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Self-coordinated Phthalocyanine Nanoaggregates

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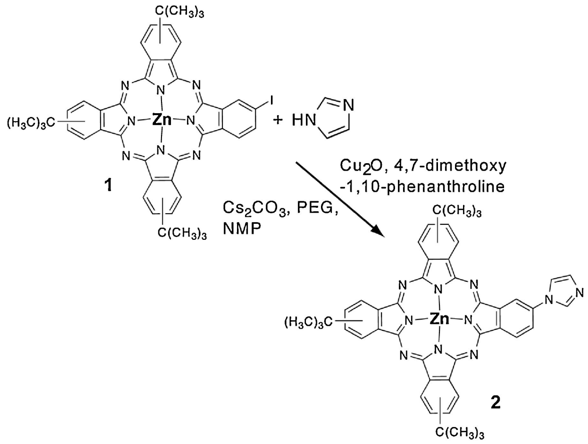
Asymmetric zinc phthalocyanine (ZnPc) **2**, in which one imidazole unit is attached to a ZnPc ring, assembles into supramolecular polymers through intermolecular metal–ligand interactions.

The self-organization of discrete functional molecules into specific assembled architectures is an important process for constructing molecular-based electronic and optical devices.[1] Control of the spatial arrangement and orientation of building molecular units within organized systems enhances the properties and functions of the devices. Phthalocyanines (Pcs) have been used as building molecular units for constructing molecular devices.[2] Owing to their extended flat aromatic surface, Pcs and their metal complexes (MPcs) can be assembled into one-dimensional columnar assemblies using π–π stacking interactions.[3] Furthermore, intermolecular noncovalent interactions such as metal–ligand, hydrogen-bonding, and donor–acceptor interactions have also been used for the formation of long-range supramolecular structures.[4] Torres et al. reported the formation of one-dimensional nanoaggregates using the complementary donor–acceptor interactions among Pc heterodimers.[5] Kobuke et al. succeeded the formation of highly fluorescent Pc dimers by the coordination of the imidazole group from one MPc with the central metal ion of the second MPc.[6] In spite of the extensive research in MPcs assemblies,[4] metal–ligand interactions have never been explored to construct nanoaggregates in MPcs systems. In this study, we describe the self-organization of imidazole-substituted ZnPc **2** into nanoaggregates.

Asymmetric tri-*tert*-butyliodophthalocyaninatozinc(II) **1** was prepared by using the statistical condensation of 4-iodophthalonitrile and 4-*tert*-butylphthalonitrile in the presence of $ZnCl_2$ according to a literature method reported by Torres et al.[7] The target imidazole-substituted ZnPc **2** was prepared by the copper-catalyzed *N*-arylation reaction of imidazole with **1** in the presence of Cu_2O and 4,7-dimethoxy-1,10-phenanthroline (Scheme 1).[8] The synthesized ZnPc **2** was isolated by column chromatography on activated alumina with ethyl acetate/acetic acid (10:1) as eluent and characterized by MALDI-TOF-MS and ^{1}H NMR spectroscopy. MALDI-TOF mass spectrum of **2** revealed a peak for the molecular ion at m/z 811 $[M + H]^+$ as well as a set of peaks corresponding to m/z 1622 (dimer), 2434 (trimer), and 3244 (tetramer). While the ^{1}H NMR spectrum in $CDCl_3$ of **1** showed a resolved set of resonances, the spectrum of **2** showed the typical broadened resonances of Pc aggregates.



Scheme 1.

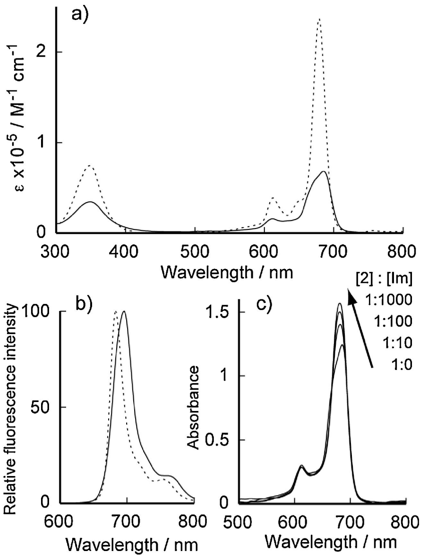
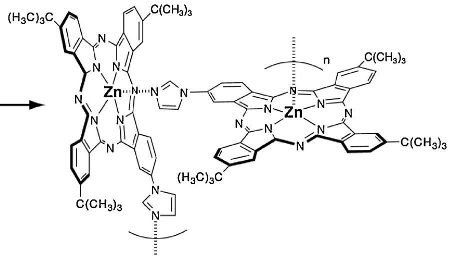


Figure 1. a) Absorption and b) fluorescence spectra in $CHCl_3$ of **1** (dashed line) and **2** (solid line). c) Changes in the spectra of **2** upon addition of Im.

Absorption spectroscopy provides us information on the type of aggregated structures for MPcs in a solution or a solid.[9] The absorption spectra of **1** and **2** in $CHCl_3$ are shown in Figure 1a. While **1** exhibits a sharp Q band at 679 nm, which is typical of monomeric ZnPcs, the spectrum of **2** revealed a significant hypochromicity of the Soret and Q bands.[9] The maximum of Q band was red-shifted by 9 nm compared to that of **1** and the Q band possessed a shoulder peak at around 660 nm. Moreover, the emission maximum of **2** was also red-shifted ($\lambda_{em} = 696$ nm) as shown in Figure 1b and the fluorescence quantum yield of **2** was 0.09. The observed change in absorption spectra and the red-shifted emission peak of **2** indicate the formation of Pc aggregates in $CHCl_3$. As the imidazole lies on

2 →



Scheme 2.

the same plane as the ZnPc ring, the metal–ligand interactions between imidazolyl substituent and central Zn ion lead to the formation of a supramolecular polymer (Scheme 2).[10] The red-shift of the Q band and the presence of the shoulder peak results from the interaction among ZnPcs in the supramolecular polymers.[6,11] No significant changes in the UV–vis spectra of **2** were detected in the range of 5×10^{-8} to 1×10^{-4} M, suggesting the high association constant of supramolecular polymers made up of **2**. When methanol was added to the solution of **1**, its Q band of **1** was broadened and the maximum of the Q band was blue-shifted to 620 nm with the increase in methanol content.[9] This spectral change can be ascribed to the formation of phthalocyanine aggregates having a coafacial stacking and the formed aggregates are not fluorescent. In contrast, the absorption and fluorescence spectra of **2** were unaltered by the addition of methanol. The association constant for the axial ligation was evaluated by the titration study of **1** with *N*-methylimidazole (Im). By the addition of Im, the absorption spectra of **1** changed and the change showed clear isosbestic points. Titration of **1** with Im using Job's method indicated the formation of a 1:1 complex and the association constant was 2.1×10^4 M^{-1}.[6] Titration of **2** with Im resulted in a small blue shift of the Q band from 686 to 681 nm and the intensity of the Q band was increased (Figure 1c). The final converged spectrum resembles that of **1** with an axial coordination of Im. This spectral change suggests the dissociation of the supramolecular polymer for the each molecular component with the addition of Im. From the absorption and fluorescence spectra, the imidazole-substituted ZnPc **2** assembled into fluorescent supramolecular polymers driven by intermolecular metal–ligand interactions between the central metal of the ZnPc ring and the peripheral imidazole ligand.

The size and morphology of the Pc aggregates were examined by using TEM and AFM (Figure 2). One drop of the CHCl$_3$ solution of **1** or **2** (0.2 mM) was placed on carbon-coated grids (400 mesh) or mica substrates, and dried in vacuo, and then underwent TEM and AFM observations. The characteristic structure could not be observed in **1**, but **2** showed spherical aggregates with a diameter range of 20–100 nm. Moreover, spherical aggregates were observed in a sample prepared from a diluted solution of **2** (0.01 mM), suggesting that the observed aggregates were formed in the solution. Therefore, the supramolecular polymers made of imidazole-substituted ZnPc **2** organize into larger nanoaggregates in solution.

In summary, we have synthesized and characterized the novel asymmetric ZnPc **2**, in which the imidazole unit is attached to a ZnPc ring at the β position. The absorption and fluorescence analyses in solution suggest an intermolecular connection of **2** through metal–ligand interactions. The assembled supramolecular polymers organized into spherical nanoaggregates as observed by TEM and AFM. We believe that the formation of these novel self-coordinated nanoaggregates provides a new approach for creating functional components to fabricate organic electronic or photonic devices. We are currently investigating the carrier transportation properties of the self-coordinated phthalocyanine nanoaggregates.

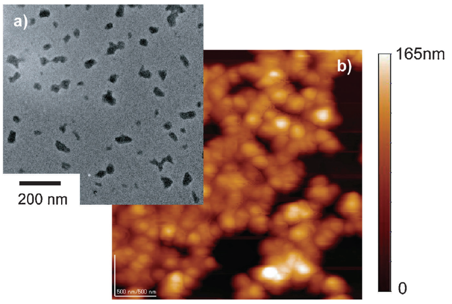


Figure 2. a) TEM and b) AFM (5 × 5 µm) images of **2** aggregates.

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