Self-Assembly of *meso*-Pyridylporphyrins and Zinc Phthalocyanines Through Axial Coordination

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Molecular assemblies of *meso*-pyridylporphyrins and zinc(II) 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine held through axial coordination are reported. Their formation has been revealed by ^{1}H NMR spectroscopy and photophysical measurements.

Introduction

Photo-induced electron- and energy-transfer in noncovalently bonded supramolecular assemblies has been studied extensively with the primary aim of harvesting solar energy and gaining a better understanding of photosynthesis, which is a marvellous but highly complex biological process.[1] Noncovalent assemblies containing porphyrins are of special importance because of their resemblance to nature, which also relies on supramolecular methods of assembly,[2] and the rich redox and photochemistry of this intriguing class of pigments.[3] Numerous porphyrin systems linked to a variety of electron acceptors, in particular quinone[4] and C_{60} derivatives,[5] have been examined. Supramolecular aggregates involving phthalocyanines, however, have received little attention despite the fact that these tetrapyrrole derivatives also exhibit fascinating physico-chemical properties.[6] Arrays of mixed porphyrin and phthalocyanine are mainly confined to the few examples of covalently linked systems,[7,8] sandwich-type complexes,[9] and face-to-face aggregates held by electrostatic interactions.[8] We describe herein the first edge-to-face arrays assembled through axial ligation of pyridyl substituents in porphyrins to zinc phthalocyanines. Although it is well-known that pyridine can relieve the extent of aggregation of zinc phthalocyanines (probably via axial coordination[10]) and that the formation of edge-to-face assemblies of the zinc(II) tribenzo(pyridino)porphyrazine has been inferred,[11] there has been a shortage of concrete experimental evidence supporting the axial coordination of zinc phthalocyanines which forms the basis of this work.[12]

Results and Discussion

The *meso*-tetra(4-pyridyl)porphyrin (**1**) and 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninatozinc(II) (**2**) were selected to construct multi(tetrapyrrole) arrays as the former is an excellent square-shaped building block[13] and the latter gives distinct and well-resolved ^{1}H NMR spectra, which facilitates the spectral analysis.[14] Figure 1 shows the ^{1}H NMR spectral changes of these macrocycles upon complexation. It can be seen that by adding one equiv. of **2** to **1** in $CDCl_3$, the three sets of aromatic signals for **2** experience a downfield shift ($\Delta\delta = 0.32$ for H_a, 0.11 for H_b, 0.10 for H_c), retaining the original multiplicity [Figure 1 (b) and (c)]. The multiplets for the 3-pentyloxy substituents (not shown) are also shifted downfield by ca. 0.1−0.2 ppm. The signals for the β-pyrrole, pyridyl and N−H protons of **1**, however, are shifted upfield and become broad [Figure 1 (a) and (c), the N−H band shifts from $\delta = -2.92$ to -3.03]. The broad signal at $\delta = 8.44$ is tentatively assigned to the β-pyrrole protons, while the broad band at $\delta = 7.70$ and the very weak tail around the solvent peak may be due to the pyridyl protons. These data are consistent with an edge-to-face dyad in which the phthalocyanine is deshielded by the ring current generated by the porphyrin macrocycle which falls into the shielding region of phthalocyanine. Similar spectral features have also been observed for related porphyrin aggregates.[13b,15] The broad nature of the porphyrin signals, in particular for the pyridyl protons, suggests that there is an extensive exchange between the coordinated and the free pyridyl groups. Due to the C_{4h} symmetry of the phthalocyanine, the resulting dyad does not possess an internal mirror plane, but a C_2 axis is present passing through two opposite pyridyl nitrogen atoms and the zinc(II) centre.[16] Therefore, some of the pyridyl protons become chemically equivalent and hence a restricted rotation of the pyridyl group along the C(*meso*)−C(pyridyl) bond may not contribute to the broadening of signals. Upon addition of four equiv. of **2** to **1** in $CDCl_3$, the NMR signals due to **2** are also shifted downfield to virtually the same extent, but the signals assigned to **1** are further broadened and shifted upfield [Figure 1 (d)]. This indicates that higher aggregates up to pentad [Figure 2 (a)] may be formed, which also exhibit relatively fast dynamic exchange processes.

The electronic absorption spectra of **1** (4×10^{-6} M), upon titration with **2** (from 4×10^{-6} to 2×10^{-5} M) in $CHCl_3$, and vice versa ([**2**] = 1×10^{-6} M, [**1**] from 1×10^{-6} to $1 \times$

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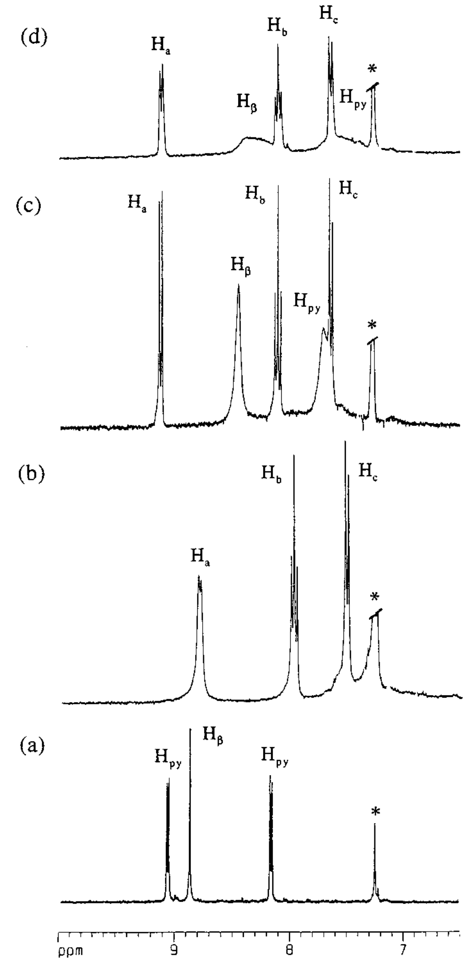


Figure 1. ^{1}H NMR spectra (aromatic region) of (a) **1**, (b) **2**, and mixtures of **1** and **2** in a (c) 1:1 and (d) 1:4 ratio in $CDCl_3$; * indicates residual solvent peak

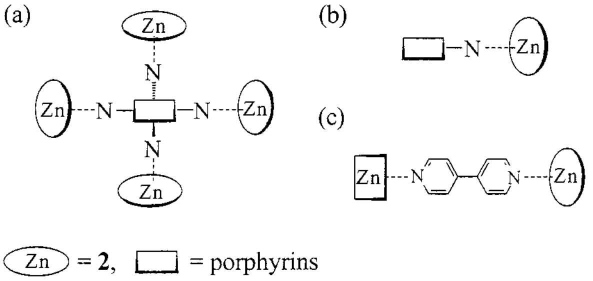
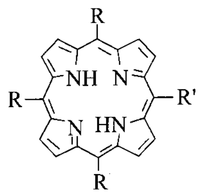
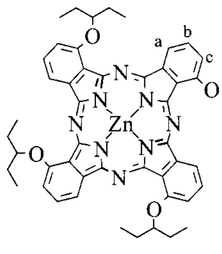


Figure 2. Schematic diagrams showing the structure of (a) **1**-(**2**)$_4$ pentad, (b) **4**−**2** dyad and (c) Zn(**5**)-bipy-**2**

10^{-5} M), remains essentially unchanged showing that the ground state π-π interactions between the perpendicularly disposed **1** and **2** are insignificant. The absence of interactions was also observed for oligoporphyrin systems linked in a similar fashion.[16] However, the fluorescence of **1** at 649 and 709 nm, upon excitation at 515 nm, diminishes gradually during titration with **2** in $CHCl_3$ (Figure 3). A similar fluorescence quenching is also observed by titrating a $CHCl_3$ solution of **2** (λ_{ex} = 615 nm, λ_{em} = 714 nm) with **1**. This mutual quenching phenomenon is likely to be due to a photo-induced electron transfer, as it is well-known that both porphyrins and phthalocyanines can act as electron donors or acceptors,[8,17] and no emission due to **2** is observed when **1** is excited which precludes an energy transfer pathway. In a control experiment, **1** was replaced with *meso*-tetraphenylporphyrin (**3**) of which the fluorescence spectra were recorded under identical conditions. There is no observable change in the fluorescence intensity of **3** upon titration with **2** which provides strong evidence for axial coordination of the pyridyl groups to the zinc(II) metal centre in **2**.



Compound	R	R'
1	C_5H_4N	C_5H_4N
3	Ph	Ph
4	Ph	C_5H_4N
5	C_6H_4Me	C_6H_4Me



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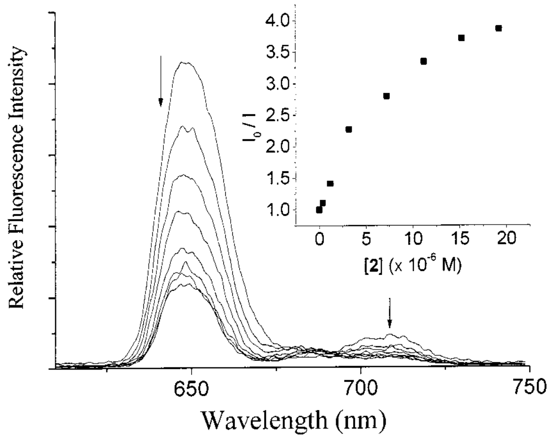

Figure 3. Fluorescence spectra of **1** (4 × 10^{-6} M) upon titration with **2** in $CHCl_3$. [**2**]: 0, 0.4, 1.2, 3.2, 7.2, 11.2, 15.2 and 19.2 × 10^{-6} M. The inset shows the Stern−Volmer plot for the fluorescence quenching at 649 nm

The association of *meso*-triphenyl(4-pyridyl)porphyrin (**4**) and **2** was also studied in which there is only one axial ligation [Figure 2 (b)]. Similarly, all the ^{1}H NMR signals due to **2** are shifted downfield while the signals assigned to **4** are slightly broadened and shifted upfield (see the Experimental Section). The fluorescence of **4** was also quenched by **2** and the association constant (*K*) for this edge-to-face dyad was determined by the Benesi−Hildebrand equation: $I_o/(I_o - I) = 1/A + 1/KA[\mathbf{2}]$, where I_o and I are the fluorescence intensity of **4** without and with the addition of **2**, respectively, and A is a constant related to the difference in the emission quantum yield of the complexed and uncomplexed **4**.[5b,18] By plotting $I_o/(I_o - I)$ vs. 1/[**2**] (Figure 4), a perfect straight line was obtained from which the value of *K* was determined to be 4.2×10^4 M^{-1} which is comparable with the values reported for related porphyrin systems.[1c]

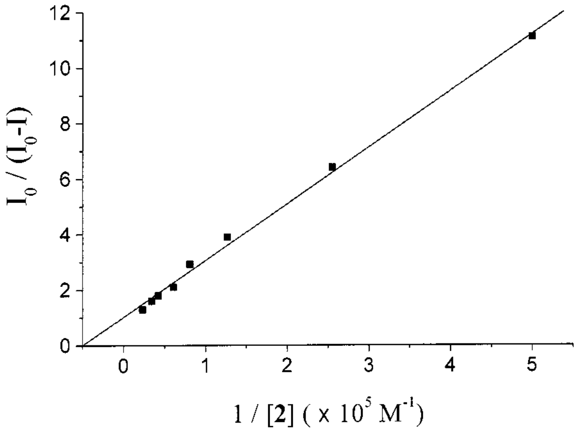

Figure 4. The Benesi−Hildebrand plot for determining the association constant between **2** and **4** (4×10^{-6} M) by fluorescence titration in $CHCl_3$

In an attempt to construct a face-to-face dyad of phthalocyanine and porphyrin linked through axial coordination, a mixture of zinc(II) *meso*-tetra(4-tolyl)porphyrin Zn(**5**), **2** and 4,4′-bipyridine (bipy) was examined. As zinc(II) tetrapyrroles normally bind to an additional ligand forming five coordinated species,[4b,13a] it was expected that apart from the hetero-dyad **2**-bipy-Zn(**5**) [Figure 2 (c)], the homo-dyads **2**-bipy-**2** and Zn(**5**)-bipy-Zn(**5**) should also be formed. Due to the presence of several dyads and the fact that some exhibit diastereomerism (those involving **2**), the ^{1}H NMR spectrum recorded in $CDCl_3$ is very complicated and cannot be unambiguously assigned. However, the formation of these face-to-face dimers is supported by the appearance of several broad bands at $\delta = 3.6-5.5$, which can be assigned to the coordinated bipy and the $OCHEt_2$ protons. The fluorescence quenching experiments provide more convincing evidence. The fluorescence intensity of Zn(**5**), when excited at 515 nm in the presence of bipy in $CHCl_3$ (both in 3.4×10^{-6} M), gradually decreases during titration with **2** (from 4.0×10^{-7} to 2.3×10^{-5} M). However, in the absence of bipy, the intensity remains relatively unchanged (Figure 5), showing that bipy plays a crucial role joining **2** and Zn(**5**) through coordination bonds.

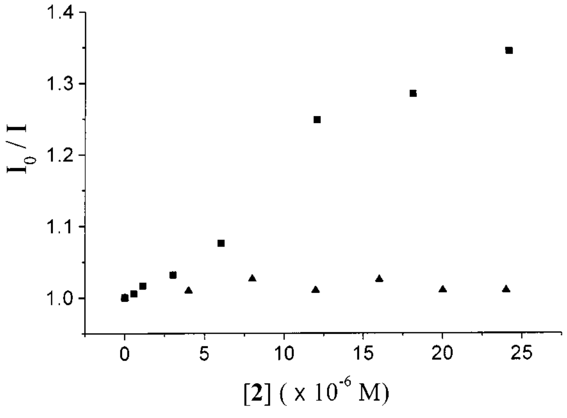

Figure 5. Stern−Volmer plots for the fluorescence quenching of Zn(**5**) by **2** with (■) or without (▲) the presence of bipy in $CHCl_3$; [Zn(**5**)] = [bipy] = 3.4×10^{-6} M

In summary, we have constructed, for the first time, assemblies of phthalocyanines and porphyrins through the relatively labile Zn(phthalocyanine)−N(pyridyl) axial ligation. Like many other supramolecules involving porphyrins, an efficient photo-induced electron transfer also occurs in these assemblies. By replacing the labile Zn^{II} ion with inert ions such as Ru^{II} and Os^{II}, it can be envisaged that more inert and diverse supramolecules based on phthalocyanines can be assembled.

Experimental Section

Compounds **2**,[14] **4**[16] and Zn(**5**)[19] were prepared by previously described methods. All other reagents and solvents were commercially available and used as received. Absorption and uncorrected fluorescence spectra were recorded on a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively, both in $CHCl_3$ at ambient temperature. Phthalocyanine **2** was excited at 615 nm, while all the porphyrins were excited at 515 nm. The fluorescence intensities of porphyrins were based on the area under the fluorescence spectra in the region of 625−730 nm.

^{1}H NMR Studies: All ^{1}H NMR data were acquired on a Bruker DPX 300 (300 MHz) spectrometer at ambient temperature in $CDCl_3$, with Me_4Si as an internal standard. The concentration of **1** and **4** was kept at 0.5 mM. For a 1:1 mixture of **1** and **2**: $\delta = 9.12$ (d, $J = 7.5$ Hz, 4 H, H_a), 8.44 (br. s, 8 H, H_β), 8.09 (t, $J = 7.5$ Hz, 4 H, H_b), 7.70 (br. s, H_{py}), 7.64 (d, $J = 8.1$ Hz, 4 H, H_c), 4.88−4.94 (m, 4 H, OCH), 2.41−2.50 (m, 8 H, CH_2), 2.23−2.32 (m, 8 H, CH_2), 1.40 (t, $J = 7.5$ Hz, 24 H, CH_3), −3.03 (br. s, 2 H, NH). For a 1:4 mixture of **1** and **2**: $\delta = 9.11$ (d, $J = 7.5$ Hz, 16 H, H_a), 8.0−8.5 (br. s, H_β), 8.09 (t, $J = 7.5$ Hz, 16 H, H_b), 7.63 (d, $J = 7.8$ Hz, 16 H, H_c), 7.3−7.8 (br. s, H_{py}), 4.87−4.94 (m, 16 H, OCH), 2.40−2.47 (m, 32 H, CH_2), 2.22−2.31 (m, 32 H, CH_2), 1.40 (t, $J = 7.5$ Hz, 96 H, CH_3), −3.10 (br. s, 2 H, NH).[20] For a 1:1 mixture of **2** and **4**: δ 9.15 (d, $J = 9.0$ Hz, 4 H, H_a), 8.73−8.78 (m, 4 H, H_β), 8.60 (br. s, 2 H, H_β), 8.06−8.14 (m, 10 H, H_b & Ph), 7.63−7.74 (m, 15 H, H_c, H_β & Ph), 7.0−7.6 (br. s, 4 H, H_{py}), 4.93 (quintet, $J = 6.0$ Hz, 4 H, OCH), 2.22−2.40 (m, 8 H, CH_2), 2.42−2.56 (m, 8 H, CH_2), 1.41 (t, $J = 7.5$ Hz, 24 H, CH_3), −3.11 (br. s, 2 H, NH).

Determination of the Association Constant of the 4−2 Dyad by Fluorescence Titration: The concentration of **4** in $CHCl_3$ was kept at 4×10^{-6} M, while that for **2** was varied from 0 to 4×10^{-5} M. Upon excitation at 515 nm (where **2** has no absorption), fluorescence due to **4** was observed, and was monitored during the titration. The absorbance values at the excitation wavelength were first normalized before the fluorescence intensities were adjusted and taken. As all the absorbance values at this position were only ca. 0.1, it could be assumed that reabsorption was not significant.

Acknowledgments

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