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A New Doubly Interlocked [2]Catenane

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Topologically interesting molecular structures can be considered as one of the areas at the forefront of chemical topology. The understanding and control of noncovalent interactions have allowed the systematic synthesis of knots, catenanes, and rotaxanes to be undertaken.[1]

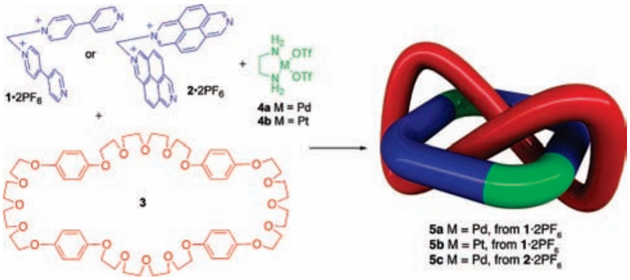
In knot theory, a knot is defined as a closed, nonself-intersecting curve that is embedded in three dimensions and cannot be untangled to produce a simple loop (i.e., the unknot). A knot can be generalized to a link, which is simply a knot collection of one or more closed strands. Therefore, links can be roughly characterized by its number of components and crossing number, the latter is the minimal number of crossings of any diagram of the link.

Only a small number of molecular knots or links have been prepared. The first synthesis of a trefoil knot (3_1^1 according to Rolfsen notation[2]), the simplest knot, was reported by Dietrich-Buchecker and Sauvage employing a metal-directed self-assembly based on helical Cu^I-phenanthroline complexes.[3] Other trefoil knots were assembled by $\pi-\pi$ interactions,[4] hydrogen bonding,[5] and folding around an octahedral center.[6] Among the links, only three types have their molecular counterparts. The simplest link with two components is the Hopf link (2_1^2) representative of [2] catenanes and it is by far the link with more molecular examples.[1b,c] The second link type, Borromean rings, (6_2^3) is characterized by three components and six crossings.[7] Finally, only three examples of the third type, the Solomon link (4_1^2), can be found in the literature: (a) a 4-crossing [2]catenane could be prepared using a metal templation strategy from two linear coordinating fragments, each containing three 1,10-phenanthroline units,[8a,b] (b) two 50-membered organogold rings were doubly interlocked from eight components to give an octagold complex,[8c] and (c) more recently, the synthesis of a Solomon link has been accomplished via metal-directed self-assembly and dynamic covalent chemistry.[8d]

Continuing our investigations on self-assembled [2] and [3]catenanes,[9] we report the structure and synthesis of a doubly braided [2]catenane, a new molecular 4_1^2 link, obtained by a 5-component-self-assembly process based on coordinative bonds and π−donor/π−acceptor interactions.

The addition of 0.5 equiv of cyclophane **3**[10] to an equimolar solution of **1**$\cdot 2PF_6$[9a] and (en)$PdOTf_2$ (**4a**) (10 mM) in CD_3CN at room temperature resulted in a color change from light yellow to intense red (Scheme 1). The ^1H NMR spectrum of the solution shows broad signals, which indicates an equilibrium situation that is close to coalescence. When the temperature was lowered to 253 K, the spectrum showed well-resolved peaks consistent with the formation of the molecular Solomon link **5a**$\cdot 4PF_6 \cdot 4OTf$. The aromatic signal of the outside dioxoaryl rings (HQ_{out}) is characteristically shifted upfield ($\Delta\delta = -0.45$ ppm) suggesting a π interaction with the bipyridine units. Two sets of resonances for the aromatic protons of the metallocycle were observed as a consequence of the slow exchange, on the NMR scale, between the bipyridine units orthogonal to the inside dioxoaryl rings (HQ_{in}) and the parallel ones. Methylene protons of the metallocycle appear as doublets at $\delta = 6.93$ ppm ($J = 13.9$ Hz) and $\delta = 7.15$ ppm ($J = 13.9$ Hz). The DOSY measurement of the solution showed that all signals have the same log D, indicating the existence of a single species. The formation of the [2]catenane from different starting stoichiometries was studied by ^1H NMR. The [2]catenane was self-assembled in presence of either an excess of cyclophane **3** or metallocycle (**1**$\cdot 2PF_6$ + (en)$PdOTf_2$), signals attributable to unbound **3** in the former case and the metallocycle in the latter are shown in the ^1H NMR spectrum (see Supporting Information). In the latter case, a ^1H DOSY experiment was carried out to determine the relative size of the two species in solution. DOSY measurement showed that the observed D values of the signals of the [2]catenane are in the same order of magnitude as those of the metallocycle, indicating that both species have similar hydrodynamic radii.

Scheme 1. Synthesis of Molecular Solomon Links **5a**−**c**



Employing a similar strategy to that we used in the above cases and taking advantage of "molecular lock" strategy,[11] Pt catenane was isolated as its hexafluorophosphate salt in a 61% yield. A solution of the bipyridine ligand **1**$\cdot 2PF_6$, (en)$PtOTf_2$, and macrocycle **3** in CH_3CN was heated at 50 °C for 7 d. The formation of **5b**$\cdot 8PF_6$ was supported by NMR and MS. The ^1H NMR spectrum recorded at 253 K shows two doublets for NCH_2N, multiplets attributable to amine protons, and the inequivalence for the aromatic hydrogens of the alongside dioxoaryl. In both Pd and Pt catenanes, the loss of symmetry of the structure can be explained by assuming the formation of a doubly interlocked [2]catenane structure, which implicates the loss of the symmetry plane formed by the four corners of the cationic macrocycle. The rotation of the bipyridine system was quicker along the N−N axis than the NMR time scale averaged the signals for its protons, and only four doublets appear for each bipyridine. A fast "rocking process" for the dioxoaryl rings could average these signals but the topology of the complex precludes this process. The ^1H NMR spectrum of **5b**$\cdot 8PF_6$ measured in CD_3COCD_3 at 188 K showed at least thirteen resonances for the bipyridine protons, suggesting that the rotation is almost frozen. The HR-ESI features signals resulting from the loss of between two and five hexafluorophosphate ions, which match the simulated isotopic patterns.

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It is well-known that 2,7-diazapyrene is a good electron acceptor, so we carried out the synthesis of ligand **2**•2PF$_6$ from 2,7-diazapyrene and dibromomethane. As expected, the formation of the square metallocycle from **2**•2PF$_6$ and (en)PdOTf$_2$ (2.5 mM) proceed at room temperature in CD$_3$NO$_2$. The spectroscopic characteristics are very similar to those of the bipyridine metallocycle (see Supporting Information).[9a]

The diazapyrenium catenane was self-assembled from ligand **2**•2PF$_6$, cyclophane **3**, and (en)PdOTf$_2$ in CD$_3$NO$_2$. The ^{1}H NMR spectrum recorded at room temperature shows again separated resonances for the parallel (DZP$_{par}$) and orthogonal (DZP$_{ort}$) π-acceptor system. Interestingly, each set shows eight resonances due to the inequivalence of the eight diazapyrene protons, four singlets for the α protons, and four doublets for the γ (Figure 1).

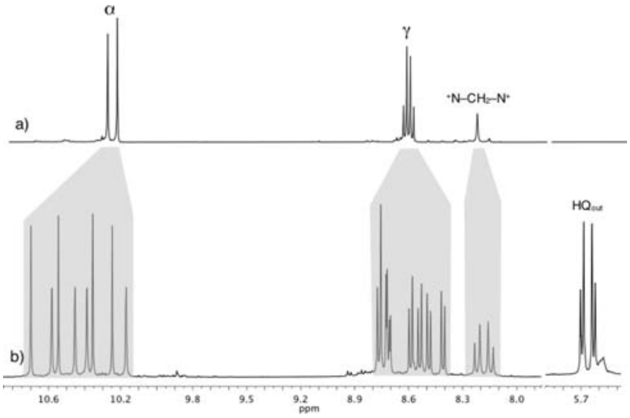

Figure 1. Partial ^{1}H NMR (500 MHz, 298 K, CD$_3$NO$_2$) spectra of (a) ligand **2**•2PF$_6$ (2.5 mM) and **4a** (2.5 mM); (b) Same + **3** (1.25 mM).

Therefore, the rotation of the diazapyrenes along the N−N axis at room temperature is slow in the NMR time scale. The HQ$_{out}$ protons are more shielded ($\Delta\delta \approx -1.10$ ppm) than the corresponding protons in the bipyridine catenanes **5a**,**b**.

The X-ray crystal study revealed a [2]catenane structure with the metallocycle doubly encircled by the cyclophane **3** (Figure 2).[12]

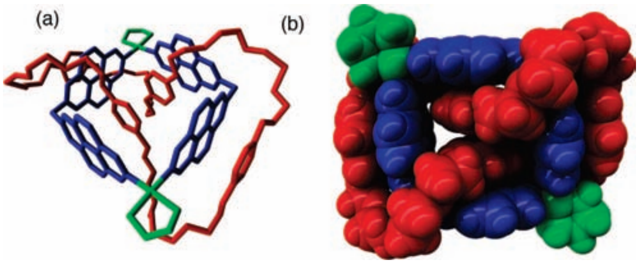

Figure 2. Crystal structure of **5c**•4OTf •4PF$_6$. (a) Cylinder model (ligand **2**, blue; (en)Pd, green; cyclophane, **3** red). Hydrogen atoms, solvent molecules, and counteranions were omitted for clarity. (b) Space-filling model.

Two of the dioxoaryl rings are inserted into the metallocycle displaying a $\pi-\pi$ stacking arrangement of four components (DZP$_{par}$/HQ$_{in}$/HQ$_{in}$/DZP$_{par}$) with interplanar distances of 3.52, 3.72, and 3.52 Å, respectively. The other two donor rings are located outside of the metallocycle but involved in $\pi-\pi$ interactions with DZP$_{ort}$ (interplanar distance 3.38 Å). The catenane is also stabilized by [N−H•••O] bonds between ethylenediamine nitrogens and polyether oxygens, [C−H•••O] bonds between the α-CH diazapyrene and $^+$NCH$_2$ hydrogens and the oxygen atoms of **3**.

In conclusion, we have achieved the self-assembly of a molecular Solomon link formed by the union of five components, and in the case of link **5b** its isolation. It is particularly interesting how π-interactions, hydrogen bonding, and metal coordination led to an unusual molecular topology. These findings can be useful to develop the synthesis of higher order molecular links.

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Supporting Information Available: Experimental procedures, ^{1}H NMR, ^{13}C NMR, and 2D experiments for all compounds, and crystallographic file (in CIF format) of **5c**•4OTf•4PF$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) Rolfsen notation, here C_k^r denotes the kth r-component link with crossing number C. For a complete list of knots and links see: Rolfsen, D. *Knots and Links*; Publish or Perish: Wilmington, DE, 1976.

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(12) Crystal data for **5c**•4OTf•4PF$_6$•4CH$_3$CN•4H$_2$O: formula, C$_{130}$H$_{144}$F$_{36}$N$_{16}$O$_{36}$P$_4$Pd$_2$S$_4$; formula weight, 3655.53; crystal system, monoclinic, space group, $C2/c$; $a = 44.661(5)$, $b = 13.570(5)$, $c = 29.304$ Å, $\alpha = 90.000(5)$, $\beta = 114.204(5)$, $\gamma = 90.000(5)°$, $V = 16198(7)$ Å^3, $Z = 4$, reflections measured 82038, unique reflections 16451 ($R_{int} = 0.0872$), $T = 100$ K, $R1$ ($I > 2\sigma(I)$) = 0.2033, w$R2$ (all data) = 0.3910.

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