Pergamon

Tetrahedron Letters, Vol. 38, No. 20, pp. 3635-3638, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00688-6

A Self-Complexing Macrocycle Acting as a Chromophoric Receptor

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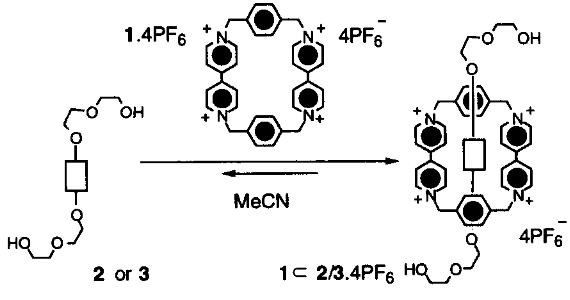
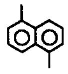
Abstract: The self-complexing macrocycle **4**.4PF$_6$ has been shown to behave as a chromophoric receptor for the 1,5-dioxynaphthalene derivative **3**, which is able to displace the hydroquinone ring out from the cavity of the self-complexing macrocycle **4**.4PF$_6$ and in so doing produces a 1:1 complex. This process is accompanied by an alteration in the UV/Vis absorbance which is reflected in a change in the colour of the solution — from red to purple. © 1997 Elsevier Science Ltd.

Since the advent of supramolecular chemistry[1] — the domain where noncovalent bonding interactions[2] become important — chemists have not only created molecules displaying fascinating topological features,[3] but they have also constructed a series of molecular and supramolecular switches.[4] The importance of materials functioning at a molecular level was first highlighted by the late Richard P Feynman[5] back in 1960. Since then, numerous examples of molecules exhibiting switching properties have appeared in the chemical literature.[6]

The design and synthesis of chemical sensors utilising host-guest chemistry is still in its infancy. Moreover, in the majority of the systems reported so far, the sensing action is addressed by complex electrochemical and/or photochemical means.[7] In this communication, we report a chromophoric receptor[8] in which the sensing action can be monitored directly by a dramatic change in the colour of the solution.

The stability constant (K_a) for the formation (**Scheme 1**) of a 1:1 complex between the tetracationic cyclophane **1**.4PF$_6$ and the substituted hydroquinone derivative **2** is 2200 L mol^{-1} in MeCN.[9] This complex gives rise to a red coloration [λ_{max} (ε) 470 nm (350)] arising from the noncovalent charge-transfer interactions between the π-electron rich hydroquinone ring included in the cavity and the π-electron deficient bipyridinium units of $\mathbf{1}^{4+}$. However, the stability constant for the formation of a 1:1 complex between the same parent cyclophane **1**.4PF$_6$ and the 1,5-dioxynaphthalene derivative **3** in MeCN is[10] very much higher: in fact, K_a = 20000 ± 4000 L mol^{-1}. In this case, the absorbance maximum associated with the charge-transfer interaction is[8,11] λ_{max} (ε) 515 nm (650), an absorption which confers a purple coloration upon the solution.[12]

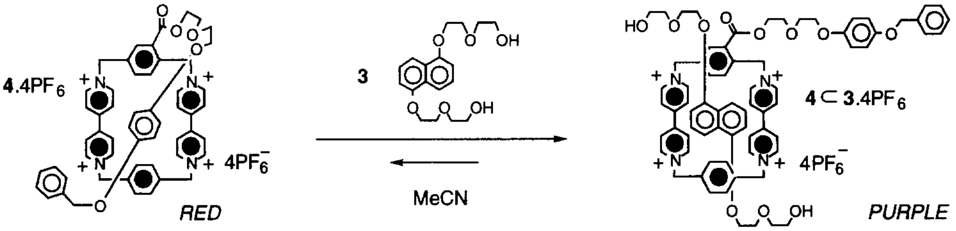


	☐	K_a (L mol^{-1})	λ_{max}	ε
2		2200	470	350
3		20000	515	650

Scheme 1. Binding constants for the parent tetracationic cyclophane **1**.4PF$_6$ with substrates **2** and **3**

Recently, we have reported[11] the template-directed synthesis of the self-complexing macrocycle **4**.4PF$_6$ as a result of the noncovalent bonding interactions[9] between the π-electron rich hydroquinone ring and the π-electron deficient bipyridinium units. The fact that **4**.4PF$_6$ exhibits a rare scorpion-like topology, as depicted in **Scheme 2**, has been shown by (a) mass spectrometry in the gas phase, (b) ^{1}H NMR spectroscopy, UV/Vis spectroscopy, and electrochemistry in solution, and (c) X-ray crystallography in the solid state.[11] A MeCN solution of **4**.4PF$_6$ has an absorbance maximum in the visible region at λ_{max} (ε) 466 nm (350) commensurate with the red colour of the solution.[9]

When one equivalent of the 1,5-dioxynaphthalene derivative **3** is added to a MeCN solution of **4**.4PF$_6$, it undergoes an immediate change of colour from red to purple. This change indicates that, initially, **4**.4PF$_6$ is a self-complexing macrocycle in which the hydroquinone ring is intramolecularly bound within the cavity of the tetracationic cyclophane. The presence of one equivalent of the more strongly bound 1,5-dioxynaphthalene derivative **3** causes the expulsion of the hydroquinone ring from the cavity of the tetracationic component of **4**.4PF$_6$ to form (**Scheme 2**) the 1:1 complex **4**$\subset$**3**.4PF$_6$ where the 1,5-dioxynaphthalene moiety of **3** is threaded through the cavity of the tetracationic cyclophane **4**.4PF$_6$ in a pseudorotaxane-like fashion.



Scheme 2. The self-complexing macrocycle **4**.4PF$_6$ functioning as a chromophoric receptor

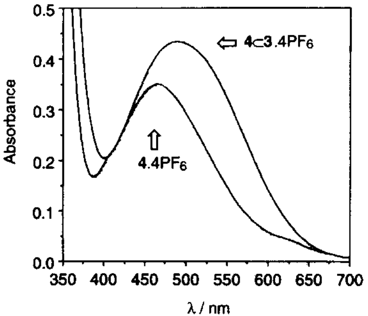


Figure 1. UV/Vis Absorption spectra of **4**.4PF$_6$ and the 1:1 complex **4**$\subset$**3**.4PF$_6$.

The process can be monitored by UV/Vis spectroscopy. The self-complexing macrocycle **4**.4PF$_6$ shows (**Figure 1**) a charge-transfer band at λ_{max} (ε) 467 nm (350), which renders the solution red. After one equivalent of the 1,5-dioxynaphthalene derivative **3** has been added to the MeCN solution of **4**.4PF$_6$, the absorbance maximum is shifted bathochromically to λ_{max} (ε) 495 nm (433). This change in the absorbance maximum associated with the charge-transfer interactions indicates that the hydroquinone ring is no longer self-complexed within the cavity of the tetracationic cyclophane. A dynamic equilibrium process is clearly taking place (**Scheme 2**) as a result of which the more π-electron donating 1,5-dioxynaphthalene moiety is involved in charge-transfer interactions with the π-electron deficient bipyridinium units of the tetracationic cyclophane component of **4**.4PF$_6$, thus at least partially replacing the hydroquinone ring in the cavity of the tetracationic cyclophane and forming a 1:1 complex.

Attempts to quantify the binding ability of the self-complexing macrocycle **4**.4PF$_6$ with the 1,5-dioxynaphthalene derivative **3** by titration UV/Vis spectroscopic experiments in MeCN failed to produce a reliable K_a value because the absorbance maximum related to the charge-transfer band underwent hypsochromic shifts when less than one molar equivalent of **3** was added.

Further evidence for the formation of this 1:1 complex can be obtained from mass spectrometric studies. The Liquid Secondary Ion Mass Spectrum of a 1:1 mixture of the self-complexing macrocycle **4**.4PF$_6$ and the 1,5-dioxynaphthalene derivative **3** shows a peak for *m/z* at 1605 which corresponds to the molecular ion of the 1:1 complex $\mathbf{4}\subset\mathbf{3}.4PF_6$ less one of the hexafluorophosphate counterions.

The 1:1 complex $\mathbf{4}\subset\mathbf{3}.4PF_6$ also possesses thermochromic behaviour as indicated by variable temperature UV/Vis spectroscopic studies. When the temperature is increased, complexation of **3** is disfavoured and therefore a decrease of the intensity of the absorbance of the charge transfer band at 495 nm is to be expected. In addition, an hypsochromic shift is observed (**Figure 2**) as the temperature is increased — ranging from λ_{max} (ε) 495 nm (477) at 10 °C to λ_{max} (ε) 474 nm (310) at 60 °C. This observation indicates that, when the temperature is raised, not only is the complexation of **3** hindered, but also intramolecular binding is preferred to 1:1 complex formation, *i.e.*, the equilibrium depicted in **Scheme 2** is shifted to the left-hand side.

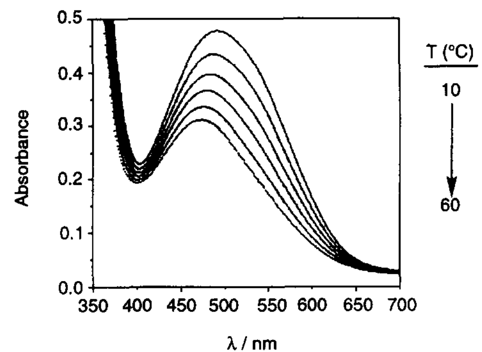


Figure 2. Temperature dependent UV/Vis spectra of the 1:1 complex $\mathbf{4}\subset\mathbf{3}.PF_6$.

In summary, we have shown that the self-complexing macrocycle **4**.4PF$_6$ behaves as a chromophoric receptor for the 1,5-dioxynaphthalene derivative **3**. The variable temperature UV/Vis spectroscopic studies suggest that the equilibrium is dynamic. The main advantage of this system is the ease with which the sensing action can be addressed, *i.e.* a change of colour of the solution from red to purple. Our next goal will be the construction of a reversible system in which the complexation will be switched off and on again when it is perturbed by some external stimuli which could be either chemical, electrochemical or photochemical in nature.

Acknowledgments. This research was supported by the Engineering and Physical Sciences Research Council in the United Kingdom. We also thank Eusko Jaurlaritza, Unibersitate, Hizkuntza eta Ikerketa Saila in the Basque Country (Spain) for their support of a Postgraduate Fellowship (to M.G.-L.) and the European Community (Human Capital and Mobility Programme, ERBCHBICT941744) for their support of a Postdoctoral Fellowship to (J.A.P.).

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(*Received in UK* 19 *March* 1997; *accepted* 10 *April* 1997)