Supplementary Information

A water-stable lanthanide-organic framework as recyclable luminescent probe for detecting pollutant phosphorus anions

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Experimental Section

Materials and methods

All reagents and reactants were purchased commercially and were used directly without further purification. The C, H and N microanalyses were obtained at the Institute of Elemental Organic Chemistry, Nankai University. Powder X-ray diffraction and thermodiffractogram measurements were carried out on an Ultima Ⅳ X-ray diffractometer using Cu-Kα radiation. Thermogravimetric analyses (TGA) were recorded with a Netzsch TG 209 TG-DTA analyzer under a nitrogen atmosphere. The fluorescent spectra were measured on an F-4500 FL Spectrophotometer.

Synthesis of $\{[Eu_{1.5}(BTB)_{1.5}(H_2O)]\cdot 3DMF\}_n$.

A mixture of $Eu(OAc)_3\cdot 4H_2O$ (0.1 mmol, 40.1 mg), H_3BTB (0.1 mmol, 43.8 mg) and $LiOH\cdot H_2O$ (0.2 mmol, 8.4 mg) in DMA (3.5 mL) and H_2O (1 mL) were sealed in a 15 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 130 ℃ for 3 days under autogenous pressure and then cooled to room temperature 2 ℃/h under ambient conditions. The colorless crystals were obtained and washed with DMF. Yield: 80 %, based on $Eu(OAc)_3\cdot 4H_2O$. Elemental analysis (%) Calcd for compound **1**: C 53.15, H 4.07, N 3.76. Found: C 54.13, H 4.27, N 3.91.

X-Ray crystallography

Suitable crystal **1** was paced in a cooled N_2 gas stream at ~130 K for crystallographic data collection on a SuperNova Single Crystal Diffractometer equipped with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å). Data reduction included absorption was performed by using the SAINT program.[1] The structures were solved by direct methods and refined by full-matrix least squares on F^2 with SHELXS-97 and SHELXL-97 programs.[2] All the hydrogen atoms were placed geometrically and refined using a riding model.

We used PLATON/SQUEEZE[3] to calculate the contribution to the diffraction from the solvent region. The number of isolated DMF molecules was determined by TG analyses and elemental microanalyses. Detailed crystal data and structure refinement for **1** are shown in Table 1S.

Table 1S Crystal data and structure refinement for **1**

Identification code	**1**
Empirical formula	$C_{81}H_{49}O_{20}Eu_3$
Formula weight	1798.08
Temperature/K	121(2)
Crystal system	monoclinic
Space group	*P*2/*c*
a/Å	10.8511(6)
b/Å	28.8803(13)
c/Å	19.1550(8)
α/°	90.00
β/°	123.902(3)
γ/°	90.00
Volume/Å^3	4982.3(4)
Z	2
F(000)	1768.0
Goodness-of-fit on F^2	0.967
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0821, wR_2 = 0.2107
Final *R* indexes [all data]	R_1 = 0.1009, wR_2 = 0.2297

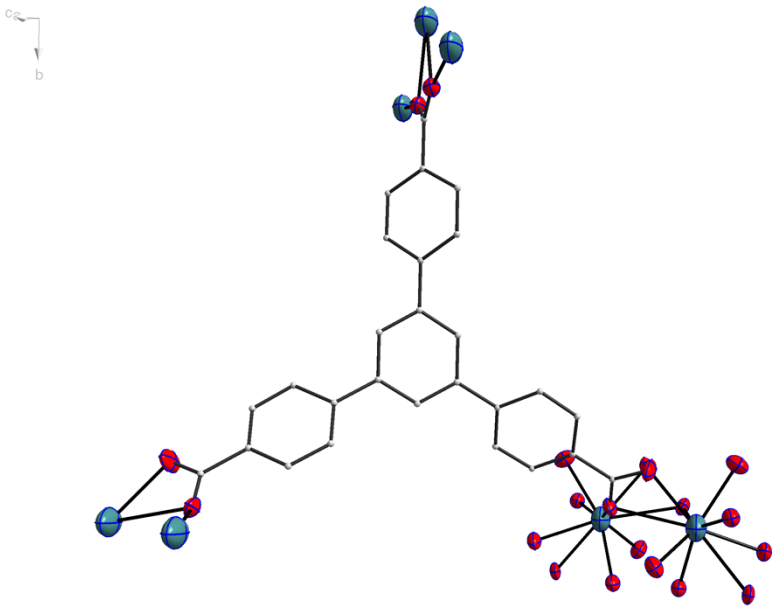

Fig. S1. The coordinated environments of Eu^{3+} and BTB^{3-} ligand in **1**.

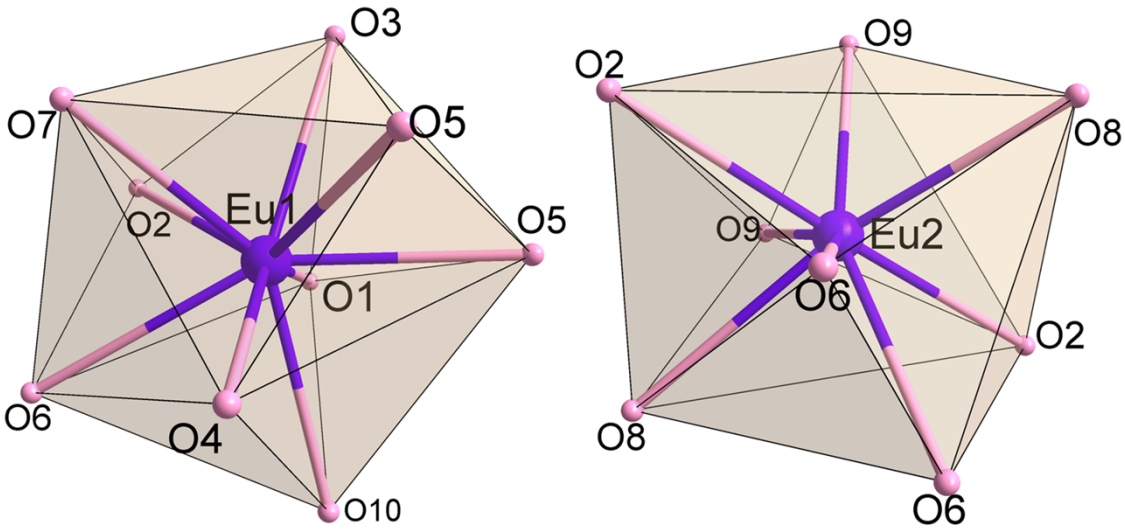

Fig. S2. The coordinated environments and the polyhedral representation of Eu^{3+}.

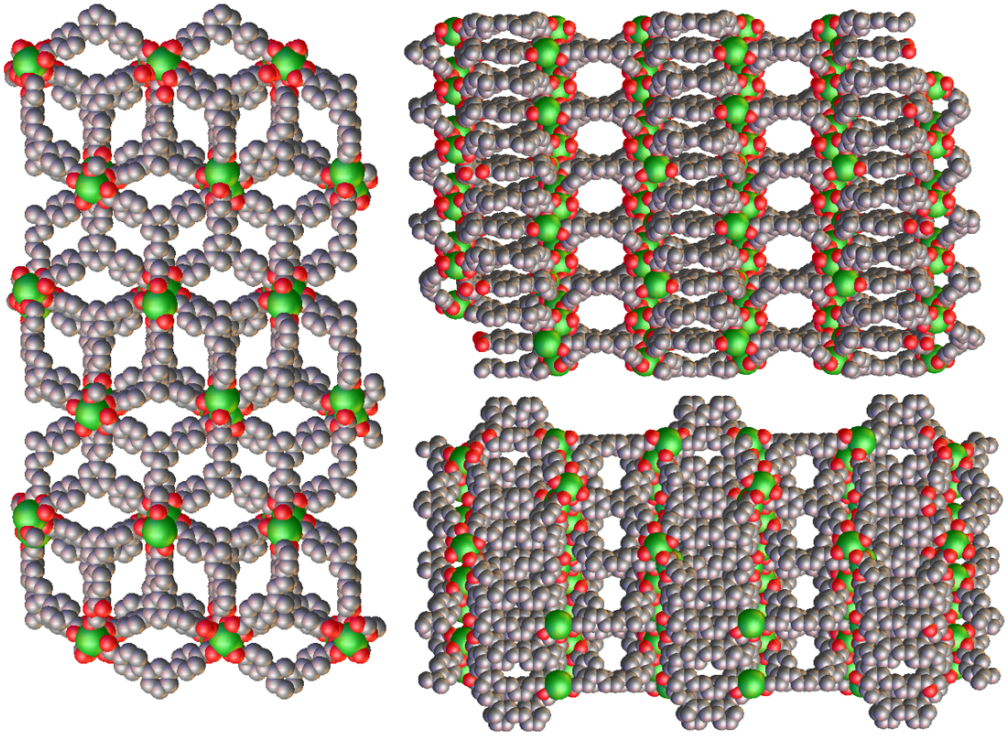

Fig. S3. The 3D framework of **1** exhibits three types of channels in packing mode.

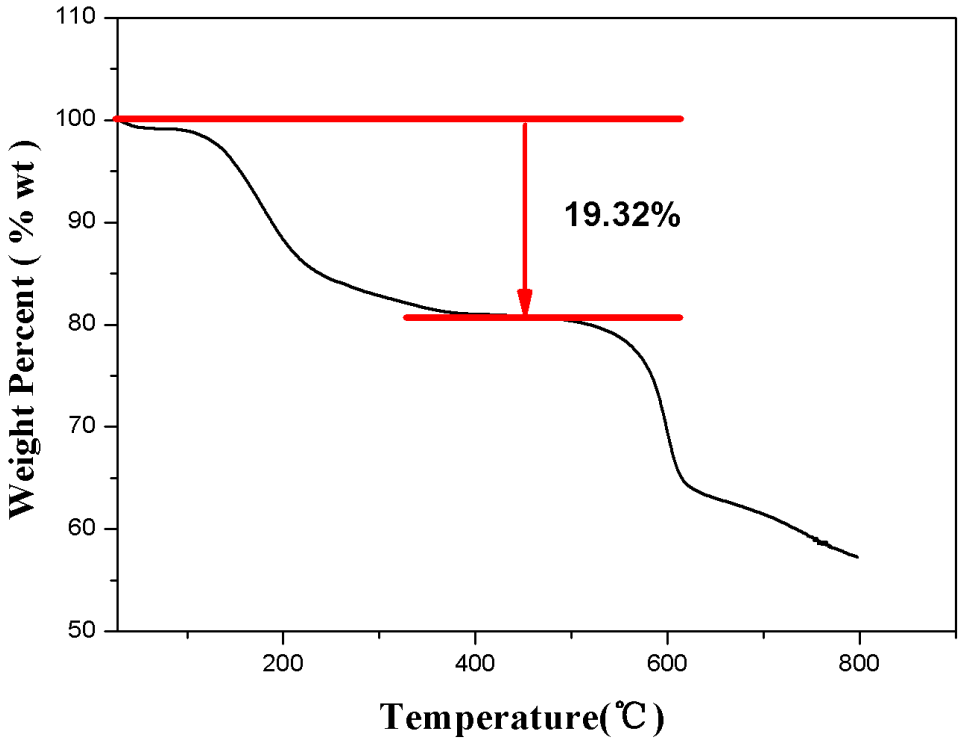

Fig. S4. Thermogravimetric analyses curve of **1**, the weight loss of 19.32% is close to the calculated value (19.60%).

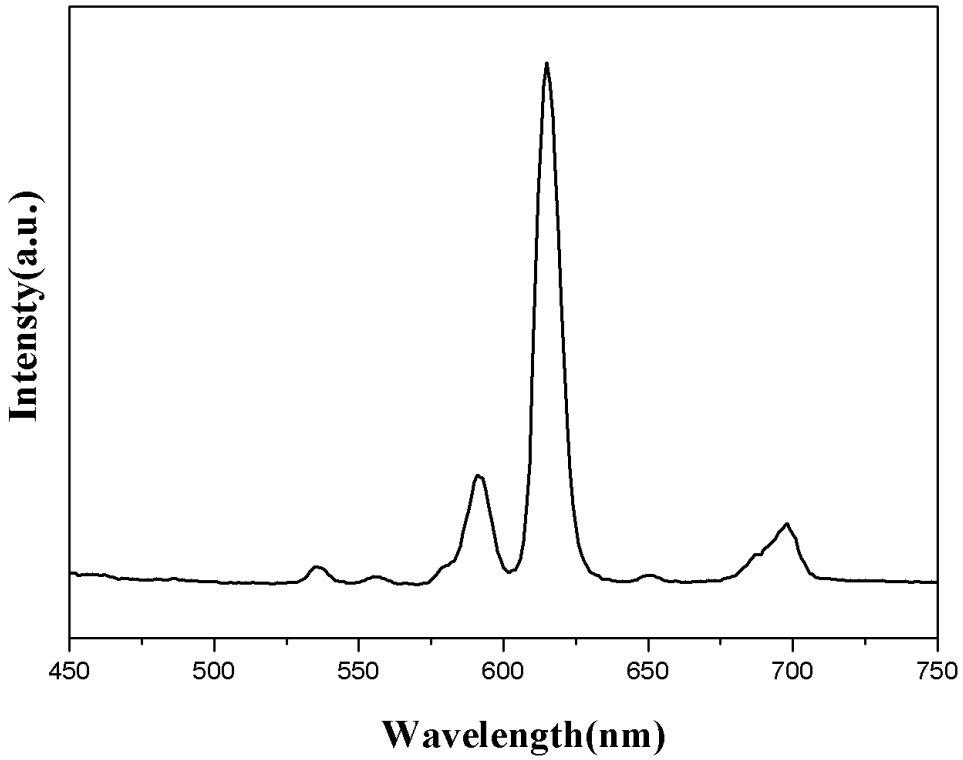

Fig. S5. The emission spectra of **1** ($\lambda_{excited}$ = 305 nm)

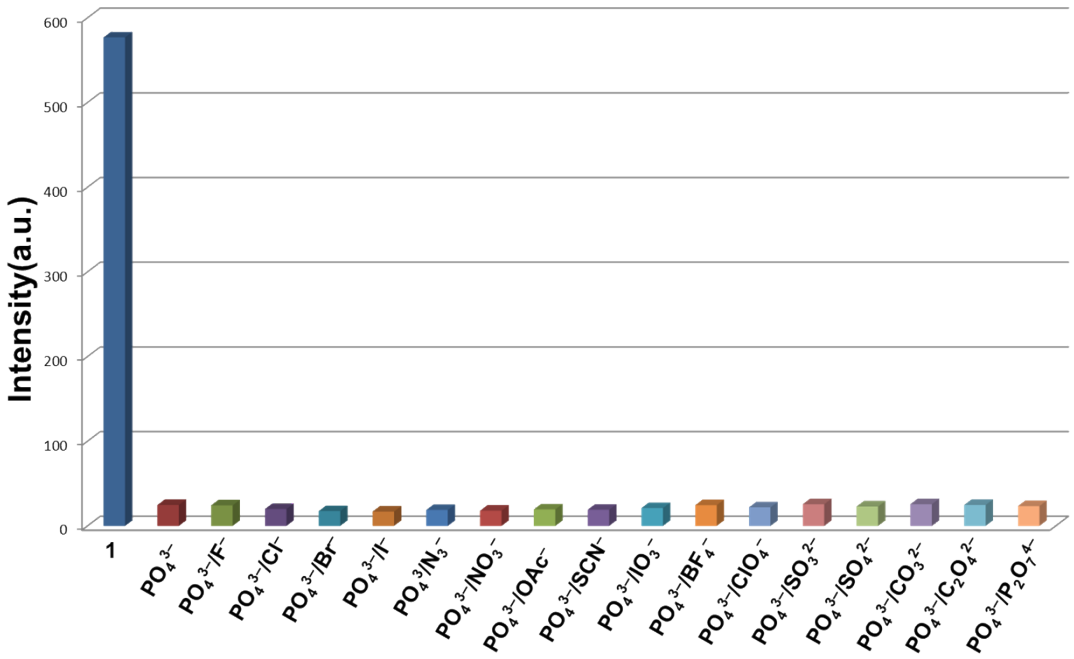

Fig. S6. Comparison of the luminescence intensity of **1** under mixed anions (10^{-3} M).

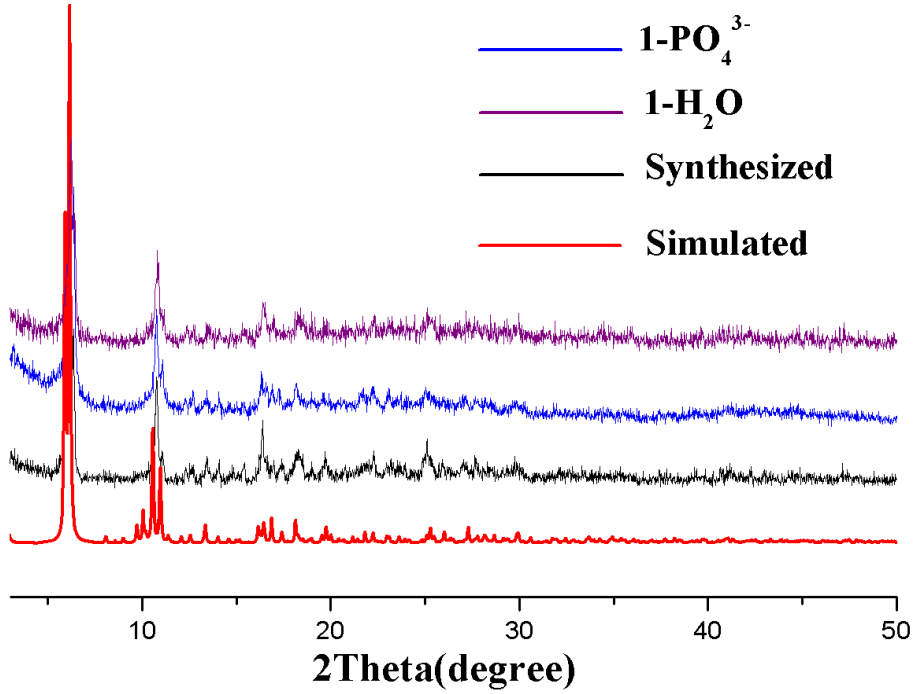

Fig. S7. Powder XRD of simulated from the single-crystal data of **1** (red), as-synthesized compound **1** (black), **1** immersing in H_2O (**1**-H_2O, purple) and **1**-PO_4^{3-} (blue).

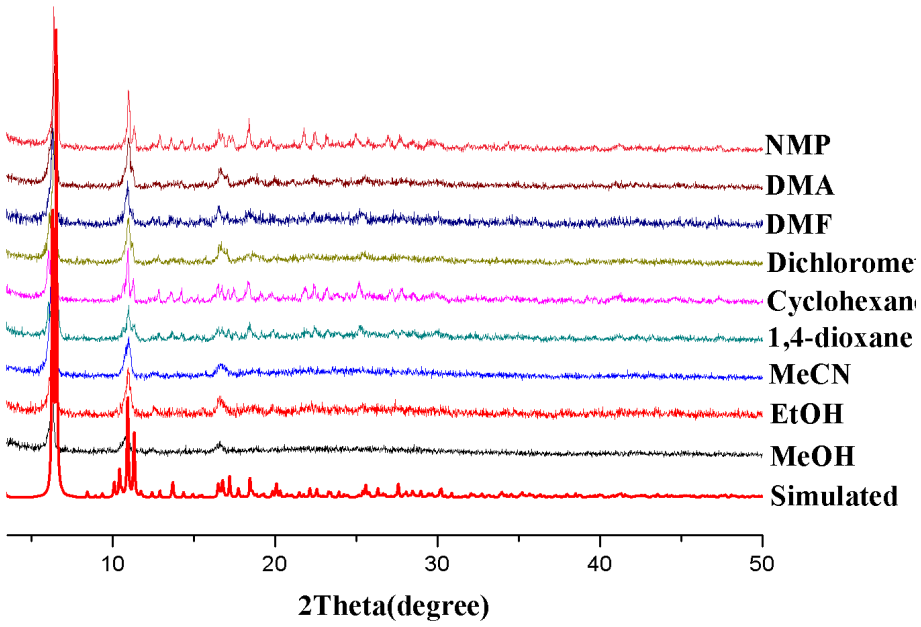

Fig. S8 The PXRD patterns of compound 1 after immersing in various organic solvent.

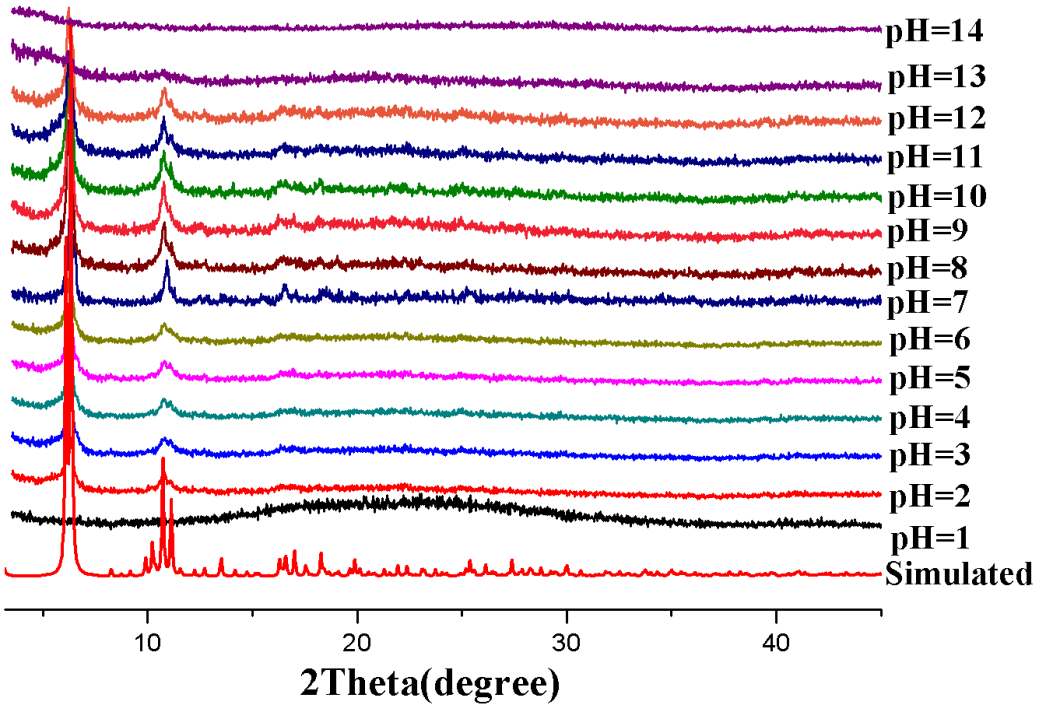

Fig. S9. The PXRD patterns of **1** after exposure to aqueous solution with various pH values from 1.0 to 14.0.

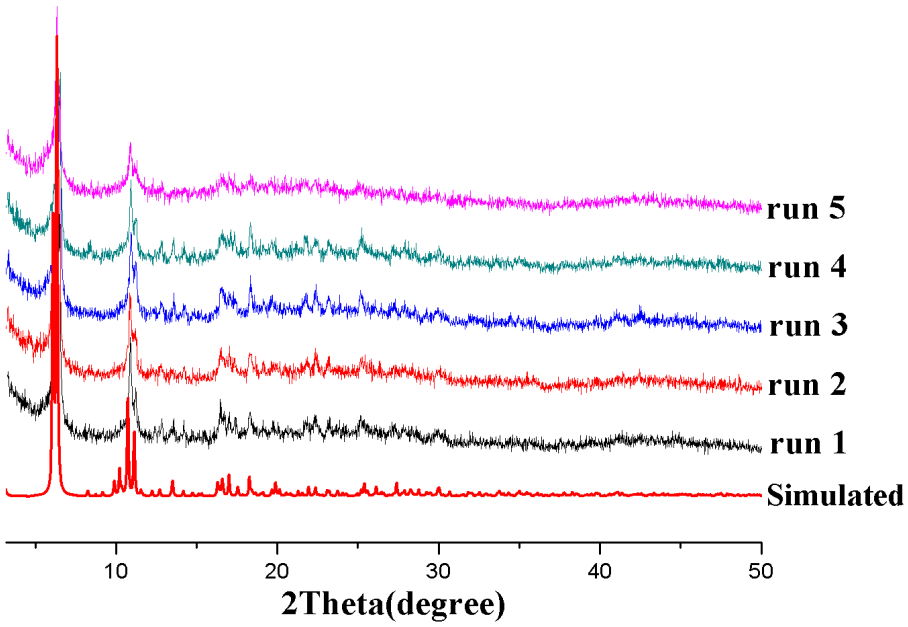

Fig. S10. The PXRD patterns of **1** after five recyclings.

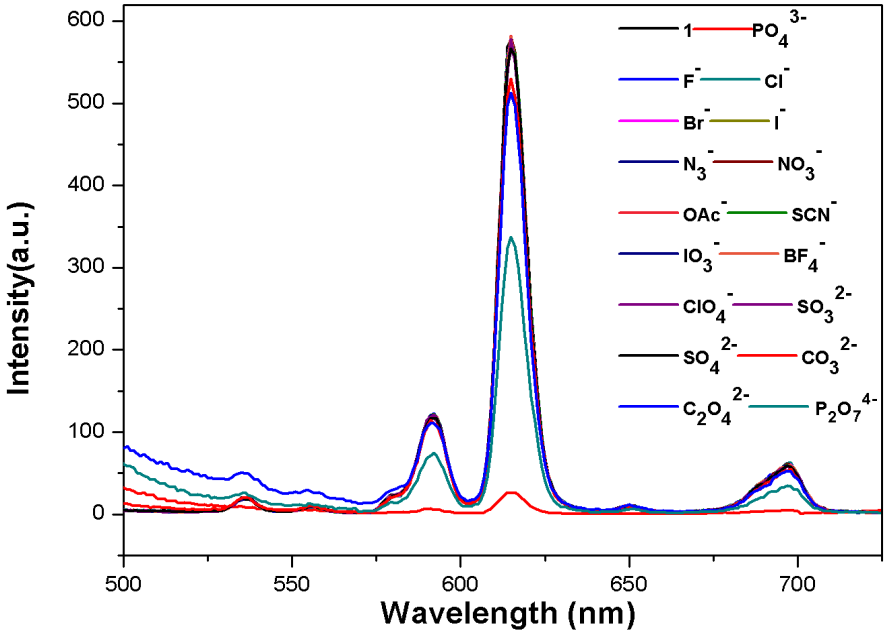

Fig. S11. Comparison of the luminescence intensity of **1-X** in 10^{-3} M different anions

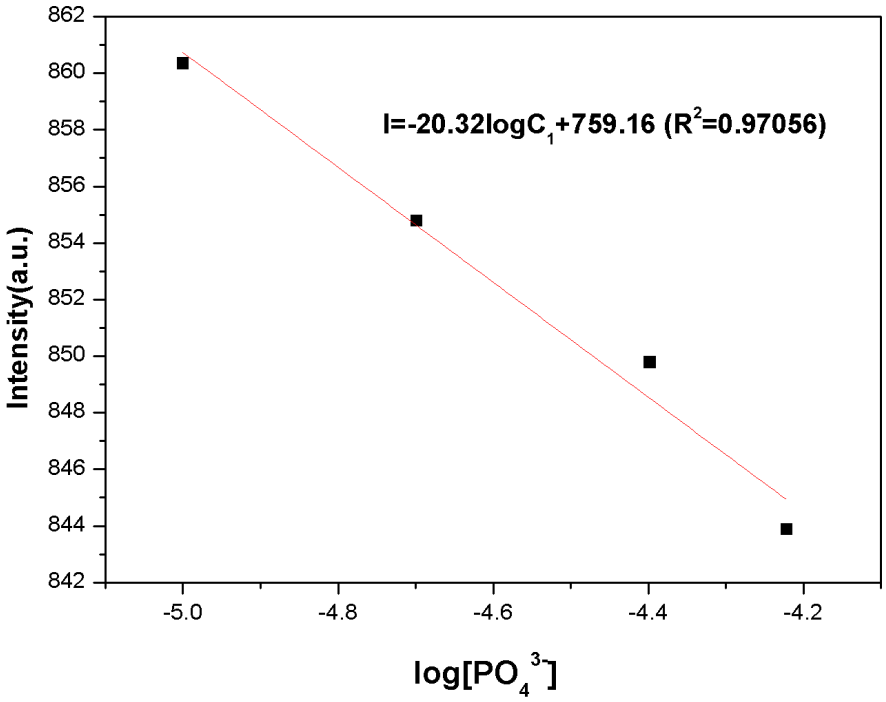

Fig. S12. The intensity plots of **1** *vs* log[PO_4^{3-}].

1 SAINT+, version 6.22; Bruker AXS: Madison, 2001.

2 G. Sheldrick,*Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008,**64**, 112.

3 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2001.