Supporting Information

Structural Variability, Unusual Thermochromic Luminescence and Nitrobenzene Sensing Property of Five Zn(II) Coordination Polymers Assembled from a Terphenyl-Hexacarboxylate Ligand

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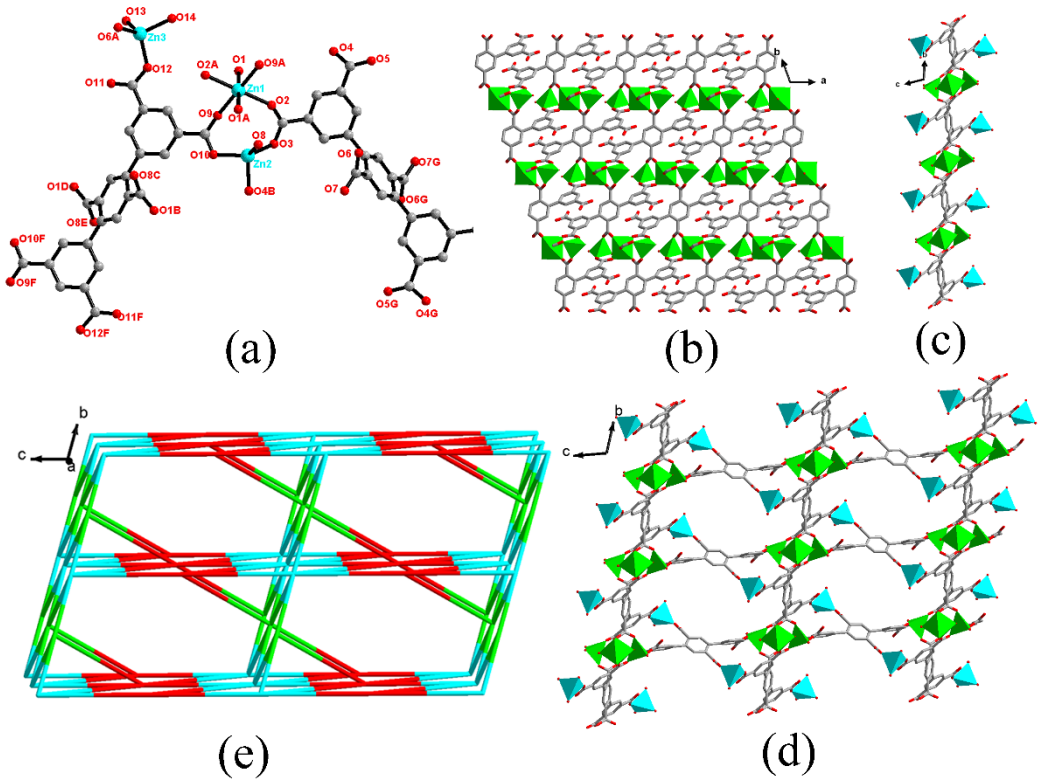


Figure S1. (a) The coordination environments for Zn(Ⅱ) ions in **1**; (b) The 2D layer in *bc* plane formed by hourglass clusters connected by ligands with MODE Ⅰ (polyhedron: green for Zn1 and Zn2, cyan for Zn3); (c) View of the layer structure along *a* axis; (d) Schematic representation of ligands pillaring the 2D layer to form 3D framework; (e) Schematic representation of topology of **1**.

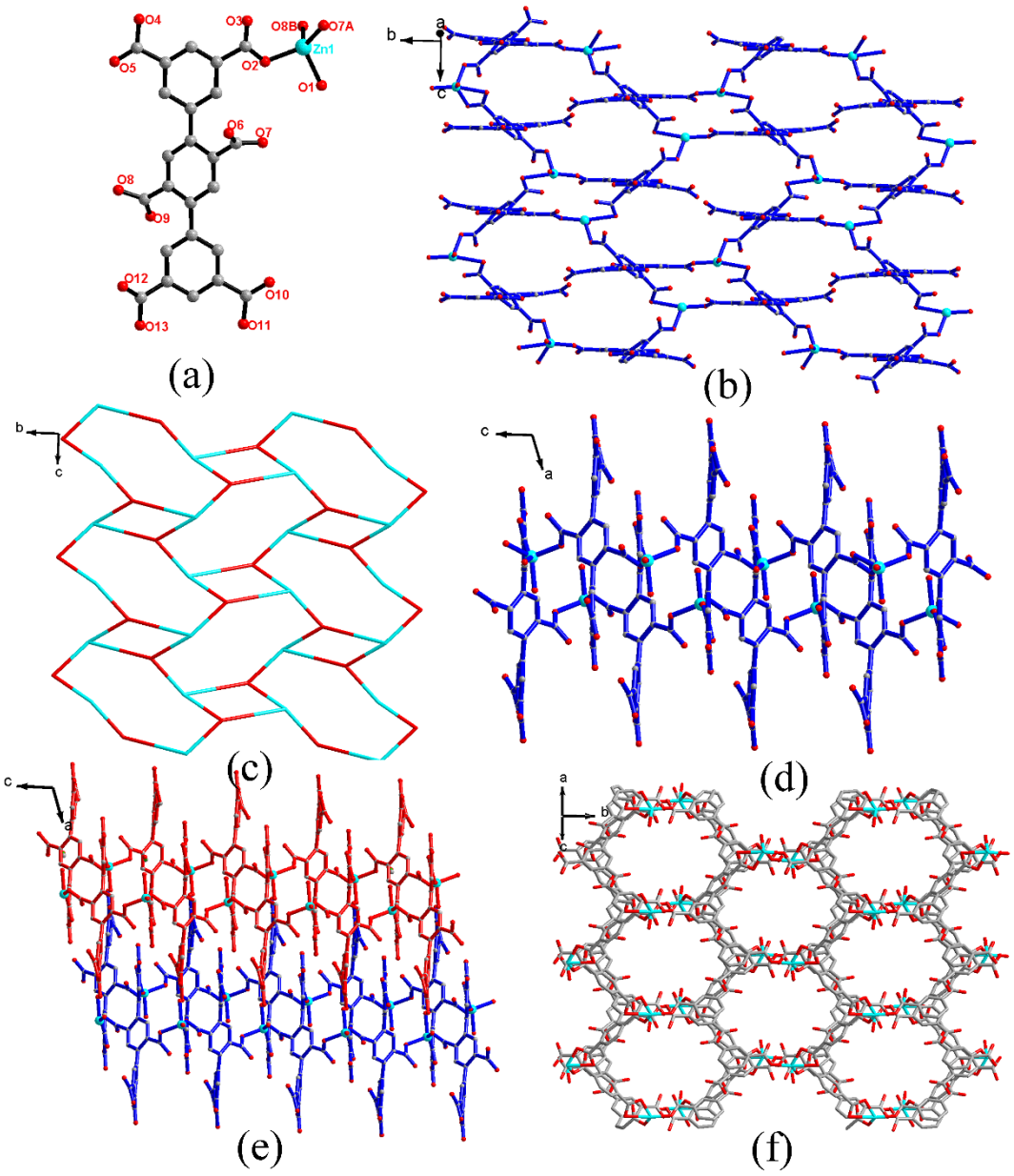


Figure S2. (a) The coordination environments for Zn(Ⅱ) ions in **2**; (b) The 2D layer formed by Zn centers and ligands; (c) The 2D Shubnikov plane net viewed along *a* axis; (d) The thick layer consisted of two parallel Zn(Ⅱ) layers viewed along *b* axis; (e) The 3D framework stacked in zipping way viewed along *b* axis; (f) View of hexagon channels in **2**.

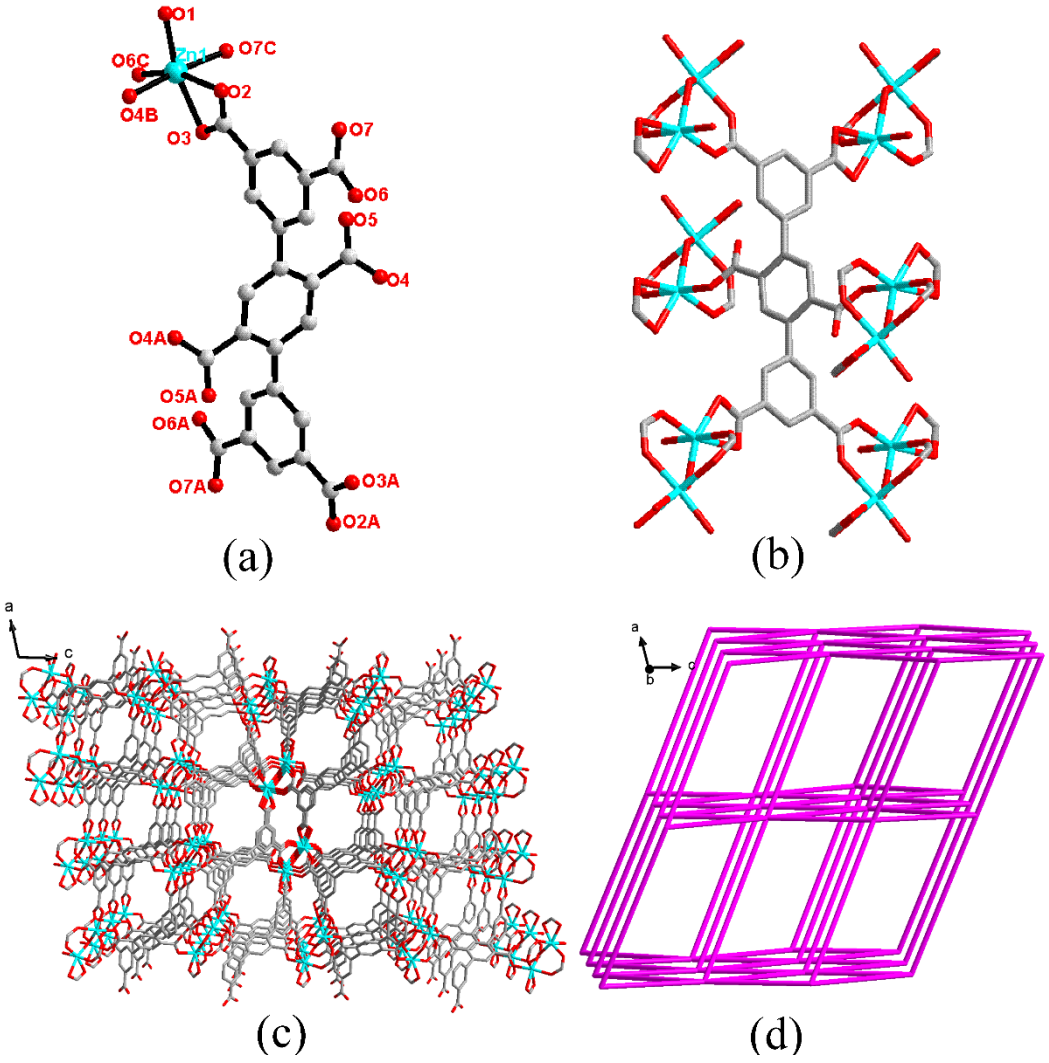


Figure S3. (a) The coordination environments for Zn(Ⅱ) ions in **3**; (b) The repeated units formed by Zn centers and ligands; (c) The 3D framework viewed along *b* axis; (d) Schematic representation of topology of **3**.

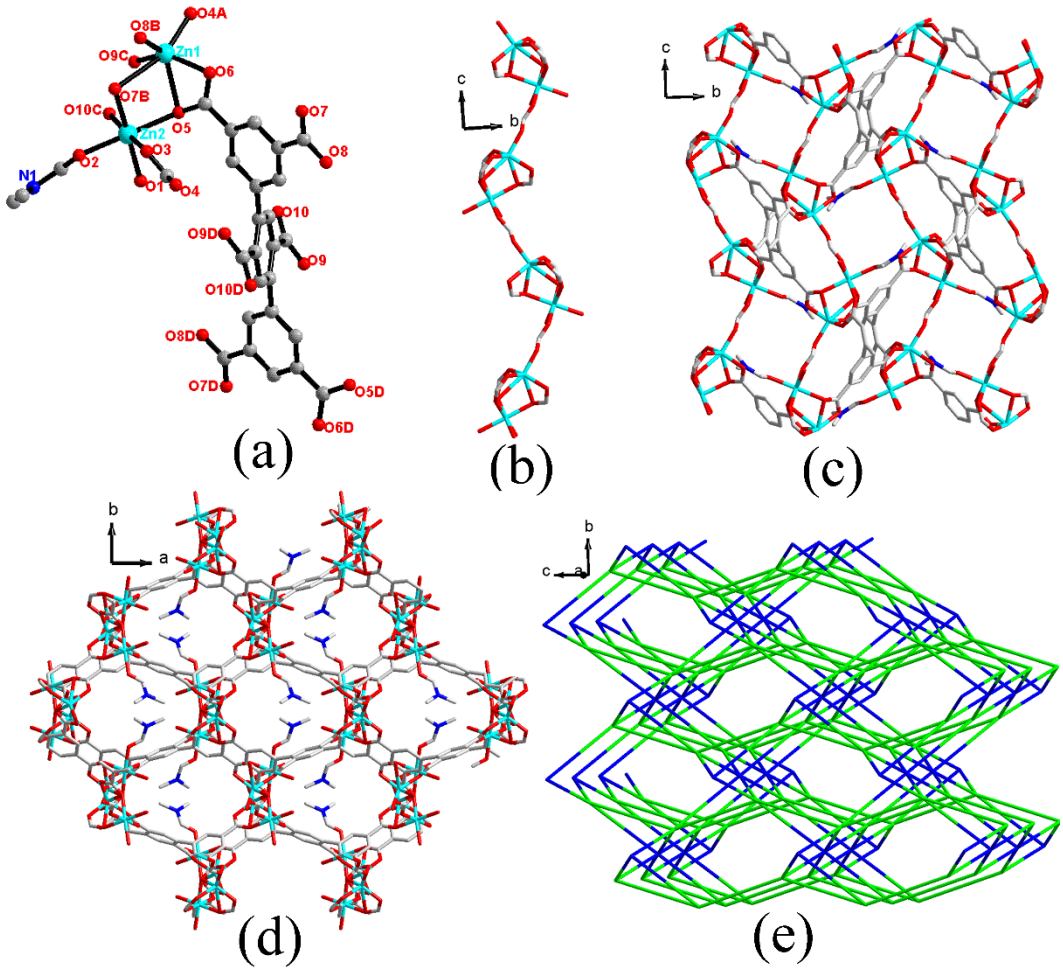


Figure S4. (a) The coordination environments for Zn(Ⅱ) ions in **4**; (b) The 1D chain formed by binuclear Zn centers and μ-COO^-. (c) the quasi-plane generated by linked 1D chains with ligands; (d) The 3D framework with a distorted quadrangular channel viewed along *c* axis; (e) Schematic representation of topology of **4**.

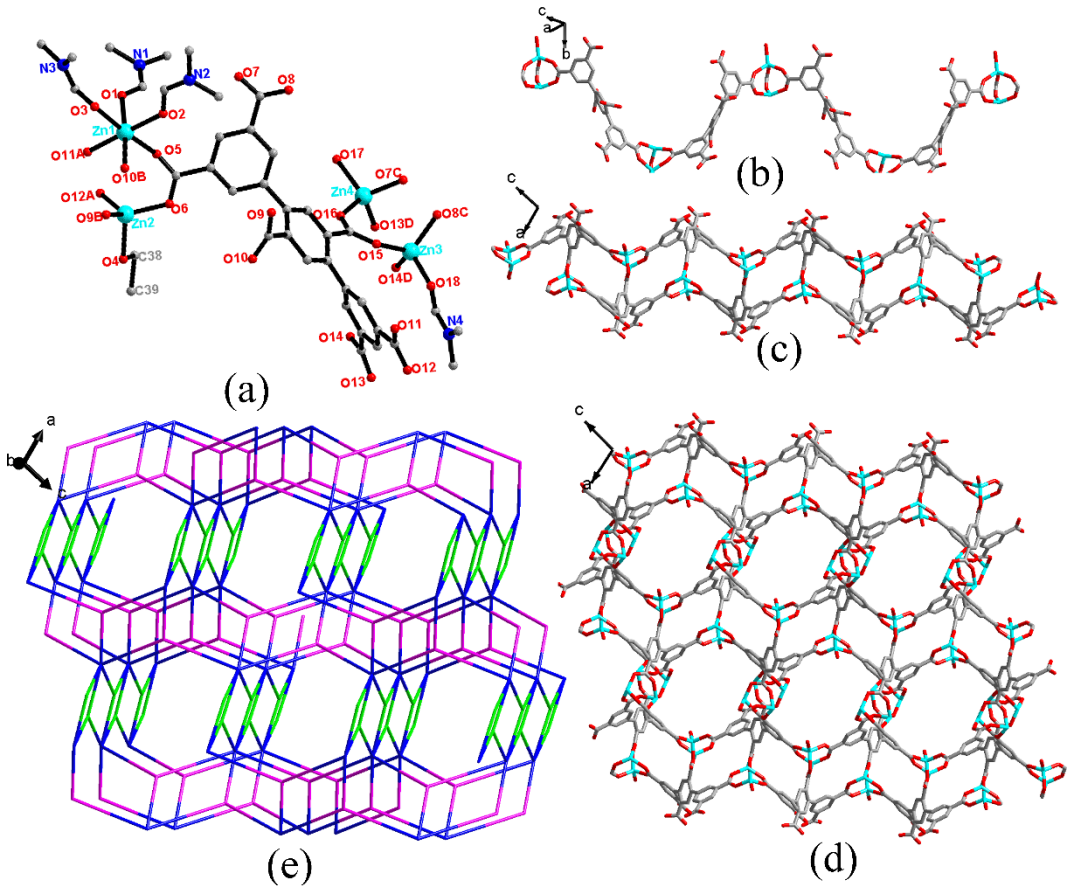
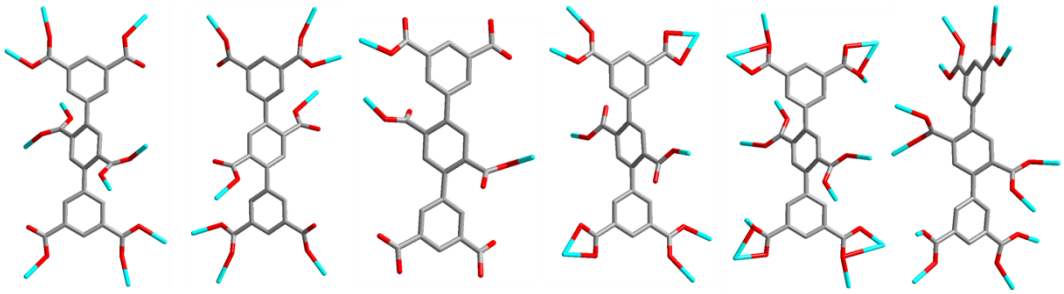
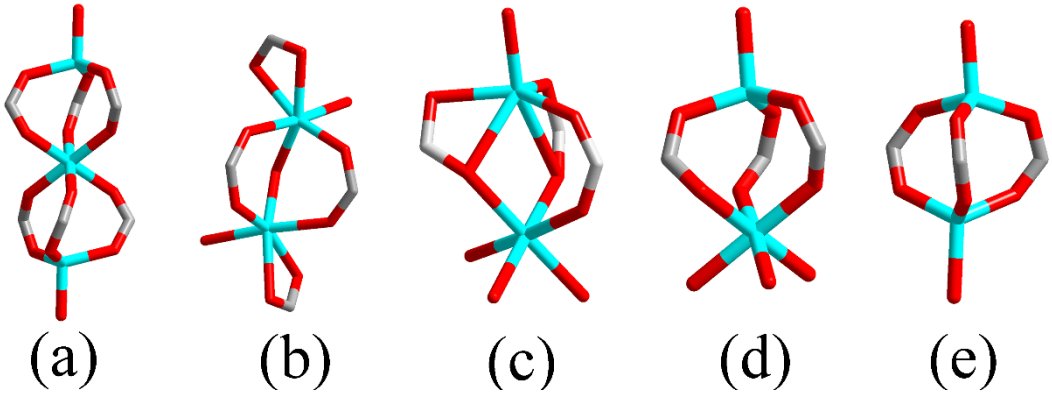


Figure S5. (a) The coordination environments for Zn(Ⅱ) ions in **5**; (b) The 1D chain formed by binuclear clusters B and ligands; (c) Thick wave-like layers with two kind of rhombus channels which are mirror images; (d) The 3D porous framework of compound **5** (The coordinated DMF molecules and ethanol molecules have been removed to get a better insight of the structure); (e) Schematic representation of topology of **5**.



MODE Ⅰ **MODE** Ⅱ **MODE** Ⅲ **MODE** Ⅳ **MODE** Ⅴ **MODE** Ⅵ

Scheme S1. The coordination modes of ligands in compounds **1**-**5**.



Scheme S2. The metal clusters in compounds **1**, **3-5**. (a) Trinuclear hourglass cluster in **1**. (b) Binuclear paddle-wheel cluster in **3**. (c) Binuclear paddle-wheel cluster in **4**. (d) Binuclear paddle-wheel cluster A in **5**. (e) Binuclear paddle-wheel cluster B in **5**.

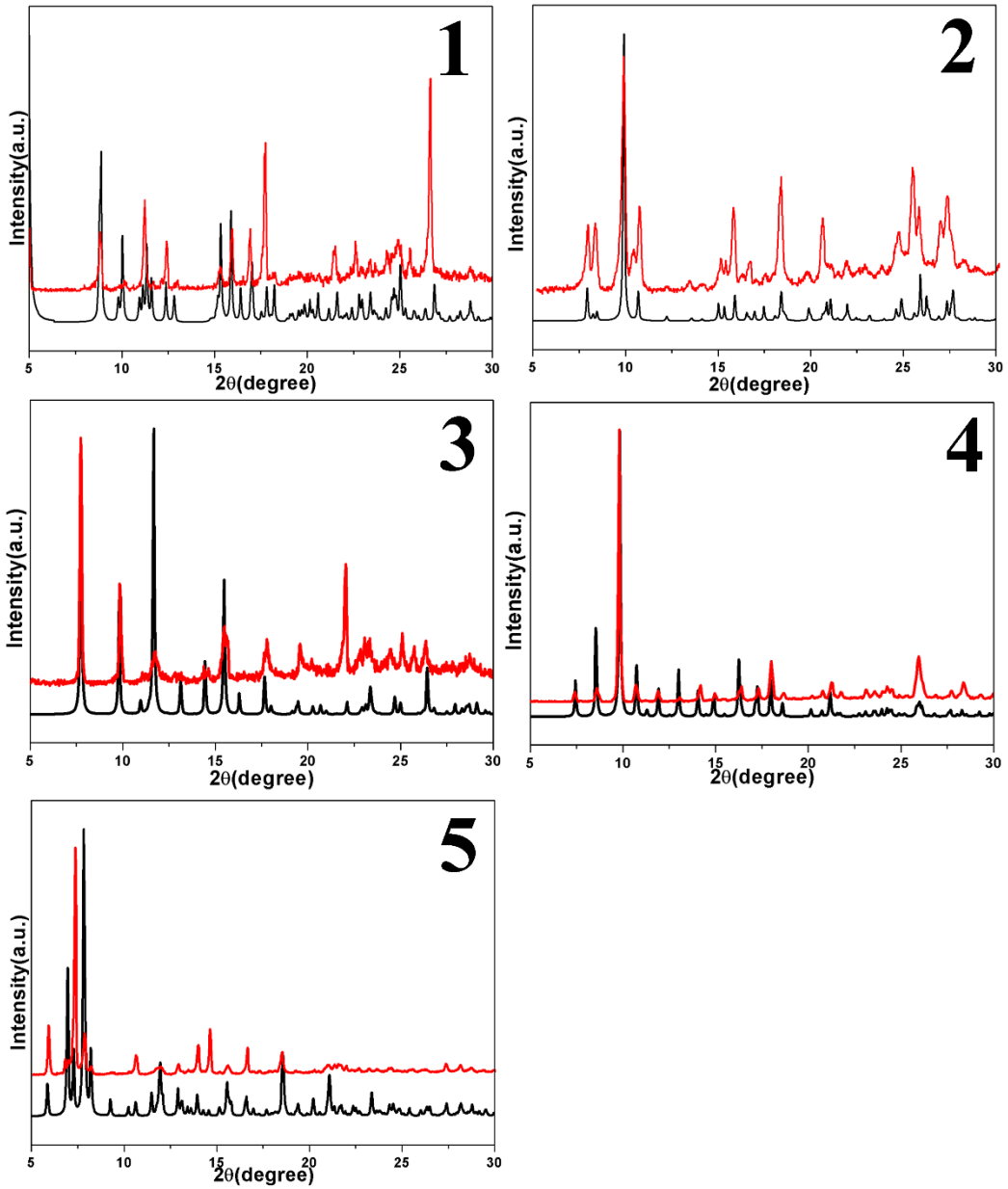


Figure S6. The simulated (black) and experimental (red) PXRD patterns for the compounds **1**−**5**.

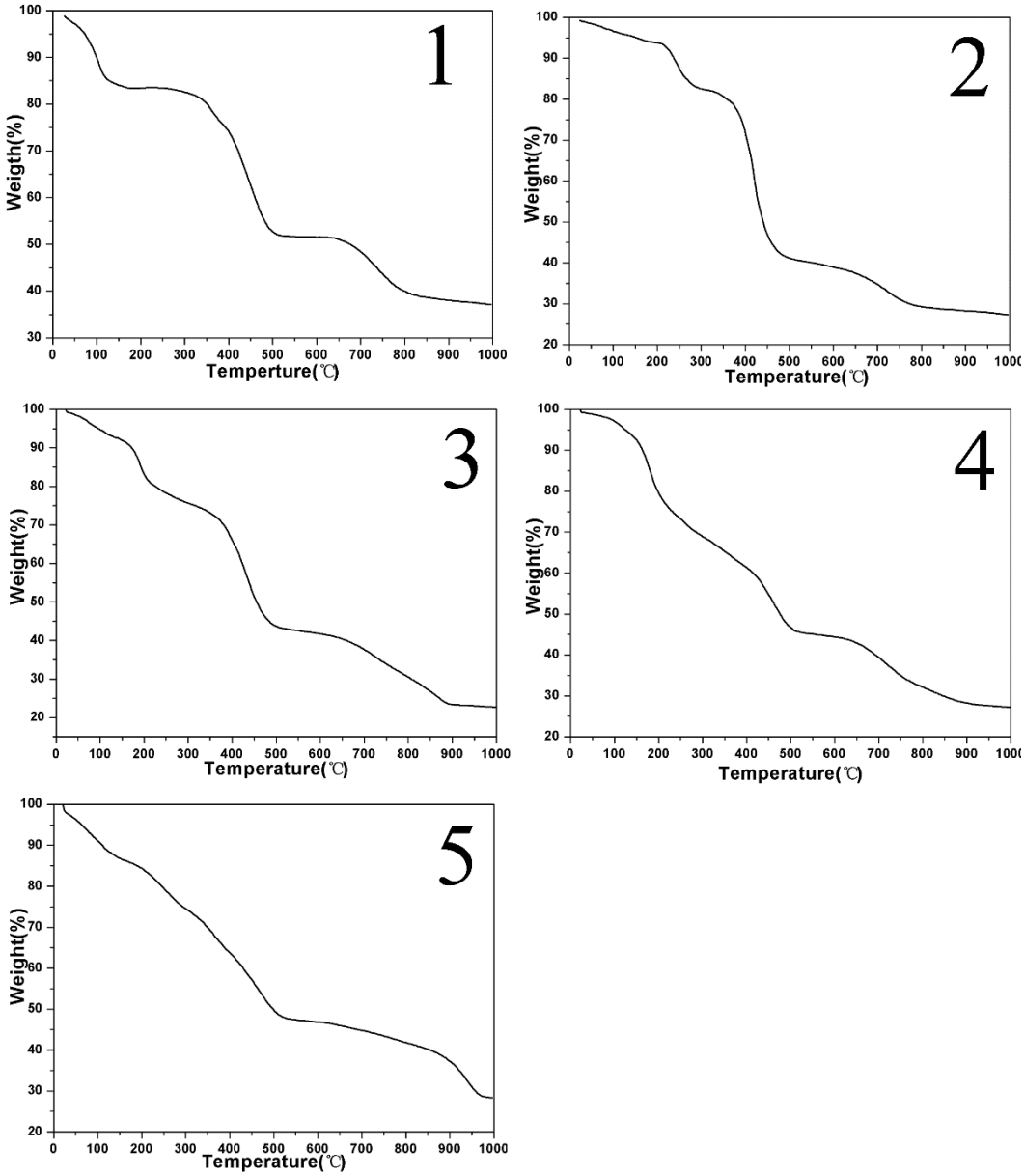


Figure S7. TGA curves of compounds**1**−**5**.

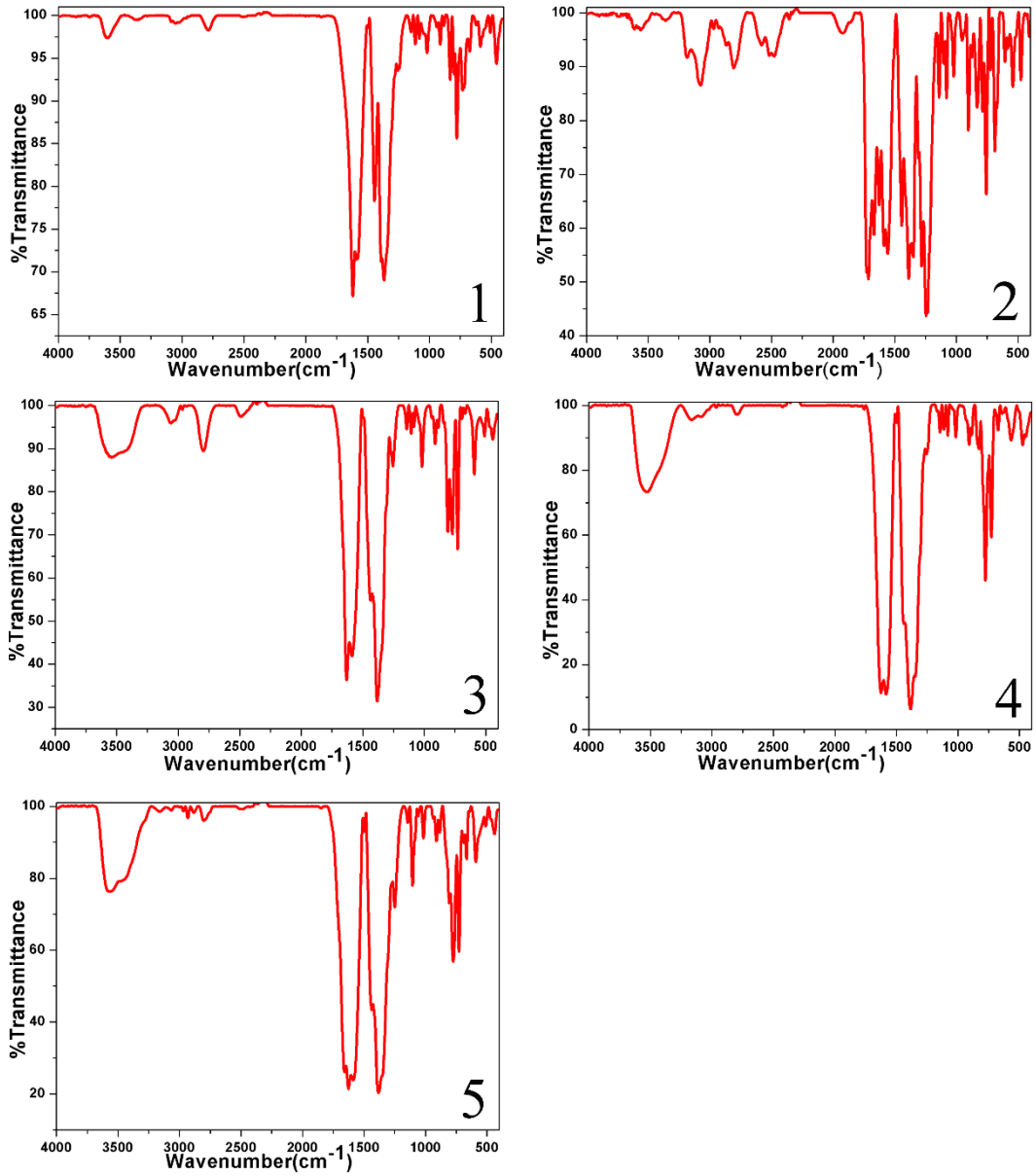


Figure S8. IR spectra of compounds**1**−**5**.

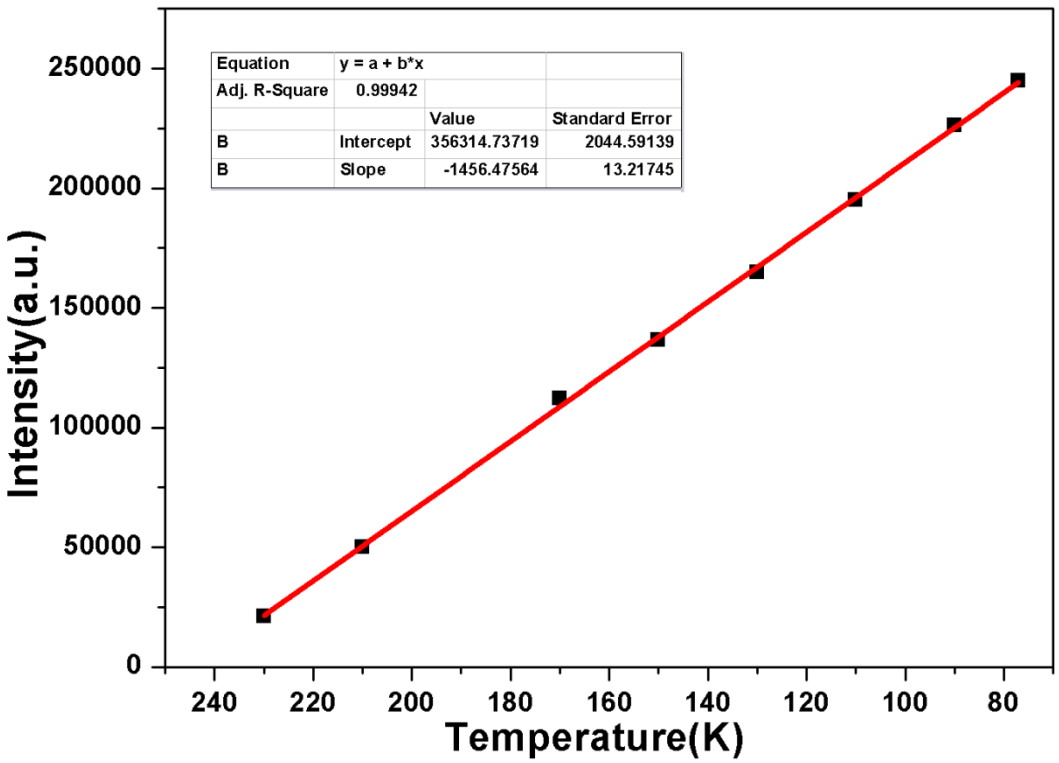


Figure S9. The scatterplot of luminescent intensity (LE band) of **3** response to temperature (rectangle box: the fitting equation y=-1456x+356314 (x≤250)).

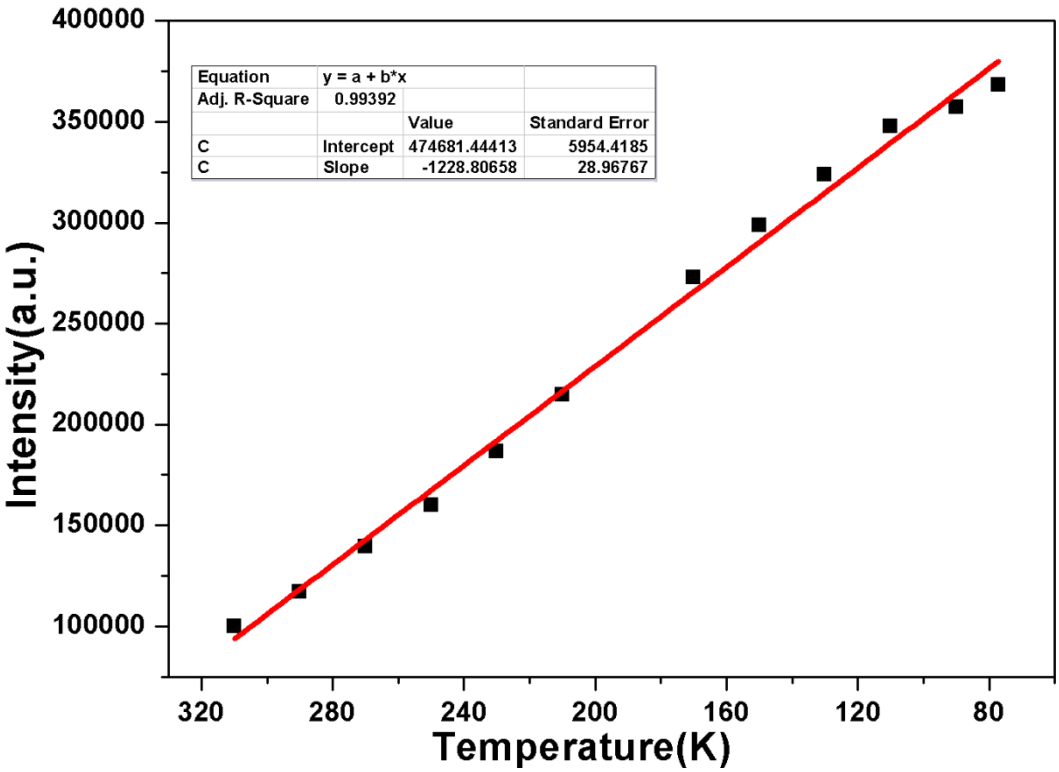


Figure S10. The scatterplot of luminescent intensity (HE band) of **5** response to temperature (rectangle box: the fitting equation y= -1229x+474681).

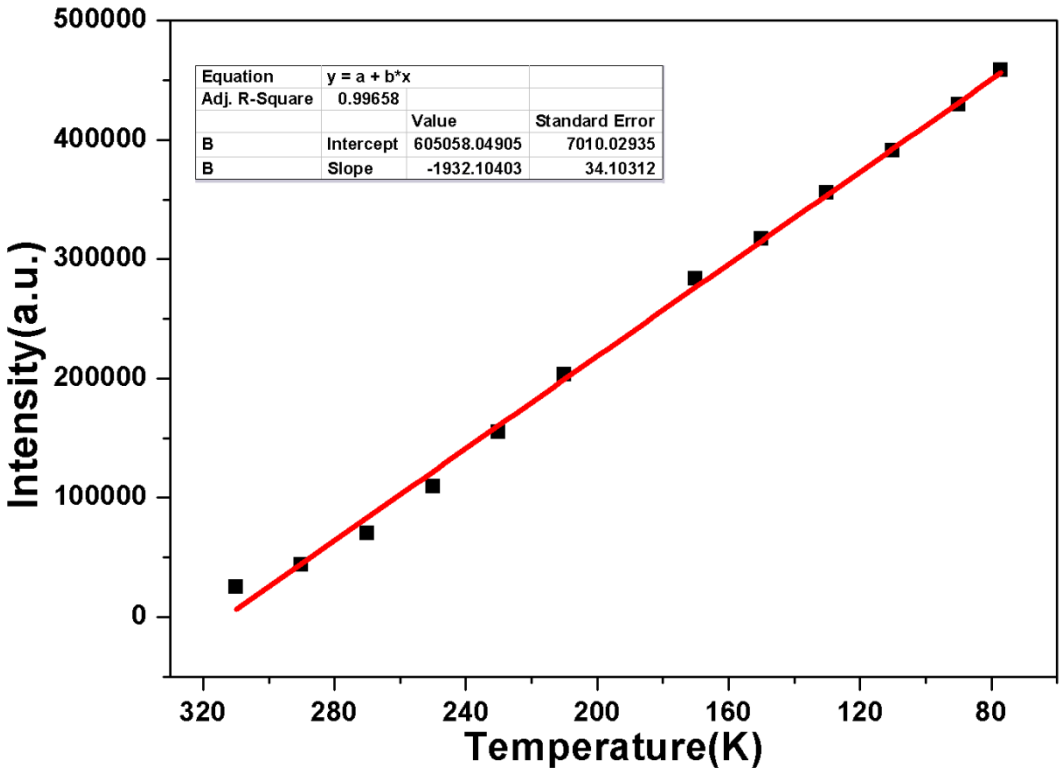


Figure S11. The scatterplot of luminescent intensity (LE band) of **5** response to temperature (rectangle box: the fitting equation y= -1932x+605058).

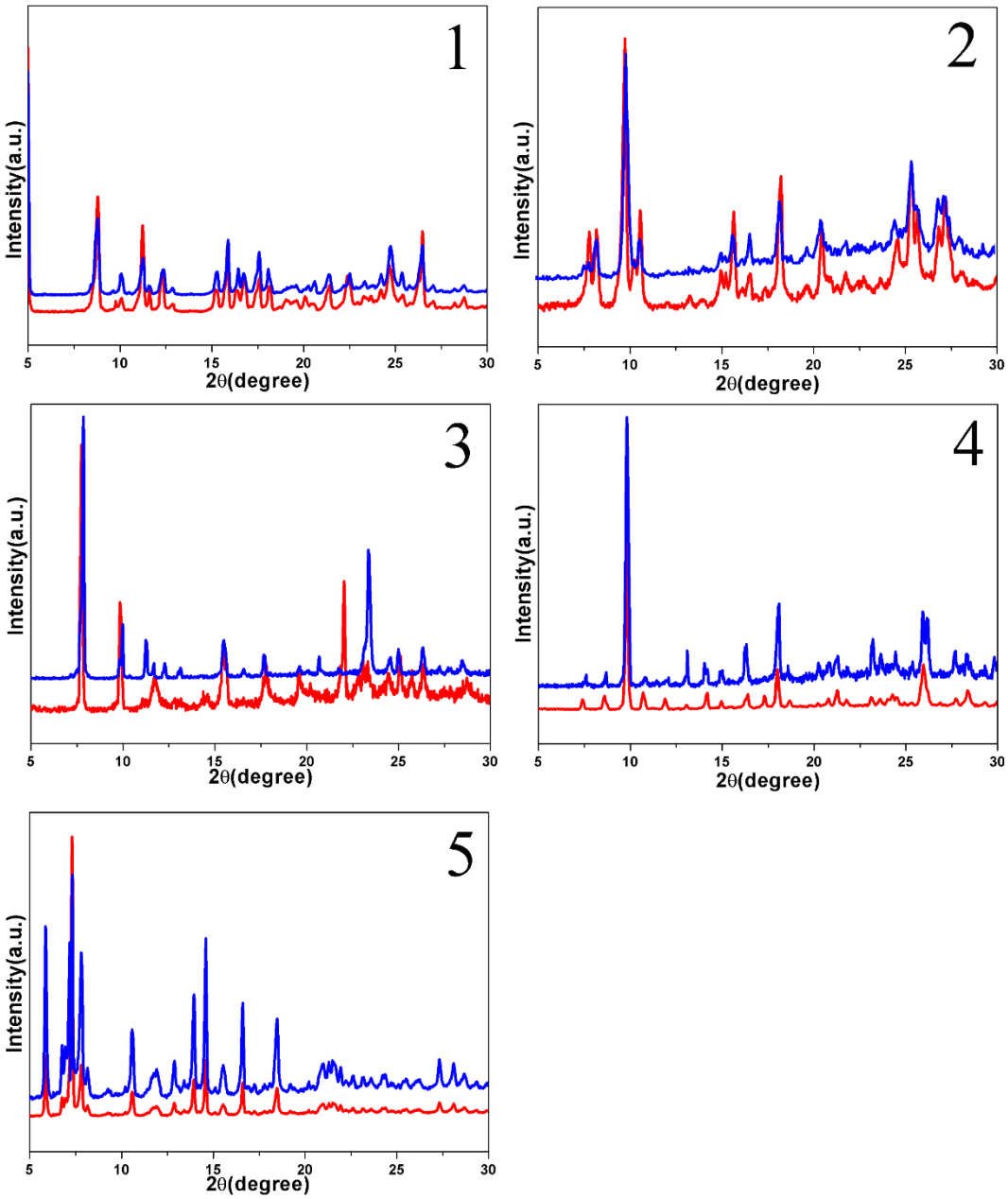


Figure S12. PXRD patterns of compounds **1-5** before (red) and after heated at 330 K for 30 min (blue).

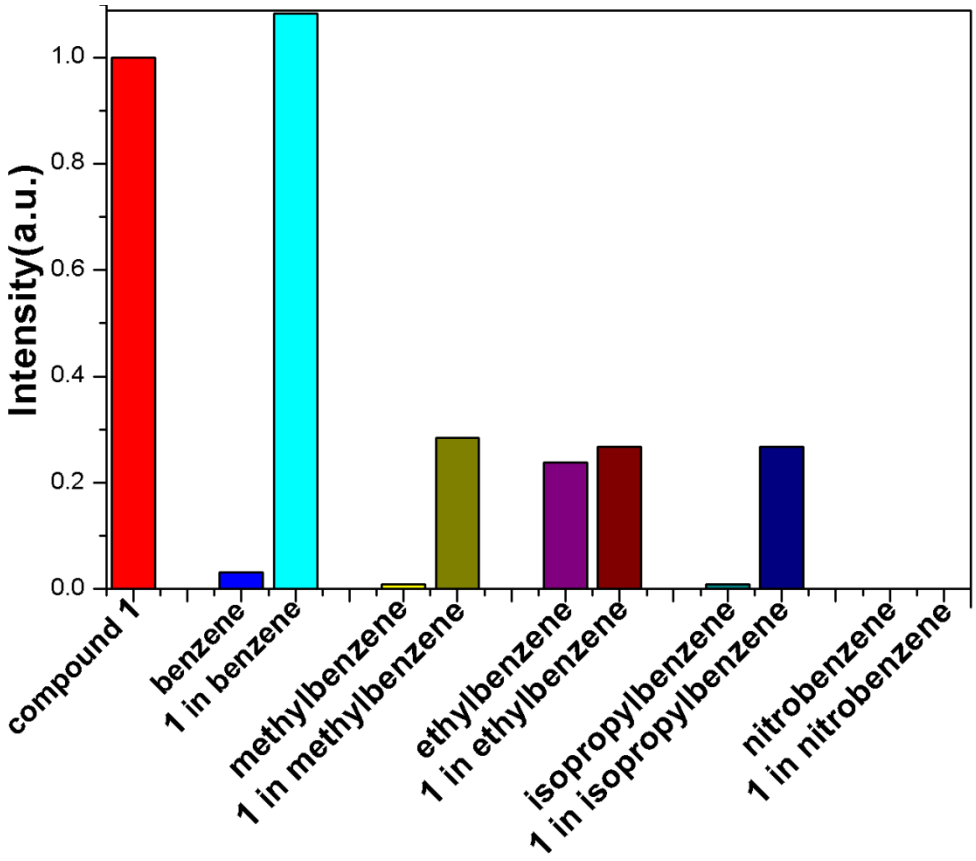


Figure S13. Comparison of emission intensities of different solvents and emulsions for **1**.

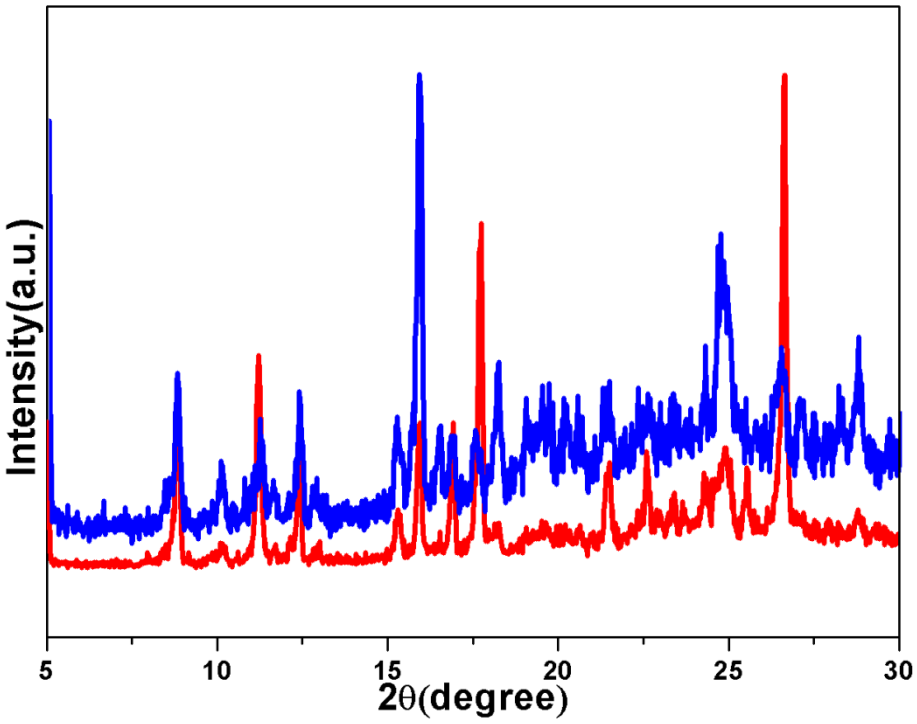


Figure S14. PXRD patterns of **1** before (red) and after (blue) sensing experiments.

Table S1. Crystal Data and Structure Refinements for compounds **1-5**.

Compounds	***1***	***2***	***3***	***4***	***5***
Empirical formula	$C_{52}H_{72}N_2O_{44}Zn_5$	C28H37NO19Zn	$C_{34}H_{46}N_4O_{18}Zn_2$	$C_{41}H_{56}N_4O_{24}Zn_4$	$C_{41}H_{57}N_5O_{23}Zn_4$
Formula weight	1756.16	756.10	929.56	1294.54	1249.55
Temperature (K)	100 (2)	100 (2)	100 (2)	100 (2)	100 (2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	*C*2/c	$P2_1/c$	$P2_1/n$
a [Å]	9.3789(3)	11.0076(4)	18.3439(3)	12.024(3)	17.0549(3)
b[Å]	10.9247(4)	21.4138(8)	8.80900(10)	13.773(4)	15.3986(3)
c [Å]	18.8993(6)	13.7391(6)	23.4388(4)	15.850(4)	23.0104(5)
α [°]	104.858(3)	90.00	90.00	90.00	90.00
β [°]	94.314(2)	108.520(5)	101.965(2)	99.093(5)	102.754(2)
γ [°]	107.714(3)	90.00	90.00	90.00	90.00
V [Å^3]	1758.09(10)	3070.8(2)	3705.22(10)	2591.8(11)	5893.9(2)
Z	2	4	8	8	4
Dc[g/cm^{-3}]	1.292	1.243	1.630	1.302	1.243
μ [mm^{-1}]	2.519	1.616	2.324	1.891	2.348
F(000)	678	1164	1880	1016	2252
θ range (°)	4.4–76.1	3.97–74.51	4.9–76.0	2.2–27.4°	3.9–72.9°
GOF on F²	1.108	1.001	0.955	1.071	1.093
Parameters	367	347	257	264	490
$R_1(I >2\sigma(I))^a$	0.0465	0.0457	0.0551	0.0433	0.0824
$wR_2(I >2\sigma(I))^b$	0.1534	0.1056	0.1513	0.1284	0.2626

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes **1-5**.

Compound 1

Bond	Dist.	Bond	Dist.
Zn1—O9	2.0816 (19)	Zn2—O3	1.935 (2)
Zn1—O9^{i}	2.0816 (19)	Zn2—O4^{ii}	1.946 (2)
Zn1—O2	2.0935 (19)	Zn2—O8	1.955 (2)
Zn1—O2^{i}	2.0935 (19)	Zn3—O12	1.911 (2)
Zn1—O1^{i}	2.1054 (18)	Zn3—O6^{i}	1.946 (3)
Zn1—O1	2.1054 (18)	Zn3—O13	1.958 (4)
Zn2—O10	1.924 (2)	Zn3—O14	1.962 (3)
Angle	(°)	Angle	(°)
O9—Zn1—O9^{i}	180.0	O10—Zn2—O4^{ii}	94.14 (10)
O9—Zn1—O2	94.13 (8)	O3—Zn2—O4^{ii}	110.01 (9)
O9^{i}—Zn1—O2	85.87 (8)	O10—Zn2—O8	116.63 (10)
O9—Zn1—O2^{i}	85.87 (8)	O3—Zn2—O8	101.42 (9)
O9^{i}—Zn1—O2^{i}	94.13 (8)	O4^{ii}—Zn2—O8	105.01 (10)

O2—Zn1—O2^{i}	180.00 (11)	O12—Zn3—O6^{i}	108.02 (12)
O9—Zn1—O1^{i}	95.30 (8)	O12—Zn3—O13	116.18 (14)
O9^{i}—Zn1—O1^{i}	84.70 (8)	O6^{i}—Zn3—O13	109.24 (18)
O2—Zn1—O1^{i}	92.77 (7)	O12—Zn3—O14	102.92 (12)
O2^{i}—Zn1—O1^{i}	87.23 (7)	O6^{i}—Zn3—O14	112.13 (13)
O9—Zn1—O1	84.70 (8)	O13—Zn3—O14	108.31 (18)
O9^{i}—Zn1—O1	95.30 (8)	C1—O2—Zn1	147.87 (18)
O2—Zn1—O1	87.23 (7)	C13—O9—Zn1	142.62 (19)
O2^{i}—Zn1—O1	92.77 (7)	C13—O10—Zn2	116.16 (18)
O1^{i}—Zn1—O1	180.0	C1—O3—Zn2	120.01 (18)
O10—Zn2—O3	127.56 (10)		

Symmetry codes: (i) 2-x, 2-y, -z; (ii) 1+x, y, z.

Compound 2

Bond	Dist.	Bond	Dist.
Zn1—O2	1.931 (2)	Zn1—O7^{i}	1.988 (2)
Zn1—O1	1.9861 (15)	Zn1—O8^{ii}	1.992 (2)
Angle	(°)	Angle	(°)
O2—Zn1—O1	97.60 (8)	O1—Zn1—C16^{i}	95.44 (8)
O2—Zn1—O7^{i}	115.42 (10)	O7^{i}—Zn1—C16^{i}	28.80 (9)
O1—Zn1—O7^{i}	114.46 (10)	O8^{ii}—Zn1—C16^{i}	99.47 (9)
O2—Zn1—O8^{ii}	111.12 (10)	C1—O2—Zn1	124.4 (2)
O1—Zn1—O8^{ii}	103.41 (10)	C16—O7—Zn1^{i}	102.86 (17)
O7^{i}—Zn1—O8^{ii}	113.23 (8)	C12—O8—Zn1^{iii}	118.58 (18)
O2—Zn1—C16^{i}	142.69 (10)		

Symmetry codes: (i) 2-x, 2-y, 1-z; (ii) 2-x, 1/2+y, 3/2-z; (iii) 2-x, -1/2+y, 3/2-z.

Compound 3

Bond	Dist.	Bond	Dist.
Zn1—O1	2.019 (2)	Zn1—O5^{iii}	2.133 (2)
Zn1—O3	2.084 (2)	Zn1—O4^{iii}	2.237 (2)
Zn1—O2^{i}	2.086 (2)	Zn1—C5^{iii}	2.505 (3)
Zn1—O7^{ii}	2.101 (2)		
Angle	(°)	Angle	(°)
O1—Zn1—O3	105.25 (9)	O5^{iii}—Zn1—O4^{iii}	60.35 (9)
O1—Zn1—O2^{i}	92.43 (10)	O1—Zn1—C5^{iii}	128.75 (11)
O3—Zn1—O2^{i}	88.72 (8)	O3—Zn1—C5^{iii}	125.99 (10)
O1—Zn1—O7^{ii}	90.48 (11)	O2^{i}—Zn1—C5^{iii}	88.15 (10)
O3—Zn1—O7^{ii}	90.63 (8)	O7^{ii}—Zn1—C5^{iii}	89.93 (10)
O2^{i}—Zn1—O7^{ii}	177.09 (11)	O5^{iii}—Zn1—C5^{iii}	30.01 (10)
O1—Zn1—O5^{iii}	98.76 (9)	O4^{iii}—Zn1—C5^{iii}	30.34 (10)
O3—Zn1—O5^{iii}	155.89 (9)	C12—O7—Zn1^{iv}	127.6 (2)

O2^{i}—Zn1—O5^{iii}	88.09 (9)	Zn1—O3—Zn1^{i}	107.00 (14)
O7^{ii}—Zn1—O5^{iii}	91.35 (10)	C1—O2—Zn1^{i}	131.3 (2)
O1—Zn1—O4^{iii}	159.04 (9)	C5—O5—Zn1^{v}	91.6 (2)
O3—Zn1—O4^{iii}	95.69 (8)	C5—O4—Zn1^{v}	86.60 (19)
O2^{i}—Zn1—O4^{iii}	88.72 (9)	C1—O1—Zn1	124.9 (2)
O7^{ii}—Zn1—O4^{iii}	88.52 (10)		

Symmetry codes: (i) 1-x, y, 3/2-z; (ii) x, 1+y, z; (iii) -1/2+x, 1/2+y, z; (iv) x, -1+y, z; (v) 1/2+x, -1/2+y, z.

Compound 4

Bond	Dist.	Bond	Dist.
Zn1—O8^{i}	1.947 (2)	Zn2—O3	2.052 (2)
Zn1—O9^{ii}	1.954 (2)	Zn2—O7^{i}	2.085 (2)
Zn1—O4^{iii}	1.977 (2)	Zn2—O2	2.106 (3)
Zn1—O6	2.107 (3)	Zn2—O1	2.118 (3)
Zn1—O5	2.342 (3)	Zn2—O5	2.222 (3)
Zn2—O10^{ii}	2.045 (2)		
Angle	(°)	Angle	(°)
O8^{i}—Zn1—O9^{ii}	111.79 (11)	O3—Zn2—O7^{i}	86.21 (10)
O8^{i}—Zn1—O4^{iii}	107.25 (11)	O10^{ii}—Zn2—O2	90.57 (10)
O9^{ii}—Zn1—O4^{iii}	98.78 (9)	O3—Zn2—O2	90.62 (12)
O8^{i}—Zn1—O6	99.20 (12)	O7^{i}—Zn2—O2	90.29 (12)
O9^{ii}—Zn1—O6	142.35 (10)	O10^{ii}—Zn2—O1	91.00 (10)
O4^{iii}—Zn1—O6	91.57 (11)	O3—Zn2—O1	93.31 (11)
O8^{i}—Zn1—O5	114.86 (10)	O7^{i}—Zn2—O1	178.81 (12)
O9^{ii}—Zn1—O5	88.60 (9)	O2—Zn2—O1	88.62 (13)
O4^{iii}—Zn1—O5	130.75 (11)	O10^{ii}—Zn2—O5	87.30 (9)
O6—Zn1—O5	58.31 (10)	O3—Zn2—O5	91.59 (11)
O8^{i}—Zn1—C2	110.11 (11)	O7^{i}—Zn2—O5	90.91 (11)
O9^{ii}—Zn1—C2	115.59 (11)	O2—Zn2—O5	177.55 (10)
O4^{iii}—Zn1—C2	112.62 (12)	O1—Zn2—O5	90.19 (12)
O6—Zn1—C2	29.41 (11)	C13—O9—Zn1^{iv}	133.34 (19)
O5—Zn1—C2	28.91 (10)	C13—O10—Zn2^{iv}	135.0 (2)
O10^{ii}—Zn2—O3	175.56 (9)	C6—O7—Zn2^{v}	155.0 (3)
O10^{ii}—Zn2—O7^{i}	89.51 (10)	C6—O8—Zn1^{v}	113.4 (2)

Symmetry codes: (i) 3-x, -1/2+y, 1/2-z; (ii) 2-x, -1/2+y, 1/2-z; (iii) x, 1/2-y, 1/2+z; (iv) 2-x, 1/2+y, 1/2-z; (v) 3-x, 1/2+y, 1/2-z.

Compound 5

Bond	Dist.	Bond	Dist.
Zn1—O2	2.0593 (12)	Zn2—O4	2.0011 (11)

Zn1—O5	2.0737 (12)	Zn3—O14^{iii}	1.911 (2)
Zn1—O10^{i}	2.0839 (11)	Zn3—O8^{iv}	1.945 (2)
Zn1—O11^{ii}	2.0856 (12)	Zn3—O15	1.9628 (13)
Zn1—O3	2.0956 (11)	Zn3—O18	1.9803 (12)
Zn1—O1	2.0975 (11)	Zn4—O16	1.9363 (13)
Zn2—O6	1.9465 (12)	Zn4—O7^{iv}	1.959 (2)
Zn2—O12^{ii}	1.9485 (11)	Zn4—O13^{iii}	1.9599 (17)
Zn2—O9^{i}	1.9585 (12)	Zn4—O17	2.1643 (12)
Angle	(°)	Angle	(°)
O2—Zn1—O5	86.5	O8^{iv}—Zn3—O18	108.74 (7)
O2—Zn1—O10^{i}	89.0	O15—Zn3—O18	98.25 (7)
O5—Zn1—O10^{i}	94.4	O16—Zn4—O7^{iv}	110.07 (8)
O2—Zn1—O11^{ii}	178.66 (6)	O16—Zn4—O13^{iii}	110.12 (9)
O5—Zn1—O11^{ii}	92.1	O7^{iv}—Zn4—O13^{iii}	105.5
O10^{i}—Zn1—O11^{ii}	91.1	O16—Zn4—O17	111.24 (6)
O2—Zn1—O3	91.0	O7^{iv}—Zn4—O17	110.83 (6)
O5—Zn1—O3	175.09 (6)	O13^{iii}—Zn4—O17	108.91 (5)
O10^{i}—Zn1—O3	89.8	C30—O12—Zn2^{v}	123.3 (2)
O11^{ii}—Zn1—O3	90.3	C20—O10—Zn1^{i}	135.44 (13)
O2—Zn1—O1	93.5	C30—O11—Zn1^{v}	129.1 (2)
O5—Zn1—O1	89.7	C20—O9—Zn2^{i}	119.84 (13)
O10^{i}—Zn1—O1	175.3	C10—O6—Zn2	116.83 (12)
O11^{ii}—Zn1—O1	86.5	C10—O5—Zn1	135.50 (12)
O3—Zn1—O1	86.2	C33—O13—Zn4^{iii}	134.7 (3)
O6—Zn2—O12^{ii}	114.82 (6)	C24—O15—Zn3	133.9 (2)
O6—Zn2—O9^{i}	115.7	C14—O7—Zn4^{vi}	143.0 (2)
O12^{ii}—Zn2—O9^{i}	112.8	C14—O8—Zn3^{vi}	124.29 (19)
O6—Zn2—O4	105.19 (6)	C7—O3—Zn1	121.0 (2)
O12^{ii}—Zn2—O4	104.12 (6)	C35—O18—Zn3	123.8 (3)
O9^{i}—Zn2—O4	102.34 (5)	C4—O2—Zn1	128.1 (4)
O14^{iii}—Zn3—O8^{iv}	123.68 (6)	C33—O14—Zn3^{iii}	130.2 (2)
O14^{iii}—Zn3—O15	110.36 (9)	C1—O1—Zn1	125.6 (3)
O8^{iv}—Zn3—O15	105.22 (8)	C24—O16—Zn4	130.8 (3)
O14^{iii}—Zn3—O18	107.65 (9)	C38—O4—Zn2	87.9 (4)

Symmetry codes: (i) 2-x, 1-y, 1-z; (ii) x, -1+y, z; (iii) 1-x, 2-y, 1-z; (iv) 3/2-x, 1/2+y, 3/2-z; (v) x, 1+y, z; (vi) 3/2-x, -1/2+y, 3/2-z.