

Supporting information

**A heterometallic sodium(I)-europium(III)-organic layer exhibiting dual-responsive luminescent sensing for nitrofurantoin antibiotics,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{MnO}_4^-$  anions**

Shan Xu,<sup>a</sup> Jing-Jing Shi,<sup>a</sup> Bo Ding,<sup>a</sup> Zheng-Yu Liu,<sup>a</sup> Xiu-Guang Wang,<sup>a</sup> Xiao-Jun Zhao<sup>\*a, b</sup> and En-Cui

Yang<sup>\*a</sup>

**Table S1** Selected bond lengths (Å) and angles (deg) for **1**<sup>a</sup>

Eu(1)–O(1)	2.441(5)	Eu(2)–O(10)	2.374(5)
Eu(1)–O(2)	2.467(5)	Eu(2)–O(11) <sup>#1</sup>	2.511(4)
Eu(1)–O(5)	2.473(5)	Eu(2)–O(12) <sup>#1</sup>	2.437(5)
Eu(1)–O(6)	2.523(4)	Eu(2)–O(14)	2.431(5)
Eu(1)–O(8) <sup>#1</sup>	2.392(5)	Eu(2)–O(16)	2.312(5)
Eu(1)–O(9)	2.315(5)	Na(1)–O(2)	2.506(5)
Eu(1)–O(13)	2.341(6)	Na(1)–O(4) <sup>#5</sup>	2.371(5)
Eu(1)–O(15)	2.422(5)	Na(1)–O(6)	2.292(6)
Eu(2)–O(3) <sup>#3</sup>	2.463(5)	Na(1)–O(11) <sup>#2</sup>	2.285(6)
Eu(2)–O(4) <sup>#3</sup>	2.453(5)	Na(1)–O(14) <sup>#4</sup>	2.546(6)
Eu(2)–O(7) <sup>#1</sup>	2.280(5)	Na(1)–O(15)	2.406(5)
O(1)–Eu(1)–O(2)	52.66(15)	O(7) <sup>#1</sup> –Eu(2)–O(12) <sup>#1</sup>	81.8(2)
O(1)–Eu(1)–O(5)	79.45(19)	O(7) <sup>#1</sup> –Eu(2)–O(14)	80.47(19)
O(1)–Eu(1)–O(6)	102.53(17)	O(7) <sup>#1</sup> –Eu(2)–O(16)	110.70(18)
O(2)–Eu(1)–O(5)	92.22(18)	O(10)–Eu(2)–O(3) <sup>#2</sup>	79.99(18)
O(2)–Eu(1)–O(6)	71.35(17)	O(10)–Eu(2)–O(4) <sup>#2</sup>	132.04(17)
O(5)–Eu(1)–O(6)	51.73(16)	O(10)–Eu(2)–O(11) <sup>#1</sup>	129.42(17)

---

O(8) <sup>#1</sup> –Eu(1)–O(1)	81.75(17)	O(10)–Eu(2)–O(12) <sup>#1</sup>	78.55(17)
O(8) <sup>#1</sup> –Eu(1)–O(2)	134.31(17)	O(10)–Eu(2)–O(14)	149.13(17)
O(8) <sup>#1</sup> –Eu(1)–O(5)	80.88(17)	O(12) <sup>#1</sup> –Eu(2)–O(3) <sup>#2</sup>	78.93(19)
O(8) <sup>#1</sup> –Eu(1)–O(6)	129.54(17)	O(12) <sup>#1</sup> –Eu(2)–O(4) <sup>#2</sup>	96.22(19)
O(8) <sup>#1</sup> –Eu(1)–O(15)	147.05(16)	O(12) <sup>#1</sup> –Eu(2)–O(11) <sup>#1</sup>	52.00(16)
O(13)–Eu(1)–O(6)	148.25(18)	O(14)–Eu(2)–O(3) <sup>#2</sup>	122.30(18)
O(9)–Eu(1)–O(2)	141.91(16)	O(14)–Eu(2)–O(4) <sup>#2</sup>	71.41(16)
O(9)–Eu(1)–O(5)	84.55(19)	O(14)–Eu(2)–O(11) <sup>#1</sup>	72.53(17)
O(9)–Eu(1)–O(6)	77.17(16)	O(14)–Eu(2)–O(12) <sup>#1</sup>	123.65(17)
O(9)–Eu(1)–O(8) <sup>#1</sup>	82.72(18)	O(16)–Eu(2)–O(3) <sup>#2</sup>	82.10(18)
O(9)–Eu(1)–O(13)	107.29(19)	O(16)–Eu(2)–O(4) <sup>#2</sup>	86.36(18)
O(9)–Eu(1)–O(15)	79.45(18)	O(16)–Eu(2)–O(10)	80.37(19)
O(13)–Eu(1)–O(1)	84.07(19)	O(16)–Eu(2)–O(11) <sup>#1</sup>	149.97(18)
O(13)–Eu(1)–O(2)	89.63(19)	O(16)–Eu(2)–O(14)	82.02(18)
O(13)–Eu(1)–O(8) <sup>#1</sup>	81.94(19)	O(4) <sup>#5</sup> –Na(1)–O(2)	105.04(18)
O(13)–Eu(1)–O(15)	77.28(18)	O(4)–Na(1)–O(14) <sup>#4</sup>	70.75(17)
O(15)–Eu(1)–O(1)	120.62(17)	O(15)–Na(1)–O(14) <sup>#4</sup>	113.59(19)
O(15)–Eu(1)–O(2)	71.20(16)	O(6)–Na(1)–O(2)	74.53(19)
O(15)–Eu(1)–O(5)	124.26(16)	O(6)–Na(1)–O(4) <sup>#5</sup>	100.1(2)
O(15)–Eu(1)–O(6)	72.65(16)	O(6)–Na(1)–O(14) <sup>#4</sup>	111.1(2)
O(3) <sup>#2</sup> –Eu(2)–O(11) <sup>#1</sup>	98.02(17)	O(6)–Na(1)–O(15)	77.15(18)
O(4) <sup>#2</sup> –Eu(2)–O(3) <sup>#2</sup>	52.50(16)	O(11) <sup>#3</sup> –Na(1)–O(4) <sup>#5</sup>	76.26(19)
O(4) <sup>#2</sup> –Eu(2)–O(11) <sup>#1</sup>	70.79(17)	O(11) <sup>#3</sup> –Na(1)–O(14) <sup>#4</sup>	74.26(18)
O(7) <sup>#1</sup> –Eu(2)–O(4) <sup>#2</sup>	144.78(17)	O(11) <sup>#3</sup> –Na(1)–O(15)	106.0(2)

---

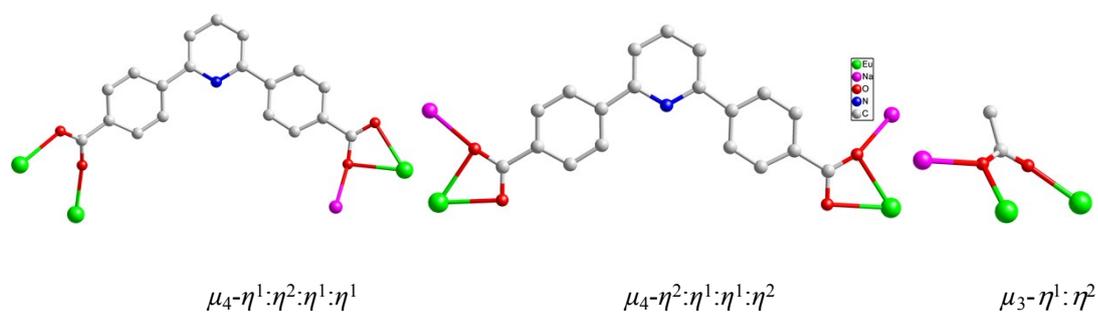
---

O(7)<sup>#1</sup>-Eu(2)-O(10)    82.32(19)    O(15)-Na(1)-O(2)    70.79(17)

O(7)<sup>#1</sup>-Eu(2)-O(11)<sup>#1</sup>    80.97(16)

<sup>a</sup> Symmetry codes: #1  $x, y + 1, z$ ; #2  $x - 1, 3/2 - y, z - 1/2$ ; #3  $-x, y + 1/2, 3/2 - z$ ; #4  $-x, y - 1/2, 3/2 - z$ ; #5  $1 - x, 1 - y, 2 - z$ ; #6  $1 + x, 3/2 - y, z + 1/2$ ; #7  $x, y - 1, z$ .

---

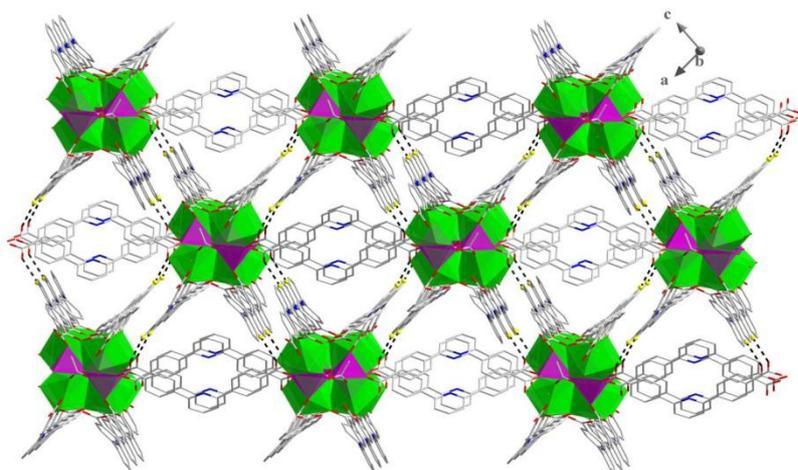


**Fig. S1** Binding modes of pddb<sup>2-</sup> and acetate anion.

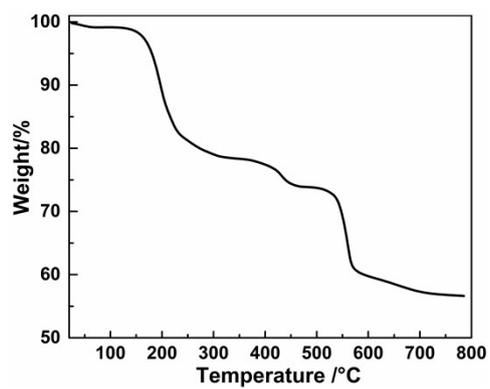
**Table S2** Hydrogen-bonding parameters (Å, deg) in **1**<sup>a</sup>

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(D–H···A)
C28–H28···O1	0.93	2.56	3.209	128
C48–H48···O3	0.93	2.41	3.304	162

<sup>a</sup> Symmetry codes: #1 – *x*, 1 – *y*, 2 – *z*.



**Fig. S2** 3D supramolecular framework of **1**.



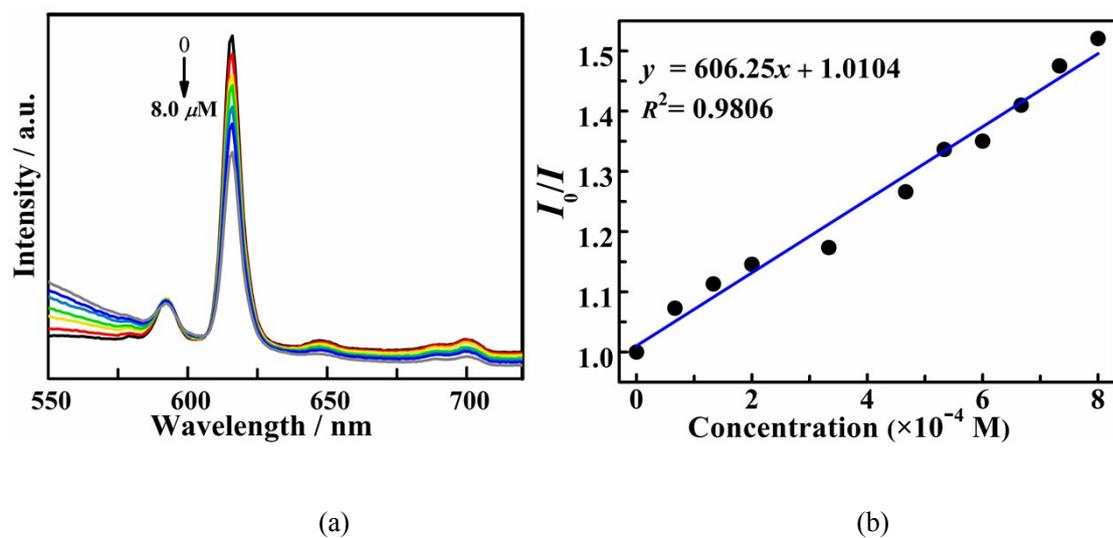
**Fig. S3** TGA curve of **1**.

**Table S3** Fluorescence lifetime of **1** in the solid state and dispersed in DMF in the absence and presence of NFZ, NFT and  $\text{Cr}_2\text{O}_7^{2-}$

Sample	$\tau_1$ ( $\mu\text{s}$ )	%	$\tau_2$ ( $\mu\text{s}$ )	%	Lifetime ( $\mu\text{s}$ )
<b>1</b>	317	2.19	971	97.81	1018.78
<b>1</b> -DMF suspension	87	2.77	959	97.23	956.36
<b>1</b> + NFZ (0.13 mM)	95	2.46	958	97.56	958.07
<b>1</b> + NFT (0.13 mM)	85	2.07	954	97.93	951.56
<b>1</b> + FZD (0.13 mM)	94	2.26	951	97.74	950.51
<b>1</b> + $\text{Cr}_2\text{O}_7^{2-}$ (0.67 mM)	109	2.73	955	97.27	958.71
<b>1</b> + $\text{MnO}_4^-$ (0.67 mM)	89	1.68	955	98.32	953.71

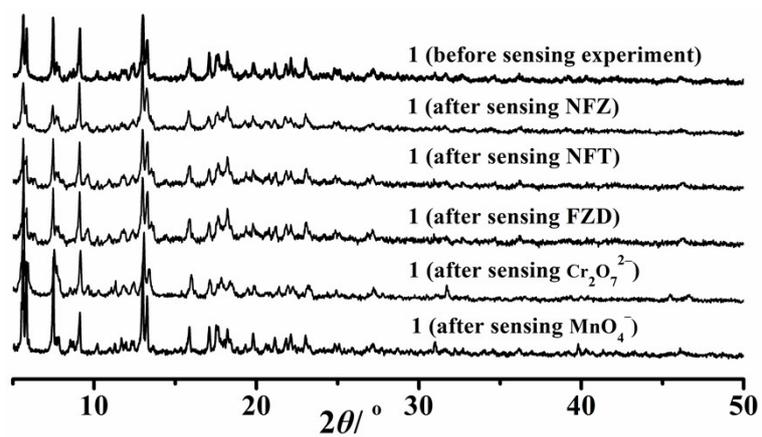
**Table S4** Standard deviation ( $\sigma$ ) calculated from the five blank measurements.

Blank Readings	NFZ	NFT	FDZ	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	MnO <sub>4</sub> <sup>-</sup>
#1 Fluorescence Intensity (CPS)	1114385	1114385	1114385	1056255	1056255
#2 Fluorescence Intensity (CPS)	1110000	1110000	1110000	1067350	1067350
#3 Fluorescence Intensity (CPS)	1111070	1111070	1111070	1057650	1057650
#4 Fluorescence Intensity (CPS)	1108240	1108240	1108240	1055530	1055530
#5 Fluorescence Intensity (CPS)	1093660	1093660	1093660	1048050	1048050
Standard Deviation ( $\sigma$ )	8038.767	8038.767	8038.767	6898.514	6898.514

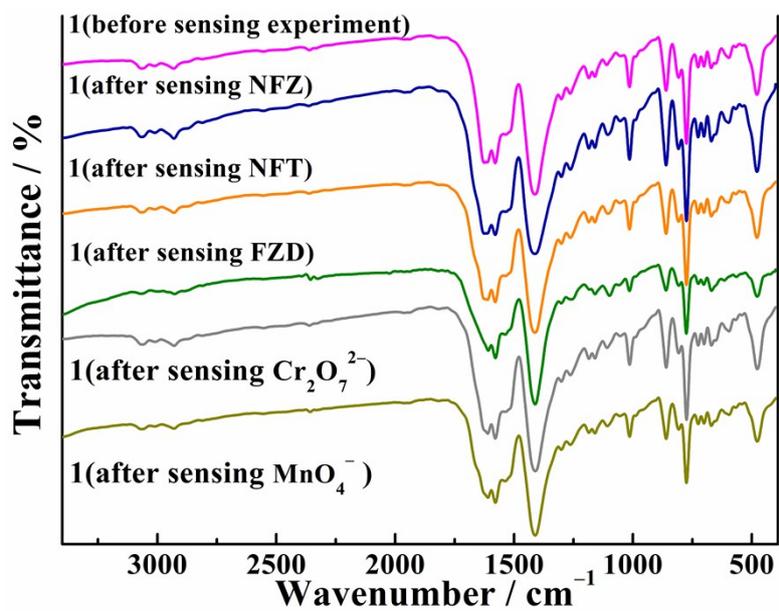


**Fig. S4** (a) Fluorescence spectra of **1** upon incremental addition of  $\text{Cr}_2\text{O}_7^{2-}$  in alkaline DMF solution. (b)

Plot of  $I_0/I$  vs.  $[\text{Cr}_2\text{O}_7^{2-}]$  in alkaline DMF solution (The blue solid lines represent the linear fit to the Stern–Volmer equation).



**Fig. S5** XRD patterns of **1** before after detecting of NFs,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{MnO}_4^-$ .



**Fig. S6** FT-IR spectra of **1** before and after the detection of NFs, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and MnO<sub>4</sub><sup>-</sup>.