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

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A [2]pseudorotaxane is formed from a Zn^{II}-phthalocyanine with polyether substituents containing π-electron rich hydroquinone segments and a cyclobis(paraquat-*p*-phenylene) tetracation containing π-electron-deficient bipyridinium units; fluorescence quenching of the Zn^{II}-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.[1] 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.[2] 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.[3] 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;[4] the π-donor–π-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.

The new zinc(II)-phthalocyanine derivative 3 was prepared from 2-methoxyphenol according to Scheme 1. Bromination of 2-methoxyphenol in CH_2Cl_2 at -78 °C gave the dibromo derivative 4 in 85% yield. Reaction of 2-[2-(2-chloroethoxy)-ethoxy]ethanol 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 ¹H 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 λ_{max} 674 nm (log ε 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 4PF₆. The formation of the [2]-pseudorotaxane was also monitored by ¹H NMR in CD₃CN 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 4PF₆ shift upfield by 2.71 ppm, while the resonances corresponding to the phthalocyanine ring's protons (δ 6.81–8.42) remain unaffected. ¹H NMR titration studies

1   2

3

$R^1 =$

$R^2 =$ OMe

3

7

Scheme 1 *Reagents and conditions*: i, Br₂, CH_2Cl_2, -78 °C, 85%; ii, Cl(CH₂CH₂O)₃H, MeCN, K₂CO₃, reflux, 5 d, 72%; iii, TsCl, CH_2Cl_2, Et₃N, 85%; iv, MeO(CH₂CH₂O)₃C₆H₄OH, NaH, THF, reflux, 2 d, 52%; v, CuCN, DMF, reflux, 6 h, 62%; vi, ZnCl₂, DBU, C₅H₁₁OH, 140 °C, 24 h, 21%

show that **2** binds **3** with an association constant of 1200 ± 200 dm³ mol in CD₃CN at 25 °C. The dominant species in a mixture of a 5 mmol dm⁻³ solution of **2** and a 1 mmol dm⁻³ solution of **3** is the 1 : 4 complex determined by a Job plot of the ¹H NMR data.[6] From these results, it can be seen that [2]psuedorataxane **2·3** 4PF₆ is formed by the π-donor–π-acceptor interaction between **2** and the hydroquinol groups of **3**.

Zinc(II)-phthalocyanine complex **3** exhibits a strong fluorescence peak at 674 nm with excitation at 370 nm, which is
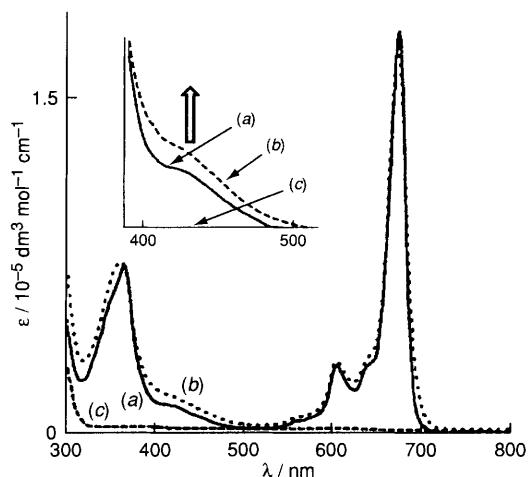
Fig. 1 UV–VIS absorption spectra of (a) **3**, (b) **2** + **3** and (c) **2** in MeCN, [**3**] = 1.12 × 10⁻⁵ mol dm⁻³, [**2**] = 5.12 × 10⁻⁵ mol dm⁻³
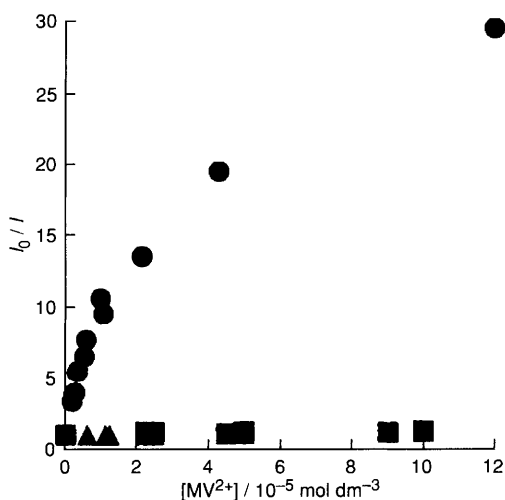
Fig. 2 Steady-state fluorescence titration of **2** into: (●) **3** (1.2 × 10⁻⁵ mol dm⁻³), excitation 370 nm, emission 674 nm; (▲) ZnTBPc (1.2 × 10⁻⁵ mol dm⁻³), excitation 370 nm, emission 674 nm; and (■) titration of PQ²⁺·2PF₆ into **3** (1.2 × 10⁻³ mol dm⁻³). In MeCN at 25 °C

quenched by addition of **2**. The photochemical properties of [2]psuedorotaxane **2·3** 4PF₆ were investigated using steady-state 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 (PQ²⁺) 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** 4PF₆ 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_{SD} value was 820 000 dm³ mol⁻¹ for **2·3** 4PF₆ which is 300 times as large as 3-PQ²⁺ (K_{SD} 2500 dm³ mol⁻¹) and ZnTBPc-**2** (K_{SD} 2600 dm³ mol⁻¹).

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