

## Assembly of a Photoactive Supramolecule using Porphyrin Co-ordination Chemistry

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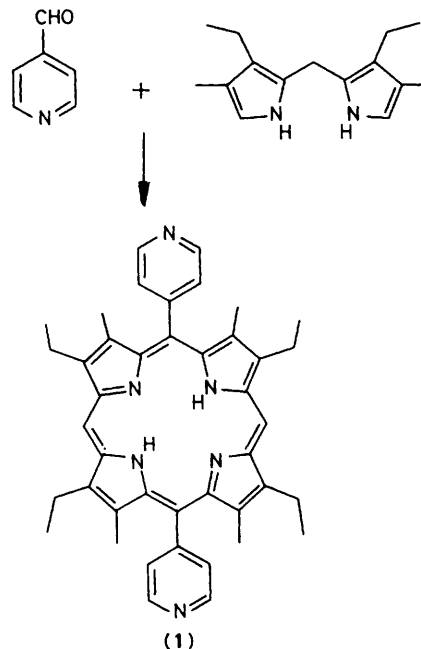
A bis(4-pyridyl)-porphyrin has been synthesised and shown to bind within the cavity of a host metalloporphyrin–pyromellitimide dimer; fluorescence quenching of the bound guest implies a photoinduced electron transfer to the pyromellitimide moieties of the host molecule.

Any attempt to model the behaviour of biological photosynthetic reaction centres should feature strict control of the relative geometries of the various photoactive components.<sup>1</sup> Synthetic organic chemistry permits the incorporation of many different photoactive subunits in a single supramolecular system,<sup>2</sup> but conformational control of such systems has proved exceedingly difficult.<sup>3</sup> We recently used the co-ordination properties of metalloporphyrins in macrocycles to control their conformations,<sup>4</sup> and we now apply this approach to the design and assembly of a supramolecular photochemical device.

The bis(4-pyridyl)porphyrin (**1**) was synthesised in 51% yield by acid-catalysed reaction of pyridine-4-carbaldehyde and 3,3'-diethyl-4,4'-dimethyldipyrromethane, followed by *in situ* DDQ oxidation of the porphyrinogen (Scheme 1).<sup>5</sup> We have already reported the synthesis and some co-ordination properties of the bis-zinc porphyrin dimer (**2**).<sup>4</sup>

Over a wide range of concentrations ( $10^{-6}$  to  $10^{-3}$  M) (**1**) binds within the cavity of (**2**), as shown in Figure 1. The conformation of the important components of the complex should be fixed by their intermolecular interactions: co-ordination of zinc by pyridine, and donor–acceptor  $\pi$ – $\pi$  attraction between pyromellitimide and (**1**). The structure and properties of the complex were established by <sup>1</sup>H n.m.r., u.v.–visible absorption and emission spectroscopy.

Titration of (**1**) with (**2**) was followed by difference



Scheme 1. Reagents: *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, MeOH, then dichlorodicyanobenzoquinone (DDQ).

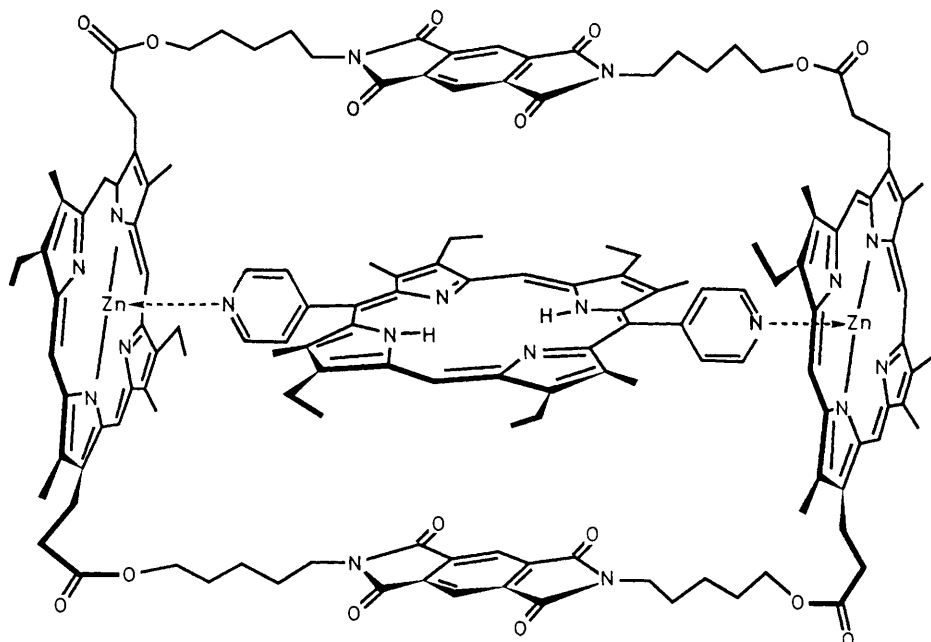
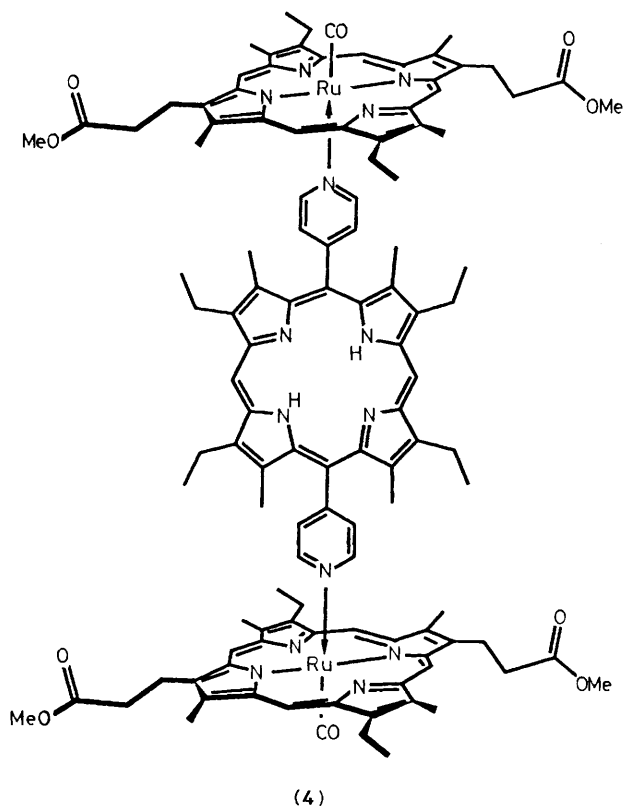
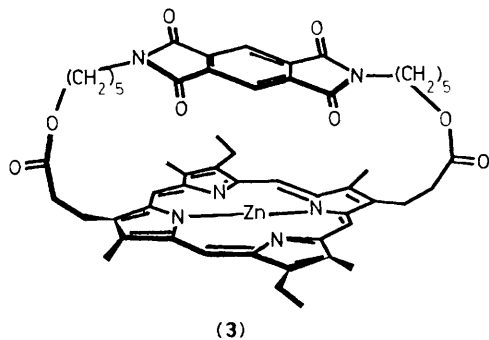


Figure 1. Complex between guest porphyrin (**1**) and host dimer (**2**).



absorption spectroscopy.† A Hill plot yields a slope of 0.96 ( $\pm 0.05$ ), indicating that a simple 1:1 complex is formed.<sup>6,7</sup> The binding constant is  $2.6 (\pm 0.2) \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ ; this is two orders of magnitude larger than the value for the binding of (1) to the corresponding monomeric zinc porphyrin (3). Indeed, it is also two orders of magnitude larger than the binding constants of other bispyridyl ligands inside the cavity of (2).<sup>8</sup> We believe that this difference is largely due to the strong

donor-acceptor  $\pi$ - $\pi$  attraction between the pyromellitimide subunits and the bound (1).

The 400 MHz  $^1\text{H}$  n.m.r. spectrum of the complex is broad at room temperature, but at 250 MHz a fast exchange spectrum between the free and bound species is observed. This exchange is slower than for pyridine because of the greater binding energy of (1). All the signals of (1) experience large upfield shifts when bound in the cavity of (2) as a result of the combined ring currents of the two porphyrin and the two pyromellitimide moieties; the ring methyl protons of (1) appear at  $\delta$  0.50, essentially the same shift as is observed in the ternary complex (4);<sup>9</sup> the chemical shifts of the metalloporphyrin subunits of (2) in the complex also match those of (4). However, the *meso* signals of (1) are at  $\delta$  9.30, shifted 0.25 p.p.m. upfield relative to (4) by the proximate pyromellitimide moieties. The slow exchange spectrum is obtained at 200 K at 400 MHz; intermolecular nuclear Overhauser enhancements are now observed between the host dimer protons and the bound protons of (1). Taken together, these results confirm the essential features of the geometry shown in Figure 1 and provide strong evidence for the expected<sup>4</sup>  $\pi$ - $\pi$  interaction between bound (1) and the pyromellitimide walls of the host.

Observation of the fluorescence at 630 nm [which is mainly due to (1)] during the titration of (1) with (2) shows that the fluorescence of bound (1) is at least 90% quenched. Similar titrations of (1) with simple zinc porphyrins or with (3) show no change in the fluorescence of bound (1). The quenching in the dimer complex can thus be ascribed to photoinduced electron transfer between bound (1) and the pyromellitimide groups that we know are very close in space. A more detailed investigation of the photochemical properties of this complex is in progress.

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† Binding of pyridine to a zinc porphyrin induces substantial shifts in the Soret and *Q*-bands.<sup>6</sup>