Supplementary Material (ESI) for *CrystEngComm*
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Polyoxometalate-directed assembly of various multinuclear metal–organic complexes with 4-amino-1,2,4-triazole and selective photocatalysis for organic dyes degradation

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Table S1 Selected bond distances (Å) and angles (°) for compounds **1**–**5**.

Compound **1**			
Cu(1)–N(1)	1.986(4)	Cu(2)–N(9)	1.988(5)
Cu(1)–N(5)	2.025(4)	Cu(2)–N(6)	2.017(5)
Cu(1)–O(1)	2.441(3)	Cu(2)–N(2)	2.032(5)
Cu(2)–O(1W)	2.313(5)	Cu(2)–O(1)	2.590(2)
Cu(2)–N(13)	1.980(5)		
N(1)–Cu(1)–N(1)#1	180.0	N(9)–Cu(2)–N(2)	87.6(2)
N(1)–Cu(1)–N(5)	90.03(18)	N(6)–Cu(2)–N(2)	87.53(19)
N(13)–Cu(2)–N(9)	91.1(2)	N(13)–Cu(2)–O(1W)	87.5(2)
N(13)–Cu(2)–N(6)	94.2(2)	N(9)–Cu(2)–O(1W)	94.9(2)
N(9)–Cu(2)–N(6)	170.3(2)	N(6)–Cu(2)–O(1W)	93.5(2)
N(13)–Cu(2)–N(2)	177.0(2)	N(2)–Cu(2)–O(1W)	89.9(2)
Symmetry code: #1 $-x+1, -y+2, -z+1$.			
Compound **2**			
Cu(1)–N(5)#1	1.96(3)	Cu(1)–N(6)	2.00(3)
Cu(1)–N(9)	1.98(4)	Cu(1)–O(1W)	2.40(4)
Cu(1)–N(2)	1.99(4)	Cu(1)–O(16)	2.46(8)
N(5)#1–Cu(1)–N(9)	171.8(16)	N(2)–Cu(1)–N(6)	177.4(16)
N(5)#1–Cu(1)–N(2)	89.9(16)	N(5)#1–Cu(1)–O(1W)	82.8(12)
N(9)–Cu(1)–N(2)	92.3(17)	N(9)–Cu(1)–O(1W)	104.9(14)
N(5)#1–Cu(1)–N(6)	87.9(13)	N(2)–Cu(1)–O(1W)	94.0(13)
N(9)–Cu(1)–N(6)	90.1(15)	N(6)–Cu(1)–O(1W)	84.5(12)
Symmetry code: #1 $-x+1/2, y, -z$			
Compound **3**			
Cu(1)–O(25)	1.945(6)	Cu(2)–N(2)	2.049(8)
Cu(1)–N(1)	1.980(8)	Cu(2)–N(14)#2	2.286(8)
Cu(1)–O(1)	2.397(7)	Cu(3)–N(13)	2.012(8)
Cu(2)–O(25)	1.929(6)	Cu(3)–N(9)	2.047(8)
Cu(2)–N(5)	1.998(8)	Cu(3)–N(6)	2.447(9)
Cu(2)–N(10)#2	2.028(8)		

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O(25)–Cu(1)–N(1)	87.6(3)	O(25)–Cu(2)–N(14)#2	103.9(3)
O(25)–Cu(1)–N(1)#1	92.4(3)	N(5)–Cu(2)–N(14)#2	90.4(3)
O(25)–Cu(1)–O(1)	92.1(3)	N(10)#2–Cu(2)–N(14)#2	90.4(3)
N(1)–Cu(1)–O(1)	85.4(3)	N(2)–Cu(2)–N(14)#2	91.7(3)
O(25)–Cu(1)–O(1)#1	87.9(3)	N(13)–Cu(3)–N(9)	91.6(3)
N(1)–Cu(1)–O(1)#1	94.6(3)	N(13)–Cu(3)–N(9)#2	88.4(3)
O(25)–Cu(2)–N(5)	165.7(3)	N(13)–Cu(3)–N(6)	88.9(3)
O(25)–Cu(2)–N(10)#2	88.0(3)	N(9)–Cu(3)–N(6)	92.2(3)
N(5)–Cu(2)–N(10)#2	93.1(3)	N(13)#2–Cu(3)–N(6)#2	88.9(3)
O(25)–Cu(2)–N(2)	86.4(3)	N(13)–Cu(3)–N(6)#2	91.1(3)
N(5)–Cu(2)–N(2)	92.1(3)	N(9)–Cu(3)–N(6)#2	87.8(3)
N(10)#2–Cu(2)–N(2)	174.3(3)		
Symmetry codes: #1 $-x+1, -y, -z+1$; #2 $-x+2, -y, -z$.			
Compound **4**			
Cu(1)–N(10)	1.945(6)	Cu(2)–O(7W)	2.045(5)
Cu(1)–N(1)	1.951(6)	Cu(2)–O(9W)	2.314(6)
Cu(1)–O(1)	1.996(5)	Cu(2)–O(10W)	2.327(8)
Cu(1)–O(7W)	1.998(5)	Cu(3)–N(2)	1.985(6)
Cu(1)–O(13)#1	2.310(5)	Cu(3)–O(27)	1.946(5)
Cu(1)–O(20)	2.782(5)	Cu(3)–O(7W)	1.989(5)
Cu(2)–N(6)	1.969(6)	Cu(3)–N(5)	1.993(6)
Cu(2)–N(9)	1.976(6)	Cu(3)–O(12)#2	2.387(5)
Cu(2)–O(8W)	2.020(7)		
N(10)–Cu(1)–N(1)	176.6(2)	O(8W)–Cu(2)–O(9W)	88.6(3)
N(10)–Cu(1)–O(1)	89.8(2)	O(7W)–Cu(2)–O(9W)	88.6(2)
N(1)–Cu(1)–O(1)	93.5(2)	N(6)–Cu(2)–O(10W)	89.7(3)
N(10)–Cu(1)–O(7W)	88.7(2)	N(9)–Cu(2)–O(10W)	90.9(3)
N(1)–Cu(1)–O(7W)	87.9(2)	O(8W)–Cu(2)–O(10W)	88.3(3)
O(1)–Cu(1)–O(7W)	168.2(2)	O(7W)–Cu(2)–O(10W)	94.5(3)
N(10)–Cu(1)–O(13)#1	91.8(2)	O(9W)–Cu(2)–O(10W)	176.8(3)
N(1)–Cu(1)–O(13)#1	88.9(2)	O(27)–Cu(3)–N(2)	94.3(2)
O(1)–Cu(1)–O(13)#1	89.92(19)	O(27)–Cu(3)–O(7W)	145.9(2)
O(7W)–Cu(1)–O(13)#1	101.87(19)	N(2)–Cu(3)–O(7W)	88.9(2)
N(6)–Cu(2)–N(9)	176.5(3)	O(27)–Cu(3)–N(5)	96.5(2)
N(6)–Cu(2)–O(8W)	92.8(3)	N(2)–Cu(3)–N(5)	164.6(2)
N(9)–Cu(2)–O(8W)	90.7(3)	O(7W)–Cu(3)–N(5)	88.3(2)
N(6)–Cu(2)–O(7W)	87.1(2)	O(27)–Cu(3)–O(12)#2	90.84(19)
N(9)–Cu(2)–O(7W)	89.4(2)	N(2)–Cu(3)–O(12)#2	85.2(2)
O(8W)–Cu(2)–O(7W)	177.3(3)	O(7W)–Cu(3)–O(12)#2	123.30(18)
N(6)–Cu(2)–O(9W)	89.5(3)	N(5)–Cu(3)–O(12)#2	83.7(2)
N(9)–Cu(2)–O(9W)	90.1(3)		
Symmetry codes: #1 $x-1, y, z$; #2 $x-1, -y+1/2, z-1/2$.			
Compound **5**			
Cu(1)–O(1)	1.940(3)	Cu(2)–O(2W)	2.383(4)

Cu(1)–N(5)	1.966(4)	Cu(2)–O(8)	2.488(1)
Cu(1)–N(1)	1.983(4)	Cu(3)–O(13)#3	1.897(3)
Cu(1)–O(15)	1.995(3)	Cu(3)–N(10)	1.972(4)
Cu(1)–O(12)#1	2.225(4)	Cu(3)–N(6)	1.979(4)
Cu(2)–O(5)#2	1.936(3)	Cu(3)–O(15)	2.000(3)
Cu(2)–N(9)	1.982(4)	Cu(3)–O(16)	2.468(1)
Cu(2)–N(2)	1.991(4)	Cu(3)–O(14)	2.659(2)
Cu(2)–O(15)	2.025(3)		
V(1)–O(2)	1.619(4)	V(3)–O(9)	1.789(4)
V(1)–O(1)	1.680(4)	V(3)–O(6)	1.802(3)
V(1)–O(11)	1.775(4)	V(4)–O(16)	1.616(4)
V(1)–O(3)	1.789(4)	V(4)–O(13)	1.663(3)
V(2)–O(4)	1.606(4)	V(4)–O(10)	1.765(3)
V(2)–O(5)	1.676(3)	V(4)–O(9)	1.806(3)
V(2)–O(3)	1.767(4)	V(5)–O(14)	1.637(3)
V(2)–O(6)	1.773(3)	V(5)–O(12)	1.642(4)
V(3)–O(7)	1.630(4)	V(5)–O(10)	1.789(3)
V(3)–O(8)	1.647(4)	V(5)–O(11)#4	1.810(4)
O(1)–Cu(1)–N(5)	90.43(16)	O(5)#2–Cu(2)–O(15)	170.71(15)
O(1)–Cu(1)–N(1)	91.70(15)	N(9)–Cu(2)–O(15)	89.07(14)
N(5)–Cu(1)–N(1)	170.66(17)	N(2)–Cu(2)–O(15)	87.48(14)
O(1)–Cu(1)–O(15)	165.73(14)	O(5)#2–Cu(2)–O(2W)	97.56(15)
N(5)–Cu(1)–O(15)	89.27(14)	N(9)–Cu(2)–O(2W)	85.91(16)
N(1)–Cu(1)–O(15)	86.43(14)	N(2)–Cu(2)–O(2W)	99.96(16)
O(1)–Cu(1)–O(12)#1	93.77(14)	O(15)–Cu(2)–O(2W)	91.64(14)
N(5)–Cu(1)–O(12)#1	97.11(16)	O(13)#3–Cu(3)–N(10)	91.89(16)
N(1)–Cu(1)–O(12)#1	91.82(16)	O(13)#3–Cu(3)–N(6)	91.20(16)
O(15)–Cu(1)–O(12)#1	100.42(14)	N(10)–Cu(3)–N(6)	166.44(17)
O(5)#2–Cu(2)–N(9)	92.86(16)	O(13)#3–Cu(3)–O(15)	171.09(14)
O(5)#2–Cu(2)–N(2)	89.65(16)	N(10)–Cu(3)–O(15)	89.78(15)
N(9)–Cu(2)–N(2)	173.26(17)	N(6)–Cu(3)–O(15)	89.20(14)
O(2)–V(1)–O(1)	107.4(2)	O(7)–V(3)–O(6)	106.13(18)
O(2)–V(1)–O(11)	109.5(2)	O(8)–V(3)–O(6)	111.41(19)
O(1)–V(1)–O(11)	110.49(18)	O(9)–V(3)–O(6)	112.29(18)
O(2)–V(1)–O(3)	108.6(2)	O(16)–V(4)–O(13)	111.95(19)
O(1)–V(1)–O(3)	107.45(18)	O(16)–V(4)–O(10)	110.40(19)
O(11)–V(1)–O(3)	113.19(19)	O(13)–V(4)–O(10)	109.19(17)
O(4)–V(2)–O(5)	108.4(2)	O(16)–V(4)–O(9)	108.88(19)
O(4)–V(2)–O(3)	108.9(2)	O(13)–V(4)–O(9)	106.84(18)
O(5)–V(2)–O(3)	112.09(19)	O(10)–V(4)–O(9)	109.50(18)
O(4)–V(2)–O(6)	110.4(2)	O(14)–V(5)–O(12)	108.95(19)
O(5)–V(2)–O(6)	107.71(19)	O(14)–V(5)–O(10)	108.72(18)
O(3)–V(2)–O(6)	109.36(18)	O(12)–V(5)–O(10)	109.84(18)
O(7)–V(3)–O(8)	107.8(2)	O(14)–V(5)–O(11)#4	110.30(19)

O(7)–V(3)–O(9)	106.87(19)	O(12)–V(5)–O(11)#4	109.80(19)
O(8)–V(3)–O(9)	111.9(2)	O(10)–V(5)–O(11)#4	109.21(18)

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

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

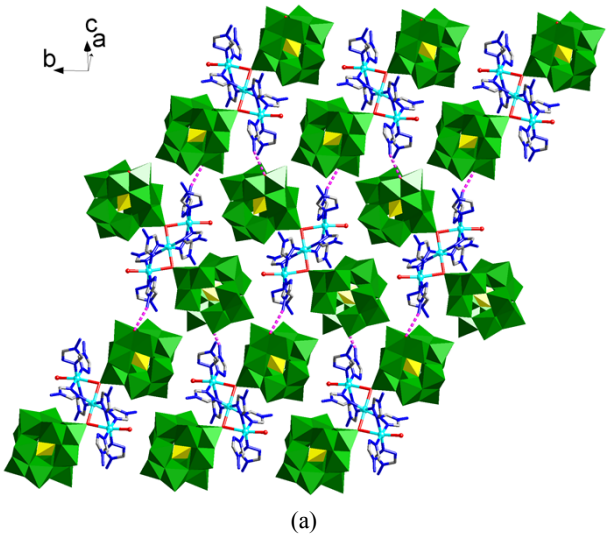
D–H···A	D–H	H···A	D···A	D–H···A
N(16)–H(16B)···O(27)	0.87	2.47	2.874	109
N(12)–H(12B)···O(26)	0.87	2.27	3.012	143

Table S3 Selected hydrogen bonding geometry (Å, º) for compound **3**.

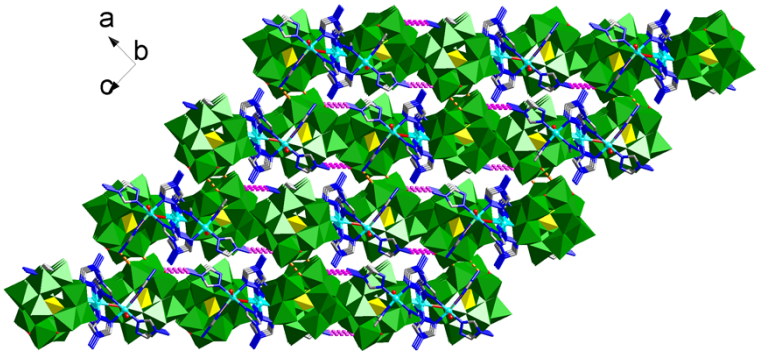
D–H···A	D–H	H···A	D···A	D–H···A
N(12)–H(12A)···O(6)	0.89	2.16	2.994	156
C(5)–H(5)···O(9)	0.93	2.20	3.131	175

Table S4 Selected hydrogen bonding geometry (Å, º) for compound **4**.

D–H···A	D–H	H···A	D···A	D–H···A
N(8)–H(8A)···O(16)	0.86	2.12	2.908	153

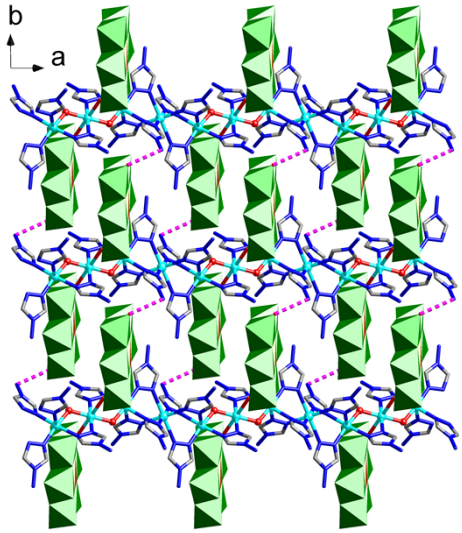


(a)

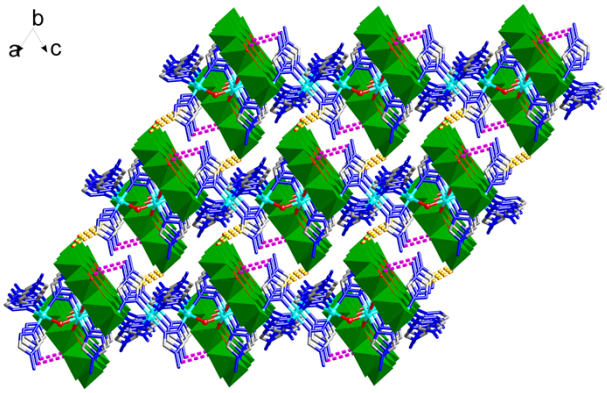


(b)

Fig. S1 (a) View of 2D layer formed by intermolecular hydrogen bonds in **1**. (b) View of 3D supramolecular skeleton formed by intermolecular hydrogen bonds in **1**. (H-bond codes: N(16)–H(16B)···O(27), pink bond; N(12)–H(12B)···O(26), yellow bond)



(a)



(b)

Fig. S2 (a) View of 2D supramolecular layer formed through H-bond interactions in **3**. (H-bond code: N(12)–H(12A)···O(6), pink bond); (b) View of 3D supramolecular framework of **3** through hydrogen bonds. (H-bond codes: N(12)–H(12A)···O(6), pink bond; C(5)–H(5)···O(9), yellow bond)

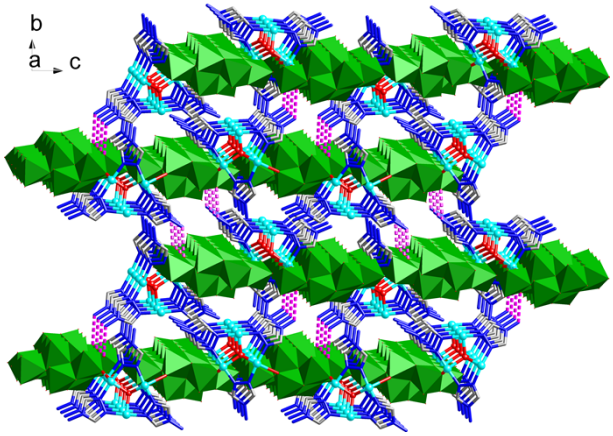


Fig. S3 View of 3D supramolecular framework of **4** formed through hydrogen-bonding interactions. (H-bond code: N(8)–H(8A)···O(16), pink bond)

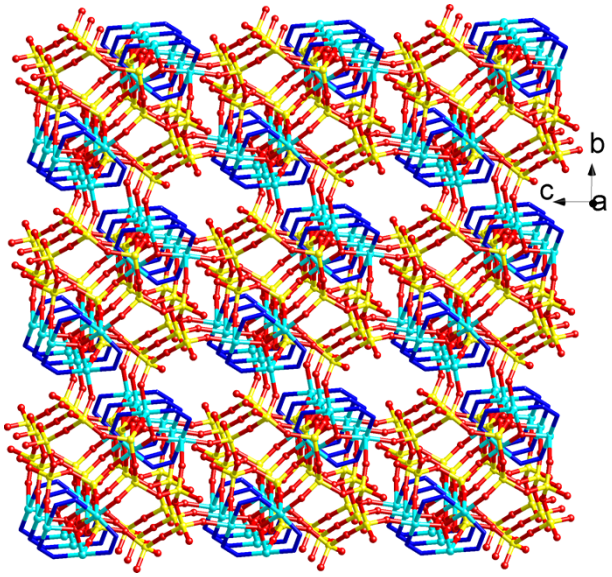
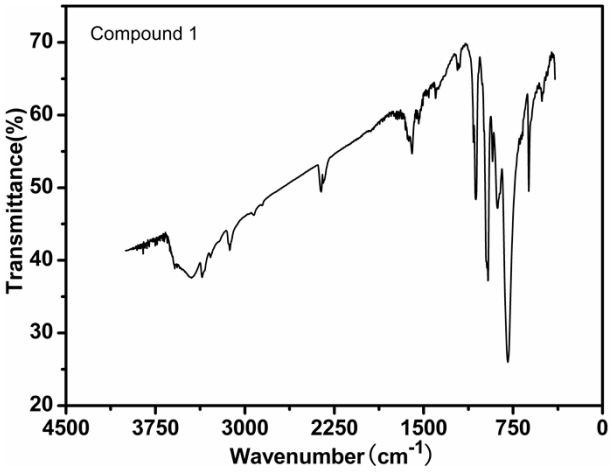
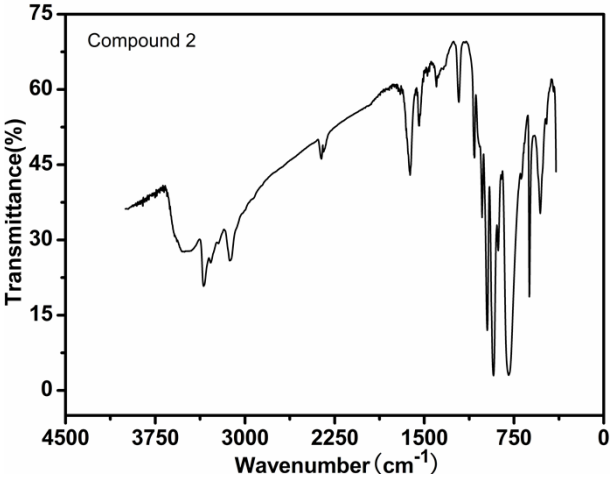


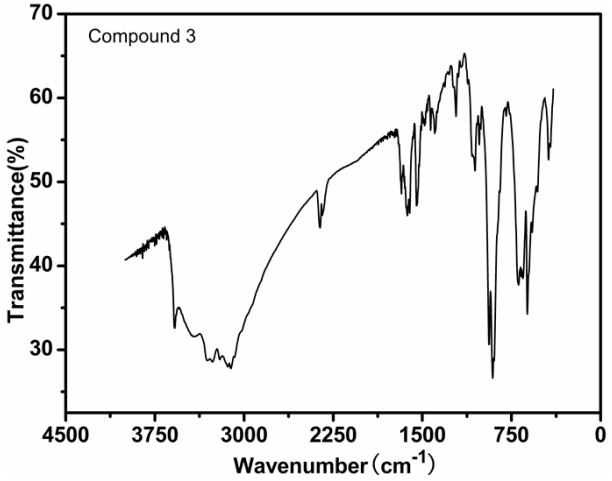
Fig. S4 View of 3D metal organic framework of **5**.



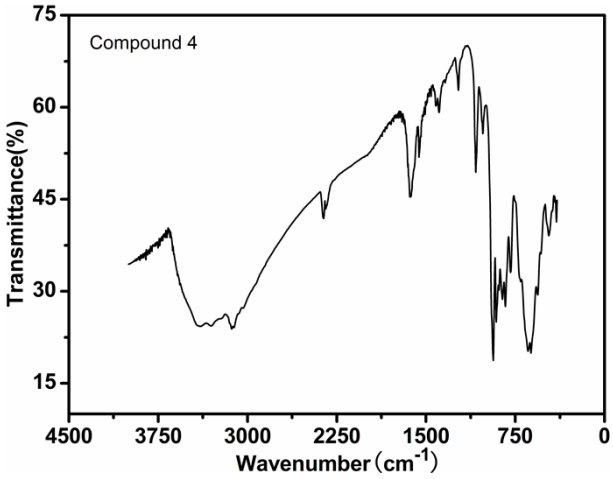
(a)



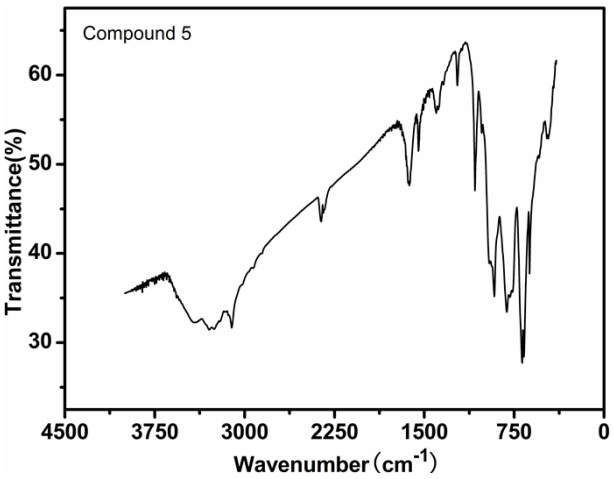
(b)



(c)

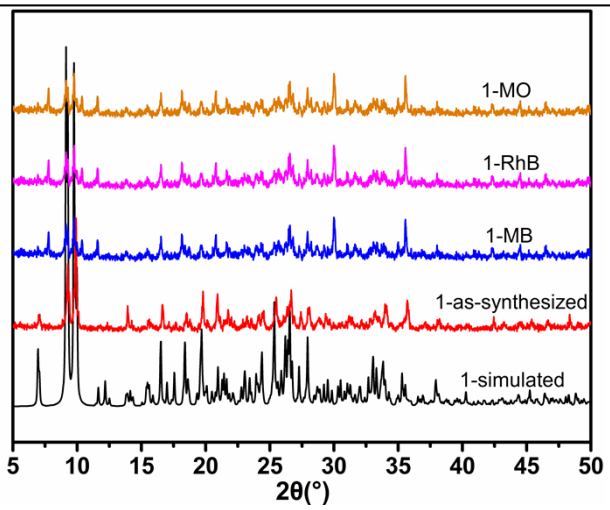


(d)

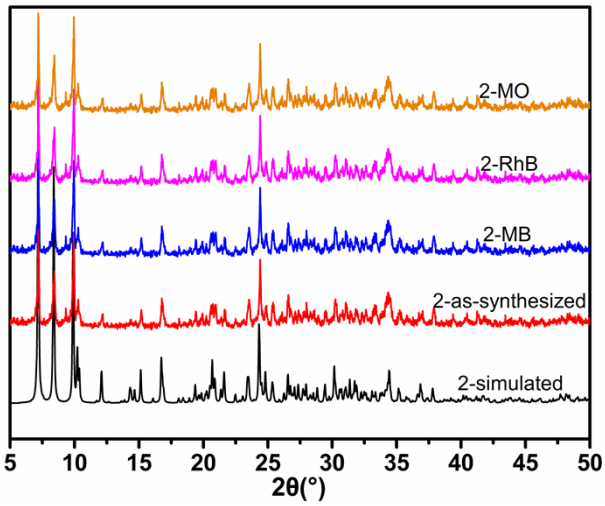


(e)

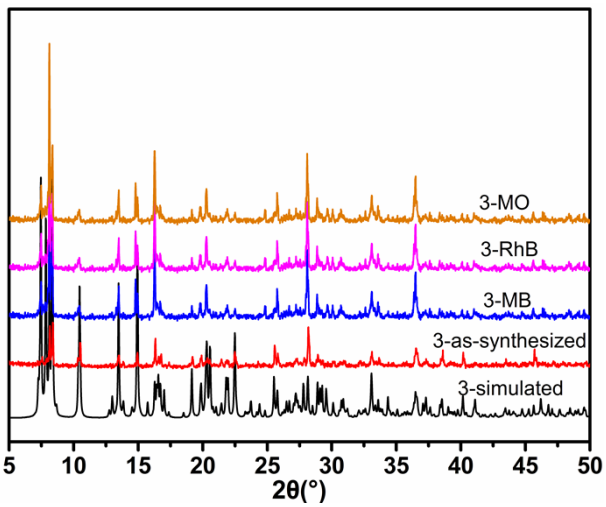
Fig. S5 IR spectra of compounds **1**−**5**.


1-MO
1-RhB
1-MB
1-as-synthesized
1-simulated
5
10
15
20
25
30
35
40
45
50
2θ(°)

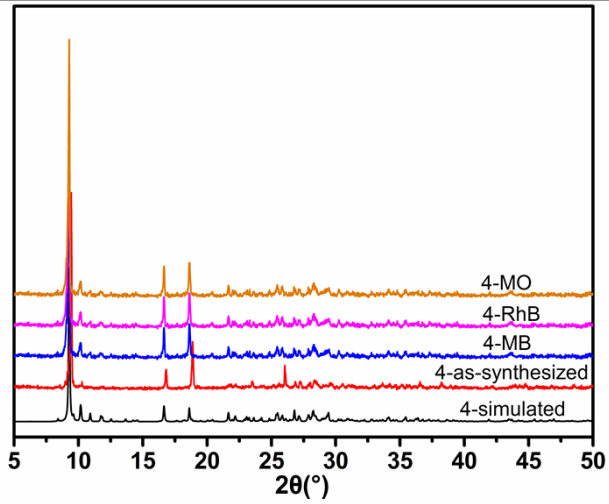
(a)


2-MO
2-RhB
2-MB
2-as-synthesized
2-simulated
5
10
15
20
25
30
35
40
45
50
2θ(°)

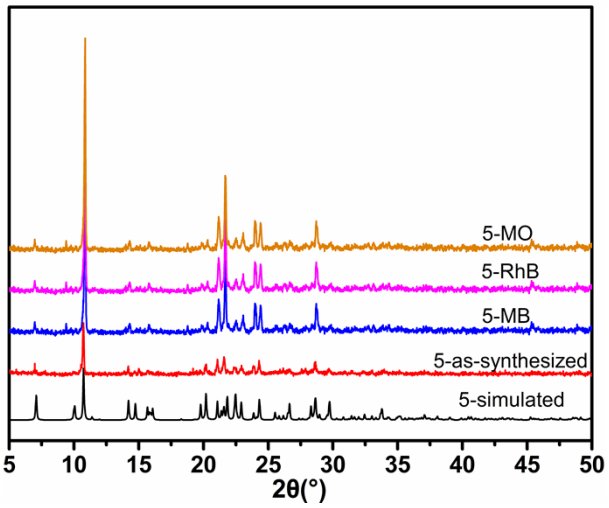
(b)


3-MO
3-RhB
3-MB
3-as-synthesized
3-simulated
5
10
15
20
25
30
35
40
45
50
2θ(°)

(c)



(d)



(e)

Fig. S6 X-ray powder diffraction patterns of compounds **1**−**5** (a−e) (simulated from single-crystal X-ray data, as-synthesized and after photocatalytic reaction towards MB, RhB and MO).

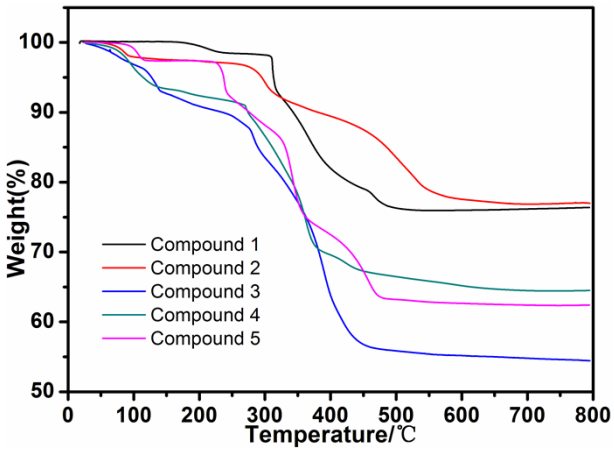
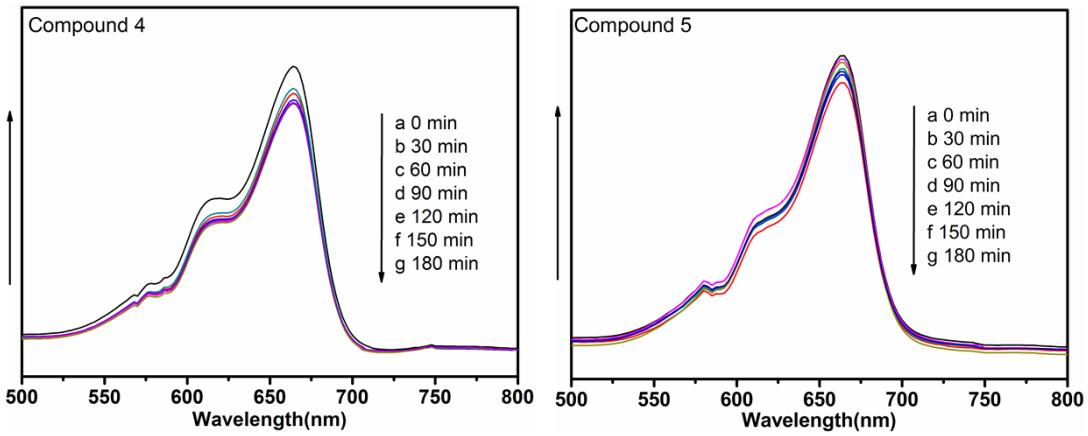
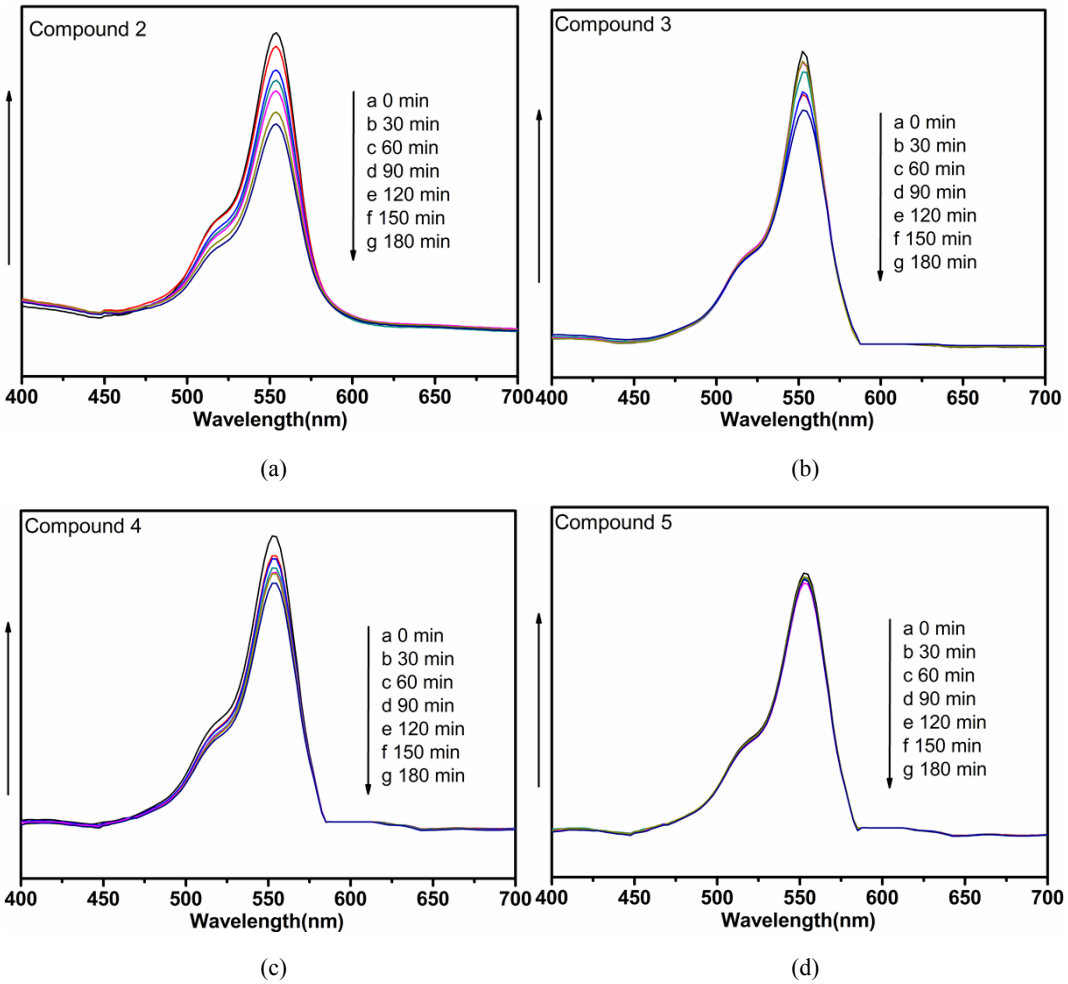


Fig. S7 TGA curves of compounds **1**–**5**.



(a) (b)

Fig. S8 Absorption spectra of the MB solution in the presence of compound **4** (a) and **5** (b), during the decomposition reaction under UV irradiation.



(a) (b)

(c) (d)

Fig. S9 Absorption spectra of the RhB solution (a−d) in the presence of compounds **2**−**5**, during the decomposition reaction under UV irradiation.

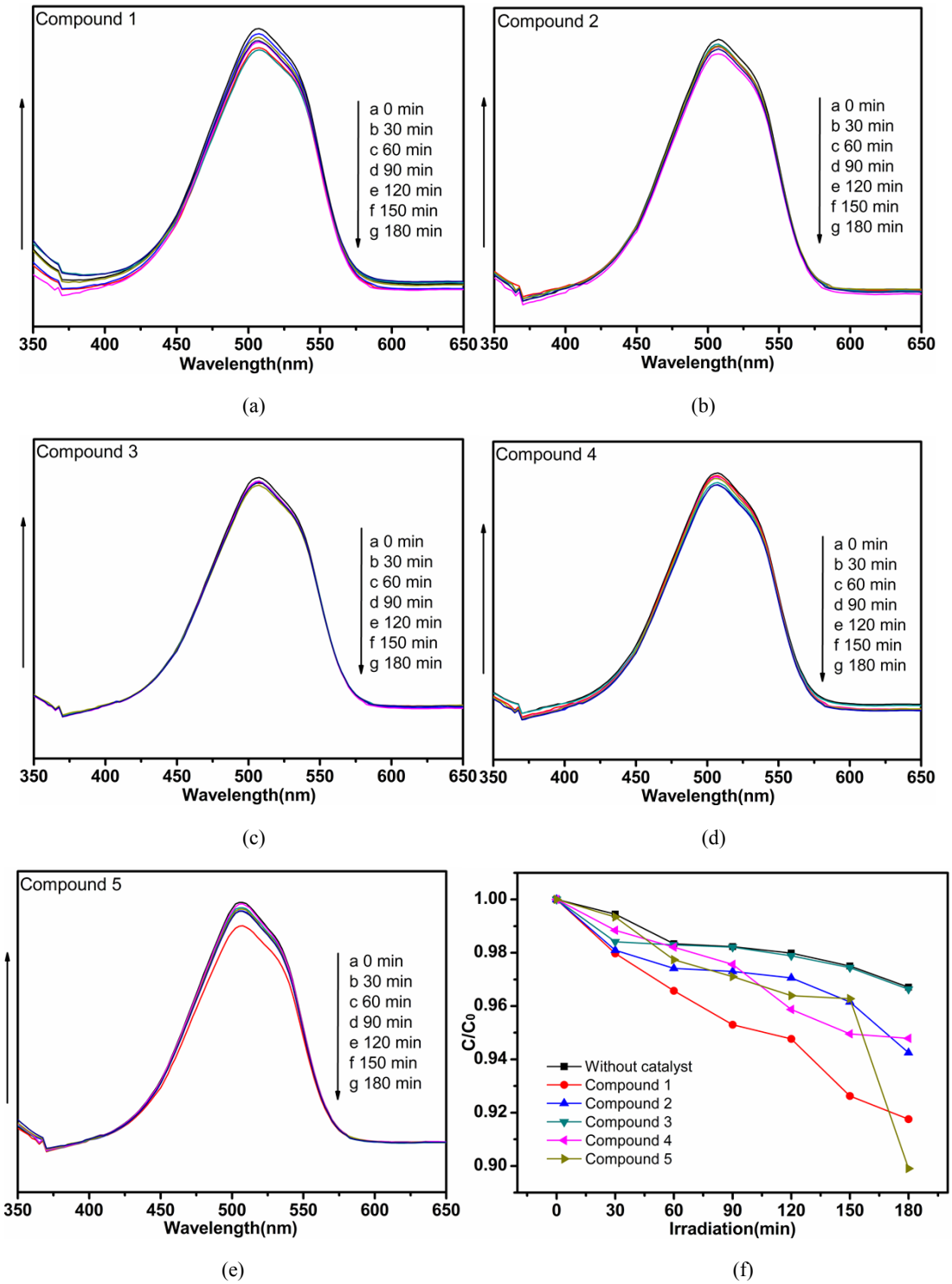


Fig. S10 Absorption spectra of the MO solution (a−e) in the presence of compounds **1**−**5**, during the decomposition reaction under UV irradiation. (f) Photocatalytic decomposition rate of the MO solution under UV irradiation with the use of compounds **1**–**5** and without catalyst in the same conditions.