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Half-rotation in a kinetically locked [2]catenane induced by transition metal ion substitution†

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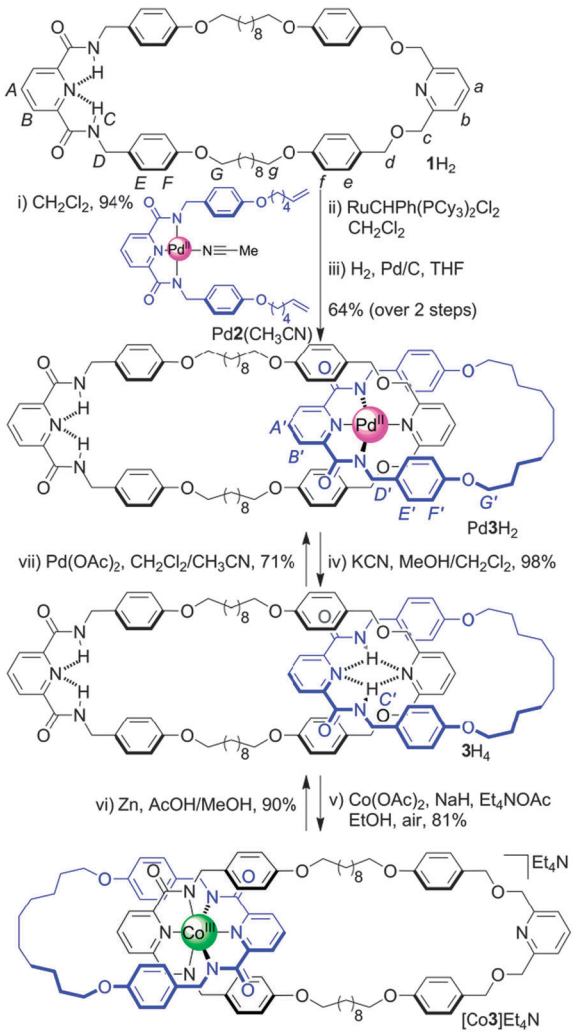
We report on a heterocircuit [2]catenane in which a reversible half-rotation of one ring about the other can be induced, and locked in place, by switching the coordination of the interlocked rings between Pd(II) and Co(III).

Reversible control of large amplitude sub-molecular motions is a feature of many of the structures considered to be prototypical elements of synthetic molecular machines.[1] Although many methods to efficiently assemble mechanically interlocked molecules have been developed,[2] there are relatively few examples through which the interlocked macrocycles can be 'locked' in different co-conformations.[3–7] Sauvage and colleagues have exploited the different coordination preferences of Cu(I) (tetrahedral) and Cu(II) or Zn(II) (trigonal bipyramidal) in the switching of catenanes,[3] rotaxanes[4] and so-called "molecular muscles".[5,6] Here we report on a heterocircuit [2]catenane that can be kinetically fixed in two different co-conformations through binding of both macrocycles to non-labile transition metal ions with different coordination requirements, specifically square planar Pd(II) and octahedral Co(III). The mechanism of formal rotation is a two stage process: (i) 'unlocking' of the system by removing the chelated metal ion, allowing relative movement of the interlocked rings, followed by (ii) addition of a different metal ion to lock the molecule in its new co-conformational arrangement.

Metal template synthesis is a powerful tool for the assembly of mechanically interlocked molecular structures.[8] A '3 + 1' donor set enables square planar Pd(II) ions to form kinetically robust heteroleptic complexes in which the ligands can be preorganised for the synthesis of both rotaxanes[9] and catenanes.[10] We used this strategy to prepare [2]catenane Pd**3**H_2 by coordination of Pd**2**(CH_3CN) to the 2,6-bis(oxymethylene)pyridine moiety of macrocycle **1**H_2 (Scheme 1, i) and subsequent ring closing metathesis and hydrogenation (Scheme 1, ii, iii).



Scheme 1 Synthesis and reversible interconversion of Pd**3**H_2, **3**H_4 and [Co**3**]Et_4N.

Comparison of the ^{1}H NMR spectra of macrocycle **1**H_2 and Pd**3**H_2 (Fig. 1a and b) shows a significant upfield shift of several signals corresponding to aromatic resonances closest to the 2,6-bis(oxymethylene)pyridine motif (H_e and H_f) in the [2]catenane whereas signals close to the 2,6-dicarboxamide unit (*e.g.* H_D) are essentially unchanged. Although the large macrocycle is bound to the metal centre by a single coordination

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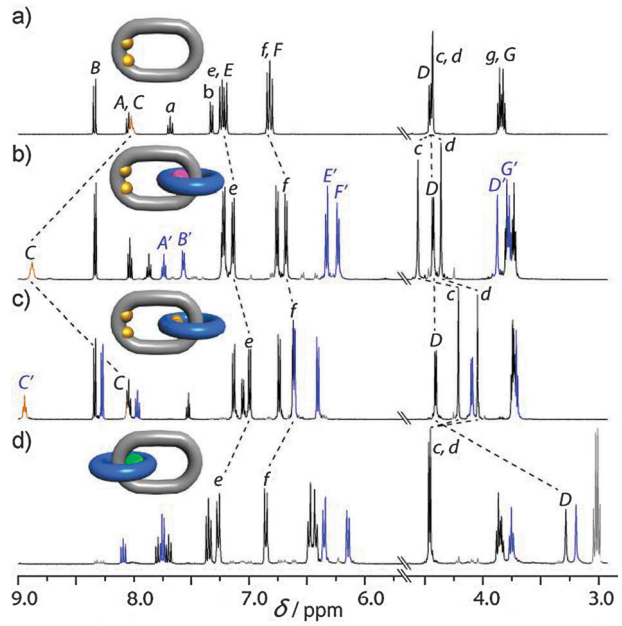

Fig. 1 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of (a) macrocycle $\mathbf{1}H_2$, (b) Pd$\mathbf{3}H_2$, (c) $\mathbf{3}H_4$ and (d) [Co$\mathbf{3}$]Et_4N. The assignments of the signals correspond to those shown in Scheme 1. Signals corresponding to residual solvent peaks, trace impurities and the Et_4N counterion are shown in grey.

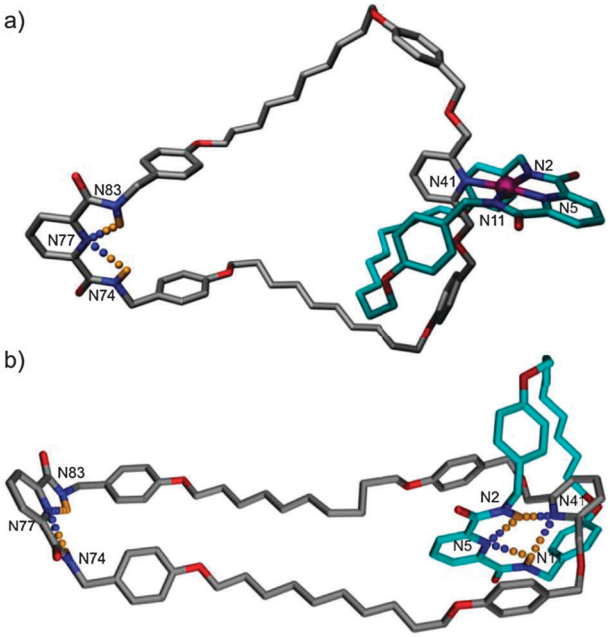

Fig. 2 X-Ray crystal structures of (a) Pd$\mathbf{3}H_2$ (CCDC 874998) and (b) $\mathbf{3}H_4$ (CCDC 874997). Carbon atoms of the smaller macrocycle are shown in light blue and those of the larger macrocycle in grey, oxygen atoms are red, nitrogen dark blue, hydrogen gold, and palladium pink. For clarity non-amide hydrogen atoms are not shown. Selected bond lengths for Pd$\mathbf{3}H_2$ [Å]: Pd-N2 2.06; Pd-N5 1.92; Pd-N11 2.04; Pd-N41 2.08; N77-H74 2.45; N77-H83 2.01; other selected distance [Å]: N5-N41 4.00. Selected bond angles for Pd$\mathbf{3}H_2$ [°]:N2-Pd-N11 161.1; H74N-N77-H83N 77.1. Selected bond lengths for $\mathbf{3}H_4$ [Å]: H2N-N5 2.45; H11N-N5 2.34; H2N-N41 2.28; H11N-N41 2.43. Selected bond angles for $\mathbf{3}H_4$ [°]: H2N-N5-H11N 75.2; H2N-N41-H11N 76.8.

bond this motif is kinetically stable.[10] A large downfield shift of the amide protons (H_C) of the $\mathbf{1}H_2$ macrocycle in the [2]catenane is also observed suggesting that intercomponent hydrogen bonding occurs, probably to the carboxamido oxygens of the other ring through folding in solution. The topology of Pd$\mathbf{3}H_2$ was confirmed by X-ray crystallography of a single crystal grown from slow cooling of a hot saturated solution of the complex in acetonitrile (Fig. 2a). The intercomponent hydrogen bonding interaction observed in solution is satisfied intermolecularly in the solid state (see ESI†).

Macrocycle $\mathbf{1}H_2$ also contains a 2,6-pyridinedicarboxamide binding site that in its deprotonated (carboxamido) form has been previously shown to bind a selection of 'hard' transition metal ions,[11] including Co(III).[12] Conversion of [2]catenane Pd$\mathbf{3}H_2$ into the corresponding octahedral Co(III) complex was carried out in two steps (Scheme 1, iv, v). Removal of the Pd(II) ion with KCN furnished the free ligand $\mathbf{3}H_4$ in 98% yield (Scheme 1, iv). The downfield shift of the amide signal $H_{C'}$ and the pronounced shielding of signals H_c and H_d in the ^{1}H NMR spectrum (Fig. 1c) indicates that the general co-conformation of Pd$\mathbf{3}H_2$ is retained in the metal-free catenane $\mathbf{3}H_4$ in CD_2Cl_2 through an intercomponent pyridine-NH-pyridine bifurcated H-bond motif.[13] The X-ray structure of a single crystal of the demetalated catenane, grown by slow diffusion of diethyl ether into a saturated solution of $\mathbf{3}H_4$ in CH_2Cl_2, confirms that this arrangement is maintained in the solid state (Fig. 2b).

Treatment of $\mathbf{3}H_4$ with $Co(OAc)_2$, Et_4NOAc and sodium ethoxide followed by stirring under air generated [Co$\mathbf{3}$]Et_4N in 81% yield (Scheme 1, v). Introduction of the Co(III) ion introduces several pronounced changes to the ^{1}H NMR spectrum of [Co$\mathbf{3}$]Et_4N (Fig. 1d) verifying that the two macrocycles have undergone a significant shuttling motion in order to accommodate the trivalent metal ion. Resonances corresponding to benzylic protons H_D and $H_{D'}$ are heavily shielded in [Co$\mathbf{3}$]Et_4N with respect to Pd$\mathbf{3}H_2$ and $\mathbf{3}H_2$, whilst the chemical shifts of the H_c and H_d signals are similar to those in $\mathbf{3}H_2$, indicating that they are no longer in close proximity to the aromatic groups of the small amide macrocycle. The calculated minimum energy structure (Spartan 06, MMFF) of [Co$\mathbf{3}$]Et_4N, showing the 180° half-turn indicated by the ^{1}H NMR data, is shown in Fig. 3.

To return the heterocircuit catenane back to its original state [Co$\mathbf{3}$]Et_4N was stirred first with Zn in acetic acid and then treated with $Pd(OAc)_2$ in a mixture of CH_2Cl_2 and CH_3CN (Scheme 1, vi, vii). We attribute the modest yield (71%)

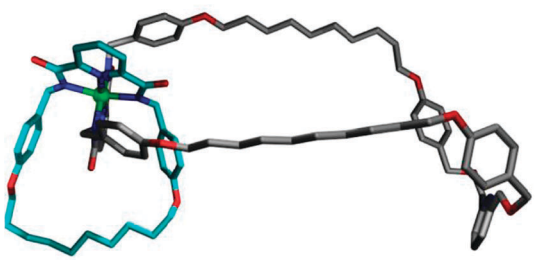

Fig. 3 Energy minimised structure of [Co$\mathbf{3}$] (Spartan 06, MMFF). The colour scheme is as for Fig. 2 with the addition of cobalt (green). For clarity hydrogen atoms and the Et_4N counterion are not shown.

of the final step to small amounts of Pd(II) binding to the 2,6-pyridine dicarboxamide of the large macrocycle.

In summary, a switchable [2]catenane has been prepared for which the co-conformation is controlled by the coordination preference of the transition metal ion the interlocked macrocycles bind to. The [2]catenane is co-conformationally locked when bound to either metal; switching between the two sites is permitted by first abstracting the transition metal ion (Pd(II) or Co(III)), which allows the sub-molecular fragments to rotate more freely, and then locking the structure again through metal ion re-coordination. Easily operated and reversible systems for controlling the co-conformation of heterocircuit [2]catenanes could prove useful in the design of more complex pieces of synthetic molecular machinery.

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