# 'Molecular Chinese blinds': self-organization of tetranitrato lanthanide complexes into open, chiral hydrogen bonded networks

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**Lanthanide ions, with their unique electronic properties, rich stereochemistry, and consistent structural patterns offer a novel approach to the design of polar/chiral networks.**

In recent years a wide variety of networks have been designed using the two major branches of crystal engineering (*i.e.* organic solids and inorganic coordination polymers), yet the rational design of polar/chiral networks continues to be an elusive and challenging goal for crystal engineers.[1–5] The difficulty results from synthetic strategies which rely upon the propagation of molecular symmetry into crystalline symmetry through rigid directional forces (hydrogen bonds and/or metal-coordination bonds), because such symmetry driven open networks tend to crystallize in *centrosymmetric* space groups.[3,6] However, using lanthanides, one can easily induce dissymmetry at metal centers simply by coordination with suitable ligand(s) which may thus result in controllable 1D, 2D, or 3D chiral networks with the aid of complementary hydrogen bonding functional groups.

In order to explore the role of lanthanide metal complexes in the context of crystal engineering, we have synthesized lanthanum nitrate metal complexes of 1,2-bis(4-pyridyl)ethane (bpe). $La(NO_3)_3 \cdot 6H_2O$ (0.433 g, 1 mmol) was reacted with bpe (0.368 g, 2 mmol) in EtOH (25 mL) and heated until both the reactants were completely dissolved. Crystals of **1**, $[bpeH]^+[La(NO_3)_4(OH_2)(bpe)]^-$, were obtained within 2–3 days. Complex **1** is also formed when $La(NO_3)_3$ and bpe are reacted in 1:2 or 1:3 molar ratios in 3:1 solvent mixtures of MeCN–MeOH.[7]†

Compound **1** crystallizes in the chiral space group $C222_1$.‡ The lanthanum cations are 11-coordinate, complexed with four bidentate nitrate anions, two bridging bpe ligands, and one water molecule resulting in an anionic 1D coordination polymer. The two protons of the water molecule along with oxygen atoms of adjacent nitrate anions constitute complementary divergent hydrogen bonding recognition sites on the backbone of the 1D coordination polymer (Fig. 1).

The hydrogen bonded nature of the 1D polymers [H···O, O···O, O-H···O; 2.155(3), 2.818(3) Å, 135.7(2)°] leads to the formation of a pleated-sheet structure with unusual cavities (Fig. 2). Each of these cavities is threaded by two linear 1D hydrogen bonded chains of the monoprotonated $bpeH^+$ molecules (N···N, 2.664(3) Å) resulting in an unprecedented polypseudo-rotaxane-type architecture.[8] To the best of our knowledge, this is the first structure to be reported with these unique 2D threading/interweaving structural features, *i.e.* threaded pleated-sheets, or a 'chinese blinds' structure. Also, formation of **1** under different experimental conditions, sug-

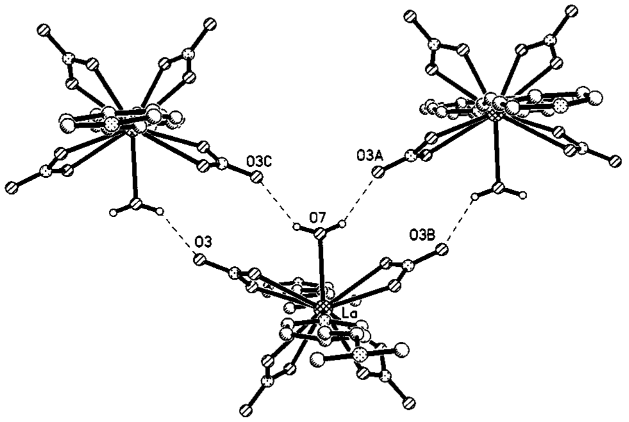

**Fig. 1** Hydrogen bonded self-assembly of $[La(NO_3)_4(OH_2O)(bpe)]^-$ anions in **1**. The 1D coordination polymers run perpendicular to plane of the paper.

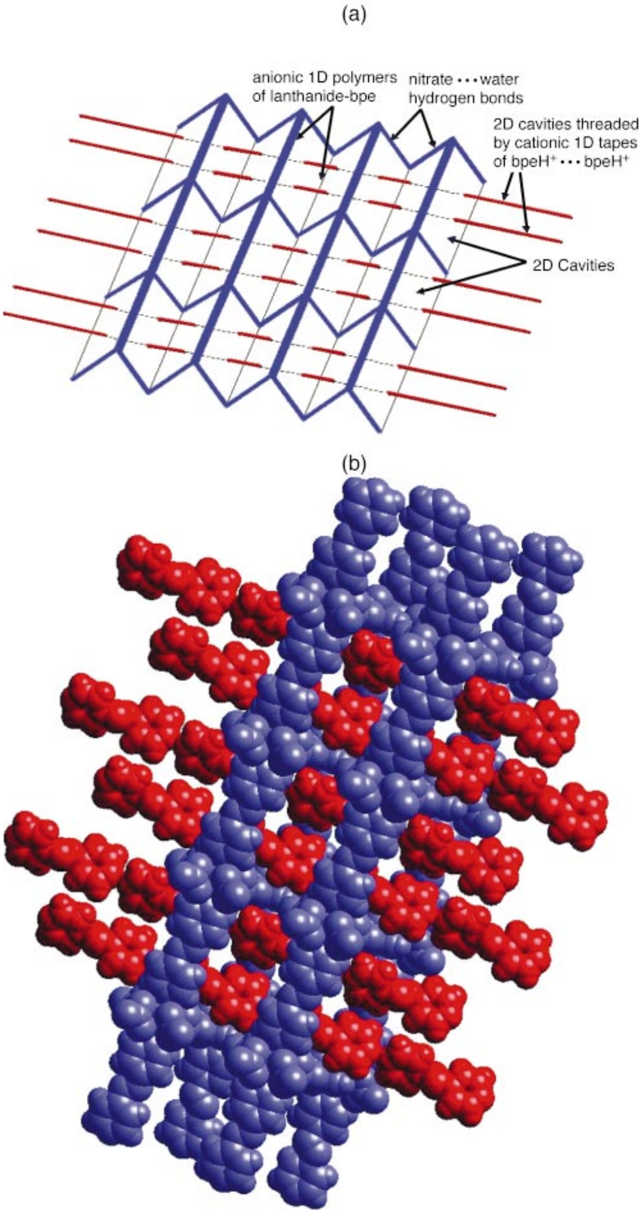

**Fig. 2** Schematic (a) and space-filling (b) representations of a single sheet of **1** with the chiral 2D pleated-sheet of $[La(NO_3)_4(OH_2)(bpe)]^-$ (blue) threaded by 1D linear chains of $bpeH^+ \cdots bpeH^+$ (red).

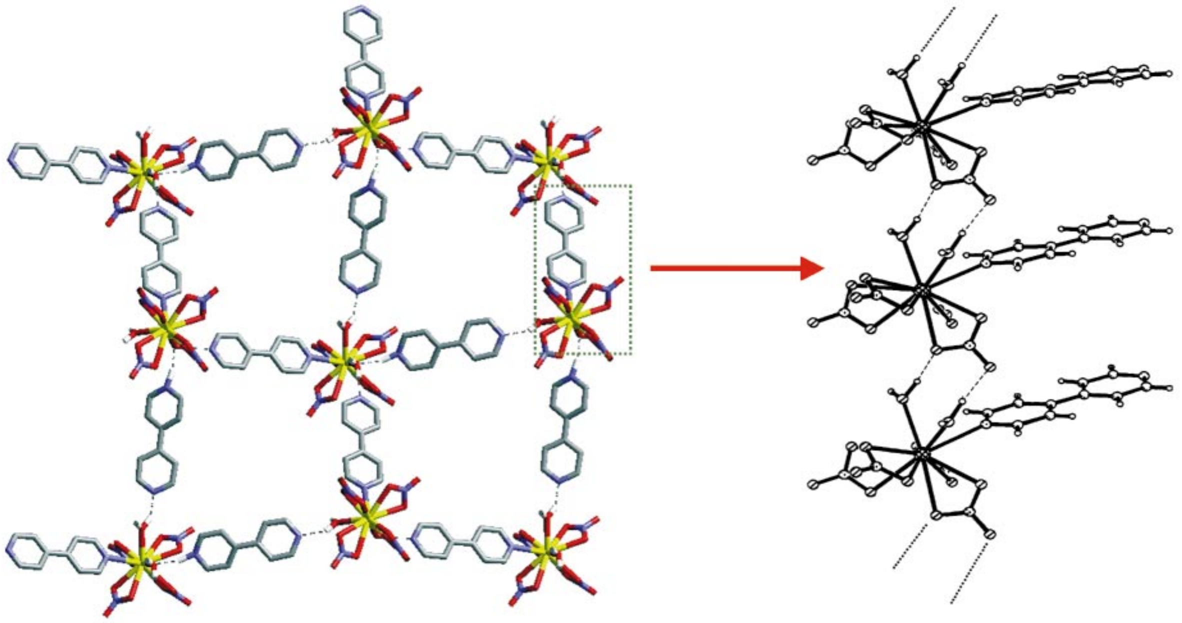

**Fig. 3** A portion of the chiral, open 3D grids formed by **2a** resulting from hydrogen bonding between the complex anion, $[La(NO_3)_4(OH_2)_2(bipy)]^-$, and cation, $bipyH^+$. Two such independent networks interpenetrate.[9] The square grids are locked into place by hydrogen bonding between $NO_3^-$ and $H_2O$ groups in the third dimension.

gests strong complementary interactions among the various building blocks associated in the self-organization. Further, the nitro groups that are not part of the hydrogen bonding network interdigitate with neighboring 2D pleated-sheets through off-set stacking for efficient close packing.

The interesting open, chiral networks in **1** prompted us to carefully examine the 20 (many of them isostructural) $Ln(NO_3)_3$ complexes in the Cambridge Structural Database (April 1997 release) with the more rigid 4,4′-bipyridine (bipy). These complexes may be classified into three structurally distinct series: neutral hydrogen bonded cocrystals, metal–ligand coordination complexes, and organic cation–inorganic anion pairs. Two different isostructural series are particularly important to the crystal engineer in the design of open, chiral networks, each crystallizing in the chiral space group $P2_12_12_1$: the charged coordination complexes $[bipyH]^+[Ln(NO_3)_4(OH_2)_2(bipy)]^-$ (Ln = La, Ce, Pr, Nd: **2a**-**d**) and the neutral, hydrogen bonded cocrystals $[Ln(NO_3)_3(OH_2)_3]\cdot 2bipy\cdot H_2O$ (Ln = Nd, Pr: **3a**,**b**). In the former series complementary hydrogen bonding of the complex anions and $bipyH^+$ results in a well defined infinite chiral 3D open architecture (Fig. 3) that undergoes self-interpenetration.[9] The latter complexes form hydrogen bonded layered structures where bipy molecules function as pillars between the layers.[10]

We have synthesized further examples of **2** and **3** to determine the commonality of this approach. $La(NO_3)_3\cdot 6H_2O$ (0.433 g, 1 mmol) was reacted with 4,4′-bipyridyl (0.312 g, 2 mmol) in MeOH (15 mL) and single crystals of $[bipyH]^+[La(NO_3)_4(OH_2)_2(bipy)]^-$ **2a**, were obtained over a period of two weeks. The neutral hydrogen bonded crystals of $[La(NO_3)_3(OH_2)_3]\cdot 2bipy\cdot H_2O$ **3c**, were obtained when $La(NO_3)_3$ and bipy were reacted in 1:2 molar ratio in a solution mixture of xylene and MeOH.§

The crystal structures of **1-3** suggest a simple and efficient way to design chiral crystals with predictable networks and further suggest that lanthanides form exotic supramolecular networks which are of importance not only for their aesthetic appeal, but also for their potential use in the design of functional solids. Lanthanides, with their interesting electronic, spectral, and magnetic properties coupled with their availability, propensity to form isostructural complexes, and range in ionic radii are thus, attractive targets for exploring such structure–function correlations.

## Notes and references

† The complexation properties of $Ln(NO_3)_3$ with softer N-donor ligands (*e.g.* 4,4′-bipyridyl) are sensitive to the solvent of crystallization. Any slight variations in nature of the solvent, acidity, basicity, or solvent:water ratio leads to drastic changes in the complex formed.

‡ *Crystal data* for **1**, $M$ = 774.4, orthorhombic, space group $C222_1$, $a$ = 14.9977(2), $b$ = 16.3302(1), $c$ = 11.8663(2) Å, $V$ = 2906.24(6) Å$^3$, $D_c$ = 1.770 Mg m$^{-3}$ for $Z$ = 4. 3369 unique absorption corrected reflections measured at 173 K with a Siemens CCD area detector diffractometer ($4 < \theta < 56°$), on convergence gave final values of $R$ = 0.019, $R_w$ = 0.046. The sp$^3$ C atoms of the bpe ligand coordinated to the lanthanide exhibit ± *gauche* disorder. CCDC 182/1081

§ Complexes **2a** and **3c** crystallize in the orthorhombic space group $P2_12_12_1$. The unit cell parameters of **2a** have been reported previously at room temperature,[7] while **3c** is a new member of the complex **3** series. We have crystallographically characterized both **2a** and **3c** at −100 °C utilizing a Siemens CCD area detector diffractometer with molybdenum radiation: **2a**: $a$ = 7.2658(4), $b$ = 18.5137(11), $c$ = 19.9204(12) Å. **3c**: $a$ = 7.1228(3), $b$ = 16.1694(6), $c$ = 24.7284(10) Å. CCDC 182/1081

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