Metallophthalocyanines

Highly Fluorescent Self-Coordinated Phthalocyanine Dimers**

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Phthalocyanines have been studied for many possible applications because of their excellent optical and electronic properties as well as their chemical, thermal, and light stability.[1] Their expanded π orbitals create the large oscillator strength in the Q band (S_1) region and result in high quantum yields of fluorescence. Pigments, dyes, nonlinear optics,[2] and optical data storage devices are important applications for phthalocyanines. Phthalocyanines are also ideal for applications in electronic conduction[3] as a result of the extra stabilization of electrons/holes in their large π-electronic frameworks.

In the related field of porphyrin chemistry, Kobuke et al. previously reported a methodology for supramolecular organization. For imidazolyl-substituted porphyrins, complementary coordination of the imidazolyl group from one porphyrin molecule to the central Zn^{II} ion in a second porphyrin molecule causes a “slipped cofacial dimer”, with an extremely large stability constant of $10^{11}\,\text{M}^{-1}$. This organization has served as a basic building block of linear and macrocyclic porphyrin arrays, which have increased the utilities of porphyrins for photosynthesis and functional dyes.[4]

The organization of phthalocyanines into controlled structures has been the target of extensive investigations. Besides π–π interactions in solution,[5] in thin films,[6] and in the solid state,[7] metal–ligand,[8] hydrogen-bonding,[9] and donor–acceptor interactions[10] have been reported for the phthalocyanines. It is well-known that J-aggregates of organic dyes are fluorescent[11] whereas H-aggregates are not.[12] Therefore, head-to-tail dimers and J-aggregates are highly desirable to maximize their optical properties. However, except for a few fluorescent phthalocyanines[13,14] only face-to-face dimers and H-aggregates have been observed. Herein, we report highly fluorescent phthalocyanine dimers that result from complementary coordination of imidazolyl groups to zinc and magnesium ions.

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Zinc(II) hexa-*n*-butoxyimidazolylphthalocyanine (**1**) was prepared from the condensation of 6-cyanodiiminoisoindoline with 5 equivalents of 6,7-dibutoxydiiminoisoindoline in the presence of $Zn(OAc)_2$, followed by treatment with *N*-methylethylenediamine to convert the cyano groups into imidazolinyl substituents (29 % yield based on 6-cyanodiiminoisoindoline). Oxidation of the imidazolinyl derivative with 5 % Pt/C in boiling diphenyl ether afforded **1** in 95 % yield (see Supporting Information). The MALDI-TOF mass spectrum of purified **1** revealed a peak for the molecular ion at $m/z = 1091.6$ $[M+H]^+$ as well as a peak for the dimer $[\mathbf{1}]_2$ at $m/z = 2182.0$ $[M+H]^+$ in a ratio of 6:5. Similarly, zinc(II) and magnesium(II) tri-*tert*-butylimidazolylphthalocyanines **2** and **3** were synthesized from zinc(II) and magnesium(II) tri-*tert*-butylcyanophthalocyanines, respectively.

The self-association behavior of **1**–**3** was first examined with UV/Vis spectroscopy by performing titrations in toluene. Phthalocyanine **1** (1.07×10^{-6} M) showed split Q bands at 670 and 700 nm (Figure 1 a, solid line). If we assume that dimer $[\mathbf{1}]_2$ forms (Scheme 1),[15] the split Q bands are best interpreted in terms of exciton interactions of Q_x and Q_y transition dipoles to give red-shifted Q_x and blue-shifted Q_y bands (Figure 1 c).[16] These Q bands converged into a single peak through isosbestic points at 624, 650, and 693 nm upon addition of *N*-methylimidazole (Im; Figure 1 b), and the spectra reached a stationary state after adding 1.44×10^{-2} M Im. The final converged spectrum (Figure 1 a, dashed line) resembles that of zinc(II) octa-*n*-butoxyphthalocyanine (**4**) in toluene with axial coordination of Im.

On the basis of the association constants determined for **4** with Im ($K_{\mathbf{4}\text{-Im}} = 2.8 \times 10^5\,\text{M}^{-1}$) from another titration experiment (data not shown), the constant for self-association of **1** in toluene was evaluated as $K_{\mathbf{1}\text{-}\mathbf{1}} = 1.1 \times 10^{12}\,\text{M}^{-1}$. The extremely large association constant is thought to originate from the

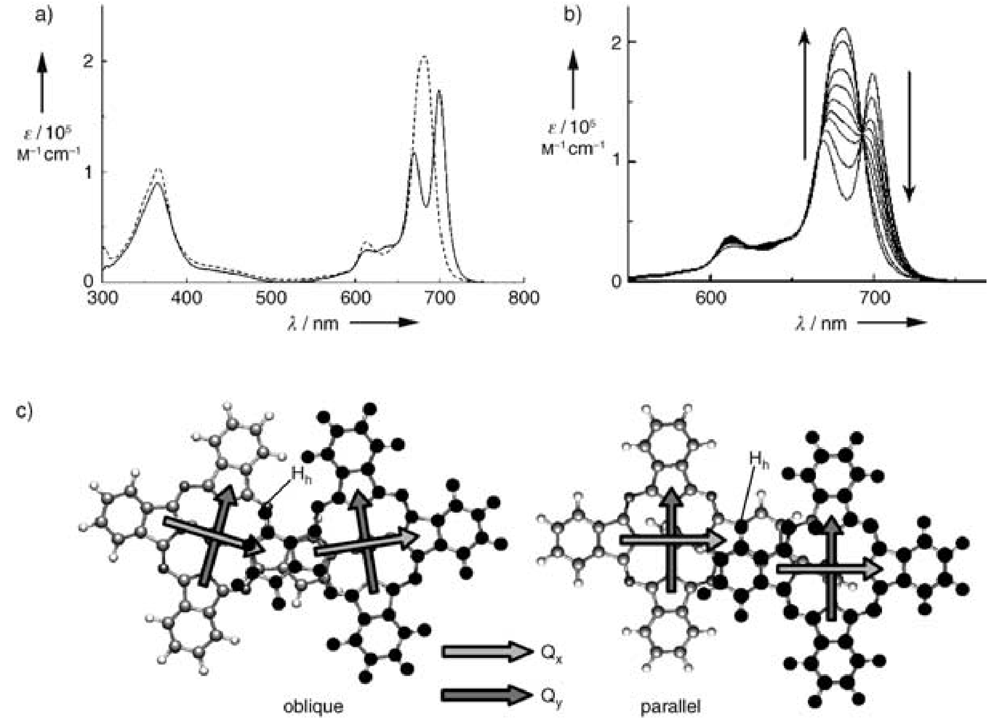
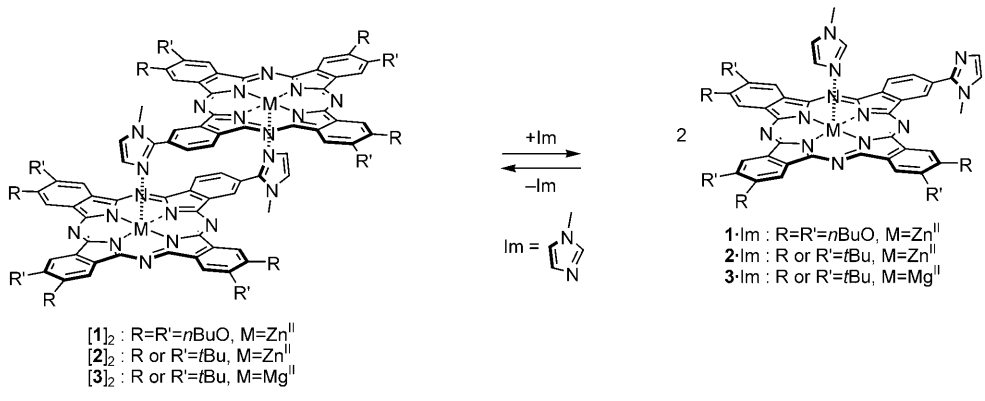


Figure 1. a) UV/Vis spectra of dimer $[\mathbf{1}]_2$ (——) and dissociated monomer **1**·Im (-----) in toluene. b) Changes in the spectra of $[\mathbf{1}]_2$ upon addition of Im (0.00, 0.32×10^{-3}, 0.73×10^{-3}, 1.04×10^{-3}, 1.44×10^{-3}, 2.01×10^{-3}, 2.93×10^{-3}, 4.45×10^{-3}, and 1.44×10^{-2} M). c) Oblique and parallel geometric isomers of $[\mathbf{1}]_2$, and the directions of the transition dipoles. Hydrogen atom H_h is highlighted (see Figure 2).



Scheme 1. Dimer⇌monomer equilibrium of metalloimidazolylphthalocyanines **1**–**3**.

complementary nature of the coordination. Dilution of [**1**]$_2$ down to 1.03×10^{-9} M did not lead to any spectral changes, which is in accord with the high association constant. As the UV/Vis spectra followed Beer's law, at least, up to 2×10^{-4} M,[17] further aggregation of [**1**]$_2$ caused by commonly observable π–π stacking is considerably suppressed relative to zinc tetra-*tert*-butylphthalocyanine (dimerization constant in toluene, $K = 2.5\times10^{4}\,\text{M}^{-1}$).[18]

The formation of stable dimers was also observed in other noncoordinating solvents such as $CHCl_3$ and CH_2Cl_2. Furthermore, **2** and **3** also showed similar split Q bands at 671 and 700 nm for **2** and at 672 and 701 nm for **3**, and their self-association constants in toluene were $K_{\mathbf{2}\text{-}\mathbf{2}} = 1.7\times10^{11}$ and $K_{\mathbf{3}\text{-}\mathbf{3}} = 1.4\times10^{11}\,\text{M}^{-1}$. These results indicate that the Zn and Mg imidazolylphthalocyanine motifs lead to stable dimeric complexes of defined structure, regardless of the nature of the peripheral substituents.

A detailed structural analysis was carried out by NMR spectroscopy using various techniques. As the imidazolyl substituent does not lie along the symmetry axis defined by the pyrrolic N⋯N atoms, two isomeric dimers should emerge upon coordination: one parallel, with the two metallophthalocyanine units aligned but slip-stacked; and the other oblique, with the imidazolyl group of one unit aligned with the pyrrolic symmetry axis of the other (see Figure 1 c). The presence of two dimeric structures was clearly displayed in the ^{1}H NMR (Figure 2) and heteronuclear multiple quantum coherence (HMQC) spectra. The hydrogen atom H_k, which lies closest to the plane of the second phthalocyanine unit upon coordination, appeared characteristically as two highly shielded peaks at $\delta = 2.91$ and 2.83 ppm. The second closest hydrogen atom H_j and imidazolyl-*N*-methyl H_i atoms were observed as moderately shielded pairs of peaks at $\delta = 5.57$ and 5.47 ppm and at $\delta = 2.55$ and 2.39 ppm, respectively. When trifluoroacetic acid (TFA) was gradually added to the dimer, the two peaks for H_k at $\delta = 2.91$ and 2.83 ppm shifted downfield and converged at $\delta = 7.71$ ppm. Similarly, the peaks for the other imidazolyl protons, H_i and H_j, also shifted downfield and converged as indicated by arrows in Figure 2 b. These results reveal that the coordinated dimers dissociates into the corresponding monomer upon addition of TFA and that the twin peaks originate from two isomeric dimers upon coordination.

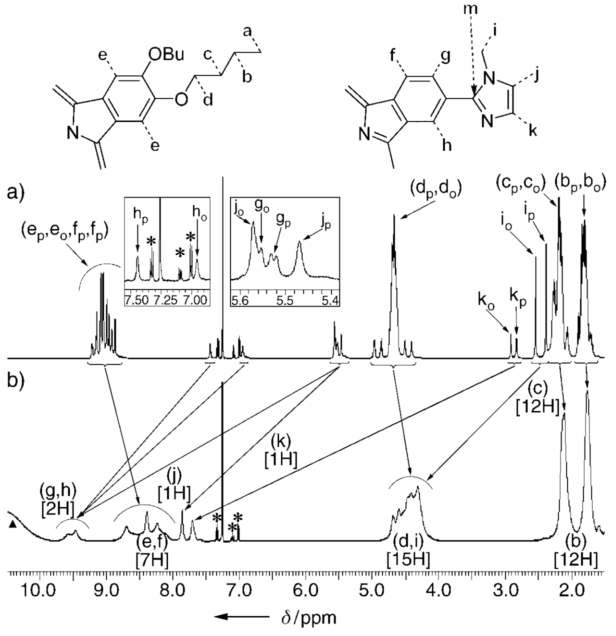


Figure 2. ^{1}H NMR spectra of a) dimer [**1**]$_2$ (20 mM) in $CDCl_3$ at room temperature and b) monomer **1**·TFA, from the dissociation of the dimer by the addition of 10% TFA. The subscripts o and p denote oblique and parallel, respectively, and refer to the isomers shown in Figure 1. Symbols * and ▲ indicate the residual peaks of the solvent (diphenyl ether) and TFA, respectively. Relative integration intensities are provided in square parentheses in (b).

Two sets of signals for all the protons were assigned by total correlation and heteronuclear multiple bond coherence NMR spectroscopy (TOCSY and HMBC). Proton H_h was the most sensitive to the isomeric structures and appeared at $\delta =$ 6.96 and 7.44 ppm. The proton H_h in the oblique configuration is located closer to the center of the molecule, and the signal for H_h at $\delta = 6.96$ ppm was assigned to the oblique isomer whereas that at $\delta = 7.44$ ppm was assigned to the parallel isomer. The ratio of parallel to oblique dimers for [**1**]$_2$ was approximately 1:1 from the integration of the areas for various well-separated peaks. All the NMR signals were consistent with the expected J-type phthalocyanine dimers. ^{1}H NMR spectra of dimers **2** and **3** were assigned to similar isomeric dimers.

All of the J-type dimers emit strong fluorescence in toluene. The quantum yield of [**1**]$_2$ ($\Phi_F = 0.45$) is identical to that of the dissociated monomer **1**·Im ($\Phi_F = 0.45$), and the same pattern is observed for the other dimers, with $\Phi_F = 0.26$ for [**2**]$_2$ ($\Phi_F = 0.27$ for **2**·Im) and $\Phi_F = 0.76$ for [**3**]$_2$ ($\Phi_F = 0.76$ for **3**·Im). These results indicate that both the oblique and parallel conformational isomers emit in the same way as the monomeric metallophthalocyanines. In the case of a previously reported noncomplementary coordination dimer,[13b] the fluorescence quantum yield was decreased by a half as a result of its flexible structure. Other supramolecular motifs reported so far have weaker interactions, such that J-type dimerization only occurred under specific conditions of concentration, composition of solvent mixture, and temperature.[13] The orientation and spatial position of the two phthalocyanines units were not reported in those cases, but the imidazolylphthalocyanine motif developed here constitutes a unique basis set for supramolecular expression.

Analysis by differential pulse voltammetry of [**1**]$_2$ showed split oxidation waves at 510 and 619 mV (versus Ag/AgCl)[19] for oxidation of the phthalocyanine ring that correspond to one- and two-electron oxidations from the dimer, respectively. The first oxidation potential was almost identical to that of the dissociated monomer **1**·Im, and the second wave appeared at a higher potential. This pattern suggests delocalization of the cation radical over the two π–π interacting phthalocyanine units. Such so-called charge–resonance interaction[20] is effective in lowering the charge density of the cation generated on the phthalocyanine rings and decreases the solvent reorganization energy and is therefore beneficial for efficient charge separation.[4b]

In conclusion, we have demonstrated a complementary phthalocyanine dimer. This report is the first example of a noncovalent J-type dimer of fluorescent phthalocyanines with well-defined structural analysis. This supramolecular dimer unit will be useful in applications that require efficient excitation-energy transfer, charge separation, and hole-transfer reactions, as was shown previously with a porphyrin dimer.[4] The present methodology which employs a slipped-cofacial dimer of imidazolyl-appended phthalocyanine is expected to produce advanced materials with excellent fluorescence properties combined with stabilities toward various external sources.

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