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A homochiral triple helix constructed from an axially chiral bipyridine†

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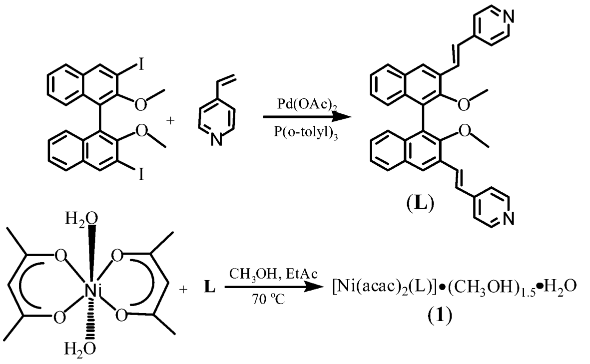
A homochiral triple helix was self-assembled from an axially chiral bipyridine and a linear metal-connecting point, which further assembles into a 2D network *via* infinite π···π stacking interactions and acts as a host for the inclusion of guest molecules.

The field of discrete metallohelicates and infinite metal-containing helical chains[1] has attracted much attention as a result of the interest in building novel supramolecular architectures with potential applications in second-order nonlinear optics[2] and host–guest interactions.[3] Ubiquitous in nature and as the foundation of genetic codes, helices are also the best example of chirality that can be readily induced by metal–ligand coordination.[4] Although achiral and racemic ligands can be used to form intrinsically chiral helical chains, the overall chirality of the bulk product is much less predictable (or controllable). When achiral or racemic ligands are employed to form helices, bulk racemates typically result with only a few exceptions where spontaneous resolution upon crystallisation occurs.[5,6] The use of enantiopure ligands will on the other hand necessarily lead to the stereoselective synthesis of helices with the same handedness.

We have recently focused on the synthesis of chiral supramolecular systems based on axially chiral multitopic ligands.[7] We envisage that the twisted nature of the binding sites in these axially chiral ligands can induce the self-assembly of helical architectures when coordinated to linear metal-connecting points. The axially chiral ligand used for this study is 2,2′-dimethoxy-1,1′-binaphthyl-3,3′-bis(4-vinylpyridine), **L**, while $Ni(acac)_2$ (acac is acetylacetonate) with *trans* binding sites is used as the linear metal-connecting point.[8] Lützen *et al.* recently reported the stereoselective self-assembly of double- and triple-stranded discrete metallohelicates based on a 1,1′-binaphthyl-derived bis(bipyridyl) ligand with a similar configuration.[9] Capó *et al.* more recently reported the stereoselective assembly of a trinuclear Na/Li triple helix based on a modified 1,1′-bi-2-naphthol ligand.[10] We report here the self-assembly of a homochiral triple helix built from alternating $Ni(acac)_2$ and **L**. These homochiral triple helices further assemble into a 2D network *via* infinite π···π stacking interactions and act as a host for the inclusion of guest molecules.

2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-bis(4-vinylpyridine), **L**, was synthesized by a Pd-catalyzed Heck coupling reaction between 4-vinylpyridine and known 3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthalene[11] in 50% yield (Scheme 1). **L** has been characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Single-crystals of $[Ni(acac)_2(\mathbf{L})]\cdot(CH_3OH)_{1.5}\cdot H_2O$, **1**, were obtained in 70% yield by heating a mixture of $[Ni(acac)_2(H_2O)_2]$, **L**, methanol and ethyl acetate at 70 °C for two days.‡ Thermogravimetric analysis shows that **1** experiences a 7.3% weight loss by 260 °C, corresponding to the loss of one and a half CH_3OH and one water molecules (expected 7.8%). Further heating led to the decomposition of the framework of **1** slowly. The formulation of **1** was supported by elemental microanalysis. The IR spectrum of **1** exhibits strong signals at ~1600 and 1400 cm^{-1} for the coordinating acac groups in addition to the signals that are attributed to coordinated **L**. A broad peak at ~3437 cm^{-1} is consistent with the presence of hydroxyl functionalities in **1**. The phase purity of the sample was confirmed by powder XRD.



Scheme 1 Synthesis of **L** and **1**.

A single-crystal X-ray diffraction study of (*S*)-**1** reveals the formation of a homochiral helical chain constructed from **L** and $Ni(acac)_2$.§ **1** crystallizes in the chiral space group *C*2, with one $Ni(acac)_2$ unit, one **L** ligand, one and a half methanol and one water guest molecules in the asymmetric unit. The distorted octahedral Ni center coordinates to two chelating acac groups in the equatorial plane and to two pyridyl groups from different **L** ligands in a *trans* fashion with an N–Ni–N angle of 177.1(2)°. Adjacent $Ni(acac)_2$ units are bridged by binaphthyl backbones of **L** groups to form an infinite helical chain running along the *b*-axis (Figure 1). The left-handed helix is generated around the crystallographic 2_1 axis with a helical pitch of 34.22(1) Å, which is thrice of the *b*-axis length. The naphthyl rings of the **L** ligand are twisted along the pivotal 1,1′-bond with a dihedral angle of 90.78°; the bulk of the naphthol moieties are pointing away the helical axis and are thus well positioned to intertwine with other helices.

Three left-handed helical strands intertwine one another *via* van der Waals interactions to form a triple helix as shown in Figure 2.[12] A careful examination indicated that there exist strong infinite π···π stacking interactions among the inter-

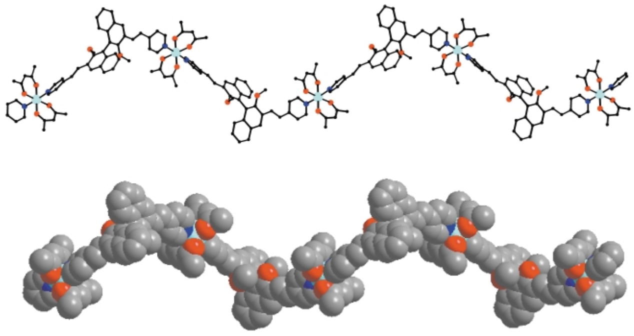


Fig. 1 Top, a view of a left-handed 2_1 helix of **1**. Bottom, a space-filling model of the helical chain.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b212781d/

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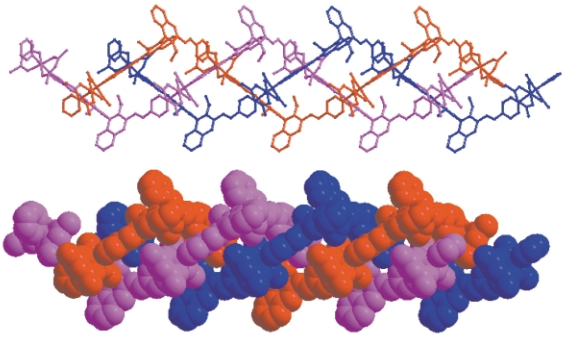

Fig. 2 Top, a view of the triple helix of **1** formed by van der Waals interations. Bottom, a space-filling model of the triple helix.

twined vinylnaphthyl groups of **L** from adjacent triple helices in a non-parallel fashion with the nearest carbon to carbon separation of 3.351(1) Å.[13] Adjacent triple helices are thus assembled into a 2D network in the *bc* plane *via* the π···π stacking interactions. The 2D slabs stack on top of each other in a staggered fashion (by 1/2b) along the *a*-axis forming a lamellar solid. The void space between the layers is occupied by MeOH and water guest molecules. Interestingly, methanol molecules are hydrogen-bonded to the oxygen atoms of acac anions with O–O distances of 2.974 and 2.966 Å.

We have also prepared **1** using (*R*)-**L**. As shown in Figure 4, CD spectra of **1** made from (*R*)- and (*S*)-**L** are mirror images of each other, indicating that the triple helix built from (*R*)-**L** is right-handed. Compound **1** made from (*R*)- and (*S*)-**L** are thus supramolecular enantiomer of each other. Enantiopure bridging ligands will thus steer the formation of homochiral helices of predictable handedness.

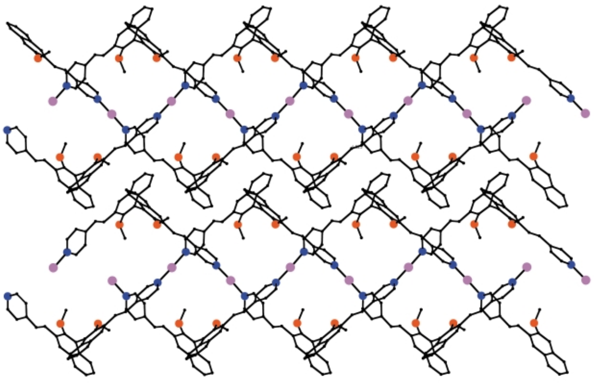

Fig. 3 A view showing the π···π stacking interactions between adjacent triple helices.

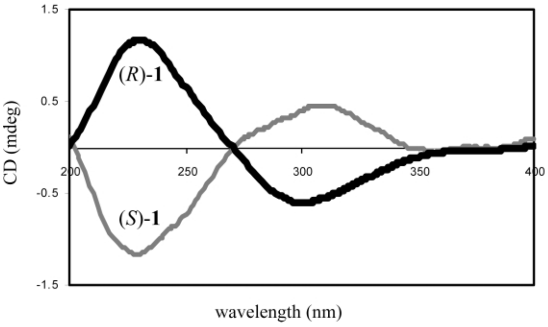

Fig. 4 Solid-state circular dichroism spectra of **1**.

In conclusion, we have developed a rational synthetic approach toward a homochiral triple helix using Ni(acac)$_2$ and a *C*2 symmetric ligand **L** as the building blocks. The helices spontaneously self-assembled into a 2D lamellar structure through strong interhelical π···π stacking interactions. We are currently extending this strategy to the synthesis of other chiral helices and using them as building blocks for supramolecular frameworks suitable for enantiospecific processes.

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Notes and references

‡ Synthesis of [Ni(acac)$_2$(L)]·(CH$_3$OH)$_{1.5}$·(H$_2$O), **1**. A mixture of Ni(acac)$_2$(H$_2$O)$_2$ (2.9 mg, 0.1 mmol) L (5.2 mg, 0.1 mmol), methanol (2 mL) and ethyl acetate (2 mL) in a capped vial was heated at 70 °C. After two days, single-crystals suitable for X-ray diffraction were obtained, washed with diethyl ether and dried in air. Yield: 5.7 mg (70%). Anal. calc. for C$_{47.5}$H$_{50}$N$_2$NiO$_{8.5}$: C, 67.63; H, 5.97; N, 3.32%. Found: C, 69.03; H, 5.21; N 3.42%. IR (cm^{-1}): 3437(mb), 1605(s), 1550(w), 1590(s), 1515(s), 1459(ms), 1408(s), 1358(m), 1256(m), 1236(m), 11135(w), 1102(w), 1015(m), 976(w), 922(w), 975(w), 922(w), 870(w), 814(w), 750(w).

§ X-ray single-crystal diffraction data for **1** were collected on a Siemens SMART CCD diffractometer. Crystal data: monoclinic, space group *C*2, $a = 26.4314(7)$, $b = 11.4071(3)$, $c = 16.5957(4)$ Å, $\beta = 114.379(2)$, $U = 4557.5(2)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.256$ g cm^{-3}, μ(MoKα) = 0.482 mm^{-1}. Least-squares refinements based on 6327 reflections with $I > 2\sigma(I)$ and 520 parameters led to convergence, with a final $R1 = 0.073$, $wR2 = 0.185$, and GOF = 1.06. CCDC 200587. See http://www.rsc.org/suppdata/cc/b2/b212781d/ for crystallographic data in .cif or other electronic format

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