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Supporting information

Two-dimensional Layered Lanthanide Diphosphonates: Synthesis, Structures and Sensing Properties towards Fe^{3+} and $Cr_2O_7^{2-}$

Xiaomin Hou,[a] Chong-Chong Yan,[b] Xiu-Ling Xu,[b] Ai-Qin Liang[b], Zu-Wei Song[b] and Si-Fu Tang*[,b]

[a]Shandong Province Key Laboratory of Applied Mycology, College of Life Science, and [b]College of Chemistry and Pharmaceutical Sciences Qingdao Agricultural University, Changcheng Road 700, Chengyang District, Qingdao 266109, China.

Table S1. Hydrogen bonds in compounds **1**-**4**.

Donor-H···Acceptor	D - H	H...A	D...A	D - H...A
Compound **1**				
O(1W)-H(1W)···O(6)_$1	0.85	2.55	3.0292	117
O(1W)-H(1W)···O(2W)_$2	0.85	2.33	3.1325	157
O(1W)-H(2W)···O(4)_$1	0.85	2.06	2.9013	173
O(2W)-H(3W)···O(3)_$3	0.85	2.24	2.8919	134
O(2W)-H(3W)···O(2)_$4	0.85	2.28	2.9992	142
O(2W)-H(4W)···O(5)_$3	0.85	2.54	3.1550	130
O(6)-H(6B)···O(2) _$4	0.82	1.82	2.6229	167
Compound **2**				
O(1W)-H(1W)···O(6)_$1	0.85	2.55	3.0292	117
O(1W)-H(1W)···O(2W)_$2	0.85	2.33	3.1325	157
O(1W)-H(2W)···O(4)_$1	0.85	2.06	2.9013	173
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O(2W)-H(4W)···O(5)_$3	0.85	2.54	3.1550	130
O(6)-H(6B)···O(2)_$4	0.82	1.82	2.6229	167
Compound **3**				
O(1W)-H(1W)···O(3)_$3	0.85	2.52	3.00(3)	116
O(1W)-H(1W)···O(5)	0.85	2.16	2.79(2)	130
O(2)-H(2B)···O(1W)_$4	0.82	1.52	2.35(2)	178
O(2W)-H(3W)···O(6)_$1	0.85	2.16	2.99(3)	164
O(2W)-H(3W)···O(4)_$2	0.85	2.06	2.40(2)	103
O(2W)-H(4W)···O(4)_$2	0.85	1.77	2.40(2)	129
Compound **4**				
O(1W)-H(1W)···O(6)_$1	0.84	2.54	3.0108	117
O(1W)-H(1W)···O(2W)_$2	0.84	2.35	3.1376	157
O(1W)-H(2W)···O(4)_$1	0.84	2.12	2.9526	171

O(2W)-H(3W)···O(3)_$3	0.84	2.59	3.0108	112
O(2W)-H(3W)···O(2)_$4	0.84	2.25	2.8778	132
O(2W)-H(4W)···O(5)_$3	0.84	2.23	2.9423	142
O(6)-H(6B)···O(2) _$4	0.84	2.52	3.1466	132
O(1W)-H(1W)···O(6)_$1	0.82	1.82	2.6317	168

Symmetry transformations used to generate equivalent atoms:
For **1**, **2** and **4**: $1 = x, 1+y, z; $2 = 1-x, 1/2+y, 3/2-z; $3 = 1-x, -y, 1-z; $4 = x, 1/2-y, 1/2+z
For **3**: $1 =1+x, y, z; $2 =1-x, -1/2+y, -z; $3 =x, -1+y, z; $4 =x, 1+y, z.

Table S2. π···π interactions in compounds **1**-**4** with Cg-Cg Distances < 6.0 Angstrom and Beta < 60.0Deg.

Cg(I)···Cg(J)	Cg-Cg	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp
Compound **1**						
Cg(1)···Cg(1)_$1	5.7061	37	41.5	73.5	1.6181	4.2758
Compound **2**						
Cg(1)···Cg(1)_$1	5.7228	37	41.8	73.5	-1.6250	-4.2662
Compound **3**						
Cg(1)···Cg(1) _$1	5.747(14)	36	42.2	73.1	-1.674(9)	-4.259(9)
Compound **4**						
Cg(1)···Cg(1) _$1	5.7515	36	42.8	73.4	-1.6435	-4.2186

Cg(I) = Plane number I (= ring number in () above)
Alpha = Dihedral Angle between Planes I and J (Deg)
Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
Cg-Cg = Distance between ring Centroids (Ang.)
CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).
6-Membered Ring (1): C(1)→C(2) →C(3) →C(4) →C(5) →C(6) →
Symmetry transformations used to generate equivalent atoms:
For **1**: $1= 1-x, -1/2+y, 1/2-z;
For **2** and **4**: $1= -x, 1/2+y, 1/2-z;
For **3**: $1= -x, -1/2+y, -1-z.

Table S3. O-H···π interactions in compounds **1**-**4** with H···Cg < 3.0 Å and Gamma < 30.0 Deg.

X-H(I)···Cg(J)	H···Cg	H-Perp	Gamma	X-H···Cg	X···Cg	X-H,Pi
Compound **1**						
O(2W) -H(4W)···Cg(1) _$1	2.49	-2.44	11.57	153	3.2696	74
Compound **2**						
O(2W) -H(4W)···Cg(1)_$1	2.70	2.58	17.33	130	3.3136	57
Compound **4**						
O(2W) -H(4W)···Cg(1)_$1	2.79	2.64	18.79	130	3.3902	59

Cg(J) = Center of gravity of ring J (Plane number above)

H-Perp = Perpendicular distance of H to ring plane J
Gamma = Angle between Cg-H vector and ring J normal
X-H···Cg = X-H-Cg angle (degrees)
X···Cg = Distance of X to Cg (Angstrom)
X-H, Pi = Angle of the X-H bond with the Pi-plane
Symmetry transformations used to generate equivalent atoms:
For **1**: $1= -X, 1-Y, -Z;
For **2** and **4**: $1= 1-X, -Y, 1-Z.

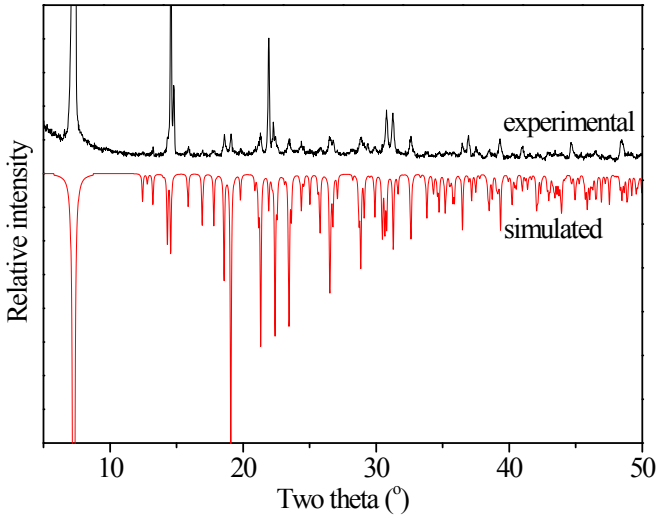


Figure S1. Comparison of simulated and experimental PXRD pattern of compound **1**.

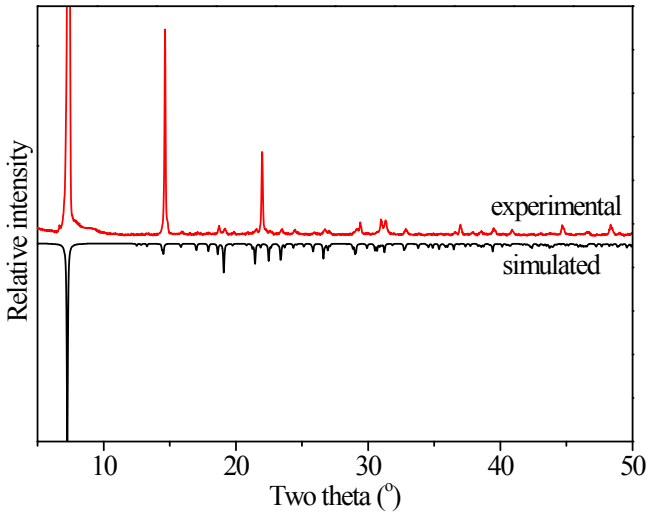


Figure S2. Comparison of simulated and experimental PXRD pattern of compound **2**.

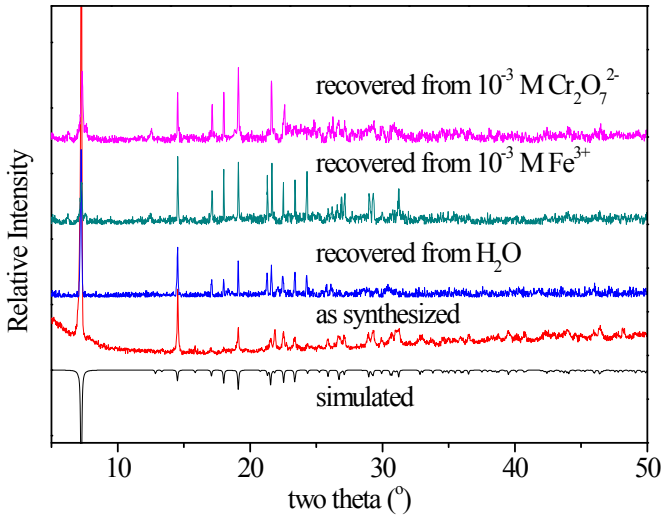


Figure S3. Comparison of the PXRD patterns of dry samples compound **3**.

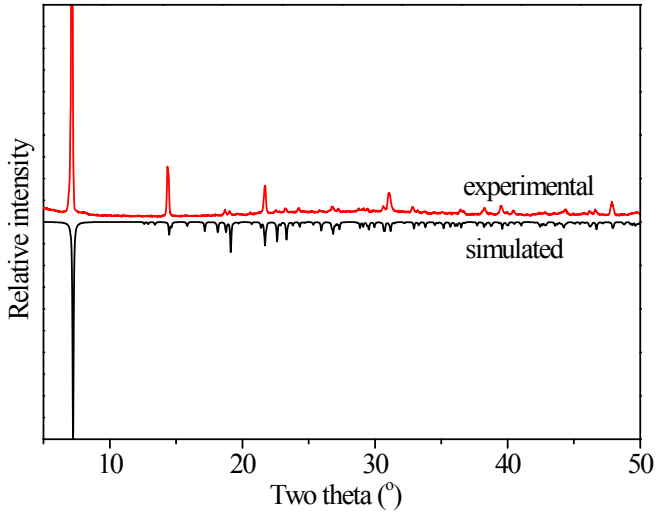


Figure S4. Comparison of simulated and experimental PXRD pattern of compound **4**.

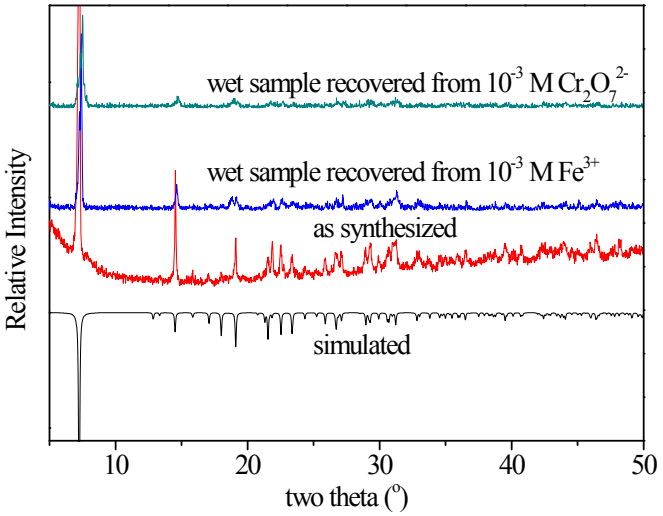


Figure S5. Comparison of the PXRD patterns of dry samples compound **3**.

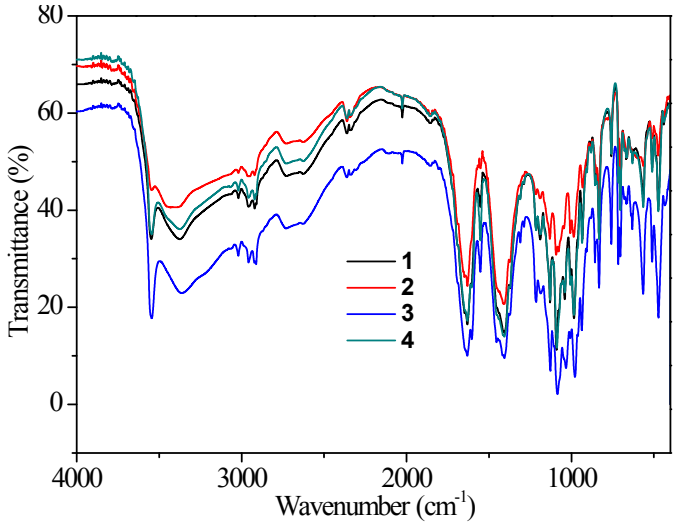


Figure S6. IR spectra of compounds **1**-**4**.

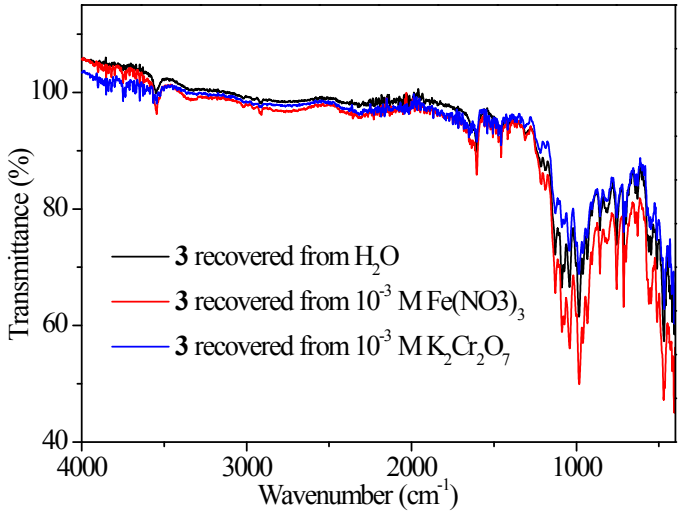


Figure S7. IR spectra of compound **3** recovered from H_2O, 10^{-3} M $Fe(NO_3)_3$ and 10^{-3} $K_2Cr_2O_7$.

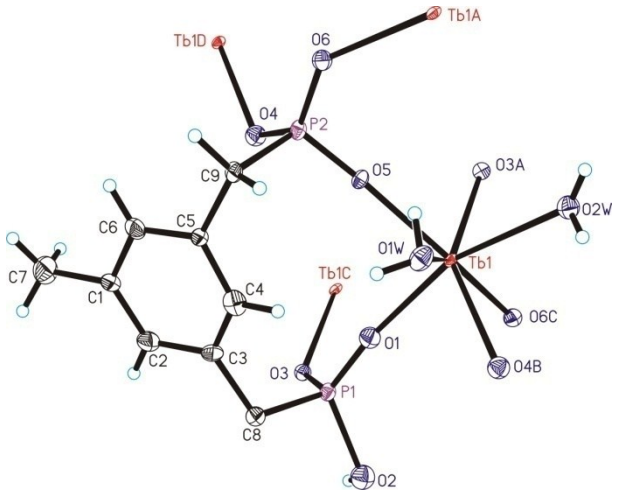
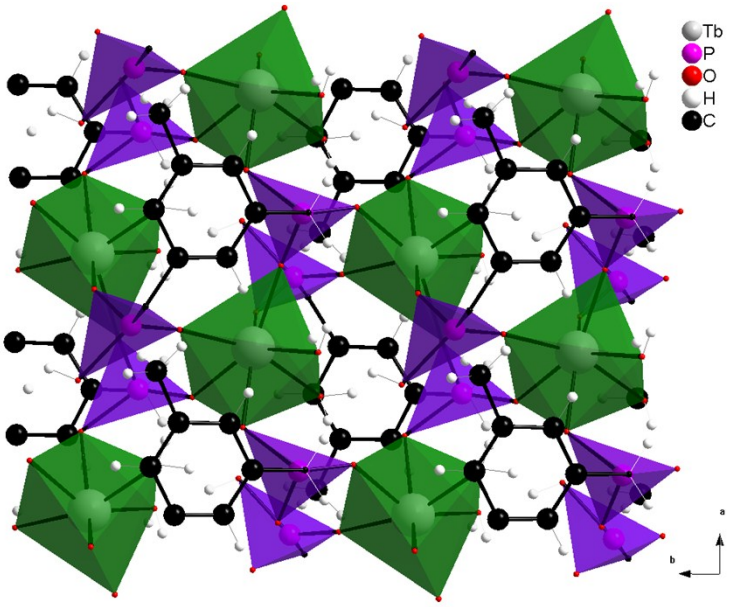
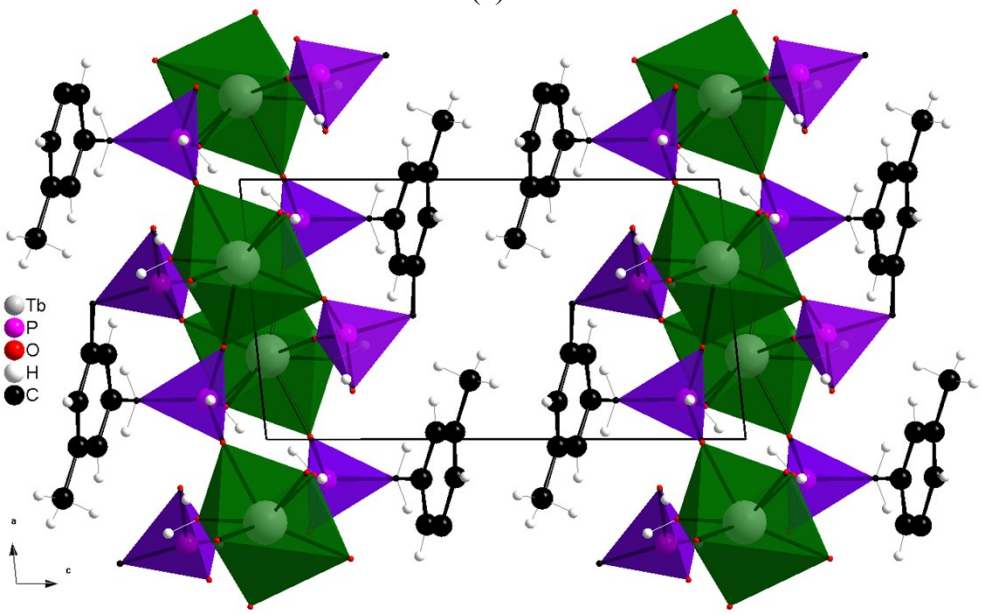


Figure S8. The coordination environments of the bisphosphonate ligand and Tb(III) ions in **3** (thermal ellipsoids are given at 30% probability). A: 1-x, -0.5+y, -z; B: 1+x, y, z; C: 1-x, 0.5+y, -z; D: -1+x, y, z.



(a)



(b)

Figure S9. Two-dimensional layer in *ab*-plane (a) and three-dimensional packing structure of compound **3** viewing along *b*-axis (b). The TbO_7 and $–CPO_3$ polyhedrons are shaded in green and purple, respectively.

Table S4. Detection limit calculation of compound **3** toward Fe^{3+} and $Cr_2O_7^{2-}$.

Blank samples	Luminescence intensity
Test 1	2275
Test 2	2270

Test 3	2288
Test 4	2269
Test 5	2271
Standard deviation (σ)	7.83
Detection limit towards Fe^{3+}	
Slope (S)	30348.026 mM^{-1}
Detection limit (3σ/S)	0.000774 mM
Detection limit towards $Cr_2O_7^{2-}$	
Slope (S)	36441.024 M^{-1}
Detection limit (3σ/S)	0.000665 mM

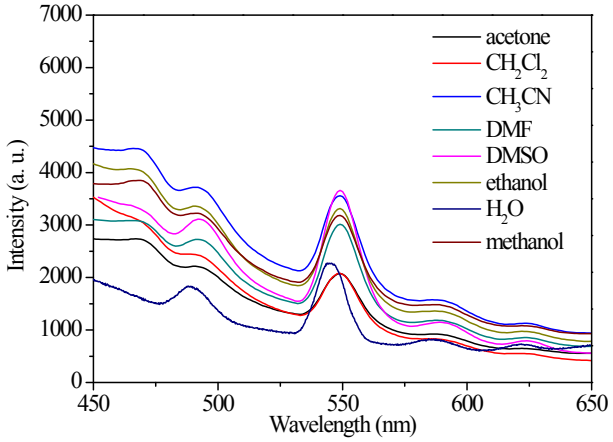


Figure S10. Emission spectra of the suspensions of compound **3** in different solvents under excitation of 354 nm.

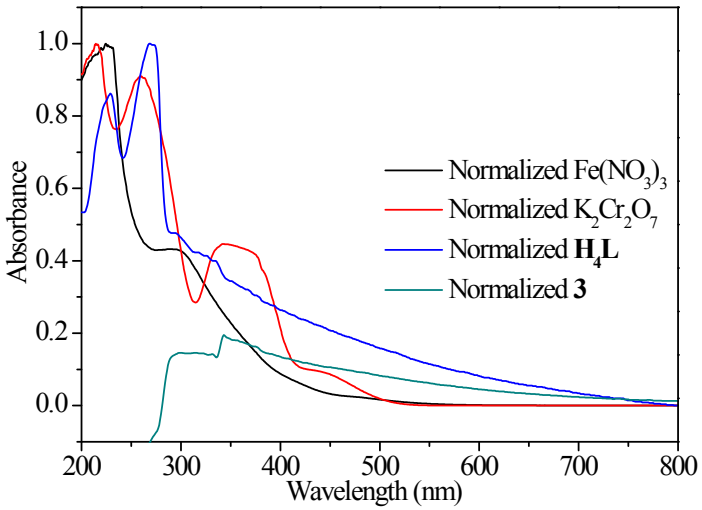


Figure S11. UV-Vis absorption spectra of $Fe(NO_3)_3$, $K_2Cr_2O_7$ solutions, H_4L and compound **3**.