First direct assembly of molecular helical complexes into a coordination polymer†

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Luminescent triple-stranded helicates, formed between Tb(III) ions and bis-acylpyrazolones, were directly assembled into a 1-D polymeric system.

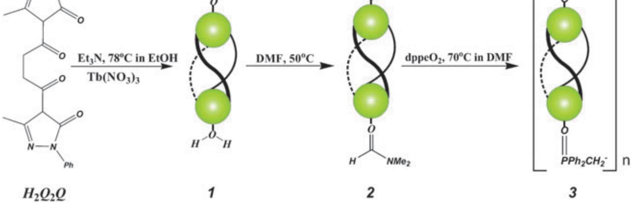
During the last decade lanthanide supramolecular complexes have been intensively investigated due to the possibility to combine unique spectroscopic and magnetic properties of lanthanide ions with specific features belonging to supramolecular edifices.[1] Thus, these compounds allow to achieve desired functionality and open the way for application in many areas, for instance, gas sorption, liquid crystals, catalysis, fluoroimmunoassays and biomedical imaging.[2] The directed design of functional lanthanide supramolecular architectures requires structural blocks with defined properties leading to adequate coordination strength and geometry. Furthermore, mastering of the coordination number can lead to edifices with unsaturated coordination sites, enabling further intermolecular interactions and the potential formation of extended structures.

One of the most fascinating types of rigid structures are the helicates,[3] a large number of which have been investigated, including self-assembled polymetallic lanthanide helicates.[4] A predictive thermodynamic model for their formation has also been developed.[5] Tridentate benzimidazole pyridyl ligands are among the most widely used coordination units for designing lanthanide helicates because three of these moieties saturate the inner coordination sphere of the lanthanides. On the other hand, the resulting molecular structures are not amenable to further interaction leading to more complicated supramolecular architectures. In this respect, bis-β-diketones, are more suitable. Indeed, β-diketones form stable complexes with most metal ions and the neutral tris complexes with lanthanide ions feature unsaturated six-coordination allowing interaction with ancillary ligands; helicates based on bis-β-diketones can therefore act as building blocks for designing extended functional supramolecular architectures. Only a few examples of triple-stranded helicates based on bis-β-diketones are documented, namely, M(III) binuclear helicates (M = Mn, Fe, Ga) and a Mn(II) trinuclear triple-helical complex.[6] Similar edifices incorporating lanthanides have been evidenced by NMR and ESI mass spectrometry,[7] but no X-ray crystal structure is available. Finally, bis-acylpyrazolones, which are the structural analogues of bis-β-diketones, have also been used in design of mono-[8] and bimetallic[9] lanthanide complexes, and have been successfully applied in engineering supramolecular architectures such as a unique lanthanum(III) octanuclear complex or quadruple-stranded thorium(IV) helicates.[10]

In this work we report the synthesis of terbium complexes with triple-helical structure, based on bis-acylpyrazolone ligands H_2Q_2Q (**1, 2**, Scheme 1), as well as, for the first time, a direct assembly of these helical blocks into the 1-D coordination polymer **3** mediated by diphenylphosphinethane dioxide ($dppeO_2$) acting as bridging ligand. All compounds were fully characterized by various physico-chemical methods and their structures were determined by single-crystal X-ray diffraction. To confirm the possibility of using the helical fragments as building blocks with predetermined coordination geometry in the design of supramolecular architectures, model DFT calculations were also performed.

A general scheme of the reaction path is presented on Scheme 1.

Several ligands with general formula H_2Q_nQ (where n is a number of bridging methylene groups, n = 2–5) were tested for assembling triple-stranded helical complexes. However, only the ligand with n = 2 was found to form the sought for lanthanide containing structures with the predetermined adequate geometry. This observation is in a good agreement with previously published data,[6] where it was clearly



Scheme 1 Reaction path for **1–3**.

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established that Ga(III) and Fe(III) ions gave triple-helical structures only with ligands containing double-unit bridges. The coordination sphere of the metal ions in these complexes is fully saturated while for lanthanides ions an additional coordination possibility exists. Thus, in $Tb_2(Q_2Q)_3(H_2O)_2$ (**1**) and $Tb_2(Q_2Q)_3(DMF)_2$ (**2**) (Scheme 1) each terbium(III) atom coordinates a water or DMF molecule, respectively, along the 3-fold axis in addition to the bis-acylpyrazolone ligand. This specific feature was used in building infinite helical chains bridged by $dppeO_2$ ligands, which offer a strong binding to Ln(III) ions by two oxygen donor monodentate binding sites and could lead to improving the luminescent properties.[11]

The final polymeric product $[Tb_2(Q_2Q)_3(dppeO_2)]_n$ (**3**) was obtained in crystalline form as a result of slow substitution of DMF in **2** by $dppeO_2$. Alternatively, complex **3** can be prepared as a bulky material by direct assembly of the mixture of ligands and the metal salt. The samples prepared by both methods were structurally identical according to powder diffraction data (see ESI† for details).

According to X-ray single-crystal analysis,§ complexes **1** and **2** possess a molecular structure and consist of the idealized D_3-symmetrical fragment $\{Tb_2(Q_2Q)_3\}$ capped by two ancillary ligands, H_2O and DMF, respectively (Fig. 1). Both terbium atoms in **1** and **2** are seven coordinated. The coordination polyhedron can be described as a mono-capped octahedron, consistent with the C_3 symmetry of the coordination environment. There are no significant differences in Tb–O distances for anionic and ancillary ligands and their average value of 2.31 Å is close to that found for similar coordination environments.[11] In both structures, the two terbium atoms and the oxygen atoms from ancillary ligands are aligned along the pseudo 3-fold axis. A detailed analysis of the helical portions delimited by the four parallel facial planes containing the coordinated oxygen atoms (see Fig. S2, ESI†) shows the helical pitches to be similar for **1** and **2** and the usual tightening of their values around the complexed metal centres and its straightening within the intermetallic domains (see ESI† for details).[4,10] The total length of the helix is equal to 7.0 and 7.4 Å for **1** and **2**, respectively, which corresponds to a 1/3 turn per molecule. Thus, the average pitch for both structures is approximately equal to 21 Å, that is larger than the values reported for helicates based on benzimidazole pyridyl ligands[4] and smaller than those for thorium(IV) quadruple-stranded helicates.[10]

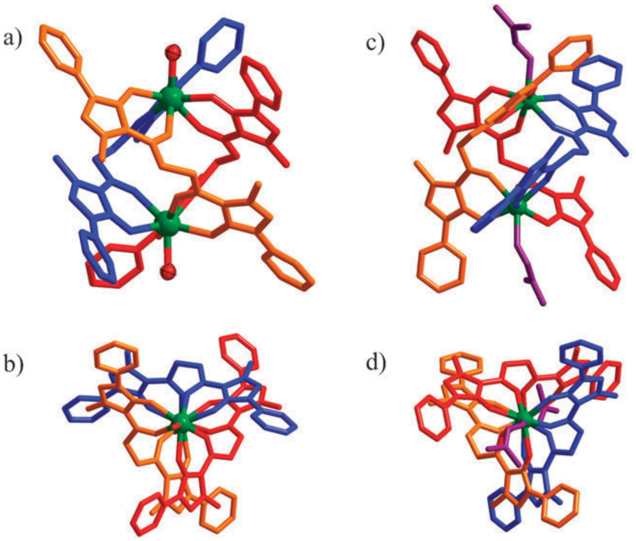

Fig. 1 Ball-and-stick representation of: (a) **1** perpendicular to a 3-fold axis; (b) **1** along a 3-fold axis; (c) **2** perpendicular to a 3-fold axis; (d) **2** along a 3-fold axis. Terbium atoms are shown as green spheres, ligands are presented in different colors, oxygen atoms of water molecules are colored in red, and those of coordinated DMF ones are violet.

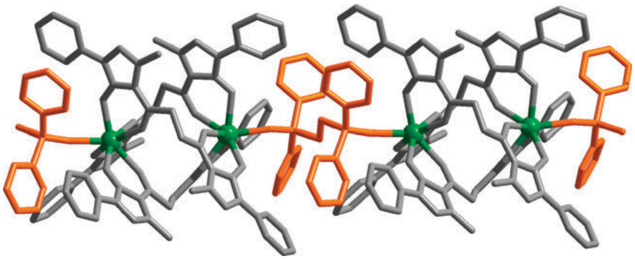

Fig. 2 Fragment of the polymeric chain in **3**. Ligands forming helices and bridges are presented in different colors.

The crystal structure of **3** consists in infinite parallel chains formed by the helical units $\{Tb_2(Q_2Q)_3\}$ bridged by $dppeO_2$ ligands (Fig. 2). The structure of the helical part is overall the same as those in **1** and **2**. The relevant helical parameters are presented in Table S1 (ESI†). Ordinarily, a distortion from the ideal helix decreases with increasing the volume of an ancillary ligand. This can be demonstrated by the values of $\angle TbTbO_{terminal}$ as well as by angles between the facial planes for all the complexes **1–3** (see ESI† for details).

There are two types of chains in **3** corresponding to the two different optical isomers of the helix (left and right-handed, respectively). The length of the repetitive unit in the chain is 16.28(1) Å, whereas the Tb···Tb distance between neighbouring helical molecules amounts to 10.08 Å, that is slightly larger than the Ln···Ln distances in $[Ln(NO_3)_3(dppeO_2)_{1.5}]_n$ (*ca.* 9.2 Å).[12]

Terbium complexes show an intense metal-centred characteristic green luminescence due to ligand-to-metal energy transfer upon UV excitation.[13] The quantum yield of an ethanol solution of **1** was determined by a comparison method with Rhodamine B as standard[14] and amounts to 18 ± 3%.

To demonstrate the specificity of the additional coordination sites along the 3-fold axis in $\{Tb_2(Q_2Q)_3\}$ fragment and to estimate the coordination ability of the ancillary ligand to each metal ion in **1**, theoretical modeling was performed using the DFT/BP86 method (see ESI† for details). For the sake of simplicity, two gadolinium complexes with different number of coordinated water molecules, as the smallest ancillary ligand, namely, $[Gd_2(Q_2Q)_3(H_2O)_2]$ and $[Gd_2(Q_2Q)_3(H_2O)_4]$, were taken into consideration. The starting geometry of the latter complex was estimated from the structure of **1** by completing the coordination sphere of each Gd ion with an additional water molecule. Geometry optimization for $[Gd_2(Q_2Q)_3(H_2O)_4]$ results in the second water molecule being pushed into an outer position (Fig. S8, ESI†). However, it is noteworthy that the geometrical parameters of the bis-acylpyrazolone ligands, as well as of the metal environment in this complex, sustain only minute changes with respect to the same parameters calculated for [$Gd_2(Q_2Q)_3(H_2O)_2$]. As a consequence, the theoretical modelling clearly indicates that coordination of the second ancillary ligand to the studied helical fragment is impossible and proves the {$Ln(Q_2Q)_3$} unit being an unique rigid building block with tailored open coordination sites.

In conclusion, the first direct assembly of molecular helical complexes into a polymeric system is reported in the case of terbium bis-acylpyrazolonates. The proposed synthetic approach can be extended to other systems and opens the way to the design of new fascinating lanthanide supramolecular architectures with tunable functional properties by varying both the helix-forming and ancillary ligands.

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Notes and references

§ *Crystal data* for [$Tb_2(Q_2Q)_3(H_2O)_2$]·$(H_2O)_{7/3}(C_2H_5OH)_{1/3}$: M = 1693.33, triclinic, $P\bar{1}$, a = 17.257(4), b = 27.225(5), c = 28.140(6) Å, α = 115.55(3), β = 104.56(3), γ = 97.14(3)°, V = 11 126(4) Å^3, Z = 6. 103 098 measured reflections, 52 881 unique reflections (R_{int} = 0.128), R_1 = 0.0816, wR_2 = 0.211 for 2745 parameters and 40 004 contributing reflections ($|F_o| > 4\sigma(F_o)$). Hydrogen atoms of the crystal water molecules O43–O50 were not observed nor calculated. CCDC 670980. *Crystal data* for [$Tb_2(Q_2Q)_3(DMF)_2$]: M = 1695.21, triclinic, $P\bar{1}$, a = 12.807(3), b = 14.379(3), c = 21.830(4) Å, α = 96.03(3), β = 90.17(3), γ = 111.71(3)°, V = 3710.4(13) Å^3, Z = 2. 101 982 measured reflections, 16 377 unique reflections (R_{int} = 0.088), R_1 = 0.0785, wR_2 = 0.161 for 893 variables and 12 763 contributing reflections ($|F_o| > 4\sigma(F_o)$). CCDC 670981. *Crystal data* for [$Tb_2(Q_2Q)_3(dppeO_2)$]$_n$: M = 2035.57, triclinic, $P\bar{1}$, Z = 2, a = 14.674(3), b = 16.276(3), c = 18.847(4) Å, α = 83.63(3), β = 82.24(3), γ = 76.43(3)°, V = 4320.9(15) Å^3. 58 840 measured reflections, 17 652 unique reflections (R_{int} = 0.106), R_1 = 0.056, wR_2 = 0.113 for 1153 variables and 6137 contributing reflections ($|F_o| > 4\sigma(F_o)$). CCDC 670982. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719171e

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