(3)
Co(2)–N(10)	2.153(3)	V(3)–O(6)	1.792(3)
		V(3)–O(7)	1.616(3)
		V(3)–O(8)	1.789(3)
		V(3)–O(9)	1.643(3)
O(1)–Co(1)–O(5)#1	90.62(13)	O(2)–V(1)–O(1)	109.55(18)
O(1)–Co(1)–O(9)#2	91.95(13)	O(2)–V(1)–O(3)	111.0(2)
O(5)#1–Co(1)–O(9)#2	84.10(14)	O(1)–V(1)–O(3)	107.20(16)
O(1)–Co(1)–N(5)	87.91(13)	O(2)–V(1)–O(8)#3	107.50(19)
O(5)#1–Co(1)–N(5)	171.56(14)	O(1)–V(1)–O(8)#3	110.87(16)

O(9)#2–Co(1)–N(5)	87.64(14)	O(3)–V(1)–O(8)#3	110.7(2)
O(1)–Co(1)–N(1)	89.41(13)	O(4)–V(2)–O(5)	107.1(2)
O(5)#1–Co(1)–N(1)	94.72(14)	O(4)–V(2)–O(3)	108.7(2)
O(9)#2–Co(1)–N(1)	178.21(14)	O(5)–V(2)–O(3)	108.8(2)
N(5)–Co(1)–N(1)	93.58(13)	O(4)–V(2)–O(6)	110.7(2)
O(1)–Co(1)–N(9)	173.36(12)	O(5)–V(2)–O(6)	109.69(17)
O(5)#1–Co(1)–N(9)	93.33(14)	O(3)–V(2)–O(6)	111.74(17)
O(9)#2–Co(1)–N(9)	93.77(14)	O(7)–V(3)–O(9)	108.92(19)
N(5)–Co(1)–N(9)	88.95(14)	O(7)–V(3)–O(8)	108.0(2)
N(1)–Co(1)–N(9)	84.95(14)	O(9)–V(3)–O(8)	109.55(18)
N(6)–Co(2)–N(6)#4	180	O(7)–V(3)–O(6)	109.54(18)
N(6)–Co(2)–N(10)	90.52(13)	O(9)–V(3)–O(6)	110.10(17)
N(6)–Co(2)–N(10)#4	89.48(13)	O(8)–V(3)–O(6)	110.68(16)
N(10)–Co(2)–N(10)#4	180.000(1)		
N(6)–Co(2)–N(2)	90.82(13)		
N(10)–Co(2)–N(2)	88.29(13)		
N(6)–Co(2)–N(2)#4	89.18(13)		
N(10)–Co(2)–N(2)#4	91.71(13)		
N(2)–Co(2)–N(2)#4	180		

Symmetry codes: #1 $–x + 2, –y, –z + 1$; #2 $x, y + 1, z$; #3 $–x + 1, –y – 1, –z + 1$; #4 $–x + 1, –y, –z$.

4

Zn(1)–O(1)	2.0913(19)	V(1)–O(1)#1	1.6491(19)
Zn(1)–O(2)	2.123(2)	V(1)–O(3)	1.608(2)
Zn(1)–O(5)	2.052(2)	V(1)–O(4)	1.774(2)
Zn(1)–N(1)	2.144(2)	V(1)–O(8)#2	1.785(2)
Zn(1)–N(5)	2.138(2)	V(2)–O(4)	1.769(2)
Zn(1)–N(9)	2.138(2)	V(2)–O(5)	1.645(2)
Zn(2)–N(2)	2.163(2)	V(2)–O(6)	1.604(3)
Zn(2)–N(6)	2.167(2)	V(2)–O(7)	1.790(2)
Zn(2)–N(10)	2.185(2)	V(3)–O(2)#4	1.640(2)
		V(3)–O(7)	1.793(2)
		V(3)–O(8)	1.785(2)
		V(3)–O(9)	1.625(2)
O(5)–Zn(1)–O(1)	90.71(9)	O(3)–V(1)–O(1)#1	109.48(12)
O(5)–Zn(1)–O(2)	83.20(10)	O(3)–V(1)–O(4)	111.40(16)
O(1)–Zn(1)–O(2)	91.58(8)	O(1)#1–V(1)–O(4)	106.82(12)
O(5)–Zn(1)–N(9)	96.45(9)	O(3)–V(1)–O(8)#2	107.57(14)
O(1)–Zn(1)–N(9)	89.16(8)	O(1)#1–V(1)–O(8)#2	110.97(11)
O(2)–Zn(1)–N(9)	179.18(8)	O(4)–V(1)–O(8)#2	110.62(15)
O(5)–Zn(1)–N(5)	169.14(10)	O(6)–V(2)–O(5)	107.62(15)
O(1)–Zn(1)–N(5)	86.91(8)	O(6)–V(2)–O(4)	108.64(18)
O(2)–Zn(1)–N(5)	86.27(9)	O(5)–V(2)–O(4)	108.54(14)
N(9)–Zn(1)–N(5)	94.12(9)	O(6)–V(2)–O(7)	110.62(15)

O(5)–Zn(1)–N(1)	94.45(9)	O(5)–V(2)–O(7)	109.81(12)
O(1)–Zn(1)–N(1)	173.01(8)	O(4)–V(2)–O(7)	111.50(12)
O(2)–Zn(1)–N(1)	93.71(9)	O(9)–V(3)–O(2)#4	108.68(13)
N(9)–Zn(1)–N(1)	85.58(9)	O(9)–V(3)–O(8)	107.88(15)
N(5)–Zn(1)–N(1)	88.87(9)	O(2)#4–V(3)–O(8)	109.73(12)
N(2)–Zn(2)–N(2)#3	180	O(9)–V(3)–O(7)	110.01(13)
N(2)–Zn(2)–N(6)#3	89.43(9)	O(2)#4–V(3)–O(7)	109.99(11)
N(2)–Zn(2)–N(6)	90.57(9)	O(8)–V(3)–O(7)	110.50(11)
N(6)#3–Zn(2)–N(6)	180		
N(2)–Zn(2)–N(10)#3	91.43(9)		
N(6)–Zn(2)–N(10)#3	89.03(9)		
N(2)–Zn(2)–N(10)	88.57(9)		
N(6)–Zn(2)–N(10)	90.97(9)		
N(10)#3–Zn(2)–N(10)	180		

Symmetry codes: #1 *–x* – 1, *–y* + 1, *–z* – 1; #2 *–x* – 2, *–y*, *–z* – 1; #3 *–x*, *–y* + 1, *–z*; #4 *–x* – 1, *–y*, *–z* – 1.

Table S2 Selected hydrogen bonding geometry (Å, °) for compound **1**.

D–H···A	D–H	H···A	D···A	D–H···A
N(4)–H(4B)···O(3)	0.86	2.43	2.80	107

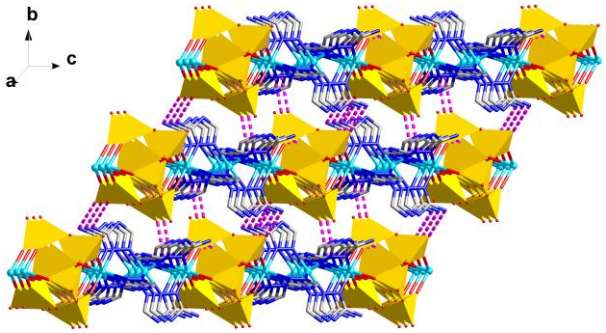

Fig. S1 The 3D supramolecular framework formed by the hydrogen bonding interactions in **1**.

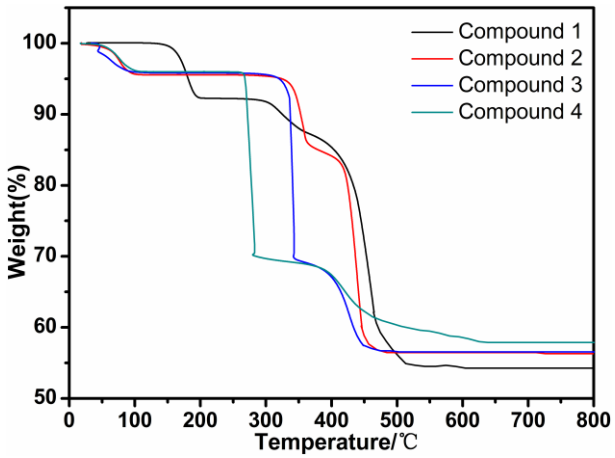

Fig. S2 TG curves of compounds **1**–**4**.

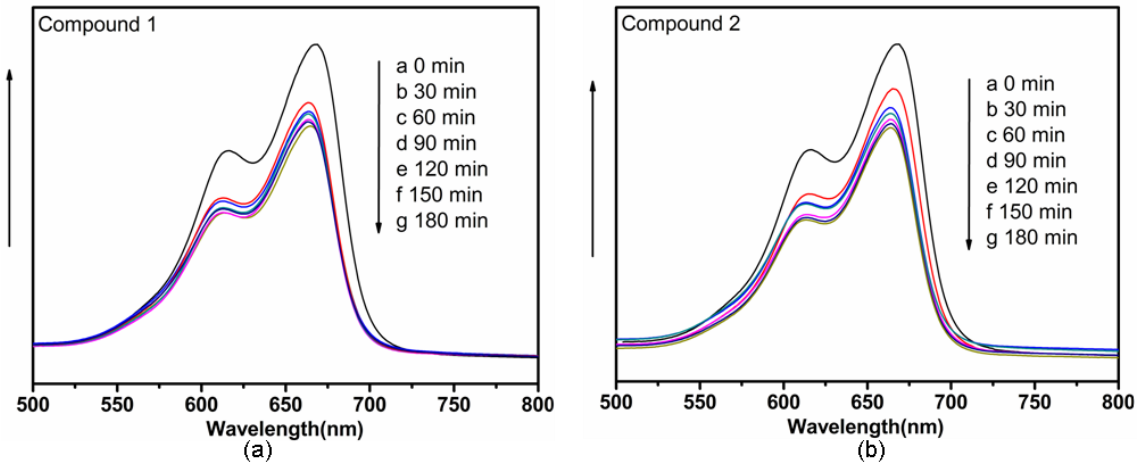

Fig. S3 Absorption spectra of the MB solution during the decomposition reaction under UV irradiation with the presence of compounds **1** (a) and **2** (b).

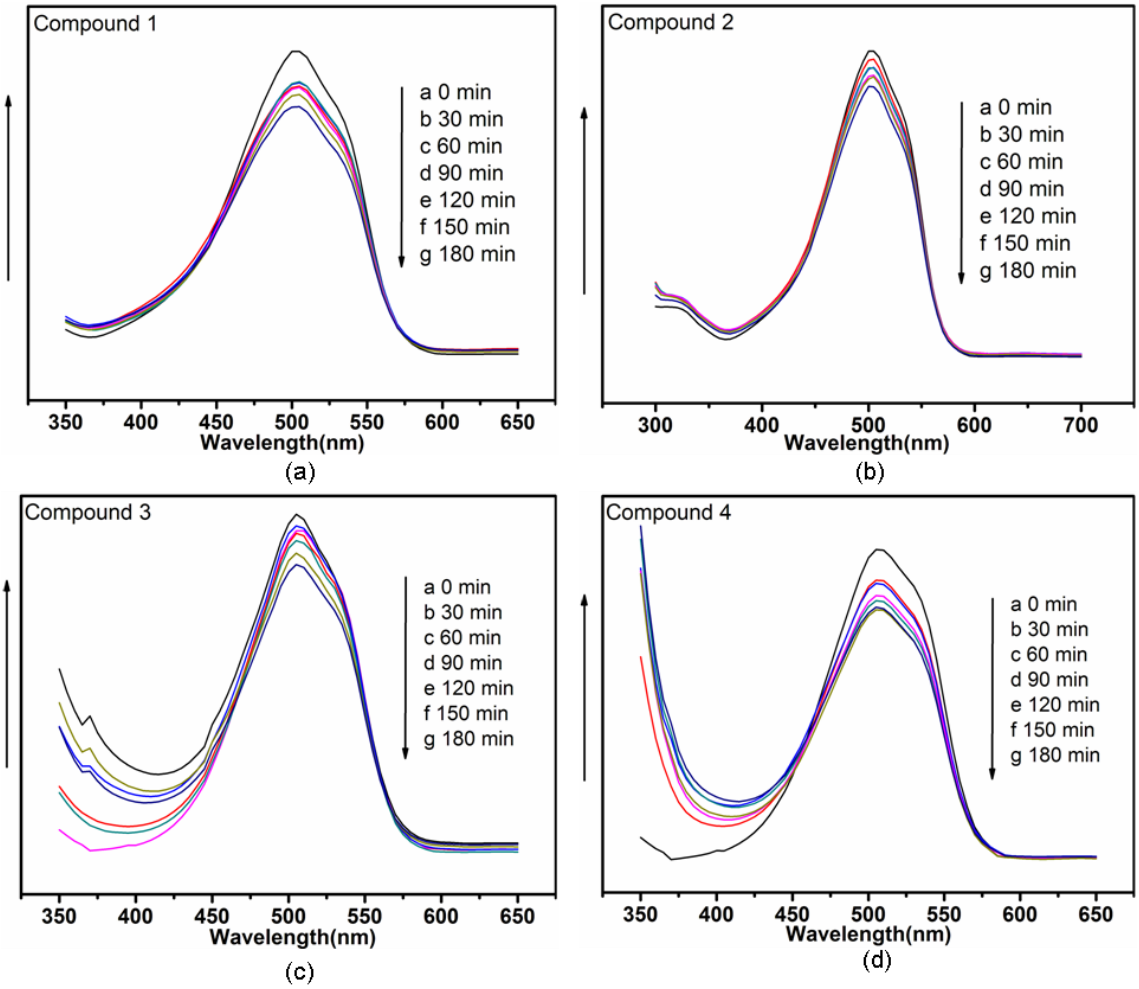

Fig. S4 Absorption spectra of the MO solution during the decomposition reaction under UV irradiation with the presence of compounds **1** (a), **2** (b), **3** (c), **4** (d).

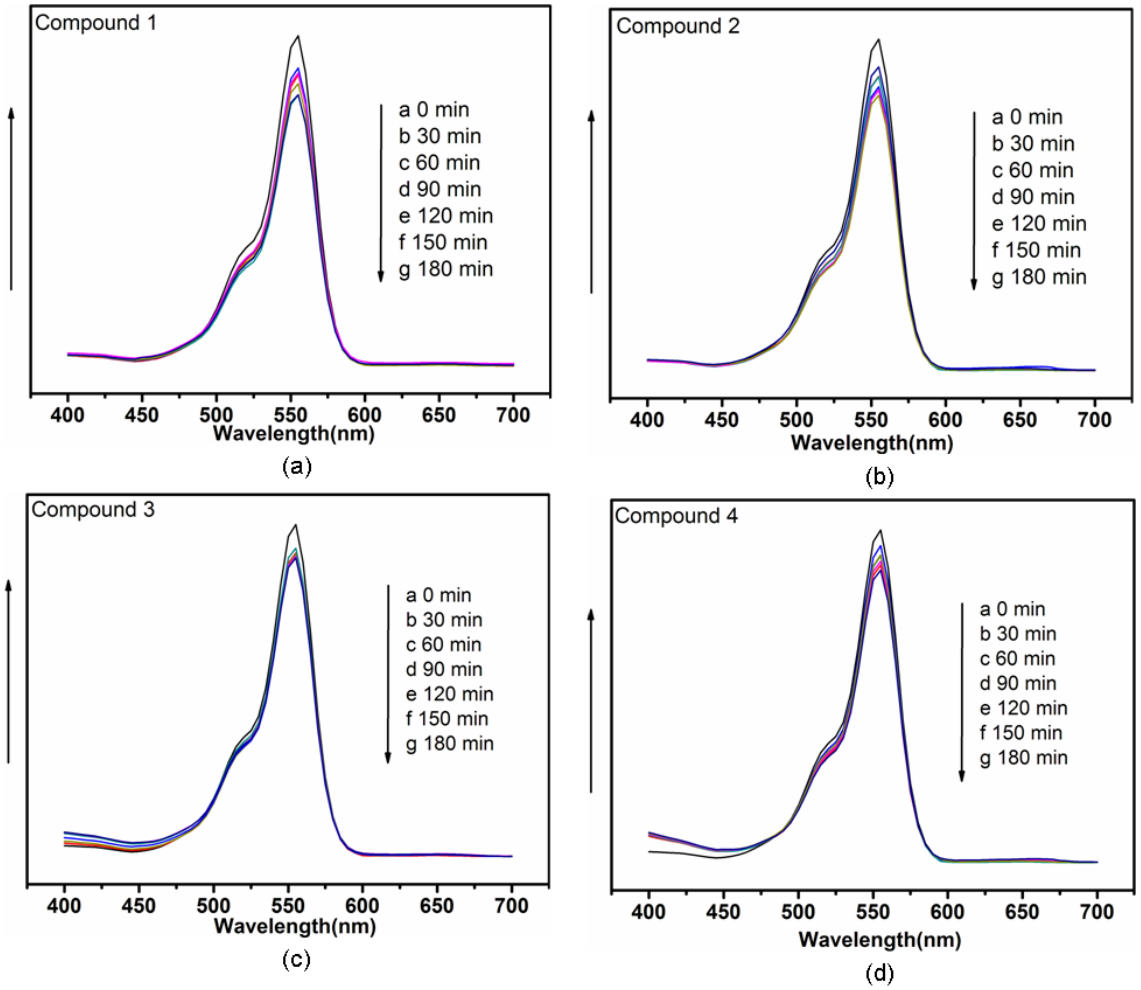

Fig. S5 Absorption spectra of the RhB solution during the decomposition reaction under UV irradiation with the presence of compounds **1** (a), **2** (b), **3** (c), **4** (d).

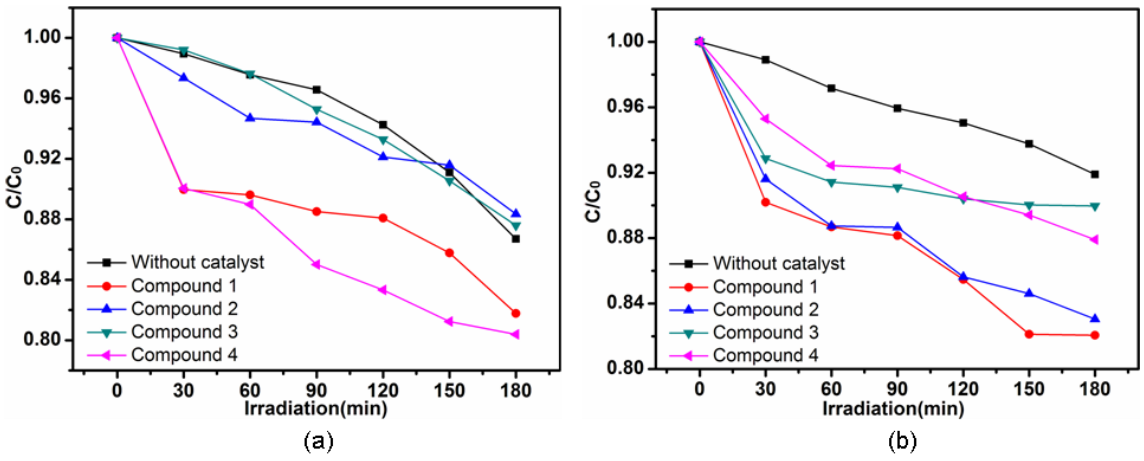

Fig. S6 Photocatalytic decomposition rate of the MO solution (a) and RhB solution (b) under UV irradiation with the use of compounds **1**–**4** and without catalyst in the same conditions.

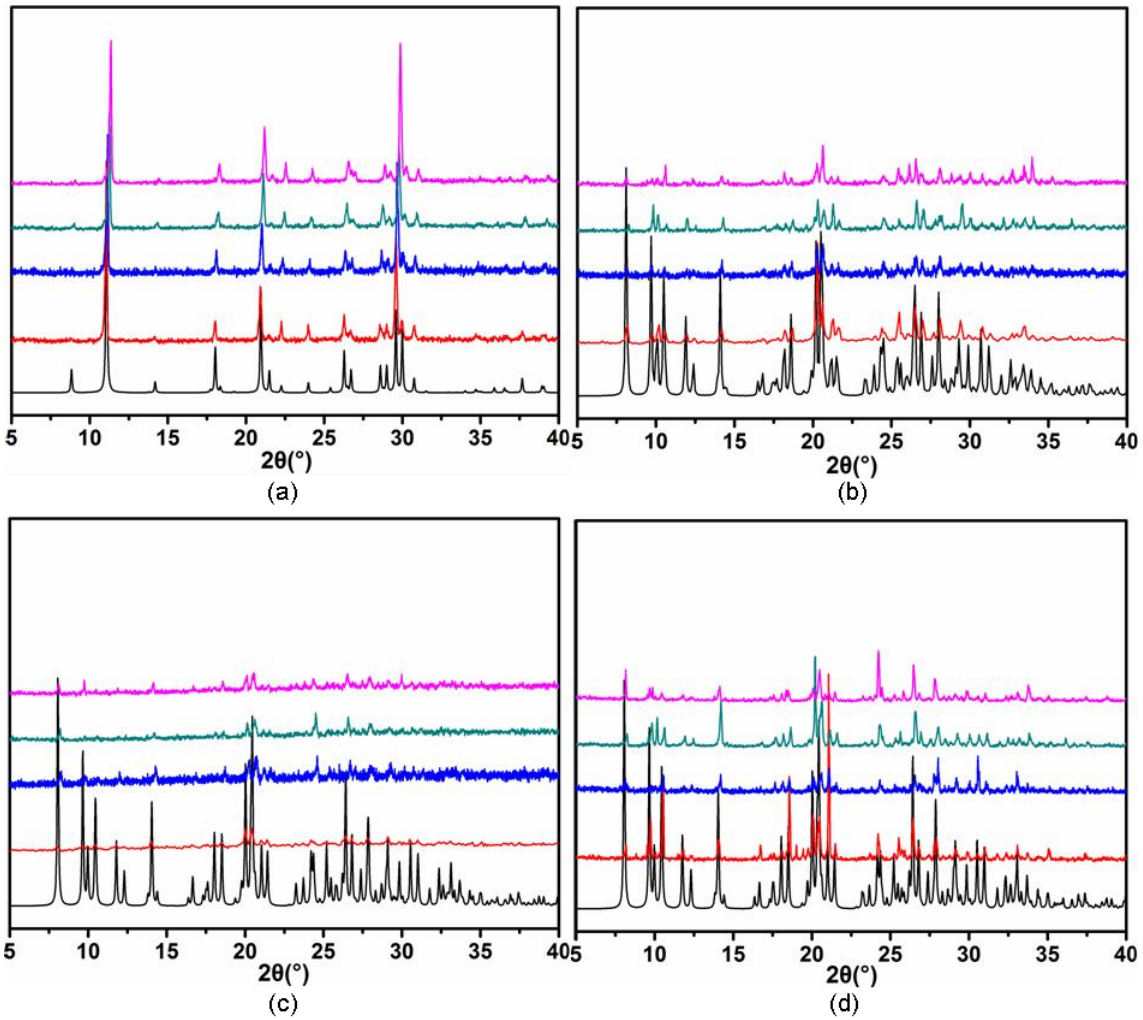

Fig. S7 X-ray powder diffraction patterns of compounds **1** (a), **2** (b), **3** (c) and **4** (d) simulated from single-crystal X-ray data (black line), as-synthesized (red line) and after the photocatalytic reaction-MB (blue line), MO (dark cyan line) and RhB (magenta line).