Supporting information

The luminescent sensing profiles based on anion-responsive

lanthanide(III) quinolinecarboxylate materials: solid-state structures,

photophysical properties, and anionic species recognition

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	2	3	4	5
Formula	C ₅₄ H ₄₈ N ₃ O ₉ Pr	C ₅₄ H ₄₈ N ₃ O ₉ Nd	$C_{54}H_{48}N_3O_9Sm$	C ₅₄ H ₄₈ N ₃ O ₉ Eu
Formula weight	1023.86	1027.19	1033.30	1034.91
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	11.9877(3)	11.9730(2)	11.9586(3)	11.9567(5)
<i>b</i> (Å)	12.8636(5)	12.8879(5)	12.8019(4)	12.8560(5)
<i>c</i> (Å)	15.9294(6)	15.9094(6)	15.9246(5)	15.8977(6)
α(°)	86.856(3)	87.030(7)	87.217(3)	87.548(3)
β(°)	73.942(3)	73.854(6)	74.158(2)	74.215(4)
γ(°)	83.926(3)	83.803(7)	83.990(2)	83.653(3)
Volume(Å ³)	2346.46(14)	2343.71(13)	2331.95(12)	2336.9 (2)
<i>T</i> (K)	100(18)	293(2)	100.0(3)	100(15)
Ζ	2	2	2	2
$D_{\rm c} ({\rm g}\cdot{\rm cm}^{-3})$	1.449	1.456	1.472	1.471
μ (mm ⁻¹)	8.467	1.169	9.961	10.111
<i>F</i> (000)	1048	1050	1054	1056
R _{int}	0.0222	0.0593	0.0349	0.0445
$R_1^{a}/wR_2^{b} \left[I \ge 2\sigma(I)\right]$	0.0331/ 0.0864	0.0437/ 0.1121	0.0341/ 0.0866	0.0504/0.1374
R_1/wR_2 (all data)	0.0361/0.0888	0.0487/ 0.1169	0.0406/ 0.0905	0.0560/0.1406
GOF	1.052	1.116	1.062	1.106

Table S1. Crystallographic data and refinements for 2–5

^{*a*} $R_1 = \sum ||F_o|| - |F_c|| / \sum ||F_o||; wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$

Complex 2			
Bond	Dist.(Å)	Bond	Dist.(Å)
Pr(1)-O(6)#1	2.428(2)	Pr(1)-O(4)	2.566(2)
Pr(1)-O(1)#1	2.431(2)	Pr(1)-O(2)	2.568(2)
Pr(1)-O(5)	2.472(2)	Pr(1)-O(1)	2.613(2)
Pr(1)-O(7)	2.482(2)	O(1)-Pr(1)#1	2.431(2)
Pr(1)-O(3)	2.511(2)	O(6)-Pr(1)#1	2.428(2)
Pr(1)-O(8)	2.559(2)		
Angle	(°)	Angle	(°)
O(6)#1-Pr(1)-O(1)#1	71.51(7)	O(7)-Pr(1)-O(4)	100.13(8)
O(6)#1-Pr(1)-O(5)	134.81(7)	O(3)-Pr(1)-O(4)	51.18(8)
O(1)#1-Pr(1)-O(5)	74.00(7)	O(8)-Pr(1)-O(4)	76.10(9)
O(6)#1-Pr(1)-O(7)	144.12(7)	O(6)#1-Pr(1)-O(2)	81.67(8)
O(1)#1-Pr(1)-O(7)	143.92(7)	O(1)#1-Pr(1)-O(2)	119.67(7)
O(5)-Pr(1)-O(7)	72.48(7)	O(5)-Pr(1)-O(2)	91.03(8)
O(6)#1-Pr(1)-O(3)	127.22(8)	O(7)-Pr(1)-O(2)	74.01(8)
O(1)#1-Pr(1)-O(3)	76.86(8)	O(3)-Pr(1)-O(2)	151.08(8)
O(5)-Pr(1)-O(3)	69.89(7)	O(8)-Pr(1)-O(2)	69.07(9)
O(7)-Pr(1)-O(3)	79.46(8)	O(4)-Pr(1)-O(2)	145.02(8)
O(6)#1-Pr(1)-O(8)	72.33(8)	O(6)#1-Pr(1)-O(1)	72.38(7)
O(1)#1-Pr(1)-O(8)	140.64(8)	O(1)#1-Pr(1)-O(1)	70.10(8)
O(5)-Pr(1)-O(8)	145.08(8)	O(5)- $Pr(1)$ - $O(1)$	68.99(7)
O(7)-Pr(1)-O(8)	74.50(8)	O(7)-Pr(1)-O(1)	109.00(7)
O(3)-Pr(1)-O(8)	114.64(9)	O(3)-Pr(1)-O(1)	132.62(7)
O(6)#1-Pr(1)-O(4)	84.90(8)	O(8)-Pr(1)-O(1)	112.48(8)
O(1)#1-Pr(1)-O(4)	85.72(8)	O(4)-Pr(1)-O(1)	150.85(8)
O(5)-Pr(1)-O(4)	120.66(8)	O(2)-Pr(1)-O(1)	50.30(7)
Symmetry codes: (#1) -x+2,-	-y+1,-z		

Table S2. Selected bond lengths (Å) and bond angles (°) for 2--5

Complex 3			
Bond	Dist.(Å)	Bond	Dist.(Å)
Nd(1)-O(5)	2.411(3)	Nd(1)-O(1)	2.543(3)
Nd(1)-O(4)#1	2.414(3)	Nd(1)-O(3)	2.557(3)
Nd(1)-O(6)#1	2.454(3)	Nd(1)-O(4)	2.591(3)
Nd(1)-O(8)	2.469(3)	O(4)-Nd(1)#1	2.414(3)
Nd(1)-O(2)	2.493(3)	O(6)-Nd(1)#1	2.454(3)
Nd(1)-O(7)	2.541(4)		
Angle	(°)	Angle	(°)
O(5)-Nd(1)-O(4)#1	71.72(10)	O(8)-Nd(1)-O(1)	100.53(11)
O(5)-Nd(1)-O(6)#1	135.23(10)	O(2)-Nd(1)-O(1)	51.32(11)
O(4)#1-Nd(1)-O(6)#1	74.02(9)	O(7)-Nd(1)-O(1)	75.47(13)
O(5)-Nd(1)-O(8)	143.97(10)	O(5)-Nd(1)-O(3)	81.77(11)
O(4)#1-Nd(1)-O(8)	143.92(9)	O(4)#1-Nd(1)-O(3)	120.00(10)
O(6)#1-Nd(1)-O(8)	72.47(9)	O(6)#1-Nd(1)-O(3)	91.35(11)
O(5)-Nd(1)-O(2)	127.10(10)	O(8)-Nd(1)-O(3)	73.95(10)
O(4)#1-Nd(1)-O(2)	77.22(10)	O(2)-Nd(1)-O(3)	151.03(11)
O(6)#1-Nd(1)-O(2)	70.14(10)	O(7)-Nd(1)-O(3)	69.32(13)
O(8)-Nd(1)-O(2)	79.17(10)	O(1)-Nd(1)-O(3)	144.54(12)
O(5)-Nd(1)-O(7)	72.80(11)	O(5)-Nd(1)-O(4)	72.49(9)
O(4)#1-Nd(1)-O(7)	141.09(10)	O(4)#1-Nd(1)-O(4)	70.11(10)
O(6)#1-Nd(1)-O(7)	144.74(10)	O(6)#1-Nd(1)-O(4)	69.29(9)
O(8)-Nd(1)-O(7)	73.89(10)	O(8)-Nd(1)-O(4)	109.23(10)
O(2)-Nd(1)-O(7)	113.31(13)	O(2)-Nd(1)-O(4)	133.23(10)
O(5)-Nd(1)-O(1)	84.07(11)	O(7)-Nd(1)-O(4)	113.19(12)
O(4)#1-Nd(1)-O(1)	85.46(10)	O(1)-Nd(1)-O(4)	150.23(10)
O(6)#1-Nd(1)-O(1)	120.96(10)	O(3)-Nd(1)-O(4)	50.61(10)
Symmetry codes: (#1) -x+1,-y	r+2,-z		

Complex 4			
Bond	Dist.(Å)	Bond	Dist.(Å)
Sm(1)-O(4)#1	2.381(2)	Sm(1)-O(3)	2.512(3)
Sm(1)-O(6)#1	2.389(2)	Sm(1)-O(2)	2.519(3)
Sm(1)-O(5)	2.423(2)	Sm(1)-O(4)	2.591(2)
Sm(1)-O(8)	2.436(2)	O(4)-Sm(1)#1	2.381(2)
Sm(1)-O(1)	2.468(2)	O(6)-Sm(1)#1	2.389(2)
Sm(1)-O(7)	2.505(3)		
Angle	(°)	Angle	(°)
O(4)#1-Sm(1)-O(6)#1	72.35(8)	O(8)-Sm(1)-O(3)	74.16(9)
O(4)#1-Sm(1)-O(5)	74.28(8)	O(1)-Sm(1)-O(3)	149.29(9)
O(6)#1-Sm(1)-O(5)	135.43(8)	O(7)-Sm(1)-O(3)	69.79(9)
O(4)#1-Sm(1)-O(8)	143.27(8)	O(4)#1-Sm(1)-O(2)	85.74(8)
O(6)#1-Sm(1)-O(8)	144.22(8)	O(6)#1-Sm(1)-O(2)	83.73(8)
O(5)-Sm(1)-O(8)	72.43(8)	O(5)-Sm(1)-O(2)	122.23(8)
O(4)#1-Sm(1)-O(1)	76.93(9)	O(8)-Sm(1)-O(2)	99.14(9)
O(6)#1-Sm(1)-O(1)	127.57(9)	O(1)-Sm(1)-O(2)	52.23(8)
O(5)-Sm(1)-O(1)	70.44(8)	O(7)-Sm(1)-O(2)	75.06(9)
O(8)-Sm(1)-O(1)	77.70(9)	O(3)-Sm(1)-O(2)	144.74(9)
O(4)#1-Sm(1)-O(7)	140.98(8)	O(4)#1-Sm(1)-O(4)	70.10(9)
O(6)#1-Sm(1)-O(7)	72.02(9)	O(6)#1-Sm(1)-O(4)	72.09(8)
O(5)-Sm(1)-O(7)	144.51(9)	O(5)-Sm(1)-O(4)	69.28(8)
O(8)-Sm(1)-O(7)	74.33(9)	O(8)-Sm(1)-O(4)	111.05(8)
O(1)-Sm(1)-O(7)	113.92(9)	O(1)-Sm(1)-O(4)	133.20(8)
O(4)#1-Sm(1)-O(3)	120.63(8)	O(7)-Sm(1)-O(4)	112.64(9)
O(6)#1-Sm(1)-O(3)	83.07(9)	O(3)-Sm(1)-O(4)	50.91(8)
O(5)-Sm(1)-O(3)	89.36(9)	O(2)-Sm(1)-O(4)	149.81(8)
Symmetry codes: (#1) -x+2	2,-y,-z		

Complex 5				
Bond	Dist.(Å)	Bond	Dist.(Å)	
Eu(1)-O(5)	2.366(3)	Eu(1)-O(4)	2.498(4)	
Eu(1)-O(2)#1	2.368(4)	Eu(1)-O(8)	2.496(4)	
Eu(1)-O(6)#1	2.416(3)	Eu(1)-O(2)	2.576(3)	
Eu(1)-O(7)	2.421(4)	O(2)-Eu(1)#1	2.368(4)	
Eu(1)-O(3)	2.456(4)	O(6)-Eu(1)#1	2.416(3)	
Eu(1)-O(1)	2.492(4)			
Angle	(°)	Angle	(°)	O(5)-
Eu(1)-O(2)#1	72.54(12)	O(7)-Eu(1)-O(4)	99.46(14)	
O(5)-Eu(1)-O(6)#1	135.69(12)	O(3)-Eu(1)-O(4)	52.34(13)	
O(2)#1-Eu(1)-O(6)#1	74.40(12)	O(1)-Eu(1)-O(4)	144.84(14)	
O(5)-Eu(1)-O(7)	143.97(12)	O(5)-Eu(1)-O(8)	72.08(14)	
O(2)#1-Eu(1)-O(7)	143.36(12)	O(2)#1-Eu(1)-O(8)	141.08(13)	
O(6)#1-Eu(1)-O(7)	72.50(12)	O(6)#1-Eu(1)-O(8)	144.33(13)	
O(5)-Eu(1)-O(3)	127.57(13)	O(7)-Eu(1)-O(8)	74.00(13)	
O(2)#1-Eu(1)-O(3)	76.89(13)	O(3)-Eu(1)-O(8)	113.56(16)	
O(6)#1-Eu(1)-O(3)	70.50(12)	O(1)-Eu(1)-O(8)	69.90(15)	
O(7)-Eu(1)-O(3)	77.63(13)	O(4)-Eu(1)-O(8)	75.07(16)	
O(5)-Eu(1)-O(1)	83.30(14)	O(5)-Eu(1)-O(2)	72.25(12)	
O(2)#1-Eu(1)-O(1)	120.99(12)	O(2)#1-Eu(1)-O(2)	70.14(14)	
O(6)#1-Eu(1)-O(1)	89.26(13)	O(6)#1-Eu(1)-O(2)	69.27(11)	
O(7)-Eu(1)-O(1)	73.95(13)	O(7)-Eu(1)-O(2)	111.24(12)	
O(3)-Eu(1)-O(1)	149.04(14)	O(3)-Eu(1)-O(2)	133.20(13)	
O(5)-Eu(1)-O(4)	83.27(13)	O(1)-Eu(1)-O(2)	51.21(12)	
O(2)#1-Eu(1)-O(4)	85.23(13)	O(4)-Eu(1)-O(2)	149.30(13)	
O(6)#1-Eu(1)-O(4)	122.34(13)	O(8)-Eu(1)-O(2)	113.00(14)	
Symmetry codes: (#1)	-x+1,-y+1,-z+1			

Table S3 The calculated energy and interaction energy about $HSO_4^-/H_2PO_4^-$ with ligand by DFTmethod at B3LYP-D3/6-31++G* level,

	HSO ₄ -L	H ₂ PO ₄ -L
$E(HSO_4/H_2PO_4-L)$ (a.u.)	-1521.38928	-1465.30232
E(L) (a.u.)	-821.63408	
$E(HSO_{4}^{-}/H_{2}PO_{4}^{-})$ (a.u.)	-699.73284	-643.64658
E(HSO ₄ /H ₂ PO ₄ ^L) (kcal/mol)	-3.35569	-3.25048

1 a.u.=627.51 kJ/mol = 150.05 kcal/mol, E(HSO₄/H₂PO₄^L)=E(HSO₄/H₂PO₄-L)- E(HSO₄-/H₂PO₄-) - E(L)

Table S4 calculated hydrogen bond length between $HSO_4^-/H_2PO_4^-$ and PQC

	C-H	С-НО	НО	O-H	O-HN	HN
L	1.08499					
HSO ₄ -				0.96931		
HSO ₄ -L	1.09065	3.14557	2.05772	0.98225	2.95102	1.96891
H ₂ PO ₄ -				0.96638		
H ₂ PO ₄ -L	1.09562	3.07134	1.97948	0.97669	2.99027	2.01643

Table S5 The calculated energy and interaction energy about HSO_4 -/ H_2PO_4 - with Eu^{3+} inmonodentate mode by DFT method at B3LYP/6-31G**(ECP52MWB) level

	$Eu(HSO_4)_3(H_2O)_5$	$Eu(H_2PO_4)_3(H_2O)_5$		
E(Eu ³⁺) (a.u.)	-33.	-33.81557		
$E(H_2O)$ (a.u.)	-76.4	41974		
$E(HSO_4/H_2PO_4)$ (a.u.)	-699.69269	-643.59804		
$E[Eu(HSO_4/H_2PO_4)_3(H_2O)_5]$ (a.u.)	-2516.73106	-2348.53679		
$E(H_2O^{Eu^{3+}})$ (a.u.)	-0.1	1017		
E(HSO ₄ /H ₂ PO ₄ ^Eu ³⁺) (kcal/mol)	-59.16024	-63.62655		

Table S6 The calculated energy and interaction energy about $HSO_4^-/H_2PO_4^-/L$ with Eu^{3+} in bidentate mode by DFT method at B3LYP/6-31G**(ECP52MWB) level

	$Eu(HSO_4)_3(H_2O)_2$	$Eu(H_2PO_4)_3(H_2O)_2$	$Eu(L)_3(H_2O)_2$
$E(Eu^{3+})$ (a.u.)	-33.81557		
E(H ₂ O) (a.u.)	-76.41974		
$E(HSO_4/H_2PO_4/L)$ (a.u.)	-699.69269	-643.59804	-821.02425
$E[Eu(HSO_4/H_2PO_4/L)_3(H_2O)_2]$ (a.u.)	-2287.37066	-2119.17105	-2651.38530
$E(H_2O^{Eu^{3+}})$ (a.u.)	-0.11017		
E(HSO ₄ /H ₂ PO ₄ /L^Eu ³⁺) (kcal/mol)	-70.58065	-74.78070	-71.57474



Fig. S1 The coordination environment around Eu(III) in Eu_2PQC_6 with the thermal ellipsoid at the 30% probability level. Symmetry codes: A: 1-x, 1-y, 1-z.



Fig. S2 3D framework of Eu_2PQC_6 propagates through the $\pi \cdots \pi$ interactions (denoted by the green dotted lines) with the intercentroid distances being 3.621 Å and 3.493 Å respectively.





Fig. S4 IR spectra of PQC ligand, complex 1-5 in solid state and 5 in solution.



Fig. S5 TGA diagram of 5 under $N_{2}\,atmosphere.$



Fig. S6 PXRD diagram of 1-5.



Fig. S7 Room-temperature emission spectra of ligand and complexes 1-4 (λ_{ex} = 345 nm).



Fig. S8 The CIE chromaticity coordinates of Eu₂PQC₆ in solid state and solution.



Fig. S9 Fluorescence emission spectra of (a) Eu_2PQC_6 solution with different concentrations as calibration, (b) Eu_2PQC_6 -HSO₄⁻ solution with different mol fractions, (c) Eu_2PQC_6 -H₂PO₄⁻ solution with different mol fractions. The insets in the upper-right show Job's plots after calibration for the determination of the stoichiometry of Eu_2PQC_6 to HSO₄^{-/} H₂PO₄⁻.



Fig. S10 The UV-vis absorption spectra of 5 (5 μ M) in ETOH solution upon addition of F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, SCN⁻ and HCO₃⁻ anions (6.0 equiv).



Fig. S11 Fluorescence of Eu_2PQC_6 in EtOH–DMSO (95:5 v/v) solution (16.7 μ M) under λ_{ex} = 343 nm and its complexation with H₂PO₄⁻ and HSO₄⁻ (3 equiv) in the presence of different anions (6 equiv).



Fig. S12 The changes in the excitation spectra of Eu_2PQC_6 (16.7 µM) in ETOH-DMSO (v/v = 95:5) solution upon addition of $H_2PO_4^-$ and HSO_4^- (0 – 22 equiv).



Fig. S13 Response parameter values (α) as a function of the logarithm of H₂SO₄⁻ and HPO₄⁻ concentration.



Fig. S14 The double logarithm plot of the Eu^{III} emission in the presence of increasing amounts of HSO_4^- and $H_2PO_4^-$, and the corresponding linear fitting.



Fig. S15 The changes of emission intensity (at 617 nm) of Eu_2PQC_6 with different concentrations of $H_2PO_4^-$ and HSO_4^- added, where I_0 and I are the emission intensities of Eu_2PQC_6 in the absence of $H_2PO_4^-$ and HSO_4^- and at varying amounts of $H_2PO_4^-$ and HSO_4^- , respectively.



Fig. S16 The respond time of Eu_2PQC_6 to $H_2PO_4^-$ and $HSO_4^-(3.0 \text{ equiv})$.



Fig. S17 The changes in emission from PQC ligand upon addition of $H_2PO_4^-$ and HSO_4^- , respectively. Inset: intensity at 387 nm as a function of $H_2PO_4^-$ and HSO_4^- concentration.



Fig.S18 (a) P $2p_{1/2}$ and $2p_{3/2}$ spectra obtained for [TBA]H₂PO₄ and 5-H₂PO₄⁻ sample, (b) Eu $3d_{5/2}$

spectra obtained for **5** and **5**-H₂PO₄⁻ sample, respectively.



Fig. S19 ¹H-NMR spectra of PQC, **5**, **5** addition with 1.0 equiv of $H_2PO_4^-$ and HSO_4^- in DMSO- d_6 solution.



Fig. S20 The optimized structures of investigated PQC-HSO₄⁻/H₂PO₄⁻ hydrogen-bonding interaction and Eu-HSO₄⁻/H₂PO₄⁻ coordination-bonding interaction by DFT method.



Fig. S21 The evolution of the fluorescence emission of Eu_2PQC_6 (50µM) in H₂O-DMSO solution ($\lambda_{ex} = 343$ nm).



Fig. S22 Luminescence decay curve excited at 343 nm at 77 K of Eu_2PQC_6 (50 μ M) in D₂O-DMSO (v/v =10:90) and H₂O-DMSO (v/v =10:90) solution, respectively.



Fig. S23 Emission spectra of 5 (16.7 μ M) against AMP and ATP in 10:90 (v/v) H₂O-DMSO solution. The inset shows the linear fit related to the binding constant determination.