Electronic Supporting Information

Assembly of two novel $Cd_3/(Cd_3+Cd_5)$-cluster-based metal–organic frameworks: structures, luminescence and photocatalytic degradation of organic dyes

Ya-Pan Wu[†,‡], Xue-Qian Wu[†], Jian-Fang Wang[†], Jun Zhao[†],Wen-Wen Dong[†], Dong-Sheng Li[†]*, Qi-Chun Zhang[§]*

[†] *College of Materials and Chemical Engineering, Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, Key laboratory of inorganic nonme tallic crystalline and energy conversion materials,China Three Gorges University, Yichang, 443002, P. R. China,* [‡]*Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, P. R. China, and* [§]*School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore*

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Table S1. Selected bond lengths (Å) and bond angles (deg) for **1**.

Cd(1)- O(5)A	2.258(4)	Cd(1)-O(9)A	2.291(4)
Cd(1)-O(2)	2.328(4)	Cd(1)-O(13)	2.385(5)
Cd(1)-O(1)	2.411(4)	Cd(1)-O(8)	2.500(4)
Cd(1)-O(10)A	2.518(5)	Cd(2)-O(3)B	2.247(4)
Cd(2)-O(14)	2.248(5)	Cd(2)-O(5)A	2.273(4)
Cd(2)-O(7)	2.281(4)	Cd(2)-O(12)B	2.338(5)
Cd(2)-O(8)	2.627(4)	Cd(2)-O(4)B	2.635(4)
Cd(3)-O(11)B	2.219(5)	Cd(3)-O(15)	2.248(5)
Cd(3)-N(1)	2.313(5)	Cd(3)-O(16)	2.335(6)
Cd(3)-O(4)B	2.355(4)	Cd(3)-O(7)	2.439(4)
O(3)-Cd(2)C	2.247(4)	O(4)-Cd(3)C	2.355(4)
O(4)-Cd(2)C	2.635(4)	O(5)-Cd(1)D	2.258(4)
O(5)-Cd(2)D	2.273(4)	O(9)-Cd(1)D	2.291(4)
O(10)-Cd(1)D	2.518(5)	O(11)-Cd(3)C	2.219(5)
O(12)-Cd(2)C	2.338(5)		
O(5)A-Cd(1)-O(9)A	115.59(16)	O(5)A-Cd(1)-O(2)	148.99(14)
O(9)A-Cd(1)-O(2)	95.23(16)	O(5)A-Cd(1)-O(13)	97.64(15)
O(9)A-Cd(1)-O(13)	82.06(16)	O(2)-Cd(1)-O(13)	82.61(17)
O(5)A-Cd(1)-O(1)	94.63(13)	O(9)A-Cd(1)-O(1)	144.33(15)
O(2)-Cd(1)-O(1)	55.24(13)	O(13)-Cd(1)-O(1)	75.19(16)
O(5)A-Cd(1)-O(8)	76.53(12)	O(9)A-Cd(1)-O(8)	123.66(14)
O(2)-Cd(1)-O(8)	89.61(15)	O(13)-Cd(1)-O(8)	153.84(15)
O(1)-Cd(1)-O(8)	79.84(13)	O(5)A-Cd(1)-O(10)A	83.04(15)
O(9)A-Cd(1)-O(10)A	53.86(15)	O(2)-Cd(1)-O(10)A	120.68(15)
O(13)-Cd(1)-O(10)A	129.44(16)	O(1)-Cd(1)-O(10)A	155.37(14)
O(8)-Cd(1)-O(10)A	75.77(13)	O(3)B-Cd(2)-O(14)	93.17(19)
O(3)B-Cd(2)-O(5)A	105.52(15)	O(14)-Cd(2)-O(5)A	88.6(2)
O(3)B-Cd(2)-O(7)	130.21(14)	O(14)-Cd(2)-O(7)	134.1(2)
O(5)A-Cd(2)-O(7)	92.29(14)	O(3)B-Cd(2)-O(12)B	82.37(17)
O(14)-Cd(2)-O(12)B	92.6(3)	O(5)A-Cd(2)-O(12)B	171.94(16)
O(7)-Cd(2)-O(12)B	81.13(19)	O(3)B-Cd(2)-O(8)	176.96(13)
O(14)-Cd(2)-O(8)	83.88(17)	O(5)A-Cd(2)-O(8)	73.71(13)
O(7)-Cd(2)-O(8)	52.83(12)	O(12)B-Cd(2)-O(8)	98.50(15)
O(3)B-Cd(2)-O(4)B	53.12(13)	O(14)-Cd(2)-O(4)B	146.21(17)
O(5)A-Cd(2)-O(4)B	101.68(14)	O(7)-Cd(2)-O(4)B	78.10(13)
O(12)B-Cd(2)-O(4)B	81.60(18)	O(8)-Cd(2)-O(4)B	129.85(11)
O(11)B-Cd(3)-O(15)	162.8(2)	O(11)B-Cd(3)-N(1)	91.35(18)
O(15)-Cd(3)-N(1)	103.06(19)	O(11)B-Cd(3)-O(16)	87.2(3)
O(15)-Cd(3)-O(16)	83.1(3)	N(1)-Cd(3)-O(16)	91.9(2)
O(11)B-Cd(3)-O(4)B	82.51(17)	O(15)-Cd(3)-O(4)B	85.22(19)
N(1)-Cd(3)-O(4)B	166.52(16)	O(16)-Cd(3)-O(4)B	99.7(2)

O(11)B-Cd(3)-O(7)	106.8(2)	O(15)-Cd(3)-O(7)	83.00(17)

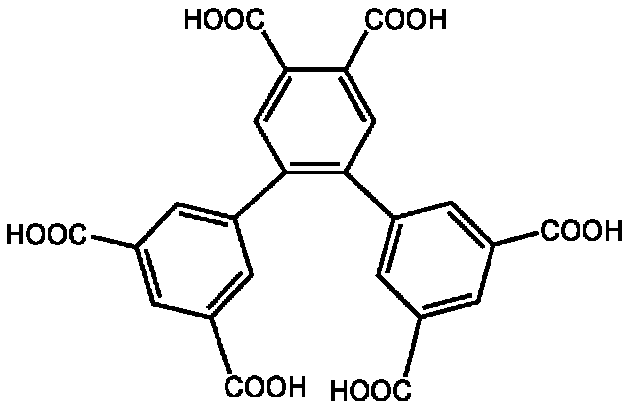
Symmetry codes: A, x-1/2, y, -z+1; B, x, y, z+1; C, x, y, z-1/2; D, x, -y+3/2,-z+1/2.

Table S2. Selected bond lengths (Ǻ) and bond angles (deg) for **2**.

Cd(1)-O(13)	2.266(7)	Cd(1)-O(2)	2.272(8)
Cd(1)-O(12)A	2.282(11)	Cd(1)-O(19)B	2.412(8)
Cd(1)-O(4)C	2.438(9)	Cd(1)-O(3)C	2.452(8)
Cd(1)-O(1)	2.634(9)	Cd(2)-O(5)	2.185(10)
Cd(2)-O(7)D	2.253(9)	Cd(2)-O(23)E	2.282(7)
Cd(2)-O(9)F	2.357(9)	Cd(2)-O(27)	2.382(11)
Cd(2)-O(8)D	2.435(9)	Cd(3)-O(20)B	2.246(9)
Cd(3)-O(3)C	2.257(8)	Cd(3)-O(14)	2.279(9)
Cd(3)-O(18)G	2.330(9)	Cd(3)-O(29)	2.331(10)
Cd(3)-O(17)G	2.582(9)	Cd(4)-O(15)	2.250(8)
Cd(4)-O(22)H	2.250(9)	Cd(4)-O(11)A	2.251(10)
Cd(4)-O(25)	2.274(11)	Cd(4)-O(10)A	2.352(8)
Cd(4)-O(30)	2.458(13)	Cd(5)-O(21)H	2.192(8)
Cd(5)-O(16)	2.237(8)	Cd(5)-O(23)I	2.261(7)
Cd(5)-O(6)J	2.283(9)	Cd(5)-O(10)A	2.301(7)
Cd(5)-O(24)I	2.603(9)	Cd(6)-O(28)	2.262(11)
Cd(6)-O(28)G	2.262(11)	Cd(6)-O(26)	2.291(12)
Cd(6)-O(26)G	2.291(12)	Cd(6)-O(17)G	2.386(9)
Cd(6)-O(17)	2.386(9)	O(3)-Cd(3)D	2.257(8)
O(3)-Cd(1)D	2.452(8)	O(4)-Cd(1)D	2.438(9)
O(6)-Cd(5)K	2.283(9)	O(7)-Cd(2)C	2.253(9)
O(8)-Cd(2)C	2.435(9)	O(9)-Cd(2)F	2.357(9)
O(10)-Cd(5)A	2.301(7)	O(10)-Cd(4)A	2.352(8)
O(11)-Cd(4)A	2.251(10)	O(12)-Cd(1)A	2.282(11)
O(17)-Cd(3)G	2.582(9)	O(18)-Cd(3)G	2.330(9)
O(19)-Cd(1)B	2.412(8)	O(20)-Cd(3)B	2.246(9)
O(21)-Cd(5)H	2.192(8)	O(22)-Cd(4)H	2.250(9)
O(23)-Cd(5)I	2.261(7)	O(23)-Cd(2)E	2.282(7)
O(24)-Cd(5)I	2.603(9)		
O(13)-Cd(1)-O(2)	133.3(3)	O(13)-Cd(1)-O(12)A	96.2(5)
O(2)-Cd(1)-O(12)A	86.8(4)	O(13)-Cd(1)-O(19)B	79.1(3)
O(2)-Cd(1)-O(19)B	83.3(3)	O(12)A-Cd(1)-O(19)B	160.8(4)
O(13)-Cd(1)-O(4)C	143.6(3)	O(2)-Cd(1)-O(4)C	81.7(3)
O(12)A-Cd(1)-O(4)C	95.5(5)	O(19)B-Cd(1)-O(4)C	99.2(4)
O(13)-Cd(1)-O(3)C	90.6(3)	O(2)-Cd(1)-O(3)C	129.8(3)
O(12)A-Cd(1)-O(3)C	115.5(4)	O(19)B-Cd(1)-O(3)C	83.3(3)
O(4)C-Cd(1)-O(3)C	53.4(3)	O(13)-Cd(1)-O(1)	83.5(3)
O(2)-Cd(1)-O(1)	52.1(3)	O(12)A-Cd(1)-O(1)	75.1(4)
O(19)B-Cd(1)-O(1)	85.9(3)	O(4)C-Cd(1)-O(1)	132.8(3)

O(3)C-Cd(1)-O(1)	168.5(3)	O(5)-Cd(2)-O(7)D	142.8(4)
O(5)-Cd(2)-O(23)E	121.5(4)	O(7)D-Cd(2)-O(23)E	95.7(3)
O(5)-Cd(2)-O(9)F	85.4(5)	O(7)D-Cd(2)-O(9)F	100.3(4)
O(23)E-Cd(2)-O(9)F	79.9(3)	O(5)-Cd(2)-O(27)	89.9(5)
O(7)D-Cd(2)-O(27)	94.5(4)	O(23)E-Cd(2)-O(27)	87.2(4)
O(9)F-Cd(2)-O(27)	161.2(4)	O(5)-Cd(2)-O(8)D	87.3(4)
O(7)D-Cd(2)-O(8)D	55.8(3)	O(23)E-Cd(2)-O(8)D	151.0(3)
O(9)F-Cd(2)-O(8)D	108.4(4)	O(27)-Cd(2)-O(8)D	89.5(4)
O(20)B-Cd(3)-O(3)C	128.1(3)	O(20)B-Cd(3)-O(14)	84.2(4)
O(3)C-Cd(3)-O(14)	84.0(3)	O(20)B-Cd(3)-O(18)G	135.4(3)
O(3)C-Cd(3)-O(18)G	96.5(3)	O(14)-Cd(3)-O(18)G	105.0(4)
O(20)B-Cd(3)-O(29)	90.8(4)	O(3)C-Cd(3)-O(29)	90.6(3)
O(14)-Cd(3)-O(29)	168.2(4)	O(18)G-Cd(3)-O(29)	86.1(4)
O(20)B-Cd(3)-O(17)G	83.3(3)	O(3)C-Cd(3)-O(17)G	148.0(3)
O(14)-Cd(3)-O(17)G	95.0(3)	O(18)G-Cd(3)-O(17)G	52.8(3)
O(29)-Cd(3)-O(17)G	95.1(3)	O(15)-Cd(4)-O(22)H	88.9(3)
O(15)-Cd(4)-O(11)A	92.9(4)	O(22)H-Cd(4)-O(11)A	177.4(4)
O(15)-Cd(4)-O(25)	174.6(4)	O(22)H-Cd(4)-O(25)	87.3(4)
O(11)A-Cd(4)-O(25)	91.0(4)	O(15)-Cd(4)-O(10)A	89.1(3)
O(22)H-Cd(4)-O(10)A	98.7(4)	O(11)A-Cd(4)-O(10)A	83.2(4)
O(25)-Cd(4)-O(10)A	87.7(4)	O(15)-Cd(4)-O(30)	81.8(4)
O(22)H-Cd(4)-O(30)	102.2(5)	O(11)A-Cd(4)-O(30)	76.2(4)
O(25)-Cd(4)-O(30)	102.8(5)	O(10)A-Cd(4)-O(30)	157.0(4)
O(15)-Cd(4)-Cd(5)	67.8(2)	O(22)H-Cd(4)-Cd(5)	64.3(3)
O(11)A-Cd(4)-Cd(5)	118.2(3)	O(25)-Cd(4)-Cd(5)	107.0(3)
O(10)A-Cd(4)-Cd(5)	41.13(18)	O(30)-Cd(4)-Cd(5)	146.2(4)
O(21)H-Cd(5)-O(16)	91.5(4)	O(21)H-Cd(5)-O(23)I	139.0(3)
O(16)-Cd(5)-O(23)I	90.9(3)	O(21)H-Cd(5)-O(6)J	87.5(4)
O(16)-Cd(5)-O(6)J	173.1(4)	O(23)I-Cd(5)-O(6)J	94.3(3)
O(21)H-Cd(5)-O(10)A	120.0(3)	O(16)-Cd(5)-O(10)A	89.8(3)
O(23)I-Cd(5)-O(10)A	101.0(3)	O(6)A0-Cd(5)-O(10)A	84.8(3)
O(21)H-Cd(5)-O(24)I	86.5(3)	O(16)-Cd(5)-O(24)I	83.9(3)
O(23)I-Cd(5)-O(24)I	53.1(3)	O(6)A0-Cd(5)-O(24)I	102.8(4)
O(10)A-Cd(5)-O(24)I	153.0(3)	O(21)H-Cd(5)-Cd(4)	79.4(3)
O(16)-Cd(5)-Cd(4)	78.7(2)	O(23)I-Cd(5)-Cd(4)	140.9(2)
O(6)A0-Cd(5)-Cd(4)	94.4(3)	O(10)A-Cd(5)-Cd(4)	42.3(2)
O(24)I-Cd(5)-Cd(4)	157.2(2)	O(28)-Cd(6)-O(28)G	180.000(2)
O(28)-Cd(6)-O(26)	93.7(5)	O(28)G-Cd(6)-O(26)	86.3(5)
O(28)-Cd(6)-O(26)G	86.3(5)	O(28)G-Cd(6)-O(26)G	93.7(5)
O(26)-Cd(6)-O(26)G	180.000(2)	O(28)-Cd(6)-O(17)G	95.9(4)
O(28)G-Cd(6)-O(17)G	84.1(4)	O(26)-Cd(6)-O(17)G	100.6(4)
O(26)G-Cd(6)-O(17)G	79.4(4)	O(28)-Cd(6)-O(17)	84.1(4)
O(28)G-Cd(6)-O(17)	95.9(4)	O(26)-Cd(6)-O(17)	79.4(4)
O(26)G-Cd(6)-O(17)	100.6(4)	O(17)G-Cd(6)-O(17)	180.000(2)

Symmetry codes: A, -x, -y+2, -z; B, -x, -y+2, -z+1; C, x+1, y, z; D, x-1, y, z; E, -x-1, -y+2, -z+1; F, –x-1, -y+3, -z; G, –x+1, -y+2, -z+1; H, –x+1, -y+1,-z+1; I, -x, -y+1, -z+1; J, x+1, y-1, z; K, x-1, y+1, z



Scheme S1.View of the symmetric hexatopic 3,4-di(3,5-dicarboxyl phenyl)phthalic acid(H_6dccpa) ligand.

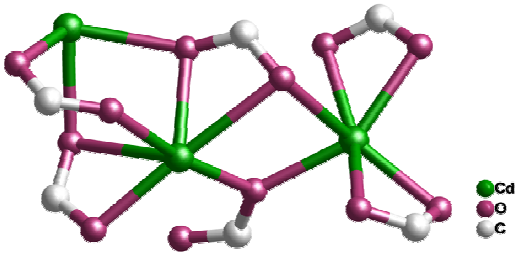
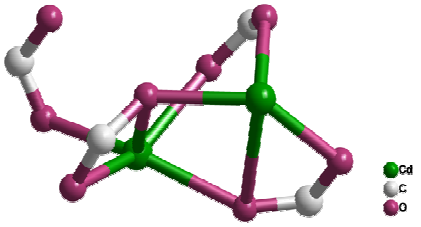


Figure S1 View of the trinuclear $[Cd_3(COO)_6]$ units.

(a)



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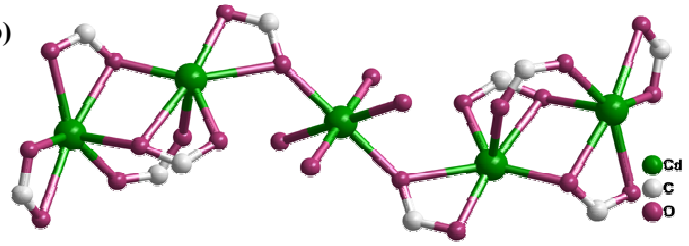

(c)

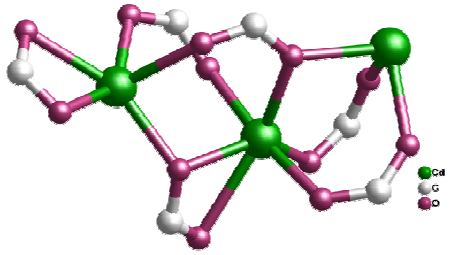

Figure S2 (a) View of the binuclear $[Cd_2(COO)_4]$ SBU-a unit; (b) the pentanuclear $[Cd_5(COO)_{10}]$ SBU-b; (c) the trinuclear $[Cd_3(COO)_6]$ SBU-c unit.

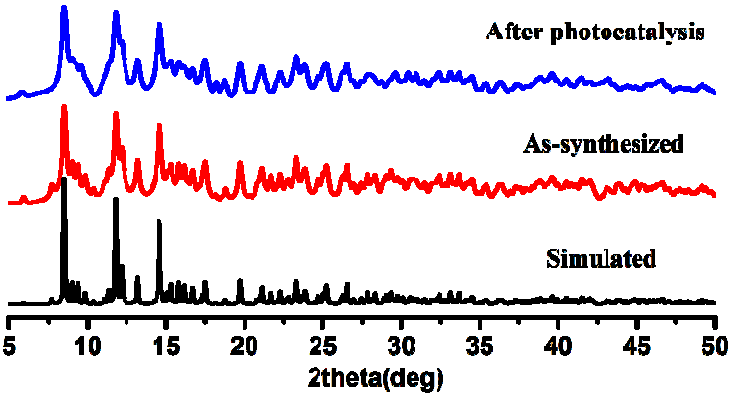

Figure S3 X-Ray power diffraction diagram of the simulated spectra from single crystal data of **1** (black), compound **1** (red), **1** after a photocatalysis process (blue).

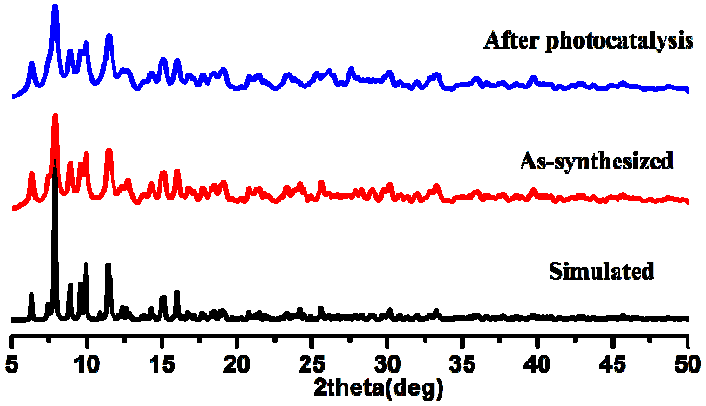

Figure S4 X-Ray power diffraction diagram of the simulated spectra from single crystal data of **2** (black), compound **2** (red), **2** after a photocatalysis process (blue).

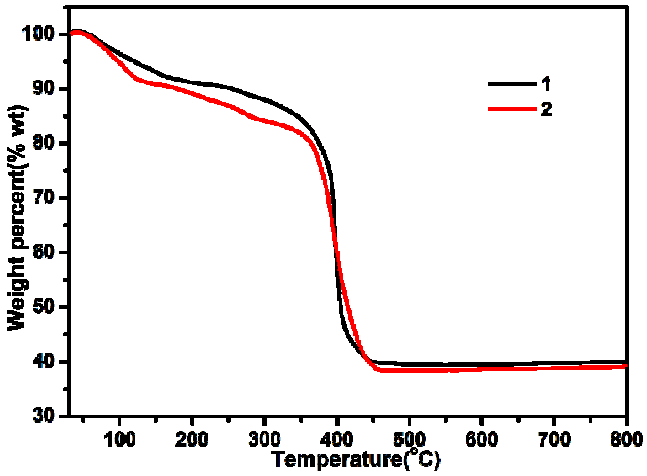

Figure S5 Thermogravimetric analysis of **1** and **2**.

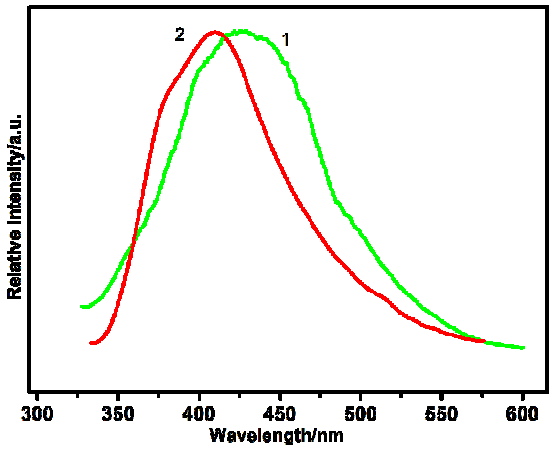

Figure S6 The emission spectra of **1** λ_{em}= 425nm (λ_{ex}=330nm) and **2**, λ_{em}= 413nm (λ_{ex}=320nm) .

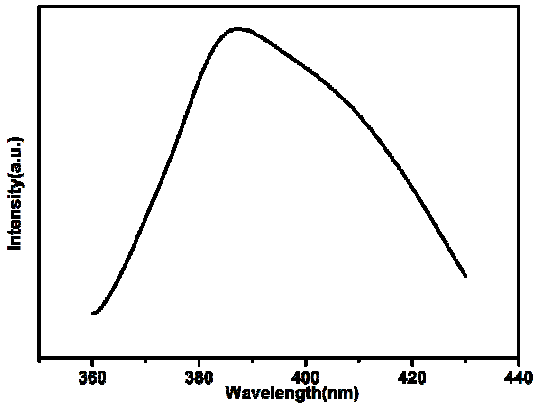

Figure S7 Solid-state luminescent emission spectra of free H_6dccpa ligand at room temperature (λ_{ex}= 300nm).

Photocatalytic experiments

The UV−vis absorption spectra of the **1** and **2** are depicted in Fig. S8. **1** and **2** show strong absorption from 200 to 800 nm. Comparably, the absorption edge of **2** is obviously red-shift than that of **1**. Besides, the optical band gap (E_g) was one principal factor affecting the speed of the photocatalysis degradation process of the organic dye. The band gaps (E_g) of **1** and **2** were investigated through the measurements of their diffuse reflectivity. The F *vs* E plots are revealed in Fig. S9, and the Eg values evaluated from the steep absorption edge are 2.87eV for **1**, and 2.79 eV for **2**, indicating that **1** and 2 are potential semiconductive characteristics.

Possible photocatalytic mechanism of 1 and 2

The photocatalytic possible mechanism is speculated as follows: the electrons of compounds were excited from the valence band (VB) to the conduction band (CB). The same number of holes have oxidation remained in the valence band. Furthermore, hydroxyl adsorbed on the surfaces of complexes could interact with the electrons on the CB or the hole on the VB, respectively, which probably generated the activated hydroxyl radicals (·OH). Consequently, the ·OH radicals could degrade the organic dye effectively to achieve the photocatalytic process.[1,2]

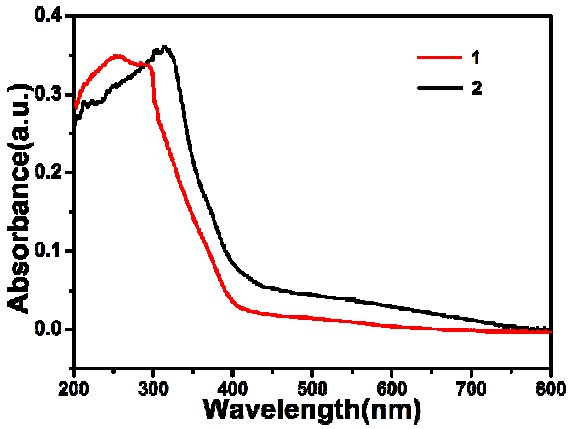

Figure S8 Solid-state optical diffuse-reflection spectra of **1** and **2**.derived from diffuse reflectance data at ambient temperature.

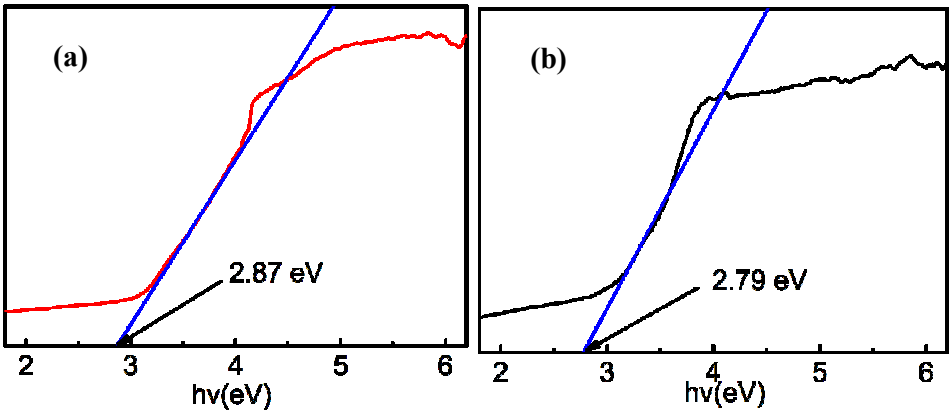

Figure S9 The $\alpha h\nu^2$ vs $h\nu$ curve of **1**(a) and **2** (b).

References:

1 F. Wang, Z. S. liu, H. Yang, Y. X. Tan, J. Zhang, Angew. Chem., Int. Ed., 2011, 50, 450.

2 L. L. Wen, L. Zhou, B. G. Zhang, X. G. Meng, H. Qu and D. F. Li, J. Mater. Chem., 2012, 22, 22603.