

## **Supporting Information**

### **Anion Dependent Self-assembly of Drum-like 30- and 32-metal Cd-Ln Nanoclusters: Visible and NIR luminescent Sensing of Metal Cations**

Chengri Wang,<sup>a</sup> Xiaoping Yang,<sup>\*a</sup> Shiqing Wang,<sup>a</sup> Ting Zhu,<sup>a</sup> Le Bo,<sup>a</sup> Lijie Zhang,<sup>a</sup> Hongfen  
Chen,<sup>a</sup> Dongmei Jiang,<sup>a</sup> Xiaomei Dong<sup>a</sup> and Shaoming Huang <sup>\*a</sup>

## **Contents**

|                                                                                                                    |     |
|--------------------------------------------------------------------------------------------------------------------|-----|
| 1. Synthesis of H <sub>2</sub> L and <b>1-4</b> .....                                                              | S2  |
| 2. Energy dispersive X-ray (EDX) spectra of <b>2-4</b> .....                                                       | S4  |
| 3. Enclosed solvent molecules in the drum-like structures.....                                                     | S5  |
| 4. Powder XRD patterns of <b>1</b> and <b>4</b> .....                                                              | S6  |
| 5. The thermogravimetric analysis of <b>1</b> and <b>4</b> and the <sup>1</sup> H NMR spectrum of <b>1</b> .....   | S7  |
| 6. Photophysical properties of the free H <sub>2</sub> L.....                                                      | S8  |
| 7. Excitation and NIR luminescence emission spectra of <b>1-4</b> in CHCl <sub>3</sub> and CDCl <sub>3</sub> ..... | S9  |
| 8. Visible and NIR luminescence lifetimes of <b>1-4</b> .....                                                      | S10 |
| 9. Visible and NIR emission response of <b>1</b> to the addition of metal ions.....                                | S12 |
| 10. Visible emission response of <b>3</b> to the addition of metal ions.....                                       | S17 |
| 11. MS(ESI) spectra of <b>1</b> before and after the addition of Zn <sup>2+</sup> ion.....                         | S18 |
| 12. X-Ray Crystallography.....                                                                                     | S19 |

## 1. Synthesis of H<sub>2</sub>L and 1-4

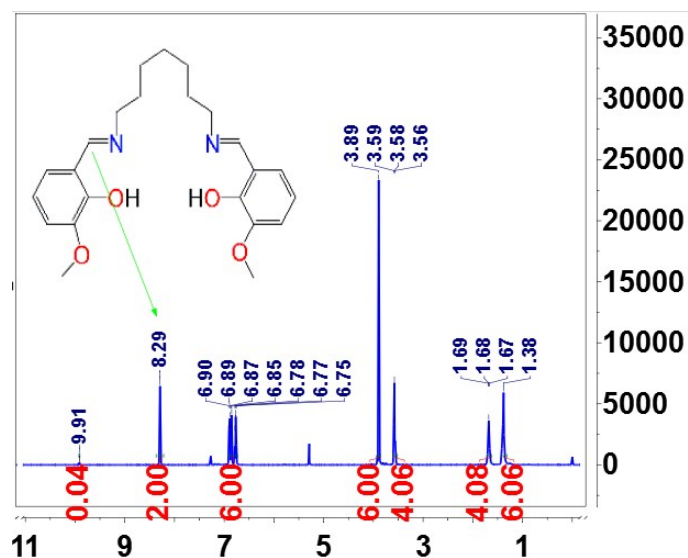


Figure S1. The <sup>1</sup>H NMR spectrum of H<sub>2</sub>L.

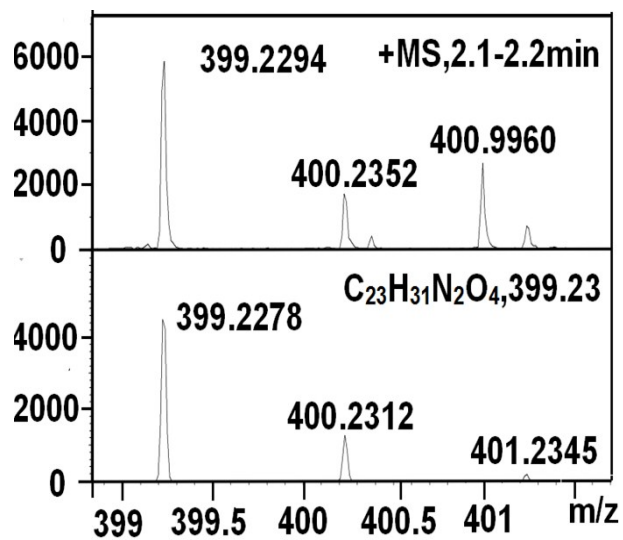
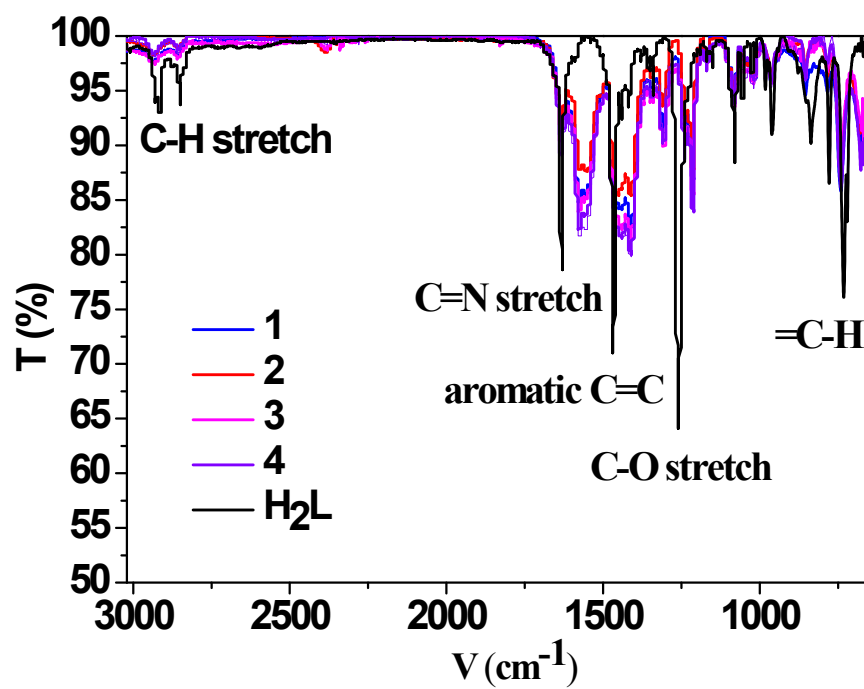
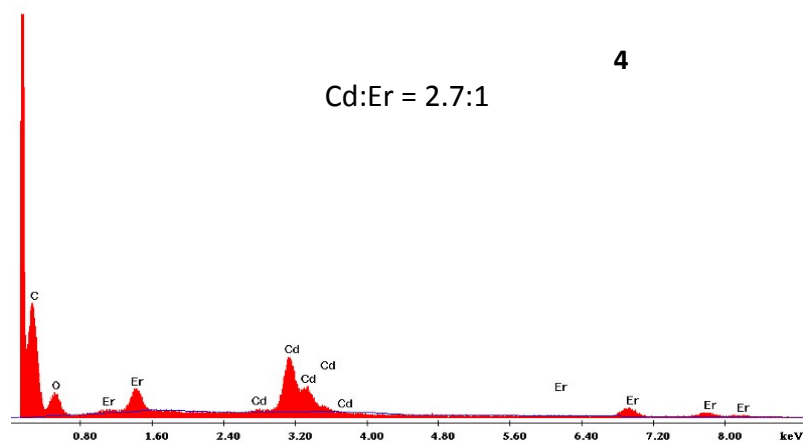
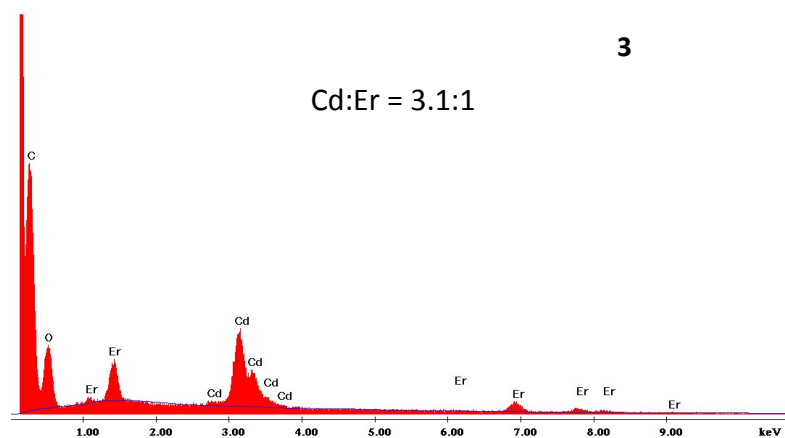
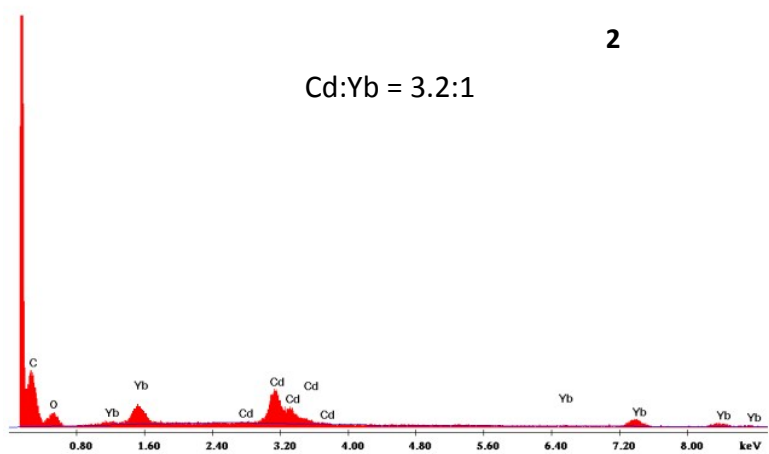


Figure S2. The high resolution mass spectrometry of H<sub>2</sub>L.



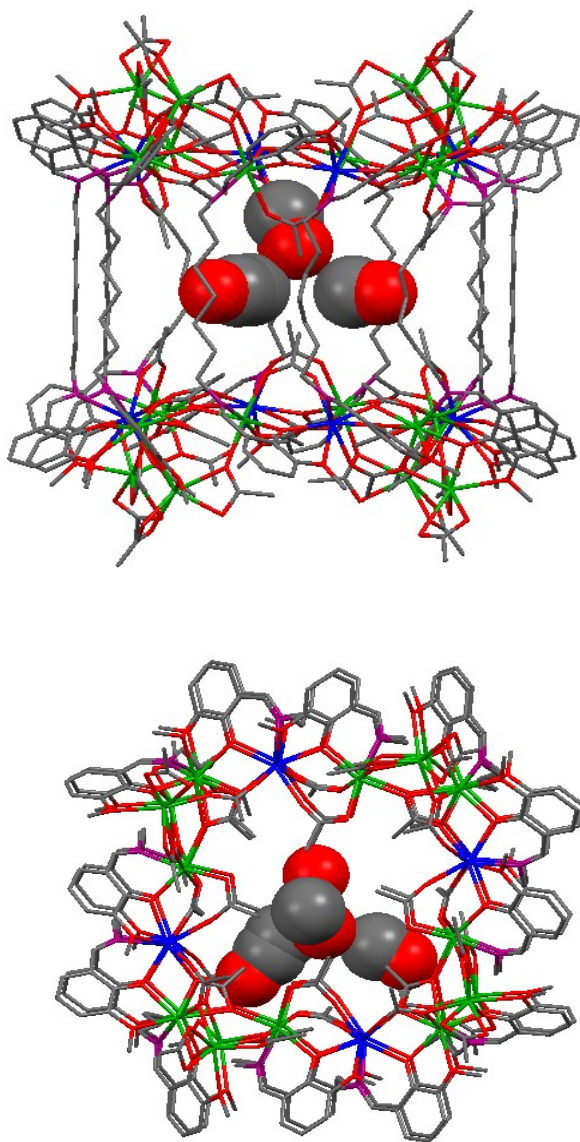
**Figure S3.** The Infrared absorption spectra of H<sub>2</sub>L and 1-4.

## 2. Energy dispersive X-ray (EDX) spectra of 2-4.



**Figure S4.** Energy dispersive X-ray (EDX) spectra of 2-4.

### 3. Enclosed solvent molecules in the drum-like structures



**Figure S5.** Enclosed solvent molecules such as H<sub>2</sub>O, MeOH and EtOH in the drum-like structures.

#### 4. Powder XRD patterns of 1 and 4.

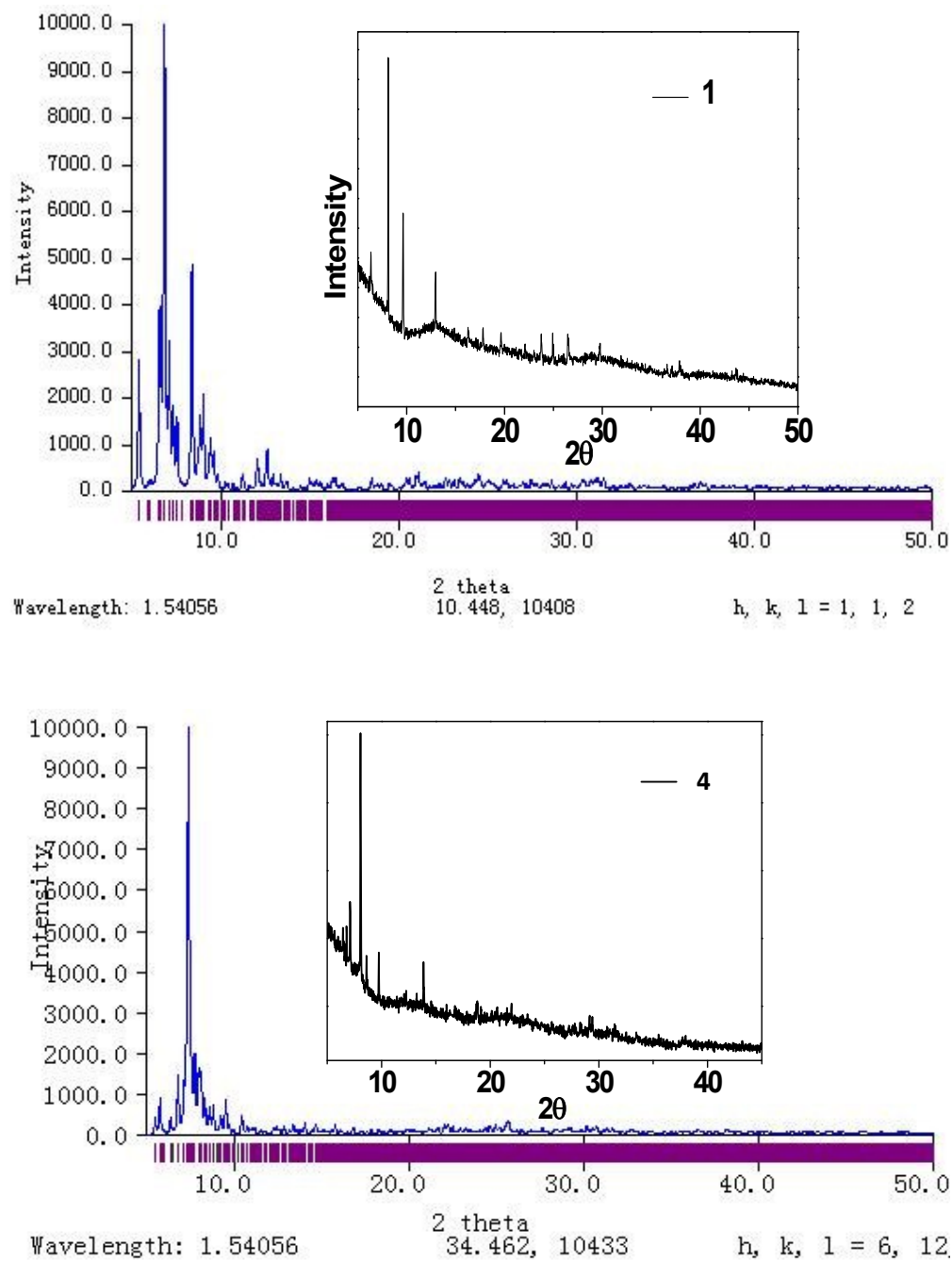
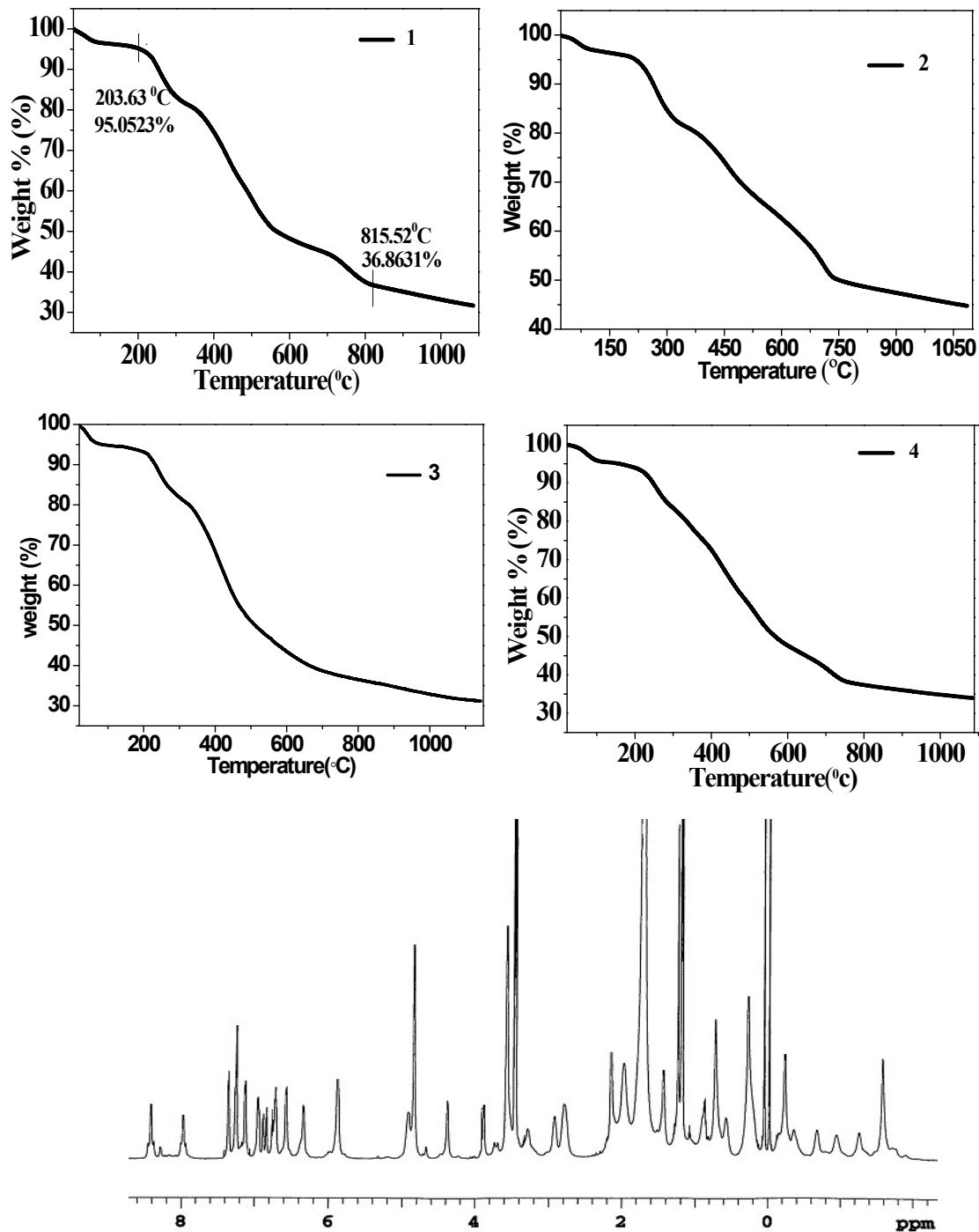


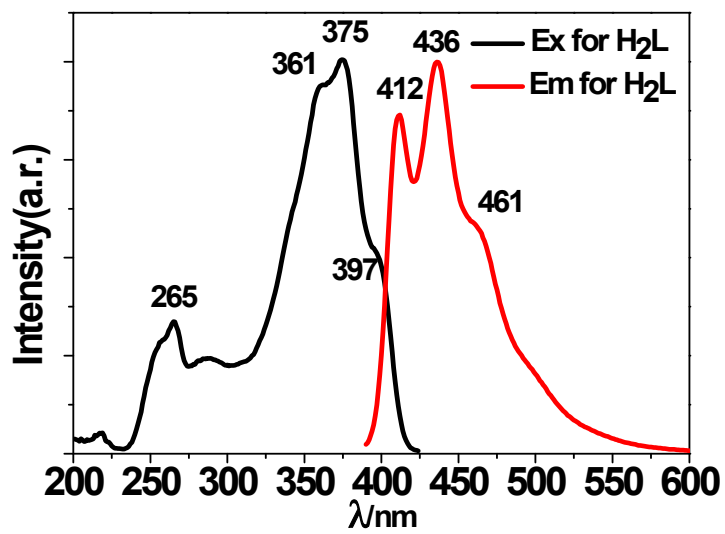
Figure S6. Powder XRD patterns of 1 and 4.

## 5. The thermogravimetric analysis of 1-4 and the $^1\text{H}$ NMR spectrum of 1



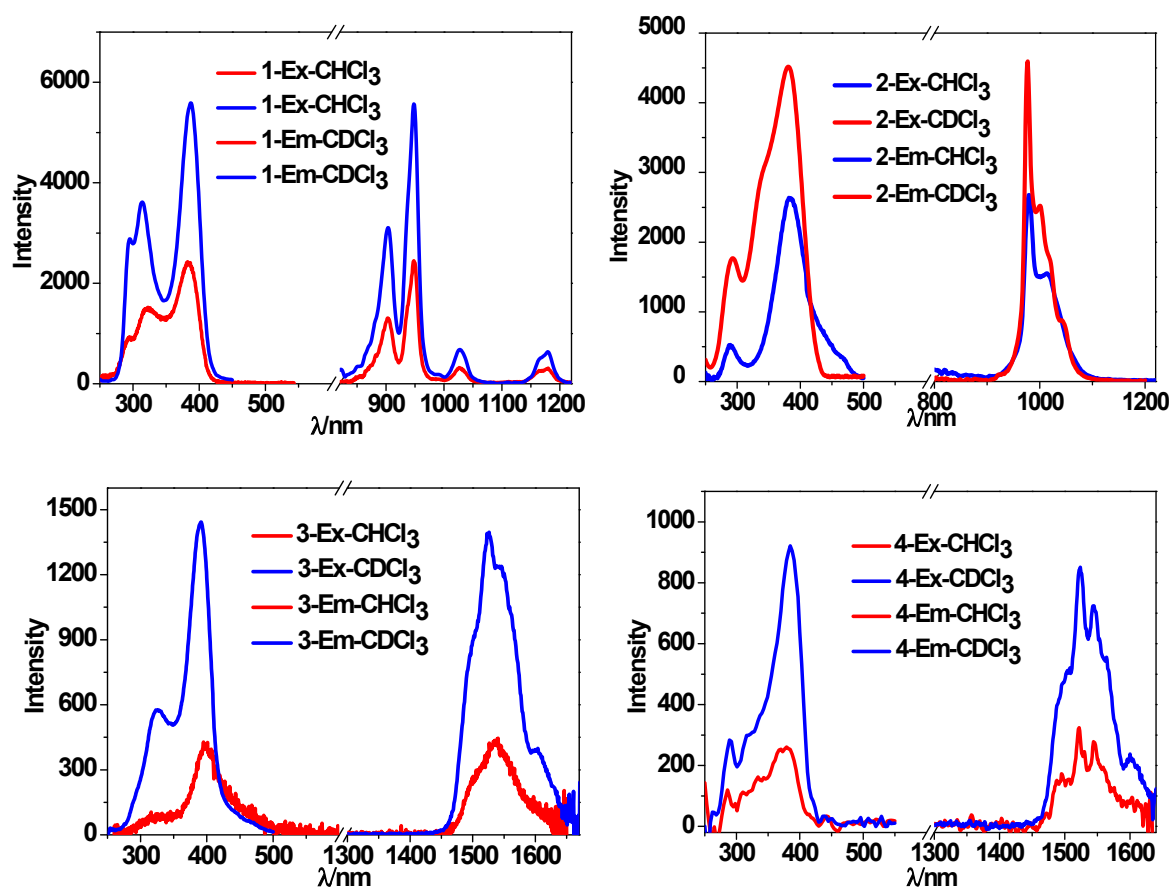
**Figure S7.** The thermogravimetric analysis of **1** and **4** and the  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$ .

## 6. Photophysical properties of the free $H_2L$



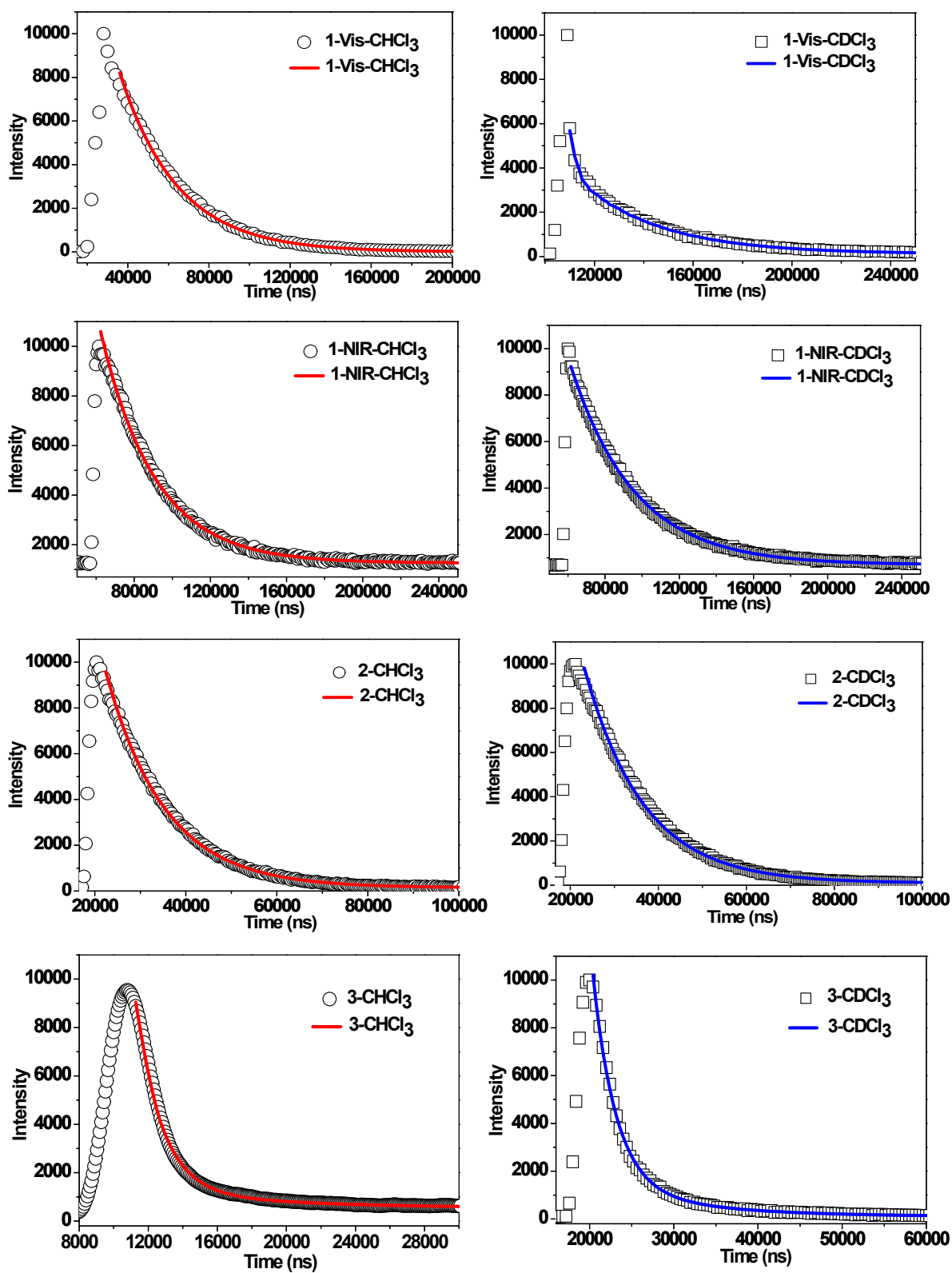
**Figure S8.** Excitation and emission spectra of the free ligand  $H_2L$  in  $CHCl_3$ .

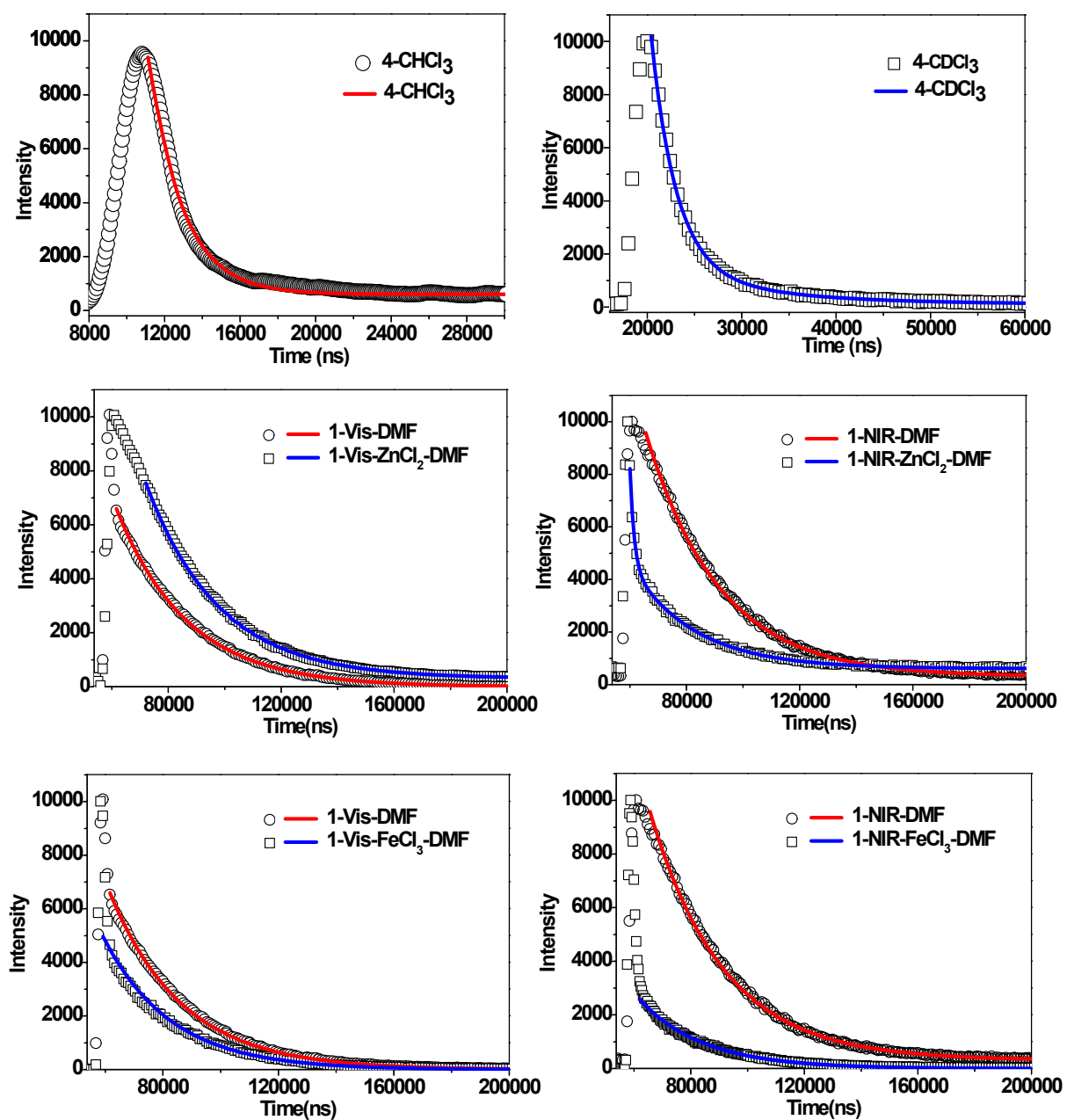
## 7. Excitation and NIR luminescence emission spectra of 1-4 in $\text{CHCl}_3$ and $\text{CDCl}_3$



**Figure S9.** Excitation and NIR luminescence emission spectra of **1-4** in  $\text{CHCl}_3$  and  $\text{CDCl}_3$ .

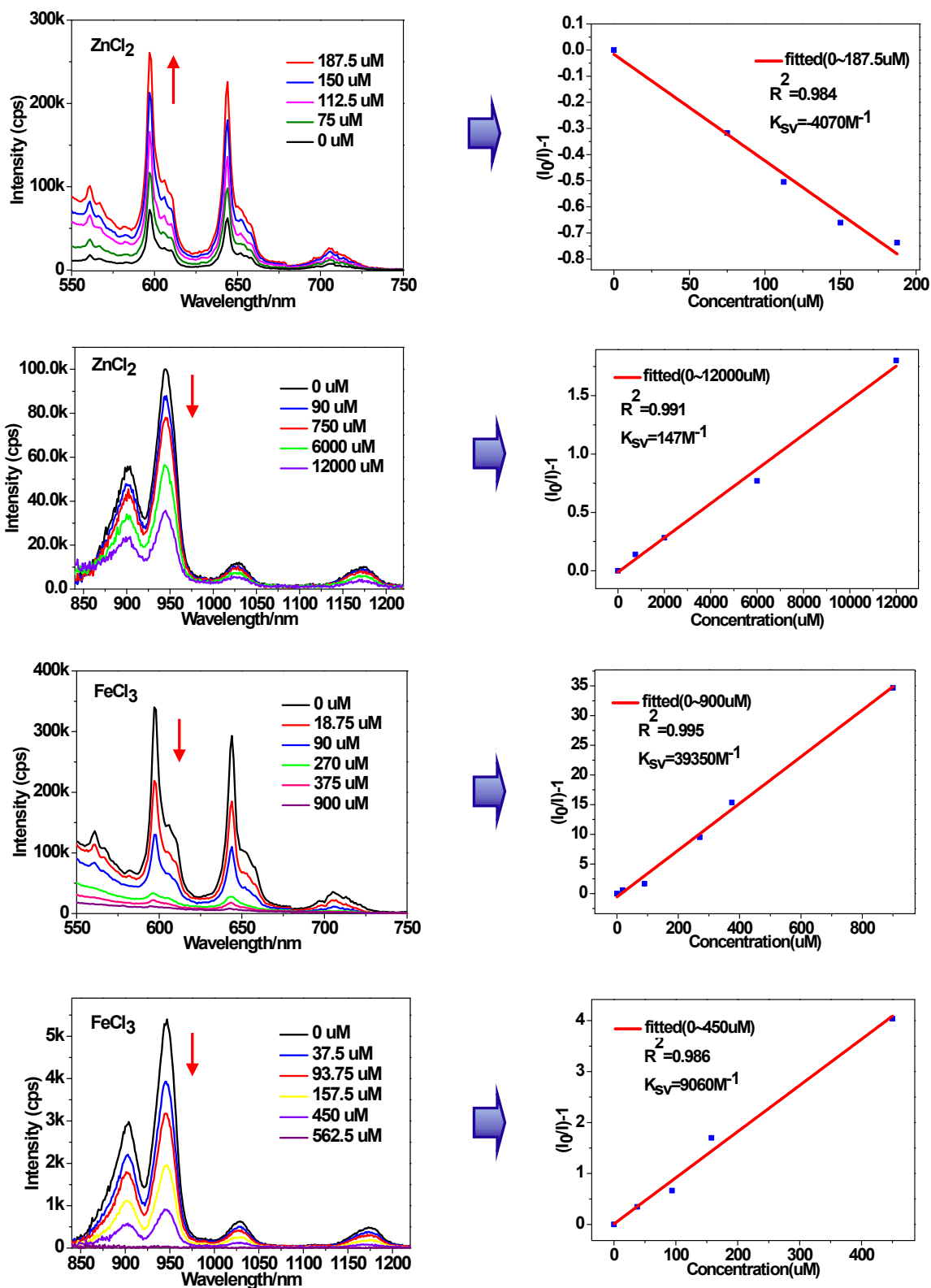
## 8. Visible and NIR luminescence lifetimes of 1-4

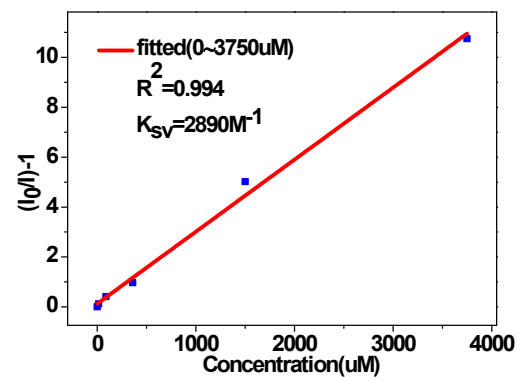
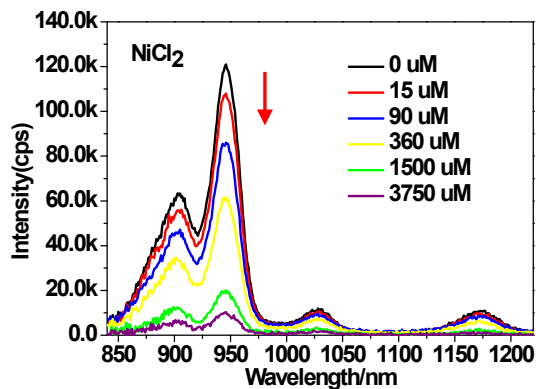
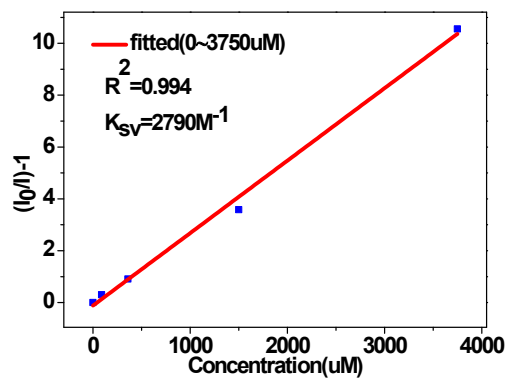
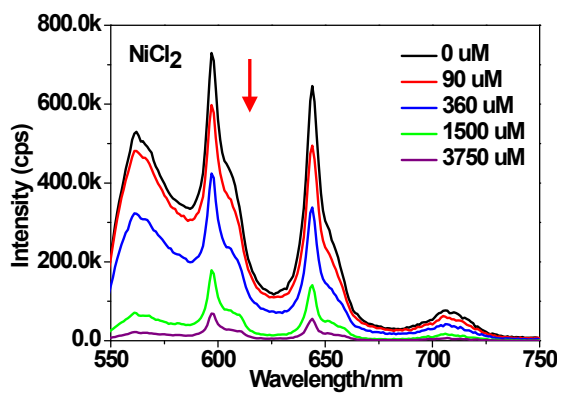
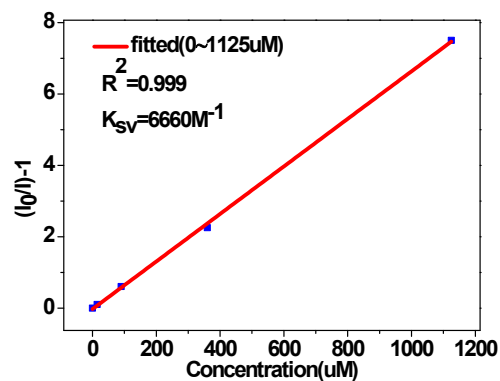
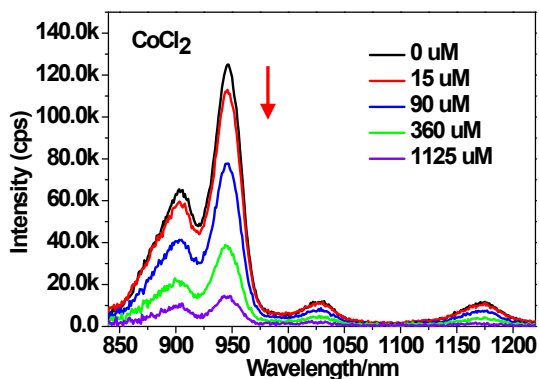
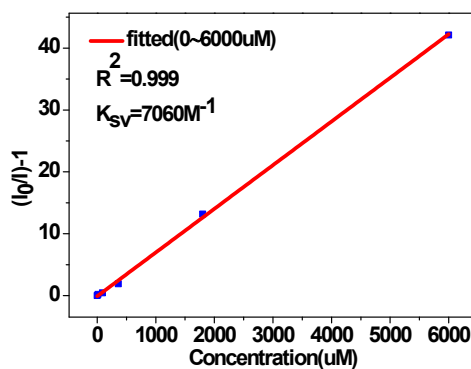
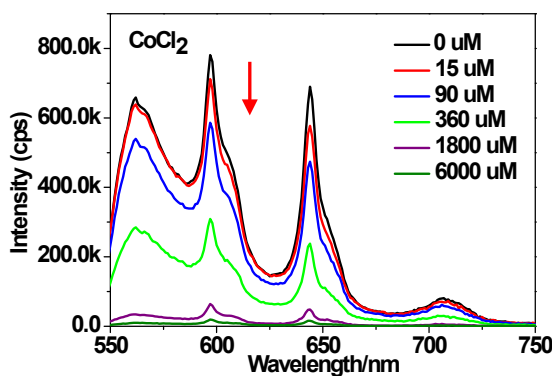


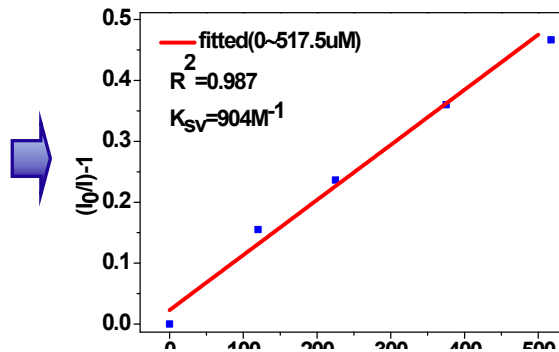
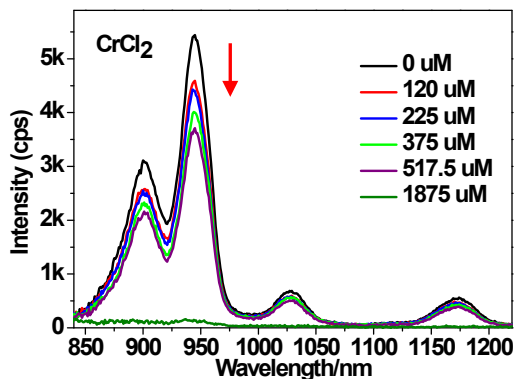
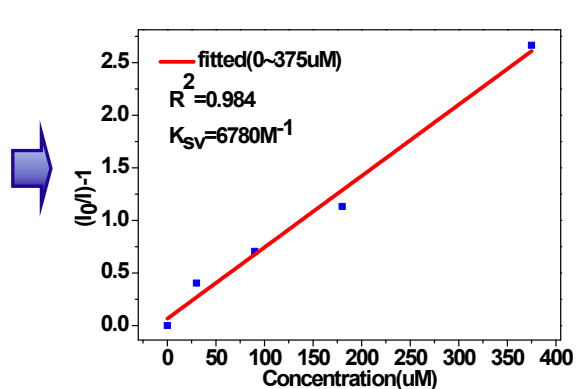
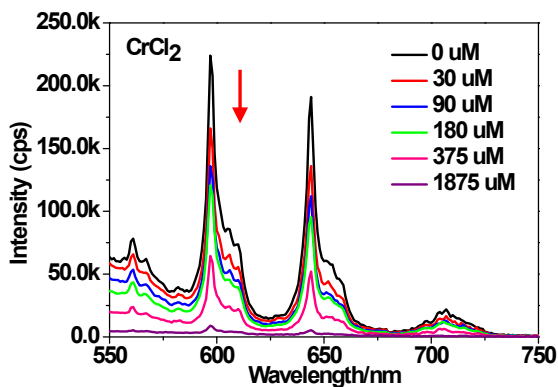
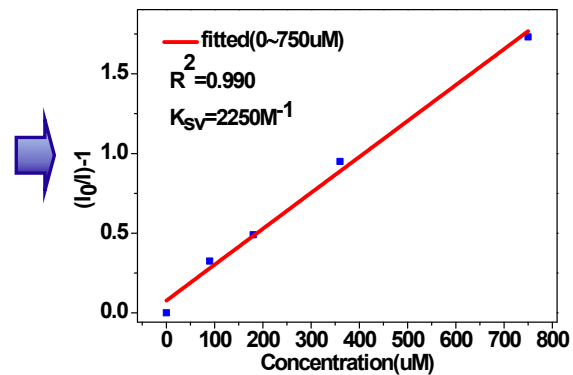
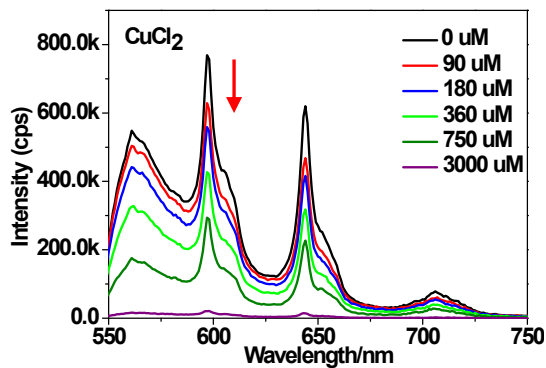
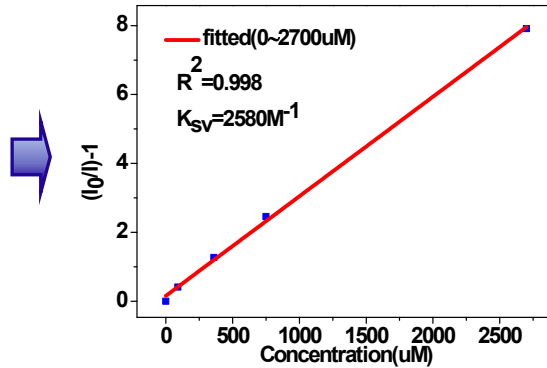
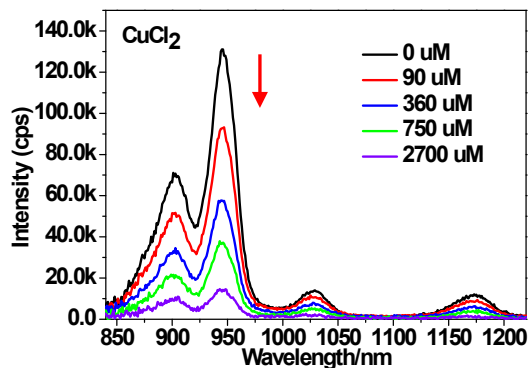


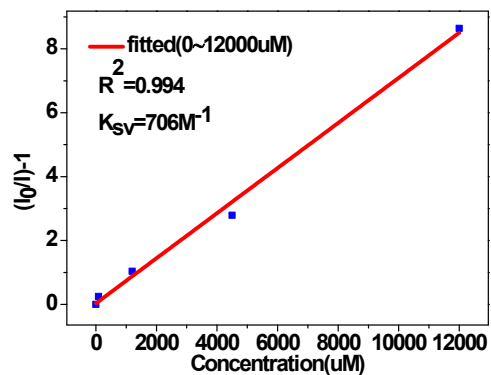
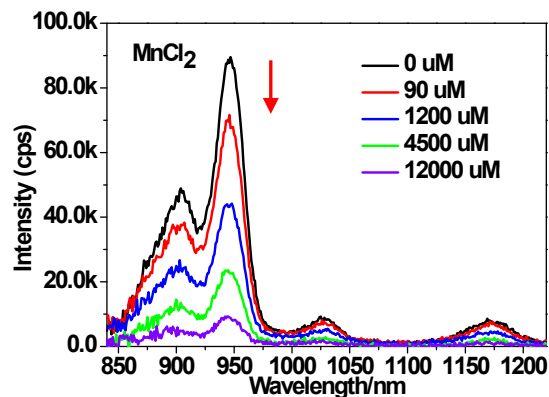
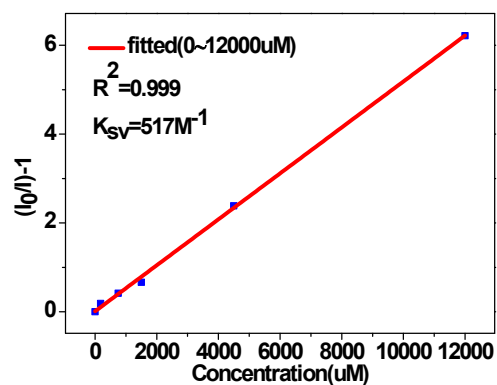
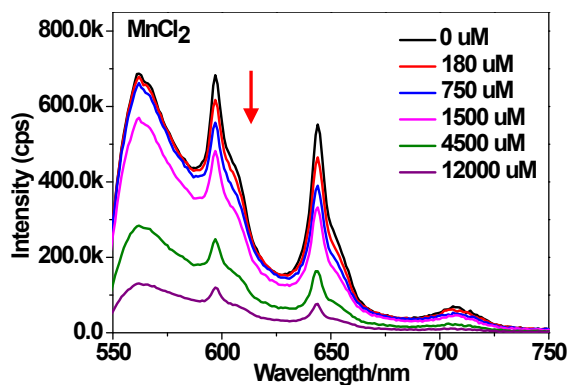
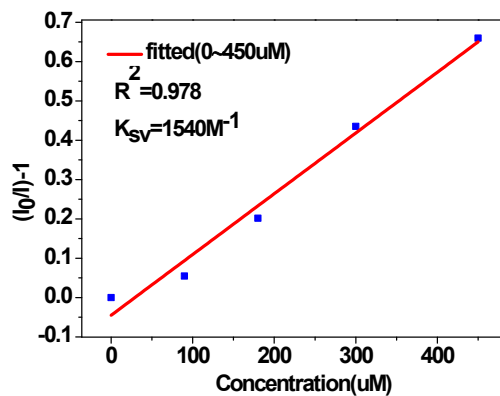
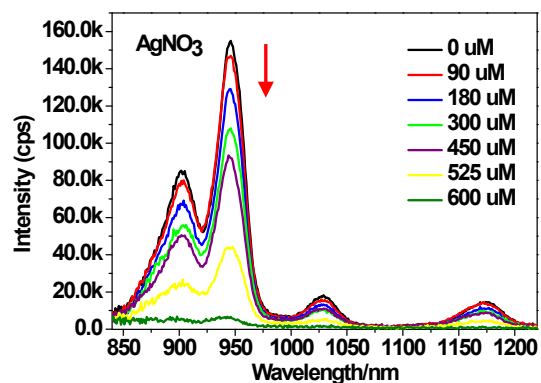
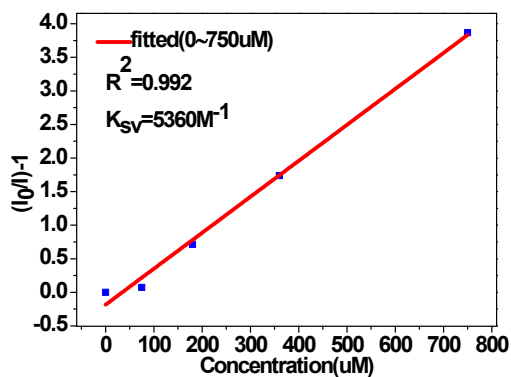
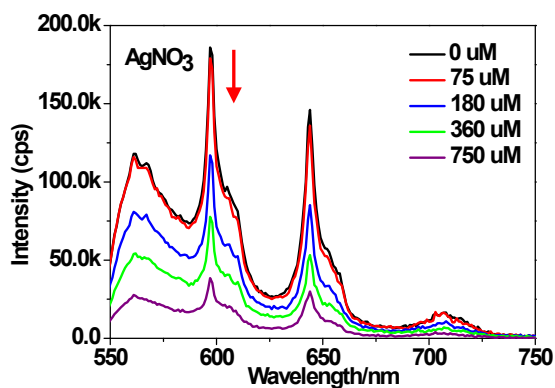
**Figure S10.** The visible and NIR luminescence decay curves of **1-4** in  $\text{CHCl}_3$  and  $\text{CDCl}_3$ .

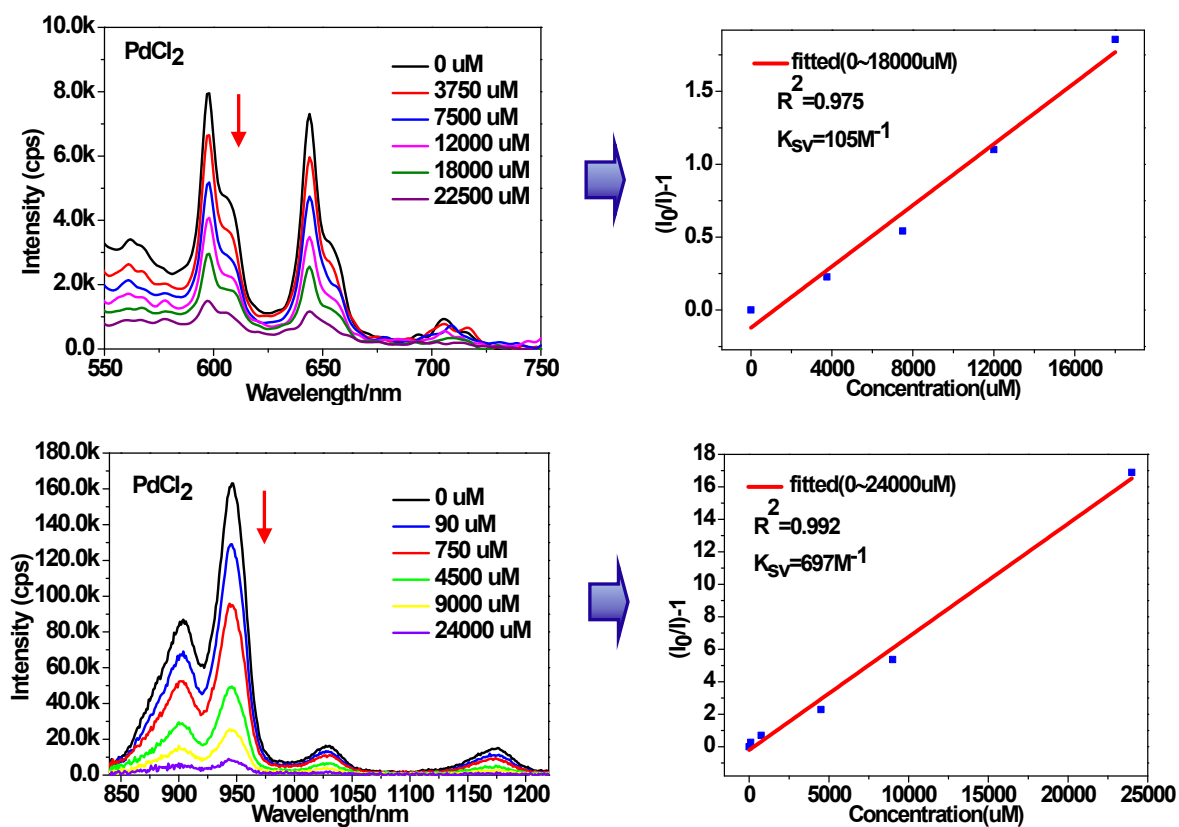
## 9. Visible and NIR emission response of 1 to the addition of metal ions





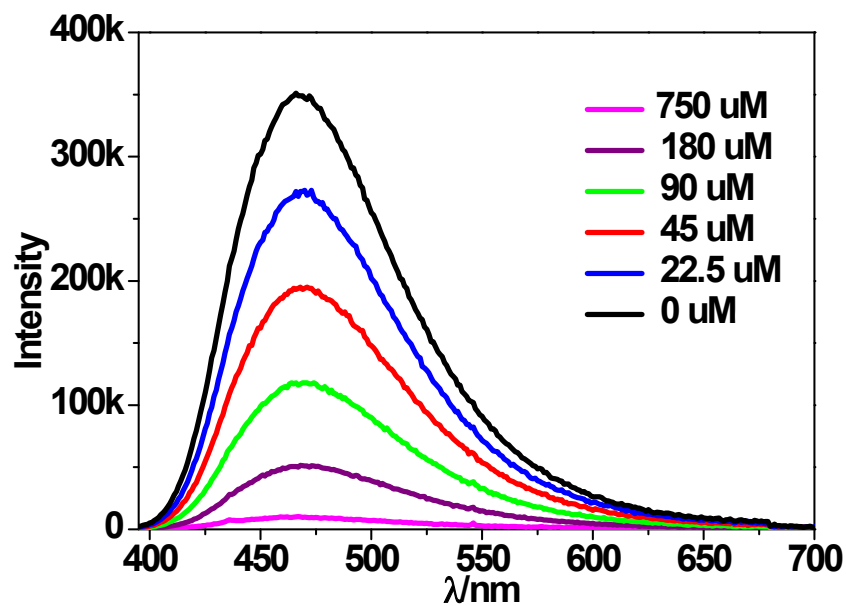






**Figure S11.** Luminescent sensing of metal cations of **1** in DMF ( $1.0 \times 10^{-4}$  M). ( $\lambda_{\text{ex}} = 382$  nm)

## 10. Visible emission response of 3 to the addition of metal ions

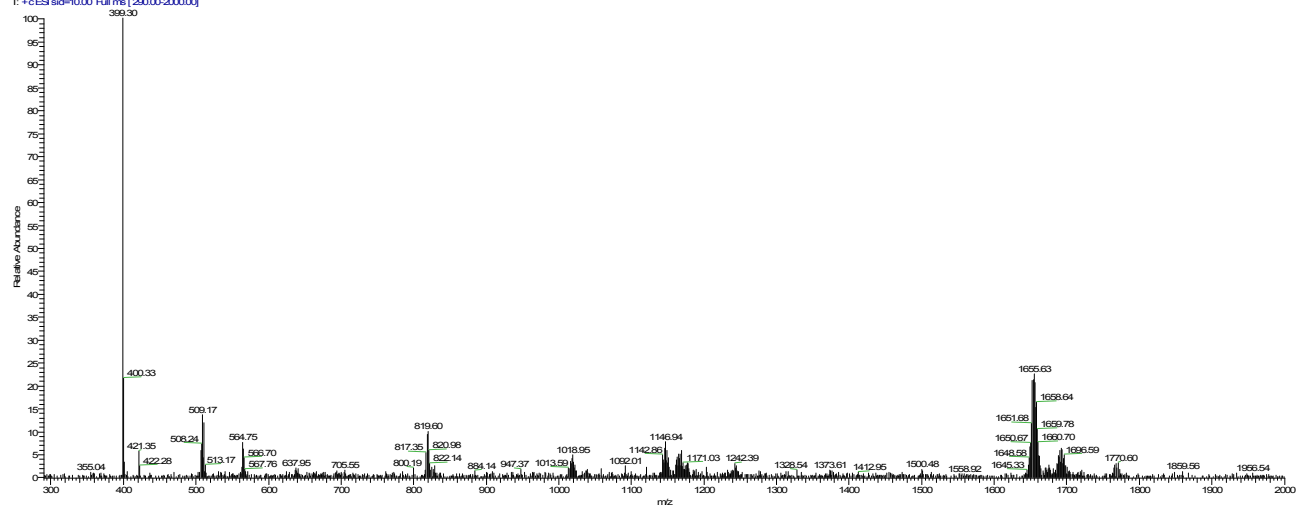


**Figure S12.** Visible emission response of **3** to Fe<sup>3+</sup> ion in DMF.

## 11. MS(ESI) spectrum of 1 before and after the addition of Zn<sup>2+</sup> ion

CPO 975444\_171101194613  
Type: Unknown ID: Unknown Row: 1  
Sample Name:  
Lot #:  
MW:  
Sample Type:  
Operator: 2Q

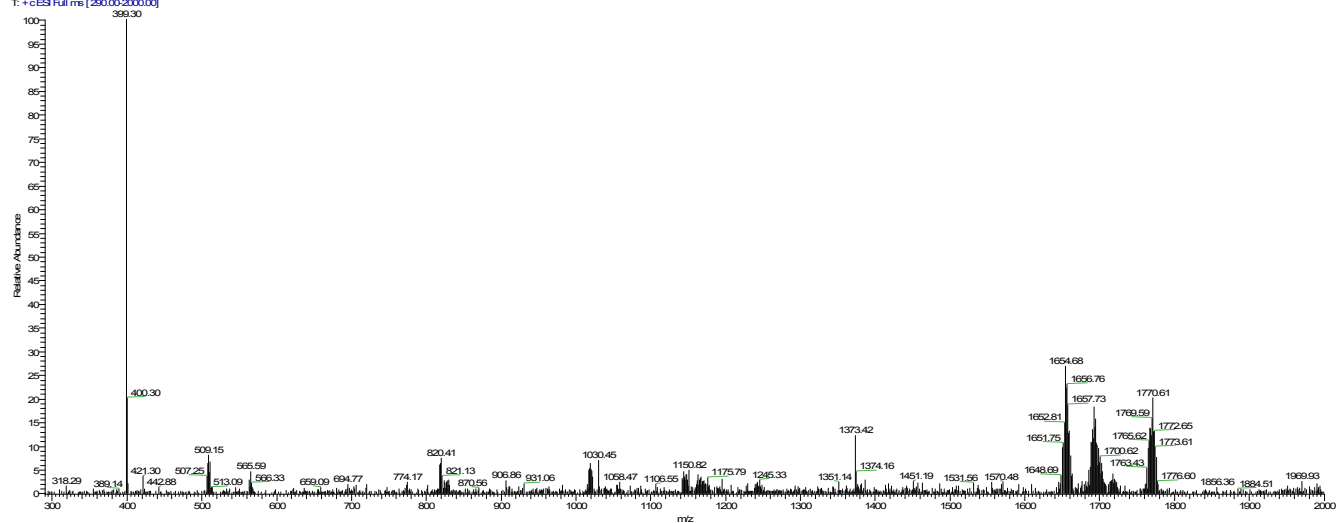
CHO975444\_171101194613 #2:28 RT: 0.03-0.64 AV: 27 NL: 1.25E5  
T: +cESI.sid=10.00 Full.ms [280.00-2000.00]



(a)

CPO 975444  
Type: Unknown ID: Unknown Row: 1  
Sample Name:  
Lot #:  
MW:  
Sample Type:  
Operator: 2Q

CHO975444 #2:33 RT: 0.03-0.76 AV: 32 NL: 9.61E4  
T: +cESI Full.ms [280.00-2000.00]



(b)

**Figure S13.** MS(ESI) spectra of **1** before (a) and after (b) the addition of Zn<sup>2+</sup> ion (C = 375  $\mu$ M).

## 12. X-Ray Crystallography

**Table S1.** Selected Bond Lengths (Å) for **1**.

|               |           |               |           |
|---------------|-----------|---------------|-----------|
| Sm(1)-O(16)   | 2.269(8)  | Cd(2)-O(20)   | 2.628(10) |
| Sm(1)-O(2)    | 2.284(9)  | Cd(3)-O(6)    | 2.263(10) |
| Sm(1)-O(14)   | 2.308(12) | Cd(3)-O(24)   | 2.283(10) |
| Sm(1)-O(4)    | 2.327(11) | Cd(3)-O(22)   | 2.313(11) |
| Sm(1)-O(19)   | 2.352(9)  | Cd(3)-O(18)   | 2.312(9)  |
| Sm(1)-O(17)   | 2.390(9)  | Cd(3)-O(23)   | 2.424(9)  |
| Sm(1)-N(2)    | 2.516(12) | Cd(3)-O(5)    | 2.469(10) |
| Sm(1)-O(1)    | 2.587(11) | Cd(3)-O(21)   | 2.488(12) |
| Sm(2)-O(8)    | 2.275(9)  | Cd(4)-O(25)   | 2.262(10) |
| Sm(2)-O(28)   | 2.277(11) | Cd(4)-O(8)    | 2.277(9)  |
| Sm(2)-O(26)   | 2.290(9)  | Cd(4)-O(27)   | 2.296(9)  |
| Sm(2)-O(10)   | 2.328(9)  | Cd(4)-N(4)    | 2.318(12) |
| Sm(2)-O(29)   | 2.349(11) | Cd(4)-O(20)   | 2.329(9)  |
| Sm(2)-O(31)   | 2.367(10) | Cd(4)-O(23)   | 2.382(9)  |
| Sm(2)-N(5)    | 2.563(16) | Cd(5)-O(12)   | 2.220(10) |
| Sm(2)-O(7)    | 2.572(10) | Cd(5)-O(10)   | 2.228(10) |
| Cd(1)-O(13)   | 2.245(10) | Cd(5)-O(30)   | 2.237(11) |
| Cd(1)-O(2)    | 2.262(10) | Cd(5)-N(6)    | 2.253(13) |
| Cd(1)-O(15)   | 2.298(10) | Cd(5)-O(31)   | 2.308(10) |
| Cd(1)-N(1)    | 2.361(12) | Cd(5)-O(9)    | 2.490(11) |
| Cd(1)-O(36)   | 2.360(12) | Cd(5)-O(32)   | 2.602(10) |
| Cd(1)-O(32)#1 | 2.365(11) | Cd(6)-O(35)   | 2.259(15) |
| Cd(2)-O(6)    | 2.232(8)  | Cd(6)-O(12)   | 2.269(11) |
| Cd(2)-N(3)    | 2.238(12) | Cd(6)-O(30)   | 2.319(11) |
| Cd(2)-O(4)    | 2.275(10) | Cd(6)-O(33)   | 2.342(19) |
| Cd(2)-O(18)   | 2.285(9)  | Cd(6)-O(36)#1 | 2.421(12) |
| Cd(2)-O(19)   | 2.301(10) | Cd(6)-O(11)   | 2.485(12) |
| Cd(2)-O(3)    | 2.523(9)  |               |           |

**Table S2.** Selected Bond Lengths (Å) for **2**.

|               |           |               |           |
|---------------|-----------|---------------|-----------|
| Yb(1)-O(16)   | 2.322(8)  | Cd(3)-O(6)    | 2.235(9)  |
| Yb(1)-O(2)    | 2.326(9)  | Cd(3)-O(22)   | 2.286(10) |
| Yb(1)-O(4)    | 2.331(11) | Cd(3)-O(18)   | 2.300(8)  |
| Yb(1)-O(14)   | 2.341(11) | Cd(3)-O(24)   | 2.304(10) |
| Yb(1)-O(19)   | 2.361(9)  | Cd(3)-O(23)   | 2.415(8)  |
| Yb(1)-O(17)   | 2.389(8)  | Cd(3)-O(21)   | 2.468(11) |
| Yb(1)-O(1)    | 2.584(9)  | Cd(3)-O(5)    | 2.500(9)  |
| Yb(1)-N(2)    | 2.586(11) | Cd(4)-O(25)   | 2.270(9)  |
| Yb(2)-O(8)    | 2.252(10) | Cd(4)-O(8)    | 2.298(9)  |
| Yb(2)-O(26)   | 2.305(9)  | Cd(4)-O(27)   | 2.301(8)  |
| Yb(2)-O(28)   | 2.311(10) | Cd(4)-N(4)    | 2.324(12) |
| Yb(2)-O(10)   | 2.341(9)  | Cd(4)-O(20)   | 2.330(8)  |
| Yb(2)-O(29)   | 2.346(10) | Cd(4)-O(23)   | 2.382(9)  |
| Yb(2)-O(31)   | 2.384(9)  | Cd(5)-O(12)   | 2.198(10) |
| Yb(2)-N(5)    | 2.576(15) | Cd(5)-O(10)   | 2.227(10) |
| Yb(2)-O(7)    | 2.578(9)  | Cd(5)-O(30)   | 2.247(11) |
| Cd(1)-O(2)    | 2.227(8)  | Cd(5)-N(6)    | 2.264(12) |
| Cd(1)-O(13)   | 2.268(10) | Cd(5)-O(31)   | 2.340(8)  |
| Cd(1)-O(15)   | 2.280(10) | Cd(5)-O(9)    | 2.537(11) |
| Cd(1)-O(32)#1 | 2.356(9)  | Cd(5)-O(32)   | 2.605(8)  |
| Cd(1)-N(1)    | 2.375(11) | Cd(6)-O(33)   | 2.256(17) |
| Cd(1)-O(36)   | 2.391(11) | Cd(6)-O(12)   | 2.292(11) |
| Cd(2)-O(6)    | 2.223(8)  | Cd(6)-O(35)   | 2.290(14) |
| Cd(2)-N(3)    | 2.228(13) | Cd(6)-O(30)   | 2.314(11) |
| Cd(2)-O(4)    | 2.284(9)  | Cd(6)-O(36)#1 | 2.387(11) |
| Cd(2)-O(18)   | 2.287(9)  | Cd(6)-O(11)   | 2.505(12) |
| Cd(2)-O(19)   | 2.297(9)  | Cd(6)-O(34)   | 2.643(19) |
| Cd(2)-O(3)    | 2.560(9)  |               |           |

**Table S2.** Selected Bond Lengths (Å) for **3**.

|             |           |               |           |
|-------------|-----------|---------------|-----------|
| Er(1)-O(2)  | 2.296(6)  | Cd(2)-O(20)   | 2.631(7)  |
| Er(1)-O(16) | 2.297(6)  | Cd(3)-O(6)    | 2.231(7)  |
| Er(1)-O(4)  | 2.310(7)  | Cd(3)-O(22)   | 2.276(7)  |
| Er(1)-O(14) | 2.312(8)  | Cd(3)-O(18)   | 2.297(7)  |
| Er(1)-O(19) | 2.368(6)  | Cd(3)-O(24)   | 2.297(7)  |
| Er(1)-O(17) | 2.383(7)  | Cd(3)-O(23)   | 2.407(6)  |
| Er(1)-N(2)  | 2.559(9)  | Cd(3)-O(21)   | 2.463(8)  |
| Er(1)-O(1)  | 2.575(6)  | Cd(3)-O(5)    | 2.473(7)  |
| Er(2)-O(8)  | 2.263(7)  | Cd(4)-O(25)   | 2.257(7)  |
| Er(2)-O(28) | 2.275(7)  | Cd(4)-O(8)    | 2.288(6)  |
| Er(2)-O(10) | 2.304(6)  | Cd(4)-O(27)   | 2.300(6)  |
| Er(2)-O(26) | 2.326(6)  | Cd(4)-N(4)    | 2.317(9)  |
| Er(2)-O(29) | 2.344(7)  | Cd(4)-O(20)   | 2.330(6)  |
| Er(2)-O(31) | 2.372(7)  | Cd(4)-O(23)   | 2.385(6)  |
| Er(2)-O(7)  | 2.568(7)  | Cd(5)-O(12)   | 2.223(7)  |
| Er(2)-N(5)  | 2.597(10) | Cd(5)-N(6)    | 2.238(9)  |
| Cd(1)-O(13) | 2.251(7)  | Cd(5)-O(30)   | 2.247(8)  |
| Cd(1)-O(2)  | 2.255(7)  | Cd(5)-O(10)   | 2.268(8)  |
| Cd(1)-O(15) | 2.284(7)  | Cd(5)-O(31)   | 2.311(6)  |
| Cd(1)-N(1)  | 2.321(8)  | Cd(5)-O(9)    | 2.519(8)  |
| Cd(1)-O(36) | 2.400(8)  | Cd(5)-O(32)   | 2.575(6)  |
| Cd(2)-O(6)  | 2.231(6)  | Cd(6)-O(33)   | 2.271(12) |
| Cd(2)-N(3)  | 2.233(9)  | Cd(6)-O(12)   | 2.281(7)  |
| Cd(2)-O(18) | 2.262(7)  | Cd(6)-O(35)   | 2.285(11) |
| Cd(2)-O(4)  | 2.272(7)  | Cd(6)-O(30)   | 2.303(8)  |
| Cd(2)-O(19) | 2.313(7)  | Cd(6)-O(36)#1 | 2.413(8)  |
| Cd(2)-O(3)  | 2.542(7)  | Cd(6)-O(11)   | 2.479(9)  |

**Table S4.** Selected Bond Lengths (Å) for **4**.

|             |           |              |           |
|-------------|-----------|--------------|-----------|
| Er(1)-O(24) | 2.309(12) | Cd(4)-O(10)  | 2.196(15) |
| Er(1)-O(64) | 2.362(12) | Cd(4)-O(38)  | 2.249(16) |
| Er(1)-O(66) | 2.408(15) | Cd(4)-O(39)  | 2.289(16) |
| Er(1)-O(25) | 2.429(15) | Cd(4)-O(8)   | 2.295(16) |
| Er(1)-O(2)  | 2.440(12) | Cd(4)-N(5)   | 2.296(13) |
| Er(1)-O(27) | 2.471(12) | Cd(4)-O(7)   | 2.48(2)   |
| Er(1)-N(1)  | 2.543(13) | Cd(4)-O(40)  | 2.506(19) |
| Er(1)-O(23) | 2.646(12) | Cd(5)-O(12)  | 2.265(14) |
| Er(2)-O(36) | 2.342(14) | Cd(5)-O(41)  | 2.268(13) |
| Er(2)-O(6)  | 2.362(11) | Cd(5)-O(43)  | 2.301(16) |
| Er(2)-O(34) | 2.383(14) | Cd(5)-N(6)   | 2.342(15) |
| Er(2)-O(8)  | 2.391(14) | Cd(5)-O(67)  | 2.38(2)   |
| Er(2)-O(39) | 2.400(14) | Cd(5)-O(40)  | 2.407(16) |
| Er(2)-O(37) | 2.442(14) | Cd(6)-O(16)  | 2.199(13) |
| Er(2)-N(4)  | 2.585(17) | Cd(6)-O(14)  | 2.249(15) |
| Er(2)-O(5)  | 2.633(18) | Cd(6)-N(8)   | 2.255(18) |
| Er(3)-O(44) | 2.353(13) | Cd(6)-O(46)  | 2.257(14) |
| Er(3)-O(42) | 2.354(13) | Cd(6)-O(47)  | 2.322(11) |
| Er(3)-O(45) | 2.379(13) | Cd(6)-O(13)  | 2.539(14) |
| Er(3)-O(12) | 2.401(16) | Cd(6)-O(48)  | 2.637(10) |
| Er(3)-O(14) | 2.417(14) | Cd(7)-O(16)  | 2.260(15) |
| Er(3)-O(47) | 2.464(14) | Cd(7)-O(53)  | 2.266(15) |
| Er(3)-N(7)  | 2.627(14) | Cd(7)-O(50)  | 2.266(17) |
| Er(3)-O(11) | 2.635(16) | Cd(7)-O(46)  | 2.273(12) |
| Er(4)-O(56) | 2.348(10) | Cd(7)-O(15)  | 2.429(17) |
| Er(4)-O(18) | 2.350(9)  | Cd(7)-O(54)  | 2.486(13) |
| Er(4)-O(52) | 2.364(14) | Cd(7)-O(49)  | 2.53(3)   |
| Er(4)-O(20) | 2.395(12) | Cd(8)-O(51)  | 2.274(14) |
| Er(4)-O(57) | 2.438(16) | Cd(8)-O(18)  | 2.279(11) |
| Er(4)-O(59) | 2.470(13) | Cd(8)-O(55)  | 2.285(13) |
| Er(4)-N(10) | 2.59(2)   | Cd(8)-N(9)   | 2.305(17) |
| Er(4)-O(17) | 2.655(12) | Cd(8)-O(48)  | 2.379(9)  |
| Cd(1)-O(2)  | 2.215(13) | Cd(8)-O(54)  | 2.385(13) |
| Cd(1)-O(4)  | 2.220(15) | Cd(9)-N(11)  | 2.23(2)   |
| Cd(1)-O(26) | 2.243(12) | Cd(9)-O(22)  | 2.245(11) |
| Cd(1)-N(2)  | 2.246(15) | Cd(9)-O(58)  | 2.277(16) |
| Cd(1)-O(27) | 2.311(13) | Cd(9)-O(20)  | 2.302(11) |
| Cd(1)-O(1)  | 2.567(13) | Cd(9)-O(59)  | 2.332(12) |
| Cd(1)-O(28) | 2.647(11) | Cd(9)-O(19)  | 2.496(13) |
| Cd(2)-O(4)  | 2.197(12) | Cd(10)-O(69) | 2.25(2)   |
| Cd(2)-O(32) | 2.237(13) | Cd(10)-O(22) | 2.249(16) |
| Cd(2)-O(26) | 2.268(15) | Cd(10)-O(58) | 2.305(12) |
| Cd(2)-O(31) | 2.416(13) | Cd(10)-O(61) | 2.34(2)   |
| Cd(2)-O(30) | 2.42(2)   | Cd(10)-O(68) | 2.38(2)   |
| Cd(2)-O(3)  | 2.432(16) | Cd(10)-O(62) | 2.386(12) |
| Cd(2)-O(29) | 2.448(16) | Cd(10)-O(21) | 2.414(14) |
| Cd(3)-O(33) | 2.245(13) | Cd(11)-O(63) | 2.259(11) |
| Cd(3)-O(6)  | 2.291(14) | Cd(11)-O(65) | 2.275(10) |
| Cd(3)-O(28) | 2.311(12) | Cd(11)-N(12) | 2.294(16) |
| Cd(3)-O(35) | 2.314(14) | Cd(11)-O(60) | 2.322(14) |
| Cd(3)-N(3)  | 2.325(14) | Cd(11)-O(24) | 2.337(11) |
| Cd(3)-O(31) | 2.392(16) |              |           |