A Novel Phthalocyanine-based Dimer Linked by a Silver Ion: Structural Control of Self-assembled Dimers

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A novel phthalocyanine-based dimer, which is a di-nuclear pyridino-tri-*tert*-butylbenzotetraazaporphinatozinc linked by a silver ion, has been synthesized to control the states of assembly and characterized using electronic absorption and magnetic circular dichroism spectroscopy.

Since porphyrins reveal useful electronic and photonic properties, it is an attractive strategy to assemble porphyrins for constructing functional arrays, and therefore, a number of self-assembled porphyrin oligomers have been reported.[1] While phthalocyanines (Pcs) are analogous to porphyrins, Pc oligomers are expected to be superior to those of porphyrins in the following two aspects. (i) Pcs are more stable and robust. (ii) Characteristic photophysical properties are expected for Pc oligomers, since the oscillator strength of the Q band is much larger in Pcs than in porphyrins. However, there have been only a few studies on self-assembled Pc oligomers.[2–4] We report here a novel Pc-based dimer, which is a di-nuclear pyridino-tri-*tert*-butylbenzotetraazaporphinatozinc (ZnPcPy) linked by a silver ion, $[(ZnPcPy)_2Ag]PF_6$. In contrast to a number of self-assembled porphyrin or Pc oligomers linked by pyridine-metal-pyridine bridges reported to date,[1] this ZnPcPy complex contains a pyridine moiety in the π system. Accordingly, interactions between the Pc chromophores become relatively strong. In addition, it is known that ZnPcPy forms a self-assembled dimer ($(ZnPcPy)_2$) in a non-polar solvent, while it returns to a constituting monomer when pyridine (Py) is added.[4,5] Therefore, we have attempted to control the states of assembly by preparing $[(ZnPcPy)_2Ag]PF_6$. This self-assembled dimer is investigated by electronic absorption and magnetic circular dichroism (MCD) spectroscopy, in order to clarify the electronic structure in the excited states.

ZnPcPy was synthesized according to the methods previously reported.[4,5] UV-vis absorption spectra were measured with a Hitachi U3410 spectrometer. MCD measurements were made with a JASCO J-720 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields of up to 1.1 T (T = tesla) with parallel and then antiparallel fields.

It was found that an electronic absorption spectrum of ZnPcPy in CH_2Cl_2/MeOH (10 : 1 v/v) immediately changed by adding $AgPF_6$.[6–8] The absorption spectrum in the presence of sufficient $AgPF_6$ was clearly different not only from that of the monomeric ZnPcPy in the absence of $AgPF_6$ but also from that of $(ZnPcPy)_2$. After adding NH_4Cl which can remove silver ions as AgCl, it reverted to the same absorption spectrum as the monomer. These results indicate that ZnPcPy forms a complex with $AgPF_6$. Indeed, in a FAB mass spectrum, the +1 species resulting from $[(ZnPcPy)_2Ag]$ (1601) and $[(ZnPcPy)_2Ag]PF_5$ (1728) were observed, from which a formation of $[(ZnPcPy)_2Ag]PF_6$ was clearly confirmed.

Figures 2a and 2b show the electronic absorption and MCD spectra, respectively, in the Q band region of $[(ZnPcPy)_2Ag]PF_6$. The electronic absorption spectrum of $[(ZnPcPy)_2Ag]PF_6$

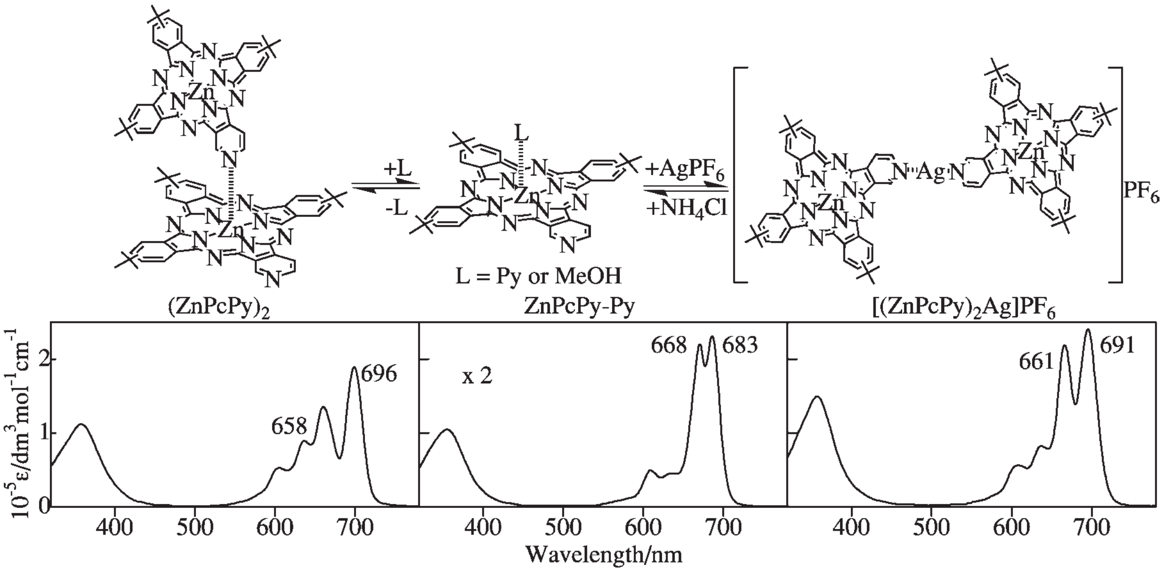

Figure 1. Molecular structure of ZnPcPy complexes and electronic absorption spectra. These absorption spectra of $(ZnPcPy)_2$, ZnPcPy-Py, and $[(ZnPcPy)_2Ag]PF_6$ were measured in CH_2Cl_2, CH_2Cl_2/MeOH (10 : 1 v/v), and CH_2Cl_2/MeOH (10 : 1 v/v), respectively.

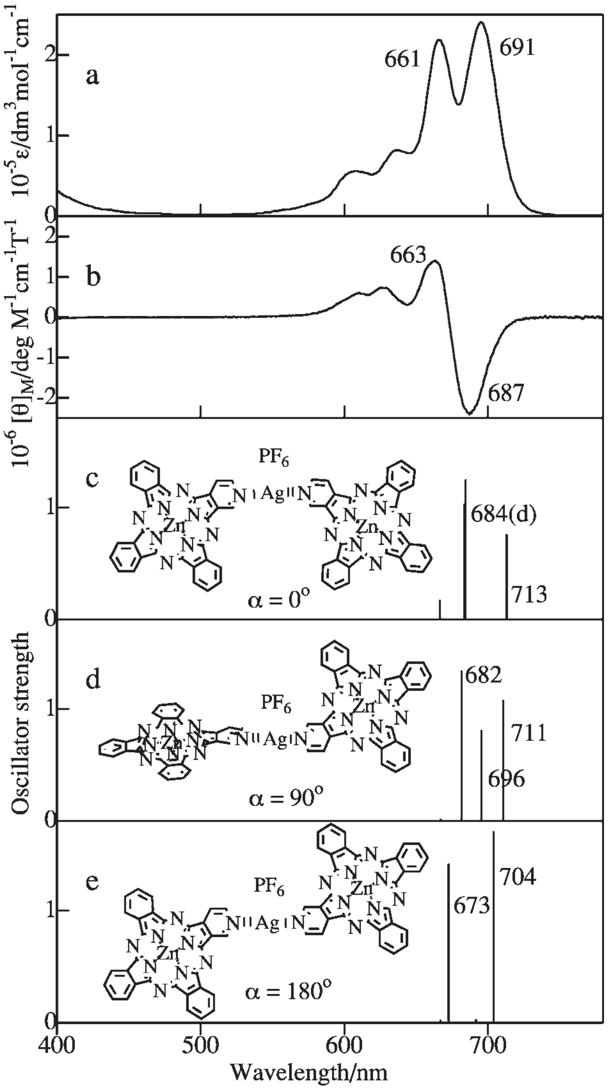

Figure 2. Elecronic absorption (a) and MCD (b) spectra with CI calculations for $\alpha = 0°$ (c), 90° (d), 180° (e).

exhibits two intense peaks at 661 and 691 nm. These two absorption peaks coincide with positive and negative MCD peaks (663 and 687 nm), which indicate the Faraday *B* terms originating from non-degenerate transitions. For [(ZnPcPy)$_2$Ag]PF$_6$, various dihedral angles between the two Pc planes, α, are considered possible. While exciton interactions resulting in the main spectral changes in the Q bands are strongly dependent on the α value,[11] only two sharp bands are seen in the electronic absorption and MCD spectra, suggesting that a conformational freedom between ZnPcPy constituents is relatively restricted. In order to clarify this electronic absorption spectrum, configuration interaction (CI) calculations were carried out for conformations with $\alpha = 0°$ (*cis*-configuration), 90°, and 180° (*trans*-configuration) using the ZINDO/S Hamiltonian.[12] The calculated spectra are shown in Figure 2c–e. When $\alpha = 90°$ (Figure 2d), three intense bands (682, 696, and 711 nm) exist at intervals of about 15 nm. When $\alpha = 0°$ (Figure 2c), two main bands are seen at 684 and 713 nm, but the former band is more intense and predicted to be degenerate. These calculated spectra are obviously different from the observed spectrum. On the other hand, two intense Q bands (673 and 704 nm) are seen in the spectrum calculated for $\alpha = 180°$, which reproduces the following experimental trends: (i) Two intense bands are spaced about 30 nm. (ii) An absorption band at the lower energy side is more intense than that at the higher energy side. These results suggest that [(ZnPcPy)$_2$Ag]PF$_6$ mainly forms a planar- and *trans*-conformation. This conformational selectivity of the planarity and *trans*-configuration may originate from the π stabllization and steric hindrance of *tert*-butyl substituents, respectively.

In summary, we have realized a novel self-assembled Pc dimer. The electronic absorption and MCD properties have been investigated by the CI calculations, which show that [(ZnPcPy)$_2$Ag]PF$_6$ mainly forms a planar- and *trans*-conformation. In addition, we have succeeded in controlling the states of assembly of ZnPcPy complexes, as shown in Figure 1. This study is not only important in exemplifying the structural control of Pc chromophores but also useful as a strategy for constructing novel functional arrays.

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6 Experimental conditions for the formation of [(ZnPcPy)$_2$Ag]PF$_6$ were examined using tetra-*tert*-butylphthalocyaninatozinc (ZnPc). By adding AgPF$_6$,[7,8] the electronic absorption spectrum of ZnPc did not change in CH$_2$Cl$_2$/MeOH (10 : 1 v/v), while in CH$_2$Cl$_2$ it exhibited an immediate formation of the cation radical,[9] indicating that ZnPc is not oxidized by AgPF$_6$ in the former mixed solvent, and that AgPF$_6$ does not coordinate to the *meso*-nitrogens.[10] Here, the electronic absorption spectrum of ZnPcPy in CH$_2$Cl$_2$/MeOH was obviously different from that in CH$_2$Cl$_2$, indicating that ZnPcPy exists as monomer and dimer in CH$_2$Cl$_2$/MeOH and CH$_2$Cl$_2$ solutions, respectively.

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