Crown ether functionalization of a porphyrin-based "molecular square": induction of fluorescence sensitivity to alkali metal cations

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Abstract

A porphyrin-based "molecular square" (**1**), prepared by reaction of a dipyridylporphyrin species with $Re(CO)_5Cl$ and subsequently with Zn^{II} acetate, was functionalized with 2-(methylene-15-crown-5-ether)-nicotinoyl ester (**2**). Functionalization was achieved by axially ligating each of the four available Zn^{II} sites within the porphyrins. (**2**) was synthesized by reaction of 2-(hydroxymethyl)-15-crown-5-ether and nicotinoyl chloride in CH_2Cl_2. Functionalization renders the square's fluorescence emission intensity responsive to added Na^+ and, to a lesser extent, K^+. © 2001 Published by Elsevier Science B.V.

Keywords: Porphyrin square; Methylene crown; Luminescence; Binding constant

1. Introduction

The advantages of molecular fluorescence or luminescence for sensing have been summarized [1] and many of the structural features which control fluorescence efficiency have been delineated [2,3]. Rigid macrocycles (molecular squares) based on *cis* bridging ligation of transition metals represent an unusual class of compounds having significant promise in solution-phase host–guest, inclusion and molecular recognition chemistry [4–7]. The 50 or so available squares have been constructed from platinum, palladium, nickel, tungsten, and rhenium precursors and have been assembled in both homometallic and heterometallic forms [4–7]. In addition, selected neutral squares have been evaluated in the solid state as thin films. In film form, the compounds exhibit exceptional nanometer-scale porosity, enormous internal surface areas, and useful molecular binding properties — where binding can be followed, for example, by quartz crystal microgravimetry [7].

In solution, on the other hand, host–guest binding is typically monitored via NMR spectroscopy. In a few cases, binding has also been monitored via changes in host luminescence.

In this paper, we report on (a) the reversible functionalization of a porphyrin-based molecular square (**1**) with a known cation receptor (2-(methylene-15-crown-5-ether)-nicotinoyl ester (**2**)), and (b) the use of the functionalized

square as a solution-phase sensing assembly (fluorescent assembly) for alkali metal ions.

2. Experimental

As described previously [8], the free base form of the tetraporphyrin square was obtained in high yield by stoichiometrically combining 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis-(4-pyridyl)porphyrin and $Re(CO)_5Cl$ in 100 ml of freshly distilled 4:1 THF–toluene as solvent, and then heating at reflux for 48 h. The analogous tetra-zinc metallated square was obtained quantitatively by treating the tetraporphyrin square with zinc acetate in methanol + CH_2Cl_2. (**2**) was obtained from 2-(hydroxymethyl)-15-crown-5-ether and nicotinoyl chloride. Absorption and emission spectra were recorded by using a Cary 3 UV–VIS absorption spectrophotometer and an SPEX Flouromax spectrofluorimeter.

3. Results and discussion

Fig. 1 illustrates the structure of the tetraporphyrin square. A key feature is the use of tricarbonylrhenium chloro fragments as corners. Despite the fact that rhenium is a third-row transition metal, heavy-metal quenching of the porphyrin-based luminescence appears to be absent. Indeed, the room temperature luminescence lifetime of the photo-
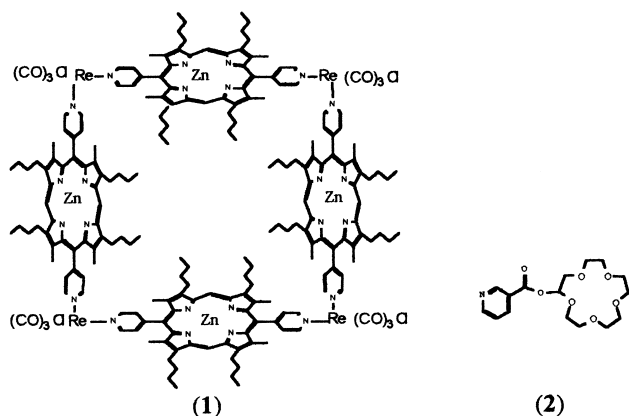

Fig. 1. Structure of porphyrin square (**1**) and methylene crown ether (**2**).

Fig. 3. Porphyrin square fluorescence emission intensity vs. methylene crown ether concentration.

Fig. 4. Fluorescence emission from the porphyrin square–crown ether mixture as a function of [NaSCN].

excited square assembly is nearly identical to that of the free porphyrin ligand [8]. Interestingly, closely related porphyrin squares featuring Pt(II) or Pd(II) corners are nonemissive [9,10], apparently because of efficient redox quenching by the corner entities [7] (Fig. 2).

As indicated in Fig. 3, emission from the zinc metallated square decreases upon addition of the pyridine-functionalized crown ether in CH_2Cl_2 as solvent. While the guest lacks obvious energy-transfer or electron-transfer quenching capabilities, a ligation-induced decrease in host luminescence intensity is not unexpected [11,12]. An observed 5 nm limiting red shift in the emission spectrum of (**1**) supports the contention that (**2**) interacts with the square via axial ligation. From additional measurements at lower host concentrations, the host (**1**)–guest (**2**) binding constant is $1.1 \times 10^7 \text{ M}^{-1}$. Further insight into the binding is provided by electronic absorption measurements. Host–guest mixtures in the ratio of 1:4 exhibit a quantitative shift of host Q bands to longer wavelength at micromolar host concentrations. The absorption studies are consistent, therefore, with a binding geometry which entails pyridine–crown ligation of all available Zn sites [13–15]. As shown in Fig. 4, the emission is enhanced by NaSCN addition. The emission
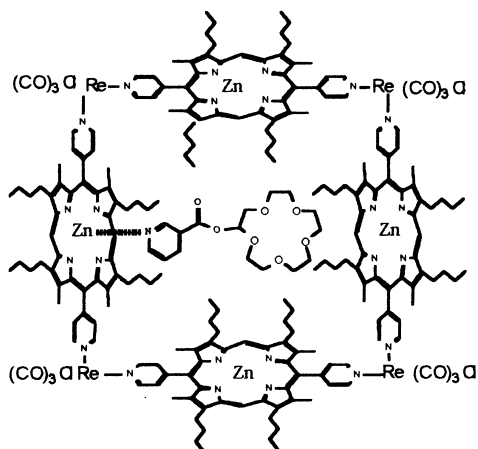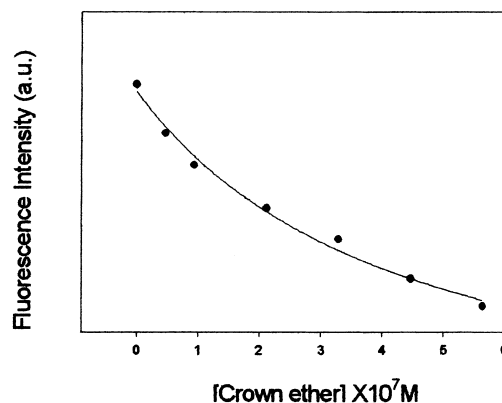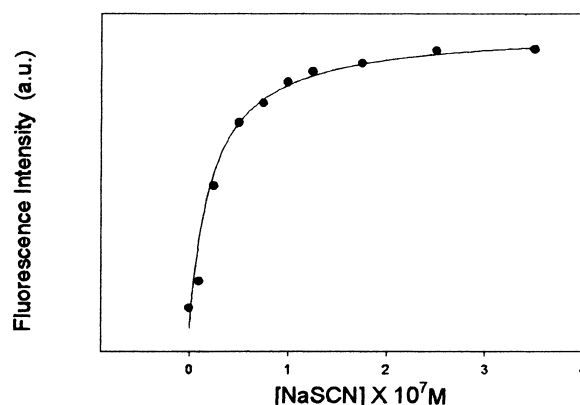
energy, however, is unchanged. A control experiment, where the receptor ligand is omitted, yields no change in emission intensity with added NaSCN. We ascribe the effect, therefore, to a subtle tuning of Zn–N interactions brought about by Na^+ binding within the crown ether. From Fig. 4, the apparent binding constant is $4 \times 10^7 \text{ M}^{-1}$. Because the measurements were made at concentrations near the host (**1**)–guest (**2**) dissociation limit, it is conceivable that the true Na^+ binding constant is higher. A similar experiment with KSCN yields a smaller intensity enhancement and a binding constant of ca. $8 \times 10^6 \text{ M}^{-1}$.

Acknowledgements

Fig. 2. Porphyrin square with one methylene crown ether moiety.

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