

Electronic Supplementary Information (ESI)

Luminescent Sequence-Dependent Materials through step by step assembly of RE^{1-1,4} Benzendicarboxylate-RE² (RE^x=Y³⁺, Eu³⁺ and Tb³⁺) architectures on silica surface

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SI 1-X-ray structure determination

Single-crystal X-ray diffraction studies of [H₂NBu₂]₂[T]·H₂T were performed on a Bruker Smart Breeze diffractometer with Apex II area detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal data are listed in Table S1. The collected intensities were corrected for Lorentz and polarization effects and for absorption through a multi-scan method.¹ The structure solution was found by means of the automatic direct methods contained in SHELX97 programme.² The hydrogen atoms were placed in calculated positions and were refined with the condition of riding motion. The final refinement cycles with anisotropic thermal parameters for non-hydrogen atoms gave the reliability factors listed in Table S1.

Table S1. Crystal data and refinement summary.

Identification code	1
CCDC number	1884399
Empirical formula	C ₃₂ H ₅₀ N ₂ O ₈
Formula weight	590.74
Crystal system	Monoclinic
Space group	C 2/c
<i>a</i> (Å)	22.420(5)
<i>b</i> (Å)	11.633(2)
<i>c</i> (Å)	13.542(3)
β (°)	102.187(6)
Volume (Å ³)	3452.3(12)
<i>Z</i>	4
ρ_{calc} (g cm ⁻³)	1.137
μ (mm ⁻¹)	0.081
<i>F</i> (000)	1280
θ range (°)	2.6 to 25.0
Reflections collected	11993
Independent reflections	2989
Goodness-of-fit on <i>F</i> ²	1.013

¹ G. M. Scheldrick, SADABS, Program for empirical absorption correction, University of Göttingen, Germany, **1996**.

² G. M. Sheldrick, A short history of SHELX *Acta Crystallogr. Sect. A: Found. Crystallogr.* 2008, **64**, 112-122.

Final R_1 [$I \geq 2\sigma(I)$]	0.0589
Final wR_2 [$I \geq 2\sigma(I)$]	0.1821
Final R_1 [all data]	0.0836
Final wR_2 [all data]	0.2078
Largest peak\hole ($e \text{ \AA}^{-3}$)	0.549, -0.215

The chemical literature reports the structures of ammonium,³ dimethylammonium⁴ and diethylammonium⁵ terephthalates. Our species can be represented by the formula $[\text{H}_2\text{NBu}_2]_2[\text{T}] \cdot \text{H}_2\text{T}$ that, similarly to the diethylammonium salt, presents a molecule of terephthalic acid for every terephthalate anion. The asymmetric unit consists in an ammonium cation, one half terephthalate anion and one half terephthalic acid. One of the two independent carboxylic groups showed a smaller difference in the CO bond distances, C–O(1) and C–O(2), 1.244(3) and 1.267(2) Å, respectively, compared to the other, having C–O(3) and C–O(4) bond distances of 1.314(3) and 1.206(3) Å, respectively. So the hydrogen atom has been considered bonded to O(3), at a longer distance from the carbon atom. The crystal structure of bisdibutylammonium terephthalate terephthalic acid solvate is tied together, in addition to ionic interactions, by London dispersion forces and a rather complex network of hydrogen bonds. Fig. S1 shows a sketch of this network. It is possible to identify columns in the b direction formed by the succession of T^{2-} anions, each accepting four hydrogen bonds from four dibutylammonium cations arranged in two pairs above and under the dianion. The two $\text{NH}\cdots\text{O}$ distances are 1.837 and 2.013 Å, respectively. Both the two halves of each dianion and each cation pair are related by inversion centers, as shown in the Figure. The molecules of 1,4-benzenedicarboxylic acid contribute to the structural architecture through hydrogen bonds with the oxygen atoms of the dicarboxylate anions belonging to neighboring columns. The two halves of each H_2T acid are related by twofold axes. The $\text{OH}\cdots\text{O}$ distance is 1.742 Å.

³ J. A. Kaduk, *Acta Crystallogr. Sect. B.*, 2000, **56**, 474-485.

⁴ E. V. Karpova, M. A. Zakharov, S. I. Gutnikov and R. S. Alekseyev, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **60**, o2491-o2492.

⁵ S. Hausdorf, J. Wagler, R. Mossig and F. O. R. L. Mertens, *J. Phys. Chem.*, 2008, **112**, 7567-7576.

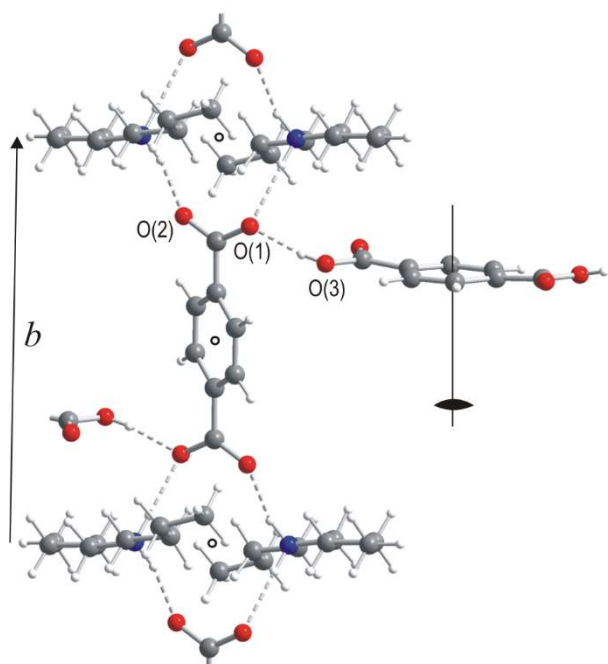


Figure S1. View of the hydrogen bond network in the crystal structure of $[(\text{H}_2\text{NBu}_2)_2\text{C}_6\text{H}_4(\text{COO})_2] \cdot \text{C}_6\text{H}_4(\text{COOH})_2$.

Table S2. Lanthanide loading of silica determined by titration

Sample	RE^{I} mmol/g SiO_2	RE^{II} mmol/g SiO_2
1Eu	0.30 ± 0.01	-
1Tb	0.33 ± 0.01	-
1Y	0.30 ± 0.01	-
1(Eu+Tb)	0.32 ± 0.01	
3Eu-T-Tb	0.30 ± 0.01	0.31 ± 0.01^a
3Y-T-Tb	0.30 ± 0.01	0.35 ± 0.01

In present work, analyses were routinely carried out titrating the excess of lanthanide ions after grafting (the amount of the unreacted metal precursor present in the filtrate). The values reported in Table S2 are the mean values of three successive titrations. The metal content of silica has been established subtracting the moles of lanthanide ions determined by titration from the used amount of metal carbamate complex. To validate our analysis protocol we carried out an ICP and EDX studies on the sample 3Eu-T-Tb. The Eu/Tb molar ratio has been found to be 1.13 ± 0.02 by ICP and 1 by EDX. The values of RE loading determined by both ICP and EDX are in agreement, within the experimental error, with the volumetric results.

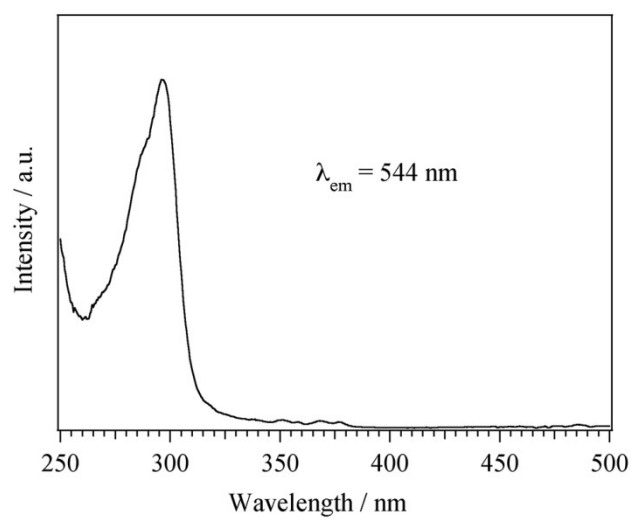


Figure S2. Terbium excitation spectra monitored at 544 nm for sample **3Eu-T-Tb**.