A series of Ln\textsuperscript{iii}\textsubscript{4} clusters: Dy\textsubscript{4} single molecule magnet and Tb\textsubscript{4} multi-responsive luminescent sensor for Fe\textsuperscript{3+}, CrO\textsubscript{4}\textsuperscript{2−}/Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−} 4-nitroaniline

Yaru Qin, Yu Ge, Shasha Zhang, Hao Sun, Yu Jing, Yahong Li* and Wei Liu

College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.
E-mail: liyahong@suda.edu.cn

Content

Fig. S1-S3 \textsuperscript{1}H, \textsuperscript{13}C NMR and IR spectra of H\textsubscript{2}L…………………………………………………………………………………………………………………2

Table S1 Selected bond lengths and angles for 1-5……………………………………………………………………………………………………………………………………..3

Fig. S4 PXRD patterns for 1-5……………………………………………………………………………………………………………………………………………………………………...6

Fig. S5 IR spectra of 1-5………………………………………………………………………………………………………………………………………………………………………………7

Table S2 Results of Continuous Shape Measures (SHAPE) calculation……………………………………………………………………………………………………………….8

Fig. S6 The Curie-Weiss law fit of 1……………………………………………………………………………………………………………………………………………………………………9

Fig. S7 Temperature dependence of the out-of-phase ($\chi''$) ac susceptibility for 3……………………………………………………………………………………………………………….9

Fig. S8 The excitation and emission spectra of H\textsubscript{2}L and emission spectra of 1-5 in solid state………………………………………………………………………………9

Fig. S9 Excitation spectrum and emission spectrum of 2 in solid state……………………………………………………………………………………………………10

Fig. S10-S11 PXRD patterns of 2 for pH and stability experiments………………………………………………………………………………………………………………..10

Fig. S12 SEM images and particle size distribution of 2 ……………………………………………………………………………………………………………………………………….11

Fig. S13 Plots of $I_0/I-1$ and fluorescence intensity of 2 versus low concentration of Fe\textsuperscript{3+}………………………………………………………………………………11

Fig. S14 The XPS spectra of 2 and 2-Fe\textsuperscript{3+}…………………………………………………………………………………………………………………………………………………….12

Fig. S15 PXRD patterns for 2 after the detection of Fe\textsuperscript{3+}, CrO\textsubscript{4}\textsuperscript{2−} and Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−}……………………………………………………………………………….12

Fig. S16 Luminescent responses of 2 towards different concentrations of CrO\textsubscript{4}\textsuperscript{2−} and Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−}, respectively………..12

Fig. S17 Plot of $I_0/I-1$ and fluorescence intensity of 2 versus low concentration of CrO\textsubscript{4}\textsuperscript{2−} and Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−}…………………..13

Fig. S18 Luminescent responses of 2 towards different concentrations of 4-NA………………………………………………………………………………………………………………..13

Fig. S19 Plot of $I_0/I-1$ and fluorescence intensity of 2 for 4-NA in low concentration region………………………………………………………………………………14
Fig. S20 PXRD patterns of 2 for free and 4-NA ethanol stability experiments.

Table S3 Comparison of various Ln-complexes fluorescent sensors for Fe$^{3+}$, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$.

Table S4 Comparison of various complexes fluorescent sensors for 4-NA.

---

Fig. S1 $^1$H NMR spectrum of H$_2$L.

Fig. S2 $^{13}$C NMR spectrum of H$_2$L.
Fig. S3 FT-IR spectrum of H$_2$L.

|      | Length/Å |      | Length/Å |      | Length/Å |
|------|----------|------|----------|------|----------|
| Gd(1)-O(1) | 2.310(3) | Tb(1)-O(1) | 2.293(2) | Dy(1)-O(1) | 2.293(2) |
| Gd(1)-O(3) | 2.202(3) | Tb(1)-O(3) | 2.181(2) | Dy(1)-O(3) | 2.169(3) |
| Gd(1)-O(5) | 2.451(3) | Tb(1)-O(5) | 2.427(2) | Dy(1)-O(5) | 2.405(2) |
| Gd(1)-O(6) | 2.444(3) | Tb(1)-O(6) | 2.435(2) | Dy(1)-O(6) | 2.429(3) |
| Gd(1)-O(10) | 2.368(3) | Tb(1)-O(10) | 2.358(2) | Dy(1)-O(10) | 2.355(3) |
| Gd(1)-O(11) | 2.548(4) | Tb(1)-O(11) | 2.533(3) | Dy(1)-O(11) | 2.534(3) |
| Gd(1)-O(12) | 2.478(4) | Tb(1)-O(12) | 2.474(3) | Dy(1)-O(12) | 2.455(3) |
| Gd(1)-N(1) | 2.509(4) | Tb(1)-N(1) | 2.495(3) | Dy(1)-N(1) | 2.491(3) |
| Gd(2)-O(1) | 2.332(3) | Tb(2)-O(1) | 2.314(2) | Dy(2)-O(1) | 2.298(2) |
| Gd(2)-O(2) | 2.586(3) | Tb(2)-O(2) | 2.578(2) | Dy(2)-O(2) | 2.575(3) |
| Gd(2)-O(5) | 2.391(3) | Tb(2)-O(5) | 2.379(2) | Dy(2)-O(5) | 2.378(2) |
| Gd(2)-O(7) | 2.305(3) | Tb(2)-O(7) | 2.289(2) | Dy(2)-O(7)#1 | 2.303(2) |
| Gd(2)-O(7)#1 | 2.332(3) | Tb(2)-O(7)#1 | 2.312(2) | Dy(2)-O(7) | 2.281(2) |
| Gd(2)-O(8)#1 | 2.634(4) | Tb(2)-O(8)#1 | 2.640(3) | Dy(2)-O(8)#1 | 2.635(3) |
| Gd(2)-O(9) | 2.280(3) | Tb(2)-O(9) | 2.258(2) | Dy(2)-O(9) | 2.249(3) |
| Gd(2)-N(2) | 2.479(5) | Tb(2)-N(2) | 2.450(3) | Dy(2)-N(2) | 2.443(3) |
| Ho(1)-O(1) | 2.276(3) | Ho(1)-O(6) | 2.408(3) | Ho(1)-O(12) | 2.430(3) |
| Ho(1)-O(3) | 2.167(3) | Ho(1)-O(10) | 2.334(3) | Ho(1)-N(1) | 2.472(4) |
| Ho(1)-O(5) | 2.393(3) | Ho(1)-O(11) | 2.519(3) | Ho(2)-O(1) | 2.285(3) |
| Ho(2)-O(2) | 2.568(3) | Ho(2)-O(5) | 2.359(3) | Ho(2)-O(7) | 2.268(3) |
| Ho(2)-O(7)#1 | 2.289(3) | Ho(2)-O(8)#1 | 2.618(3) | Ho(2)-O(9) | 2.234(3) |
| Ho(2)-N(2) | 2.429(4) |      |          |      |          |
| Er(1)-O(1) | 2.264(3) | Er(1)-O(10) | 2.328(3) | Er(2)-O(1) | 2.276(3) |
| Er(2)-O(7)#1 | 2.277(3) | Er(1)-O(3) | 2.160(3) | Er(1)-O(11) | 2.519(3) |
| Er(2)-O(2)    | 2.572(3) | Er(2)-O(8)#1 | 2.614(3) | Er(1)-O(5) | 2.389(3) |
|--------------|---------|--------------|---------|-----------|---------|
| Er(1)-O(12)  | 2.417(3) | Er(2)-O(5)   | 2.344(3) | Er(2)-O(9) | 2.224(3) |
| Er(1)-O(6)   | 2.400(3) | Er(1)-N(1)   | 2.457(3) | Er(2)-O(7) | 2.262(3) |
| Er(2)-N(2)   | 2.424(4) |              |         |           |         |

1

| Angle/°     | 2       | Angle/°     | 3       | Angle/°     |
|-------------|---------|-------------|---------|-------------|
| O(1)-Gd(1)-O(5) | 73.48(11) | O(1)-Dy(1)-O(5) | 72.91(8) |
| O(1)-Gd(1)-O(6) | 138.17(12) | O(1)-Dy(1)-O(6) | 138.57(9) |
| O(1)-Gd(1)-O(10) | 84.17(12)  | O(1)-Dy(1)-O(10) | 84.34(9) |
| O(1)-Gd(1)-O(11) | 134.50(12) | O(1)-Dy(1)-O(11) | 134.32(9) |
| O(1)-Gd(1)-O(12) | 87.23(12)  | O(1)-Dy(1)-O(12) | 87.05(9) |
| O(1)-Gd(1)-N(1) | 75.32(13)  | O(1)-Dy(1)-N(1) | 75.46(10) |
| O(3)-Gd(1)-O(1) | 127.73(12) | O(3)-Dy(1)-O(1) | 127.96(10) |
| O(3)-Gd(1)-O(5) | 146.01(12) | O(3)-Dy(1)-O(5) | 146.22(9) |
| O(3)-Gd(1)-O(6) | 85.60(12)  | O(3)-Dy(1)-O(6) | 85.07(9) |
| O(3)-Gd(1)-O(10) | 79.87(13)  | O(3)-Dy(1)-O(10) | 79.57(9) |
| O(3)-Gd(1)-O(11) | 76.43(13)  | O(3)-Dy(1)-O(11) | 76.19(10) |
| O(3)-Gd(1)-O(12) | 122.70(13) | O(3)-Dy(1)-O(12) | 123.41(10) |
| O(3)-Gd(1)-N(1) | 72.92(13)  | O(3)-Dy(1)-N(1) | 73.68(10) |
| O(5)-Gd(1)-O(11) | 108.61(12) | O(5)-Dy(1)-O(11) | 109.29(9) |
| O(5)-Gd(1)-O(12) | 79.59(12)  | O(5)-Dy(1)-O(12) | 78.73(9) |
| O(5)-Gd(1)-N(1) | 140.90(12) | O(5)-Dy(1)-N(1) | 139.97(9) |
| O(6)-Gd(1)-O(5) | 65.86(11)  | O(6)-Dy(1)-O(5) | 70.75(9) |
| O(6)-Gd(1)-O(11) | 70.75(12)  | O(6)-Dy(1)-O(11) | 70.75(9) |
| O(6)-Gd(1)-O(12) | 94.58(13)  | O(6)-Dy(1)-O(12) | 94.05(10) |
| O(6)-Gd(1)-N(1) | 145.51(13) | O(6)-Dy(1)-N(1) | 144.74(10) |
| O(10)-Gd(1)-O(5) | 76.27(12)  | O(10)-Dy(1)-O(5) | 76.52(9) |
| O(10)-Gd(1)-O(6) | 77.31(12)  | O(10)-Dy(1)-O(6) | 77.57(9) |
| O(10)-Gd(1)-O(10) | 141.26(12) | O(10)-Dy(1)-O(10) | 141.31(9) |
| O(10)-Gd(1)-O(11) | 155.79(13) | O(10)-Dy(1)-O(11) | 155.21(9) |
| O(10)-Gd(1)-N(1) | 123.11(13) | O(10)-Dy(1)-N(1) | 123.94(10) |
| O(12)-Gd(1)-O(11) | 50.58(12)  | O(12)-Dy(1)-O(11) | 50.10(9) |
| N(1)-Gd(1)-O(11) | 75.94(13)  | O(12)-Dy(1)-N(1) | 75.73(10) |
| O(1)-Gd(2)-O(2) | 64.51(11)  | O(1)-Dy(2)-O(2) | 65.13(9) |
| O(1)-Gd(2)-O(5) | 74.22(11)  | O(1)-Dy(2)-O(5) | 73.38(9) |
| O(1)-Gd(2)-O(7)#1 | 89.14(12)  | O(1)-Dy(2)-O(7)#1 | 88.98(9) |
| O(1)-Gd(2)-O(8)#1 | 76.69(11)  | O(1)-Dy(2)-O(8)#1 | 76.44(9) |
| O(1)-Gd(2)-N(2) | 151.17(13) | O(1)-Dy(2)-N(2) | 150.93(10) |
| O(2)-Gd(2)-O(8)#1 | 120.64(11) | O(2)-Dy(2)-O(8)#1 | 121.43(9) |
| O(5)-Gd(2)-O(2) | 127.31(11) | O(5)-Dy(2)-O(2) | 126.88(9) |
| O(5)-Gd(2)-O(8)#1 | 76.77(11)  | O(5)-Dy(2)-O(8)#1 | 76.11(8) |
| O(5)-Gd(2)-N(2) | 77.00(13)  | O(5)-Dy(2)-N(2) | 77.62(10) |
| O(7)-Gd(2)-O(1) | 138.07(12) | O(7)-Dy(2)-O(1) | 138.07(9) |
| O(7)-Gd(2)-O(2) | 75.87(12)  | O(7)-Dy(2)-O(2) | 74.38(9) |
| Bond          | Angle/°  | Bond          | Angle/°  | Bond          | Angle/°  |
|---------------|----------|---------------|----------|---------------|----------|
| O(7)#1-Gd(2)-O(2) | 73.95(12) | O(7)-Tb(2)-O(2) | 75.73(9) | O(7)-Dy(2)-O(2) | 75.52(9) |
| O(7)-Gd(2)-O(5) | 146.00(12) | O(7)-Tb(2)-O(5) | 146.76(8) | O(7)-Dy(2)-O(5) | 147.05(9) |
| O(7)#1-Gd(2)-O(5) | 138.09(11) | O(7)#1-Tb(2)-O(5) | 137.70(8) | O(7)#1-Dy(2)-O(5) | 137.43(9) |
| O(7)-Gd(2)-O(7)#1 | 66.35(14) | O(7)-Tb(2)-O(7)#1 | 66.09(10) | O(7)-Dy(2)-O(7)#1 | 66.22(10) |
| O(7)#1-Gd(2)-O(8)#1 | 61.90(11) | O(7)#1-Tb(2)-O(8)#1 | 61.85(8) | O(7)#1-Dy(2)-O(8)#1 | 62.03(8) |
| O(7)-Gd(2)-O(8)#1 | 115.29(11) | O(7)-Tb(2)-O(8)#1 | 115.03(8) | O(7)-Dy(2)-O(8)#1 | 115.26(9) |
| O(7)-Gd(2)-N(2) | 69.97(14) | O(7)#1-Tb(2)-N(2) | 113.93(9) | O(7)#1-Dy(2)-N(2) | 70.37(10) |
| O(7)#1-Gd(2)-N(2) | 113.92(13) | O(7)-Tb(2)-N(2) | 70.41(9) | O(7)-Dy(2)-N(2) | 113.84(10) |
| O(9)-Gd(2)-O(1) | 92.28(12) | O(9)-Tb(2)-O(1) | 92.48(9) | O(9)-Dy(2)-O(1) | 92.89(9) |
| O(9)-Gd(2)-O(2) | 71.67(12) | O(9)-Tb(2)-O(2) | 71.79(9) | O(9)-Dy(2)-O(2) | 71.77(9) |
| O(9)-Gd(2)-O(5) | 79.03(12) | O(9)-Tb(2)-O(5) | 78.92(9) | O(9)-Dy(2)-O(5) | 79.06(9) |
| O(9)-Gd(2)-O(7) | 87.72(12) | O(9)-Tb(2)-O(7) | 88.16(9) | O(9)-Dy(2)-O(7) | 87.96(9) |
| O(9)-Gd(2)-O(7)#1 | 141.02(12) | O(9)-Tb(2)-O(7)#1 | 141.45(9) | O(9)-Dy(2)-O(7)#1 | 141.57(9) |
| O(9)-Gd(2)-O(8)#1 | 155.34(12) | O(9)-Tb(2)-O(8)#1 | 155.05(8) | O(9)-Dy(2)-O(8)#1 | 154.87(9) |
| O(9)-Gd(2)-N(2) | 80.60(14) | O(9)-Tb(2)-N(2) | 80.50(10) | O(9)-Dy(2)-N(2) | 80.36(11) |
| N(2)-Gd(2)-O(2) | 136.43(13) | N(2)-Tb(2)-O(2) | 136.50(9) | N(2)-Dy(2)-O(2) | 136.27(10) |
| N(2)-Gd(2)-O(8)#1 | 98.39(13) | N(2)-Tb(2)-O(8)#1 | 98.07(10) | N(2)-Dy(2)-O(8)#1 | 97.86(10) |

4 Angle/°  4 Angle/°  4 Angle/°
| Bond                  | Angle (°) 1          | Bond                  | Angle (°) 2          | Bond                  | Angle (°) 3          |
|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| O(1)-Er(1)-O(11)     | 134.56(10)           | O(1)-Er(1)-O(12)     | 86.88(10)            | O(1)-Er(1)-N(1)      | 75.87(10)            |
| O(3)-Er(1)-O(1)      | 128.17(10)           | O(3)-Er(1)-O(5)      | 145.47(10)           | O(3)-Er(1)-O(6)      | 84.16(10)            |
| O(3)-Er(1)-O(10)     | 78.79(10)            | O(3)-Er(1)-O(11)     | 76.26(10)            | O(3)-Er(1)-O(12)     | 124.30(10)           |
| O(3)-Er(1)-N(1)      | 74.47(11)            | O(5)-Er(1)-O(6)      | 67.24(9)             | O(5)-Er(1)-O(11)     | 109.70(10)           |
| O(5)-Er(1)-O(12)     | 78.55(10)            | O(5)-Er(1)-N(1)      | 139.93(10)           | O(6)-Er(1)-O(11)     | 70.65(10)            |
| O(6)-Er(1)-O(12)     | 94.25(11)            | O(6)-Er(1)-N(1)      | 144.04(10)           | O(10)-Er(1)-O(5)     | 76.59(10)            |
| O(10)-Er(1)-O(6)     | 77.67(10)            | O(10)-Er(1)-O(11)    | 141.18(10)           | O(10)-Er(1)-O(12)    | 155.08(10)           |
| O(10)-Er(1)-N(1)     | 124.31(11)           | O(12)-Er(1)-O(11)    | 51.57(10)            | O(12)-Er(1)-N(1)     | 75.43(11)            |
| N(1)-Er(1)-O(11)     | 76.30(11)            | O(1)-Er(2)-O(2)      | 65.43(9)             | O(1)-Er(2)-O(5)      | 73.41(9)             |
| O(1)-Er(2)-O(7)#1    | 88.60(10)            | O(1)-Er(2)-O(8)#1    | 76.82(9)             | O(1)-Er(2)-N(2)      | 151.00(11)           |
| O(2)-Er(2)-O(8)#1    | 122.45(9)            | O(5)-Er(2)-O(2)      | 127.27(9)            | O(5)-Er(2)-O(8)#1    | 75.27(9)             |
| O(5)-Er(2)-N(2)      | 77.63(11)            | O(7)-Er(2)-O(1)      | 137.73(10)           | O(7)-Er(2)-O(2)      | 74.96(10)            |
| O(7)#1-Er(2)-O(2)    | 74.19(10)            | O(7)-Er(2)-O(5)      | 147.38(10)           | O(7)#1-Er(2)-O(5)    | 137.14(9)            |
| O(7)-Er(2)-O(7)#1    | 66.24(12)            | O(7)#1-Er(2)-O(8)#1  | 62.70(9)             | O(7)-Er(2)-O(8)#1    | 115.46(9)            |
| O(7)-Er(2)-N(2)      | 70.62(11)            | O(7)#1-Er(2)-N(2)    | 114.29(11)           | O(9)-Er(2)-O(2)      | 92.77(10)            |
| O(9)-Er(2)-O(2)      | 71.29(10)            | O(9)-Er(2)-O(5)      | 79.56(10)            | O(9)-Er(2)-O(7)      | 87.92(10)            |
| O(9)-Er(2)-O(7)#1    | 141.19(10)           | O(9)-Er(2)-O(8)#1    | 154.58(10)           | O(9)-Er(2)-N(2)      | 80.46(11)            |

Symmetry transformation: #1 -X, 2-Y, 1-Z for 1, #1 2-X, -Y, 1-Z for 2-5
Fig. S4 PXRD patterns of 1(a), 2(b), 3(c), 4(d), 5(e).
Fig. S5 IR spectra of 1(a), 2(b), 3(c), 4(d), 5(e).

Table S2. Agreement factor between the coordination polyhedron of the LnIII and the various ideal polyhedral calculated by the SHAPE program

|       | HBPY-8 | CU-8 | SAPR-8 | TDD-8 | JGBF-8 | JBTAPR | BTPR-8 | JSD-8 | TT-8 |
|-------|--------|------|--------|-------|--------|--------|--------|-------|------|
| Gd1   | 14.779 | 8.898| 1.686  | 2.836 | 14.348 | 2.716  | 1.948  | 5.147 | 9.501 |
| Gd2   | 14.482 | 11.904| 3.123  | 2.877 | 11.858 | 2.745  | 2.428  | 4.685 | 12.131 |
| Tb1   | 14.941 | 8.967| 1.635  | 2.787 | 14.521 | 2.674  | 1.858  | 5.070 | 9.572 |
| Tb2   | 14.587 | 11.972| 3.095  | 2.913 | 11.953 | 2.721  | 2.435  | 4.625 | 12.156 |
| Dy1   | 15.029 | 9.008| 1.635  | 2.709 | 14.552 | 2.604  | 1.787  | 4.952 | 9.590 |
| Dy2   | 14.735 | 12.056| 3.038  | 2.904 | 12.026 | 2.668  | 2.416  | 4.549 | 12.224 |
| Ho1   | 15.177 | 9.091| 1.567  | 2.688 | 14.556 | 2.534  | 1.741  | 4.917 | 9.670 |
| Ho2   | 14.872 | 12.189| 2.967  | 2.924 | 11.996 | 2.572  | 2.313  | 4.515 | 12.306 |
| Er1   | 15.298 | 9.127| 1.525  | 2.645 | 14.588 | 2.447  | 1.685  | 4.823 | 9.686 |
| Er2   | 14.918 | 12.242| 2.990  | 2.925 | 12.031 | 2.566  | 2.323  | 4.478 | 12.406 |

1 HBPY-8 Hexagonal bipyramid D6h
2 CU-8 Cube Oh
3 SAPR-8 Square antiprism D4d
4 TDD-8 Triangular dodecahedron D2d
5 JGBF-8 Johnson – Gyrobifastigium (J26) D2d
Fig. S6 Plot of $1/\chi_M$ versus $T$ for 1, the linear fit is the Curie-Weiss law fit at 1 kOe field.

Fig. S7 Temperature dependence of the out-of-phase ($\chi''$) ac susceptibility for 3 under zero dc field at 1000 Hz.

Fig. S8 (a) The excitation and emission spectra of H$_2$L ligand. (b) Emission spectra of 1-5 in solid state at room temperature.
Fig. S9 Excitation spectrum (a) and emission spectrum (b) of 2 in solid state at room temperature.

Fig. S10 PXRD patterns for the simulated and experimental samples of 2 soaked in aqueous solutions with pH values in the range of 3-14 for two days.

Fig. S11 PXRD patterns for the simulated and experimental samples of 2 soaked in water for 2 days and 14 days.
Fig. S12 SEM images (left) and particle size distributions of 2 (right) after being sonicated for 8 (a), 15 (b) and 30 (c) minutes.

Fig. S13 (a) Stern-Volmer plot of $I_0/I - 1$ versus low Fe$^{3+}$ concentration in the aqueous suspension of 2. (b) Linear region of fluorescence intensity for the suspensions of 2 in water upon incremental addition of Fe$^{3+}$ solutions.
**Fig. S14** Comparison of XPS spectra of 2 before (black) and after (red) its immersion in the Fe$^{3+}$ aqueous solution.

**Fig. S15** PXRD patterns for 2 after the detection of Fe$^{3+}$, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ ions.

**Fig. S16** Luminescent responses of a water suspension of 2 (2 mg/2 mL) towards different concentrations of (a) CrO$_4^{2-}$ ions ($2 \times 10^{-3}$ M, 0 µL-2000 µL) and (b) Cr$_2$O$_7^{2-}$ ($2 \times 10^{-3}$ M, 0 µL-2000 µL).
Fig. S17 Stern-Volmer plot of $I_0/I - 1$ versus low concentration of $\text{CrO}_4^{2-}$ (a) and $\text{Cr}_2\text{O}_7^{2-}$ (b) in the aqueous suspension of $\mathbf{2}$, and linear region of fluorescence intensity for the suspensions of $\mathbf{2}$ in water upon incremental addition of $\text{CrO}_4^{2-}$ (c) or $\text{Cr}_2\text{O}_7^{2-}$ (d) solutions.

Fig. S18 Luminescence responses of an ethanol suspension of $\mathbf{2}$ (2 mg/2 mL) towards different concentrations of 4-NA ($1 \times 10^{-3}$ M, 0 µL-2000 µL).
Fig. S19 (a) Stern-Volmer plot of $I_0/I - 1$ versus low concentration of 4-NA in the ethanol suspension of 2. (b) Linear region of fluorescence intensity for the suspensions of 2 in ethanol upon incremental addition of 4-NA solutions.

Fig. S20 PXRD patterns for 2 after the detection of 4-NA and being soaked in ethanol for 10 days

Table S3 The comparison of various Ln-complexes fluorescent sensors for Fe$^{3+}$, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$

| Ln based complexes                       | Analyte     | Quenching constant ($K_{SV}$, M$^{-1}$) | Detection limits | Solvent | Ref     |
|-----------------------------------------|-------------|----------------------------------------|------------------|---------|---------|
| [Tb$_4$(NO$_3$)$_4$(Piv)$_4$]·2CH$_3$OH  | Fe$^{3+}$   | $1.86 \times 10^4$                    | 10µM             | water   | This    |
|                                          | CrO$_4^{2-}$| $2.998 \times 10^3$                   | 52µM             | work    |         |
|                                          | Cr$_2$O$_7^{2-}$ | $7.44 \times 10^1$               | 27µM             |         |         |
| {[Tb$_2$(Ccbp)$_3$·6H$_2$O]·3Cl$_{-}$·4H$_2$O) | Fe$^{3+}$   | $1.143 \times 10^5$               | ethanol          | 1       |         |
| {[Eu(L1)(BPDC)$_{1/2}$·(NO$_3$)]·H$_2$O)$_n$ | Fe$^{3+}$   | $5.16 \times 10^4$                   | DMF              | 2       |         |
| {[Tb(L1)(BPDC)$_{1/2}$·(NO$_3$)]·H$_2$O)$_n$ | Fe$^{3+}$   | $4.30 \times 10^4$                   | DMF              | 2       |         |
| {[Eu(1,5-Nds)$_{0.5}$(ox)(phen)(H$_2$O)]·H$_2$O} | Fe$^{3+}$   | $1.3070 \times 10^3$               | water            | 3       |         |
| Nds$_{3.5}$(ox)(phen)(H$_2$O)]·H$_2$O) | Fe$^{3+}$   | $1.5374 \times 10^3$               | 1.2 µM           | Water   | 7       |
| {[Eu(1,5-Nds)$_{0.5}$(ox)(phen)(H$_2$O)]·H$_2$O} | CrO$_4^{2-}$| $1.3734 \times 10^3$               | 130 µM           | water   | 6       |
| {[Tb(TBOT)(H$_2$O)]·4H$_2$O} | CrO$_4^{2-}$| $5.51 \times 10^3$                   | 130 µM           | water   | 6       |
| {[CH$_3$$_2$NH$_2$][Tb(bptc)]·xsolvents | Cr$_2$O$_7^{2-}$ | $1.37 \times 10^4$ | 340 µM |         | 6       |
| {[Eu(L2)(HCOO)(H$_2$O)]} | CrO$_4^{2-}$| $1.3070 \times 10^3$               | 1.8 µM           | Water   | 7       |
| {[Tb(L2)(HCOO)(H$_2$O)]} | CrO$_4^{2-}$| $2.1335 \times 10^3$               | 2.1 µM           | water   | 7       |
| Coordination complex | Quenching constant ($K_{sv}$, M$^{-1}$) | Detection limits | λ<sub>ex</sub>(nm) | λ<sub>em</sub>(nm) | Solvent | Ref |
|----------------------|-------------------------------------|-----------------|----------------|---------------|--------|-----|
| [CuL$\text{II}$(NO$_3$)$_2$]·2CH$_3$OH | 1.14 × 10$^4$ | 8.5µM | 360 | 544 | ethanol | This work |
| [Cd$_2$(L$\text{III}$)$_2$(bib)$_2$·(H$_2$O)$_2$]$_n$ | 6.6 × 10$^4$ | 325 | DMSO | 14 |
| ([Cd$_2$(L$\text{III}$)$_2$(bib)$_2$]·3H$_2$O)$_n$ | 1.1 × 10$^4$ | 375 | DMSO | 14 |
| [Cd$_2$(H$_2$L$\text{II}$)$\text{II}$]·5H$_2$O·2DMF | 1.81 × 10$^4$ | 480 | isopropanol | 15 |
| ([Zn4(O$_2$)(L7)(H$_2$O)]$\text{II}$·2DMF)$_n$ | 350 | 400 red-shifted about 40 nm. | DMF | 16 |
| [Zn$_\text{II}$L$\text{I}$·(1,10-phen·H$_2$O)]·2H$_2$O | 6556 | 330 | 456 | DMA | 17 |
| [Zn$_\text{II}$L$\text{I}$·(1,10-phen·H$_2$O)]·2H$_2$O | 3955 | 318 | 396 | DMA | 17 |

| CrO$_2$$_\text{II}$ | 4.85 × 10$^3$ | 0.33 ppm | water | 8 |
| CrO$_2$$_\text{II}$ | 1.04 × 10$^4$ | 1.07 ppm | water | 9 |
| Fe$_\text{III}$ | 2.942 × 10$^3$ | 10 µM | DMF | 10 |
| CrO$_2$$_\text{II}$ | 1.526 × 10$^3$ | 10 µM | DMF | 11 |
| Fe$_\text{III}$ | 3667 | 1 µM | water | 12 |
| CrO$_2$$_\text{III}$ | 11106 | 5 µM | water | 13 |
| [Eu(HPIDC)(m-bdc)·1.5H$_2$O]$_n$ | Cr$_\text{II}$O$_2$$_\text{II}$ | 4.1 × 10$^4$ | water | 13 |
| [Eu(HPIDC)(m-bdc)·1.5H$_2$O]$_n$ | Cr$_\text{II}$O$_2$$_\text{II}$ | 6.1 × 10$^4$ | water | 13 |

Ccb$^+$ = 4-carboxy-1-((4-carboxybenzyl)pyridinium; H$_2$L$\text{I}$ = 2,5-di(pyridin-4-yl)terephthalic acid; BPDC = biphenyl-4,4$'$-dicarboxylic acid; 1,5-Nds = 1,5-naphthalenedisulfonate disulfonate; ox = oxalate; phen = 1,10-phenanthroline; m-H$_2$bdc = 1,3-benzenedicarboxylic acid; H$_2$bpptc = benzophenone-3,3,3$'$,4,4$'$,4$'$-tetracarboxylic acid; H$_2$PIDC = 2-(4-pyridyl)-1H-imidazole-4,5-dicarboxylic acid; H$_2$MFDA = 9,9-dimethyl-fluorene-2,7-dicarboxylic acid; H$_2$TPbpc = 4,4$'$-[(2$'$-cyano-[1,1$'$-biphenyl]-4-yl)methoxy]isophthalic acid; H$_2$L$\text{III}$ = 5,5$'$-(carbonylbis(azanediyl))diisophthalic acid; H$_2$BPDC = 4,4$'$-bis(imidazol-1-yl)benzene; H$_2$L$\text{III}$ = 5,5$'$-bis(imidazol-1-yl)biphenyl; H$_2$L$\text{IV}$ = 2,5-bis(3,5-dicarboxyphenyl)thiopheneamide; H$_2$L$\text{V}$ = [1,1$'$,4,1$'$]terphenyl-3,3,5,2,5,2$'$,3$'$,5$'$-hexacarboxylic acid; H$_2$L$\text{VI}$ = bis-(3,5-dicarboxyphenyl)terephthalamide; DMA = N,N-dimethylacetamide; DMSO = dimethyl sulfoxide

Table 54 The comparison of various coordination complexes fluorescent sensors for 4-NA
References

S1. K.-M. Wang, L. Du, Y.-L. Ma, J.-S. Zhao, Q. Wang, T. Yan and Q.-H. Zhao, CrystEngComm, 2016, 18, 2690-2700.
S2. W. Yan, C. Zhang, S. Chen, L. Han and H. Zheng, ACS Appl. Mater. Interfaces, 2017, 9, 1629-1634.
S3. R. Li, X.-L. Qu, Y.-H. Zhang, H.-L. Han and X. Li, CrystEngComm, 2016, 18, 5890-5900.
S4. X. H. Zhou, L. Li, H. H. Li, A. Li and W. Huang, Dalton Trans., 2013, 42, 12403-12409.
S5. X. L. Zhao, D. Tian, Q. Gao, H. W. Sun, J. Xu and X. H. Bu, Dalton Trans., 2016, 45, 1040-1046.
S6. M. Chen, W. -M. Xu, J. -Y. Tian, H. Cui, J.-X. Zhang, C. -S. Liu and M. Du, J. Mater. Chem. C, 2017, 5, 2015-2021.
S7. Z. Sun, M. Yang, Y. Ma and L. Li, Cryst. Growth Des., 2017, 17, 4326-4335.
S8. J. Liu, G. Ji, J. Xiao and Z. Liu, Inorg. Chem., 2017, 56, 4197-4205.
S9. W. Liu, X. Huang, C. Xu, C. Chen, L. Yang, W. Dou, W. Chen, H. Yang and W. Liu, Chem. –Eur. J., 2016, 22, 18769-18776.
S10. G. X. Wen, M. L. Han, X. Q. Wu, Y. P. Wu, W. W. Dong, J. Zhao, D. S. Li and L. F. Ma, Dalton Trans., 2016, 45, 15492-15499.
S11. G. P. Li, G. Liu, Y. Z. Li, L. Hou, Y. Y. Wang and Z. Zhu, Inorg. Chem., 2016, 55, 3952-3959.
S12. W. Gao, F. Liu, B. Y. Zhang, X. M. Zhang, J. P. Liu, E. Q. Gao and Q. Y. Gao, Dalton Trans., 2017, 46, 13878-13887.
S13. X. H. Huang, L. Shi, S. M. Ying, G. Y. Yan, L. H. Liu, Y. Q. Sun and Y. P. Chen, CrystEngComm, 2018, 20, 189-197.
S14. L. Huo, J. Zhang, L. Gao, X. Wang, L. Fan, K. Fang and T. Hu, CrystEngComm, 2017, 19, 5285-5292.
S15. F. Wang, Z. Yu, C. Wang, K. Xu, J. Yu, J. Zhang, Y. Fu, X. Li and Y. Zhao, Sen. Actuators B Chem., 2017, 239, 688-695.
S16. X.-Y. Wan, F.-L. Jiang, C.-P. Liu, K. Zhou, L. Chen, Y.-L. Gai, Y. Yang and M.-C. Hong, J. Mater. Chem. A, 2015, 3, 22369-22376.
S17. F. Wang, C. Wang, Z. Yu, Q. He, X. Li, C. Shang and Y. Zhao, RSC Adv., 2015, 5, 70086-70093.