Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2021

Supplementary Information

Multifunctional luminescence sensing and white light adjustment of lanthanide metal-organic frameworks constructed from the flexible cyclotriphosphazene-derived hexacarboxylic acid ligand

Meng Wang[a], Hong Wei Gao[b], Jin Xiao Li[a], Feng Ying Bai[a], Yong Heng Xing[a], Zhan Shi[c]*

[a]*College of Chemistry and Chemical Engineering, Liaoning Normal University, Huanghe Road 850#, Dalian, 116029, P. R. China*

[b]*School of Life Science, Ludong University, Hongqi Mid-road 186#, Yantai, 264025, P. R. China*

[c]*State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China*

* *Corresponding authors E-mail address: baifengying2003@163.com (F. Y. Bai)*

Materials and Measurements

All chemicals for the synthesis were obtained commercially and used without further purification. Analyses of C, H and N were carried out on a Perkin-Elmer 240C automatic analyzer. The power X-ray diffraction (PXRD) measurements were recorded with a Bruker Advance-D8 equipped by using Cu-Kα radiation in the range of 5° < 2θ < 50° in 0.02° steps at 2 s per step. Thermogravimetric analyses (TG) were performed by a Perkin Elmer Diamond TG/DTA in a N_2 atmosphere at a heating rate of 10 °C min^{-1}. The N_2 adsorption measurements were conducted using a Autosorb-IQ-XR. The contents of Eu^{3+} and Tb^{3+} ions in the mixed Ln-MOFs materials were determined by a Prodigy XP inductively coupled plasma atomic emission spectroscopy (ICP-AES). IR spectra (KBr pellets) were recorded in the range of 400-4000 cm^{-1} with a Bruker AXS TENSOR-27 FT-IR spectrometer. UV-vis absorption spectra of solid samples were collected on a JASCO V-570 spectrophotometer and Lambda 35 spectrometer was applied to record the UV-vis absorption spectra of suspension samples and detectors solutions in 200-800 nm. The fluorescence spectra of the compounds were measured on a HORIBA Fluoromax-4-TCSPC spectrofluorometer equipped with Pulsed LED sources (200-1000 nm) at room temperature. The morphological characteristics of the compounds before and after adding detectors were studied by Scanning Electron Microscope (SEM, SU8010).

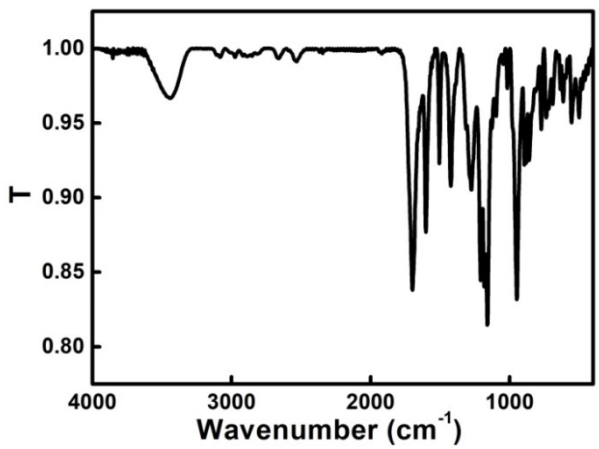


Figure S1 The IR spectrum of the HCPCP ligand

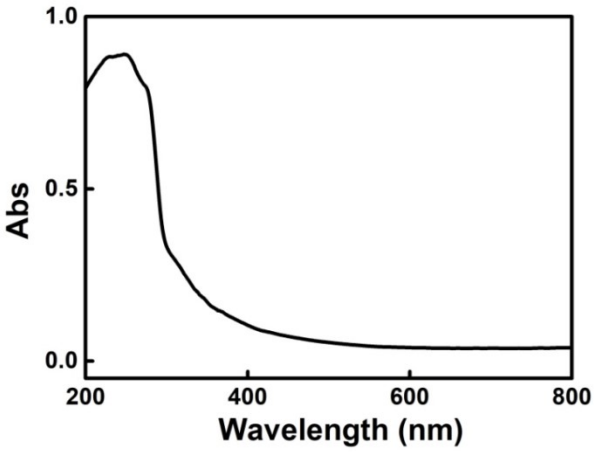


Figure S2 The UV-vis spectrum of the HCPCP ligand

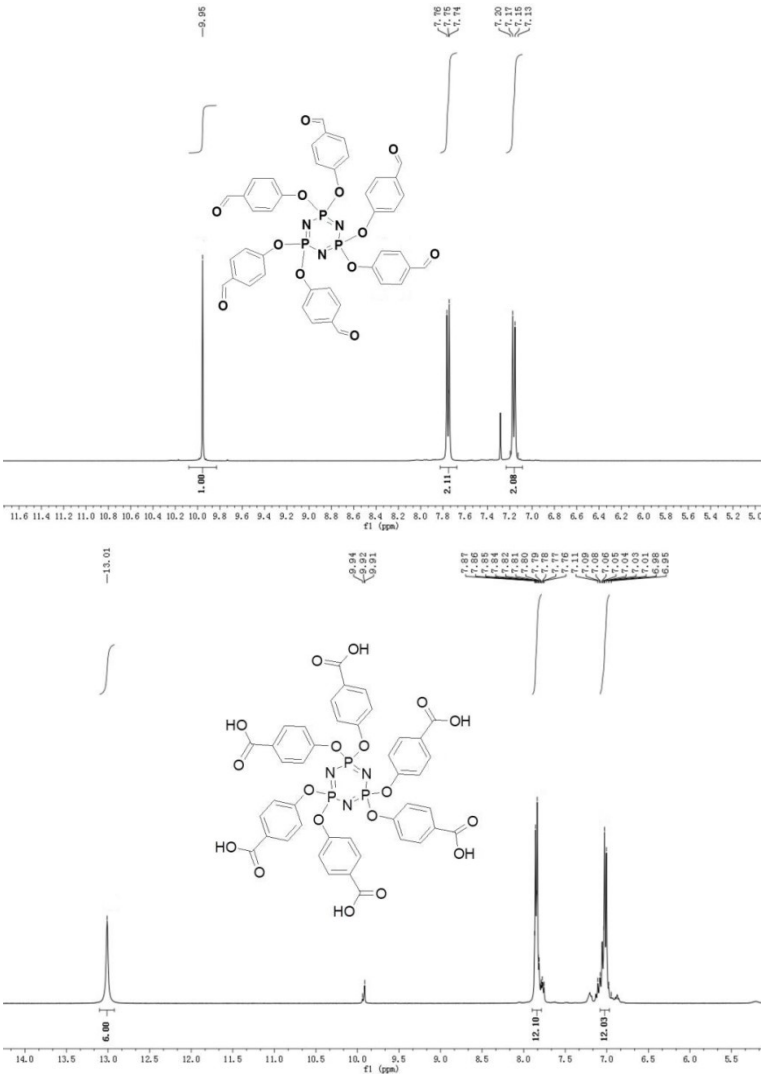


Figure S3 ^{1}H NMR spectra of HAPCP and HCPCP ligand

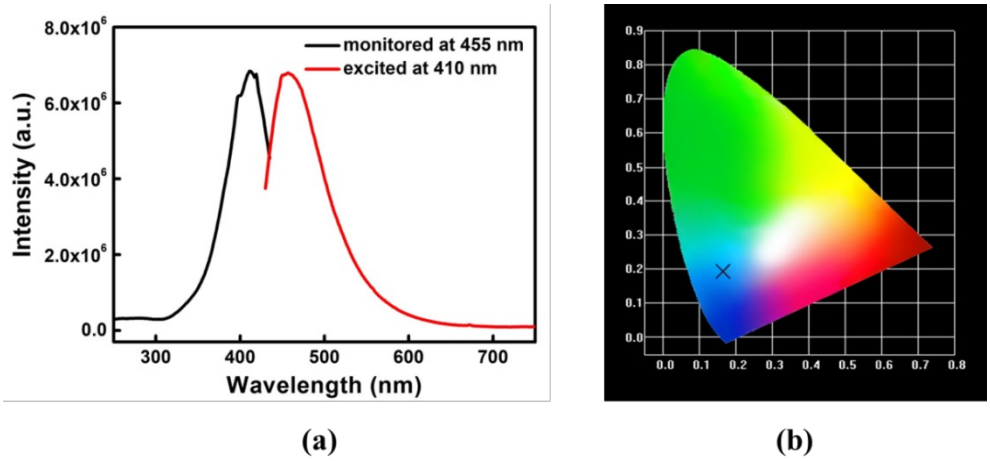


Figure S4 (a) The excitation spectrum and emission spectrum of the HCPCP ligand; (b) CIE-1931 chromaticity diagrams of the HCPCP ligand

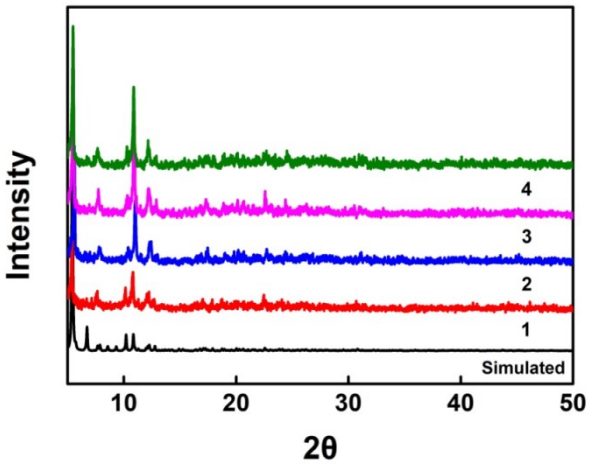


Figure S5 PXRD patterns of compounds **1-4**

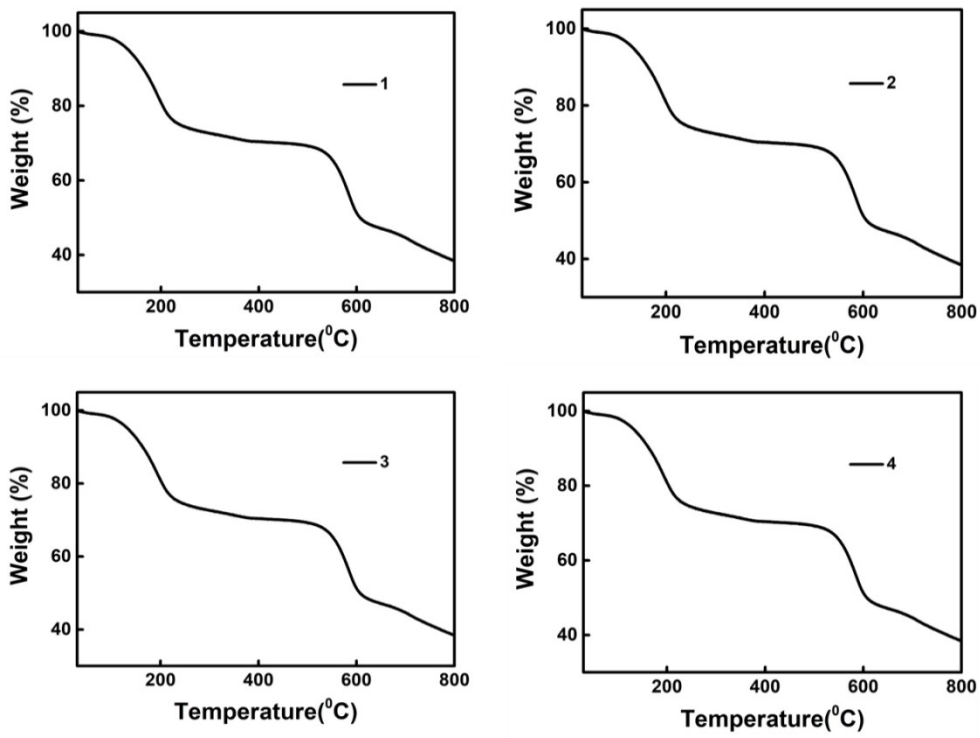


Figure S6 The TG curves of compounds **1-4**

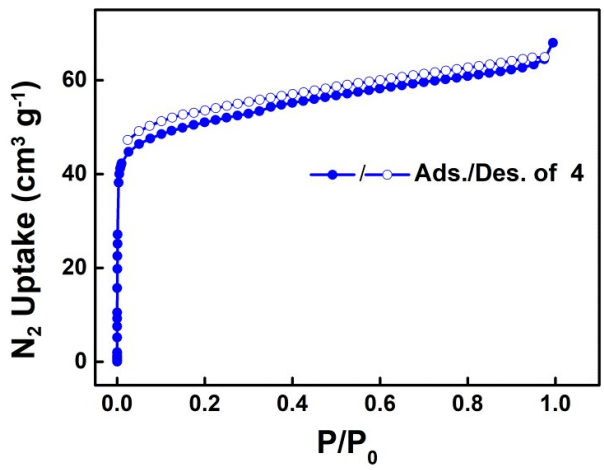


Figure S7 N_2 adsorption and desorption isotherms of compound **4** at 77 K

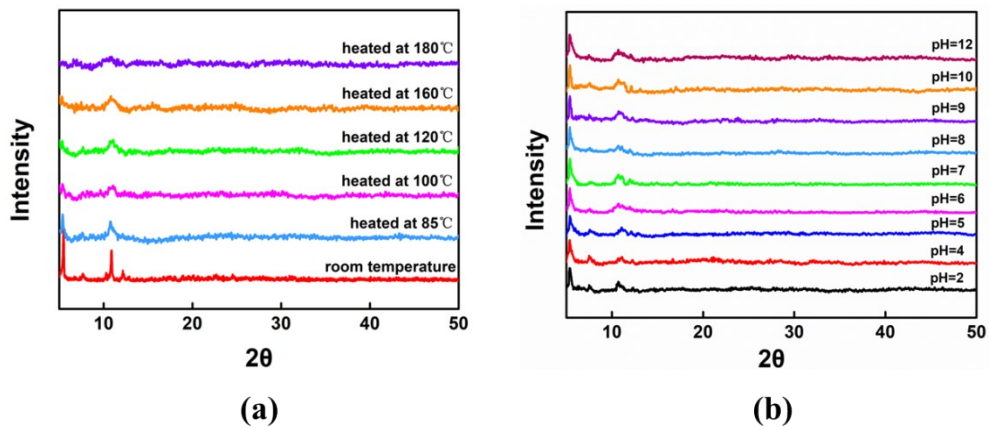


Figure S8 PXRD patterns of compound **4** at different temperatures (a) and pH values (b)

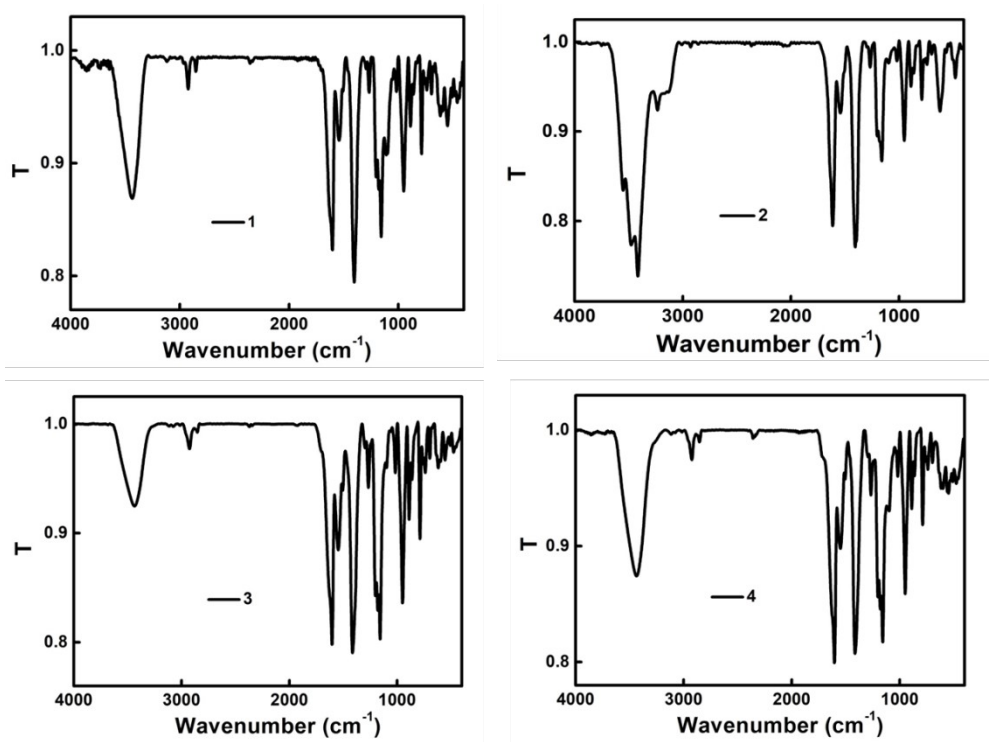


Figure S9 The IR spectra of compounds **1-4**

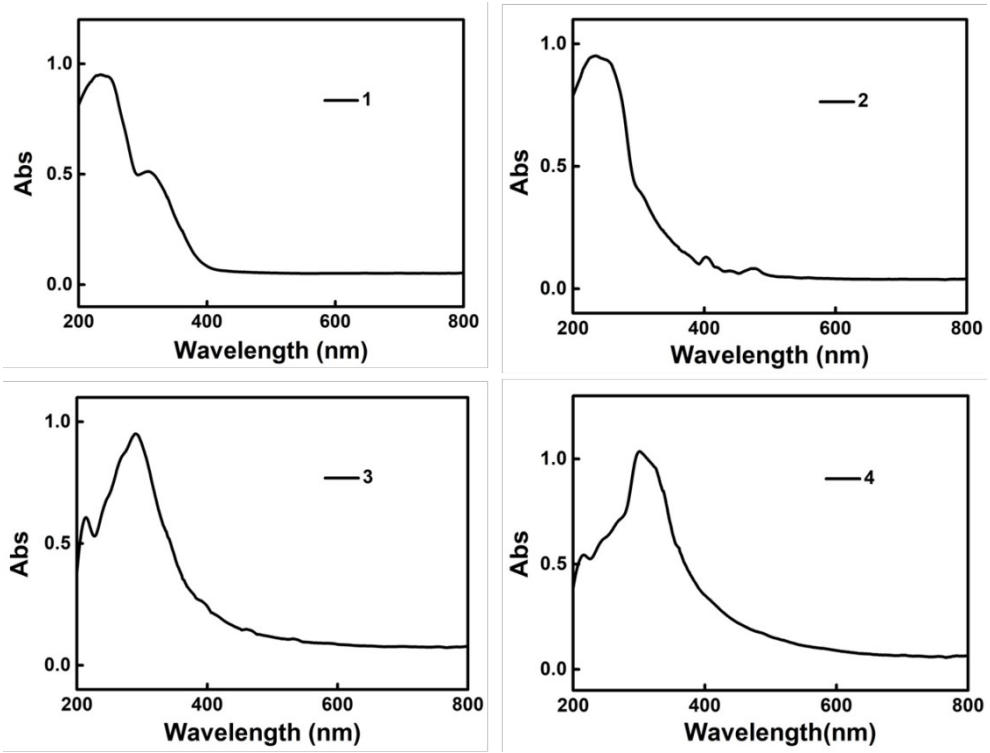


Figure S10 The UV-Vis absorption spectra of compounds **1-4**

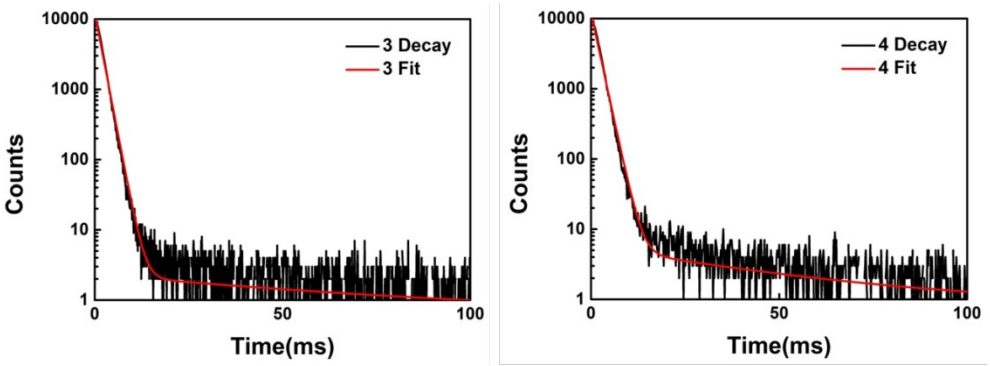


Figure S11 Lifetime decay curves of compounds **3** and **4**

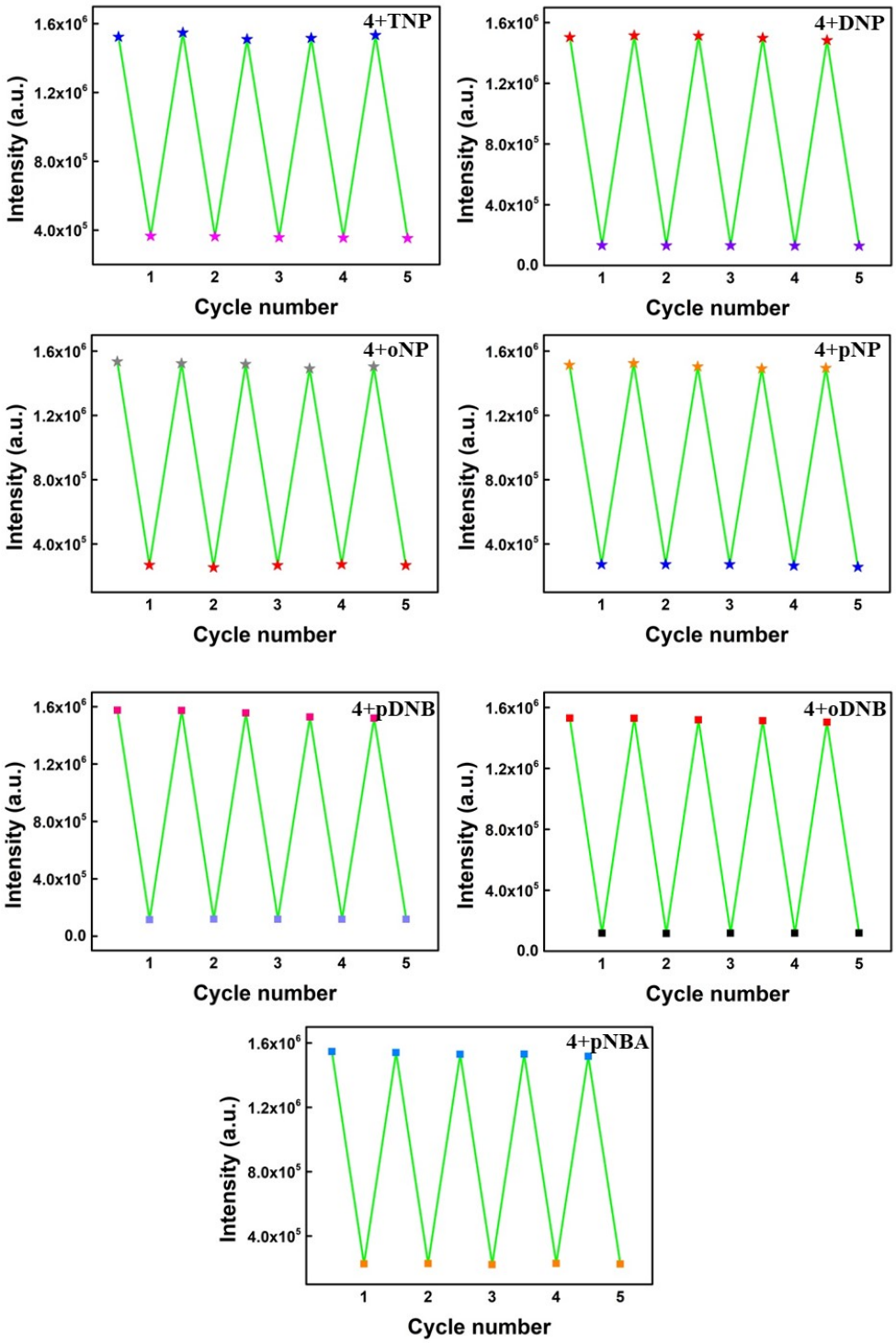


Figure S12 Recyclability tests of detecting seven kinds of NACs

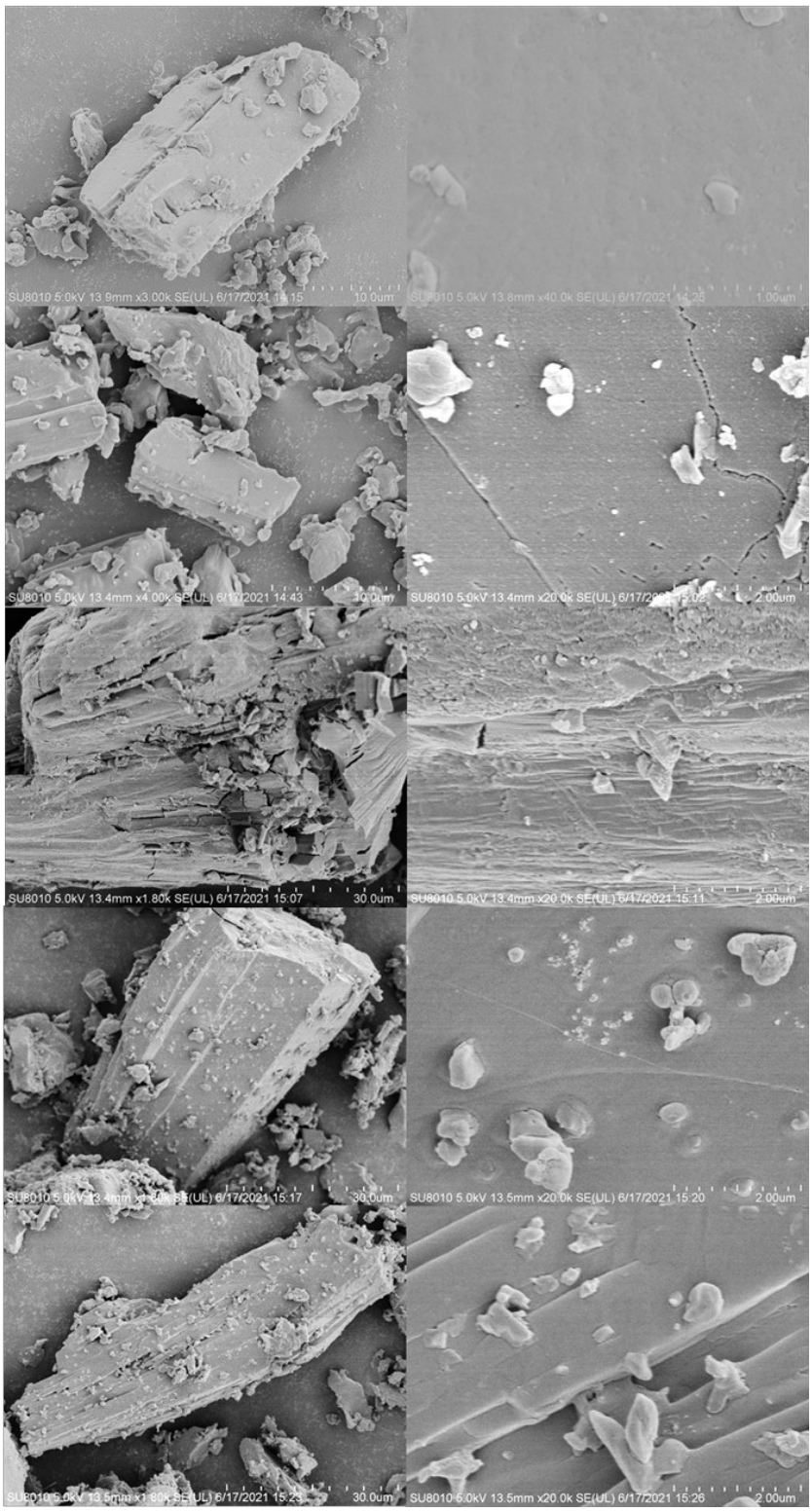
(a)

(b)

(c)

(d)

(e)


SU8010 5.0kV 13.9mm x3.00k SE(UL) 6/17/2021 14:15 10.0um
SU8010 5.0kV 13.8mm x40.0k SE(UL) 6/17/2021 14:25 1.00um
SU8010 5.0kV 13.4mm x4.00k SE(UL) 6/17/2021 14:43 30.0um
SU8010 5.0kV 13.4mm x20.0k SE(UL) 6/17/2021 15:02 2.00um
SU8010 5.0kV 13.4mm x1.80k SE(UL) 6/17/2021 15:07 30.0um
SU8010 5.0kV 13.4mm x20.0k SE(UL) 6/17/2021 15:11 2.00um
SU8010 5.0kV 13.4mm x1.80k SE(UL) 6/17/2021 15:17 30.0um
SU8010 5.0kV 13.5mm x20.0k SE(UL) 6/17/2021 15:20 2.00um
SU8010 5.0kV 13.5mm x1.80k SE(UL) 6/17/2021 15:23 30.0um
SU8010 5.0kV 13.5mm x20.0k SE(UL) 6/17/2021 15:26 2.00um

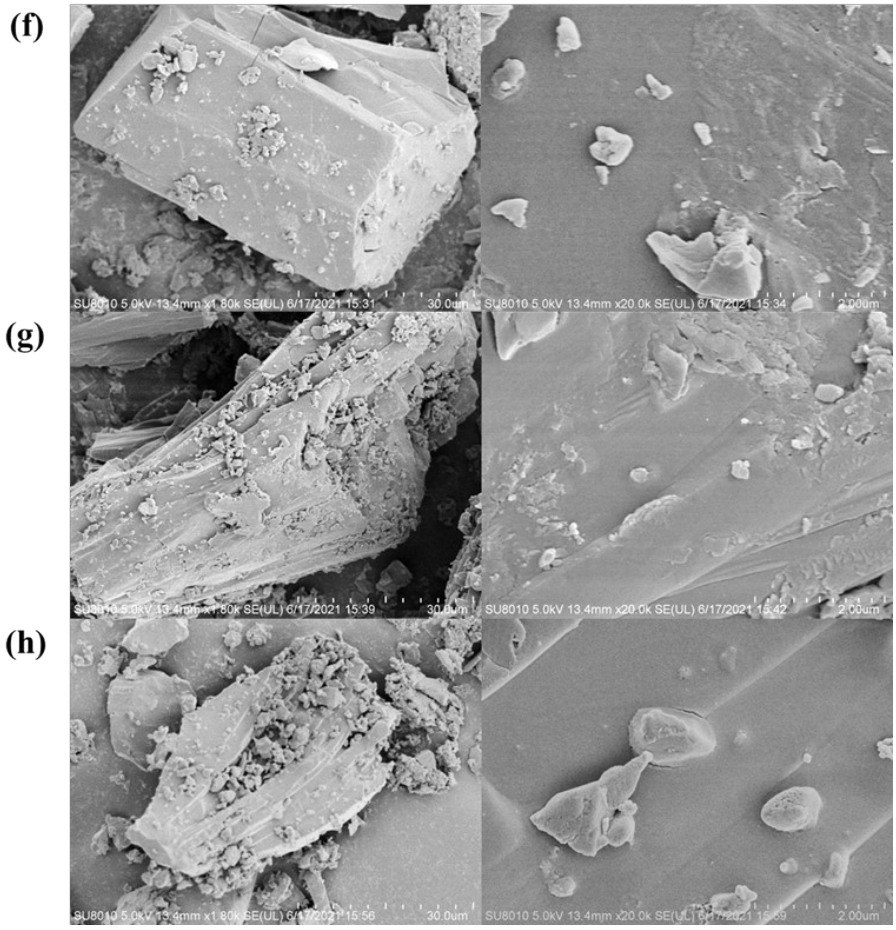


Figure S13 The SEM images of compound **4** before and after detecting different NACs: (a) **4**; (b) **4**+TNP; (c) **4**+DNP; (d) **4**+oNP; (e) **4**+pNP; (f) **4**+pDNB; (g) **4**+oDNB; (h) **4**+pNBA

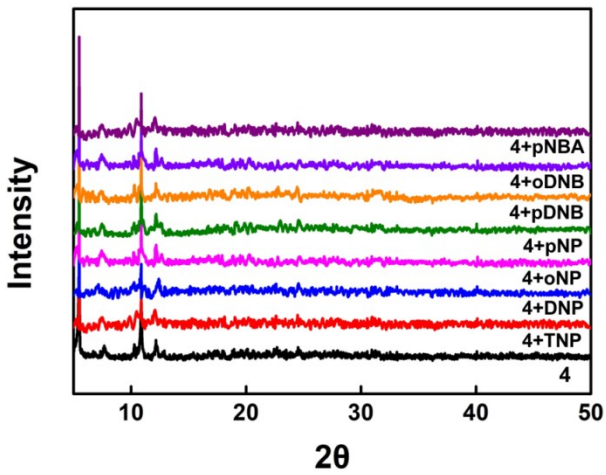


Figure S14 PXRD patterns of compound **4** before and after the addition of different NACs

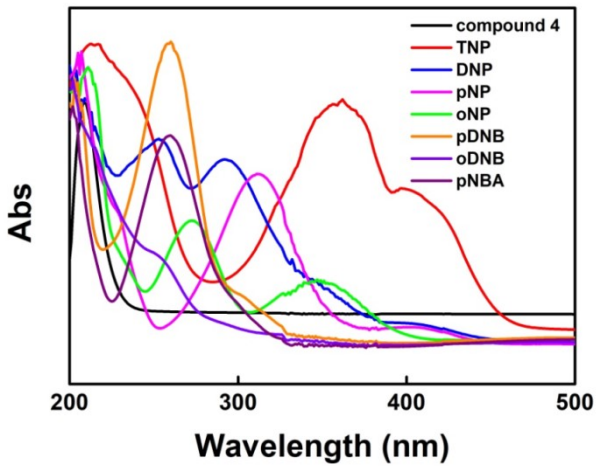


Figure S15 The UV-Vis absorption spectra of compound **4** suspension and NACs solutions

Table S1 ICP analysis data of x%Eu^{3+}@**4**

	Eu^{3+} (wt%)	Tb^{3+} (wt%)	Eu^{3+}/Tb^{3+} molar ratio	original Eu^{3+}/Tb^{3+} molar ratio
0.5%Eu^{3+}@**4**	0.094	18.742	1:190.64	0.005:0.995=1:199
2.5%Eu^{3+}@**4**	0.452	18.513	1:39.16	0.025:0.975=1:39
5%Eu^{3+}@**4**	0.913	17.957	1:18.81	0.05:0.95=1:19
7.5%Eu^{3+}@**4**	1.377	17.549	1:12.19	0.075:0.925=1:12.3
10%Eu^{3+}@**4**	1.923	17.024	1:8.46	0.1:0.9=1:9
15%Eu^{3+}@**4**	2.837	16.641	1:5.61	0.15:0.85=1:5.67
20%Eu^{3+}@**4**	3.672	15.116	1:3.94	0.2:0.8=1:4

Table S2 Single crystal structure data for compounds **1-3**

Compounds	**1**	**2**	**3**
Formula	$C_{91}H_{101}N_{11.5}O_{35}P_{4.5}Ce_3$	$C_{91}H_{101}N_{11.5}O_{35}P_{4.5}Sm_3$	$C_{91}H_{101}N_{11.5}O_{35}P_{4.5}Eu_3$
M (g mol^{-1})	2475.59	2506.32	2511.13
Crystal system	*Tetragonal*	*Tetragonal*	*Tetragonal*
Space group	*P*4(1)2(1)2	*P*4(1)2(1)2	*P*4(1)2(1)2
a (Å)	23.0481	23.0966	23.1017
b (Å)	23.0481	23.0966	23.1017
c (Å)	47.9933	47.2483	47.0681
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å^3)	25494	25204	25119
Z	8	8	8
D_{calc} (g cm^{-3})	0.994	1.021	1.027
F(000)	7472	7568	7592
μ (Mo-Kα)/mm^{-1}	1.159	1.487	1.588
2θ (°)	4.596-50.728	4.658-51.484	4.672-51.676
Reflections collected	115694	115694	115657
Independent reflections(I>2σ(I))	23323(17677)	23323(17677)	23319(17673)
Parameters	960	960	957
$\Delta(\rho)$ (e Å^{-3})	-31.15 and -0.61	-31.30 and -0.81	-31.33 and -0.85
Goodness of fit	1.026	1.022	1.014
Flack	-0.004(6)	0.071(5)	0.088(5)
R^a	0.0430(0.0675)^b	0.0464(0.0707)^b	0.0474(0.0716)^b
wR_2^a	0.1020(0.1135)^b	0.1158(0.1285)^b	0.1183(0.1317)^b

$^a R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$, $wR_2=[\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$; [$Fo$>4σ($Fo$)]. ^{b}Based on all data.

Table S3 Selected bond distances (Å) of compounds **1-3**

		1			
Ce(1)-O(13)	2.387(8)	Ce(1)-O(26)	2.431(6)	Ce(1)-O(7)	2.709(6)
Ce(1)-O(12)	2.441(5)	Ce(1)-O(16)	2.685(5)	Ce(1)-O(25)	2.614(6)
Ce(1)-O(24)	2.622(4)	Ce(1)-O(15)	2.543(6)	Ce(1)-O(8)	2.480(6)
Ce(2)-O(17)	2.405(6)	Ce(2)-O(23)	2.381(6)	Ce(2)-O(26)	2.644(5)
Ce(2)-O(12)	2.700(5)	Ce(2)-O(24)	2.503(6)	Ce(2)-O(11)	2.549(7)
Ce(2)-O(9)	2.400(6)	Ce(2)-O(27)	2.646(9)	Ce(3)-O(10)	2.394(6)
Ce(3)-O(7)$^{\#1}$	2.573(6)	Ce(3)-O(16)$^{\#1}$	2.460(5)	Ce(3)-O(14)	2.392(7)
Ce(3)-O(22)	2.392(6)	Ce(3)-O(29)	2.637(8)	Ce(3)-O(28)	2.591(8)
Ce(3)-O(18)	2.342(6)				
		2			
Sm(1)-O(13)	2.394(8)	Sm(1)-O(26)	2.428(6)	Sm(1)-O(7)	2.675(6)
Sm(1)-O(12)	2.425(6)	Sm(1)-O(16)	2.671(6)	Sm(1)-O(25)	2.609(7)
Sm(1)-O(24)	2.586(5)	Sm(1)-O(15)	2.543(6)	Sm(1)-O(8)	2.463(7)
Sm(2)-O(17)	2.406(7)	Sm(2)-O(23)	2.356(6)	Sm(2)-O(26)	2.610(6)
Sm(2)-O(12)	2.685(6)	Sm(2)-O(24)	2.491(6)	Sm(2)-O(11)	2.556(8)
Sm(2)-O(9)	2.383(6)	Sm(2)-O(27)	2.640(10)	Sm(3)-O(10)	2.386(7)
Sm(3)-O(7)$^{\#1}$	2.576(7)	Sm(3)-O(16)$^{\#1}$	2.440(6)	Sm(3)-O(14)	2.379(8)
Sm(3)-O(22)	2.388(7)	Sm(3)-O(29)	2.621(9)	Sm(3)-O(28)	2.601(9)
Sm(3)-O(18)	2.322(7)				
		3			
Eu(1)-O(13)	2.391(8)	Eu(1)-O(26)	2.426(6)	Eu(1)-O(7)	2.668(6)
Eu(1)-O(12)	2.420(6)	Eu(1)-O(16)	2.669(6)	Eu(1)-O(25)	2.607(7)
Eu(1)-O(24)	2.576(5)	Eu(1)-O(15)	2.543(6)	Eu(1)-O(8)	2.459(7)
Eu(2)-O(17)	2.403(7)	Eu(2)-O(23)	2.349(6)	Eu(2)-O(26)	2.604(6)
Eu(2)-O(12)	2.681(6)	Eu(2)-O(24)	2.487(7)	Eu(2)-O(11)	2.556(8)
Eu(2)-O(9)	2.375(6)	Eu(2)-O(27)	2.634(10)	Eu(3)-O(10)	2.380(7)
Eu(3)-O(7)$^{\#1}$	2.575(7)	Eu(3)-O(16)$^{\#1}$	2.434(6)	Eu(3)-O(14)	2.369(8)
Eu(3)-O(22)	2.386(7)	Eu(3)-O(29)	2.615(9)	Eu(3)-O(28)	2.605(9)
Eu(3)-O(18)	2.316(7)				

*Symmetry transformations used to generate equivalent atoms: #1: -3/2-x, -1/2+y, -1/4+z.

Table S4 Selected bond angles(°) of compounds **1-3**

		1			
O(13)-Ce(1)-O(26)	148.2(2)	O(13)-Ce(1)-O(15)	126.7(3)	O(13)-Ce(1)-O(8)	121.3(3)
O(26)-Ce(1)-O(7)	129.4(2)	O(26)-Ce(1)-O(16)	121.7(2)	O(12)-Ce(1)-O(7)	148.45(18)
O(12)-Ce(1)-O(25)	113.36(17)	O(12)-Ce(1)-O(8)	152.4(2)	O(25)-Ce(1)-O(16)	151.0(2)
O(24)-Ce(1)-O(7)	138.89(19)	O(24)-Ce(1)-O(16)	142.30(18)	O(15)-Ce(1)-O(25)	154.1(2)
O(15)-Ce(1)-O(24)	129.84(18)	O(8)-Ce(1)-O(24)	118.5(2)	O(17)-Ce(2)-O(26)	136.78(19)
O(17)-Ce(2)-O(27)	147.0(3)	O(23)-Ce(2)-O(26)	128.7(2)	O(23)-Ce(2)-O(12)	135.8(3)
O(23)-Ce(2)-O(11)	142.1(2)	O(23)-Ce(2)-O(27)	129.4(3)	O(24)-Ce(2)-O(11)	110.2(2)
O(24)-Ce(2)-O(27)	115.5(2)	O(9)-Ce(2)-O(26)	121.9(2)	O(9)-Ce(2)-O(12)	127.0(2)
O(9)-Ce(2)-O(24)	167.89(19)	O(10)-Ce(3)-O(7)$^{\#1}$	151.3(3)	O(10)-Ce(3)-O(14)	138.4(3)
O(7)$^{\#1}$-Ce(3)-O(29)	125.7(3)	O(7)$^{\#1}$-Ce(3)-O(28)	138.6(3)	O(16)$^{\#1}$-Ce(3)-O(28)	122.4(3)
O(22)-Ce(3)-O(14)	141.9(3)	O(22)-Ce(3)-O(29)	133.3(3)	O(22)-Ce(3)-O(28)	145.5(3)
		2			
O(13)-Sm(1)-O(26)	148.6(2)	O(13)-Sm(1)-O(15)	126.8(3)	O(13)-Sm(1)-O(8)	121.4(3)
O(26)-Sm(1)-O(7)	129.1(2)	O(26)-Sm(1)-O(16)	121.4(2)	O(12)-Sm(1)-O(7)	148.2(2)
O(12)-Sm(1)-O(25)	114.41(19)	O(12)-Sm(1)-O(8)	152.2(3)	O(25)-Sm(1)-O(16)	151.0(2)
O(24)-Sm(1)-O(7)	138.2(2)	O(24)-Sm(1)-O(16)	142.0(2)	O(15)-Sm(1)-O(25)	154.1(3)
O(15)-Sm(1)-O(24)	129.7(2)	O(8)-Sm(1)-O(24)	117.7(2)	O(17)-Sm(2)-O(26)	137.0(2)
O(17)-Sm(2)-O(27)	147.1(3)	O(23)-Sm(2)-O(26)	128.1(2)	O(23)-Sm(2)-O(12)	135.4(3)
O(23)-Sm(2)-O(11)	142.5(3)	O(23)-Sm(2)-O(27)	129.2(3)	O(24)-Sm(2)-O(11)	110.3(2)
O(24)-Sm(2)-O(27)	115.9(3)	O(9)-Sm(2)-O(26)	121.2(2)	O(9)-Sm(2)-O(12)	126.6(3)
O(9)-Sm(2)-O(24)	168.0(2)	O(10)-Sm(3)-O(7)$^{\#1}$	151.3(3)	O(10)-Sm(3)-O(14)	138.3(3)
O(7)$^{\#1}$-Sm(3)-O(29)	126.6(3)	O(7)$^{\#1}$-Sm(3)-O(28)	138.4(3)	O(16)$^{\#1}$-Sm(3)-O(28)	122.5(3)
O(22)-Sm(3)-O(14)	141.6(3)	O(22)-Sm(3)-O(29)	133.2(3)	O(22)-Sm(3)-O(28)	146.1(3)
		3			
O(13)-Eu(1)-O(26)	148.5(2)	O(13)-Eu(1)-O(15)	127.0(3)	O(13)-Eu(1)-O(8)	121.6(3)
O(26)-Eu(1)-O(7)	129.0(2)	O(26)-Eu(1)-O(16)	121.2(2)	O(12)-Eu(1)-O(7)	148.1(2)
O(12)-Eu(1)-O(25)	114.71(19)	O(12)-Eu(1)-O(8)	152.1(3)	O(25)-Eu(1)-O(16)	150.9(2)
O(24)-Eu(1)-O(7)	138.1(2)	O(24)-Eu(1)-O(16)	141.9(2)	O(15)-Eu(1)-O(25)	154.2(3)
O(15)-Eu(1)-O(24)	129.6(2)	O(8)-Eu(1)-O(24)	117.5(2)	O(17)-Eu(2)-O(26)	137.0(2)
O(17)-Eu(2)-O(27)	147.0(3)	O(23)-Eu(2)-O(26)	127.9(2)	O(23)-Eu(2)-O(12)	135.3(3)
O(23)-Eu(2)-O(11)	142.5(3)	O(23)-Eu(2)-O(27)	128.9(3)	O(24)-Eu(2)-O(11)	110.3(2)
O(24)-Eu(2)-O(27)	116.2(3)	O(9)-Eu(2)-O(26)	120.9(2)	O(9)-Eu(2)-O(12)	126.6(3)
O(9)-Eu(2)-O(24)	168.1(2)	O(10)-Eu(3)-O(7)$^{\#1}$	151.4(3)	O(10)-Eu(3)-O(14)	138.0(3)
O(7)$^{\#1}$-Eu(3)-O(29)	127.1(3)	O(7)$^{\#1}$-Eu(3)-O(28)	138.4(3)	O(16)$^{\#1}$-Eu(3)-O(28)	122.2(3)
O(22)-Eu(3)-O(14)	141.6(3)	O(22)-Eu(3)-O(29)	133.3(4)	O(22)-Eu(3)-O(28)	146.5(3)

Table S5 IR data (cm^{-1}) for the HCPCP ligand and compounds **1-4**

	ν_{O-H}	$\nu_{as\ (COO)^-}$	$\nu_{C=C}$	$\nu_{s\ (COO)^-}$	$\nu_{P=N}$	ν_{Ar-O-P}	ν_{P-N}
HCPCP	3619-3295	1704	1574	1501	1073-1331	947	782
1	3317-3635	1603	1549	1405	1078-1316	952	789
2	3280-3662	1618	1539	1402	1076-1314	952	786
3	3286-3638	1614	1545	1408	1076-1310	954	787
4	3274-3655	1611	1543	1408	1073-1318	951	790

Table S6 UV-vis spectra identication of HCPCP ligand and compounds **1-4**

	λ/nm	λ/nm	λ/nm
HCPCP	250(π→π*, HCPCP)	315(n→π*, HCPCP)	—
1	236(π→π*, HCPCP)	307(n→π*, HCPCP)	—
2	242(π→π*, HCPCP)	302(n→π*, HCPCP)	403($^6H_{5/2}$→$^6P_{3/2}$)
	475($^6H_{5/2}$→$^4I_{11/2}$)	_	_
3	214(π→π*, HCPCP)	290(n→π*, HCPCP)	_
4	219(π→π*, HCPCP)	300(n→π*, HCPCP)	_

Table S7 CIE coordinates, quantum yields and the correlated color temperatures (CCT) of 0.5%Eu^{3+}@**4** at different excitation wavelengths

0.5%Eu^{3+}@**4**			
Ex/nm	CIE coordinate	quality yield	CCT/K
320	(0.2854,0.397)	2.28%	7204.223
330	(0.2824,0.3766)	2.3%	7543.8
340	(0.2813,0.3598)	3.13%	7823.955
350	(0.2765,0.341)	4.12%	8440.267
360	(0.2388,0.271)	5.19%	17870.42
370	(0.2448,0.2792)	5.89%	15388.96
380	(0.2257,0.2467)	6.41%	30735.59
390	(0.1935,0.206)	7.20%	362495.3

Table S8 CIE coordinates, quantum yields and the correlated color temperatures (CCT) of 2.5%Eu^{3+}@**4** at different excitation wavelengths

2.5%Eu^{3+}@**4**			
Ex/nm	CIE coordinate	quality yield	CCT/K
320	(0.2885,0.3835)	1.30%	7199.019
330	(0.2866,0.3793)	1.47%	7323.601
340	(0.2768,0.3514)	2.34%	8210.296
350	(0.2743,0.3054)	2.77%	9699.76
360	(0.2351,0.2475)	3.27%	26819.66
370	(0.2446,0.2531)	3.42%	21418.47
380	(0.2268,0.2309)	4.13%	46590.22
390	(0.1946,0.2035)	6.78%	479958.5

Table S9 CIE coordinates, quantum yields and the correlated color temperatures (CCT) of 5%Eu^{3+}@**4** at different excitation wavelengths

5%Eu^{3+}@**4**			
Ex/nm	CIE coordinate	quality yield	CCT/K
320	(0.3276,0.3625)	1.08%	5689.338
330	(0.3178,0.3419)	1.44%	6168.525
340	(0.3174,0.3248)	1.63%	6274.735
350	(0.3174,0.3098)	1.88%	6371.93
360	(0.2692,0.2545)	2.02%	15104.2
370	(0.2751,0.2585)	2.56%	13278.79
380	(0.2522,0.2341)	3.92%	28603.4
390	(0.2048,0.2017)	4.47%	514373

Table S10 CIE coordinates, quantum yields and the correlated color temperatures (CCT) of 7.5%Eu^{3+}@**4** at different excitation wavelengths

7.5%Eu^{3+}@**4**			
Ex/nm	CIE coordinate	quality yield	CCT/K
320	(0.3349,0.3612)	0.54%	5405.041
330	(0.3264,0.341)	0.69%	5768.188
340	(0.3268,0.3212)	1.03%	5784.679
350	(0.3243,0.302)	1.44%	5985.596
360	(0.2785,0.2474)	1.22%	14452.3
370	(0.2785,0.2459)	1.70%	14759.63
380	(0.2587,0.2234)	1.76%	35756.8
390	(0.2066,0.1913)	2.02%	7212685

Table S11 CIE coordinates, quantum yields and the correlated color temperatures (CCT) of 10%Eu^{3+}@**4** at different excitation wavelengths

10%Eu^{3+}@**4**			
Ex/nm	CIE coordinate	quality yield	CCT/K
320	(0.326,0.3436)	0.35%	5781.964
330	(0.3162,0.323)	0.59%	6352.084
340	(0.314,0.2974)	0.72%	6714.286
350	(0.3099,0.2754)	0.61%	7427.51
360	(0.2674,0.2342)	0.59%	22088.49
370	(0.2656,0.2327)	0.89%	23646.26
380	(0.2495,0.2196)	0.95%	49998.44
390	(0.2072,0.2016)	1.14%	499494.1

Table S12 CIE coordinates, quantum yields and the correlated color temperatures (CCT) of 15%Eu^{3+}@**4** at different excitation wavelengths

15%Eu^{3+}@**4**			
Ex/nm	CIE coordinate	quality yield	CCT/K
320	(0.3311,0.3218)	0.48%	5562.363
330	(0.3142,0.3013)	0.65%	6656.869
340	(0.3096,0.2802)	0.95%	7346.511
350	(0.3052,0.2613)	1.52%	8415.056
360	(0.272,0.2275)	1.72%	24102.63
370	(0.2626,0.2216)	2.23%	35475.2
380	(0.2541,0.2136)	2.46%	62549.15
390	(0.2107,0.1998)	2.24%	619265.7

Table S13 CIE coordinates, quantum yields and the correlated color temperatures (CCT) of 20%Eu^{3+}@**4** at different excitation wavelengths

20%Eu^{3+}@**4**			
Ex	CIE coordinate	quality yield	CCT/K
320 nm	(0.3697,0.3213)	0.32%	3885.765
330 nm	(0.349,0.3023)	0.49%	4595.522
340 nm	(0.3502,0.2892)	0.83%	4423.819
350 nm	(0.3514,0.2796)	1.24%	4254.361
360 nm	(0.3293,0.2539)	1.37%	5793.52
370 nm	(0.3134,0.2516)	2.03%	7745.56
380 nm	(0.3138,0.247)	2.64%	7878.4
390 nm	(0.2386,0.2222)	2.38%	54136.69