Supporting Information

A rare three-coordinated zinc cluster-organic framework with two types of second building units

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1. Materials and methods

Reagents and solvents employed were commercially available and used as received. Ligand H_3NTB was prepared by the literature methods [S1]. IR absorption spectra of the complexes were recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation (0.15418 nm), in which the X-ray tube was operated at 40 kV and 40 mA. Luminescent spectra were recorded with a SHIMAZU VF–320 X-ray fluorescence spectrophotometer at room temperature. The photoluminescence lifetime was measured with an Edinburgh Instruments FLS920P fluorescence spectrometer. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min^{-1} under N_2 atmosphere. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate a SHG signal. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532 nm radiation.

The solvent molecules in the structure were found to be highly disordered and were impossible to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining solvent molecules was removed by the SQUEEZE routine in PLATON [S2]. The numbers of solvent molecules were obtained by element analysis, IR and TGA.

References

[S1] J. Wang, C. He, P. Y. Wu, J. Wang, C. Y. Duan, *J. Am. Chem. Soc.*, 2011, **133**, 12402.

[S2] A. L. Spek, *Acta Crystallogr., Sect. A: Found Crystallogr*. 1990, **46**, 194.

2. Synthesis procedure

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.4 mmol), H_3NTB (0.1 mmol) and H_2NDB (0.1 mmol) is dispersed in 10 mL H_2O, and the mixture is adjusted to pH=6. The final mixture is placed in a Parr Teflon-lined stainless steel vessel (15 mL) and heated at 150 °C for 4d. Large quantities of faint yellow-block crystals is obtained, the crystals are filtered off, washed with mother liquid, and dried under ambient conditions. yield of the reaction is ~40%. Anal. Calcd for $C_{168}H_{178}N_9O_{94}Zn_{17}$: C, 40.86%, H, 3.63%, N, 2.55%; found C, 40.61%, H, 3.86%, N, 2.35%. IR (KBr, cm^{-1}): 3485(w), 3062(w), 2361(m), 1666(s), 1604(s), 1548(s), 1383(s), 1299(w), 1161(m), 1093(m), 1010(w), 844(w), 794(m), 733(s), 615(m).

3. Electronic structure calculations

Computational details

Starting from the crystal structures, geometry optimizations were performed for clusters $Zn_4H_6(\mu_4\text{-}O)(COO)_6$ and $Zn_9H_{12}(\mu_3\text{-}O)_3(COO)_{12}$ using the DFT/B3LYP/ 6-31G(d) with diffuse functions for oxygen atoms. In order to obtain the same geometry configurations with clusters in the MOFs, $Zn_4H_6(\mu_4\text{-}O)(COO)_6$ and $Zn_9H_{12}(\mu_3\text{-}O)_3(COO)_{12}$ are constrainted to have C_3 and D_3 symmetries, respectively. To further study the configuration of $Zn_9H_{12}(\mu_3\text{-}O)_3(COO)_{12}$, we calculated its structure again without any symmetry constraint. As a result, a stable configuration $Zn_9H_{12}(\mu_3\text{-}O)(\mu_4\text{-}O)_2(COO)_{12}$ was obtained. Based on the optimized geometry structures, frequency calculations were carried out at the same theoretical level and accurate electronic energies for these clusters were calculated using the DFT/B3LYP/6-311++G(d,p). Finally, we performed natural bond orbital (NBO) analysis[S3] for all the clusters. All the calculations were carried out with the Gaussian03 package[S4]. Our calculation methods have been successfully used to the similar study of the Zn clusters.[S5] The calculated results indicate that $Zn_4H_6(\mu_4\text{-}O)(COO)_6$ and $Zn_9H_{12}(\mu_3\text{-}O)(\mu_4\text{-}O)_2(COO)_{12}$ have no imaginary frequency and $Zn_9H_{12}(\mu_3\text{-}O)_3(COO)_{12}$ has five imaginary frequencies (-59.1*i*, -59.1*i*, -30.0*i*, -30.0*i*, -16.6*i*).

Cartesian coordiantes and electronic energies (E) by the B3LYP/ 6-311++G(d,p)

$Zn_4H_6(\mu_4\text{-}O)(COO)_6$ (E = -8328.43262 au)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	8	0.120544	-0.155879	0.058033
2	8	-0.010014	-0.155879	4.750175
3	8	4.118779	-0.155879	2.517170
4	8	2.375327	-0.106159	-0.129036
5	8	-1.299412	-0.106159	2.891010
6	8	3.153394	-0.106159	4.563404
7	8	-1.390279	2.459613	1.030208
8	8	1.587326	2.459613	5.572498
9	8	4.032262	2.459613	0.722672
10	8	-0.240786	4.308682	1.648424
11	8	1.547970	4.308682	4.267900
12	8	2.922125	4.308682	1.409053
13	8	1.409770	1.629354	2.441793
14	30	-0.267237	0.966355	1.616922
15	30	1.533914	0.966355	4.306558
16	30	2.962631	0.966355	1.401898
17	30	1.409770	3.612173	2.441793
18	6	1.596244	3.706913	5.376700
19	1	1.652304	4.340498	6.273167
20	6	3.858237	3.706912	0.812847
21	1	4.606570	4.340498	0.316065
22	6	-1.225172	3.706913	1.135830
23	1	-2.029565	4.340498	0.736146
24	6	1.217217	-0.454332	-0.491435
25	1	1.156951	-1.089231	-1.386717
26	6	4.046296	-0.454332	3.741651
27	1	4.851766	-1.089231	4.137100
28	6	-1.034204	-0.454332	4.075162
29	1	-1.779408	-1.089231	4.574995

$Zn_9H_{12}(\mu_3\text{-}O)_3(COO)_{12}$ (E = -18511.4158202 au)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	8	0.000000	1.845597	0.000000
2	8	-1.755508	0.597141	3.352372
3	8	-2.428078	2.430027	2.195468
4	30	0.000000	0.000000	3.014847
5	30	0.000000	0.000000	0.000000
6	30	-1.067422	3.099623	0.958902
7	30	1.067422	3.099623	-0.958902
8	8	0.360615	-1.818885	3.352372
9	8	1.394894	1.221744	3.352372
10	8	-1.598334	-0.922799	0.000000
11	8	1.598334	-0.922799	0.000000
12	8	0.215809	4.297395	1.918932
13	8	-1.894635	4.308962	-0.390260
14	8	2.428078	2.430027	-2.195468
15	8	-0.215809	4.297395	-1.918932
16	8	1.894635	4.308962	0.390260
17	30	-3.218063	-0.625397	-0.958902
18	30	-2.150641	-2.474226	0.958902
19	30	2.150641	-2.474226	-0.958902
20	30	3.218063	-0.625397	0.958902
21	8	-0.890426	-3.317791	2.195468
22	8	3.318504	0.887764	2.195468
23	8	-3.318504	0.887764	-2.195468
24	8	-3.613749	-2.335594	-1.918932
25	8	-4.678988	-0.513680	0.390260
26	8	-3.829558	-1.961801	1.918932
27	8	-2.784354	-3.795283	-0.390260
28	8	0.890426	-3.317791	-2.195468
29	8	3.829558	-1.961801	-1.918932
30	8	2.784354	-3.795283	0.390260
31	8	3.613749	-2.335594	1.918932
32	8	4.678988	-0.513680	-0.390260
33	8	1.755508	0.597141	-3.352372
34	30	0.000000	0.000000	-3.014847
35	8	-0.360615	-1.818885	-3.352372
36	8	-1.394894	1.221744	-3.352372
37	6	4.705678	-1.166716	-1.472980
38	1	5.595761	-1.021057	-2.104309
39	6	3.363245	-3.491879	1.472980
40	1	3.682142	-4.335543	2.104309
41	6	0.023131	-2.988993	-3.031493

42	1	-0.485716	-3.801782	-3.567807
43	6	2.576979	1.514529	-3.031493
44	1	3.535298	1.480248	-3.567807
45	6	-2.600110	1.474464	-3.031493
46	1	-3.049582	2.321533	-3.567807
47	6	-3.363245	-3.491879	-1.472980
48	1	-3.682142	-4.335543	-2.104309
49	6	-4.705678	-1.166716	1.472980
50	1	-5.595761	-1.021057	2.104309
51	6	-2.576979	1.514529	3.031493
52	1	-3.535298	1.480248	3.567807
53	6	-0.023131	-2.988993	3.031493
54	1	0.485716	-3.801782	3.567807
55	6	2.600110	1.474464	3.031493
56	1	3.049582	2.321533	3.567807
57	6	1.342433	4.658595	1.472980
58	1	1.913619	5.356600	2.104309
59	6	-1.342433	4.658595	-1.472980
60	1	-1.913619	5.356600	-2.104309

$Zn_9H_{12}(\mu_3\text{-}O)(\mu_4\text{-}O)_2(COO)_{12}$ (E = -18511.5053905 au)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	8	-0.036607	1.629895	0.008158
2	8	1.732262	3.137696	-2.228361
3	8	2.747912	3.189557	-0.200972
4	30	0.059473	2.183875	-1.853584
5	30	0.323373	-0.314532	-0.161126
6	30	1.194095	2.867263	0.930858
7	30	-1.653741	2.177620	0.980246
8	8	0.559327	0.313969	-2.428700
9	8	-1.587159	2.852506	-2.676913
10	8	1.932016	-1.179981	-0.079715
11	8	-1.428464	-1.206665	-0.044426
12	8	0.213967	4.636455	0.792153
13	8	1.226129	2.431427	2.822535
14	8	-3.067338	0.813996	1.337191
15	8	-1.011644	2.089301	2.926764
16	8	-1.986989	4.105348	0.747040
17	30	3.090715	-1.373630	1.406319
18	30	3.218920	-1.090502	-1.466107
19	30	-1.784282	-2.885918	-1.022239
20	30	-2.962474	-0.198372	-0.766816

21	8	2.399346	-0.706348	-3.239340
22	8	-2.776026	1.762922	-1.117377
23	8	2.239538	-1.599608	3.174344
24	8	4.205114	-2.971710	0.933413
25	8	4.360953	0.171575	1.293062
26	8	4.475838	0.395741	-0.966756
27	8	4.289055	-2.752111	-1.328645
28	8	-0.999975	-4.390380	-0.067977
29	8	-3.760459	-3.191342	-0.718958
30	8	-1.588704	-2.522708	-2.925229
31	8	-2.713772	-0.560894	-2.787822
32	8	-4.660496	-1.134798	-0.423300
33	8	-3.071030	-0.883862	2.802941
34	30	-1.557469	-1.706357	1.836160
35	8	-1.339389	-3.652407	2.049547
36	8	0.186872	-1.013570	2.472175
37	6	-4.718174	-2.399211	-0.506954
38	1	-5.712954	-2.848450	-0.373130
39	6	-2.122167	-1.479246	-3.413918
40	1	-2.053666	-1.375288	-4.507071
41	6	-1.012013	-4.521063	1.188239
42	1	-0.700573	-5.499643	1.578778
43	6	-3.448547	0.250461	2.417552
44	1	-4.173096	0.783475	3.047047
45	6	0.999781	-1.493050	3.327660
46	1	0.590915	-1.834137	4.291768
47	6	4.537423	-3.333002	-0.230867
48	1	5.117079	-4.265951	-0.302644
49	6	4.773330	0.707592	0.224991
50	1	5.473906	1.547407	0.345003
51	6	2.717070	3.334732	-1.455363
52	1	3.648209	3.667958	-1.931770
53	6	1.336702	-0.064457	-3.374425
54	1	1.037104	0.196548	-4.401209
55	6	-2.673106	2.434508	-2.192428
56	1	-3.592674	2.692023	-2.734043
57	6	-1.013912	4.919374	0.743807
58	1	-1.275390	5.985950	0.684862
59	6	0.142862	2.164349	3.426813
60	1	0.231385	1.982345	4.507652

Summary of natural population analyses

Atom	Center Number	Natural Charge	Natural Population			
			Cor	Val	Ryd	Total
$Zn_4H_6(\mu_4\text{-O})(COO)_6$						
O	1	-0.86142	1.99973	6.83757	0.02412	8.86142
O	2	-0.86143	1.99973	6.83758	0.02412	8.86143
O	3	-0.86137	1.99973	6.83753	0.02412	8.86137
O	4	-0.86105	1.99973	6.83721	0.02410	8.86105
O	5	-0.86103	1.99973	6.83720	0.02410	8.86103
O	6	-0.86101	1.99973	6.83718	0.02410	8.86101
O	7	-0.86159	1.99973	6.83774	0.02412	8.86159
O	8	-0.86162	1.99973	6.83777	0.02412	8.86162
O	9	-0.86160	1.99973	6.83775	0.02412	8.86160
O	10	-0.86114	1.99973	6.83730	0.02411	8.86114
O	11	-0.86115	1.99973	6.83731	0.02411	8.86115
O	12	-0.86113	1.99973	6.83730	0.02411	8.86113
O	13	-1.85458	1.99999	7.77981	0.07477	9.85458
Zn	14	1.74499	17.99825	10.20505	0.05170	28.25501
Zn	15	1.74497	17.99825	10.20506	0.05172	28.25503
Zn	16	1.74503	17.99825	10.20504	0.05168	28.25497
Zn	17	1.74507	17.99825	10.20499	0.05168	28.25493
		Natural Electron Configuration				
O	1	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)				
O	2	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)4p(0.01)				
O	3	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)				
O	4	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)				
O	5	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)4p(0.01)				
O	6	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)				
O	7	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)4p(0.01)				
O	8	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)4p(0.01)				
O	9	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)4p(0.01)				
O	10	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)				
O	11	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)4p(0.01)				
O	12	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)				
O	13	[core]2S(1.94)2p(5.84)3p(0.06)4p(0.01)				
Zn	14	[core]4S(0.27)3d(9.93)4p(0.01)5p(0.04)				
Zn	15	[core]4S(0.27)3d(9.93)4p(0.01)5p(0.04)				
Zn	16	[core]4S(0.27)3d(9.93)5p(0.05)				
Zn	17	[core]4S(0.27)3d(9.93)4p(0.01)5p(0.04)				
$Zn_9H_{12}(\mu_3\text{-O})_3(COO)_{12}$						

O	1	-1.79416	1.99998	7.75328	0.04090	9.79416
O	2	-0.91346	1.99971	6.88560	0.02815	8.91346
O	3	-0.83152	1.99970	6.80512	0.02670	8.83152
Zn	4	1.70598	17.99763	10.23702	0.05937	28.29402
Zn	5	1.74650	17.99874	10.19775	0.05701	28.25350
Zn	6	1.74887	17.99829	10.19684	0.05600	28.25113
Zn	7	1.74887	17.99829	10.19684	0.05600	28.25113
O	8	-0.91346	1.99971	6.88560	0.02815	8.91346
O	9	-0.91346	1.99971	6.88560	0.02815	8.91346
O	10	-1.79416	1.99998	7.75328	0.04090	9.79416
O	11	-1.79416	1.99998	7.75328	0.04090	9.79416
O	12	-0.85307	1.99973	6.82958	0.02375	8.85307
O	13	-0.85295	1.99973	6.83020	0.02301	8.85295
O	14	-0.83152	1.99970	6.80512	0.02670	8.83152
O	15	-0.85307	1.99973	6.82958	0.02375	8.85307
O	16	-0.85295	1.99973	6.83020	0.02301	8.85295
Zn	17	1.74887	17.99829	10.19684	0.05600	28.25113
Zn	18	1.74887	17.99829	10.19684	0.05600	28.25113
Zn	19	1.74887	17.99829	10.19684	0.05600	28.25113
Zn	20	1.74887	17.99829	10.19684	0.05600	28.25113
O	21	-0.83152	1.99970	6.80512	0.02670	8.83152
O	22	-0.83152	1.99970	6.80512	0.02670	8.83152
O	23	-0.83152	1.99970	6.80512	0.02670	8.83152
O	24	-0.85307	1.99973	6.82958	0.02375	8.85307
O	25	-0.85295	1.99973	6.83020	0.02301	8.85295
O	26	-0.85307	1.99973	6.82958	0.02375	8.85307
O	27	-0.85295	1.99973	6.83020	0.02301	8.85295
O	28	-0.83152	1.99970	6.80512	0.02670	8.83152
O	29	-0.85307	1.99973	6.82958	0.02375	8.85307
O	30	-0.85295	1.99973	6.83020	0.02301	8.85295
O	31	-0.85307	1.99973	6.82958	0.02375	8.85307
O	32	-0.85295	1.99973	6.83020	0.02301	8.85295
O	33	-0.91346	1.99971	6.88560	0.02815	8.91346
Zn	34	1.70598	17.99763	10.23702	0.05937	28.29402
O	35	-0.91346	1.99971	6.88560	0.02815	8.91346
O	36	-0.91346	1.99971	6.88560	0.02815	8.91346

Natural Electron Configuration

O	1	[core]2S(1.93)2p(5.82)3p(0.03)4p(0.01)
O	2	[core]2S(1.71)2p(5.17)3S(0.01)3p(0.01)3d(0.01)
O	3	[core]2S(1.71)2p(5.10)3p(0.01)3d(0.01)
Zn	4	[core]4S(0.32)3d(9.91)4p(0.02)5p(0.03)
Zn	5	[core]4S(0.31)3d(9.89)4p(0.04)5p(0.02)

Zn	6	[core]4S(0.27)3d(9.93)4p(0.04)5p(0.01)
Zn	7	[core]4S(0.27)3d(9.93)4p(0.04)5p(0.01)
O	8	[core]2S(1.71)2p(5.17)3S(0.01)3p(0.01)3d(0.01)
O	9	[core]2S(1.71)2p(5.17)3S(0.01)3p(0.01)3d(0.01)
O	10	[core]2S(1.93)2p(5.82)3p(0.03)4p(0.01)
O	11	[core]2S(1.93)2p(5.82)3p(0.03)4p(0.01)
O	12	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	13	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	14	[core]2S(1.71)2p(5.10)3p(0.01)3d(0.01)
O	15	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	16	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
Zn	17	[core]4S(0.27)3d(9.93)4p(0.03)5p(0.02)
Zn	18	[core]4S(0.27)3d(9.93)4p(0.04)5p(0.02)
Zn	19	[core]4S(0.27)3d(9.93)4p(0.04)5p(0.02)
Zn	20	[core]4S(0.27)3d(9.93)4p(0.03)5p(0.02)
O	21	[core]2S(1.71)2p(5.10)3p(0.01)3d(0.01)
O	22	[core]2S(1.71)2p(5.10)3p(0.01)3d(0.01)
O	23	[core]2S(1.71)2p(5.10)3p(0.01)3d(0.01)
O	24	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	25	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	26	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	27	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	28	[core]2S(1.71)2p(5.10)3p(0.01)3d(0.01)
O	29	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	30	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	31	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	32	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	33	[core]2S(1.71)2p(5.17)3S(0.01)3p(0.01)3d(0.01)
Zn	34	[core]4S(0.32)3d(9.91)4p(0.02)5p(0.03)
O	35	[core]2S(1.71)2p(5.17)3S(0.01)3p(0.01)3d(0.01)
O	36	[core]2S(1.71)2p(5.17)3S(0.01)3p(0.01)3d(0.01)

$Zn_9H_{12}(\mu_3\text{-}O)(\mu_4\text{-}O)_2(COO)_{12}$

O	1	-1.83001	1.99998	7.78003	0.05000	9.83001
O	2	-0.87372	1.99973	6.84994	0.02405	8.87372
O	3	-0.85444	1.99973	6.82956	0.02516	8.85444
Zn	4	1.75314	17.99807	10.19848	0.05031	28.24686
Zn	5	1.80552	17.99847	10.15923	0.03678	28.19448
Zn	6	1.74079	17.99810	10.20676	0.05435	28.25921
Zn	7	1.76228	17.99799	10.19326	0.04647	28.23772
O	8	-0.96514	1.99974	6.92366	0.04174	8.96514
O	9	-0.83041	1.99974	6.80053	0.03015	8.83041
O	10	-1.78967	1.99998	7.75863	0.03107	9.78967

O	11	-1.83393	1.99998	7.78132	0.05262	9.83393
O	12	-0.85386	1.99973	6.83025	0.02388	8.85386
O	13	-0.85635	1.99974	6.83380	0.02281	8.85635
O	14	-0.96232	1.99974	6.92402	0.03856	8.96232
O	15	-0.85635	1.99973	6.83110	0.02552	8.85635
O	16	-0.86220	1.99975	6.83887	0.02358	8.86220
Zn	17	1.74681	17.99833	10.20193	0.05293	28.25319
Zn	18	1.74220	17.99836	10.20460	0.05485	28.25780
Zn	19	1.74333	17.99810	10.20771	0.05085	28.25667
Zn	20	1.76181	17.99800	10.19422	0.04597	28.23819
O	21	-0.80041	1.99972	6.76942	0.03127	8.80041
O	22	-0.94528	1.99974	6.90741	0.03813	8.94528
O	23	-0.81700	1.99972	6.78534	0.03194	8.81700
O	24	-0.85300	1.99973	6.82989	0.02338	8.85300
O	25	-0.85263	1.99973	6.82900	0.02391	8.85263
O	26	-0.86520	1.99974	6.84105	0.02442	8.86520
O	27	-0.85829	1.99973	6.83570	0.02286	8.85829
O	28	-0.84849	1.99973	6.82540	0.02336	8.84849
O	29	-0.85406	1.99973	6.83015	0.02418	8.85406
O	30	-0.85920	1.99974	6.83624	0.02322	8.85920
O	31	-0.85142	1.99973	6.82594	0.02575	8.85142
O	32	-0.86336	1.99975	6.83993	0.02368	8.86336
O	33	-0.81826	1.99973	6.78806	0.03047	8.81826
Zn	34	1.75544	17.99808	10.19466	0.05182	28.24456
O	35	-0.87142	1.99973	6.84774	0.02394	8.87142
O	36	-0.92787	1.99973	6.88997	0.03818	8.92787

Natural Electron Configuration

O	1	[core]2S(1.93)2p(5.85)3p(0.04)4p(0.01)
O	2	[core]2S(1.72)2p(5.13)3p(0.01)3d(0.01)
O	3	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
Zn	4	[core]4S(0.27)3d(9.93)4p(0.02)5p(0.03)
Zn	5	[core]4S(0.24)3d(9.92)4p(0.02)5S(0.01)
Zn	6	[core]4S(0.28)3d(9.93)4p(0.03)5p(0.02)
Zn	7	[core]4S(0.26)3d(9.94)4p(0.02)5p(0.02)
O	8	[core]2S(1.73)2p(5.20)3S(0.01)3p(0.03)3d(0.01)
O	9	[core]2S(1.72)2p(5.08)3p(0.01)3d(0.01)
O	10	[core]2S(1.93)2p(5.83)3p(0.02)
O	11	[core]2S(1.93)2p(5.85)3p(0.04)4p(0.01)
O	12	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	13	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	14	[core]2S(1.72)2p(5.21)3S(0.01)3p(0.02)3d(0.01)
O	15	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)

O	16	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)
Zn	17	[core]4S(0.27)3d(9.93)4p(0.02)5p(0.03)
Zn	18	[core]4S(0.27)3d(9.93)4p(0.05)
Zn	19	[core]4S(0.28)3d(9.93)4p(0.04)
Zn	20	[core]4S(0.26)3d(9.94)4p(0.02)5p(0.02)
O	21	[core]2S(1.71)2p(5.05)3p(0.01)3d(0.01)
O	22	[core]2S(1.72)2p(5.19)3S(0.01)3p(0.02)3d(0.01)
O	23	[core]2S(1.72)2p(5.07)3p(0.01)3d(0.01)4p(0.01)
O	24	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	25	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	26	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)
O	27	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)4p(0.01)
O	28	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	29	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	30	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	31	[core]2S(1.72)2p(5.11)3p(0.01)3d(0.01)
O	32	[core]2S(1.72)2p(5.12)3p(0.01)3d(0.01)
O	33	[core]2S(1.72)2p(5.07)3p(0.01)3d(0.01)
Zn	34	[core]4S(0.26)3d(9.93)4p(0.03)5p(0.02)
O	35	[core]2S(1.72)2p(5.13)3p(0.01)3d(0.01)
O	36	[core]2S(1.72)2p(5.17)3S(0.01)3p(0.02)3d(0.01)

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4. CD, PXRD, TGA and luminescent and the photoluminescence lifetime patterns

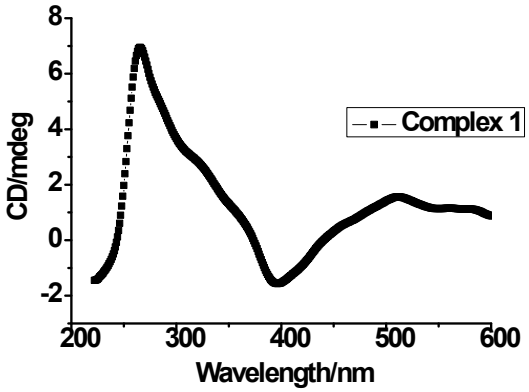

Figure S1. Solid-state circular dichroism spectrum of **1**

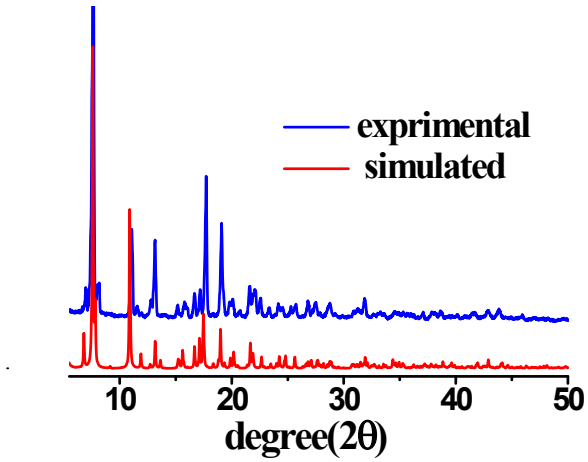

Figure S2. Powder X-ray diffraction pattern of **1**

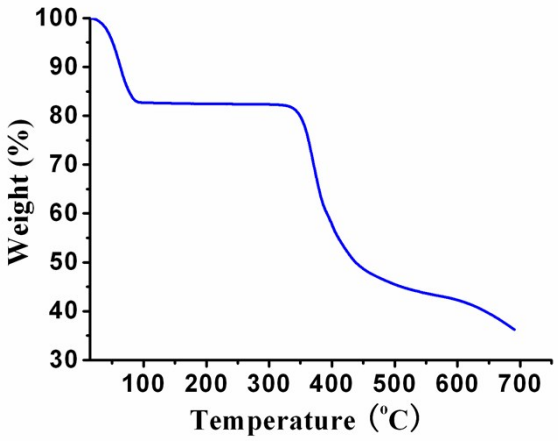

Figure S3. The TGA pattern of complex **1**

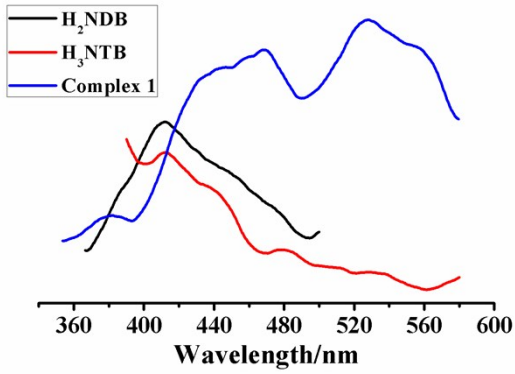

Figure S4. The solid photoluminescent patterns of complex **1**, H_3NTB and H_2NDB

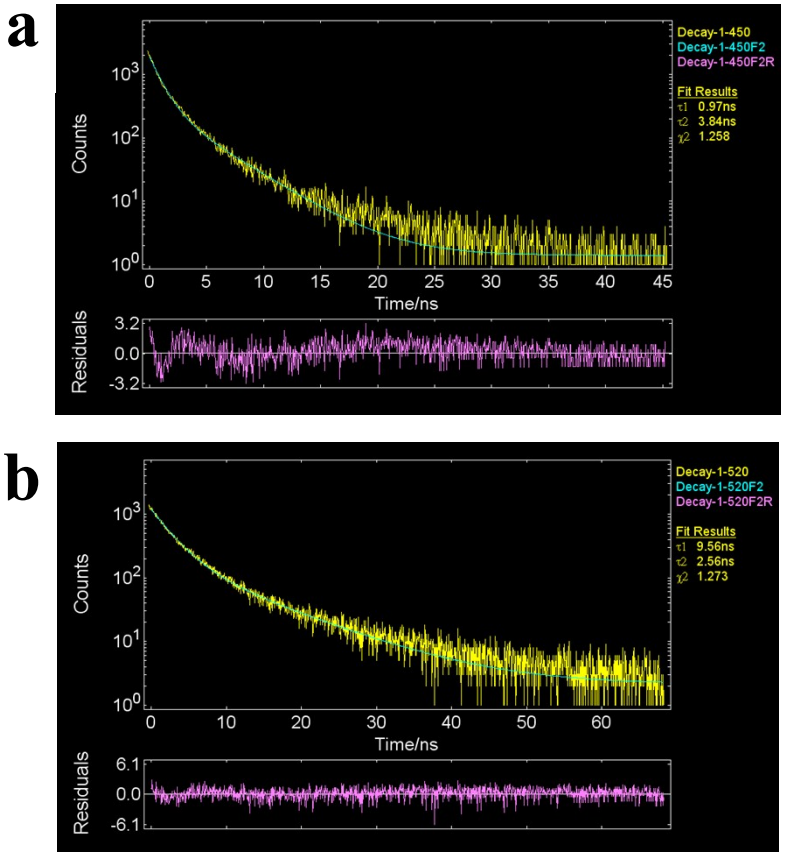

Figure S5. The fitted decay curve monitored at 450nm (**a**) and 520 nm (**b**) for complex **1** in the solid state at room temperature. The sample is excited at 370 nm. Yellow lines: experimental data; Solid line: fitted by Fit = $A+B_1\times\exp(-t/\tau_1)+B_2\times\exp(-t/\tau_2)$.

5. Bond lengths (Å) and angles (deg) of complex 1

Table S1. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Complex **1**			
O1-Zn2	1.740(5)	O1-Zn3	1.891(4)
O2-Zn1	1.949(4)	O3-Zn3	1.922(5)
O4-Zn3	1.914(4)	O5-Zn3	1.973(4)
O6-Zn4	1.909(4)	O7-Zn4	1.880(4)
O8-Zn4	1.944(4)	O9-Zn5	1.956(4)
O10-Zn5	1.884(6)	O10-Zn4	1.960(2)
O2-Zn1-O2	99.43(16)	O1-Zn2-O1	120.0
O1-Zn3#1-O4	99.02(13)	O1-Zn3#1-O3	142.45(17)
O4-Zn3#1O3	105.88(17)	O1-Zn3#1-O5	92.70(12)
O4-Zn3#1-O5	116.30(16)	O3-Zn3#1-O5	100.67(16)
O7-Zn4-O6	118.56(16)	O7-Zn4-O8	102.98(18)
O6-Zn4-O8	103.78(17)	O7-Zn4-O10	110.84(14)
O6-Zn4-O10	113.25(13)	O8-Zn4-O10	105.8(2)
O10-Zn5-O9	109.54(12)	O9-Zn5-O9	109.40(12)

#1 = *1-x, 1-x+y, -z*.