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# From rational octahedron design to reticulation serendipity. A thermally stable rare earth polymeric disulfonate family with $CdI_2$-like structure, bifunctional catalysis and optical properties

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**A new family of lanthanide disulfonates Ln(OH)(NDS)($H_2O$), (Ln = La, Pr and Nd; NDS = 1,5-naphthalenedisulfonate) was designed and hydrothermally synthesized; this is the first example of a disulfonate ligand coordinated to six different Ln atoms; these materials, with high thermal stability, act as active and selective bifunctional catalysts in oxidation and epoxide ring opening; strong luminescence from the optically active Nd center was observed.**

With such a great number of known purely inorganic structures based on octahedra, we entertained the idea of using this motif as a secondary building unit (SBU) for the creation of supramolecular assemblies that, while leading to known inorganic structure types, may have the properties of the hybrid organo-inorganic frameworks. The first such structure, based on octahedral cages, an $A_6{}^{2a}A_6{}^{3d}$ assembly, has recently been reported.[1] The formation of a hybrid octahedral SBU through one only central hexacoordinated ligand, made us establish the following conditions. For the donor connector: (i) capability of linking six different metals (hexatopic connector); (ii) the presence of an inversion center, this condition being fundamental to avoid the formation of a trigonal prism; (iii) volume and geometry such as to minimize steric hindrance among the metal coordination spheres. Regarding the acceptor, *i.e.* the metal cation, a metal with high coordinative capability is envisioned in order to favor the reticulation of octahedra into an infinite network through the same or different links. All these requirements, together with the remarkable magnetic, optical and catalytic properties of the lanthanides,[2–8] prompted us to investigate the possibility of synthesizing sulfonates of rare earth elements (Ln). This combination in a metal coordination polymer could result in a multifunctional catalyst, considering the strong catalytic activity of the rare earth elements and the relatively strong acid character of sulfonate groups. Moreover, in contrast with the rich chemistry of open framework coordination polymers formed by phosphonates and carboxylates, to the best of our knowledge, only one 3D mixed-ligand sulfonate and carboxylate-containing coordination polymer of rare earth elements has been reported.[9] We considered that 1,5-naphthalenedisulfonic acid ($H_2$NDS), with its rigid structure and two centrosymmetric, functionally active groups in the two extreme positions, could meet all the demands to engineer a material with the required structural and physico-chemical properties.

The compounds were obtained by treating an aqueous solution containing a mixture of equimolar amounts of $Ln(NO_3)_3\cdot 6H_2O$ (Ln = La, Pr and Nd) and $Na_2$NDS under hydrothermal reaction conditions (24 h, 170 °C). The crystalline product was separated by suction filtration, washed with water and dried in air, and its purity checked by X-ray powder diffraction, by comparison with the simulated pattern on the basis of the single crystal data.

Crystals of the La and Nd compounds were selected and mounted in a diffractometer equipped with a CCD detector. Upon determining the crystal structure,[10] the composition was found to be Ln(OH)(NDS)($H_2O$), a lanthanide polymeric framework, (denoted LnPF-1). An X-ray powder diffraction pattern showed that the Pr compound has the same structure. In LnPF-1 the lanthanide ion is octacoordinated to two $\mu_2$-OH groups, one water molecule and five oxygen atoms of different NDS ligands (Fig. 1). Every two of these ($LnO_8$) polyhedra share an OH–OH edge, giving rise to dimers, which are isolated in the **b** direction and joined through S atoms in the **a** direction. Connections along the **c** direction are made *via* whole NDS ligands. Hence, at a first sight the structure can be thought of as formed by $Ln_2O_{14}$ dimers that give rise to ($Ln_2O_{14}$)–NDS–($Ln_2O_{14}$)–NDS... infinite chains, kept together through the NDS connectors. Regarding the connectors, there are two differently coordinated NDS molecules, which are perpendicularly oriented along the [−210] and the [210] directions. One of them (NDS-1) (blue ligand in Fig. 2) coordinates, as expected to six distinct Ln atoms, whereas the other (NDS-2) (grey in Fig. 2) is

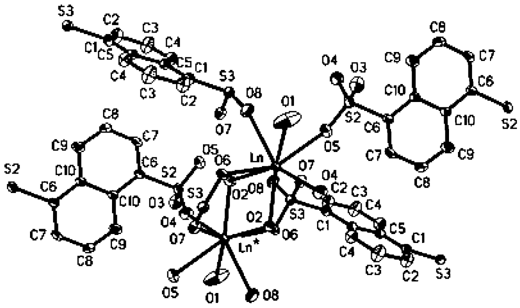

**Fig. 1** ORTEP plot of the building unit showing more than the asymmetric unit.

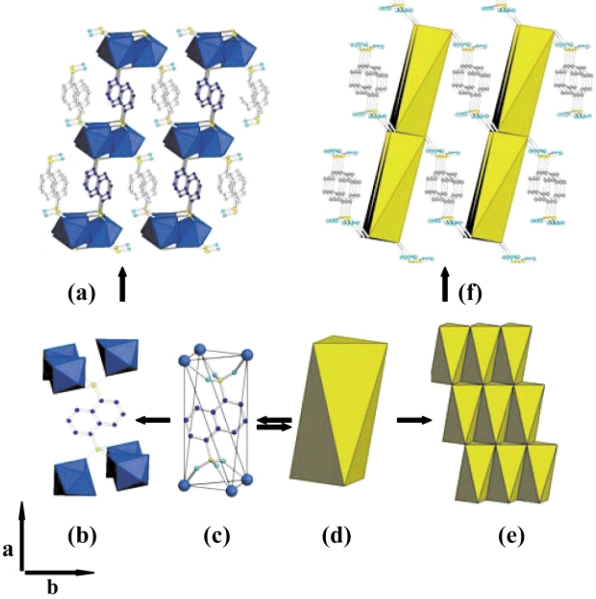

**Fig. 2** Formation of the crystal structure of Ln(OH)(NDS)($H_2O$) (in blue) based on octahedra and idealised $I_2Cd$ structure type (in yellow).

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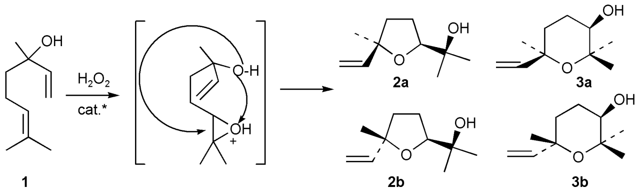
bonded only to four lanthanide atoms, leaving thus, one free oxygen atom for each sulfonate group. By considering the centre of the NDS-1 ligand, which is an inversion centre of the organic molecule and of the unit cell, as a hypothetical atom A coordinated to the six rare-earth atoms that are bonded to this ligand (Fig. 2(b) and (c)), an $ALn_6$ polyhedron arises. Given that the six Ln atoms are 3 to 3 related by the inversion centre, trigonal prismatic geometry is not present, and therefore it is an irregular octahedron, which defines the SBU (Fig. 2(d)).

In doing that, the structure could be also described in terms of layers of $ALn_6$ octahedra, each sharing an edge with each of six adjacent ones (Fig. 2(e)). This geometrical disposition corresponds to the $CdI_2$ structure,[11] with the lanthanide ions occupying the place of the I ions and the centre of the NSD-1 ligands (A) those of the cadmium ions. These layers that are perpendicular to the **b** direction are linked to each other through the four coordinated oxygen atoms of the NDS-2 connectors, in a manner closely reminiscent of other known inorganic structures based on $CdI_2$-like layers[11] (Fig. 2(f)).

The presence of hydroxy groups and water can be clearly observed in the IR spectrum (bands at *ca*. 3600, 3500–3100 and 1530 $cm^{-1}$). Besides, the aromatic C–H stretching (3080–2870 $cm^{-1}$ ) and both $\nu_{as}$ and $\nu_s$ of the $SO_3$ groups are detected at 1240–1250 and 1180 ($\nu_{as}$) and 1044 $cm^{-1}$ ($\nu_s$). Thermogravimetric analysis, and differential thermal analyses (TGA–DTA) carried out under $N_2$ (50 ml $min^{-1}$) for LnPF-1 (Ln = La, Pr and Nd) show a weight loss between 240 and 310 °C, accompanied by an endothermic effect corresponding to the loss of the coordinated water molecule per formula unit (calculated 1.9%, found 2%). No further weight loss was detected within the temperature interval 310–510 °C. Above the latter temperature both frameworks completely decomposed.

The presence in these materials of active metal (Ln), and acid (sulfonate groups) sites forming part of the framework, prompted us to test the catalytic activity of the three LnPF-1 compounds in the oxidation of linalool **1**. Linalool oxides are extensively found in nature, and are used as fragrances. They also appear to have a strong biological significance in certain pollination systems, acting as insect attractants. Although numerous multistep organic synthesis of pyranoid and furanoid linalool oxides have been reported,[12] some of them highly stereoselective,[13,14] they are usually obtained by extraction from natural products or by transformation of linalool. The samples were used as catalysts (20 mg) for the transformation of linalool (330 mg, 2.1 mmol) by $H_2O_2$ (3 mmol) in acetonitrile (10 ml) in a glass reactor at 343 K. The samples were active for the oxidation of linalool to hydroxy ethers (furanoid and piranoid form, **2**, **3** in Scheme 1), with yields after 24 h of 100, 94 and 75%, for La, Pr and Nd, respectively. This activity is comparable to that of microporous bifunctional titanium aluminosilicates.[15] The similar **2**:**3** ratios found in all cases (1.8, 2.1 and 2.2 for La, Pr and Nd compounds, respectively), show that all materials behave similarly. It seems plausible that the process involves firstly the epoxidation at the metal site of the 2,3 double bond followed by intramolecular opening of the epoxide ring by the hydroxy group at positions 6 or 7, the latter reaction being catalyzed by the acid sites. All the catalysts are very selective and no other reaction products were detected.Optical properties of active Ln ions were studied on NdPF-1.[16]

Well-resolved strong photoluminescence spectra at 10 K from the lowest energy Stark component of $^4F_{3/2}$ unequivocally confirms the existence of a single optically active ordered site for $Nd^{3+}$ in the NdPF-1 crystal host. Moreover, The *J* manifolds of $Nd^{3+}$ in this host are split in to the maximum number of Stark components, Kramers doublets, 7, 6 and 5 for $^4I_{13/2}$, $^4I_{11/2}$, Fig. 3, and $^4I_{9/2}$, respectively, in agreement with the crystal field symmetry of its site. On the other hand, the moderate measured phonon energies of this material suggests adequate non-radiative multiphonon decay rates among $Nd^{3+}$ energy levels, and consequently satisfactory radiative efficiencies for this polymeric disulfonate matrix.



**Scheme 1**

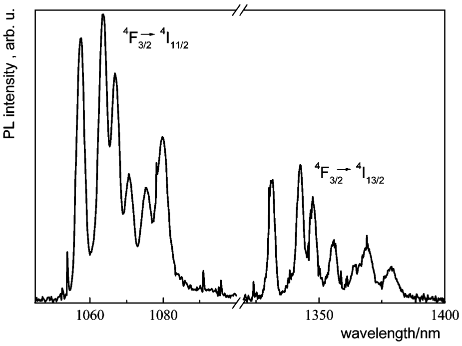


**Fig. 3** 10 K PL spectra of NdPF-1.

In summary, a novel designed polymeric structure is presented. This new family of compounds represents the first example of a disulfonate ligand coordinated to six different lanthanide atoms. These materials, with high thermal stability, act as active and selective bifunctional catalysts in oxidation and epoxide ring opening. Further studies on their optical, catalytic and magnetic properties are in progress.

## Notes and references

1 D. W. Johnson, J. Xu., R. W. Saalfrank and K. N. Raymond, *Angew. Chem., Int. Ed.*, 1999, **38**, 2882.

2 T. M. Reineke, M. Eddaoudi, M. Fehz, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651.

3 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.

4 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.

5 B. Moulton and M. J. Zaworotko, *Chem.Rev.*, 2001, **101**, 1629.

6 J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638.

7 J.-M. Lehn, *Angew. Chem., Int. Ed.*, 1990, **29**, 1304.

8 J. C. G. Bunzli and F. Ihringer, *Inorg. Chim. Acta*, 1996, **246**, 195.

9 R. G. Xiong, J. Zhang, Z. F. Chen, X. Z. You, C. M. Che and H. K. Fun, *J. Chem. Soc., Dalton Trans.*, 2001, 780.

10 *Crystal data* for LaPF-1 [NdPF-1]: $Ln^{3+}(OH)^-[C_{10}H_6O_6]^{2-}\cdot H_2O$: triclinic, space group $P1$, $a$ = 5.7263(2) [5.6745(8)], $b$ = 10.6104(4) [10.551(2)], $c$ = 11.5533(8) [11.450(2)] Å, $\alpha$ = 76.615(1) [76.456(2)], $\beta$ = 77.619(1) [77.484(2)], $\gamma$ = 87.937(1) [88.034(2)]°, $V$ = 666.94(4) [650.5(2)] $Å^3$, $T$ = 296 K, $Z$ = 2, $M_w$ = 460.2 [465.3], $D_c$ = 2.291 [2.377] Mg $cm^{-3}$, $\mu$(Mo-K$\alpha$) = 3.55 [4.35] $mm^{-1}$. CCDC reference numbers 182916 and 182917. See http://www.rsc.org/suppdata/cc/b2/b202639b/ for crystallographic data in CIF or other electronic format. Patent Registry No. 200200850.

11 A. F. Wells, *Structural Inorganic Chemistry*, Oxford Science Publications, 5th edn., 1991, p. 259.

12 Ch. Fournier-Nguefack, P. Lhoste and D. Sinou, *Tetrahedron*, 1997, **53**, 4353 and references therein.

13 G. Vidari, A. Di Rosa, G. Zanoni and C. Bicchi, *Tetrahedron*, 1999, **10**, 3547.

14 G. Vidari, A. Di Rosa, F. Castronovo, G. Zanoni and C. Bicchi, *Tetrahedron: Asymmetry*, 2000, **11**, 981.

15 A. Corma, M. Iglesias and F. Sanchez, *J. Chem. Soc., Chem. Commun.*, 1995, 1635.

16 10 K photoluminescence spectra of the Nd-sample were recorded by exciting the $^4F_{5/2}$ + $^2H_{9/2}$ multiplets with a Ti-sapphire laser ($\lambda$ = 799 ± 0.5 nm), and collecting the luminescence from $^4F_{3/2}$. The emission was dispersed with a 500 M spex monochromator and the signal recorded with suitable detectors, a Hamamatsu R636 photomultiplier ($^4I_{9/2}$), and a cooled Ge photodiode ($^4I_{11/2}$, $^4I_{13/2}$), using the lock-in amplifying technique. Raman spectra were obtained with a Reninshaw Ramascope 2000 equipped with a CCD detector. The samples were excited with the 514.5 nm line of an $Ar^+$ laser. The spectra were recorded in the backscattering geometry at room temperature, and corrected by the spectral response of the experimental set-up.