Reversible folding/unfolding of linear molecular strands into helical channel-like complexes upon proton-modulated binding and release of metal ions

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The binding of appropriate metal ions to linear ligand strands obtained by hydrazone polycondensations generates channel-like complexes by reversible coiling of the ligand, thus allowing the generation of ion-induced, acid-base neutralization fuelled, molecular nanomechanical contraction/extension motions of large amplitude.

The control of the self-organization of molecular strands into well-defined shapes has been actively investigated in recent years both in view of its relation to the folding of biopolymers and of the goal to direct the formation of specific molecular (as well as supramolecular) architectures. To this end, structure enforcing subunits may be devised that induce folding of synthetic molecular strands. In our laboratory, sequences of azaheterocyclic groups and of pyridine-dicarboxamides have been developed as helicity codons enforcing the helical wrapping of molecular chains.

On the other hand, chemical effectors may be put to use to interconvert molecular shapes as has been achieved in the realization of acid-base fuelled, large amplitude extension/contraction (folding/unfolding) molecular motions by interconversion between a free helical state and a bound linear form through metal ion complexation or protonation. One may note that this amounts to the conversion of a free helicity codon into a bound linearity codon.

The reverse process would involve the effector induced interconversion between a free linear species and a bound helical one upon ion complexation and release (Fig. 1). Here we describe such a system, which furthermore provides an approach to a self-induced functional element of a molecular ion channel.

Whereas pyridine-pyrimidine sequences undergo helical wrapping and $\alpha,\alpha'$-linked oligopyridine chains adopt a linear shape, it has been shown that a pyridine group may be replaced by the isosteric hydrazone functionality, retaining the same structure inducing features while making the synthesis of extended oligomerinc strands much more accessible via simple amine (hydrazine)-carbonyl condensation.

The 5-tridentate site (counting the hydrazone groups and the central pyridine) ligand strands 1a–c (Fig. 2) were synthesized by a pathway based on hydrazone formation. The precursor 4 was obtained by a reaction between the alkylhydrazinopyridine 3 and the 2,6-pyridinedicarboxaldehyde, in a 1 : 1 molar ratio. The final double chain-extension was performed by a condensation between a bis(alkylhydrazino)terpyridine 5 and 4, in a molar ratio of 1 : 2. Their linear shape is based on proton NMR investigations (possible for 1b and 1c: 1a is not soluble in usual NMR solvents) and on the X-ray crystallographic molecular structure determined for shorter 2-site ligand analogs (not shown). Based on the latter, its length may be estimated to lie around 40 Å.

Treatment of a suspension of 1a–c in acetonitrile with 2 equiv. lead(n) trifluoromethanesulfonate produced species 2a–c presenting NMR (1H, NOESY) spectral features in agreement with the formation of a complex containing a helically folded ligand strand. Determination of its X-ray crystallographic molecular structure on crystals grown from a solution of 1a and 2 equiv. of Pb(OTf)$_2$ in acetonitrile (see Fig. 2) showed that 2a was a dinuclear complex (confirmed also by ES-MS investigations for species 2a–c) consisting of a ligand 1a wrapped around two Pb(n) ions in about two helical turns. The helix has a height of 7.2 Å, comparable to that of a 2-turn helically folded molecular strand, based on (pyrimidine-hydrazone) units. The nuclei of lead ions are 3.9 Å apart and one of them is separated by a bound water molecule from the trflate counterions located outside the helix.
Reversible contraction/extension molecular motions were indeed sequentially effected using the ligand 1b and followed by proton NMR spectroscopy (Fig. 4). They amount to a two-stroke, linear motion-type action of very large amplitude (7 Å to 40 Å), fuelled by the neutralization energy.

The present results demonstrate the realization of periodic molecular motions, in phase opposition with respect to ion binding, compared to the systems described earlier. They offer the possibility of combining both types of motions so as to produce locally resolved on/off type mechanical changes. Such studies are in progress.

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Notes and references
† Crystallographic data: C₃₈H₃₉N₁₅Pb₂O₄·SO₄CF₃CH₃CN; 1835.61 g mol⁻¹; monoclinic; space group: P12₁/c1; a = 15.2500 (2), b = 17.5684 (2), c = 24.0749 (3) Å; β (deg) = 95.117 (5); V = 6424.4 Å³ (1); T = 173 K; Z = 4; Δνo = 1.90 cm⁻¹. F(000): 3500; number of data measured: 19130; number of data with I > 2σ (I): 11596; number of variables: 838; R = 0.071; Rw = 0.086; goodness-of-fit = 1.146; the hydrogen atoms on the coordinated water molecule could not be located.

CCDC 237616. See http://www.rsc.org/suppdata/cc/b4/b407168a/ for crystallographic data in cif format.


8 The syntheses will be described in detail in a forthcoming paper: A.-M. Stadler and J.-M. Lehn, in preparation.

