Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

New Ln-MOFs based on mixed organic ligands: synthesis, structure and efficient luminescence sensing of the Hg^{2+} ion in aqueous solutions

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Table S1 Crystal data and structure refinement for complexes **1**-**4**.

Complex	**1**	**2**	**3**	**4**
Formula	$C_{156}H_{120}Ce_4N_{10}O_{28}S_6$	$C_{156}H_{116}Pr_4N_{10}O_{26}S_6$	$C_{156}H_{120}Eu_4N_{10}O_{28}S_6$	$C_{156}H_{120}Tb_4N_{10}O_{28}S_6$
Fw	3335.45	3302.58	3382.81	3410.65
Cryst system	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a (Å)	11.58490(10)	11.6366(10)	11.49550(10)	11.47990(10)
b (Å)	22.0977(2)	22.1801(3)	22.0977(3)	22.0925(2)
c (Å)	29.3064(3)	29.5908(3)	29.0980(3)	29.0010(3)
α (°)	71.0700(10)	70.7540(10)	108.9420(10)	108.9390(10)
β (°)	89.0760(10)	89.2320(10)	90.1040(10)	90.4640(10)
γ (°)	80.4440(10)	80.4290(10)	98.5400(10)	98.1850(10)
V (Å)^3	6993.10(12)	7103.17(18)	6903.91(14)	6874.58(12)
Z	2	2	2	2
ρ_{calc} (g·cm^{-3})	1.585	1.544	1.624	1.648
μ/mm^{-1}	11.353	11.779	14.315	11.432
F(000)	3358.0	3324.0	3384.0	3412.0
Reflns collected/ independent	135072/27833	79542/28000	82789/27158	131914/27405
GOF	1.054	1.063	1.049	1.106
R indexes(*I*> 2σ(*I*))	R_1 = 0.0356 wR_2 = 0.0964	R_1 = 0.0630 wR_2 = 0.1825	R_1 = 0.0398 wR_2 = 0.1047	R_1 = 0.0455 wR_2 = 0.1246
R indexes （all data）	R_1 = 0.0383 wR_2 = 0.0979	R_1 = 0.0809 wR_2 = 0.1963	R_1 = 0.0454 wR_2 = 0.1077	R_1 = 0.0528 wR_2 = 0.1285

[A]$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [B]$wR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$.

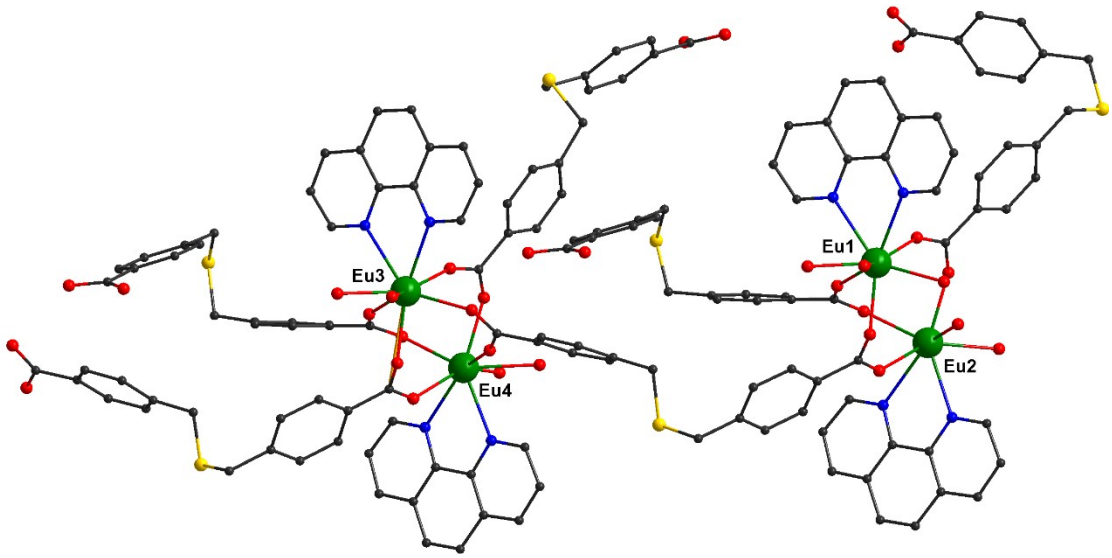

Fig. S1 The coordination environments of Eu^{3+} ions in compound **3**. The hydrogen atoms, free 1,10-phenanthroline and free water molecules were omitted for clarity.

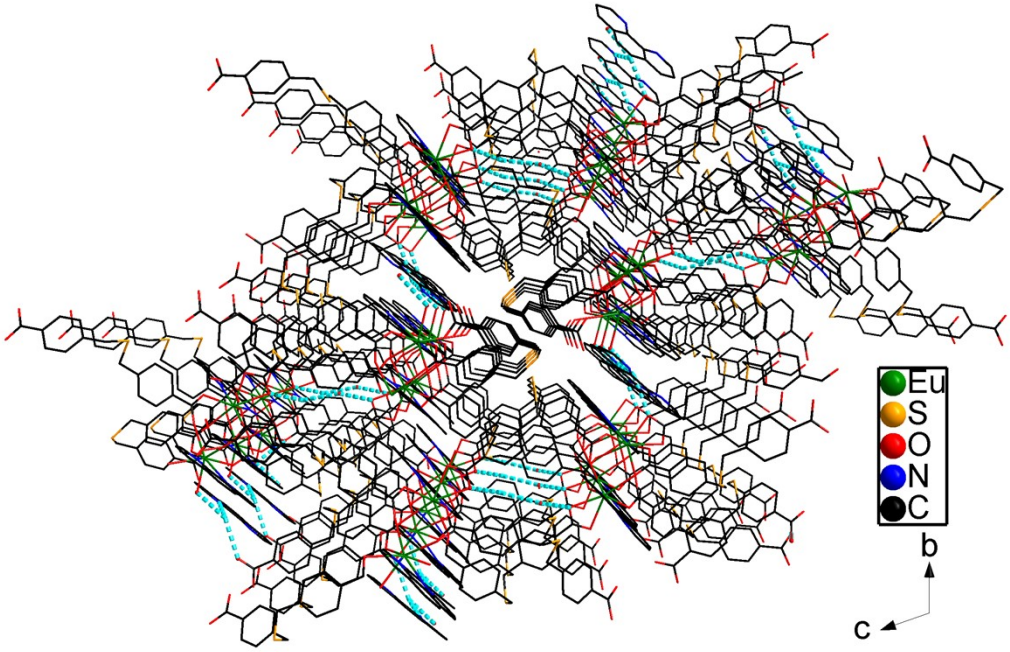

Fig. S2 Hydrogen bonding interactions in **3**.

Table S2 Selected hydrogen bonds for complex **3**.

D-H…A	*d* (D-H)/nm	*d* (H…A)/nm	(D…A)/nm	D-H…A/(°)
O(25)-H(25A)…O(19)	0.085	0.202	0.2854(7)	166
O(25)-H(25B)…O(25)	0.085	0.247	0.3198(9)	144
O(26A)-H(26C)…O(7)	0.085	0.202	0.2860(13)	171
O(26A)-H(26D)…O(26A)	0.085	0.246	0.3049(16)	127
O(27)-H(27A)…N(1)	0.085	0.208	0.2870(5)	154
O(27)-H(27B)…O(13)	0.085	0.201	0.2853(4)	172
O(28)-H(28A)…O(4)	0.085	0.193	0.2737(4)	157
O(28)-H(28B)…O(27)	0.097	0.220	0.2734(4)	113

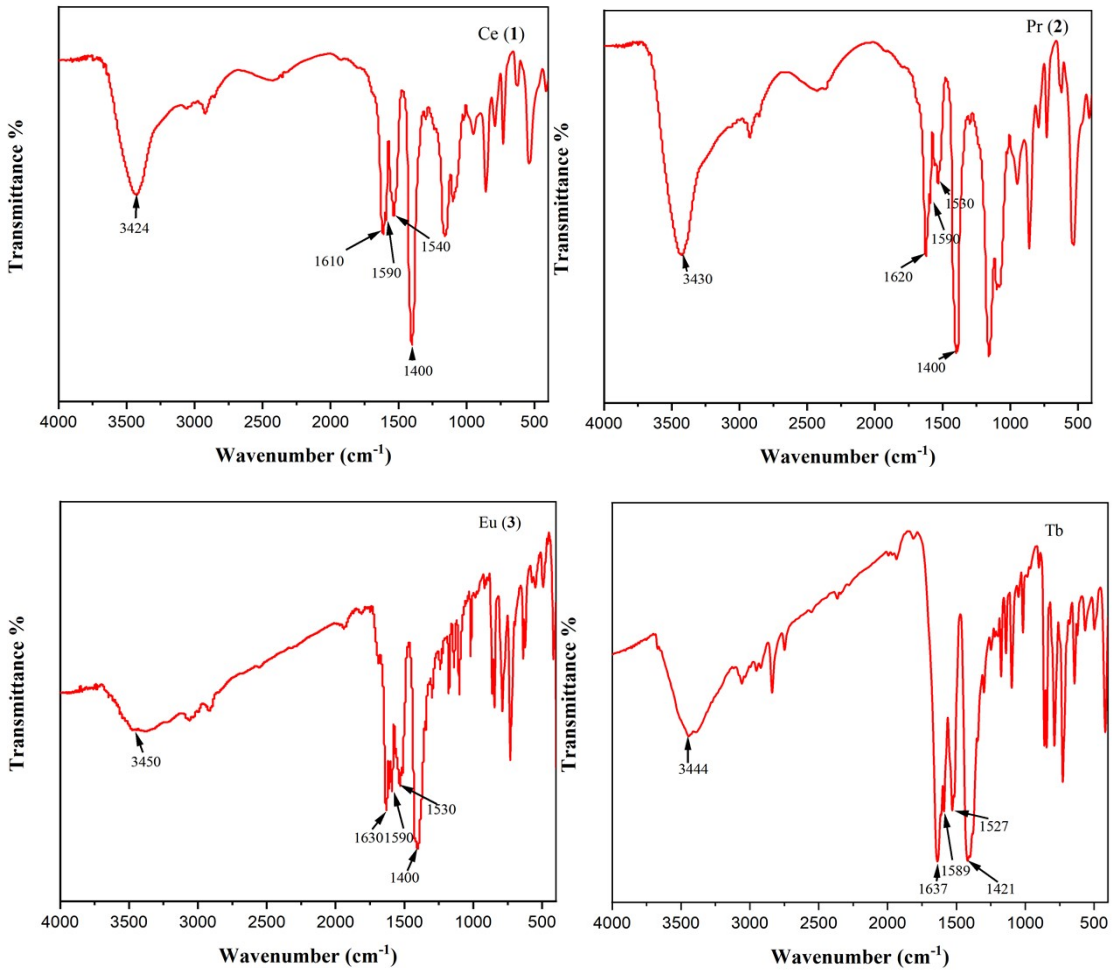

Fig. S3 Infrared spectra of **1-4**.

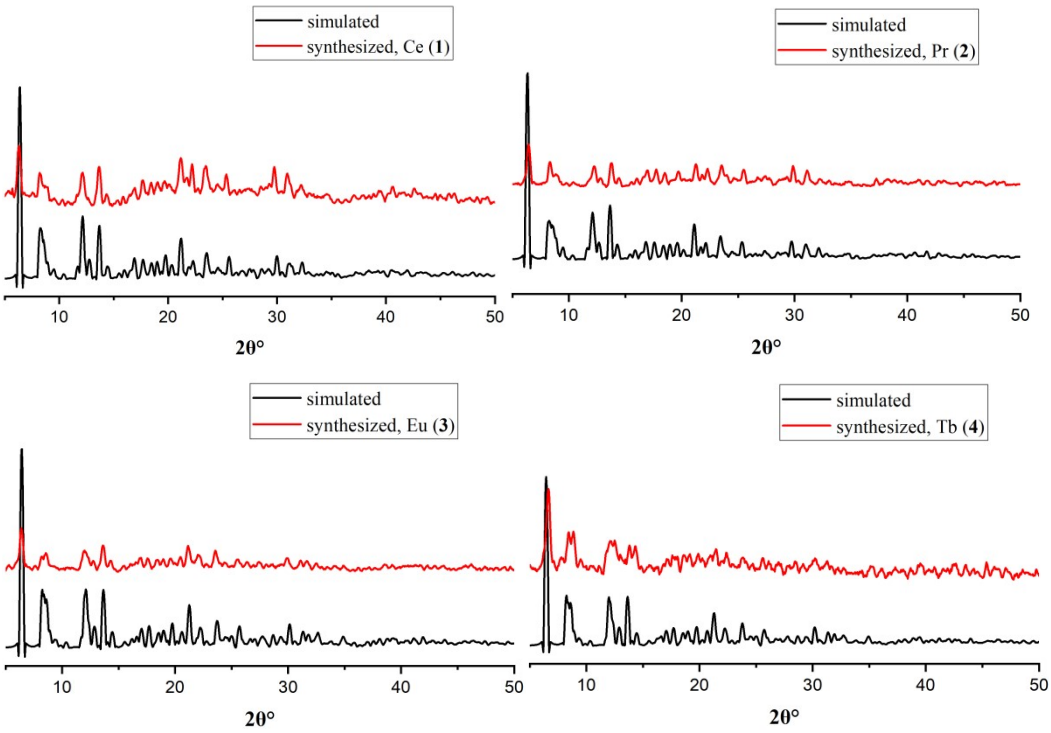

Fig. S4 PXRD patterns of **1-4**.

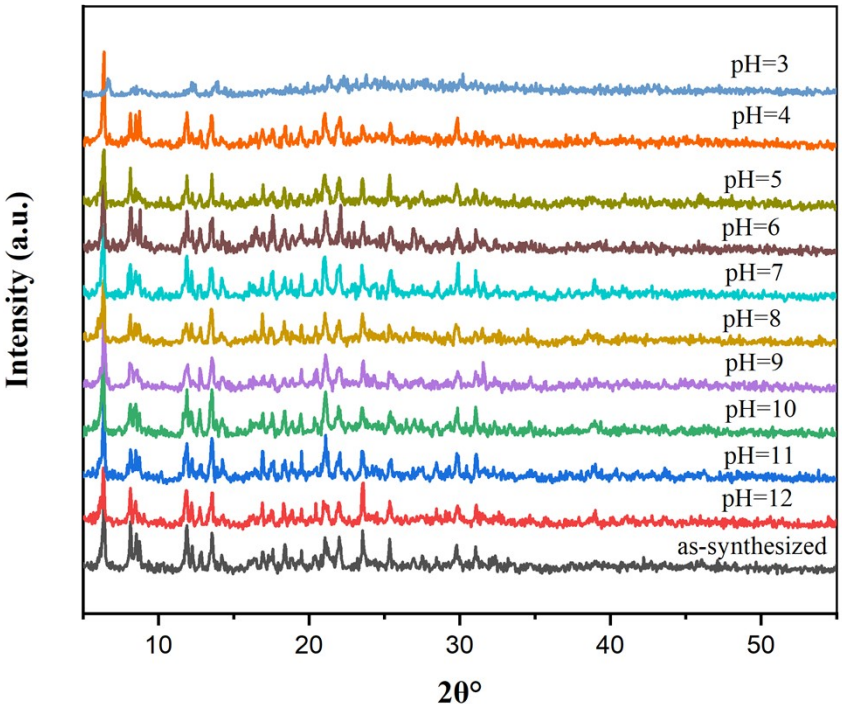

Fig. S5 PXRD patterns of as-synthesized **3** (black line) and **3** soaked in solutions with different pH.

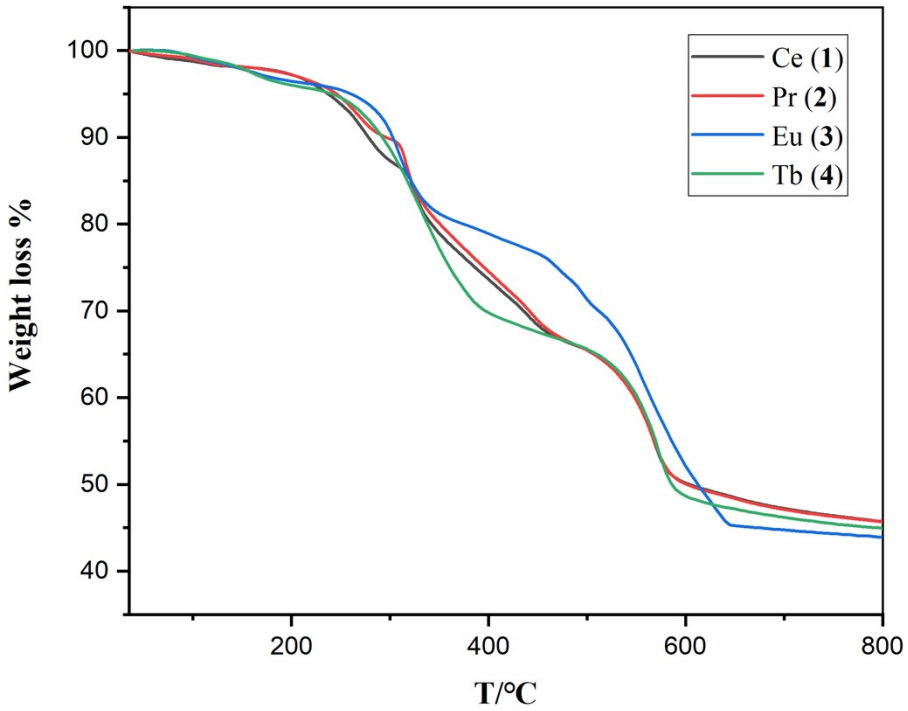

Fig. S6 Thermogravimetric analysis (TGA) curves of coordination polymer **1-4**.

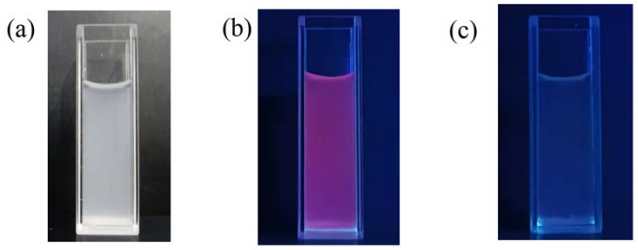

Fig. S7 The photographs of **3** dispersion in water before (a) and after (b) the excitation, (c)the sample soaking in Hg^{2+} solution upon excitation.

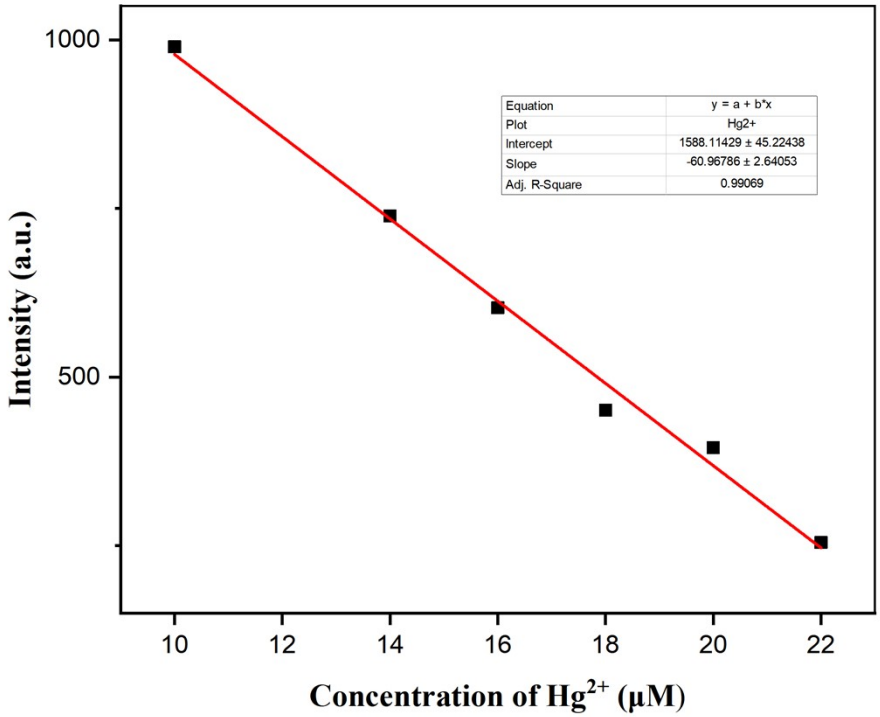

Fig. S8 Linear region of fluorescence intensity of **3** in water upon addition of Hg^{2+} solution.

Table S3 Calculation of Detection Limit.

Blank readings	**Fluorescence Intensity**
1	2035
2	1988
3	2031
4	2015
5	1998
Standard Deviation (σ)	20.38
Slope (m)	60.96786
Detection limit (3σ/m)	1.00 µM

Table S4 Comparison of the sensitivities of **3** with previously reported probes for Hg^{2+} ions.

Probe	**Target ion**	**Detection Limit (µM)**	**Reference**
$[Cd(L)(NTA)]_n$		3.05	15a
$[Ni(L)(NPTA)\cdot H_2O]_n$		2.29	15a

S, N-GQDs	9.14	15b
AuNPs@CNF	0.001	15c
SiO_2-AuNCs	0.004	15d
[Co(NPDC)(bpee)]·DMF·$2H_2O$	4.1	15e
[PCN-221]	0.01	15f
$\{[Eu_4(tmba)_6(phen)_4]\cdot 3(H_2O)(phen)\}_n$	1.00	this work

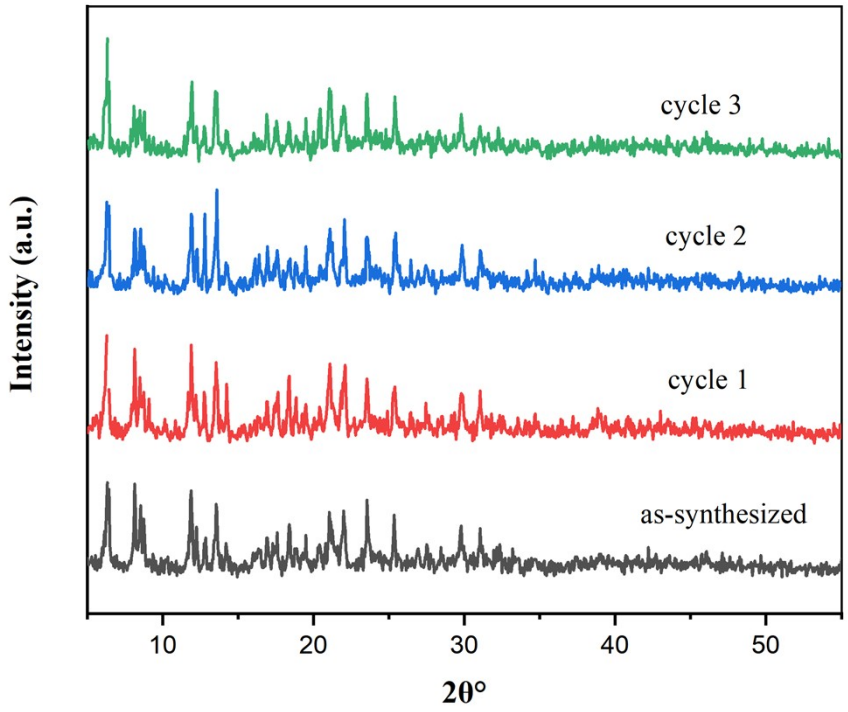

Fig. S9 PXRD patterns of compound **3**, as-synthesized (black line) and after three recycling experiments of soaking into Hg^{2+} solutions.

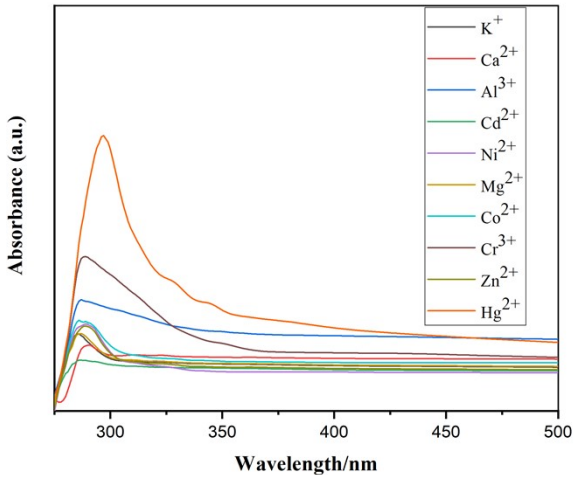

Fig. S10 UV-Vis absorption spectra of different measured ions.

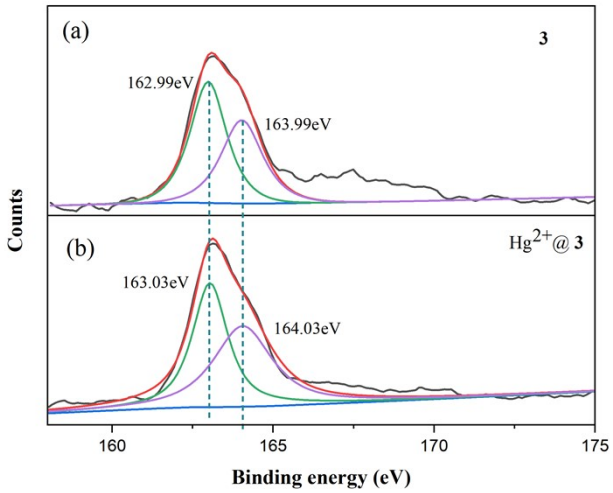

Fig. S11 (a) The XPS spectrum for the S2p region of **3**; (b) The XPS spectrum for the S2p region of **3** after soaking into a Hg^{2+} solution.

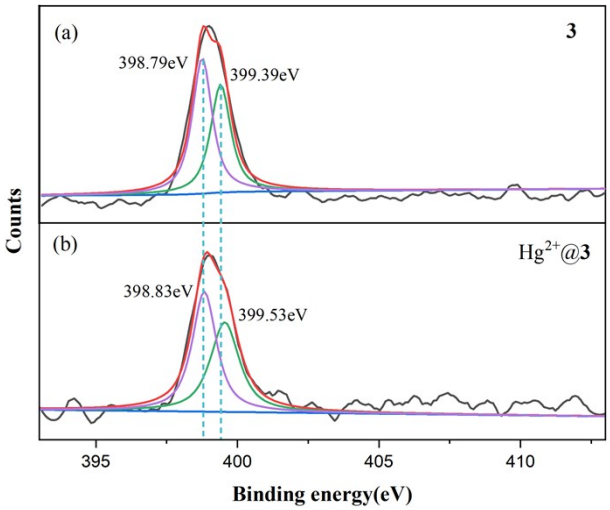

Fig. S12 (a) The XPS spectrum for the N1s region of **3**; (b) The XPS spectrum for the N1s region of **3** after soaking into a Hg^{2+} solution.