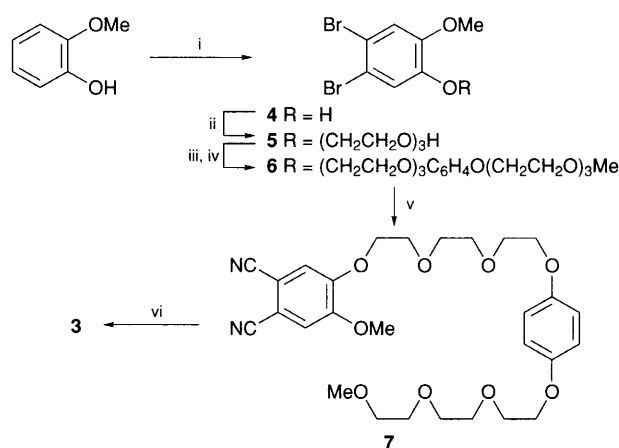


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The UV–VIS spectrum of a solution of **3** in acetonitrile at 25 °C shows a strong Q band at λ_{max} 674 nm (log ϵ 5.23) typical of a non-aggregated zinc(II)-phthalocyanine complex (Fig. 1). When **2** is added to the acetonitrile solution of **3**, 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]pseudorotaxane **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



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show that **2** binds **3** with an association constant of $1200 \pm 200 \text{ dm}^3 \text{ mol}^{-1}$ in CD_3CN 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** 4PF_6 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

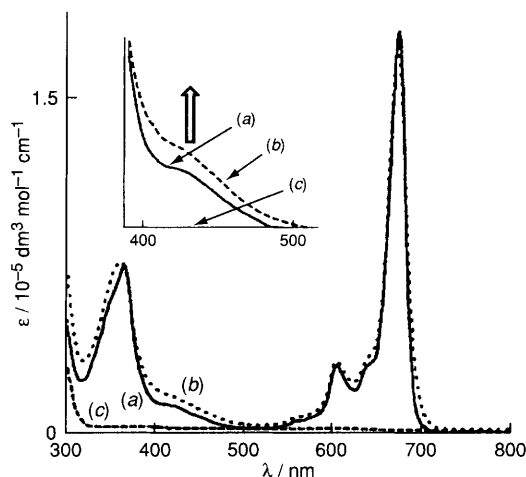


Fig. 1 UV-VIS absorption spectra of (a) **3**, (b) **2** + **3** and (c) **2** in MeCN, $[\mathbf{3}] = 1.12 \times 10^{-5} \text{ mol dm}^{-3}$, $[\mathbf{2}] = 5.12 \times 10^{-5} \text{ mol dm}^{-3}$

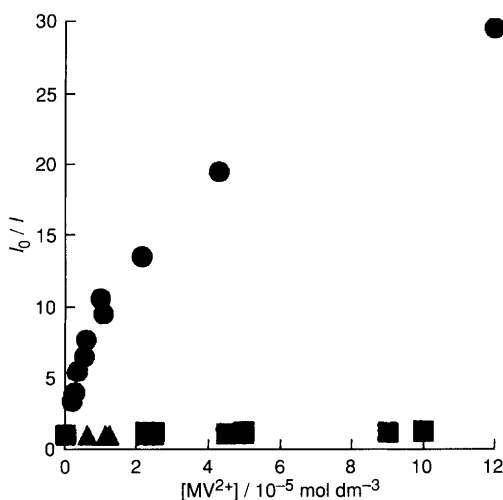


Fig. 2 Steady-state fluorescence titration of **2** into: (●) **3** ($1.2 \times 10^{-5} \text{ mol dm}^{-3}$), excitation 370 nm , emission 674 nm ; (▲) ZnTBPC ($1.2 \times 10^{-5} \text{ mol dm}^{-3}$), excitation 370 nm , emission 674 nm ; and (■) titration of $\text{PQ}^{2+} \cdot 2\text{PF}_6$ into **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_6 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 (PQ^{2+}) as electron transfer quenching agent and tetrakis(*tert*-butyl)phthalocyaninezinc(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**· PQ^{2+} 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_6 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 $820\,000 \text{ dm}^3 \text{ mol}^{-1}$ for **2**·**3** 4PF_6 which is 300 times as large as **3**· PQ^{2+} ($K_{\text{SD}} 2500 \text{ dm}^3 \text{ mol}^{-1}$) and ZnTBPC-**2** ($K_{\text{SD}} 2600 \text{ dm}^3 \text{ mol}^{-1}$).

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