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# Supporting Information for

# Eu<sup>3+</sup>/Tb<sup>3+</sup>-modified Cd(II) coordination polymers for effective detection of uric acid and lung cancer biomarker *N*-acetylneuraminic acid

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#### Materials and characterization.

Powder X-ray diffraction (PXRD) data were collected over the 20 range of 5–50° using a SmartLab diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.5418 Å) at room temperature. The FT-IR spectra (4000-400 cm<sup>-1</sup> region) were recorded from KBr pellets with a NICOLET 6700F-IR spectrometer. Thermal analyses were performed on STA 449 F5 Jupiter instrument from room temperature to 800°C with a heating rate of 10°C/min under flowing nitrogen. Emission and excitation spectra in solid state as well as lifetime luminescence were carried out on a FLS1000 spectrophotometer analyzer of Edinburgh instruments. Luminescence sensing properties were recorded on the Hitachi F-7000 Luminescence spectrophotometer. X-ray photoelectron spectroscopy (XPS) characterization was carried out by using a Thermo Fisher Scientific ESCALAB Xi+ spectrometer with Al K $\alpha$  X-rays (1486.6 eV). UV-vis measurements were conducted with a UH 4150 spectrophotometer. The SEM and EDS mapping were recorded with FIB Helios G4. The inductively coupled plasma mass spectrometer (ICP) were recorded with ThermoFisher iCAPRQ. The AFM were recorded with Multimode8 Solver P47.

## X-ray crystallographic study.

Single-crystal X-ray data for Cd-CP2 were collected on a Siemens Smart CCD diffractometer with graphite-monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298 K. The raw data frames were integrated into SHELX-format reflection files and corrected using SAINT program. Absorption corrections based on multi-scan were obtained by the SADABS program. The structure was solved with direct methods (SHELXS) and refined with full-matrix least-squares technique using the SHELXL-2018/3 programs. Displacement parameters were refined anisotropically, and the positions of the H-atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Basic information pertaining to crystal parameters and structure refinement is summarized in Table S1. Selected bond lengths and angles are listed in Table S2.

## Calculation of the HOMO and LUMO.

The HOMO–LUMO energy levels were calculated at the b3pw91/6-31g accuracy level by density functional theory (DFT), using the Gaussian 16 package of programs. The harmonic frequency was calculated to make sure that the acquired structure was the local minimum.

Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.;

Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

Cd-CP2						
Formula	$C_{35}H_{30}N_2O_9Cd$	V [Å <sup>3</sup> ]	3105.14(17)			
formula weight	735.01	Ζ	4			
T (K)	293(2)	$ ho_{ m calc} \left[ { m g} \cdot { m cm}^{-3} \right]$	1.572			
Crystal system	Monoclinic	$\mu$ [mm <sup>-1</sup> ]	6.151			
Space group	$P2_l/n$	$\theta$ range 3.858-71.193				
a [Å]	11.6644(3)		-14<=h<=11,			
b [Å]	22.9153(6)	index ranges	-28<=k<=28,			
c [Å]	12.4762(4)		-15<=1<=14			
α [°]	90	R1;wR <sub>2a</sub> [I> $2\sigma(I)$ ]	0.0377, 0.0843			
β [°]	111.388(4)	GOF	1.032			
γ [°]	90	R1;wR <sub>2a</sub> [all data]	0.0387, 0.0872			
${}^{a}R_{1} = \Sigma   F_{o}  -  F_{c}   / \Sigma  F_{o} , \ {}^{b}wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma w (F_{o}^{2})^{2}]^{1/2}$						
Table S2. Selected bond lengths [Å] and angles [°] for Cd-CP2.						
Cd(1)-O(1)	2.279(2)	Cd(1)-O(2)	2.604(3)			
Cd(1)-N(1)	2.336(3)	Cd(1)-N(2)	2.342(3)			
Cd(1)-O(4A)	2.323(2)	Cd(1)-O(5A)	2.566(2)			
Cd(1)-O(5B)	2.312(2)	O(1)-Cd(1)-O(2)	53.12(9)			
O(1)-Cd(1)-N(1)	144.28(9)	O(1)-Cd(1)-N(2)	84.42(9)			
O(1)-Cd(1)-O(4A)	110.62(9)	O(1)-Cd(1)-O(5A)	81.32(8)			
O(1)-Cd(1)-O(5B)	103.23(9)	O(4A)-Cd(1)-O(2)	86.82(9)			
O(4A)-Cd(1)-O(5A)	52.62(8)	O(4A)-Cd(1)-N(1)	85.81(8)			
O(4A)-Cd(1)-N(2)	153.82(9)	O(5B)-Cd(1)-O(2)	155.96(8)			
O(5A)-Cd(1)-O(2)	103.05(7)	O(5B)-Cd(1)-O(4A)	108.31(9)			
O(5B)-Cd(1)-O(5A)	74.00(8)	O(5B)-Cd(1)-N(1)	100.95(9)			
N(1)-Cd(1)-O(5A)	130.94(8)	N(1)-Cd(1)-N(2)	70.61(9)			
N(2)-Cd(1)-O(2)	85.69(8)	N(2)-Cd(1)-O(5A)	153.52(9)			
O(5B)-Cd(1)-N(2)	87.80(8)	N(1)-Cd(1)-O(2)	98.65(9)			

 Table S1. Crystal structure data and refinement parameters of Cd-CP2.

Symmetry transformations used to generate equivalent atoms: A: x+1, +y, 1+z. B: 1-x,1y, 1-z.

Luminescent material	Detection mechanism	$K_{ m sv}/{ m M}^{-1}$	Detection limit	Ref.
Cu <sup>2+</sup> @MIL-91(Al : Eu)	Turn-on		1.6 µM	36
ZJU-158-Tb	On-off-on	8.37× 10 <sup>3</sup>	7 nM	37
Eu-BDC@FM	On-off-on	$1.06 \times 10^4$	0.6 µM	38
MBP-SO <sub>3</sub> @Nafion			11.3 μM	39
Hf-UiO-66-Py	ratiometric		1.4 µM	40
PCN-222 (Fe)	Turn-on		3.5 µM	41
MOF-235			3.46 µM	42
<b>BTB-MOF</b>	Turn-off		4× 10 <sup>-4</sup> mg/L	43
URICASE and	Turn-on		$0.8\mu\mathrm{M}$	44
HRP@HP-DUT-5				
CD-MONT-2	Turn-on		4.3 μM	45
Eu-TDA	Turn-off	$4.15 \times 10^4$	0.689 µM	46
Cd-CP2	Turn-off	$5.162 \times 10^{4}$	$0.67\mu\mathrm{M}$	This work

Table S3. Comparison of detection capacities of Cd-CP2 toward UA with other probes.



Fig. S1. PXRD of as-synthesized Cd-CP2, Eu<sup>3+</sup>@Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2.



Fig. S2. (a) FT-IR spectra of the H<sub>3</sub>L, Cd-CP2 and Eu<sup>3+</sup>@Cd-CP2. (b) FT-IR spectra of H<sub>3</sub>L, Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2.



**(a)** 

**(b)** 



(i)







**(g)** 



Fig. S3. (a-c) SEM of Cd-CP2, Eu<sup>3+</sup>@Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2. (d-f) 2D AFM image of Cd-CP2, Eu<sup>3+</sup>@Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2. (g-i) 3D AFM image of Cd-CP2, Eu<sup>3+</sup>@Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2.

(h)



Fig. S4. (a) EDS mapping results of Eu<sup>3+</sup>@Cd-CP2. (b) EDS mapping results of Tb<sup>3+</sup>@Cd-CP2.



Fig. S5. (a) XPS spectra of Cd-CP2 and Eu<sup>3+</sup>@Cd-CP2. (b) C1s XPS, (c) N1s XPS, (d) O1s XPS, (e) Cd3d XPS, and (f) Eu3d XPS spectra of Cd-CP2 and Eu<sup>3+</sup>@Cd-CP2.



Fig. S6. (a) XPS spectra of Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2. (b) C1s XPS, (c) N1s XPS, (d) O1s XPS, (e) Cd3d XPS, and (f) Tb3d XPS spectra of Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2.



Fig. S7. Luminescence spectra and photos of aqueous suspensions of Cd-CP2, Eu<sup>3+</sup>@Cd-CP2, Tb<sup>3+</sup>@Cd-CP2 under 254 nm UV light.



Fig. S8. (a-c) PXRD of Cd-CP2,  $Eu^{3+}$ @Cd-CP2 and  $Tb^{3+}$ @Cd-CP2 after being immersed in H<sub>2</sub>O for different time.



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**Fig. S10.** (a) Emission spectra of **Eu**<sup>3+</sup> **(a)Cd-CP2** after being immersed in H<sub>2</sub>O for different time; (b) The corresponding intensity histogram diagram of  $I_{355 \text{ nm}}$  and  $I_{615 \text{ nm}}$ .



**Fig. S11.** (a) Emission spectra of  $Tb^{3+}$  (a) Cd-CP2 after being immersed in H<sub>2</sub>O for different time; (b) The corresponding intensity histogram diagram of  $I_{355 \text{ nm}}$  and  $I_{545 \text{ nm}}$ .



Fig. S12. (a-c) PXRD of Cd-CP2,  $Eu^{3+}$ @Cd-CP2 and  $Tb^{3+}$ @Cd-CP2 after being immersed in the solutions of pH = 4-9.



Fig. S13. (a) The emission spectra of Cd-CP2 after immersing in aqueous solutions with different pH values. (b) The photo of Cd-CP2 in different pH values irradiated by 254 nm UV lamp. (c) The emission spectra of  $Eu^{3+}$ @Cd-CP2 after immersing in aqueous solutions with different pH values. (d) The photo of  $Eu^{3+}$ @Cd-CP2 in different pH values irradiated by 254 nm UV lamp. (e) The emission spectra of  $Tb^{3+}$ @Cd-CP2 after immersing in aqueous solutions with different pH values solutions with different pH values. (f) The photo of  $Tb^{3+}$ @Cd-CP2 in different pH values irradiated by 254 nm UV lamp. (e) The emission spectra of  $Tb^{3+}$ @Cd-CP2 after immersing in aqueous solutions with different pH values. (f) The photo of  $Tb^{3+}$ @Cd-CP2 in different pH values irradiated by 254 nm UV lamp.



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Fig. S34. (a) PXRD of Eu<sup>3+</sup>@Cd-CP2 after being immersed in the solutions of NANA.
(b) PXRD of Tb<sup>3+</sup>@Cd-CP2 after being immersed in the solutions of NANA.



Fig. S35. (a) UV-vis absorption spectra of various urine chemicals and excitation spectra of  $Eu^{3+}$  (a) Cd-CP2. (b) UV-vis absorption spectra of various urine chemicals and excitation spectra of Tb<sup>3+</sup> (a) Cd-CP2.



Fig. S36. The calculated HOMO and LUMO energy levels of  $H_3L$  and NANA.



Fig. S37. (a) XPS of Eu<sup>3+</sup>@Cd-CP2 before and after immersing in 10<sup>-3</sup> M NANA aqueous solutions. (b) C1s XPS, (c) N1s XPS, (d) O1s XPS, (e) Cd3d XPS, and (f) Eu3d XPS of Eu<sup>3+</sup>@Cd-CP2 before and after immersing in 10<sup>-3</sup> M NANA aqueous solutions.



**Fig. S38.** (a) XPS of **Tb**<sup>3+</sup>**@Cd-CP2** before and after immersing in 10<sup>-3</sup> M NANA aqueous solutions. (b) C1s XPS, (c) N1s XPS, (d) O1s XPS, (e) Cd3d XPS, and (f) Td3d XPS of **Tb**<sup>3+</sup>**@Cd-CP2** before and after immersing in 10<sup>-3</sup> M NANA aqueous solutions.



**Fig. S39.** Simplified schematic diagram of the energy transfer from the ligand to  $Eu^{3+}$  and  $Tb^{3+}$  ions and the mechanism of luminescence quenching.



Fig. S40. (a) The luminescence lifetime decay curves of  $I_{355 \text{ nm}}$  of Eu<sup>3+</sup>@Cd-CP2 and Eu<sup>3+</sup>@Cd-CP2 with NANA. (b) The luminescence lifetime decay curves of  $I_{615 \text{ nm}}$  of Eu<sup>3+</sup>@Cd-CP2 and Eu<sup>3+</sup>@Cd-CP2 with NANA. (c) The luminescence lifetime decay curves of  $I_{355 \text{ nm}}$  of Tb<sup>3+</sup>@Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2 with NANA. (d) The luminescence lifetime decay curves of  $I_{545 \text{ nm}}$  of Tb<sup>3+</sup>@Cd-CP2 and Tb<sup>3+</sup>@Cd-CP2 with NANA. (d) The luminescence lifetime decay curves of  $I_{545 \text{ nm}}$  of Tb<sup>3+</sup>@Cd-CP2 with NANA.



**Fig. S41.** Photos of the mixture of H<sub>3</sub>L, **Cd-CP2** and Eu<sup>3+</sup> or Tb<sup>3+</sup> as well as **Eu<sup>3+</sup>@Cd-CP2** and **Tb<sup>3+</sup>@Cd-CP2** with or without NANA (10<sup>-3</sup> M) under 254 nm UV light.