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A Novel Self-aggregates of Phthalocyanine Based on Zn–O Coordination

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α-Aryl/alkoxy-substituted phthalocyanines (Pcs) were synthesized and the formation of J-type self-aggregation for zinc phthalocyanines has been observed in organic non-coordinating solvents. The mechanism of the formation of this self-assembly was studied by UV–vis spectroscopy, fluorescence spectroscopy and MALDI-TOF MS, which revealed that it was stabilized by Zn–O self-coordination.

The aromatic macrocycle phthalocyanines (Pcs) are one of the best known synthetic porphyrin analogues showing a wide range of applications in material science, medicine, catalysis, and photonics because of their exceptionally high thermal and chemical stability.[1] Molecular assemblies of chromophores play crucial roles in nature's most important systems, including light harvesting in photosynthesis,[2] and are important in technological applications.[3] The organization of phthalocyanines into controlled structures, in particular, has been attracting considerable attention. The main problem encountered during the application of molecular assemblies and aggregates is a difficulty to control the arrangement and orientation of monomers in the aggregates. The J-aggregates are one of specific molecular assemblies discovered by Jelley and Scheibe.[4,5] Intermolecular interactions based on a side-by-side arrangement lead to a characteristic narrow and intense absorption band (J-band) that shows a bathochromic shift compared to the relevant monomer band.[5] Recently, making self-organising J-aggregates of large aromatic chromophores for optoelectronic applications have also attracted much interest by a number of researchers.[6] However, there are only few reports of the Pcs J-aggregates so far. Farren et al.[7a] observed the strong aggregation of tetra-solketal-substituted zinc Pcs at low temperature. Kaneko et al.[7b] and Isago[7c] reported the observation of Pcs Q-band at longer wavelength in aqueous and non-aqueous media, respectively. Some of other cases of Pc J-aggregates are also formed under specific conditions in the solid state.[7d] Here, we report the synthesis of aryl/alkoxy substituents Pcs, and the first observation of self-assembled aggregation of zinc Pcs in organic non-coordinating solvents at room tempetature based on Zn–O self-coordination.

Aryl/alkoxy-substituted Pcs **1**–**4** (Figure 1a) were prepared according to the typical procedure by treating corresponding phthalonitriles in refluxing dimethylaminoethanol with or without $Zn(OAC)_2$. The products obtained were purified by column chromatography on silica gel and were fully characterized by UV–vis, MS spectra, ^1H NMR, and elemental analysis.[8] Figure 1b shows the electronic absorption spectra of Pcs **1**–**4** in chloroform ($CHCl_3$). In general the Q band of UV–vis spectrum shows splitted peaks for metal-free Pcs and one single peak for metal Pcs because of the different molecular symmetry.[9] As expected, metal-free Pcs **2** and **4** shows two splitted Q bands at 687, 720 nm and 692, 727 nm, respectively. However, for zinc(II) Pcs **1** and **3**, in addition to normal Q band (710 and 706 nm, respectively), an unusual red-shifted sharp band was observed at 741 and 746 nm, respectively. The formation of Pc aggregates causes significant spectral perturbations, owing to the coupling between the electronic states of individual monomeric Pc units. Therefore, the bands shifted to longer wavelength at 741 and 746 nm are ascribed to the absorption of J-aggregates. In order to understand the nature of the aggregation and test the stability of the self-aggregate, UV–vis spectra of ZnPc **1** was also measured in other solvents. Interestingly, the J-band formation is close related to the coordination behavior of solvents, i.e. it was observed in non-coordinating solvents, such as toluene, 1-chloronaphthalene, and *n*-hexane, but did not appear in coordinating solvents, such as DMF, pyridine, and methanol in which the Q band shows nomal absorption peak at ca. 690 nm (Figure 2a).

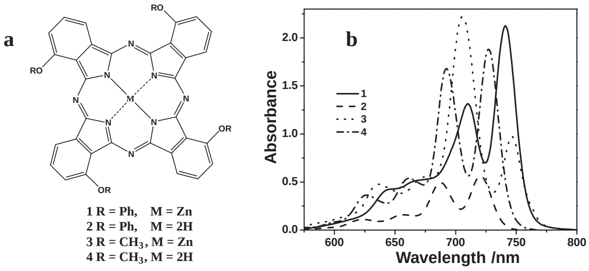

Figure 1. (a) Structures of the Pcs **1**–**4**. (b) Absorption spectra of Pcs **1**–**4** in $CHCl_3$: **1** (1.4×10^{-5} M), **2** (1.4×10^{-6} M), **3** (1.6×10^{-5} M), and **4** (2.4×10^{-5} M) at room temperature (25 °C).

The effect of concentration on the absorption spectra of ZnPc **1** in non-coordinating solvent of $CHCl_3$ was also studied.[8] It was found that the absorption spectra almost did not change with concentration (scope from 6.4×10^{-7} to 1.5×10^{-5} M) of zinc phthalocyanine in solution. The constant of self-associa-

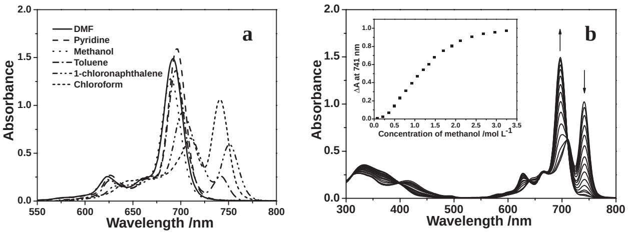

Figure 2. (a) Absorption spectra of ZnPc **1** in different solvents at room temperature (7.0×10^{-6} M). (b) Changes in the absorption spectra of ZnPc **1** in $CHCl_3$ upon addition of methanol. Inset: A plot illustrating the change in ZnPc **1** absorption at 741 nm versus increasing concentration of methanol in $CHCl_3$.

tion of ZnPc **1** in $CHCl_3$ was evaluated to be ca. $1.1 \times 10^7\,M^{-1}$ which is three orders larger than that of the aggregation of zinc tetra-*tert*-butylphthalocyanine caused by π–π stacking (dimerization constant in toluene, $K = 2.5 \times 10^{-4}\,M^{-1}$).[10] Therefore, the fact that J-aggregation appears to be complete even at the low Pc concentrations simply indicates that the coordination bonds holding the aggregate together are strong.

To investigate the de-aggregation of ZnPc **1**, a coordinating solvent of methanol was added to confirm that the solvent can interact with the ZnPc macrocycle. As methanol is titrated into a solution containing ZnPc **1** in $CHCl_3$, its absorption at 741 nm decreased gradually and then disappeared completely concomitant the increase in the absorption at 697 nm as shown in Figure 2b. In addition, the vibrational satellites corresponding to the monomeric species become more distinct. Four absorption isobetic points at 710, 666, 639, and 396 nm were observed, which suggest the existence of molecular self-aggregation. A plot of the change in absorption at 741 nm versus concentration of methanol in chloroform displays typical binding behavior (Figure 2b, inset). Recently, Smith et al.[11] reported the crystal structure of a zinc(II) porphyrin derivative in which zinc ion is ligated by methanol moleculars. In present study, upon the addition of methanol to chloroform, methanol coordinates with Zn^{2+} and destroys the self-coordination from side chain oxygen to central Zn^{2+} which causes the unusual band disappeared gradually. Peripheral substituents on Pc ring also play an important role in the formation of aggregates since phenyl-substituted Pc did not show J-aggregates formation in non-coordinating solvent toluene.[12] In addition, alkyl-substituted Pc also did not show J-aggregates formation in non-coordinating solvent 1-chloronaphthalene.[13] Accordingly, the above-mentioned UV–vis experiments indicate that oxygen atom in substituted groups and the central metal Zn are both important in aggregate formation of ZnPc **1**. A proposed mode of aggregation is illustrated in Figure 3a, wherein the J-type aggregates is stabilized by axial coordination of oxygen from side chain to the zinc(II) center between the Pc macrocycles.

It is well known that J-aggregates of organic dyes are fluorescent[4] whereas H-aggregates are not.[14] As shown in Figure 3b, a strong fluorescence emission was observed at 749 nm when excited at 630 nm. Upon gradual addition of disruptor methanol into $CHCl_3$, the intensity of fluorescence emission at 749 and 825 nm decreased together with the increase in the fluorescence emission at 711 and 777 nm with three isosbestic points appearing at 747, 756, and 810 nm. Accordingly, the fluorescence emission bands at 711 and 777 nm in $CHCl_3$ are from the monomer of ZnPc **1**, and the fluorescence peaks at 749 and 825 nm can be attributed to the fluorescence of the phthalocyanine J-type aggregates which formed by self-association of aryl/alkoxy-substituted groups to the center zinc ions and can be broke up by coordinating solvent methanol.

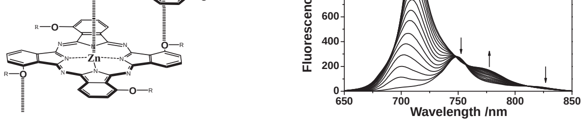

Figure 3. (a) Proposed mode of self-aggregation and (b) Changes in the fluorescence emission spectra of ZnPc **1** in $CHCl_3$ excited at 630 nm upon addition of methanol.

Furthermore, the MALDI-TOF mass spectrum of ZnPc **1** in $CHCl_3$ revealed a peak for the molecular ion at $m/z = 944.9$ $[M + H]^+$ as well as a peak for the dimer at $m/z = 1889.5$ $[M + H]^+$. This spectrum provides direct evidence for strong tendency of ZnPc **1** to aggregate. The MS of corresponding metal-free phthalocyanine **2**, on the other hand, only showed the monomer peak at m/z 883.2. This result indicates that the core metal Zinc is involved in the formation of the supramolecule which is consistent with the results of UV–vis spectra. Also, when the sample ZnPc **1** is prepared from a solution in pyridine, a well known ligand to coordinate metal zinc in Pc, no m/z peaks other than monomer could be observed. Therefore, the occurence of the unusual band is related to the formation of the J-type aggregates of phthalocyanine based on Zn–O coordination behavior, and chelating solvents can break the aggregates by coordination to zinc.

In conclusion, aryl/alkoxy-substituted Pcs were synthesized. It was found that self-aggregates of zinc Pcs formed in non-coordinating solvents at room temperature, which was characterized by MALDI-TOF MS spectra, UV–vis spectroscopy, and fluorescence spectroscopy. Further investigations on electronic absorption spectra and fluorescence spectra provided more information on molecular interaction of phthalocyanine, that is self-coordination of side chain oxygen atom to cetral metal zinc, which caused self-aggregates of phthalocyanine.

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