

Spiral frameworks firstly constructed by 1,2-phenylene-dioxydiacetic acid as highly sensitive and selective luminescent probes to detect PO₄³⁻ ions in aqueous solutions

Enjun Gao*, Na Sun, Yang Zhan, Xue Qiu, Yuqing Ding, Shaozhong Zhang, Mingchang Zhu*

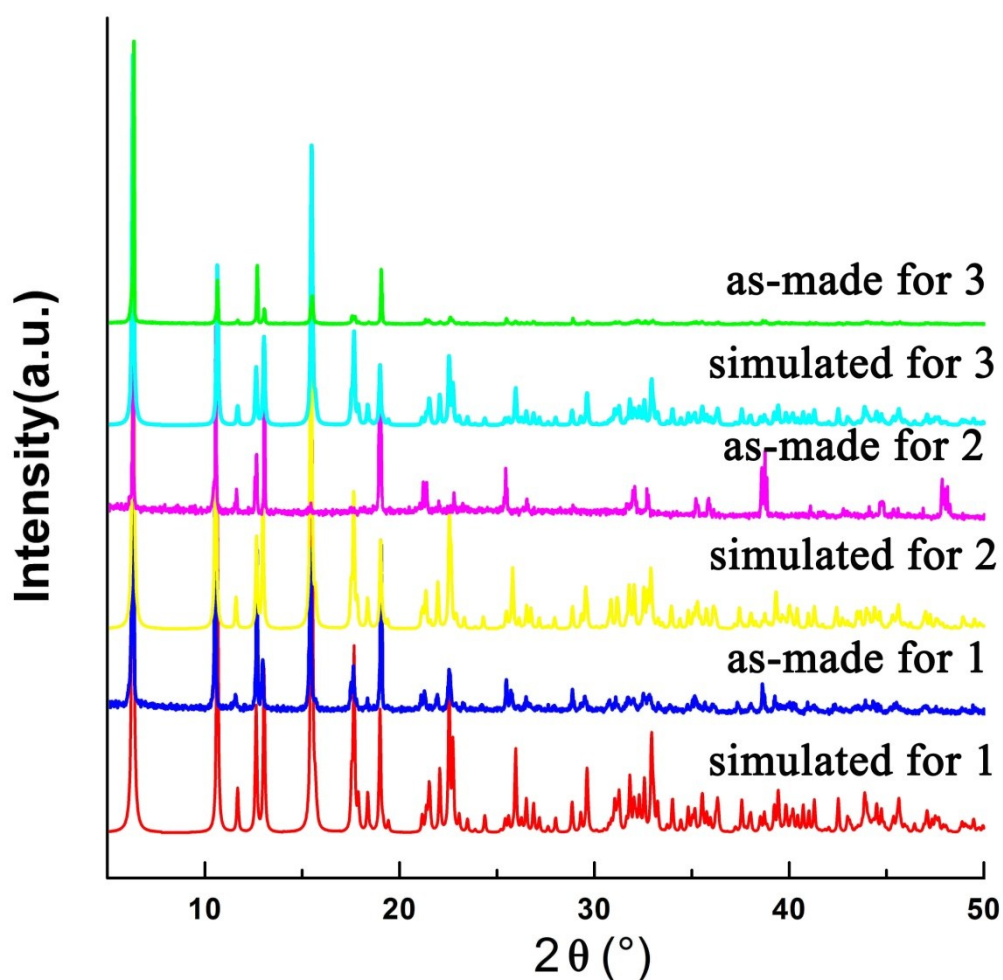


Fig.S1. Experimental and simulated powder PXRD patterns of 1–3.

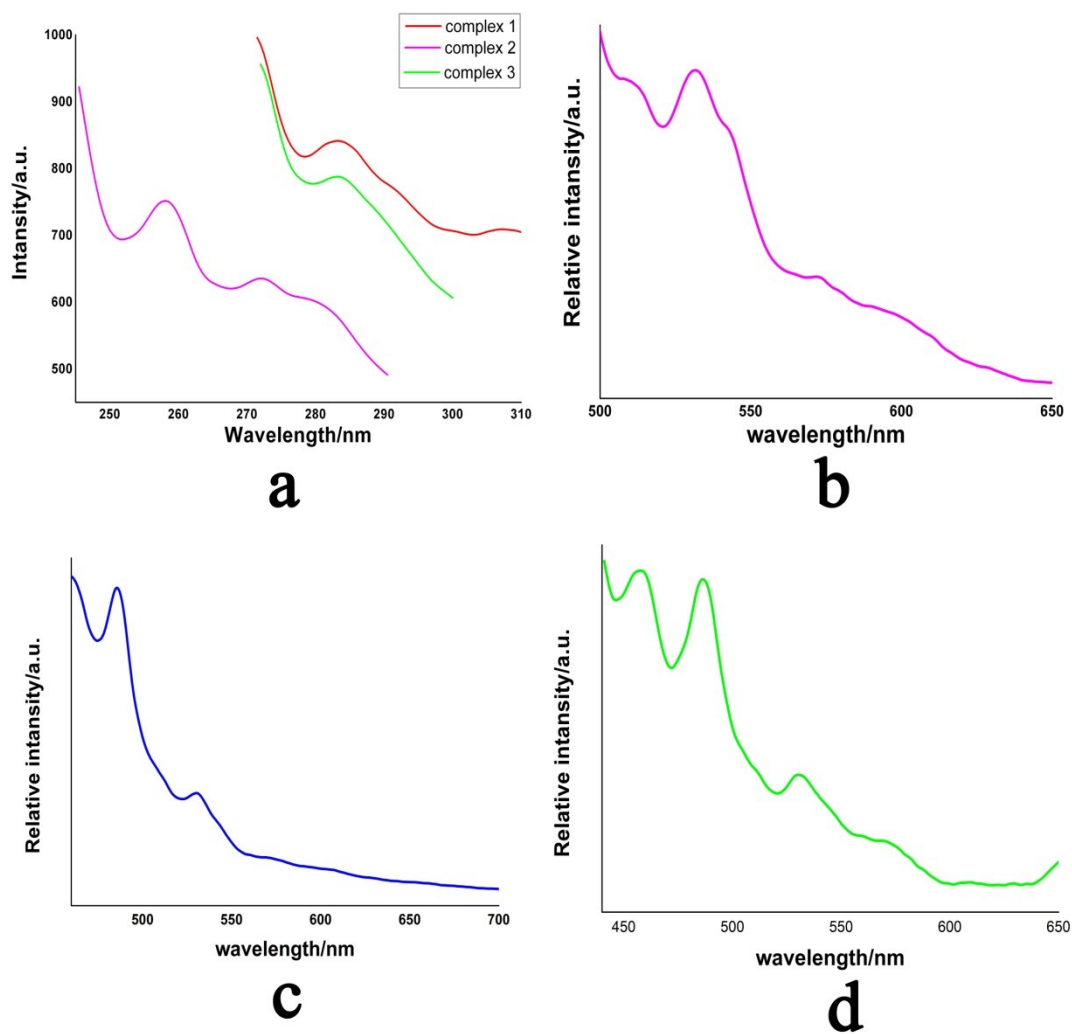


Fig.S2. a: the luminescent excitation spectrum of complex 1, 2 and 3; b and c: The luminescent emission spectrum of complex 1 and 2 excited at 301 nm; d: The luminescent emission spectrum of complex 3 excited at 413 nm.

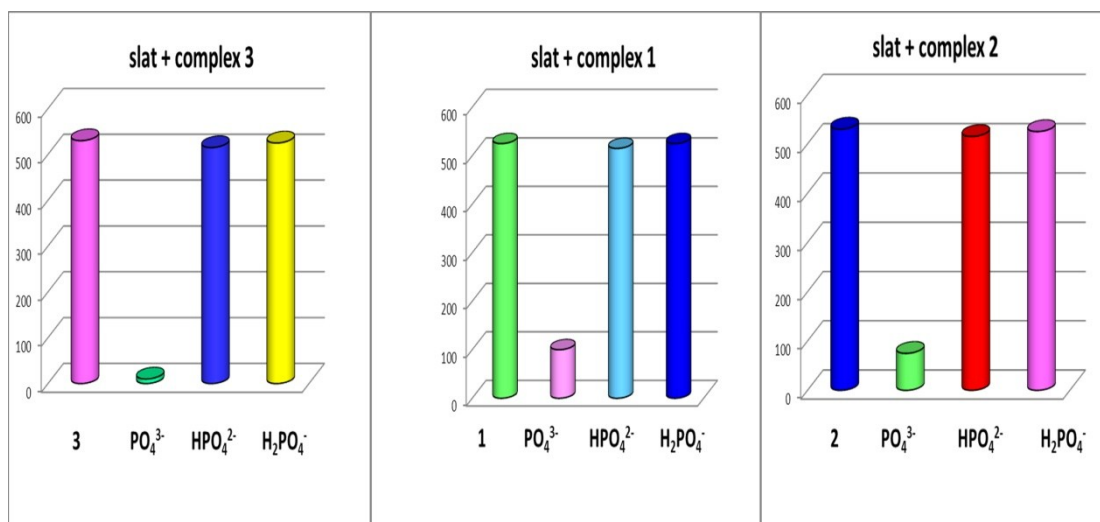


Fig.S3. Complexes comparison of the luminescence intensity of N-X in 10^{-3}M H_2PO_4^- and HPO_4^{2-} anions

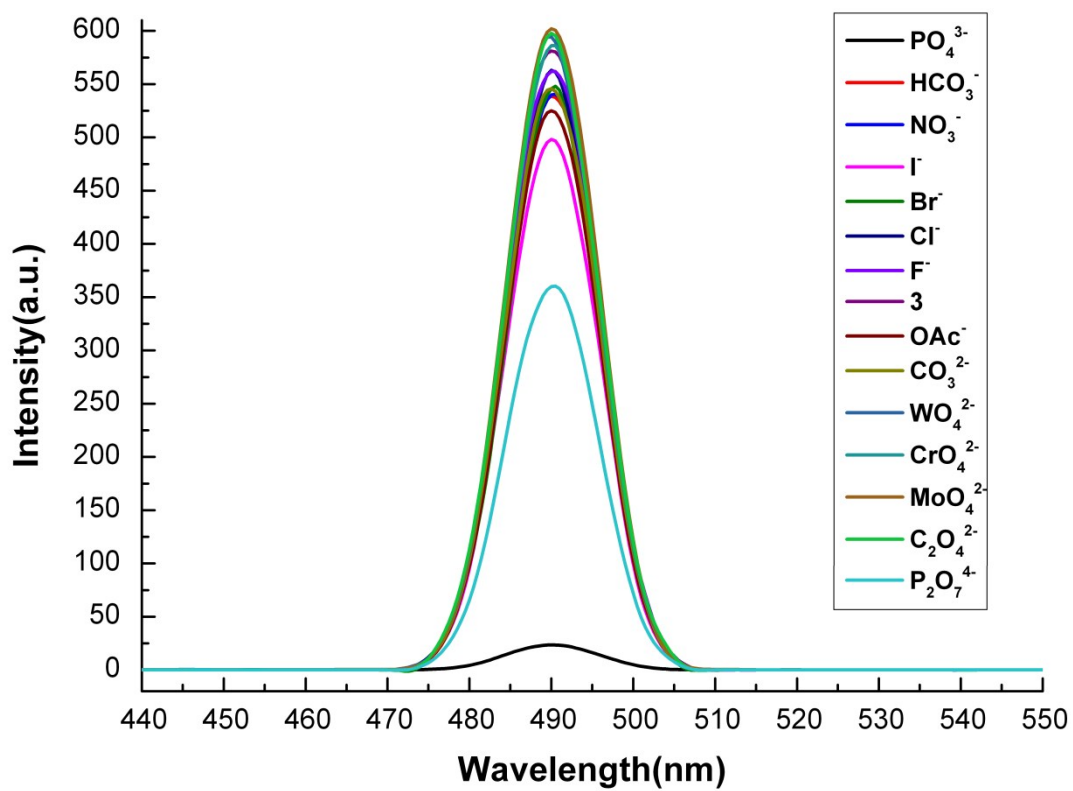


Fig.S4. Comparison of the luminescence intensity of 3-X in 10^{-3} M different anions.

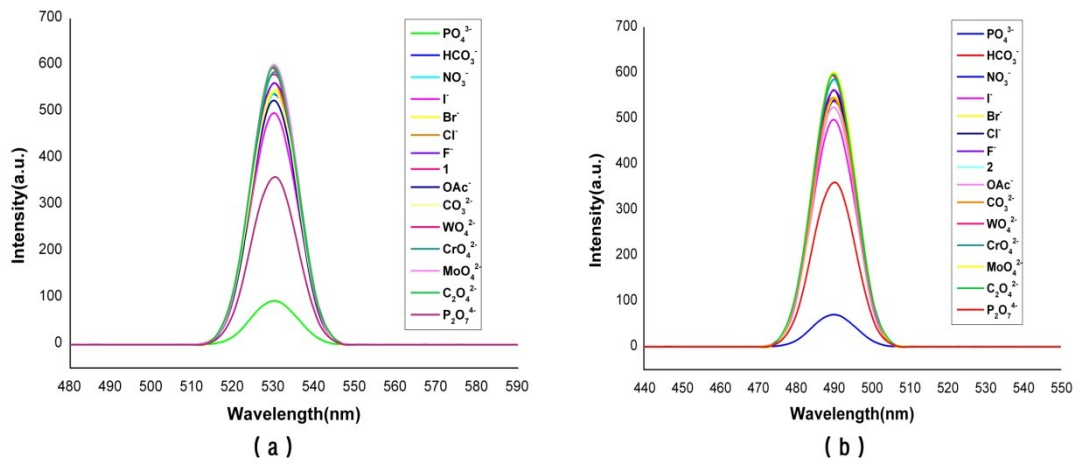


Fig.S5.Comparison of the luminescence intensity of 1-X and 2-X in 10^{-3} M different anions.

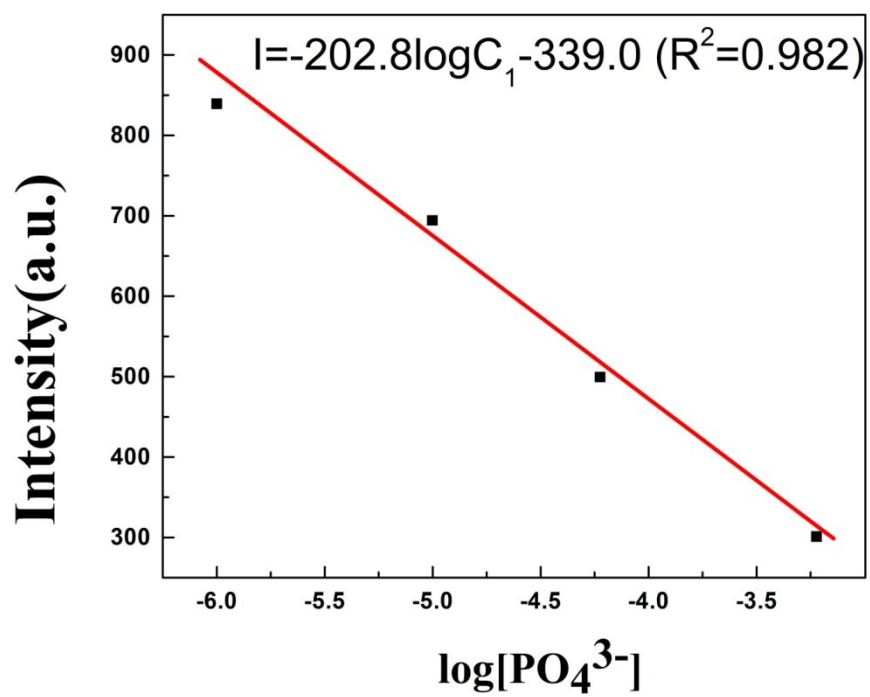


Fig. S6. The intensity plots of **1** vs log [PO₄³⁻]

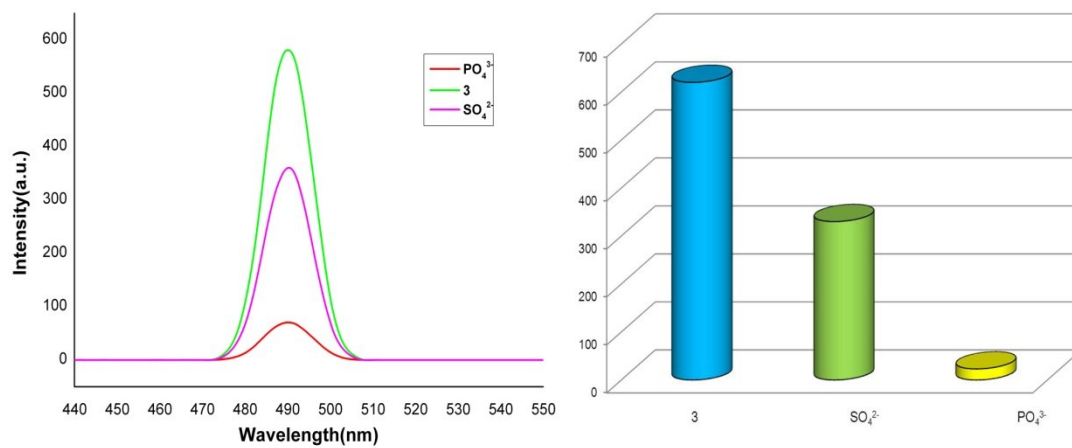
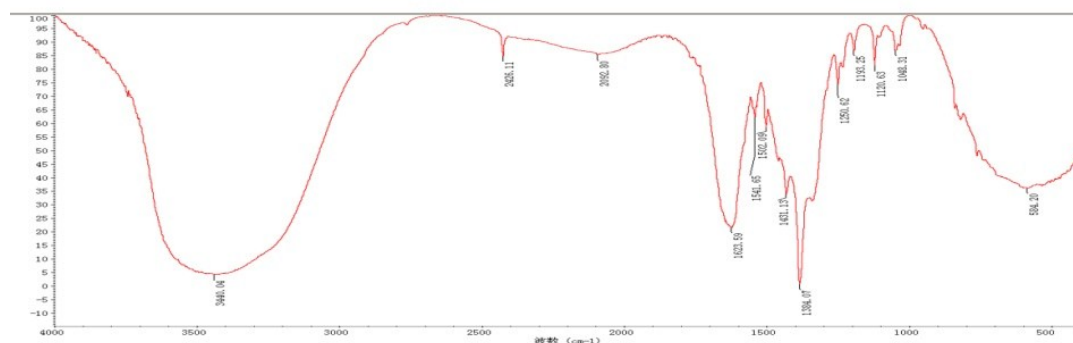
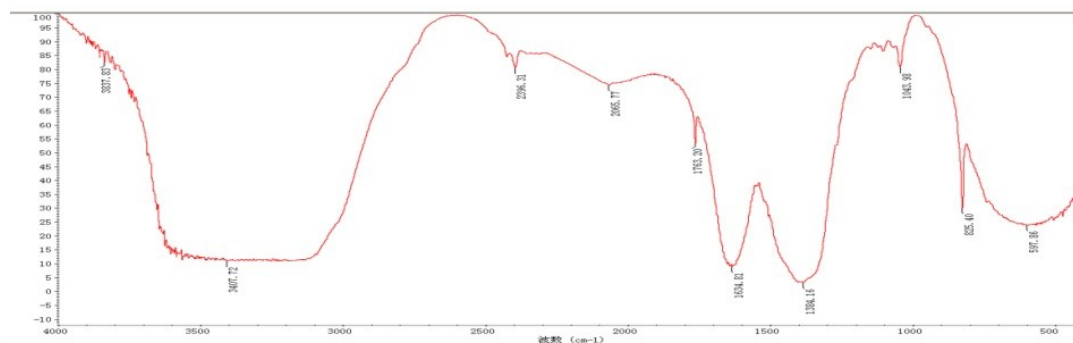


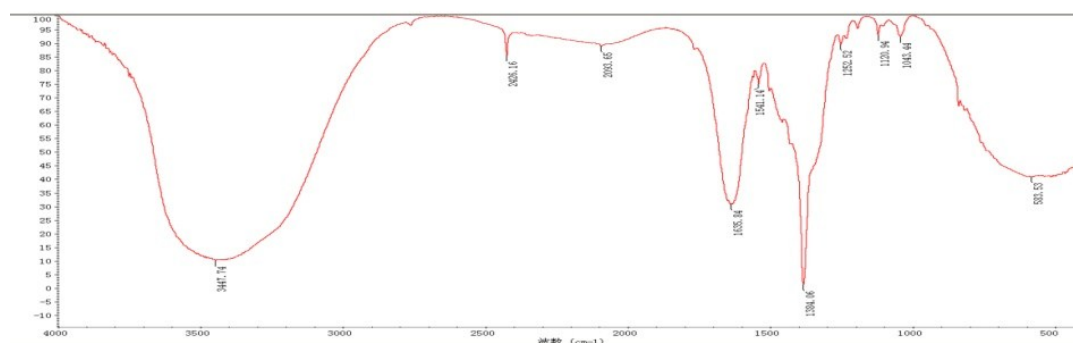
Fig.S7 complex **3** comparison of the luminescence intensity of the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transitions (487 nm) of ${}^3\text{-SO}_4^{2-}$ in 10^{-3}mol/L anions



(a)



(b)



(c)

Fig.S8. Infrared spectrum of complexes 1-3.

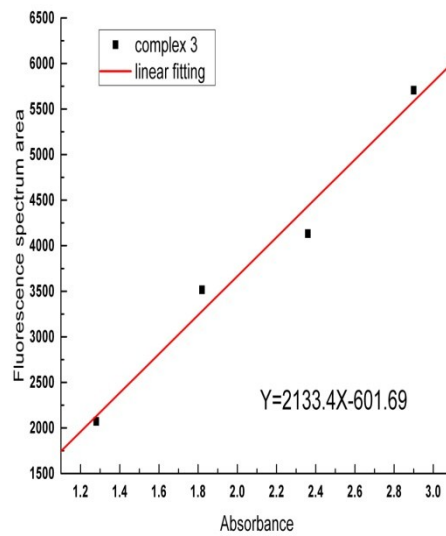
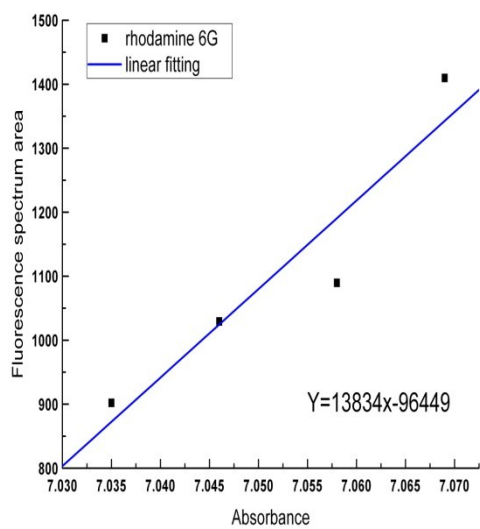


Fig.S9. Absorbance comparative fluorescence spectrum area rhodamine 6G (left) complex 3(right)

Table S1. Crystallographic data and structure refinements summary for 1-3

Complex	1	2	3
Empirical Formula	C ₁₀ H ₁₂ LaNO ₁₁	C ₁₀ H ₁₂ CeNO ₁₁	C ₁₀ H ₁₂ PrNO ₁₁
Formula weight	461.12	462.33	463.12
Crystal system, space group	Monoclinic , P2(1)/c	Monoclinic , P 2(1)/c	Monoclinic , P2(1)/c
a, (Å)	15.489(6)	15.4860(7)	15.489(6)
b, (Å)	6.174(2)	6.1777(3)	6.174(2)
c, (Å)	16.745(7)	16.8851(8)	16.745(7)
α(°)	90	90	90
β(°)	115.294(7)	115.4770(10)	115.294(7)
γ(°)	90	90	90
V, Å ³	1447.9(10)	1458.28(12)	1447.9(10)
Z	4	4	4
ρ _{calcd} , mg/cm ⁻³	2.115	2.106	2.125
Absorption coefficient, mm ⁻¹	3.011	3.182	3.426
Crystal size, mm	0.22 x 0.20 x 0.18	0.22 x 0.20 x 0.18	0.22 x 0.20 x 0.18
θ Range for data collection	1.45 to 25.40	1.457 to 27.375	2.45 to 25.13
F(000)	896	900	904
Limiting indices	-18 ≤ h ≤ 12, -7 ≤ k ≤ 7, -18 ≤ l ≤ 20	-19 ≤ h ≤ 19, -7 ≤ k ≤ 7, -16 ≤ l ≤ 21	-18 ≤ h ≤ 13, -7 ≤ k ≤ 7, -19 ≤ l ≤ 19
T	296(2)	296(2)	296(2)
Reflections collected/unique	8831/2607[R(int)=0.0192]	8349/1930[R(int)= 0.0435]	6539/2558[R(int)= 0.0492]
Completeness, %	97.7 %	99.5	98.8 %
Data/restraints / parameters	2607 / 6 / 220	3250 / 6 / 222	2558 / 6 / 220
GOF	1.080	1.303	1.089
Final R indices (I > 2σ(I))	R1 = 0.0154, wR2 = 0.0366	R1 = 0.0165, wR2 = 0.0469	R1 = 0.0455, wR2 = 0.1119
R indices (all data)	R1 = 0.0163, wR2 = 0.0371	R1 = 0.0211, wR2 = 0.0717	R1 = 0.0537, wR2 = 0.1163
Largest diff. peak and hole, e.Å ⁻³	0.524 and -0.317 e.Å ⁻³	0.652 and -0.811 e.Å ⁻³	1.902 and -1.613 e.Å ⁻³

Table S2. Selected bond lengths (Å) and angles (°) of the complex **1-3****1**

O(12)-La(1)	2.7753(18)	O(21)-La(1)	2.677(2)
O(14)-La(1)	2.4829(19)	C(10)#3-O(16)-La(1)	132.40(15)
O(16)-La(1)	2.5250(17)	O(17)-La(1)-O(14)	142.46(7)
O(20)-N(1)-La(1)	57.69(12)	O(17)-La(1)-O(16)	85.53(6)
O(18)-La(1)	2.534(2)	O(14)-La(1)-O(16)	124.00(6)
O(20)-La(1)	2.604(2)	C(10)-O(14)-La(1)	129.10(16)
O(21)-N(1)-La(1)	61.07(12)	C(6)-O(12)-La(1)	121.37(13)
C(7)-O(12)-La(1)	119.29(13)	O(14)-La(1)-O(15)	69.11(7)
O(16)-La(1)-O(18)	74.47(7)	O(17)-La(1)-O(18)	72.29(8)

2

O(1)-Ce(1)	2.659	O(2)-Ce(1)	2.789
O(3)-Ce(1)	2.440	O(4)-Ce(1)	2.518
O(5)-Ce(1)	2.509	O(6)-Ce(1)	2.471
O(7)-Ce(1)	2.530	O(8)-Ce(1)	2.529
O(9)-Ce(1)	2.605	O(10)-Ce(1)	2.689
O(2)-Ce(1)-O(3)	58.30	O(9)-Ce(1)-O(10)	47.82

3

O(18)-Pr(1)	2.518(7)	O(20)-Pr(1)	2.569(6)
N(1)-O(20)-Pr(1)	99.8(5)	O(17)-Pr(1)-O(18)	72.3(2)
O(14)-Pr(1)-O(18)	132.0(2)	O(16)-Pr(1)-O(18)	73.5(2)
O(15)-Pr(1)-O(18)	139.0(3)	O(19)-Pr(1)-O(18)	75.3(2)
O(17)-Pr(1)-O(20)	147.0(2)	O(14)-Pr(1)-O(20)	70.6(2)
O(16)-Pr(1)-O(20)	69.1(2)	O(15)-Pr(1)-O(20)	136.9(3)
O(19)-Pr(1)-O(20)	115.57(19)	O(18)-Pr(1)-O(20)	81.6(3)
O(18)-Pr(1)-O(13)	147.2(2)	O(20)-Pr(1)-O(13)	77.2(2)
O(18)-Pr(1)-O(21)	68.5(2)	O(20)-Pr(1)-O(21)	48.05(19)

#1 -x+1/2,y+1/2,-z+1/2

