## Intra-complex electron transfer in a self-assembling phthalocyanine [2]pseudorotaxane

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A [2]pseudorotaxane is formed from a Zn<sup>II</sup>-phthalocyanine with polyether substituents containing  $\pi$ -electron rich hydroquinone segments and a cyclobis(paraquat-p-phenylene) tetracation containing  $\pi$ -electron-deficient bipyridinium units; fluorescence quenching of the Zn<sup>II</sup>-phthalocyanine is enhanced dramatically in acetonitrile.

A variety of self-assembly processes exploiting non-covalent binding interactions have been used for the construction of high dimensional molecular arrays, both in solution and in the solid state. Topologically complex molecules such as catenanes, rotaxanes, pseudorotaxanes and knots have aroused interest, and their potential as the basis of molecular devices has been investigated by many chemists. Synthetic strategies for the molecular combination of these compounds have been reported. Self-assembly processes utilizing non-covalent bonds have been applied to such applications as fluorescent chemosensors and molecular switches. The preorganization between hydroquinone units containing ether chains 1 and cyclobis(paraquat*p*-phenylene) tetracation 2 was developed for the synthesis of catenanes and rotaxanes by Stoddart; the  $\pi$ -donor- $\pi$ -acceptor interaction is the driving force of the self-assembly process.

Here we describe the synthesis of zinc(II)-phthalocyanine derivative 3 containing polyether chains with hydroquinone groups as receptors, and the efficiency of fluorescence quenching caused by the formation of a [2]pseudorotaxane from 2 and 3 in acetonitrile.

OOH

OOH

$$APF_6$$
 $APF_6$ 
 $APF_6$ 

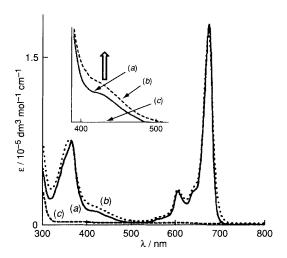
The new zinc(II)-phthalocyanine derivative 3 was prepared from 2-methoxyphenol according to Scheme 1. Bromination of 2-methoxyphenol in CH<sub>2</sub>Cl<sub>2</sub> at -78 °C gave the dibromo derivative 4 in 85% yield. Reaction of 2-[2-(2-chloroethoxy)ethoxylethanol with 4 afforded 5 in 72% yield. Tosylation of 5 proceeded in 85% yield, and reaction with 4-{2-[2-(2-methylethoxy)ethoxy|ethoxy|phenol in NaH-THF afforded 6 in 52% yield. Compound 7 was obtained in 62% yield by reaction with CuCN in refluxing DMF. Complex 3 was prepared in 21% yield by heating a mixture of anhydrous zinc(II) chloride and 7 in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 130 °C for 24 h. Compound 3 is soluble in most organic solvents (e.g. chloroform, methanol, benzene, DMF, acetonitrile) except for hexane and ethyl acetate. The purification of 3 was achieved by column chromatography and spectroscopic data were consistent with the proposed structure. The <sup>1</sup>H NMR spectrum also showed that the synthesized compound contains constitutional isomers.

The UV-VIS spectrum of a solution of 3 in acetonitrile at 25 °C shows a strong Q band at  $\lambda_{max}$  674 nm (log  $\varepsilon$  5.23) typical of a non-aggregated zinc(II)-phthalocyanine complex (Fig. 1). When 2 is added to the acetonitrile solution of 3, an increased absorbance in the region between 450 and 500 nm is observed. Stoddart reported a spectral change when 2 was added to a solution of 1 in acetonitrile; a new band which appeared at 466 nm was attributed to charge transfer between the hydroquinol group of 1 and 2.5 The change of absorbance of 3 by addition of 2 is consistent with the above result, indicating the formation of the [2]pseudorotaxane 2.3 4PF<sub>6</sub>. The formation of the [2]pseudorotaxane was also monitored by <sup>1</sup>H NMR in CD<sub>3</sub>CN solution at 25 °C. Upon addition of 2 to the solution of 3, the resonances corresponding to the hydroquinol protons in [2]psuedorotaxane 2·3 4PF<sub>6</sub> shift upfield by 2.71 ppm, while the resonances corresponding to the phthalocyanine ring's protons (δ 6.81-8.42) remain unaffected. <sup>1</sup>H NMR titration studies

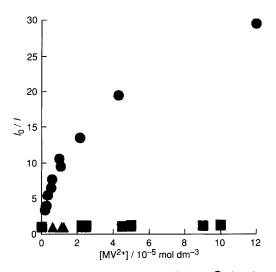
**Scheme 1** Reagents and conditions: i,  $Br_2$ ,  $CH_2Cl_2$ , -78 °C, 85%; ii,  $Cl(CH_2CH_2O)_3H$ , MeCN,  $K_2CO_3$ , reflux, 5 d, 72%; iii, TsCl,  $CH_2Cl_2$ ,  $Et_3N$ , 85%; iv,  $MeO(CH_2CH_2O)_3C_6H_4OH$ , NaH, THF, reflux, 2 d, 52%; v, CuCN, DMF, reflux, 6 h, 62%; vi,  $ZnCl_2$ , DBU,  $C_5H_{11}OH$ , 140 °C, 24 h, 21%

show that 2 binds 3 with an association constant of  $1200 \pm 200$  dm³ mol in CD<sub>3</sub>CN at 25 °C. The dominant species in a mixture of a 5 mmol dm<sup>-3</sup> solution of 2 and a 1 mmol dm<sup>-3</sup> solution of 3 is the 1:4 complex determined by a Job plot of the <sup>1</sup>H NMR data.<sup>6</sup> From these results, it can be seen that [2]psuedorataxane 2·3 4PF<sub>6</sub> is formed by the  $\pi$ -donor– $\pi$ -acceptor interaction between 2 and the hydroquinol groups of 3.

Zinc(II)-phthalocyanine complex  $\hat{3}$  exhibits a strong fluorescence peak at 674 nm with excitation at 370 nm, which is



**Fig. 1** UV–VIS absorption spectra of (a) **3**, (b) **2** + **3** and (c) **2** in MeCN,  $[3] = 1.12 \times 10^{-5}$  mol dm<sup>-3</sup>,  $[2] = 5.12 \times 10^{-5}$  mol dm<sup>-3</sup>



**Fig. 2** Steady-state fluorescence titration of **2** into: (●) **3**  $(1.2 \times 10^{-5} \text{ mol dm}^{-3})$ , excitation 370 nm, emission 674 nm; (▲) ZnTBPc  $(1.2 \times 10^{-5} \text{ mol dm}^{-3})$ , excitation 370 nm, emission 674 nm; and (■) titration of PQ<sup>2++</sup>2PF<sub>6</sub> into **3**  $(1.2 \times 10^{-3} \text{ mol dm}^{-3})$ . In MeCN at 25 °C

quenched by addition of 2. The photochemical properties of [2]psuedorotaxane 2·3 4PF<sub>6</sub> were investigated using steadystate fluorescence measurements. The fluorescent emission from 3 was monitored as 2 was titrated into a solution of 3 in degassed acetonitrile. For the fluorescence quenching of host 3 with 2, the Stern-Volmer constant  $(K_{SD})$  was obtained from the initial slope of the Stern-Volmer plots (Fig. 2). Additionally, we studied the fluorescence quenching of 3 by paraquat (PQ<sup>2+</sup>) as electron transfer quenching agent and tetrakis(tert-butyl)phthalocyaninatezinc(II) complex (ZnTBPc) by 2 as control experiments. In the control experiments, the intensities of the phthalocyanine fluorescence decrease a little on addition of the electron transfer quenching reagents, and linear Stern-Volmer plots were obtained. Normal Stern-Volmer plots of 3-PQ2+ and ZnTBPc-2 imply that this is due to intermolecular collisional (dynamic) quenching. In contrast, the addition of a small amount of 2 into the solution of 3 led to efficient fluorescence quenching. This efficient fluorescence quenching in 2.3 4PF<sub>6</sub> suggests static quenching by the formation of an associated complex. Thus efficient quenching of the phthalocyanine fluorescence only occurs via combination of 3 with the receptor part of 2. The fluorescence quenching observed is the photoinduced intra-complex electron transfer from the singlet excited state of the phthalocyanine to the noncovalently bound 2. The  $K_{\rm SD}$  value was 820 000 dm<sup>3</sup> mol<sup>-1</sup> for 2·3 4PF<sub>6</sub> which is 300 times as large as 3-PQ<sup>2+</sup> ( $K_{SD}$  2500 dm<sup>3</sup> mol<sup>-1</sup>) and ZnTBPc-2 ( $K_{SD}$  2600 dm<sup>3</sup> mol<sup>-1</sup>).

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