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Communication

New Hybrid [2]Catenanes Based on a 4,4′-Bipyridinium Ligand

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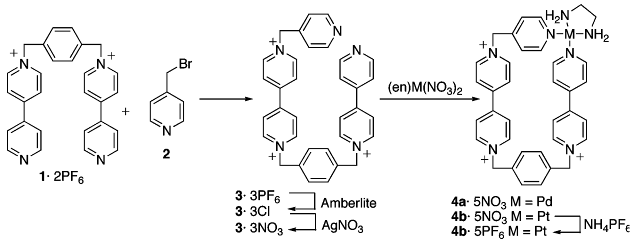
The self-assembly-mediated synthesis of metallomacrocycles **4a** and **4b** from (en)M(NO$_3$)$_2$ (M = Pd, Pt) and bipyridinium ligand **3** is described. The reaction is templated by disodium *p*-phenyldiacetic dicarboxylate, which is inserted into the macrocyclic cavity. Similarly, the self-assembly process between ligand **3**, (en)M(NO$_3$)$_2$ (M = Pd, Pt), and the macrocyclic polyether **6** resulted in the formation of hybrid catenanes **7a** and **7b**. In the [2]catenanes, the circumrotation of the macrocyclic polyether through the cavity of the metallocycle is slow on the ^{1}H NMR time scale.

Catenanes have experienced a dramatic development in the course of the last 2 decades.[1] In addition to the remarkable self-assembly formation reactions and the unusual structures, these interlocked molecules are regarded as very promising prototypes for molecular-scale memory devices, molecular machines, and motors.[2] The field of metal-containing macrocycles and their use in the formation of catenanes incorporating transition metals have been pioneered by Stang,[3] Fujita,[4] and Sauvage,[5] who have synthesized catenanes containing coordinative bonds such as M^{II}–N (M = Pd, Pt, Cu, Ru). More recently, other catenanes including metals such as Au[6] and Co[7] in their frameworks have been reported. Furthermore, a large number of synthetic strategies based on ideas such as π–π interactions, cation templation, hydrophobic forces, and H bonding have been developed to obtain catenanes with *organic* macrocycles.[8] However, the number of hybrid catenanes with *organic* and *inorganic* macrocycles has remained relatively small.[9]

Scheme 1. Synthesis of Metallocycles **4a** and **4b**



As a part of our continuing investigations with bipyridinium ligands[10] and with the aim of designing new catenanes, we decided to combine the concept of molecular lock[11] and a self-assembly process based on π–π-stacking interactions between viologens and dioxoaryls in the synthesis of a hybrid [2]catenane. Ligand **3** was obtained by the reaction of bis(hexafluorophosphate) salt **1**·2PF$_6$[12] with 4-(bromomethyl)pyridine (**2**; Scheme 1).

The addition of 1 equiv of (en)Pd(NO$_3$)$_2$ to a D$_2$O solution of **3**·3NO$_3$ (15 mM) at room temperature gave rise to

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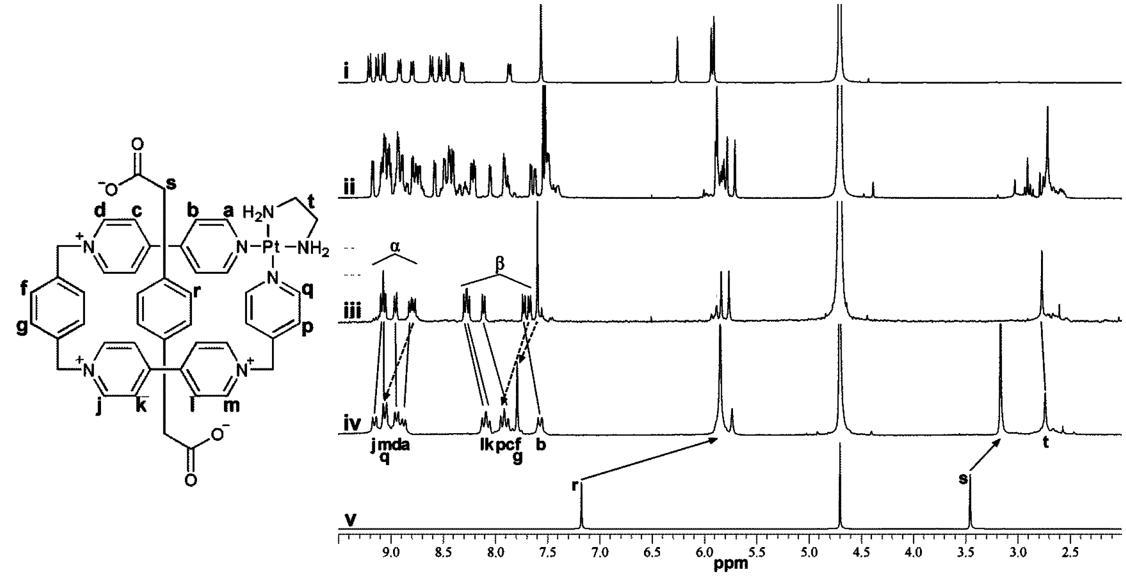


Figure 1. ^{1}H NMR (D_2O, 300 MHz, 298 K) of (i) **3**·$3NO_3$, (ii) an equimolecular solution of **3**·$3NO_3$ and (en)Pt$(NO_3)_2$ (10 mM) after heating at 373 K for 24 h, (iii) an equimolecular solution of **3**·$3NO_3$ and (en)Pt$(NO_3)_2$ (0.5 mM) after heating at 373 K for 7 days, (iv) an equimolecular solution of **3**·$3NO_3$,(en)Pt$(NO_3)_2$, and **5** (10 mM) after heating at 373 K for 12 h, and (v) **5**.

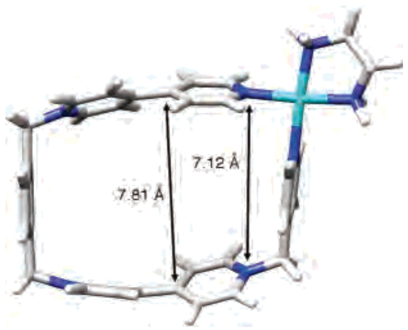
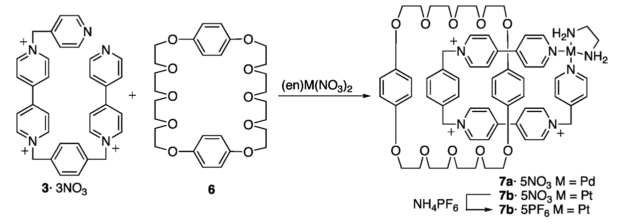


Figure 2. Optimized geometry of metallomacrocycle **4b**.

Scheme 2. Synthesis of Catenanes **7a** and **7b**



oligomeric products. Dilution of this solution showed that oligomeric products are in equilibrium with **4a**·$5NO_3$ and that dilution favors the formation of a metallocycle. Only at concentrations of 0.5 mM or lower is **4a**·$5NO_3$ the only product (see the Supporting Information). Electrospray ionization mass spectrometry (ESI−MS) of **4a**·$5NO_3$ in a CH_3OH solution at 0.5 mM concentration confirmed the structure of **4a**·$5NO_3$, showing a peak for *m*/*z* 445 $[M - (NO_3)_2]^{2+}\cdot CH_3OH$].

Pt complex **4b**·$5NO_3$ could not be self-assembled at room temperature. The formation of macrocycle **4b**·$5PF_6$ was achieved by the reaction of **3**·$3NO_3$ (0.5 mM) with 1 equiv of (en)Pt$(NO_3)_2$ at 100 °C for 7 days and subsequent anion exchange with NH_4PF_6. The ^{1}H and ^{13}C NMR spectra of **4b**·$5PF_6$, together with its 2D (COSY, HMQC, and HSQC) NMR spectra (Supporting Information), provide good evidence for the formation of the macrocycle. The ^{13}C NMR signals for C_a and C_q (Figure 1) have shifted downfield from those of the free ligand ($\Delta\delta = 5.0$ and 7.2 ppm, respectively) as a result of the formation of coordinative bonds. The formation of **4b**·$5PF_6$ was also supported by fast atom bombardment (FAB)-MS. The isolation on a preparative scale of pure macrocycle **4b**·$5PF_6$ was achieved by using disodium *p*-phenyldiacetic dicarboxylate (**5**) as a template. The heating at 100 °C for 12 h of a water solution of **5** (10 mM), **3**·$3NO_3$ (10 mM), and (en)Pt$(NO_3)_2$ (10 mM) gave, after counteranion exchange,[13] **4b**·$5PF_6$ in 76% yield. The ^{1}H NMR spectra for **3**·$3NO_3$, **5**, and **5**$\subset$**4b**·$5NO_3$ in D_2O are shown in Figure 1. The upfield shift of the signals of template **5** ($\Delta\delta = 1.33$ and 0.30 ppm, H_r and H_s, respectively) along with the upfield shift of the β protons of the bipyridine units and the downfield shift of the pyridine ($H_{p,q}$) and phenylene protons ($H_{f,g}$) strongly suggests that the template is inserted into the cavity of metallomacrocycle.

The **4b** system was characterized by means of density functional theory calculations (B3LYP model). The calculated geometry is shown in Figure 2 (see also the Supporting Information). The metal center shows a square-planar geometry, in which bond distances and angles are in the usual range.[14] Figure 2 shows distances between nonbonded atoms of the metallomacrocycles that give an estimate of the size of the macrocyclic cavity. The distance between the two pseudoparallel bipyridinium units in **4b** amounts to

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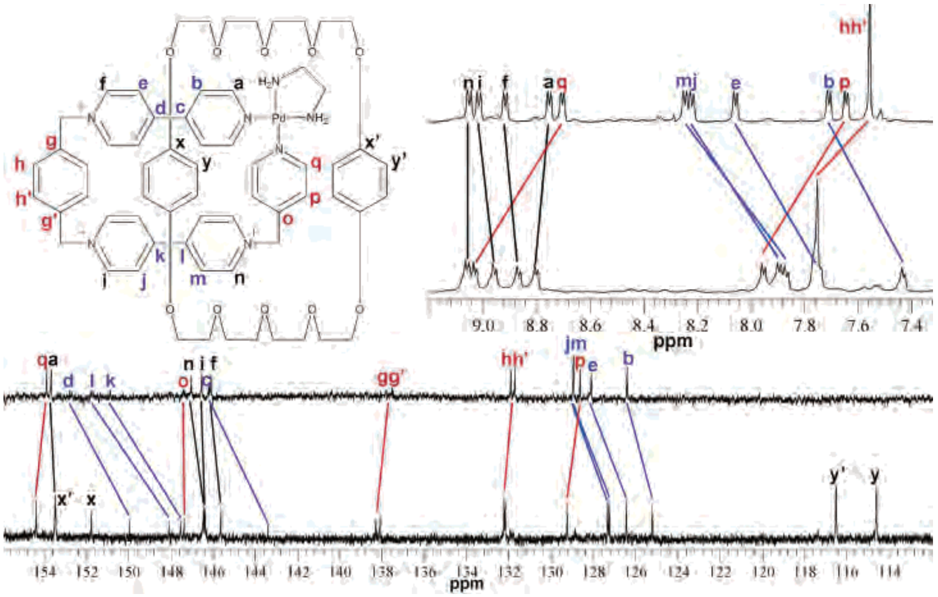

Figure 3. ^{1}H NMR (D_2O, 500 MHz, 298 K) and ^{13}C NMR (D_2O, 125 MHz, 298 K) spectra of metallocycle **4a**$\cdot 5NO_3$ (top) and catenane **7a**$\cdot 5NO_3$ (bottom).

7.1−7.8 Å, which is approximately twice the optimal π-stacking distance.[15] Thus, the macrocyclic cavity of **4b** presents a nearly optimal size to form supramolecular complexes through π-stacking interactions with electron-rich aromatic units.

When an equimolar solution (10 mM) of ligand **3**$\cdot 3NO_3$, (en)Pd$(NO_3)_2$, and macrocycle **6**[12] in D_2O was heated at 100 °C for 10 h, the solution color changed to red and no peaks other than those of catenane **7a**$\cdot 5NO_3$ could be observed in the ^{1}H NMR spectrum (Scheme 2). The diffusion coefficients obtained from DOSY[16] (diffusion-ordered NMR spectroscopy) experiments of catenane **7a**$\cdot 5NO_3$ and ligand **3**$\cdot 3NO_3$ showed that the catenane is significantly larger than its components.[17] The signals from the ligand, macrocycle **6**, and the Pd complex showed the same diffusion coefficients, indicating that the three components diffuse as a whole.

In the [2]catenane, exchange between the “inside” and “alongside” hydroquinol rings is slow at room temperature, resulting in all of the OCH_2 groups being anisochronous on the ^{1}H NMR time scale. The ^{1}H and ^{13}C NMR spectra show the upfield shift of the signals for the “inside” hydroquinol ring protons ($\delta = 3.67$ ppm)[18] and carbons (peaks labeled x and y in Figure 3) as a result of the C−H−π interaction with the pyridine and *p*-phenylene rings on the short side of the rectangle. The protons and carbons of these rings are downfield shifted from those of the macrocycle **4a**$\cdot 5NO_3$ (red lines in Figure 3). Moreover, the signals for the protons and carbons at the central positions of the bipyridine moieties have shifted upfield (blue lines in Figure 3) as a result of the shielding effect of the macrocycle **6**.

Employing the same strategy that we used in the preparation of catenane **7a**$\cdot 5NO_3$, the analogous platinum catenane could be isolated as its hexafluorophosphate salt. A solution of ligand **3**$\cdot 3NO_3$, (en)Pt$(NO_3)_2$, and macrocycle **6** (2 equiv) in H_2O was heated at 100 °C for 12 days. The addition of NH_4PF_6 made it possible to obtain **7b**$\cdot 5PF_6$ as a red powder in high yield (85%). The formation of **7b**$\cdot 5PF_6$ was confirmed by NMR and MS. The FAB-MS spectrum of **7b**$\cdot 5PF_6$ is very characteristic of interlocked molecular compounds containing bipyridinium residues.[19] Prominent peaks are observed at *m*/*z* 2024.6 $[MH]^+$, 1879.6 $[M - PF_6^-]^+$, 1734.5 $[M - 2PF_6^-]^+$, 1588.8 $[M - 3PF_6^-]^+$, 867.4 $[M - 2PF_6^-]^{2+}$, and 794.7 $[M - 3PF_6^-]^{2+}$.

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Supporting Information Available: Experimental details and characterization of **3**$\cdot 3NO_3$, **4b**$\cdot 5PF_6$, and **7b**$\cdot 5PF_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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