Supramolecular Chemistry

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A Discrete Supramolecular Conglomerate Composed of Two Saddle-Distorted Zinc(II)-Phthalocyanine Complexes and a Doubly Protonated Porphyrin with Saddle Distortion Undergoing Efficient Photoinduced Electron Transfer**

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Porphyrins (Por) and phthalocyanines (Pc) exhibit light-harvesting efficiency for producing charge-separated states as models of the reaction center in photosynthetic bacteria[1,2] and photovoltaic cells for energy conversion.[3,4] The use of supramolecular assemblies to model the functionality of the reaction center is an attractive and fruitful strategy to develop photofunctional materials and devices.[5]

Porphyrins exhibit strong Soret bands around 400 to 450 nm, whereas phthalocyanines show strong Q bands around 700 to 800 nm. Thus, the combination of those two π systems can cover nearly the whole range of the visible region and can be a useful strategy for development of photofunctional materials for efficient light-energy conversion. Attempts have so far been made to synthesize covalently linked Por–Pc heterodyad molecules[6] and construct Por–Pc heterosupramolecules.[7] Recently, ZnPor and ZnPc have been reported to form two-dimensional arrays on gold surfaces,[8] and the formation of a cofacial ZnPor–ZnPc coordination tetrad has also been reported.[9] However, a crystal structure determination of a discrete supramolecular assembly composed of both Por and Pc has yet to be reported. In addition, since the Q-band absorption of Pc usually overlaps the wavelength of fluorescence of Por, energy transfer is favored over electron transfer in most heterodyads.[10]

We have developed supramolecular assemblies based on a saddle-distorted nonplanar porphyrin, dodecaphenylporphyrin (H_2DPP), and its metal complexes.[11–13] The saddle distortion facilitates protonation of pyrrole nitrogen atoms to allow access to a stable diprotonated porphyrin, which can act as an electron acceptor.[11b] In addition, the saddle distortion affords higher Lewis acidity at the metal center to maintain axial coordination of ligands, as a result of poor overlap of the pyrrole nitrogen lone pair orbitals with d orbitals of the metal center.[12] In contrast, the Zn^{II} complex of the saddle-distorted phthalocyanine 1,4,8,11,15,18,22,25-octaphenylphthalocyanine (H_2OPPc) exhibits a lower oxidation potential relative to the corresponding porphyrin complex.[14]

To construct supramolecular conglomerates composed of both porphyrin and phthalocyanine in a well-defined manner, we have taken advantage of saddle distortion of both components. Herein, we report formation of a discrete supramolecular assembly composed of H_4DPP^{2+} and [Zn(OPPc)] connected by 4-pyridinecarboxylate (4-$PyCOO^-$) with coordination and hydrogen bonding (Figure 1).

The supramolecular conglomerate [(H_4DPP){Zn(OPPc)(κ^1-*N*-4-PyCOO)}$_2$] (**1**) was synthesized by reaction of [H_4DPP](4-PyCOO)$_2$ (**2**) and Zn(OPPc) (**3**) in toluene. We crystallized and isolated **1** in pure form by vapor diffusion of hexanes into solution of the mixture in toluene. X-ray crystallography of **1** unambiguously established its structure (Figure 2 a).[15]

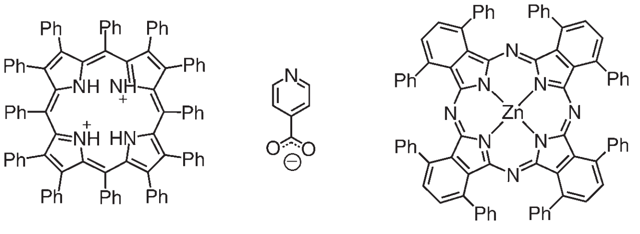
H_4DPP^{2+} 4-$PyCOO^-$ ZnOPPc

Figure 1. Components of a supramolecular assembly **1**.

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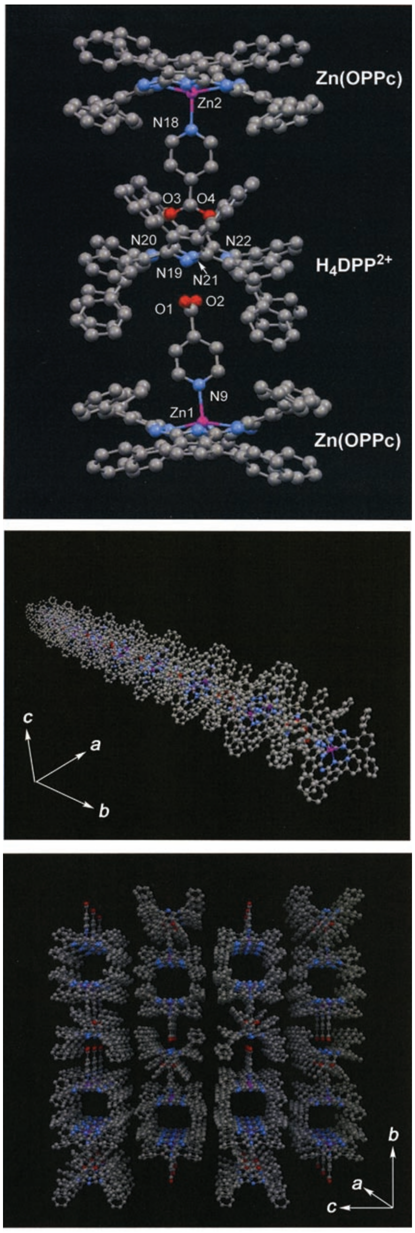

Figure 2. a) Crystal structure of **1**. Dark gray carbon, blue nitrogen, red oxygen, pink zinc. Hydrogen atoms are omitted for clarity. b) One-dimensional nanowire structure of **1** in the crystal directed to the crystallographic *b* axis; c) Crystal packing of **1**. Solvent molecules of crystallization are omitted for clarity.

The conglomerate contains one H_4DPP^{2+} ring and two [Zn(OPPc)] complexes linked by two 4-$PyCOO^-$ ions. The bridging 4-$PyCOO^-$ ion coordinates to the Zn^{II} center of [Zn(OPPc)] through the pyridine nitrogen atom, and its carboxylate group forms two-point intermolecular hydrogen bonding with two pyrrole protons of the diprotonated H_4DPP^{2+} unit.

The bond lengths Zn1–N9 and Zn2–N18 were determined to be 2.117(3) Å and 2.140(3) Å, respectively, which were comparable to that observed in [Zn(OPPc)(py)] (2.143(3) Å).[14] The dihedral angles between the carboxylate plane and the pyridine plane in 4-$PyCOO^-$ were 3.8(2)° for the ring containing N18 and 83.9(2)° for that containing N9. The interatomic distances O1···N19, O2···N21, O3···N20, and O4···N22 were 2.724(15), 2.631(9), 2.714(8), and 2.725(7) Å, respectively. These distances are suggestive of the intermolecular hydrogen bonding among the H_4DPP^{2+} unit and two 4-$PyCOO^-$ units. The Zn^{II} ions in the [Zn(OPPc)] units are located toward the pyridine ligands 0.438(2) Å (Zn1) and 0.462(3) Å (Zn2) above the least-square planes composed of the 24 atoms of each OPPc ligands.

The crystal packing of **1** exhibited a one-dimensional nanowire structure into the crystallographic *b* axis (Figure 2b) by intermolecular π–π interactions of peripheral phenyl groups of the OPPc ligand. The nanowires are extended into the direction of the crystallographic *ac* plane (Figure 2c) also with intermolecular π–π interactions.

In the absorption spectrum of **1** in benzonitrile (PhCN), absorption maxima were observed at 503 nm ($\varepsilon = 2.0 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$) for the porphyrin moiety and 773 nm ($\varepsilon = 2.1 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$) for overlapping Q bands of both the Por and the Pc moieties (see Figure S1 in the Supporting Information). These absorption maxima were intact in the solid state (Figure S2, Supporting Information). The ^1H NMR spectrum of **1** in $CDCl_3$ was different from those of **2** and **3** in that line-broadening, probably due to restricted movements, was observed. To confirm the existence of the supramolecular assembly **1** in solution, we conducted ^1H diffusion ordered spectroscopy (^1H DOSY) experiments in $CDCl_3$ for **1**–**3** to determine their diffusion constants to estimate exclude volumes (Figures S3–S5, Supporting Information). The diffusion constants for **1**–**3** were determined to be $(3.86 \pm 0.04) \times 10^{-10}$, $(5.28 \pm 0.06) \times 10^{-10}$, and $(5.98 \pm 0.04) \times 10^{-10}\,\text{m}^2\,\text{s}^{-1}$, respectively. Consequently, the molecular radii of **1**–**3** can be estimated to be 10.5, 7.70, and 6.80 Å, respectively. On the basis of these data, the exclude volumes (molecular volumes) of **1**–**3** were estimated to be 4849, 1912, and 1317 $Å^3$, respectively. The molecular volume of **1** obtained by ^1H DOSY showed good agreement with that calculated on the basis of its crystal structure ($14 \times 14 \times 26 = 5096\,Å^3$). The results strongly suggest that the supramolecular structure can be maintained even in solution.

Redox potentials of **1** were determined by cyclic voltammetry (CV), differential pulse voltammetry (DPV), and second harmonic alternating current voltammetry (SHACV) in PhCN at room temperature. An irreversible redox wave assigned to the two-electron reduction of H_4DPP^{2+} moiety with fast disproportionation was observed at −0.57 V (vs. SCE) (Figure S6, Supporting Information). One reversible and one irreversible redox wave were observed at +0.26 and +0.56 V for the stepwise oxidations of the {Zn(OPPc)} moieties. The first oxidation potential was nearly the same as that of **3**. Thus, we can determine the potential of the electron-transfer state of **1** as +0.83 eV.

The fluorescence spectrum of **2** in PhCN exhibited an emission maximum at 750 nm with 1.7% quantum yield for photoexcitation at 515 nm. The energy of the singlet excited state of **2** was determined from the absorption (743 nm; see Figure S1 in the Supporting Information) and emission (750 nm) maxima to be 1.66 eV.[16] The phosphorescence spectrum of **2** in 2-methyltetrahydrofuran (Me-THF) at 77 K showed an emission maximum at 857 nm with photoexcitation at 750 nm, allowing us to determine the energy of the triplet excited state of **2** to be 1.45 eV. The singlet and triplet energy levels of **3** were determined to be 1.52 eV[17] and 1.43 eV from the absorption maximum (781 nm) together with the fluorescence maximum (850 nm) in PhCN at room temperature and the phosphorescence of **3** (868 nm) in Me-THF at 77 K, respectively. The fluorescence of the H_4DPP^{2+} unit in **1** was completely quenched, but no fluorescence derived from the {Zn(OPPc)} unit was observed.

Femtosecond laser flash photolysis of **1** (4.0 µM) in PhCN was performed by photoexcitation at 410 nm, where both H_4DPP^{2+} and {Zn(OPPc)} are excited. We observed the formation of the singlet excited state of {Zn(OPPc)} and H_4DPP^{2+} at 4 ps after the laser pulse by the rise of the absorption maxima at 547 and 900 nm (black line in Figure 3 a).[18] At 150 ps, new absorption bands were observed at 547 and 1030 nm (red line in Figure 3 a). The absorption at 547 nm was assigned to $H_4DPP^{+\bullet}$ and that at 1030 nm was ascribed to the absorption of {Zn(OPPc$^{+\bullet}$)} with a slight overlap of $H_4DPP^{+\bullet}$, by comparison with the reference spectra of the one-electron-reduced form of **2** (($H_4DPP^{+\bullet}$)(4-PyCOO)$_2$) and the one-electron-oxidized form of **3** ([Zn(OPPc$^{+\bullet}$)]) as shown in Figure 3 b.[19] The rise of the absorption at 1030 nm gave an apparent first-order rate constant of $1.6\times10^{10}\,s^{-1}$ (Figure 3 c). This rate constant lends credence to the intrasupramolecular electron transfer from the {Zn(OPPc)} moiety to H_4DPP^{2+} to form the electron-transfer state of **1**, [{Zn(OPPc$^{+\bullet}$)(4-PyCOO)}($H_4DPP^{+\bullet}$){Zn(OPPc)(4-PyCOO)}] (Pc$^{+\bullet}$-Por$^{+\bullet}$-Pc, **1-ET**). Prior to this electron transfer, we could observe very fast decay of the absorption at a rate of $4.2\times10^{12}\,s^{-1}$ (2.4 ps). We assigned this decay to energy transfer from photoexcited $^1(H_4DPP^{2+})^*$ to {Zn(OPPc)} to give ^{1}{Zn(OPPc)}* (see the inset of Figure 3 c). The rate constant of the intrasupramolecular energy transfer was comparable to that of intramolecular energy transfer observed for a covalently linked ZnPor–ZnPc dyad.[10] After 150 ps, the absorption at 1030 nm decays to afford another first-order rate constant to be $1.5\times10^{9}\,s^{-1}$ (Figure 3 d). We assigned this process to intrasupramolecular back electron transfer from {Zn(OPPc$^{+\bullet}$)} to $H_4DPP^{+\bullet}$ to recover the ground state of **1**. Therefore, the lifetime of the electron-transfer state (**1-ET**) was determined to be 667 ps, which was much longer than that (85 ps) observed in a covalently linked ZnPc–SnPor dyad system by Odobel and co-workers.[6c]

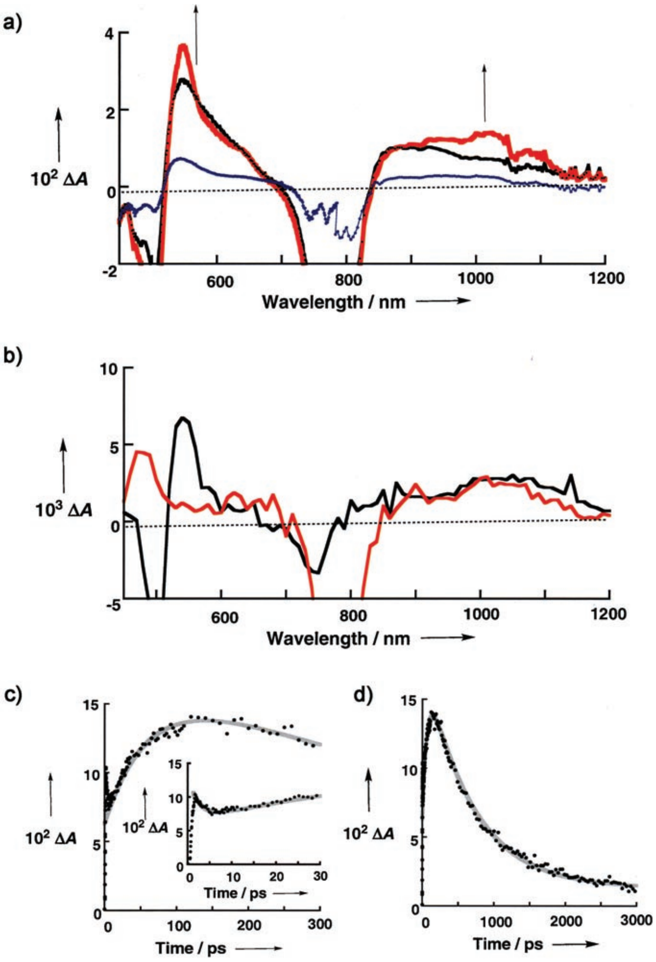

Figure 3. a) Femtosecond laser flash photolysis (excitation at 410 nm) of **1** (4.0 µM) in PhCN at room temperature: transient absorption spectra at 4 ps (black), 150 ps (red), and 3000 ps (blue): b) Reference spectra of $H_4DPP^{+\bullet}$ (black) and [Zn(OPPc$^{+\bullet}$)] (red) obtained by nanosecond laser flash photolysis of **2** (12 µM) in the presence of excess ferrocene (1 mM) and **3** (15 µM) in the presence of 2,6-dichloro-*p*-benzoquinone (0.2 mM) in PhCN at 80 µs after photoexcitation at 515 and 426 nm, respectively. c) Time course of absorption at 1030 nm (0–300 ps) for **1** (see (a)). Inset: Initial time course (0–30 ps). d) Time course of absorption at 1030 nm (0–3000 ps) for **1** (see (a)).

The energy diagram of the PET processes in **1** is summarized in Figure 4. Photoexcitation at 410 nm affords the singlet excited states of both H_4DPP^{2+} and {Zn(OPPc)} units ($^1(H_4DPP^{2+})^*$ and ^{1}{Zn(OPPc)}*) in **1**. The singlet excited state of the Por unit (1.66 eV) undergoes fast intrasupramolecular energy transfer to give that of ZnPc moiety (1.52 eV). This is followed by intrasupramolecular electron transfer from ^{1}{Zn(OPPc)}* to H_4DPP^{2+} to give the electron-transfer state **1-ET** at the energy level of 0.83 eV in 63 ps. The ET state has the lifetime of 667 ps, before going back to the ground state.

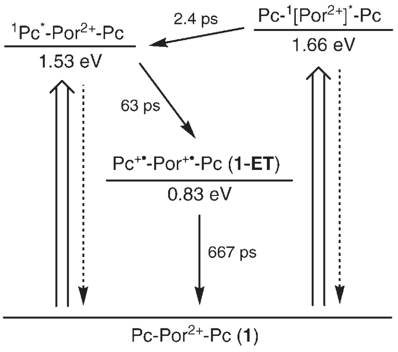

Figure 4. Energy diagram of photodynamics of **1** in PhCN. Por^{2+} and Pc represent the H_4DPP^{2+} and [Zn(OPPc)] units, respectively.

In summary, we have synthesized and determined the first structure of a discrete supramolecular assembly composed of both Por and Pc compounds. The saddle distortion of Por and

Pc cooperatively stabilizes the supramolecular assembly by virtue of the facile protonation of the Por to form strong hydrogen bonding and also by the enhanced Lewis acidity of the Zn center in the Pc to strengthen the axial coordination bond. Photoexcitation of the assembly clearly gives rise to the generation of an unprecedented intrasupramolecular electron-transfer state involving cation radicals of both one-electron-reduced diprotonated Por and one-electron-oxidized ZnPc via the singlet excited states of both the Por and the ZnPc moieties. This is the first observation of an electron-transfer state of a supramolecular conglomerate including both Por and Pc components. Our strategy described herein can be applied to construction of novel supramolecular assemblies consisting of porphyrins and phthalocyanines to develop photofunctional materials that can utilize a wide spectrum of visible light effectively.

Experimental Section

Synthesis of **2**: 4-Pyridinecarboxylic acid (15 mg, 0.12 mmol) in CH_3OH (5 mL) was added to a solution of H_2DPP (50 mg, 0.041 mmol) in CH_2Cl_2 (100 mL). The solvents were removed, and the crude product was dissolved in CH_2Cl_2 and then filtered. The solvent was again removed, and the residue was recrystallized from $CHCl_3$/hexanes to give green crystals of **2** (47 mg, 78 % yield). Elemental analysis (%) calcd for $C_{104}H_{72}N_6O_4\cdot 1.5(H_2O)$: C 83.46, H 5.05, N 5.61; found: C 83.28, H 5.04, N 5.54. Absorption maxima (λ_{max}, nm (ε, $M^{-1}cm^{-1}$)); 503 (2.0×10^5) and 743 (2.2×10^4).

Synthesis of **1**: A solution of **2** (15 mg, 0.010 mmol) and [Zn(OPPc)] (22 mg, 0.020 mmol) in toluene (30 mL) was heated at 90 °C for 4 h. The resultant solution was exposed to vapor of hexanes to afford lustrous green crystals of **1**. Elemental analysis (%) calcd for $C_{264}H_{172}N_{22}O_6Zn_2$ ($[H_4DPP\cdot\{Zn(OPPc)(4\text{-}PyCOO)\}_2]\cdot 2(H_2O)$): C 81.74, H 4.47, N 7.94; found: C 81.60, H 4.68, N 7.73. A single crystal suitable for X-ray crystallography was obtained as mentioned above.

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[15] Crystallographic data for $\mathbf{1}\cdot 7(C_7H_8)\cdot 2(C_6H_{14})$: triclinic, $P\bar{1}$, (No. 2), $a = 15.4518(4)$, $b = 27.0054(7)$, $c = 30.5422(8)$ Å, $\alpha = 90.0526(10)$, $\beta = 90.0100(10)$, $\gamma = 90.7772(10)°$, $V = 12743.5(6)$ Å^3, $Z = 2$, $T = -180$ °C, $2\theta(\text{max}) = 108.5°$ (Cu Kα radiation), $R1 = 0.1093$ ($I > 2\sigma(I)$), $Rw = 0.3299$, $GOF = 1.117$. The compound was presumed to be crystallized in a merohedrally twinned form with two domains of the space group $P\bar{1}$ (No. 2) and the structure was successfully solved with twin fraction = 0.441. The H_4DPP^{2+} ion could be resolved with the two moieties, which were heavily superimposed, so that the porphine and phenyl groups were treated as rigid groups. To improve the ratio of n(ref)/n(para), all the phenyl groups of [Zn(OPPc)] and toluene molecules were refined as rigid groups. CCDC 688606 contains the supplementary crystallographic data

for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] The fluorescence lifetime of **2** was determined to be 1.5 ns.

[17] The fluorescence lifetime of **3** was determined to be 1.2 ns.

[18] The absorption maxima of singlet excited state of **2** were seen at 590 and 960 nm and those of singlet excited state of **3** were observed at 510 and 900 nm upon photoexcitation at 410 nm in PhCN (Figure S7 in the Supporting Information).

[19] Photoexcitation at 515 nm of **2** (12 μM) in the presence of excess ferrocene (1 mM) as an electron donor led to an absorbance peak at 540 nm and broad, weak peak at 1050 nm. Those absorption bands were assigned to $H_4DPP^{+\cdot}$. The transient absorption of $[Zn(OPPc^{+\cdot})]$ was obtained by photoexcitation of **3** (15 μM) at 426 nm in the presence of 2,6-dichloro-*p*-benzoquinone (0.2 mM) as an electron acceptor: an absorption band at 1030 nm was assigned to $[Zn(OPPc^{+\cdot})]$, which is consistent with that observed for chemical oxidation with $[Ru(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) in PhCN (see Figure S8 in the Supporting Information).