Supporting Information for

A highly hydrolytically stable lanthanide organic framework as a sensitive luminescent probe for DBP and chlorpyrifos detection

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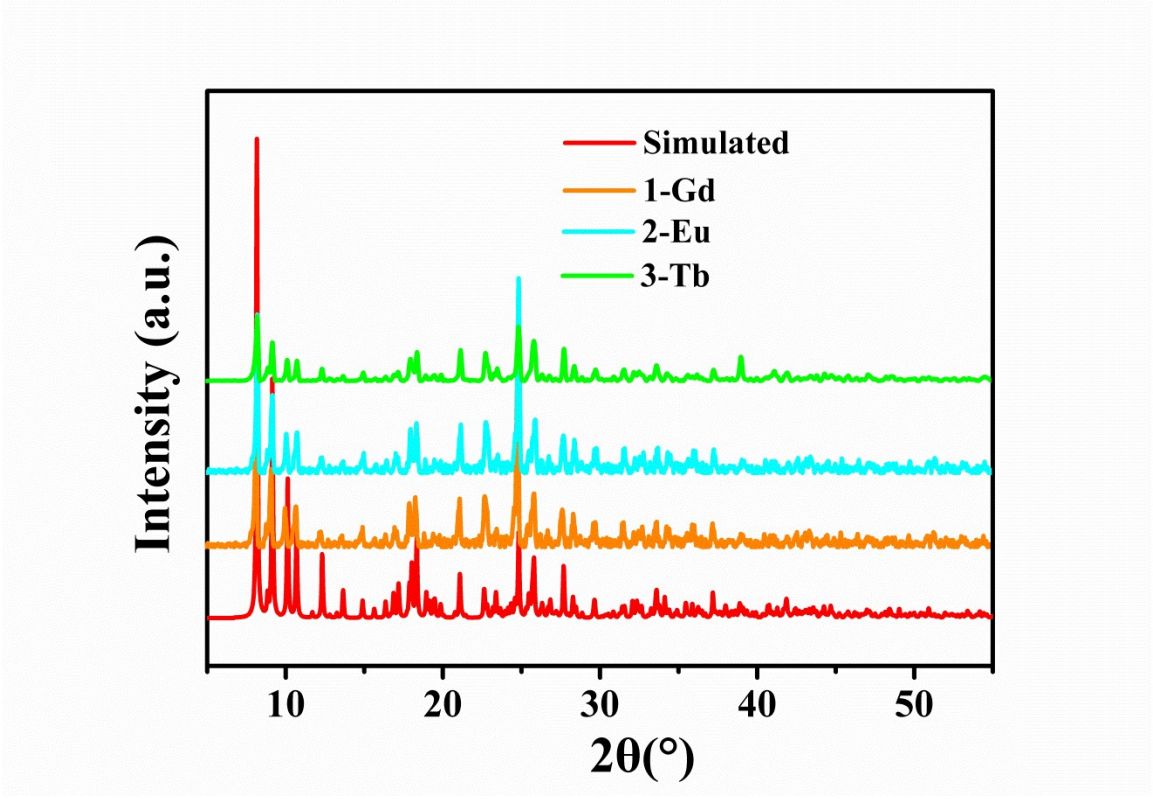


Fig. S1 Simulated and experimental XRD powder patterns for compounds **1**–**3**

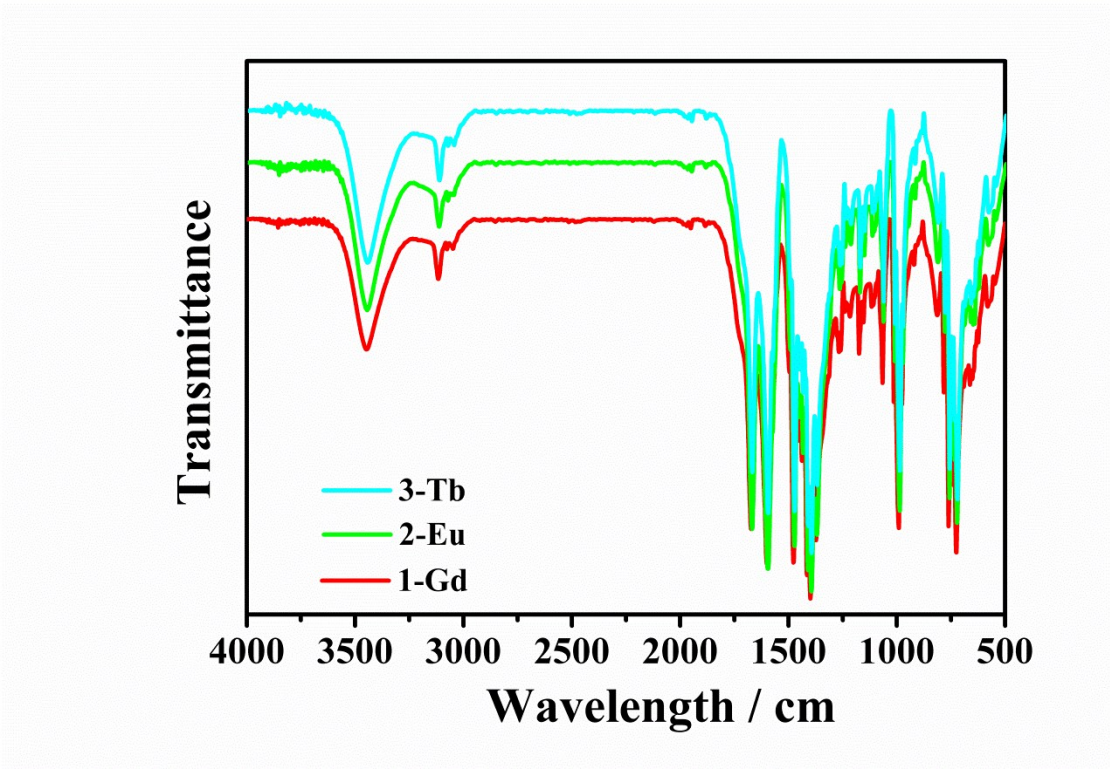


Fig. S2 View of the IR spectra of compounds **1**–**3**

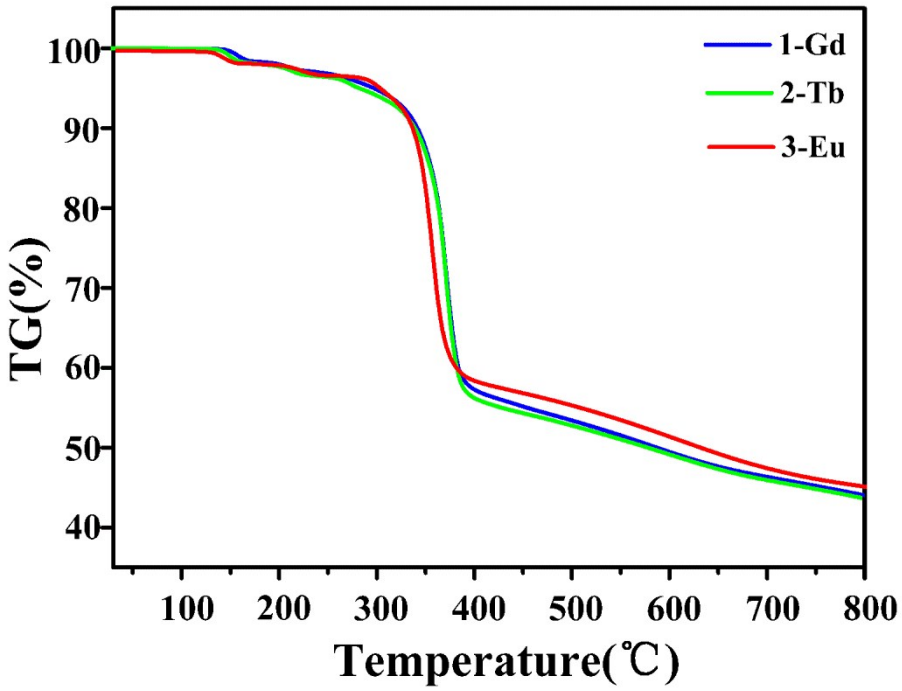


Fig. S3 TGA curves of compounds **1**−**3**

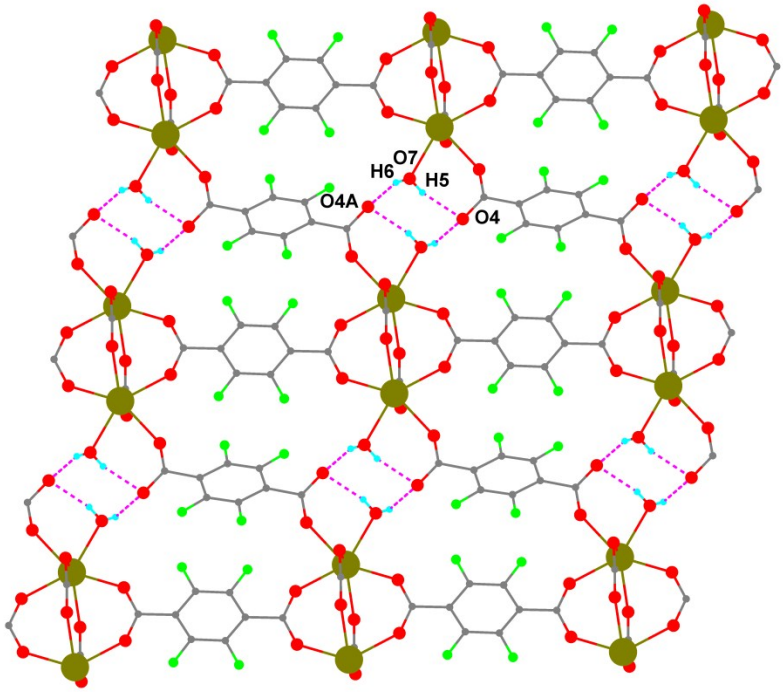
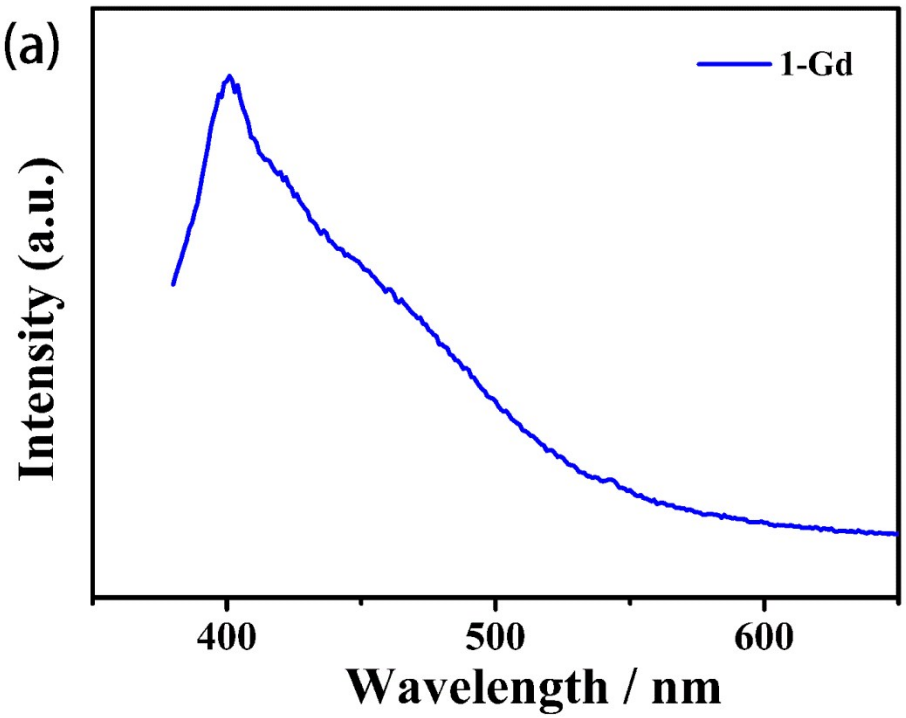


Fig. S4 View of the intralayer hydrogen bonds in **1**



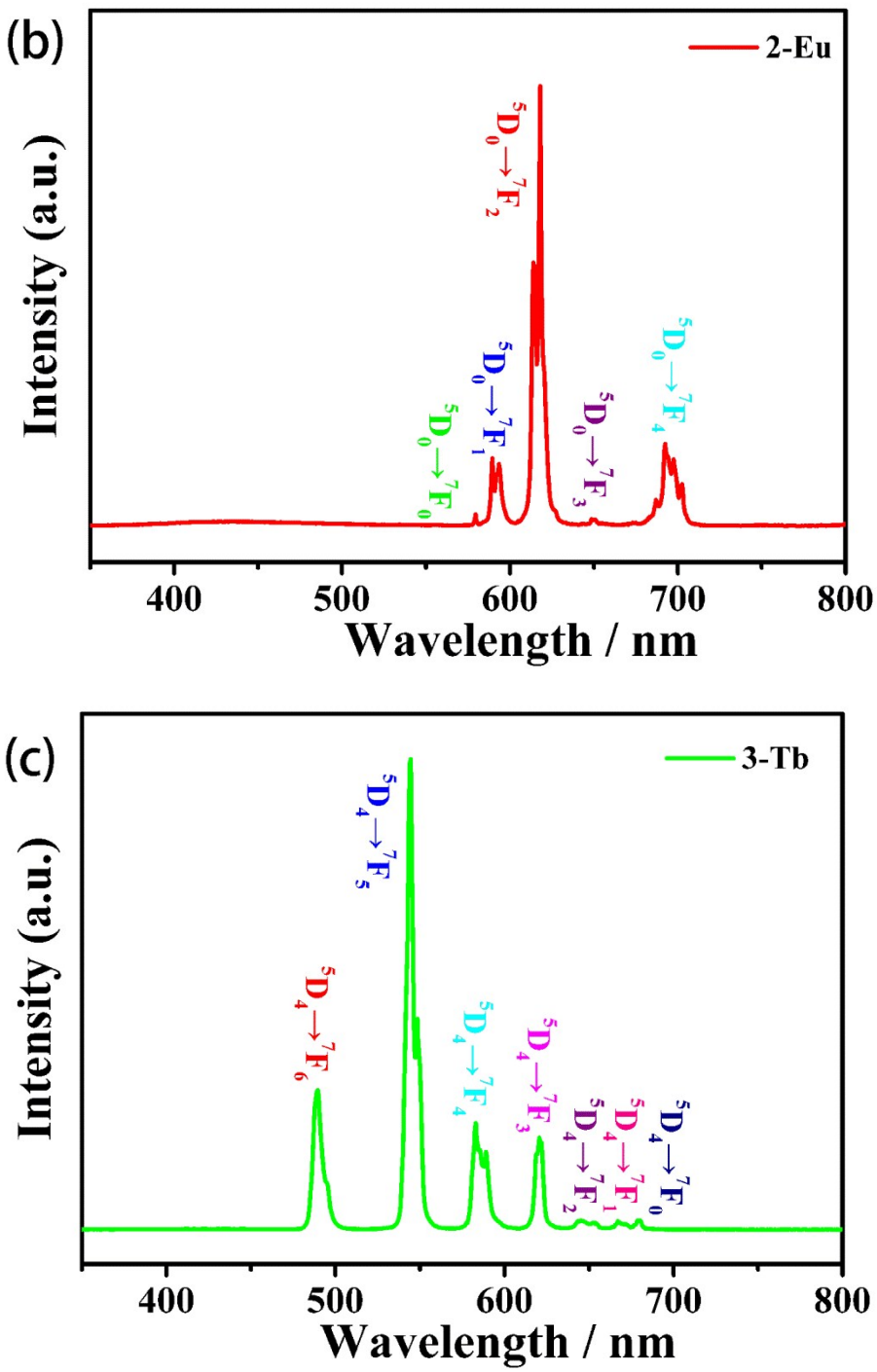


Fig. S5 Solid state luminescence emission spectra for **1** (a), **2** (b) and **3** (c) at room temperature

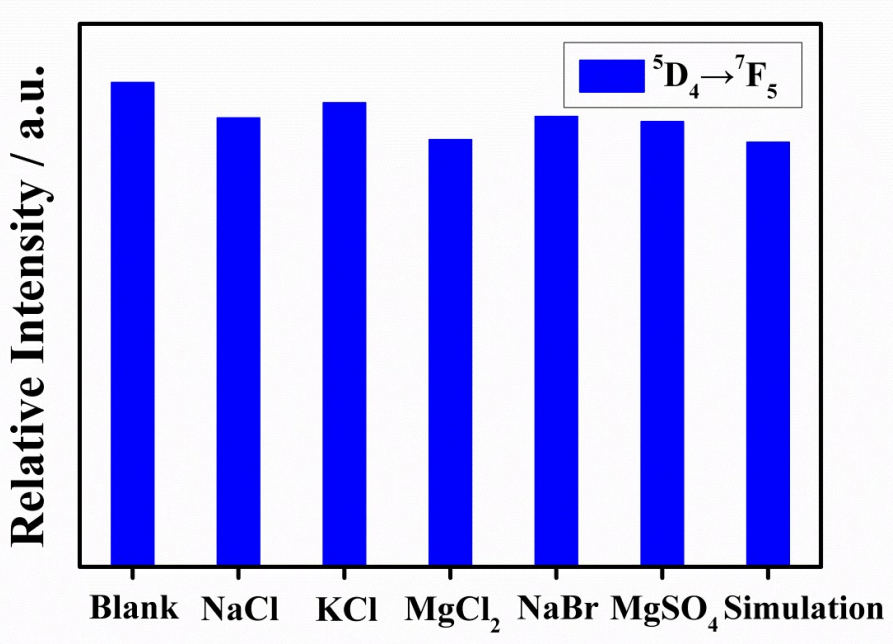


Fig. S6 Luminescent intensities of a $^5D_4 \rightarrow {}^7F_5$ transition of **3** in the presence of main compositions of seawater and simulated seawater

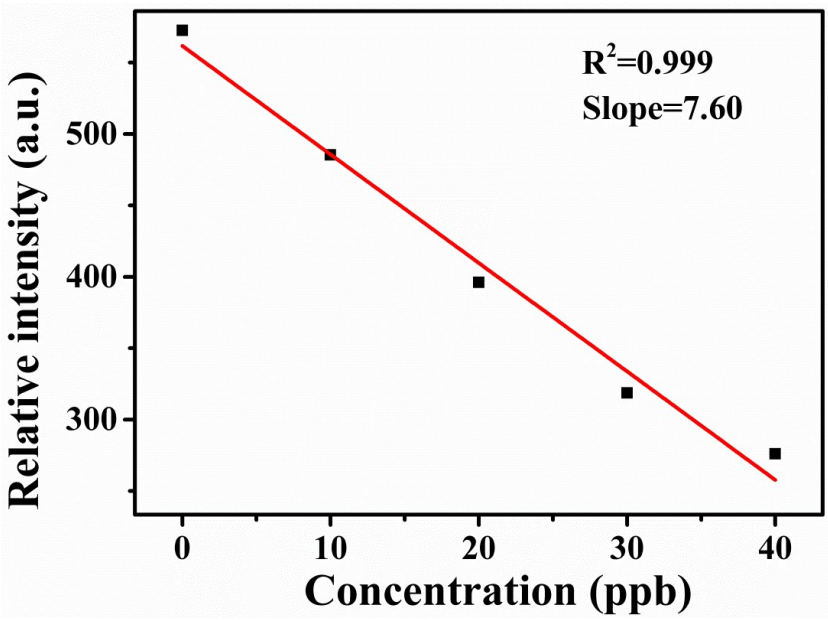


Fig. S7 Linear relationship of the emission intensity of a $^5D_4 \rightarrow {}^7F_5$ transition of **3** quenched by DBP (0–40 ppb)

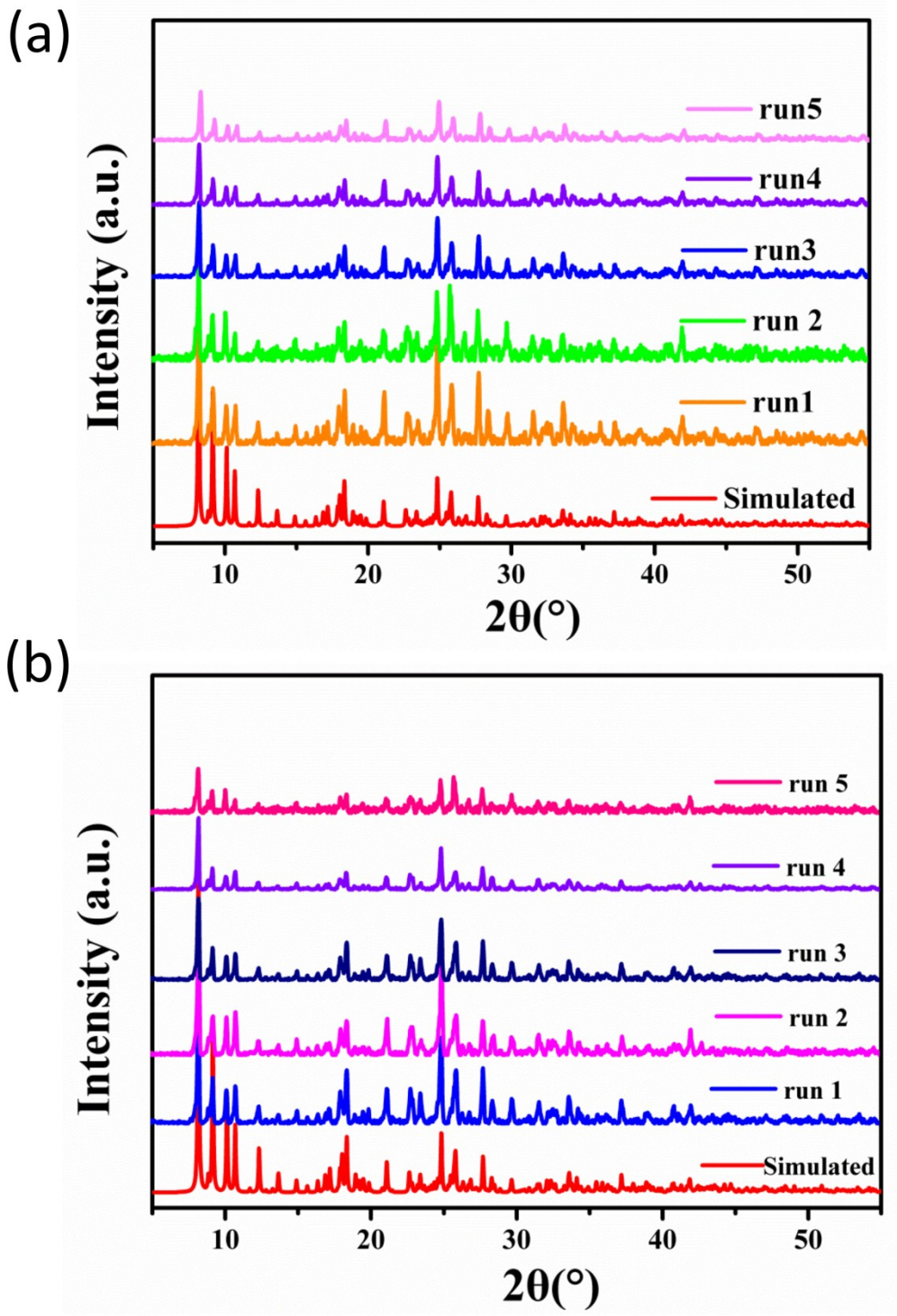


Fig. S8 PXRD patterns of **3** after recycling experiments for DBP (a) and chlorpyrifos (b)

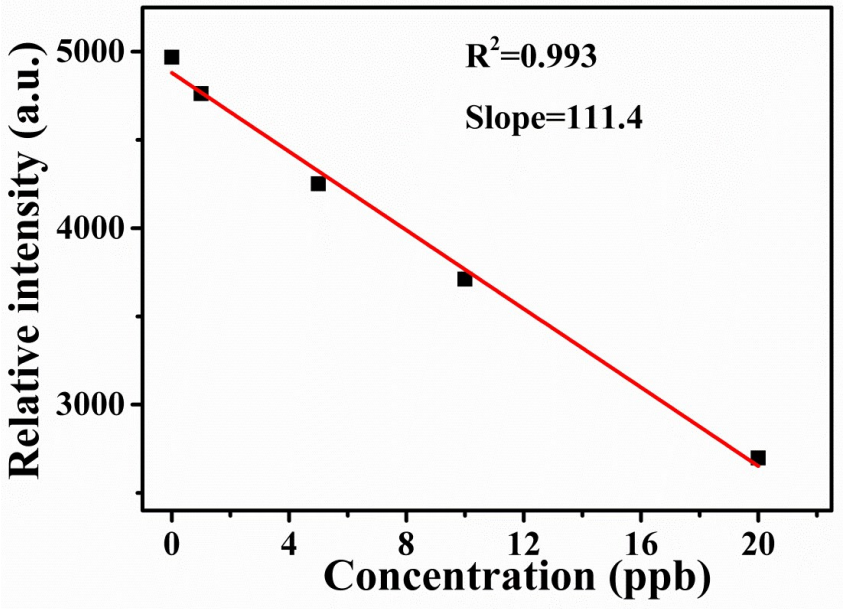


Fig. S9 Linear relationship of the emission intensity of **3** quenched by chlorpyrifos (0–20 ppb)

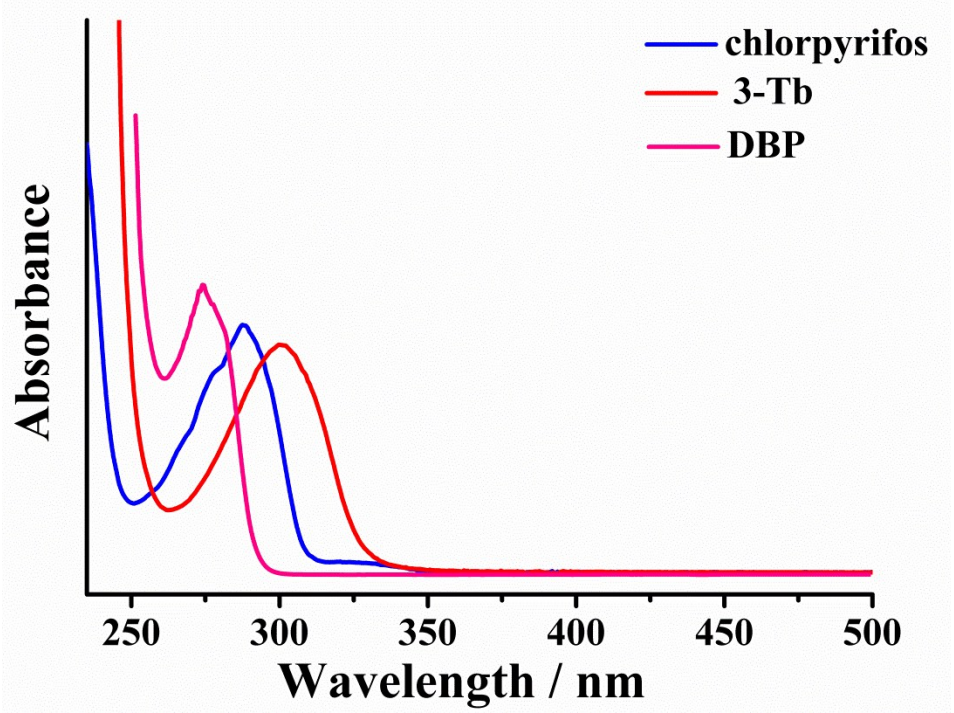


Fig. S10 The UV-vis absorption spectra of **3**, DBP and chlorpyrifos

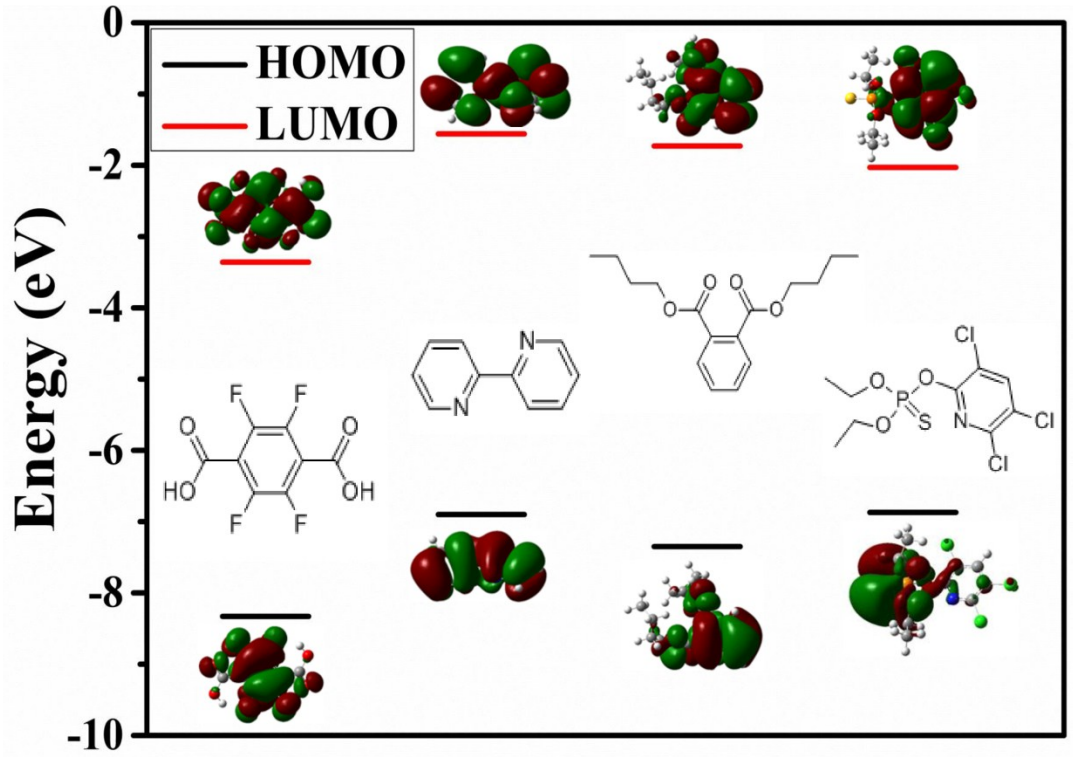


Fig. S11 HOMO and LUMO energies for selected analytes and the ligands

Table S1 Crystal data and structure refinement for compounds **1**–**3**

Compounds	**1**	**2**	**3**
Empirical formula	$C_{22}H_{10}F_6GdN_2O_7$	$C_{22}H_{10}F_6EuN_2O_7$	$C_{22}H_{10}F_6TbN_2O_7$
Formula weight	685.57	680.28	687.24
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*–1	*P*–1	*P*–1
a (Å)	10.394(2)	10.389(3)	10.3940(19)
b (Å)	10.959(2)	10.952(3)	10.943(2)
c (Å)	11.084(2)	11.108(3)	11.0626(11)
α (°)	101.158(2)	101.170(3)	101.177(4)
β (°)	90.787(2)	90.839(2)	90.560(5)
γ (°)	110.978(2)	110.841(3)	111.236(8)
V (Å^3)	1151.8(4)	1154.0(5)	1146.2(3)
Z	2	2	2
D_{calcd} (g·cm^{-3})	1.977	1.958	1.991
μ (mm^{-1})	2.975	2.814	3.182
F(000)	660	658	662
Temperature (K)	293	293	293
Refln. measured	10106	11440	11944
Independent refln.	5239	5153	5211
Observed refln.	4707	4849	4925
GOF	0.918	1.045	1.027
R_1[a] [$I > 2\sigma(I)$]	0.0222	0.0241	0.0194
wR_2[b]	0.0442	0.0510	0.0443
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e.Å^3)	0.463/–0.851	1.019/–0.908	0.378/–0.335

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

Table S2 Selected bond lengths (Å) and angles (º) for compounds **1**–**3**

Compound **1**			
Gd(1)-N(1)	2.601(2)	Gd(1)-O(3)	2.3473(18)
Gd(1)-N(2)	2.603(2)	Gd(1)-O(5)	2.3627(17)
Gd(1)-O(1)	2.4848(19)	Gd(1)-O(6)	2.3370(18)
Gd(1)-O(2)	2.3473(19)	Gd(1)-O(7)	2.432(2)
N(1)-Gd(1)-N(2)	61.88(8)	O(2)-Gd(1)-O(3)	142.01(6)
O(1)-Gd(1)-N(1)	142.33(7)	O(2)-Gd(1)-O(5)	73.78(6)
O(2)-Gd(1)-N(1)	79.45(7)	O(2)-Gd(1)-O(7)	141.40(7)
O(3)-Gd(1)-N(1)	108.55(7)	O(3)-Gd(1)-O(1)	76.86(7)
O(5)-Gd(1)-N(1)	76.29(7)	O(3)-Gd(1)-O(5)	143.96(7)
O(6)-Gd(1)-N(1)	134.04(7)	O(3)-Gd(1)-O(7)	73.23(8)
O(7)-Gd(1)-N(1)	71.68(8)	O(5)-Gd(1)-O(1)	78.97(7)
O(1)-Gd(1)-N(2)	147.52(7)	O(5)-Gd(1)-O(7)	74.87(7)
O(2)-Gd(1)-N(2)	79.07(7)	O(6)-Gd(1)-O(1)	83.63(7)
O(3)-Gd(1)-N(2)	73.24(7)	O(6)-Gd(1)-O(2)	73.69(7)
O(5)-Gd(1)-N(2)	133.43(7)	O(6)-Gd(1)-O(3)	74.99(7)
O(6)-Gd(1)-N(2)	76.71(8)	O(6)-Gd(1)-O(5)	128.14(6)
O(7)-Gd(1)-N(2)	107.79(8)	O(6)-Gd(1)-O(7)	144.76(8)
O(2)-Gd(1)-O(1)	119.89(6)	O(7)-Gd(1)-O(1)	74.73(7)
Compound **2**			
Eu(1)-N(1)	2.618(2)	Eu(1)-O(3)	2.360(2)
Eu(1)-N(2)	2.612(2)	Eu(1)-O(5)	2.3759(19)
Eu(1)-O(1)	2.5013(19)	Eu(1)-O(6)	2.347(2)
Eu(1)-O(2)	2.362(2)	Eu(1)-O(7)	2.446(2)
N(1)-Eu(1)-N(2)	61.67(8)	O(2)-Eu(1)-O(3)	142.32(7)
O(1)-Eu(1)-N(1)	142.03(8)	O(2)-Eu(1)-O(5)	73.76(7)
O(2)-Eu(1)-N(1)	79.62(8)	O(2)-Eu(1)-O(7)	141.33(8)
O(3)-Eu(1)-N(1)	108.62(8)	O(3)-Eu(1)-O(1)	76.62(7)
O(5)-Eu(1)-N(1)	75.99(7)	O(3)-Eu(1)-O(5)	143.67(7)

O(6)-Eu(1)-N(1)	133.53(8)	O(3)-Eu(1)-O(7)	73.06(8)
O(7)-Eu(1)-N(1)	71.43(8)	O(5)-Eu(1)-O(1)	79.06(7)
O(1)-Eu(1)-N(2)	147.60(8)	O(5)-Eu(1)-O(7)	74.75(8)
O(2)-Eu(1)-N(2)	79.57(7)	O(6)-Eu(1)-O(1)	84.44(7)
O(3)-Eu(1)-N(2)	73.30(7)	O(6)-Eu(1)-O(2)	73.50(8)
O(5)-Eu(1)-N(2)	133.18(7)	O(6)-Eu(1)-O(3)	75.07(7)
O(6)-Eu(1)-N(2)	76.49(8)	O(6)-Eu(1)-O(5)	128.76(7)
O(7)-Eu(1)-N(2)	107.15(8)	O(6)-Eu(1)-O(7)	145.07(8)
O(2)-Eu(1)-O(1)	119.90(7)	O(7)-Eu(1)-O(1)	74.68(7)
Compound **3**			
Tb(1)-N(1)	2.583(2)	Tb(1)-O(3)	2.3361(16)
Tb(1)-N(2)	2.589(2)	Tb(1)-O(5)	2.3488(15)
Tb(1)-O(1)	2.4600(17)	Tb(1)-O(6)	2.3246(17)
Tb(1)-O(2)	2.3213(16)	Tb(1)-O(7)	2.4142(19)
N(1)-Tb(1)-N(2)	62.36(7)	O(2)-Tb(1)-O(3)	141.83(6)
O(1)-Tb(1)-N(1)	142.48(7)	O(2)-Tb(1)-O(5)	73.89(6)
O(2)-Tb(1)-N(1)	79.01(7)	O(2)-Tb(1)-O(7)	141.10(7)
O(3)-Tb(1)-N(1)	108.84(7)	O(3)-Tb(1)-O(1)	77.26(6)
O(5)-Tb(1)-N(1)	76.40(7)	O(3)-Tb(1)-O(5)	144.02(6)
O(6)-Tb(1)-N(1)	134.90(7)	O(3)-Tb(1)-O(7)	73.58(7)
O(7)-Tb(1)-N(1)	71.72(7)	O(5)-Tb(1)-O(1)	78.49(6)
O(1)-Tb(1)-N(2)	147.67(7)	O(5)-Tb(1)-O(7)	74.73(6)
O(2)-Tb(1)-N(2)	78.49(6)	O(6)-Tb(1)-O(1)	82.62(7)
O(3)-Tb(1)-N(2)	73.32(6)	O(6)-Tb(1)-O(2)	74.08(6)
O(5)-Tb(1)-N(2)	133.82(7)	O(6)-Tb(1)-O(3)	74.94(6)
O(6)-Tb(1)-N(2)	77.11(7)	O(6)-Tb(1)-O(5)	127.39(6)
O(7)-Tb(1)-N(2)	108.45(7)	O(6)-Tb(1)-O(7)	144.60(7)
O(2)-Tb(1)-O(1)	119.72(6)	O(7)-Tb(1)-O(1)	75.06(6)

Table S3 Standard deviation and detection limit calculation of DBP and chlorpyrifos

DBP	Fluorescence intensity	chlorpyrifos	Fluorescence intensity
Test 1	572.5	Test 1	4968
Test 2	575.6	Test 2	4974
Test 3	565.1	Test 3	4961
Test 4	563.8	Test 4	4978
Test 5	576.3	Test 5	4965
Standard Deviation (σ)	5.25	Standard Deviation (σ)	5.27
Slope (K)	7.60/ppb	Slope (K)	111.4/ppb
Detection limit (3σ/K)	2.07ppb	Detection Limit (3σ/K)	0.14ppb

Table S4 HOMO and LUMO energies calculated for selected analytes and the ligands at the B3LYP/6-311+G (d,p) level.

	HOMO (eV)	LUMO (eV)	Band Gap (eV)
DBP	-7.35eV	-1.73eV	5.62eV
chlorpyrifos	-6.87eV	-2.03eV	4.84eV
Tetrafluoroterephthalic acid	-8.33eV	-3.36eV	4.97eV
2,2-bpy	-6.90eV	-1.56eV	5.34eV