Supporting Information

Nitroaromatic sensing with a new lanthanide coordination polymer $[Ln_2(C_{10}H_4O_4S_2)_3(H_2O)_6]_n$ (Ln = Sm-Yb) assembled by 2,2'-bithiophene-5,5'-dicarboxylate

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Synthesis of 2,2'-bithiophene-5,5'-dicarboxylic acid

The linker 2,2'-bithiophene-5,5'-dicarboxylic acid was synthesized according to modified literature methods (Scheme. 1).⁴¹ To a solution of 550 mg (3.30 mmol) of 2,2'-bithiophene in 50 mL dry THF was added 4.4 mL (7.04 mmol) n-BuLi solution (1.6 M in hexanes) dropwise at -78 °C using a Schlenk line under an N₂ atmosphere. After stirring for four hours, the milky white solution was poured over crushed dry ice, also under an N₂ atmosphere. The light yellow suspension was allowed to warm to room temperature under mild stirring and then acidified with 2 M aqueous HCl. The resulting yellow suspension was then filtered, washed with diethyl ether, and left to dry in air at room temperature. The same synthesis using 5,5'-dibromo-2,2'-dithiophene also produces the DTDC acid moiety in similar yields. Overall yield: 64-82%. ¹H NMR (400 MHz, DMSO, ppm) δ 7.70 (d, 2H), 7.54 (d, 2H). ¹³C NMR (101 MHz, DMSO, ppm) δ 175.84, 163.14, 142.06, 134.95, 127.08.

Scheme 1. Synthesis of DTDC linker.



Single crystal X-ray diffraction

A single crystal of the Er compound was selected and mounted atop a glass fiber. Data were collected on a Bruker D8 QUEST CMOS system equipped with a TRIUMPH curved-crystal monochromator and a Mo K α fine-focus tube ($\lambda = 0.71073$ Å). A total of 13,358 reflections up to a maximum of 56.70° were collected of which 4584 were independent. The frames were integrated with Bruker SAINT⁴² software package and the structure was solved with direct methods using the SHELXT-2014 package.⁴³ The structure was further refined using SHELX-97⁴⁴ within the WINGX⁴⁵ software suite. Crystallographic details can be found in Table S1.

Formula	$[Er_2(C_{10}H_4O_4S_2)_3(H_2O)_6]_n$		
Formula Weight (g/mol)	1199.42		
Crystal Class	Triclinic		
Space Group	<i>P</i> -1		
a (Å)	7.7389(5)		
b (Å)	9.6787(6)		
c (Å)	13.1985(8)		
α (°)	81.999(2)		
β (°)	75.000(1)		
γ (°)	75.514(2)		
Z	2		
Cell Volume (Å ³)	921.62(10)		
Density (mg m ⁻³)	2.1611(2)		
μ (mm-1)	4.941		
R _{int}	3.08%		
R ₁ ^a	2.64%		
wR ₂ ^a	6.07%		
GOF	1.113		
Total Reflections	4584		
$\overline{R_1 = \sum \frac{\left\ F_o\right - \left F_c\right }{\left F_o\right }}$; $wR_2 = (\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma[w(F_o^2)^2]})^{\frac{1}{2}}$		

 Table S1. Crystallographic Information for the Er-CP.

Table S2. Elemental analysis (%) $[Er_2(C_{10}H_4O_4S_2)_3(H_2O)_6]_n$

C(theoretical)	C(actual)	H(theoretical)	H(actual)	S(theoretical)	S(actual)
30.04	30.04	2.02	2.05	16.04	15.59



Figure S1. DTDC Product ¹H NMR (400 MHz, DMSO, ppm) δ7.70 (d, 2H), 7.54 (d, 2H).

Figure S2. DTDC Product ¹³C NMR (101 MHz, DMSO, ppm) δ175.84, 163.14, 142.06, 134.95, 127.08.



Figure S3. View of Er-CP down the [001] direction highlighting the ErO_8 monomers. Magenta polyhedra represent Er monomers, yellow spheres are sulfur atoms, red spheres are oxygen atoms, and black lines are carbon atoms. Hydrogen atoms have been omitted for clarity.



Figure S4. View of Er-CP down [100] illustrating the bridging of the carboxylate groups connecting ErO_8 polyhedra. The color scheme is the same as in Figure S3.



Thermogravimetric Analysis

Thermogravimetric analysis was conducted on the title compound from 25 to 600 °C under a nitrogen atmosphere (Figure S7) using a Mettler Toledo TGA/DSC 1. An initial weight loss of 9.8% beginning at 90 °C is due to the loss of coordinated water molecules (calculated loss of 9.0%). The second mass loss of 58.9% begins at approximately 400 °C and is attributed to the slow degradation of the three DTDC linkers minus 3 oxygen atoms to produce the final decomposition product (calculated loss of 59.1%). Overall, a mass loss of 68.7% is observed up to 500 °C. This corresponds to an expected end degradation of product of Er_2O_3 (theoretical mass loss of 68.1%).



Figure S5. Thermogram of the title compound $[Er_2(C_{10}H_4O_4S_2)_3(H_2O)_6]_n$ under a nitrogen atmosphere from 25 to 600 °C.

Figure S6. Thermogram of 1-Ln (Ln = Sm – Yb) under a nitrogen atmosphere from 25 to 500 $^{\circ}$.



IR Analysis

The IR spectra of the title compound (Figure S8) were recorded on a Thermoscientific Nicolet i55 and shows the stretching modes of the carboxylate groups at 1519 cm⁻¹ and 1395 cm⁻¹ attributed to asymmetric and symmetric C-O stretching, respectively. The absence of a peak at 1690 cm⁻¹ indicates that the carboxylic acid groups in this CP are all deprotonated. Skeletal vibrations from the thiophene groups can be observed at 1538 cm⁻¹. The broad peak centered around 3300 cm⁻¹ is attributed to the presence of the hydrogen bonding network from the bound aqua ligands.⁴⁶

Figure S7. FTIR spectrum (ATR) of title compound 1-Ln (Ln = Sm - Yb).



Table S3. Selected bond lengths for title compound.

Er-DTDC			
Er1-Ox			
X=	Å		
1	2.448		
3	2.3872		
4	2.4505		
7	2.3534		
8	2.4390		
9	2.3464		
2 ⁱ	2.2495		
5 ⁱⁱ	2.2548		
C1-O1	1.2573		
C1-O2	1.2362		
C10-O5	1.2631		
C10-O6	1.2429		
C11-O3	1.2682		
C11-O4	1.2537		

Superscript i = symmetry operator -x, 1-y, 1-z. Superscript ii = symmetry operator 1-x, 1-y, -z

Table S4. Intermolecular interactions between neighbouring centroids where Cg(1) is S(1), C(2), C(3), C(4), C(5). Cg(2) is S(2), C(6), C(7), C(8), C(9), and Cg(3) is S(3), C(12), C(13), C(14), C(15).

Centroids	Distance (Å)
Cg(1)-Cg(1)	4.4431
Cg(1)-Cg(1)	5.3538
Cg(1)-Cg(2)	3.7965
Cg(1)-Cg(2)	5.5982
Cg(1)-Cg(3)	4.8569
Cg(2)-Cg(3)	5.2304
Cg(2)-Cg(3)	5.7014
Cg(3)-Cg(1)	5.1727
Cg(3)-Cg(1)	5.3664
Cg(3)-Cg(2)	5.2574
Cg(3)-Cg(2)	5.4506

Figure S8. PXRD Patterns of isostructural 1-Ln CPs (Ln = Sm - Yb). Differences in intensities are attributed to preferred crystal orientation effects.



Figure S9. Fluorescence quenching spectrum of 1 in ethanol with 1mM 4-nitrotoluene 5 μ L increments at an excitation wavelength of 371 nm.



Figure S10. Stern-Volmer plot of 1 in ethanol with 1mM 4-nitrotoluene 5 μ L increments at an excitation wavelength of 371 nm.



Figure S11. Fluorescence quenching spectrum of **1** in ethanol with 1mM 1,3-dinitrobenzene 5 μ L increments at an excitation wavelength of 371 nm.



Figure S12. Stern-Volmer plot of **1** in ethanol with 1mM 1,3-dinitrobenzene 5 μ L increments at an excitation wavelength of 371 nm.



Figure S13. Fluorescence quenching spectrum of 1 in ethanol with 1mM 2-nitroaniline 5 μ L increments at an excitation wavelength of 371 nm.



Figure S14. Stern-Volmer plot of 1 in ethanol with 1mM 2-nitroaniline 5 μ L increments at an excitation wavelength of 371 nm.



Figure S15. Fluorescence quenching spectrum of 1 in ethanol with 1mM 4-methylphenol 5 μ L increments at an excitation wavelength of 371 nm.



Figure S16. Stern-Volmer plot of 1 in ethanol with 1mM 4-methylphenol 5 μ L increments at an excitation wavelength of 371 nm.



Figure S17. Fluorescence quenching spectrum of 1 in ethanol with 1mM phenol 5 μ L increments at an excitation wavelength of 371 nm.



Figure S18. Stern-Volmer plot of 1 in ethanol with 1mM phenol 5 μ L increments at an excitation wavelength of 371 nm.



Figure S19. Fluorescence quenching spectrum of **1** in ethanol with 1mM 4-nitrobenzonitrile 5 μ L increments at an excitation wavelength of 371 nm.



Figure S20. Stern-Volmer plot of 1 in ethanol with 1mM 4-nitrobenzonitrile 5 μ L increments at an excitation wavelength of 371 nm.



Figure S21. Fluorescence quenching spectrum of 1 in ethanol with 1mM 2-nitrophenol 5 μ L increments at an excitation wavelength of 371 nm.



Figure S22. Stern-Volmer plot of 1 in ethanol with 1mM 2-nitrophenol 5 μ L increments at an excitation wavelength of 371 nm.



Figure S23. Fluorescence quenching spectrum of 1 in ethanol with 1mM 3-nitrotoluene 5 μ L increments at an excitation wavelength of 371 nm.



Figure S24. Stern-Volmer plot of 1 in ethanol with 1mM 3-nitrotoluene 5 μ L increments at an excitation wavelength of 371 nm.



Figure S25. Fluorescence quenching spectrum of 1 in ethanol with 1mM 4-nitrophenol 5 μ L increments at an excitation wavelength of 371 nm.



Figure S26. Stern-Volmer plot of 1 in ethanol with 1mM 4-nitrophenol 5 μ L increments at an excitation wavelength of 371 nm.



Analyte	HOMO (eV)	LUMO (eV)	Band Gap (eV)
DTDC	-6.7070	-2.6082	4.0988
4-nitrotoluene	-7.4573	-2.3704	5.0869
1,3-dinitrobenzene	-8.4170	-3.3191	5.0979
2-nitroaniline	-6.4548	-2.3946	4.0602
4-methylphenol	-5.9155	-0.0587	5.8568
Phenol	-6.7070	-0.0810	6.626
4-nitrobenzonitrile	-8.1489	-3.2278	4.9211
2-nitrophenol	-7.0129	-2.2989	4.7140
3-nitrophenol	-6.7814	-2.3930	4.3884
4-nitrophenol	-6.9210	-2.2210	4.7000

Table S5. HOMO and LUMO energies calculated for DTDC linker and analytes.