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Extended molecular assembly of crown ether appended *meso–meso* coupled diporphyrin

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Abstract

Crown ether appended *meso–meso* coupled diporphyrin was synthesized and its spectroscopic studies have revealed formation of polymer architecture through interactions with potassium ion, in contrast to *face-to-face* dimerization for the corresponding porphyrin monomer. © 2000 Elsevier Science Ltd. All rights reserved.

Molecular assembly using intermolecular interactions has been of interest as a means of constructing large molecular architectures quickly and efficiently.[1] Porphyrins are attractive molecules due to their fascinating photophysical,[2] catalytic,[3] and geometrical properties.[4,5] Self-assembled systems of various porphyrin architectures via a non-covalent bond are appealing in light of solar energy harvesting and molecular device technology.[2,6,7] While most of the systems are based on assembly of a monomeric porphyrin to date, we report here new divergent assembly of porphyrins triggered by a unique disposition of the peripheral aromatic substituents in *meso–meso* coupled Zn(II) diporphyrin. Synthesis of porphyrin monomer **1** and porphyrin dimer **2** from dipyrromethane and crown ether appended benzaldehyde is outlined in Scheme 1. Treatment of unsubstituted dipyrromethane with 1 equiv. of 4′-formyl benzo-15-crown-5, followed by metalation gave the porphyrin monomer **1** in 12% yield,[9] which was in turn treated with $AgPF_6$ to provide *meso–meso* coupled Zn(II) diporphyrin **2** in 13% yield.[5]

While addition of sodium ion to the porphyrin monomer **1** induced no significant UV–vis spectral change in $CHCl_3$:MeCN (2:1), addition of potassium ion to **1** caused a blue shift of Soret band from 415 to 396 nm (Fig. 1) with an isosbectic point at 404 nm, as well as a decrease in the fluorescent intensity (not shown), suggesting construction of *face-to-face* porphyrin dimer. Formation of similar stacked diporphyrin was reported for tetrakis(5,10,15,20-benzo-15-crown-5)porphyrin.[8] In the presence of potassium ion the ^1H NMR spectrum of **1** (1.0×10^{-3} M) indicated the sharp signals that can be assigned to two kinds of *meso*-H (6.69 and 10.26 ppm)

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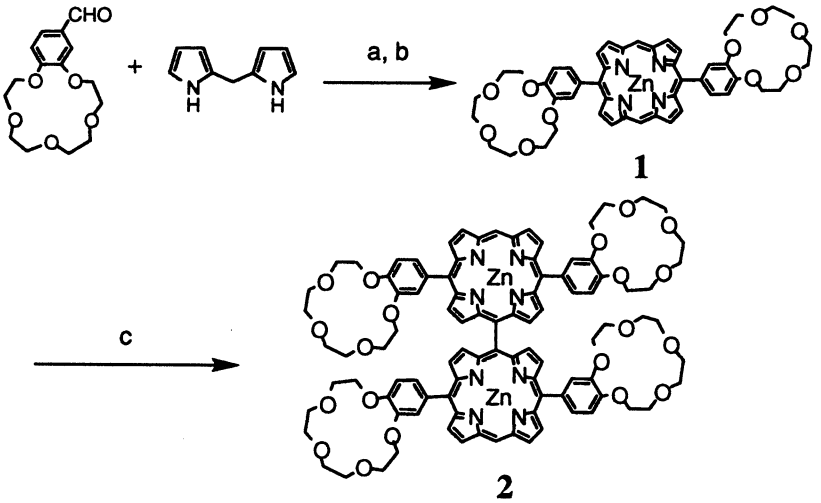


Scheme 1. Reagents and conditions: (a) $BF_3{\cdot}OEt_3$, $CHCl_3$ then DDQ; (b) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$–MeOH; (c) $AgPF_6$, $CHCl_3$–MeOH–MeCN

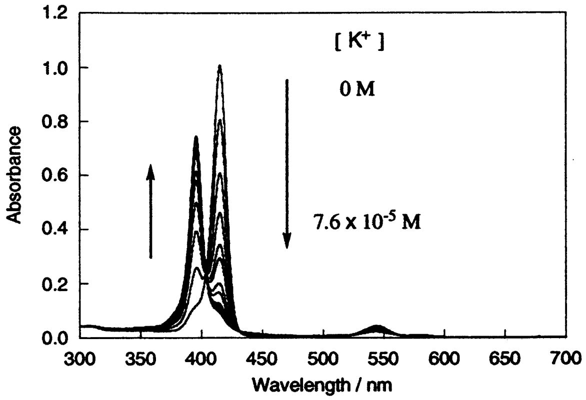


Figure 1. Absorption spectra of **1** upon addition of $KClO_4$ in $CHCl_3$:MeCN = 2:1 at room temperature; [**1**] = $1.9{\times}10^{-6}$ M

and four kinds of β-H (7.37, 8.26, 8.90 and 9.43 ppm) in the aromatic region. A singlet signal of *meso*-H (6.69 ppm) and two doublet signals of β-H (7.37 and 8.26 ppm) appeared at upfield chemical shifts compared with those of the original **1**. The upfield shifts are apparently due to the ring current effect of the porphyrin ring, suggesting that one side of porphyrin is located at upper zone of the another porphyrin ring, constituting a slip dimer.

On the other hand, the absorption spectral changes of **2** upon addition of potassium ion were more complicated (Fig. 2). In the absence of metal ion, **2** exhibited split Soret bands at 421 and 453 nm owing to exciton coupling.[5] Upon addition of potassium ion up to $1.0{\times}10^{-5}$ M, the intensity of the Soret band at 421 and 453 nm was decreased, and further addition led to a slight red-shift of the Soret band to 423 nm, followed by an increase in its absorbance. Along with these changes, a shoulder appeared at a high-energy side of the Soret band with an isosbestic point at 408 nm. The fluorescence intensity changed in a complicated manner; a steep decrease upon the addition of K^+ up to $1.0{\times}10^{-5}$ M, followed by a slight restoration upon further

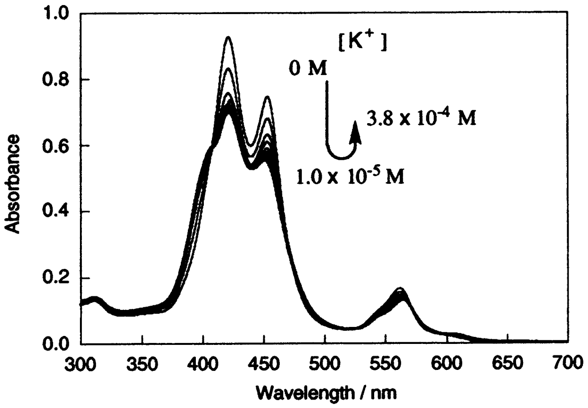


Figure 2. Absorption spectra of **2** upon addition of $KClO_4$ in $CHCl_3$:MeCN = 2:1 at room temperature; [**1**] = 3.8×10^{-6} M

addition, as shown in Fig. 3(b). These changes are in contrast to a rather monotonous and saturated fluorescence-intensity decrease of **1** upon the addition of K^+ (Fig. 3(a)). Similar absorption spectral changes and fluorescence intensity changes were observed upon the addition of Rb^+ but not observed upon the addition of Cs^+ or Na^+. Appearance of a shoulder at the high-energy side of the Soret band suggests the formation of *face-to-face* stacked diporphyrin as such for **1**. Therefore, it is plausible that the intermolecular interaction mode of the appended crown ether with potassium ion is the same for **1** and **2** but the resultant molecular architectures are entirely different between **1** and **2**. Whereas the complexation between two crown ether sites and potassium ion leads to the *face-to-face* dimerization in the case of **1**, such self-complementary complexation would be impossible for **2** and instead linear extended aggregation would be preferred. The observed complicated profiles of the absorption spectral change and the fluorescence intensity for **2** upon the addition of potassium ion indicated multi-stage equilibria, which eventually lead to extended linear assembly. The initial steep decrease in the fluorescence intensity for the complexation of **2** with potassium ion (Fig. 3(b)) might suggest the fluorescence quenching originating from the formation of the complexed *face-to-face* diporphyrin in **2**. A

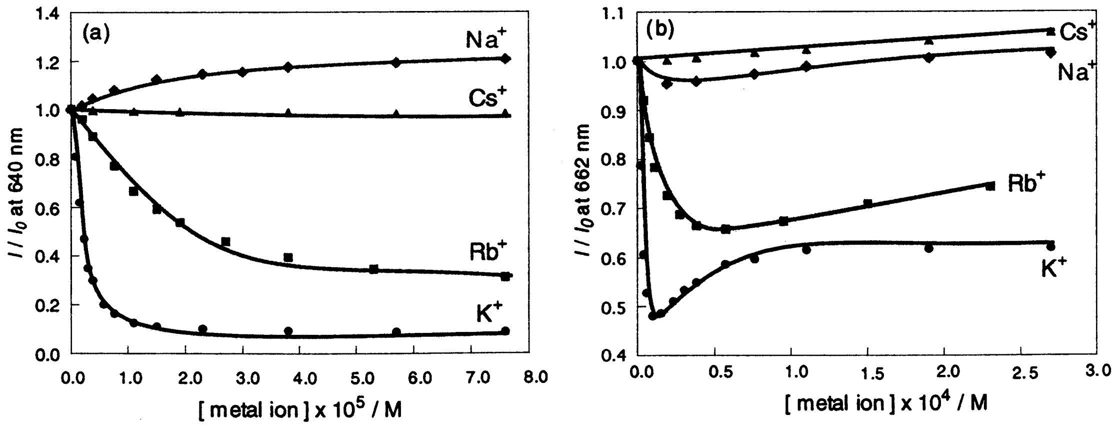
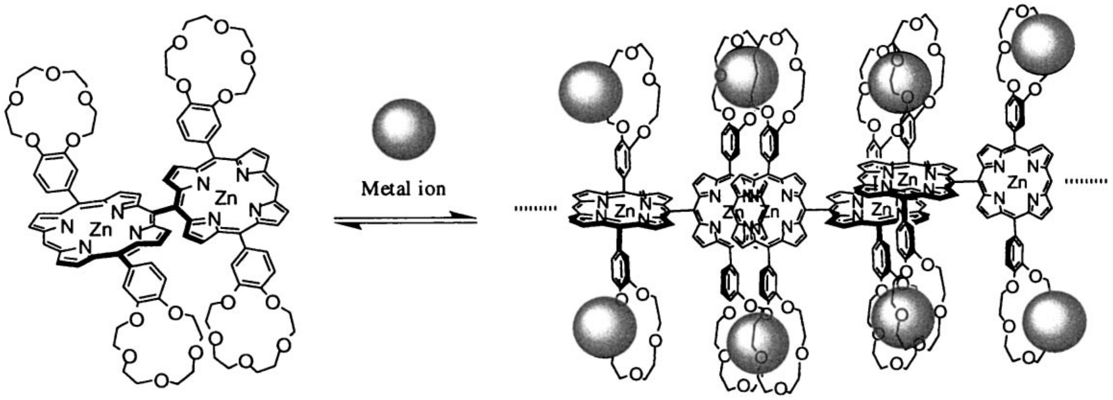


Figure 3. Plots of [metal ion] vs I/I_0 for **1** at 640 nm; (a) and **2** at 662 nm; (b) in CHCl:MeCN = 2:1 at room temperature; [**1**] = 1.9×10^{-6} M, λ_{ex} = 404 nm; [**2**] = 3.8×10^{-6} M, λ_{ex} = 408 nm

next slight increase in the fluorescence intensity might cause by the interaction between the crown ethers in the edges of the linear aggregate and metal ion. Consistent with the proposed polymeric structure, the ^{1}H NMR spectrum of **2** (1.0×10^{-3} M) became very broad upon addition of potassium ion and any assignable signals could not be detected. The polymeric nature of the aggregate formed from **2** has been confirmed by the light-scattering measurement, which indicated a molecular weight of approximately 10^5 for the aggregate, that corresponds to aggregation number of ca. 50 (Scheme 2).



Scheme 2. Proposed structure of metal assisted supramolecular assembly of **2**

Combination of the interaction of the appended crown ether with potassium ion and the unique functional-group disposition of *meso–meso* linked diporphyrin has allowed us to generate a novel divergent supramolecular assembly. This methodology can be used for constructing new molecular architectures which may lead to various excellent materials.

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