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)\textsubscript{5}Cl and subsequently with Zn\textsuperscript{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\textsuperscript{II} sites within the porphyrins. (2) was synthesized by reaction of 2-(hydroxymethyl)-15-crown-5-ether and nicotinoyl chloride in CH\textsubscript{2}Cl\textsubscript{2}. Functionalization renders the square’s fluorescence emission intensity responsive to added Na\textsuperscript{+} and, to a lesser extent, K\textsuperscript{+}. © 2001 Published by Elsevier Science B.V.

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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)\textsubscript{5}Cl 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\textsubscript{2}Cl\textsubscript{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 Fluoromax 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-
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 CH₂Cl₂ 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 × 10⁷ 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 × 10⁷ 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 × 10⁶ M⁻¹.

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References