Electronic Supplementary Material (ESI) for Dalton Transactions

Syntheses, structures, photoluminescence, photocatalysis, and photoelectronic effects of 3D mixed high-connected metal-organic frameworks based on octanuclear and dodecanuclear secondary building units

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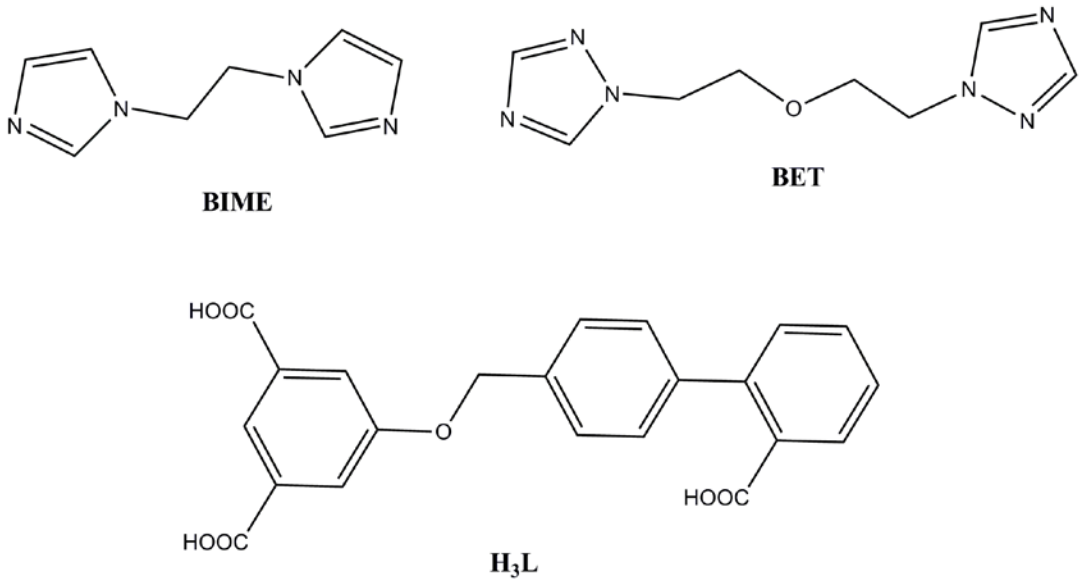
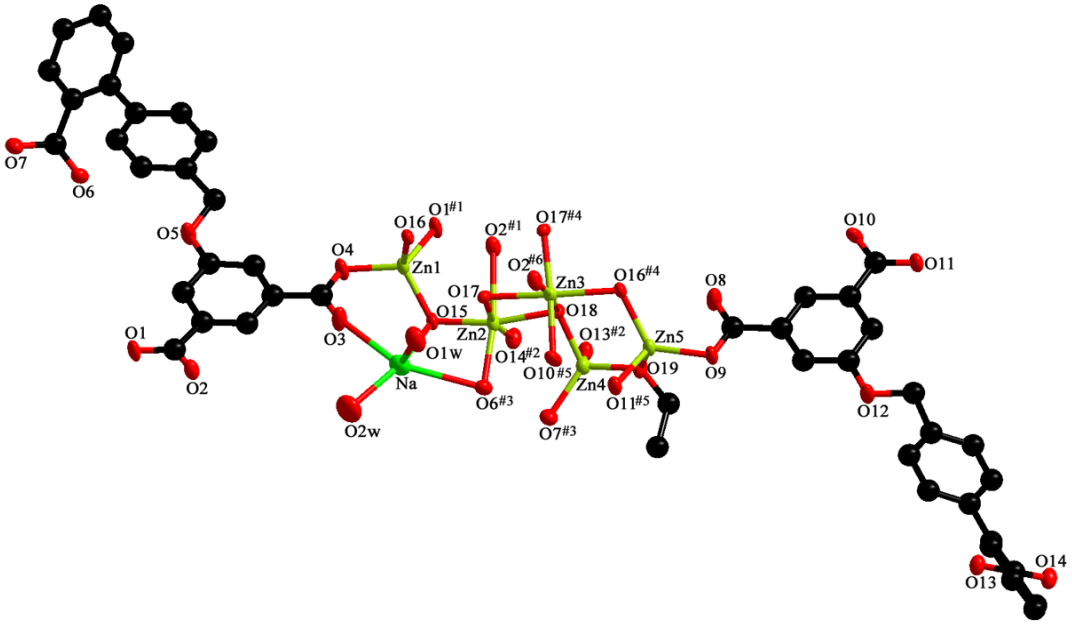
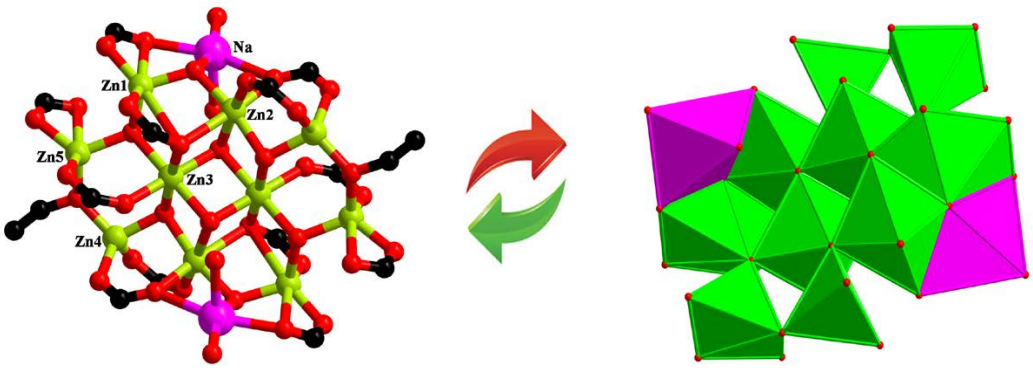


Scheme S1. Structures of H_3L and the N-donor ligands used in this work.



(a)



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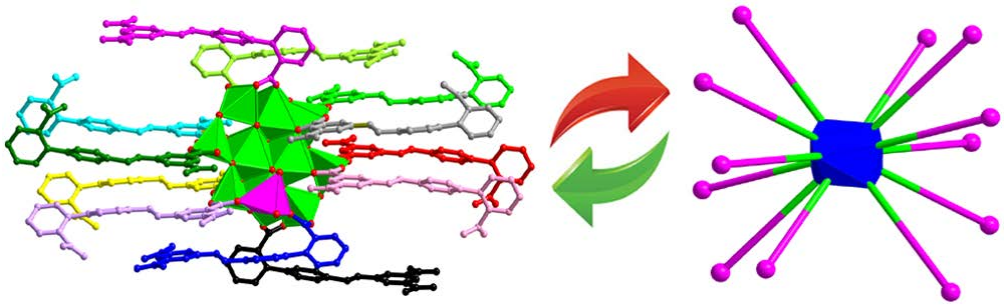
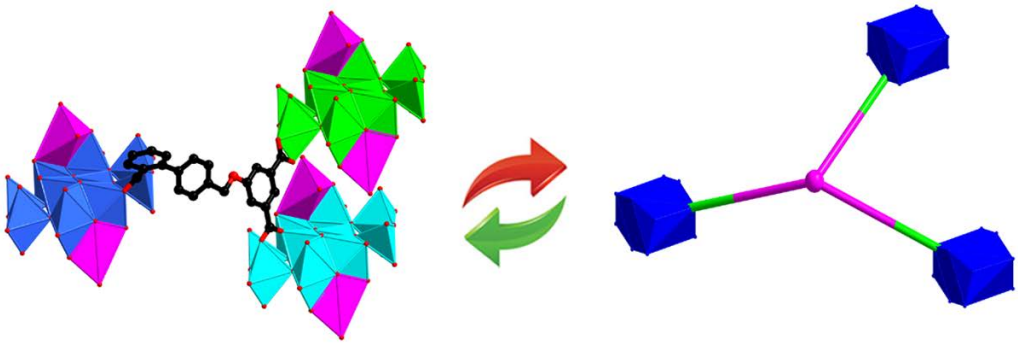
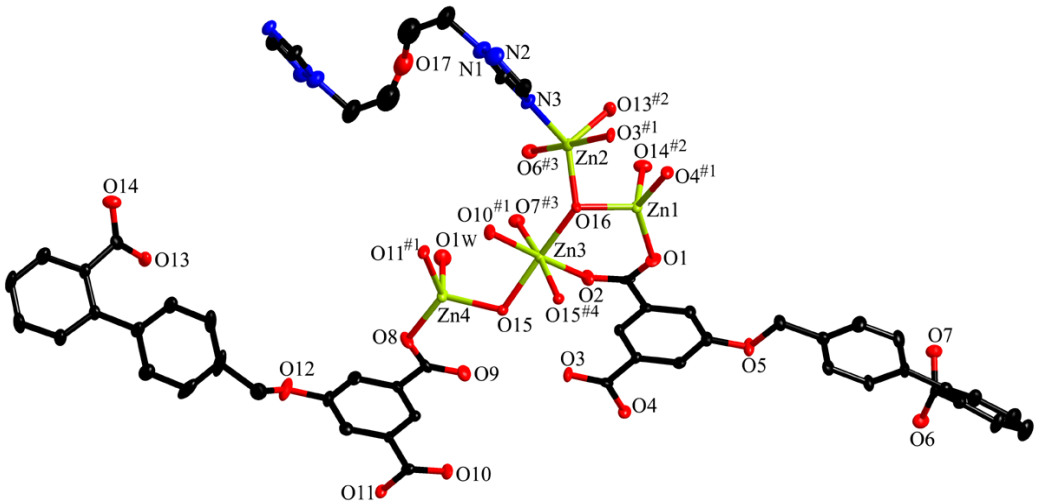


(c)

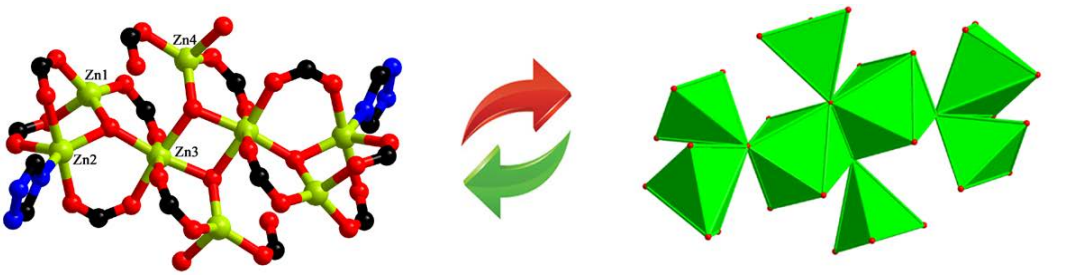


(d)

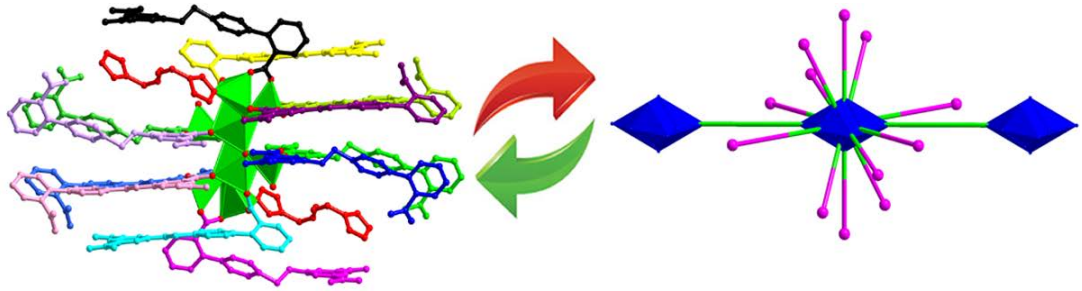
Fig. S1 (a) Coordination environments of the Zn ions in **2** (30% probability displacement ellipsoids). Symmetry code: #1 = x+1, y, z; #2 = -x+2, -y, -z; #3 = -x, -y-1, -z-1; #4 = -x+1, -y, -z-1; #5 = x-1, y, z; #6 = -x, -y, -z-1. (b) Ball-and-stick and polyhedral views of the heterometallic dodecanuclear cluster of **2**. (c) and (d) Ball-stick and polyhedral (left), and schematic (right) representations of 12-connected node and 3-connected node, respectively.



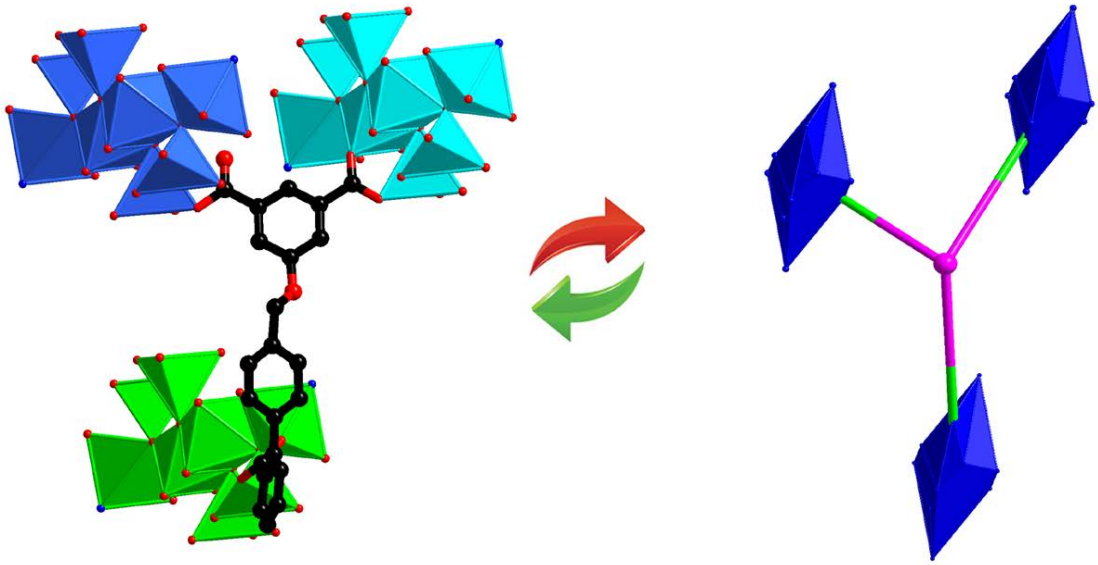
(a)



(b)



(c)



(d)

Fig. S2 (a) Coordination environments of the Zn ions in **3** (30% probability displacement ellipsoids). Symmetry code: #1 = x-1,y,z; #2 = -x,-y,-z+2; #3 = -x,-y+1,-z+1; #4 = -x,-y+1,-z+2. (b) Ball-and-stick and polyhedral views of the octanuclear zinc cluster of **3**. (c) Ball-stick and polyhedral (left), and simplified (right) representations of 3-connected node (c) and 14-connected node (d), respectively.

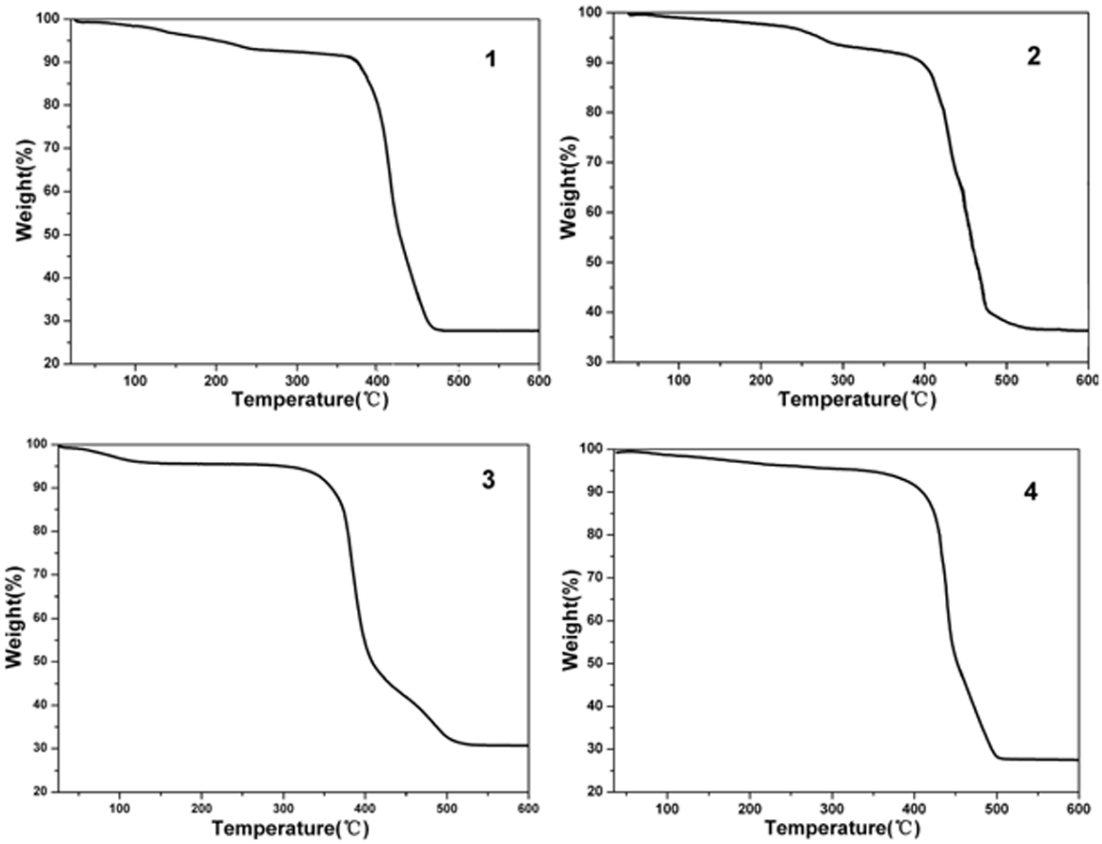


Fig. S3 The TGA curves of compounds **1-4.**

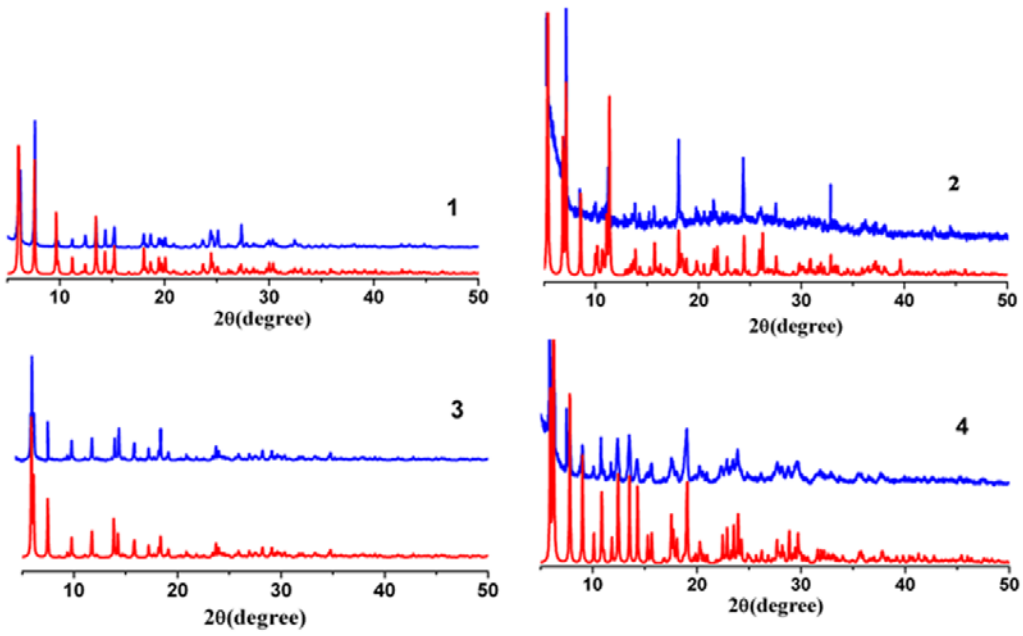


Fig. S4 The simulated (red) and experimental (black) XRD pattern for **1-4.**

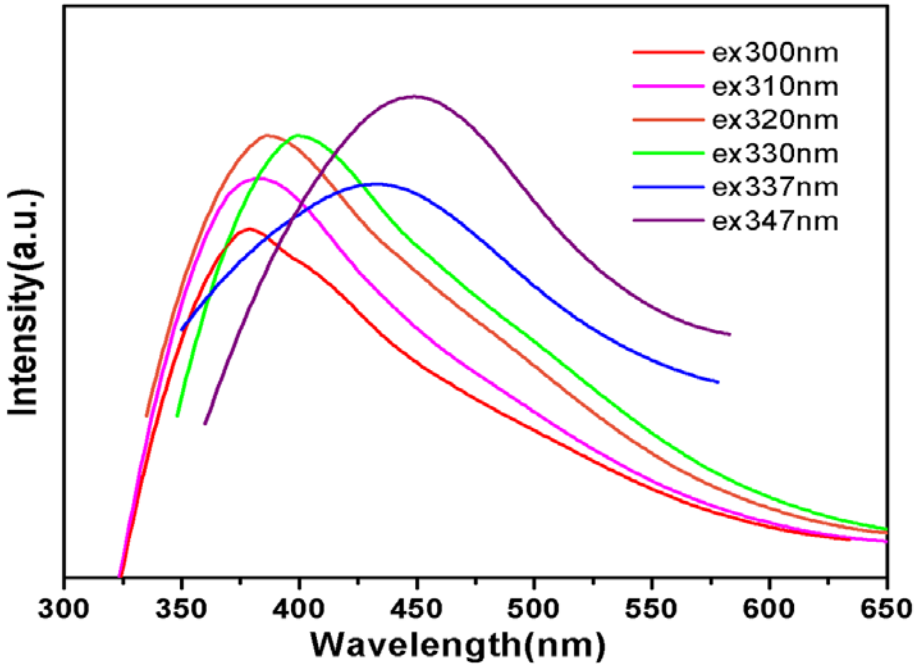


Fig. S5 Solid-state emission spectra of **3** by varying the excitation wavelengths from 300 to 347 nm under the same metrical condition.

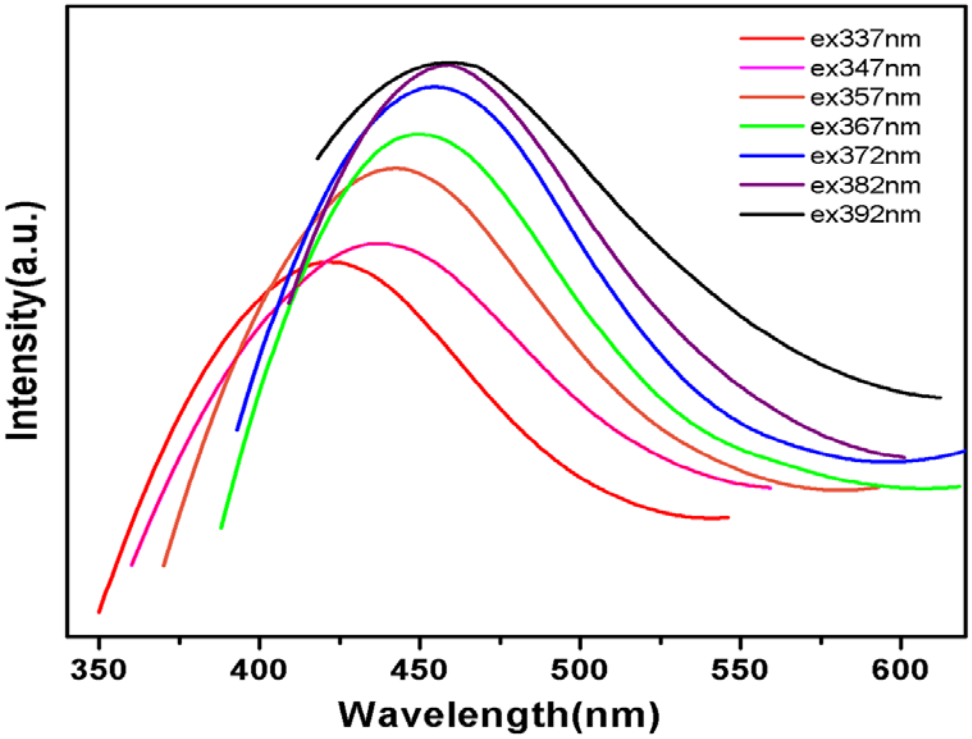


Fig. S6 Solid-state emission spectra of **4** by varying the excitation wavelengths from 337 to 392 nm under the same metrical condition.

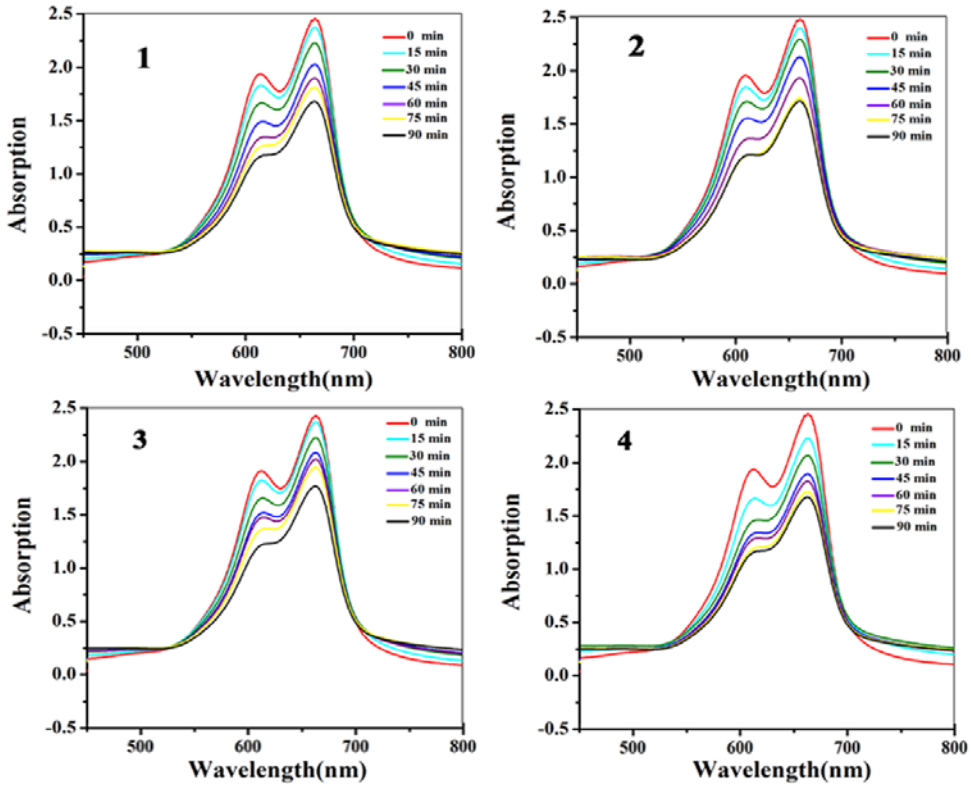


Fig. S7 Control experiments of compounds **1-4** about the absorption spectra of **MB** solution during the decomposition reaction under UV light irradiation.

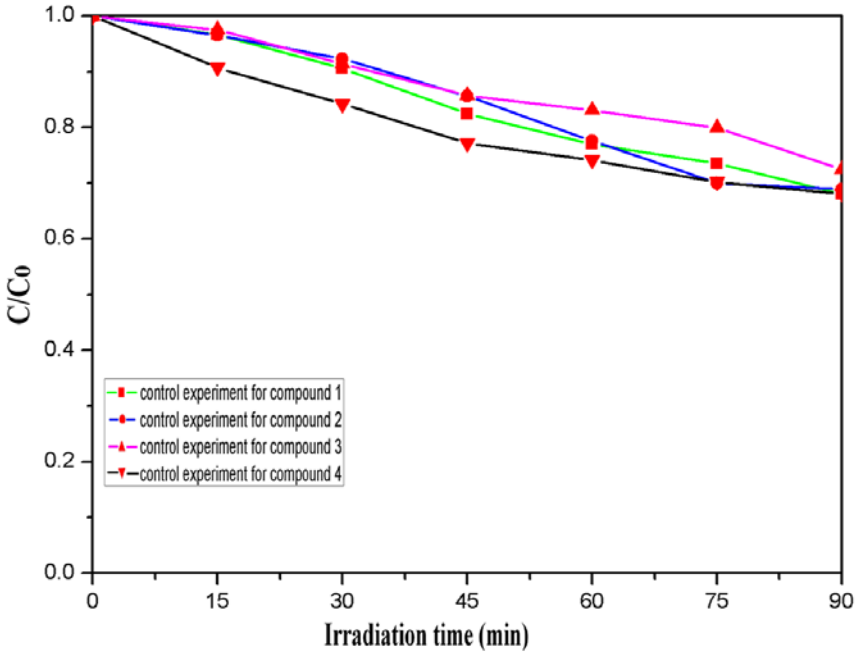


Fig. S8 Control experiments of compounds **1-4** for decomposition of **MB** under UV irradiation.

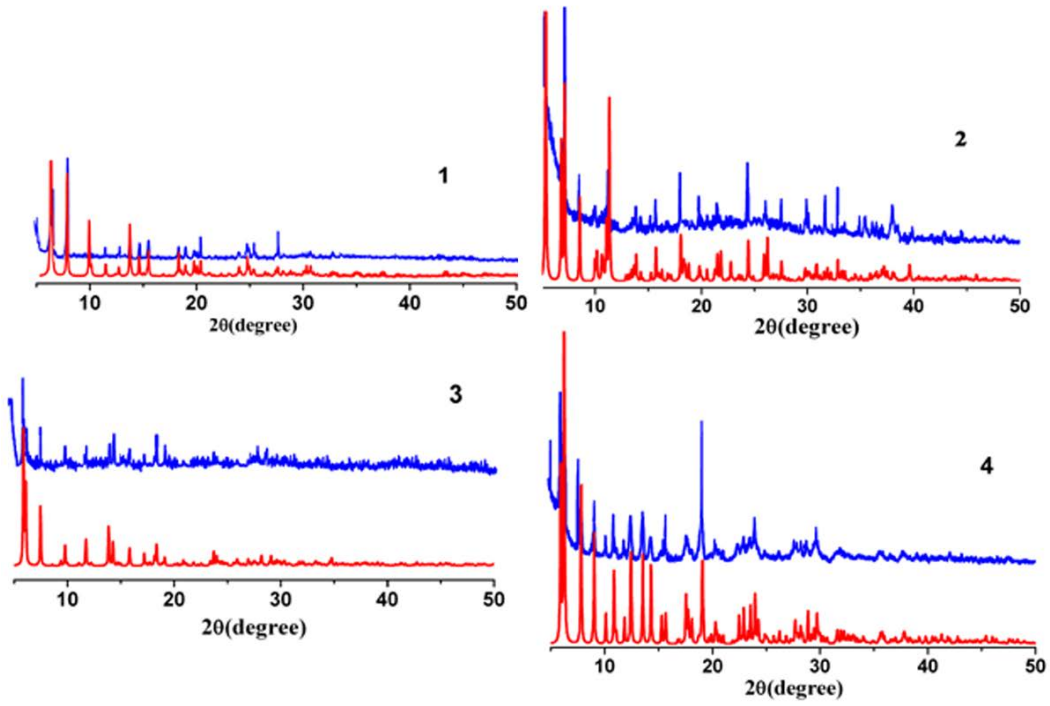


Fig. S9 The simulated (red) PXRD patterns of compounds **1**-**4**, and the PXRD patterns of compounds **1**-**4** after photocatalytic processes (blue)**.**

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

Zn(1)-O(15)	2.005(4)	Zn(1)-O(3)#1	2.007(4)
Zn(1)-O(2)#2	2.026(4)	Zn(1)-O(14)	2.053(4)
Zn(1)-O(9)#3	2.355(4)	Zn(1)-O(4)#1	2.438(4)
Zn(2)-O(6)	1.935(5)	Zn(2)-O(13)	1.941(4)
Zn(2)-O(15)	1.948(4)	Zn(2)-O(1W)	1.989(4)
Zn(3)-O(10)#4	2.066(3)	Zn(3)-O(1)#2	2.072(4)
Zn(3)-O(16)#5	2.088(4)	Zn(3)-O(16)	2.117(4)
Zn(3)-O(15)	2.126(4)	Zn(3)-O(7)	2.144(4)
Zn(4)-O(11)#6	1.947(4)	Zn(4)-O(16)	1.971(4)
Zn(4)-O(8)#3	2.009(4)	Zn(4)-O(2)#2	2.334(4)
Zn(4)-O(2W)	2.353(9)	Zn(4)-O(9)#3	2.373(4)
O(15)-Zn(1)-O(3)#1	142.40(17)	O(15)-Zn(1)-O(2)#2	106.85(15)
O(3)#1-Zn(1)-O(2)#2	108.58(16)	O(15)-Zn(1)-O(14)	94.83(18)
O(3)#1-Zn(1)-O(14)	93.33(16)	O(2)#2-Zn(1)-O(14)	96.51(16)

O(15)-Zn(1)-O(9)#3	86.07(17)	O(3)#1-Zn(1)-O(9)#3	84.62(15)
O(2)#2-Zn(1)-O(9)#3	85.35(15)	O(14)-Zn(1)-O(9)#3	177.60(14)
O(15)-Zn(1)-O(4)#1	84.96(15)	O(3)#1-Zn(1)-O(4)#1	57.74(15)
O(2)#2-Zn(1)-O(4)#1	162.53(14)	O(14)-Zn(1)-O(4)#1	95.22(15)
O(9)#3-Zn(1)-O(4)#1	82.63(14)	O(6)-Zn(2)-O(13)	108.1(2)
O(6)-Zn(2)-O(15)	113.0(2)	O(13)-Zn(2)-O(15)	114.45(17)
O(6)-Zn(2)-O(1W)	101.2(2)	O(13)-Zn(2)-O(1W)	103.11(18)
O(15)-Zn(2)-O(1W)	115.6(2)	O(10)#4-Zn(3)-O(1)#2	173.26(16)
O(10)#4-Zn(3)-O(16)#5	90.08(16)	O(1)#2-Zn(3)-O(16)#5	94.97(16)
O(10)#4-Zn(3)-O(16)	93.28(16)	O(1)#2-Zn(3)-O(16)	91.82(16)
O(16)#5-Zn(3)-O(16)	82.46(16)	O(10)#4-Zn(3)-O(15)	83.81(16)
O(1)#2-Zn(3)-O(15)	91.61(16)	O(16)#5-Zn(3)-O(15)	171.45(19)
O(16)-Zn(3)-O(15)	91.90(16)	O(10)#4-Zn(3)-O(7)	91.65(16)
O(1)#2-Zn(3)-O(7)	83.99(16)	O(16)#5-Zn(3)-O(7)	88.94(18)
O(16)-Zn(3)-O(7)	170.09(17)	O(15)-Zn(3)-O(7)	97.18(18)
O(11)#6-Zn(4)-O(16)	110.06(15)	O(11)#6-Zn(4)-O(8)#3	103.61(16)
O(16)-Zn(4)-O(8)#3	143.41(18)	O(11)#6-Zn(4)-O(2)#2	94.50(15)
O(16)-Zn(4)-O(2)#2	97.48(16)	O(8)#3-Zn(4)-O(2)#2	93.70(16)
O(11)#6-Zn(4)-O(2W)	99.9(3)	O(16)-Zn(4)-O(2W)	86.4(3)
O(8)#3-Zn(4)-O(2W)	73.9(3)	O(2)#2-Zn(4)-O(2W)	162.8(3)
O(11)#6-Zn(4)-O(9)#3	160.51(13)	O(16)-Zn(4)-O(9)#3	89.02(14)
O(8)#3-Zn(4)-O(9)#3	59.26(15)	O(2)#2-Zn(4)-O(9)#3	78.56(13)
O(2W)-Zn(4)-O(9)#3	84.8(3)		

Symmetry codes for **1**: #1 -x+2,-y+1,-z+1; #2 -x+1,-y+1,-z+1; #3 x,y,z-1; #4 -x+2,-y,-z+2; #5 -x+1,-y,-z+1; #6 x-1,y,z-1.

Table S2 Selected bond distances (Å) and angles (°) for **2.**

Zn(1)-O(4)	1.924(4)	Zn(1)-O(15)	1.935(4)
Zn(1)-O(1)#1	1.971(4)	Zn(1)-O(16)	2.013(4)

Zn(1)-Na	3.439(3)	Zn(2)-O(15)	1.966(3)
Zn(2)-O(17)	2.055(4)	Zn(2)-O(18)	2.065(3)
Zn(2)-O(14)#2	2.125(4)	Zn(2)-O(6)#3	2.134(4)
Zn(2)-O(2)#1	2.429(4)	Zn(2)-Zn(4)	3.0738(9)
Zn(2)-Zn(3)	3.1467(9)	Zn(2)-Na	3.301(3)
Zn(3)-O(17)#4	2.039(4)	Zn(3)-O(10)#5	2.048(4)
Zn(3)-O(18)	2.065(4)	Zn(3)-O(17)	2.111(3)
Zn(3)-O(16)#4	2.177(4)	Zn(3)-O(2)#6	2.192(4)
Zn(3)-Zn(3)#4	3.0877(12)	Zn(4)-O(19)	1.914(3)
Zn(4)-O(7)#3	1.933(4)	Zn(4)-O(18)	1.952(4)
Zn(4)-O(13)#2	1.990(4)	Zn(5)-O(19)	1.966(4)
Zn(5)-O(9)	1.969(4)	Zn(5)-O(11)#5	1.971(4)
Zn(5)-O(16)#4	1.998(4)	Na-O(15)	2.288(5)
Na-O(2W)	2.295(6)	Na-O(3)	2.380(5)
Na-O(1W)	2.449(5)	Na-O(6)#3	2.685(5)
O(4)-Zn(1)-O(15)	114.19(17)	O(4)-Zn(1)-O(1)#1	113.56(17)
O(15)-Zn(1)-O(1)#1	107.53(17)	O(4)-Zn(1)-O(16)	106.42(18)
O(15)-Zn(1)-O(16)	112.27(17)	O(1)#1-Zn(1)-O(16)	102.31(18)
O(15)-Zn(2)-O(17)	97.85(15)	O(15)-Zn(2)-O(18)	167.98(15)
O(17)-Zn(2)-O(18)	81.33(14)	O(15)-Zn(2)-O(14)#2	90.33(16)
O(17)-Zn(2)-O(14)#2	167.00(16)	O(18)-Zn(2)-O(14)#2	88.56(15)
O(15)-Zn(2)-O(6)#3	88.54(15)	O(17)-Zn(2)-O(6)#3	94.88(15)
O(18)-Zn(2)-O(6)#3	103.48(14)	O(14)#2-Zn(2)-O(6)#3	95.42(17)
O(15)-Zn(2)-O(2)#1	84.87(14)	O(17)-Zn(2)-O(2)#1	79.39(14)
O(18)-Zn(2)-O(2)#1	83.20(13)	O(14)#2-Zn(2)-O(2)#1	91.36(15)
O(6)#3-Zn(2)-O(2)#1	170.57(15)	O(17)#4-Zn(3)-O(10)#5	174.45(18)
O(17)#4-Zn(3)-O(18)	96.36(15)	O(10)#5-Zn(3)-O(18)	88.40(16)
O(17)#4-Zn(3)-O(17)	83.88(14)	O(10)#5-Zn(3)-O(17)	94.18(14)
O(18)-Zn(3)-O(17)	80.01(14)	O(17)#4-Zn(3)-O(16)#4	93.98(16)
O(10)#5-Zn(3)-O(16)#4	88.52(16)	O(18)-Zn(3)-O(16)#4	93.87(16)

O(17)-Zn(3)-O(16)#4	173.23(17)	O(17)#4-Zn(3)-O(2)#6	85.67(15)
O(10)#5-Zn(3)-O(2)#6	89.28(17)	O(18)-Zn(3)-O(2)#6	173.26(14)
O(17)-Zn(3)-O(2)#6	93.85(14)	O(16)#4-Zn(3)-O(2)#6	92.40(16)
O(19)-Zn(4)-O(7)#3	114.71(18)	O(19)-Zn(4)-O(18)	107.02(16)
O(7)#3-Zn(4)-O(18)	117.91(17)	O(19)-Zn(4)-O(13)#2	111.98(17)
O(7)#3-Zn(4)-O(13)#2	109.03(17)	O(18)-Zn(4)-O(13)#2	94.49(16)
O(19)-Zn(4)-Zn(2)	146.31(13)	O(7)#3-Zn(4)-Zn(2)	82.40(12)
O(18)-Zn(4)-Zn(2)	41.46(10)	O(13)#2-Zn(4)-Zn(2)	86.76(11)
O(19)-Zn(5)-O(9)	106.60(17)	O(19)-Zn(5)-O(11)#5	105.81(17)
O(9)-Zn(5)-O(11)#5	108.96(16)	O(19)-Zn(5)-O(16)#4	110.68(17)
O(9)-Zn(5)-O(16)#4	121.30(17)	O(11)#5-Zn(5)-O(16)#4	102.48(18)
O(15)-Na-O(2W)	159.8(2)	O(15)-Na-O(3)	83.09(16)
O(2W)-Na-O(3)	83.65(19)	O(15)-Na-O(1W)	110.17(18)
O(2W)-Na-O(1W)	86.2(2)	O(3)-Na-O(1W)	95.39(19)
O(15)-Na-O(6)#3	69.82(14)	O(2W)-Na-O(6)#3	123.4(2)
O(3)-Na-O(6)#3	152.66(18)	O(1W)-Na-O(6)#3	90.72(16)

Symmetry codes for **2**: #1 x+1,y,z; #2 -x+2,-y,-z; #3 -x,-y-1,-z-1; #4 -x+1,-y,-z-1; #5 x-1,y,z; #6 -x,-y,-z-1.

Table S3 Selected bond distances (Å) and angles (°) for **3.**

Cd(1)-O(4)#1	2.219(5)	Cd(1)-O(15)	2.252(5)
Cd(1)-O(1)	2.255(6)	Cd(1)-O(14)#2	2.298(5)
Cd(1)-O(2)	2.421(6)	Cd(1)-O(9)	2.488(5)
Cd(1)-C(7)	2.677(8)	Cd(1)-Cd(2)	3.4234(8)
Cd(2)-N(1)	2.155(8)	Cd(2)-O(13)#2	2.159(6)
Cd(2)-O(15)	2.176(4)	Cd(2)-O(1W)	2.321(7)
Cd(2)-O(2W)	2.436(8)	Cd(3)-O(3)#1	2.262(5)
Cd(3)-O(10)#3	2.270(6)	Cd(3)-O(16)#4	2.277(5)
Cd(3)-O(15)	2.288(5)	Cd(3)-O(16)	2.296(5)

Cd(3)-O(6)#5	2.363(6)	Cd(4)-O(11)#1	2.177(6)
Cd(4)-O(16)	2.227(5)	Cd(4)-O(8)	2.257(5)
Cd(4)-O(7)#6	2.297(6)	Cd(4)-O(9)	2.526(6)
Cd(4)-O(4)#1	2.532(5)	Cd(4)-C(29)	2.738(8)
O(4)#1-Cd(1)-O(15)	105.63(19)	O(4)#1-Cd(1)-O(1)	107.3(2)
O(15)-Cd(1)-O(1)	146.43(19)	O(4)#1-Cd(1)-O(14)#2	102.2(2)
O(15)-Cd(1)-O(14)#2	94.74(19)	O(1)-Cd(1)-O(14)#2	84.7(2)
O(4)#1-Cd(1)-O(2)	157.75(19)	O(15)-Cd(1)-O(2)	90.91(18)
O(1)-Cd(1)-O(2)	55.59(19)	O(14)#2-Cd(1)-O(2)	90.9(2)
O(4)#1-Cd(1)-O(9)	83.02(19)	O(15)-Cd(1)-O(9)	92.87(17)
O(1)-Cd(1)-O(9)	84.75(19)	O(14)#2-Cd(1)-O(9)	169.2(2)
O(2)-Cd(1)-O(9)	81.36(19)	O(4)#1-Cd(1)-C(7)	133.5(2)
O(15)-Cd(1)-C(7)	119.1(2)	O(1)-Cd(1)-C(7)	27.4(2)
O(14)#2-Cd(1)-C(7)	87.0(2)	O(2)-Cd(1)-C(7)	28.2(2)
O(9)-Cd(1)-C(7)	82.6(2)	O(4)#1-Cd(1)-Cd(2)	130.55(14)
O(15)-Cd(1)-Cd(2)	38.56(11)	O(1)-Cd(1)-Cd(2)	116.86(14)
O(14)#2-Cd(1)-Cd(2)	62.83(15)	O(2)-Cd(1)-Cd(2)	71.47(13)
O(9)-Cd(1)-Cd(2)	120.78(12)	C(7)-Cd(1)-Cd(2)	94.45(17)
N(1)-Cd(2)-O(13)#2	116.8(3)	N(1)-Cd(2)-O(15)	129.9(3)
O(13)#2-Cd(2)-O(15)	113.24(19)	N(1)-Cd(2)-O(1W)	95.3(4)
O(13)#2-Cd(2)-O(1W)	88.9(2)	O(15)-Cd(2)-O(1W)	87.6(2)
N(1)-Cd(2)-O(2W)	91.2(4)	O(13)#2-Cd(2)-O(2W)	82.3(2)
O(15)-Cd(2)-O(2W)	93.2(2)	O(1W)-Cd(2)-O(2W)	170.7(2)
N(1)-Cd(2)-Cd(1)	170.0(2)	O(13)#2-Cd(2)-Cd(1)	73.09(14)
O(15)-Cd(2)-Cd(1)	40.17(13)	O(1W)-Cd(2)-Cd(1)	85.61(17)
O(2W)-Cd(2)-Cd(1)	89.07(17)	O(3)#1-Cd(3)-O(10)#3	171.0(2)
O(3)#1-Cd(3)-O(16)#4	97.2(2)	O(10)#3-Cd(3)-O(16)#4	87.7(2)
O(3)#1-Cd(3)-O(15)	89.2(2)	O(10)#3-Cd(3)-O(15)	87.6(2)
O(16)#4-Cd(3)-O(15)	166.85(18)	O(3)#1-Cd(3)-O(16)	93.96(19)
O(10)#3-Cd(3)-O(16)	94.4(2)	O(16)#4-Cd(3)-O(16)	79.6(2)

O(15)-Cd(3)-O(16)	88.54(17)	O(3)#1-Cd(3)-O(6)#5	85.5(2)
O(10)#3-Cd(3)-O(6)#5	86.9(2)	O(16)#4-Cd(3)-O(6)#5	90.6(2)
O(15)-Cd(3)-O(6)#5	101.4(2)	O(16)-Cd(3)-O(6)#5	170.0(2)
O(11)#1-Cd(4)-O(16)	120.2(2)	O(11)#1-Cd(4)-O(8)	98.2(2)
O(16)-Cd(4)-O(8)	141.63(19)	O(11)#1-Cd(4)-O(7)#6	94.4(3)
O(16)-Cd(4)-O(7)#6	89.6(2)	O(8)-Cd(4)-O(7)#6	86.5(2)
O(11)#1-Cd(4)-O(9)	149.9(2)	O(16)-Cd(4)-O(9)	88.24(17)
O(8)-Cd(4)-O(9)	54.30(17)	O(7)#6-Cd(4)-O(9)	95.5(2)
O(11)#1-Cd(4)-O(4)#1	92.6(2)	O(16)-Cd(4)-O(4)#1	90.46(18)
O(8)-Cd(4)-O(4)#1	88.41(19)	O(7)#6-Cd(4)-O(4)#1	171.8(2)
O(9)-Cd(4)-O(4)#1	76.34(17)	O(11)#1-Cd(4)-C(29)	124.4(2)
O(16)-Cd(4)-C(29)	115.3(2)	O(8)-Cd(4)-C(29)	26.7(2)
O(7)#6-Cd(4)-C(29)	89.9(2)	O(9)-Cd(4)-C(29)	27.63(19)
O(4)#1-Cd(4)-C(29)	82.70(19)		

Symmetry codes for **3**: #1 x+1,y,z; #2 x,y,z-1; #3 -x,-y+1,-z; #4 -x+1,-y+1,-z; #5 -x,-y,-z; #6 x+1,y+1,z.

Table S4 Selected bond distances (Å) and angles (°) for **4.**

Zn(1)-O(1)	1.902(4)	Zn(1)-O(4)#1	1.935(4)
Zn(1)-O(14)#2	1.985(4)	Zn(1)-O(16)	1.995(4)
Zn(1)-Zn(2)	2.9138(11)	Zn(2)-N(3)	1.973(5)
Zn(2)-O(13)#2	1.981(4)	Zn(2)-O(16)	1.982(4)
Zn(2)-O(6)#3	2.072(4)	Zn(2)-O(3)#1	2.197(4)
Zn(3)-O(16)	2.073(4)	Zn(3)-O(15)	2.076(4)
Zn(3)-O(2)	2.086(4)	Zn(3)-O(7)#3	2.101(4)
Zn(3)-O(10)#1	2.138(4)	Zn(3)-O(15)#4	2.160(3)
Zn(4)-O(8)	1.934(4)	Zn(4)-O(11)#1	1.944(4)
Zn(4)-O(15)	1.954(4)	Zn(4)-O(1W)	2.059(4)
O(1)-Zn(1)-O(4)#1	128.50(19)	O(1)-Zn(1)-O(14)#2	102.16(17)

O(4)#1-Zn(1)-O(14)#2	96.62(16)	O(1)-Zn(1)-O(16)	112.41(18)
O(4)#1-Zn(1)-O(16)	105.64(17)	O(14)#2-Zn(1)-O(16)	109.05(19)
O(1)-Zn(1)-Zn(2)	145.10(14)	O(4)#1-Zn(1)-Zn(2)	86.12(13)
O(14)#2-Zn(1)-Zn(2)	74.17(14)	O(16)-Zn(1)-Zn(2)	42.71(11)
N(3)-Zn(2)-O(13)#2	102.6(2)	N(3)-Zn(2)-O(16)	134.02(19)
O(13)#2-Zn(2)-O(16)	122.63(18)	N(3)-Zn(2)-O(6)#3	89.8(2)
O(13)#2-Zn(2)-O(6)#3	91.65(17)	O(16)-Zn(2)-O(6)#3	96.05(17)
N(3)-Zn(2)-O(3)#1	90.54(19)	O(13)#2-Zn(2)-O(3)#1	85.03(16)
O(16)-Zn(2)-O(3)#1	86.12(16)	O(6)#3-Zn(2)-O(3)#1	176.66(16)
N(3)-Zn(2)-Zn(1)	163.74(15)	O(13)#2-Zn(2)-Zn(1)	80.22(14)
O(16)-Zn(2)-Zn(1)	43.08(12)	O(6)#3-Zn(2)-Zn(1)	106.23(13)
O(3)#1-Zn(2)-Zn(1)	73.66(11)	O(16)-Zn(3)-O(15)	169.95(14)
O(16)-Zn(3)-O(2)	93.40(16)	O(15)-Zn(3)-O(2)	91.59(16)
O(16)-Zn(3)-O(7)#3	94.81(16)	O(15)-Zn(3)-O(7)#3	94.17(15)
O(2)-Zn(3)-O(7)#3	86.85(17)	O(16)-Zn(3)-O(10)#1	86.01(16)
O(15)-Zn(3)-O(10)#1	89.46(15)	O(2)-Zn(3)-O(10)#1	176.85(17)
O(7)#3-Zn(3)-O(10)#1	90.11(17)	O(16)-Zn(3)-O(15)#4	91.40(15)
O(15)-Zn(3)-O(15)#4	79.58(15)	O(2)-Zn(3)-O(15)#4	93.55(16)
O(7)#3-Zn(3)-O(15)#4	173.74(15)	O(10)#1-Zn(3)-O(15)#4	89.56(15)
O(8)-Zn(4)-O(11)#1	125.37(18)	O(8)-Zn(4)-O(15)	115.78(18)
O(11)#1-Zn(4)-O(15)	112.77(16)	O(8)-Zn(4)-O(1W)	95.71(18)
O(11)#1-Zn(4)-O(1W)	97.29(17)	O(15)-Zn(4)-O(1W)	102.10(17)

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