ORGANIC LETTERS

2007
Vol. 9, No. 4
675−678

Synthesis of [3]Catenanes Based on Metal-Directed Self-Assembly and π-Donor/π-Acceptor Interactions

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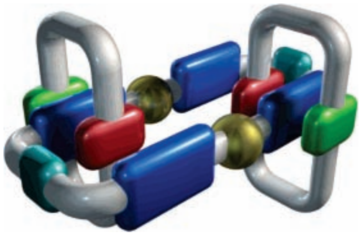
Received November 20, 2006

ABSTRACT



A metal-directed self-assembly of [3]catenanes in combination with π–π interactions was investigated. Ligands based on 4,4′-bipyridinium or 2,7-diazapyrenium were used in conjunction with dioxoaryl cyclophanes (4–6) and *trans*-$PdCl_2(CH_3CN)_2$. The [3]catenanes show a dinuclear palladium 46-membered metallomacrocycle interlocked by two π-complementary dioxoaryl macrocycles.

Metal self-assembly has been extensively utilized for the synthesis of catenanes, rotaxanes, and knots.[1] These molecules are regarded as very promising prototypes for molecular-scale memory devices, molecular machines, and motors.[2] In many cases, the synthetic strategy relies on labile metal−ligand coordination bonds and the suitable choice of the ligand and metal geometries.

4,4′-Bipyridine and 2,7-diazapyrene are ligands that have been widely employed in the construction of 2D and 3D supramolecular assemblies based on metal-directed processes.[3] However, the poor π-acceptor ability of these systems limits the use of π-acceptor/π-donor interactions in the formation of supramolecular complexes based on this type of ligands.

On the contrary, the *N*,*N*′-dialkyl-4,4′-bipyridinium or *N*,*N*′-dialkyl-2,7-diazapyrenium derivatives show a strong π-deficient character which has been successfully used by Stoddart and Balzani in the preparation of a myriad of catenanes and rotaxanes,[1a,4] although the lack of metal-binding units (coordinative nitrogen atom) precludes their usage as ligands.

To take advantage of metal-directed self-assembly and π-acceptor/π-donor interactions, we decided to explore the

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10.1021/ol062824c CCC: \$37.00

use *N*-monoalkyl-4,4′-bipyridinium or *N*-monoalkyl-2,7-diazapyrenium derivatives to synthesize supramolecular complexes. Both ligands show π-deficient aromatic surfaces that, probably, will become more π-deficient upon the formation of a coordinative bond between the nitrogen and palladium atoms.

As part of our continuing investigations on the synthesis of metallomacrocycles and catenanes based on bipyridinium ligands[5] and with the aim of designing new interlocked systems, we propose the use of $\pi-\pi$ interactions in combination with metal-directed self-assembly in the synthesis of [3]catenanes.

In this communication, we report an efficient and simple preparation of [3]catenanes by self-assembly of six components (a ligand based on 4,4′-bipyridinium or 2,7-diazapyrenium, a dioxoaryl cyclophane, and a square-planar palladium complex) in a 2:2:2 ratio (Figure 1 and Table 1).

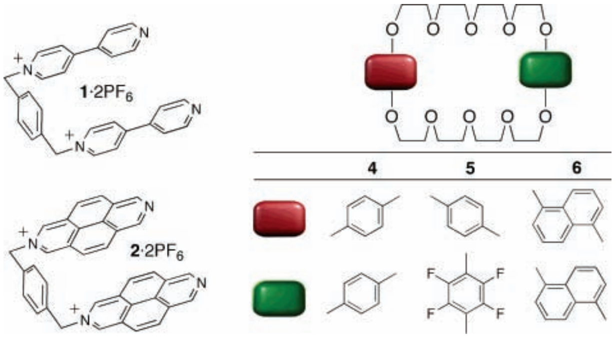


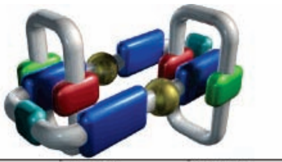
Figure 1. Structures of ligands and macrocycles **4**−**6**.

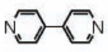
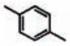
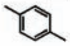
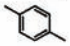
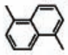
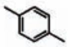
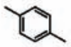
The addition of 1 equiv of *trans*-$PdCl_2(CH_3CN)_2$ (**3**) to a solution of bipyridinium ligand **1**·$2PF_6$ (2 mM) in CD_3CN at room temperature resulted in the formation of a mixture of products. However, after the addition of 12 equiv of **4**, we finally obtained a quite simple ^1H NMR spectrum that shows the expected signals for [3]catenane (Figure 2).

The upfield shift of the aromatic signals of macrocycle **4** and the β protons of the bipyridine units ($\Delta\delta = -1.28$, $\Delta\delta = -0.60$, and $\Delta\delta = -0.86$ ppm for H_k, H_b, and H_e, respectively), along with the downfield shift of the phenylene protons ($\Delta\delta = 0.18$ ppm for H_i) as the result of the $C-H\cdots\pi$ interaction with dioxoaryl rings, strongly suggest that the cyclophane **4** is inserted into the cavity of the metallomacrocycle (Figure 2). The ^{13}C NMR spectrum shows the characteristic downfield shifts for C_a, C_b, and C_c expected for coordination of the pyridyl nitrogen atoms to the Pd atoms (red arrows in Figure 3). The signals for the carbons at the pyridinium (C_{d-f}) and hydroquinol rings ($C_{j,k}$) are shifted upfield (blue arrows) as a result of the mutual shielding effect.

The 1:2 integration ratio between the signals of the metallomacrocycle and the cyclophane **4** indicates that, for each metallomacrocyclic component, there are two encircling cyclophane rings in keeping with the molecular structure of a [3]catenane. Exchange between the "inside" and "alongside" hydroquinol rings is fast at room temperature, resulting in an average signal ($\delta = 5.50$ ppm) for the aromatic protons of **4**.

Table 1. Structures of [3]Catenanes **7**−**10**·$4PF_6$



	7·$4PF_6$	**8**·$4PF_6$	**9**·$4PF_6$	**10**·$4PF_6$
●	Cl-PdCl	Cl-PdCl	Cl-PdCl	Cl-PdCl
🟦				
🟥				
🟩				
solvent	CD_3CN	CD_3NO_2	CD_3NO_2	CD_3NO_2
$c_L/c_{Pd}/c_M$[a]	2/2/24	2/2/2	2/2/3	2/2/2

[a] c_L, c_{Pd}, and c_M stand for the concentration (mM) of the ligand, $PdCl_2(CH_3CN)_2$, and macrocycles (**4**−**6**), respectively.

The diffusion coefficients obtained from DOSY[6] (diffusion-ordered NMR spectroscopy) experiments of catenane **7**·$4PF_6$ and ligand **1**·$2PF_6$ showed that the catenane is significantly larger than its components. The signals from the ligand and macrocycle **4** showed the same diffusion coefficients indicating that these components diffuse as a whole.

The location of the hydroquinol units inside the cavity of the metallomacrocycle was also confirmed by the cross-peaks between the aromatic protons of these units and bipyridinium and the phenylene protons of the ligand observed in a 2D ROESY (rotating frame Overhauser effect spectroscopy) spectrum.

The fact that, in acetonitrile, the dicationic ligand **1**·$2PF_6$ and the macrocycle **4** are in a dissociated state[7] indicates that the coordination of **1**·$2PF_6$ to palladium generates species with enough π-electron-deficient character to be inserted into **4**.

With the aim of improving the efficiency of the self-assembly process, we changed the bipyridinium π-acceptor system in ligand **1**·$2PF_6$ to a stronger one: the 2,7-diazapyrenium system. In a manner similar to that described for **7**·$4PF_6$, the catenanes **8**−**10**·$4PF_6$ were self-assembled from *trans*-$PdCl_2(CH_3CN)_2$, 2,2′-[1,4-phenylenebis(methylene)]bis-2,7-diazapyrenium hexafluorophosphate (**2**·$2PF_6$)

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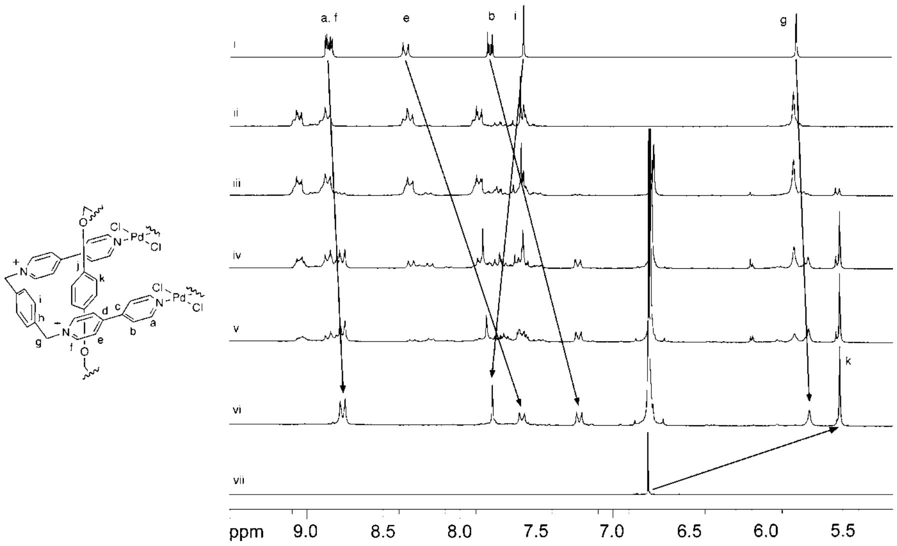

Figure 2. Partial ^{1}H NMR (CD_3CN, 300 MHz, 298 K) spectra of (i) **1**·$2PF_6$, (ii) **1**·$2PF_6$ (2 mM) + $PdCl_2(CH_3CN)_2$ (2 mM), (iii) same + **4** (1 mM), (iv) same + **4** (4 mM), (v) same + **4** (8 mM), (vi) same + **4** (24 mM), and (vii) **4**.

and macrocycles **4**−**6** (2 mM) in CD_3NO_2 (Table 1). The ^{1}H and ^{13}C NMR spectra of **8**·$4PF_6$ and **9**·$4PF_6$ indicated the formation of a [3]catenane structure, as the observed $\Delta\delta$ from those of ligand **2**·$2PF_6$ were similar to that observed in **7**·$4PF_6$. However, there are two significant differences between catenanes **7**·$4PF_6$ and **8**−**9**·$4PF_6$: (1) the self-assembly of catenane **8** required only 1 equiv of the corresponding macrocycle and 1.5 equiv of **5** for the formation of **9**, in contrast to the self-assembly of **7** that needed 12 equiv of **4** (Table 1); (2) in [3]catenane **8**, the circumrotation of the macrocyclic polyether component through the cavity of the metallocycle is slow on the ^{1}H NMR time scale resulting in all of the OCH_2 groups being anisochronous (Figure 4). Besides, two separated signals can be observed for the aromatic protons of the π-donor macrocycles ($\delta = 5.44$ ppm $H_{g'}$ and $\delta = 3.30$ ppm H_g), for alongside and inside dioxoaryl rings, respectively, in catenane **8**.[8] The larger size of the 2,7-diazapyrene system in comparison to 4,4′-bipyridine and the stronger interaction between 2,7-diazapyrenium and dioxoaryl rings can account for these facts.

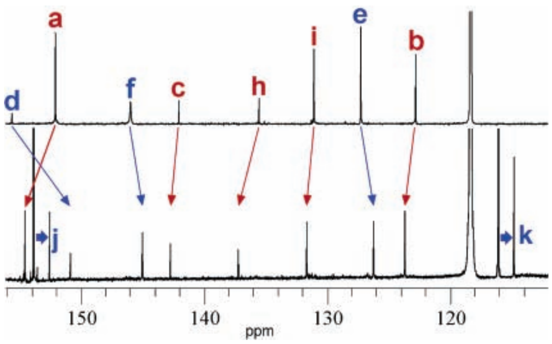

Figure 3. Partial ^{13}C NMR (CD_3CN, 125 MHz, 298 K) spectra of **1**·$2PF_6$ (top) and a solution of **1**·$2PF_6$ (2 mM) + $PdCl_2(CH_3CN)_2$ (2 mM) + **4** (24 mM) (bottom). Peak labels are defined in Figure 2.

The presence of two different aromatic units in macrocycle **5** implies the possibility of three translational isomers for catenane **9**.[9] However, only one isomer was detected in the ^{1}H NMR spectrum, which does not show any signal corresponding to the *p*-xylene moiety of **5**. This is probably due to the broadening of that signal when the aromatic ring is located inside the metallocycle. The shielding of the tetrafluoroquinone ring was observed in the ^{19}F NMR, which showed a slight upfield shift ($\Delta\delta = 0.2$ ppm) typical for the alongside position.[10] A DOSY experiment of catenane **9** also

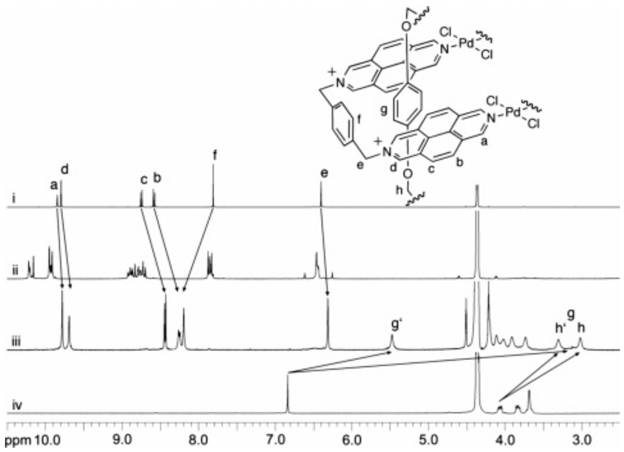

Figure 4. Partial ^{1}H NMR (CD_3NO_2, 500 MHz, 298 K) spectra of (i) **2**·$2PF_6$, (ii) **2**·$2PF_6$ (2 mM) + $PdCl_2(CH_3CN)_2$ (2 mM), (iii) same + **4** (2 mM), and (iv) **4**.

supports the formation of a [3]catenane structure showing for **9**$\cdot$4PF$_6$ a significantly smaller diffusion coefficient than that of **2**$\cdot$2PF$_6$ and **5**.

The ^{1}H NMR spectrum recorded in CD$_3$CN at 298 K for **10**$\cdot$4PF$_6$ is complex and characterized by line broadening, a phenomenon that would suggest that the alongside and inside diazapyreniums are in slow exchange on the ^{1}H NMR time scale. The introduction of the 1,5-naphthalene unit into the metallocycle results in the inequivalence of the eight diazapyrene protons and also the six protons of the naphthalene ring. These facts in addition to the relative orientations of the two π-rich components inside the metallocycle cavity can explain the complex spectrum.[11]

The assignment of products **8**−**10**$\cdot$4PF$_6$ as [3]catenanes was also made based on ESI-HRMS studies where multiply charged intact molecular ions were observed. For example, the experimental isotopic distribution for the ion [**8**$\cdot$2PF$_6$]$^{+2}$ fits very well with the theoretical calculation (Figure 5).

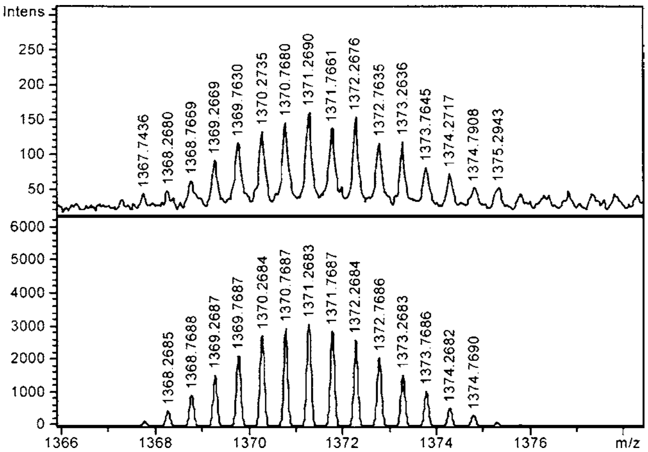

Figure 5. Observed (top) and theoretical (bottom) isotopic distribution for the fragment [**8**$\cdot$2PF$_6$]$^{2+}$.

In conclusion, we have described a very facile and efficient metal-directed self-assembly of [3]catenanes from ligands **1**$\cdot$2PF$_6$ or **2**$\cdot$2PF$_6$ and the dioxoaryl macrocycles **4**−**6**. The [3]catenanes show a dinuclear palladium 46-membered metallomacrocycle interlocked by two π-complementary dioxoaryl macrocycles. The successful catenation process relies on two key issues, namely, the lability of the palladium−nitrogen bond and the increased acceptor character of ligands **1**$\cdot$2PF$_6$ and **2**$\cdot$2PF$_6$ upon coordination to the palladium center.

Acknowledgment. This research was supported by Xunta de Galicia (PGIDIT04PXIC10307PN) and Ministerio de Educación y Cultura (BQU2003-00754). V.B. thanks Ramón Areces Foundation for a predoctoral fellowship.

Supporting Information Available: Experimental details and characterization of catenanes **7**−**10**$\cdot$4PF$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The signal at 3.30 ppm is very broad, but an exchange spectroscopy (EXSY) spectrum indicated a clear correlation between the peaks at 3.30 and 5.44 ppm.

(9) The circumrotation of the metallomacrocycle through the cavity of the macrocyclic polyether is fast on the ^{1}H NMR time scale at room temperature.

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