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Self-assembly of Perylene Bisimide Bridging Ligands to Zinc Phthalocyanine in Solution

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A novel supramolecular self-assembly, where a pyridyl-substituted perylene bisimide dye (DPyPBI) axially binds to zinc phthalocyanine (ZnPc), has been designed. Their coordination properties have been studied by UV/vis, fluorescence techniques and ^{1}H NMR spectroscopy, showing that 1:1 and 1:2 double sandwich complexes between DPyPBI and ZnPc are formed.

Keywords: Phthalocyanine; Perylene bismide; Self-assembly; Metal-mediated

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In the past decade, much attention has been paid to metal-mediated self-assembling process to provide diverse functional supramolecular architectures [1–5]. Perylene bisimide (PBI) dyes have been widely used in the construction of supramolecular arrays [6–14]. They are characterized by extremely efficient fluorescent emission, facile electrochemical reduction, and clear spectroscopic signatures [15,16]. For these useful features, PBI units have been included as photo-excitable and electron-acceptor molecular components in a variety of interesting photoactive supramolecular systems [17–23].

As one of the best known synthetic porphyrin analogues [24], phthalocyanines (Pcs) are such highly versatile and stable chromophores with unique physicochemical properties as to be made ideal building blocks in the construction of supramolecular architectures [25–31]. To the best of our knowledge, the self-assembly consisting of perylene bismide and phthalocyanine units is scarcely investigated despite the perylene bismide/porphyrin self-assembly system being generally studied [32–34].

Herein, N,N′-di(4-pyridyl)-1,6,7,12-tetra(4-tert-octylphenoxy)perylene-3,4,9,10- tetracarboxylic acid bisimide (DPyPBI) is used as a functional receptor dye, which axially binds to zinc(II) tetra-(α-2,4-dimethyl-3-pentoxy)phthalocyanine (ZnPc) to form a novel supramolecular self-assembly (see in Scheme 1). The coordination properties of this assembly are investigated by UV/vis, fluorescence techniques and ^{1}H NMR spectroscopy as below.

The coordination of DPyPBI to ZnPc was first probed by UV/vis titration in CH_2Cl_2. The absorption spectra of ZnPc displays a Soret band at 318 nm and an intense Q band at 711 nm (Fig. 1). Addition of increasing amounts of DPyPBI to a constant concentration of ZnPc induces spectral changes of ZnPc. The Q band of ZnPc at 711 nm is gradually decreased and slightly shifted to 710 nm while the absorptions at 318, 637, 675 and 766 nm are gradually increased. It is expected that the ligations of pyridyl units to zinc phthalocyanine are relatively weak and labile.

It is known that fluorescence spectrometry has higher sensitivity [35]. The spectrofluorometric titration of ZnPc with DPyPBI was carried out in CH_2Cl_2 as shown in Fig. 2. Upon excitation at 318 nm, where DPyPBI is relatively transparent, the fluorescent intensity decreasing at 727 nm and concomitantly increasing at 620 nm are observed. When the concentration of DPyPBI is over 4.0×10^{-5} M, the change of the relative fluorescence intensity is slight, showing that ZnPc has been completely coordinated to the pyridyl units of DPyPBI.

With increasing amounts of ZnPc to a constant concentration of DPyPBI, the photoluminescence

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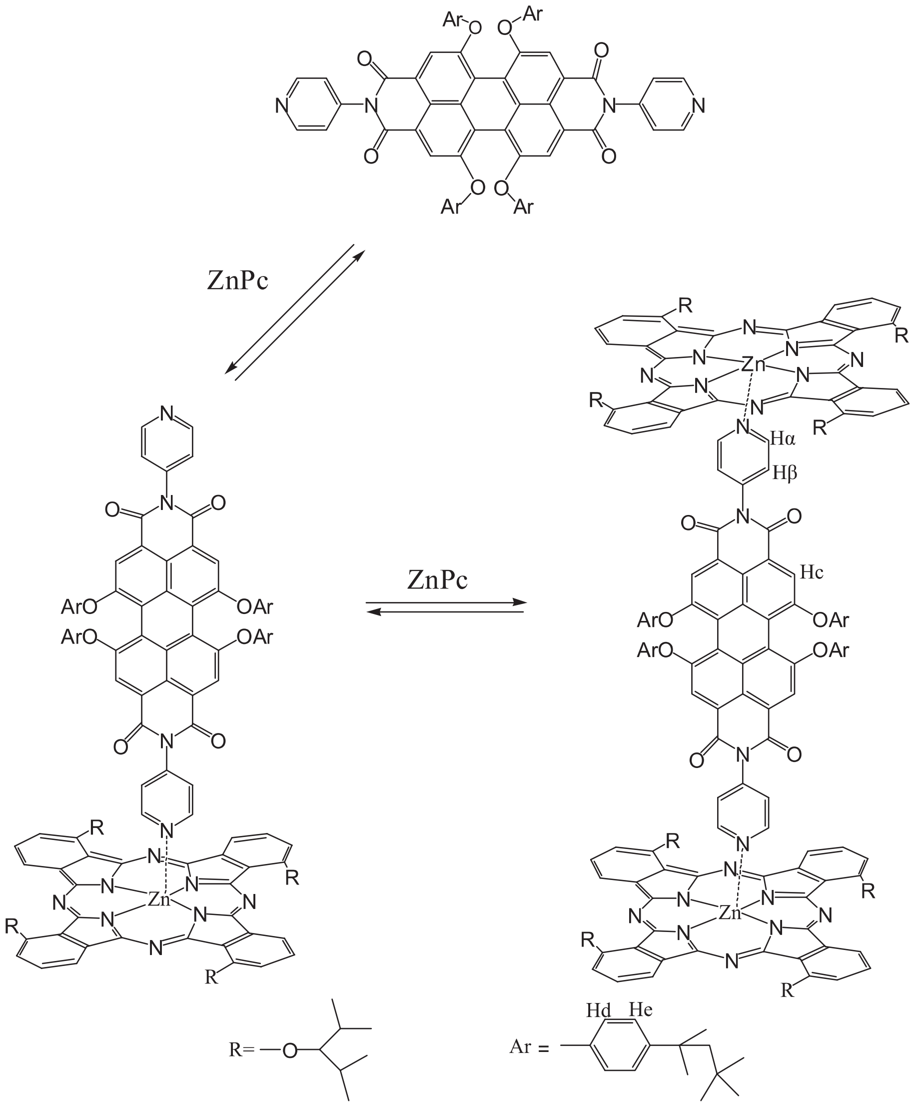

SCHEME 1

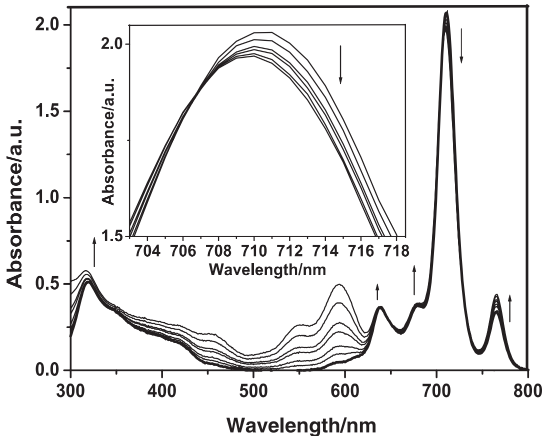

FIGURE 1 UV/vis titration of ZnPc with DPyPBI. The arrows indicate the spectral changes of ZnPc upon addition of DPyPBI. The concentration of ZnPc was kept constant at 1.0×10^{-5} M, the amounts of DPyPBI gradually increase (from 1.0×10^{-6} M to 1.0×10^{-4} M).

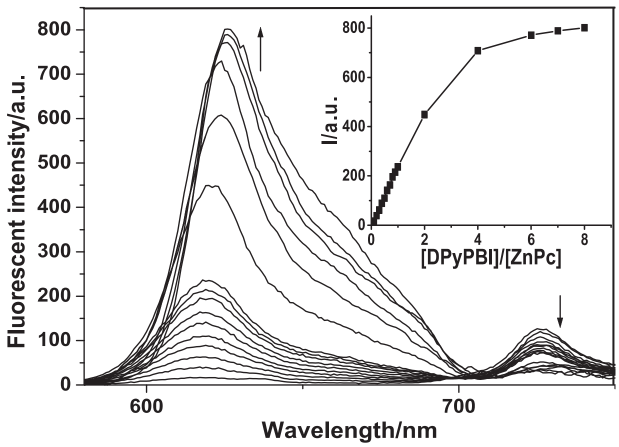

FIGURE 2 Fluorescence spectra of ZnPc ($c = 1.0 \times 10^{-5}$ M) in the presence of DPyPBI (from 1.0×10^{-6} to 1.0×10^{-4} M) (in CH_2Cl_2, $\lambda_{ex} = 318$ nm), the arrows indicate the spectral changes upon addition of DPyPBI. Inset: Plot of fluorescence intensity *vs* the molar ratio [DPyPBI]/[ZnPc].

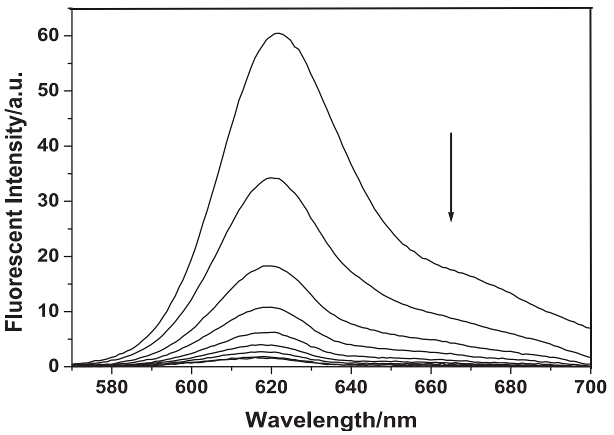

FIGURE 3 Fluorescence spectra of DPyPBI (c = 10^{-5} mol L^{-1}) in the presence of ZnPc (c = 10^{-6}–10^{-4} M) (in CH_2Cl_2, $\lambda_{ex} = 547$ nm), the arrow indicates the spectral changes upon addition of ZnPc.

of DPyPBI is almost quenched under the excitation at 547 nm (the feature absorption maximum of DPyPBI) (Fig. 3). It is probably the result of a photoinduced electron transfer process [32].

^{1}H NMR titration was carried out in $CDCl_3$ in order to further evaluate the coordination of DPyPBI to ZnPc (see in Fig. 4). The concentration of DPyPBI was kept constant, and the changes in the chemical shifts were followed as a function of increasing concentration of ZnPc. The NMR titration spectra reveal a significant upfield shift of the protons in the DPyPBI bridging unit, due to the shielding effect of the ring current of phthalocyanines. The magnitude of the shifts depends on the distance of the protons from the central macrocycle. The H_c, H_d and H_e protons, which are located further away, experience the shifts of 0.58 ppm (from 8.16 ppm to 7.58 ppm), 0.25 ppm (from 7.30 ppm to 7.05 ppm) and 0.32 ppm (from 6.87 ppm to 6.55 ppm), respectively. The H_β protons, which are more closely located, are shifted by 1.79 ppm (from 7.55 ppm to 5.76 ppm). The H_α protons, being in the closest position to the central macrocycle, are shifted by 4.76 ppm in ^{1}H NMR titration (from 8.81 ppm to 4.05 ppm). Obviously, these large upfield shifts are not a result of the coordination of Lewis acidic metal centers but are owing to the coordination of the diaza ligand within the inner core of the phthalocyanine ring. The analogous changes in the chemical shifts of protons in zinc porphyrin/perylene bisimide supramolecular system had been reported by Würthner and coworkers [32–34]. On the other hand, the coordination of DPyPBI to ZnPc is weak and ligand exchange is fast on the NMR time scale. The observed chemical shift δ is the average of the chemical shifts of the nucleus in DPyPBI and in the ZnPc/DPyPBI complex. A plot of the chemical shift of H_β protons versus the molar ratio of [ZnPc]/[DPyPBI] is given in Fig. 5. The intersection

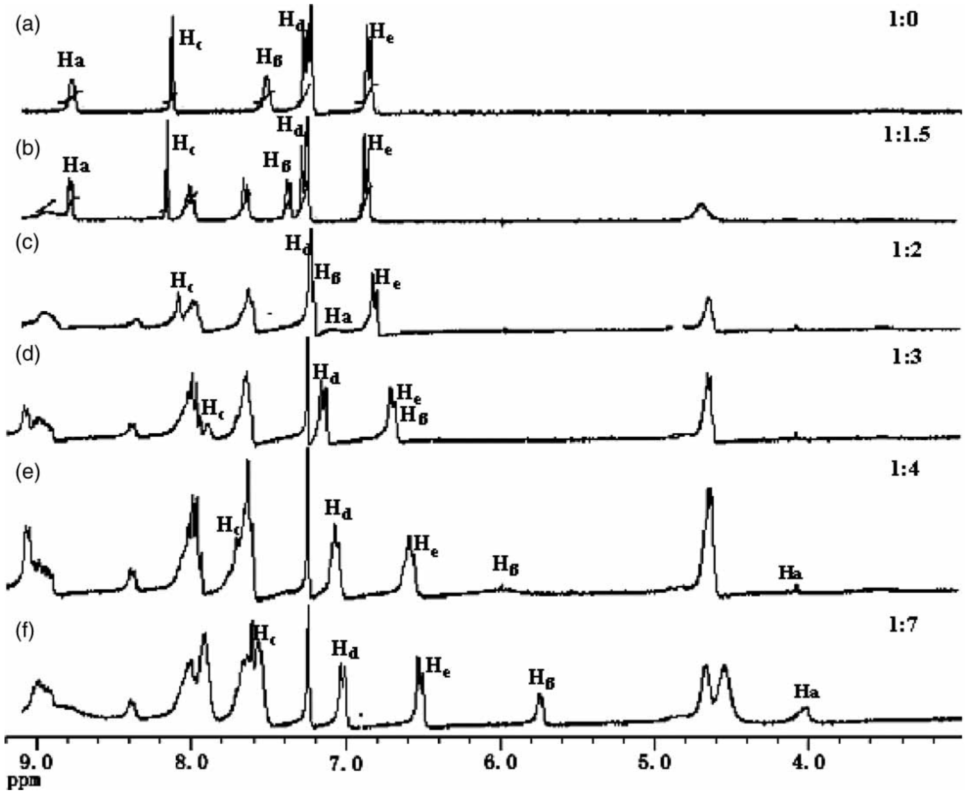

FIGURE 4 Partial ^{1}H NMR spectra of the ZnPc/DPyPBI supramolecular system in different concentration ratios in $CDCl_3$ at room temperature. The concentration of DPyPBI was kept constant at 3.0×10^{-3} M.

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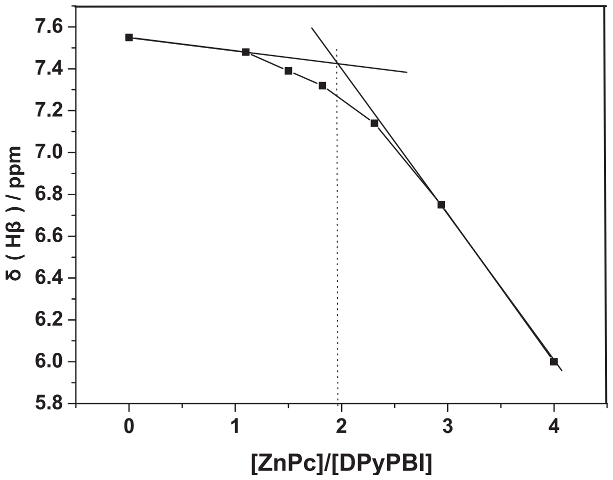

FIGURE 5 Plot of the chemical shift of H_β protons *vs* the molar ratio [ZnPc]/[DPyPBI].

of two straight lines obtained with different slopes at a mole ratio of ca. 2:1 gives unambiguous proof of the sandwich complex structure suggested in Scheme 1. And nonlinear least squares curve-fitting analysis [36] on the titration data of H_β protons reduces the binding constant of $2080\,M^{-1}$.

In summary, a novel metal-mediated supramolecular system of zinc phthalocyanine with perylene bisimide has been investigated. ^1H NMR, UV/vis and fluorescence spectra confirmed the formation of 1:1 and 1:2 double sandwich complexes between perylene bisimide and zinc phthalocyanine. The novel entities comprise the photochemically and electrochemically active phthalocyanines and perylene bisimide dyes, thus, such assemblies have potential application in molecular devices and materials.

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