Complexation of Pyrene in Aqueous Solution with a Self-Assembled Palladium Metallocycle
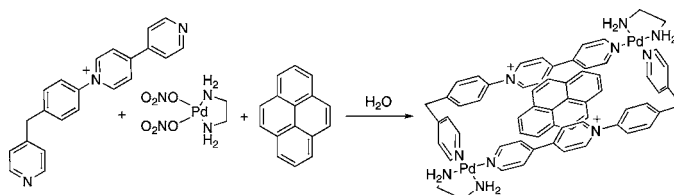
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ABSTRACT

A bidentate ligand based on *N*-monoaryl 4,4′-bipyridinium undergoes self-assembly to dinuclear rectangular metallocycles upon coordination to palladium(II) and platinum(II) centers. These metallocycles form a very stable complex with pyrene in aqueous solution and in the solid state. A crystal structure of the pyrene inclusion complex is presented. The association constants between pyrene and metallocycle 3a in organic solvents and water ($K_a = 2.3 \times 10^6$) were determined.

Polycyclic aromatic hydrocarbons (PAHs) represent a group of organic compounds with two or more fused aromatic rings.[1] Their ubiquitous distribution, environmental persistence, and potentially deleterious effect on human health have resulted in an increasing interest by the research community.[2]

Because of their hydrophobic nature, PAHs tend to be adsorbed on the organic fraction of the soils. Appropriate extraction techniques should enhance the solubility of the compounds, in order to extract their entire labile fraction. Cyclodextrin and resin extractions have shown their potential as suitable approaches for addressing the problem.[3]

Metal-directed self-assembly has proven to be a very powerful methodology to construct supramolecular structures with well-defined cavities.[4] Continuing our systematic investigation on metallomacrocyclic receptors based on bipyridinium ligands,[5] we considered the design of a larger host capable of forming an inclusion complex with a PAH such as pyrene in aqueous media.

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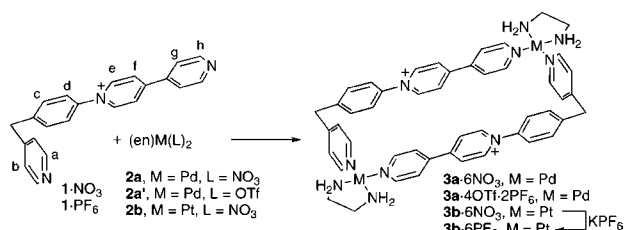
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Recently, we have reported the formation of metallocycles based on a *trans*-1,2-bis(4-pyridyl)ethylene motif and its inclusion complexes.[6] However, the extra length of these hosts provided by the double bond is not enough to allow the inclusion of pyrene.

Simple molecular calculations in order to determine the dimensions of the host and guest prompted us to synthesize a dinuclear molecular rectangle with the appropriate cavity length (ca. 11.31 Å) to bind pyrene.[7] Thus, we proposed the receptors **3a,b** as potential receptors for pyrene, where the distance between the centroids of the short sides of the rectangle grows due to the elongation of the long side from a bipyridine (in our previous metallocycles) to a phenylenebipyridine system.

The ligand **1·Cl** was obtained in a two-step synthesis from 4,4′-bipyridine following a reported procedure.[8] The nitrate and hexafluorophosphate salts were prepared by metathesis of **1·Cl**. Following a previously reported methodology,[5a–f,6] we first examined if rectangle **3a** could be self-assembled from ligand **1** and a Pd(II) metal center (Scheme 1). The

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Scheme 1. Self-Assembly of Metallocycles **3a,b**

2a, M = Pd, L = NO₃
2a', M = Pd, L = OTf
2b, M = Pt, L = NO₃

1·NO₃
1·PF₆

3a·6NO₃, M = Pd
3a·4OTf·2PF₆, M = Pd
3b·6NO₃, M = Pt
3b·6PF₆, M = Pt

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addition of 1 equiv of (en)Pd(NO₃)₂ to an 8.6 mM solution of **1·NO₃** in D₂O at room temperature gave rise to important and immediate changes in the ¹H and ¹³C NMR spectra. The chemical shifts observed are compatible with the formation of the coordinative bonds; for example, the signals for the protons H$_a$, H$_b$, and H$_h$ are downfield shifted (blue lines in Figure 1) and the protons located at the pyridinium (H$_e$ and H$_f$) and phenylene rings (H$_d$ and H$_c$) are shielded (red lines in Figure 1). The existence of the dinuclear molecular

Figure 1. Partial ¹H NMR (D₂O, 500 MHz, 298 K) spectra of ligand **1·NO₃** (top), metallocycle **3a·6NO₃** (middle), and inclusion complex PYR⊂**3a·6NO₃** (bottom). Pyrene signals are labeled as green dots.

rectangle in solution is also supported by dilution experiments monitored by ¹H NMR, which showed no changes in the 10−0.5 mM range. The rectangle **3a** was also self-assembled in acetonitrile solution from ligand **1·PF₆** and (en)PdOTf₂; the results obtained from the NMR spectra were quite similar to those described above. Platinum metallocyle **3b·6PF₆** could be self-assembled by reaction of **1·NO₃** and (en)Pt(NO₃)₂ at 100 °C for 5 days and subsequent anion exchange with KPF₆. The ¹H NMR spectrum shows similar chemical shifts to that of the palladium analogue. The formation of **3b·6PF₆** was also supported by ESI-HRMS studies where multiply charged intact molecular ions were detected: calcd for $[M − 4PF_6^-]^{4+}$ 362.0733, found 362.0740; calcd for $[M − 5PF_6^-]^{5+}$ 260.6657, found 260.6664.

To obtain structural information of metallocycle **3a** useful to evaluate its capacity as a receptor, we have performed density functional theory (DFT) calculations (B3LYP model) (see the Supporting Information for computational details). The geometry around each Pd is close to square planar with a N(py)−Pd−N(bipy) angle of 91° and a N(en)−Pd−N(en) angle of 82° (Figure 2). The three rings of the long side of

Figure 2. Calculated structure of metallocycle **3a**. The color-labeling scheme is as follows: nitrogen (blue), palladium (yellow), carbon (gray), and hydrogen (light gray).

the rectangle are not coplanar but twisted, the torsion angles of the bipyridine system and between the phenylene and the

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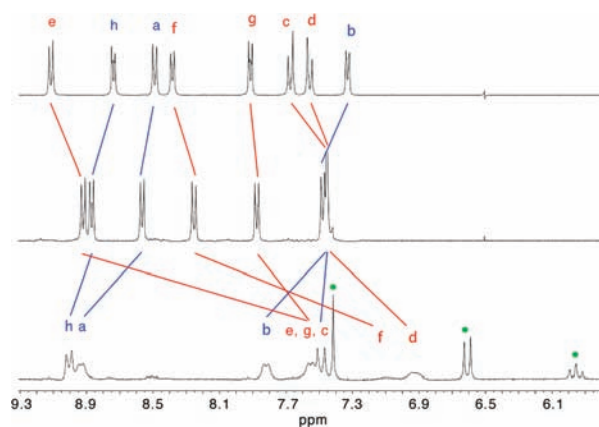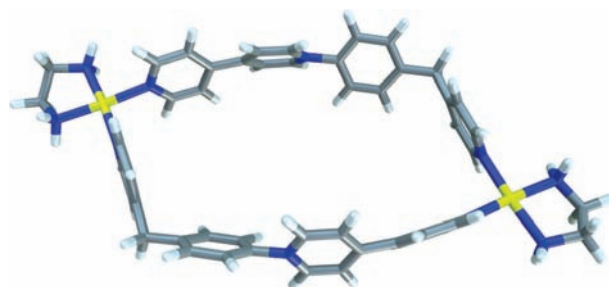
central pyridine ring are 31° and 50°, respectively. The length of the rectangle, as measured between the centroids of the pyridine rings on the short side, is 14.40 Å, while the width, defined by the distance between the centroids of the central pyridinium rings, is 9.10 Å. Considering the van der Waals radius of a sp^2 carbon to be 1.7 Å the available space for the substrate can be estimated to be $14.40 − (2 \times 1.7) = 11.00$ Å. The distance between the pyrene protons (H2 and H7) that could be potentially involved in $[C−H \cdots \pi]$ interactions is 11.31 Å,[7] and therefore a full or nearly full inclusion of the substrate within the metallocyclic cavity is possible if the structural flexibility is considered. Moreover, upon the insertion of the guest, a shortening of the separation between bipyridinium units can be expected as a consequence of a induced-fit distortion.[5a,b,9] This shortening will probably extend the length of the metallocycle to permit the insertion of pyrene. The overall dimensions of the rectangle allowed us to suppose that it could be a good receptor for polycyclic aromatic hydrocarbons such as pyrene.

The addition of 1 equiv of pyrene (PYR) to a solution of metallocycle 3a·6NO$_3$ in water (4 mM, sonication was necessary to dissolve the pyrene) results in the appearance of an intense orange color that originates from a charge-transfer band between host and guest centered at $\lambda = 457$ nm.

In the ^{1}H NMR spectrum, all the signals show the expected shifts after the inclusion of pyrene in the cavity. The protons at the central positions (H$_e$, H$_f$, and to a lesser extent H$_d$ and H$_g$) are shifted upfield; on the contrary, the protons on the short side of the rectangle (H$_a$ and H$_b$) are shifted downfield, probably as a consequence of a $[C−H \cdots \pi]$ interaction with the pyrene (Figure 1). Some of the signals in the ^{1}H NMR spectrum are broad, which indicates an equilibrium situation that is close to coalescence. To achieve more information on the geometry of the inclusion complex we carried out a VT-NMR experiment. Unfortunately, the spectrum of a solution of the complex in a 5:1 CD$_3$OD/D$_2$O solution recorded at 193 K still showed broad signals.

The formation of the 1:1 inclusion complex with pyrene in the solid state was confirmed by X-ray crystallography analysis of a single crystal obtained from a solution of pyrene and 3a·6NO$_3$ in aqueous NaNO$_3$. The resulting data were sufficient to enable an unambiguous assignment of the molecular structure (Figure 3). The pyrene molecule is clearly
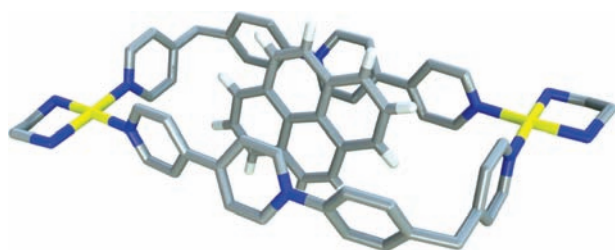
located inside the cavity: the distance between the centroid defined by the atoms of the long side of the rectangle and the plane of pyrene is 3.40 Å, exactly the optimum calculated distance for systems held by face-to-face π-stacking interactions.[10] The long side of the metallocycle measures 14.75 Å, slightly longer than the calculated one. The plane of pyrene is inclined by 70° with respect to the equatorial plane of the metallocycle defined by its four corners, while the axis defined by pyrene protons H2 and H7 forms an angle of 30° with the same plane. Another consequence is the decrease of the torsion angle in the bipyridinium moiety from 31° to 25° as a result of the $\pi−\pi$ stacking interactions.

The association constants for the 1:1 complexes formed between metallocycle 3a and pyrene in acetonitrile, MeOH, and water were measured and are shown in Table 1. In acetonitrile and methanol, these constants were determined by UV−vis spectroscopy,[11] following the corresponding charge-transfer band at λ_{max}. The Job's plot showed that maximal complexation occurred at 0.5 molar fraction of 3a·6NO$_3$ and pyrene in MeOH (see the Supporting Information).

Table 1. Association Constants K_a (L·mol^{-1}) for 1:1 Complexes Formed between 3a and Pyrene[a]

entry	metallocycle	solvent	K_a/L·mol^{-1}	λ_{max}/nm
1	3a·4OTf·2PF$_6$	CH$_3$CN	49 ± 5	460
2	3a·6NO$_3$	MeOH	145 ± 7	452
3	3a·6NO$_3$	H$_2$O	$2.3 \times 10^6 \pm 5774$	

[a] Metallocycle concentration: 1 mM.

The association constant in water was measured by liquid−liquid extraction experiments.[12] A 10 mM solution of pyrene in heptane was sonicated for 2 h at room temperature with a 1 mM solution of 3a·6NO$_3$. The concentration of pyrene in the heptane solution upon the extraction ([PYR]$_{hep}$) was determined by electronic absorption spectroscopy. The total concentration of pyrene present in the aqueous solution [PYR]$_{H_2O}$(tot) can be calculate by subtracting [PYR]$_{hep}$ from the initial concentration of pyrene (10 mM). It can be assumed that the amount of uncomplexed pyrene in the aqueous solution can be considered constant and equal to the maximum concentration of pyrene in water ([PYR]$_{H_2O} = 8.0 \times 10^{-7}$ M).[13] The concentration of pyrene complexed is [PYR]$_{H_2O}$(tot) − [PYR]$_{H_2O}$, which in a 1:1 complexation is equal to the concentration of [PYR⊂3a·6NO$_3$]$_{H_2O}$. The concentration of free metallocycle is obtained

Figure 3. Crystal structure of the inclusion complex PYR⊂3a·6NO$_3$. Hydrogen atoms from the metallocycle, solvent molecules, and counterions have been omitted for clarity.

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by subtracting $[PYR \subset \textbf{3a} \cdot 6NO_3]_{H_2O}$ from the initial concentration of $\textbf{3a} \cdot 6NO_3$ (1 mM). Therefore, all concentrations of eq 1 are known and K_a is determined from eq 2.

$$(\textbf{3a} \cdot 6NO_3)_{H_2O} + PYR_{H_2O} \rightleftharpoons (PYR \subset \textbf{3a} \cdot 6NO_3)_{H_2O} \qquad (1)$$
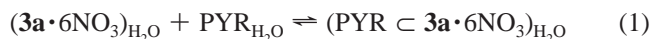
$$K_a = \frac{[PYR \subset \textbf{3a} \cdot 6NO_3]_{H_2O}}{[\textbf{3a}6NO_3]_{H_2O}[PYR]_{H_2O}} \qquad (2)$$

The host−guest association constants in acetonitrile and methanol are several orders of magnitude smaller than those in water indicating that hydrophobic forces play an important role in the complexation process.

In summary, new dinuclear metallocycles were self-assembled in aqueous media from a 4,4′-bipyridium-based ligand and square-planar palladium or platinum complexes. These rectangular metallocycles have proven to be receptors for pyrene, their cavity presents a nearly optimal size to form supramolecular complexes with pyrene through π-stacking and hydrophobic forces. The results reported in this communication open the way to the construction of new molecular receptors for PAHs.

Supporting Information Available: Synthetic procedures, NMR data, and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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