

Saddle Distortion of a Sterically Unhindered Porphyrin Ring in a Copper Porphyrin with Electron-Donating Substituents

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Two crystalline porphyrins, CuT(4'-OMePh)P (**1**) and H₂T(4'-OMePh)P (**2**) (T(4'-OMePh)P²⁻ = 5, 10, 15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphyrin dianion), have been synthesized and characterized by a single-crystal X-ray diffraction. Compound **1** is crystallized in the orthorhombic system with a space group of *Pna*2₁, but compound **2** is crystallized in the monoclinic system with a space group of *P2*/*c*. Compound **1** is characterized as an isolated structure with a saddle-distorted nonplanar porphyrin macrocycle and an embedded cupric ion coordinating to four pyrrole nitrogen atoms. Nonmetalated compound **2** also displays an isolated structure, but the macrocycle of porphyrin is close to a perfect plane. The molecules in **2** are interconnected through five C–H···π hydrogen bonding interactions to yield a 3-D supramolecular network. However, the molecules in **1** are interlinked via five C–H···π interactions and two C–H···O hydrogen bonding interactions to yield a more complex 3-D supramolecular motif. The two more C–H···O hydrogen bonding interactions are attributed to the distortion of porphyrin macrocycle, resulting from the metalation. The metalation brought changes not only in the crystal structures and supramolecular motifs but also in the properties. The photophysical and redox properties of **1** and **2** in solution have also been studied by steady-state absorption and fluorescence, cyclic voltammetry, fluorescence lifetime and nanosecond transient absorption techniques.

Introduction

Because of their resemblance to the natural photosynthetic chlorophyll pigment, easy synthetic manipulations, strong optical absorption, and emission, long lifetime of the singlet and triplet states, and favorable redox,¹ porphyrins provide

an extremely versatile synthetic base for a variety of materials for applications in many disciplines of chemistry and physics, such as solar cells and opto-electronics,^{2–6} catalysis,⁷ sensors,⁸ and molecular sieves.⁹ The role of porphyrins in photosynthetic mechanisms indicates a good capability to mediate visible photon–electron conversion processes.^{10–16}

The electronic properties of the porphyrin π-electron system can readily be altered by the peripheral substituents on the porphyrin ring and insertion of metal atoms into the center of the porphyrin ring.¹ The coordination of a metal ion at the center of porphyrin macrocycle, as well as the

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decoration of the periphery of a porphyrin ring by specific organic groups, affords abundant programming elements for the design of porphyrin supramolecular assemblies. On the basis of these unique properties and applications, much attention has been paid to porphyrin supramolecular assemblies formed via noncovalent interactions like hydrogen

bonding and π - π stacking interactions, which can be used in the industrial applications.^{12,14,15,17-20}

An increase in the number of substituents results in steric repulsive interactions among the peripheral substituents, leading to the nonplanarity of the macrocycle.²¹⁻²⁴ Unlike planar porphyrins, nonplanarity features disposition of the core nitrogen atoms above and below the faces of the macrocycle, resulting in an increase in the basicity of the macrocycle and also in the Lewis acidity of the metal center.^{25,26}

In contrast to nonplanar metalloporphyrins which are believed to require steric repulsive interactions, copper corroles are reported to be inherently saddled, even in the absence of sterically hindered substituents.²⁷ An orbital interaction between copper and the electron rich corrole

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was suggested to provide the actual driving force for a significant nonplanar distortion.²⁷ We report herein that a copper porphyrin is also saddled in the absence of sterically hindered substituents by introducing electron-donating substituents. It should be noted that many copper porphyrins even in the presence of sterically hindered substituents are planar.^{28,29} The saddle distortion of the porphyrin ring is clearly shown by the X-ray crystal structure of CuT(4'-OMePh)P (**1**) (T(4'-OMePh)P²⁻ = 5, 10, 15, 20-tetrakis-(4-methoxyphenyl)-21H, 23H-porphyrin dianion) in contrast with the planar structure of the free base porphyrin: H₂T(4'-OMePh)P (**2**). The characterization and photophysical and redox properties of **1** and **2** in solution were examined by matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF-MS), steady-state absorption and emission, electrochemical, and nanosecond transient absorption techniques.

Experimental Section

Measurements. Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL III microanalyzer. The infrared spectra were recorded on a Thermo Nicolet NEXUS 870 FT-IR spectrophotometer over the frequency range 4000–400 cm⁻¹ using the KBr pellet technique. The UV-vis absorption spectra were recorded at room temperature on a computer-controlled Hewlett-Packard 89090A UV-vis spectrometer with the wavelength range of 190–1100 nm. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra were measured on a Kratos Compact MALDI I (Shimadzu).

Fluorescence lifetime measurements were conducted using a Photon Technology International GL-3300 nitrogen laser with a Photon Technology International GL-302 dye laser and a nitrogen laser/pumped dye laser system equipped with a four-channel digital delay/pulse generator (Standard Research System Inc., model DG535) and a motor driver (Photon Technology International, model MD-5020). The excitation wavelength was 421 nm with use of a POPOP chromophore. The phosphorescent and the fluorescent studies were conducted on a Shimadzu RF-530XPC fluorescence spectroscopy instrument under 77 K and room temperature, respectively.

Measurements of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed at 298 K using a BAS 100W electrochemical analyzer in a deaerated solvent containing tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆; 0.10 M) as a supporting electrolyte. A conventional three-electrode cell was used with a carbon working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to the Ag/AgNO₃ (0.01 M). All electrochemical measurements were carried out under an atmospheric pressure of argon.

The solutions containing **1** and **2** were excited by a Panther OPO pumped by Nd:YAG laser (Continuum, SLII-10, 4–6 ns

fwhm) nm with the powers of 1.5 and 3.0 mJ per pulse. The transient absorption measurements were performed using a continuous xenon lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz).

Syntheses³⁰. All reactants of A.R. grade were obtained commercially and used without further purification.

CuT(4'-OMePh)P (1). The title compound was prepared by mixing CuCl₂·2H₂O (0.10 mmol, 17.1 mg), H₂T(4'-OMePh)P (0.10 mmol, 73.5 mg), and 10 mL of ethanol in a 23 mL Teflon-lined stainless steel autoclave and heating the mixture at 453 K for 4 d. After the mixture was cooled slowly to room temperature at 6 K/h, dark red crystals suitable for X-ray analysis were obtained. Yield: 22% (based on copper). Anal. Calcd for C₄₈H₃₆CuN₄O₄: C, 72.39; H, 4.56; N, 7.04. Found: C, 71.88; H, 4.73; N, 6.96. Fourier transform IR (KBr, cm⁻¹): 2995(w), 2929(w), 2831(w), 2360(w), 1608(s), 1536(m), 1500(vs), 1464(m), 1439(m), 1346(vs), 1289(s), 1248(vs), 1171(vs), 1104(m), 1073(w), 1038(s), 1001(vs), 847(m), 800(s), 718(m), 666(m), 636(w). *m/z* (MALDI-TOF-MS in CHCl₃ (matrix CHCA)): 795.14 (C₄₈H₃₆CuN₄O₄ requires 795.21).

H₂T(4'-OMePh)P (2). Compound **2** was prepared by the recrystallization of H₂T(4'-OMePh)P from its CHCl₃ solution. Fourier transform IR (KBr, cm⁻¹): 3319(w), 2999(w), 2932(w), 2830(w), 2361(w), 1604(s), 1526(vs), 1511(vs), 1469(s), 1439(m), 1346(vs), 1289(s), 1248(vs), 1171(vs), 1105(m), 1037(s), 965(s), 841(m), 805(s), 738(m), 702(m), 666(w).

X-ray Crystallographic Studies. The intensity data sets were collected on a Rigaku AFC-8 X-ray diffractometer with graphite monochromated Mo K α radiation (λ = 0.71073 Å) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.^{31,32a} The structures were solved by the direct methods using the Siemens SHELXTL, version 5, package of crystallographic software.^{32b} The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The hydrogen atom positions were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters. The structures were refined using a full-matrix least-squares refinement on F^2 . All atoms except for hydrogen atoms were refined anisotropically.

Results and Discussion

General Characterization. The FT-IR spectra of compound **1** and free base H₂T(4'-OMePh)P **2** display similar characters and the strong bands mainly appear between 700 and 1600 cm⁻¹. The FT-IR spectra of free base H₂T(4'-OMePh)P **2**, there are two bands occurred at ~3319 and ~965 cm⁻¹, resulting from the $\nu_{\text{N-H}}$ and $\delta_{\text{N-H}}$ vibrations of pyrrole rings (see Figure S1 in the Supporting Information). In the FT-IR spectra of compound **1**, however, these two bands disappeared due to the deprotonation and the metalation of the pyrrole rings. The MALDI-TOF-MS spectra of compound **1** in CHCl₃ (matrix CHCA; reflectron mode) exhibit its molecular

(28) Crystal structures of the parent 2,3,5,10,12,13,15,20-octaphenylporphyrin, M(TPP)(Ph)₄ (M = Co(II), Cu(II)) complexes indicated near planarity of the 24-atom core with the root-mean-square deviation value of 0.016(2) Å, whereas porphyrin rings in M(TPP)(Ph)₄·C₆₀ cocrystals revealed significant distortion with the root mean-square value as high as 0.265(2) Å, which is the average deviation of the 24 atoms core from the least squares plane; see: Bhyrappa, P.; Karunanithi, K. *Inorg. Chem.* **2010**, *49*, 8389.

(29) In CuTPP, the copper ion is located at the center of the centrosymmetric and perfectly planar porphyrin ring; see: (a) Byrn, M. P.; Goldberg, C. I.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Tendick, S. K.; Strouse, S. E. *J. Am. Chem. Soc.* **1991**, *113*, 6549. (b) He, H.-S. *Acta Crystallogr.* **2007**, *E63*, m976. (c) However, in another polymorph of CuTPP the porphyrin ring is reported to be non-planar; see: Fleischer, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1353.

(30) (a) Liston, D. J.; Kennedy, B. J.; Murray, K. S.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1561. (b) Ellison, M. K.; Schulz, C. E.; Scheidt, W. R. *Inorg. Chem.* **1999**, *38*, 100. (c) Balch, A. L.; Olmstead, M. M.; Safari, N.; St. Claire, T. N. *Inorg. Chem.* **1994**, *33*, 2815.

(31) (a) *CrystalClear*, version 1.3.5; Rigaku Corporation, 2002. (b) *CrystalStructure*, version 3.6.0; Rigaku Corporation, 2002.

(32) (a) *SAINT Software Reference Manual*; Siemens Energy & Automation, Inc.: Madison, WI, U.S.A., 1994. (b) *SHELXTL Version 5 Reference Manual*; Siemens Energy & Automation, Inc.: Madison, WI, U.S.A., 1994.

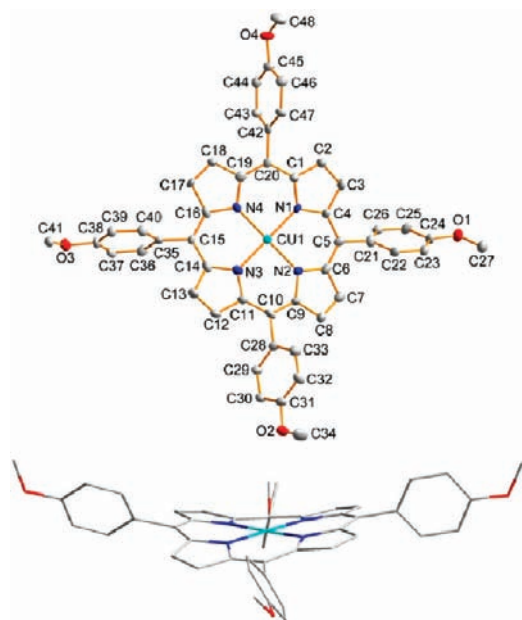


Figure 1. Face-on view (ORTEP drawing with 35% thermal ellipsoids) and edge-on view showing the saddle-distorted conformation (wire representation) of **1**. Hydrogen atoms were omitted for clarity.

peak value of 795.14, which is in good agreement with the corresponding calculated exact mass number of 795.21 (see Figure S2 in the Supporting Information). This implies that compound **1** retains its structure in solution as in the solid state.

Crystal Structures. CuT(4'-OMePh)P (1). The molecular structure of **1** is depicted as an ORTEP drawing in Figure 1. X-ray diffraction analysis reveals that compound **1** consists of neutral CuT(4'-OMePh)P molecules and crystallizes in the orthorhombic system with a space group of *Pna*2₁. All crystallographically independent atoms are in general positions. The Cu²⁺ ion resides at the center of porphyrin macrocycle and has a square geometry without an axial ligation. The bond distances from the Cu²⁺ ion (at the center of a saddle-distorted nonplanar porphyrin macrocycle) to the pyrrole nitrogens are within 1.977(3)–1.984(3) Å in **1**, which is comparable with those found for related species in the Cambridge Structural Database.^{33–36} The porphyrin macrocycle in **1** displays a saddle-distorted conformation and the four pyrrole rings appreciably distort in an alternant fashion either upward or downward with respect to the mean plane of the saddle-like porphyrin core. The displacement of each atom of the macrocyclic core 24-membered ring is from –0.374 to 0.391 Å. The displacement of the four pyrrole N atoms is within ±0.018 Å from their mean N4 plane.

For compound **1**, the dihedral angles between the planes of the four pyrrole rings distorted in the same direction are 20.62° and 22.83°. The dihedral angles between the neighboring pyrrole rings are 11.11°,

14.20°, 18.39°, and 19.43°. With respect to the N4 plane, which may represent the mean plane of the porphyrin core, the twist angles of the aryl rings are 57.13°, 73.85°, 75.64°, and 59.53°. There is no any solvent molecule in the crystal structure and the closest interplanar separation between two Cu-porphyrin planes inside one unit cell is 8.658 Å with a plane dihedral angle of 9.26°. In compound **1**, the abundant C–H···π³⁷ and C–H···O interactions bridge the molecules to construct a 3-D supramolecular network (Figure 2). The summary of the crystallographic data and structure analyses is given in Table 1. The selected bond lengths and bond angles are presented in Table 2.

H₂T(4'-OMePh)P (2). X-ray diffraction analysis reveals that the structure of **2** is comprised of neutral H₂T(4'-OMePh)P molecules, as shown in Figure 3. Compound **2** crystallizes in the space group *P2*/*c* of the monoclinic system with two formula units in a cell. The macrocyclic core 24-membered ring of the porphyrin is coplanar and the displacement of each atom in the equatorial mean plane is within ±0.071 Å. The displacement of the four pyrrole N atoms is 0 Å from their mean N4 plane, suggesting that the four pyrrole N atoms are perfectly coplanar. With respect to the N4 plane, which represents the mean plane of the porphyrin core, the twist angles of the aryl rings are 112.43°, 83.27°, 112.43°, and 83.27°. The closest porphyrin plane distance inside one unit cell is 8.675 Å with a plane dihedral angle of 31.47° that is obviously larger than that of **1**. In **2**, five C–H···π interactions interlink the molecules to yield a 3-D supramolecular motif (Figure 4). As compared with **2**, there are five C–H···π interactions and two C–H···O hydrogen bonding interactions in **1** to allow the formation of a more complex 3-D supramolecular structure. These two more C–H···O hydrogen-bonding interactions in **1** are ascribed to the saddle-distorted nonplanar porphyrin macrocycle, resulting from the metalation. Furthermore, before and after metalation, metalated compound **1** and nonmetalated compound **2** crystallize in different crystal systems with different space groups. Interestingly, all methoxy groups in compound **1** point to the same side of porphyrin macrocycle, while each pair of methoxy groups in compound **2** displays in an alternate mode either upward or downward with respect to the porphyrin core. Thus, the crystal structures and supramolecular motifs of the porphyrin are adjustable by metalation.

Steady-State Absorption and Emission Studies. Generally, metalloporphyrins exhibit two kinds of intensive absorption bands, namely, strong B band (Soret band) at around 400 nm with a molar absorption coefficient ϵ value of $\sim 10^5$ M⁻¹cm⁻¹ and several weaker Q bands in the range of 450–650 nm with the ϵ values being $\sim 10^3$ – 10^4 M⁻¹cm⁻¹. The UV–vis absorption spectra for compound **1** and free base H₂T(4'-OMePh)P in benzonitrile are shown in Figure 5. The Soret absorption band of free base H₂T(4'-OMePh)P (**2**) was observed at 426 nm, while Q-bands are observed at 523, 559, 597, and 655 nm. The Soret absorption band of compound **1** appears at 423 nm, which is blue-shifted by 3 nm as compared with that counterpart

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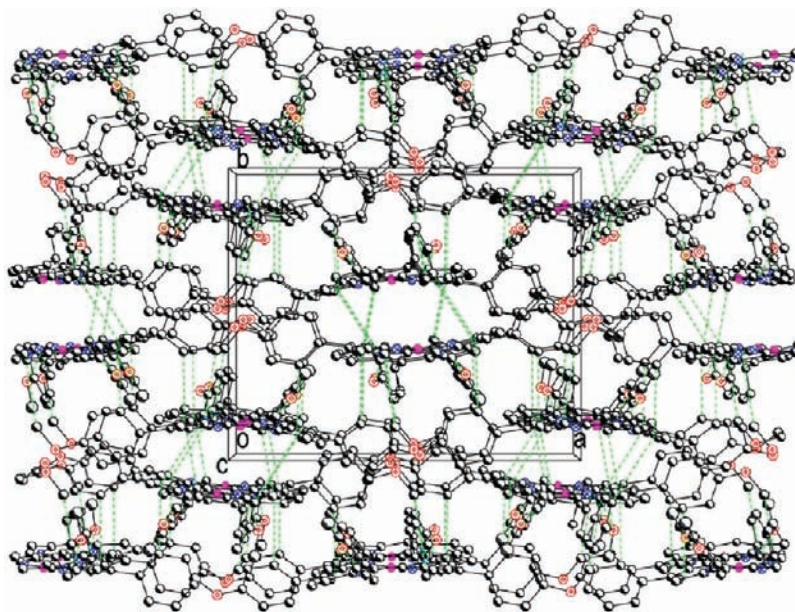


Figure 2. Packing diagram of **1** with the dashed lines representing hydrogen bonding interactions. Geometry of represented hydrogen bonding interactions: C(40)–H(40A)···C_g(1) with $d_{C\dots C_g} = 3.456(3)$ Å and $\angle(\text{DHA}) = 140.65^\circ$; C(44)–H(44A)···C_g(1) with $d_{C\dots C_g} = 3.841(3)$ Å and $\angle(\text{DHA}) = 124.72^\circ$; C(41)–H(41B)···C_g(2) with $d_{C\dots C_g} = 3.672(5)$ Å and $\angle(\text{DHA}) = 108.02^\circ$; C(22)–H(22A)···C_g(3) with $d_{C\dots C_g} = 3.354(3)$ Å and $\angle(\text{DHA}) = 108.31^\circ$; C(29)–H(29A)···C_g(3) with $d_{C\dots C_g} = 3.461(3)$ Å and $\angle(\text{DHA}) = 116.52^\circ$; C(2)–H(2A)···O(2) 3.251(4) Å and $\angle(\text{DHA}) = 156^\circ$; C(12)–H(12A)···O(4) 3.399(4) Å and $\angle(\text{DHA}) = 149^\circ$ [C_g(1), C_g(2), and C_g(3) stands for the centers of gravity of the rings N2(C6–C9), N3(C11–C14) and N4(C16–C19), respectively]. Cu, magenta; O, red; N, blue; C, gray.

Table 1. Crystal Parameters of Compounds **1** and **2**

compound	1	2
formula	C ₄₈ H ₃₆ CuN ₄ O ₄	C ₄₈ H ₃₈ N ₄ O ₄
fw	796.36	734.82
color	dark red	dark red
crystal size/mm ³	0.10 × 0.08 × 0.07	0.30 × 0.22 × 0.15
crystal system	orthorhombic	monoclinic
space group	<i>Pna</i> 2 ₁	<i>P2</i> / <i>c</i>
<i>a</i> (Å)	16.972(4)	9.860(5)
<i>b</i> (Å)	14.247(4)	13.929(2)
<i>c</i> (Å)	15.643(3)	17.350(7)
β (deg)		116.330(2)
<i>V</i> (Å ³)	3783(2)	2136(1)
<i>z</i>	4	2
$2\theta_{\text{max}}$ (deg)	50	50
reflections collected	23641	12585
independent,	5567,4047(0.0950)	3635,1800(0.0321)
observed reflections (<i>R</i> _{int})		
<i>d</i> _{calc} (g/cm ³)	1.398	1.143
μ (mm ⁻¹)	0.631	0.073
<i>T</i> (K)	123.15	123.15
<i>F</i> (000)	1652	772
<i>R</i> ₁ , <i>wR</i> ₂	0.0673,0.1455	0.0726,0.1782
<i>S</i>	1.007	1.006
largest and mean Δ/σ	0.001.0	0,0
$\Delta\rho$ (max, min) (e/Å ³)	0.889, -0.358	0.382, -0.220

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of Compound **1**

Cu(1)–N(1)	1.977(3)	N(1)–Cu(1)–N(3)	178.5(1)
Cu(1)–N(2)	1.984(3)	N(1)–Cu(1)–N(4)	89.7(1)
Cu(1)–N(3)	1.983(3)	N(2)–Cu(1)–N(3)	90.0(1)
Cu(1)–N(4)	1.977(3)	N(2)–Cu(1)–N(4)	179.4(1)
N(1)–Cu(1)–N(2)	90.0(1)	N(3)–Cu(1)–N(4)	90.2(1)

of H₂T(4'-OMePh)P. The Q-bands of **1** are observed at 544 and 583 nm. The difference in the number of Q bands of **2** compared to **1** is ascribed to an increase in the molecular symmetry, resulting from the metalation of H₂T(4'-OMePh)P. The absorption coefficient of the B band for

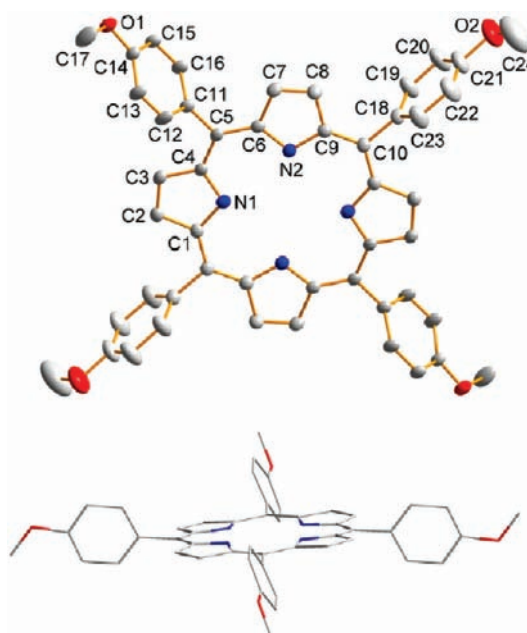


Figure 3. Face-on view (ORTEP drawing with 15% thermal ellipsoids) and edge-on view (wire representation) of H₂T(4'-OMePh)P. Hydrogen atoms were omitted for clarity.

metalloporphyrin **1** is $\sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, which is in good agreement with the conclusion drawn by Gouterman.³⁸

Solid-state porphyrins and their derivatives, in general, cannot display emission bands because of their concentration quenching, but they would usually show bright emission bands occurring around the red region of the spectrum if they were dissolved in solution. The fluorescence spectra

(38) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York: 1978; Vol. 3, Chapter 1 and references therein.

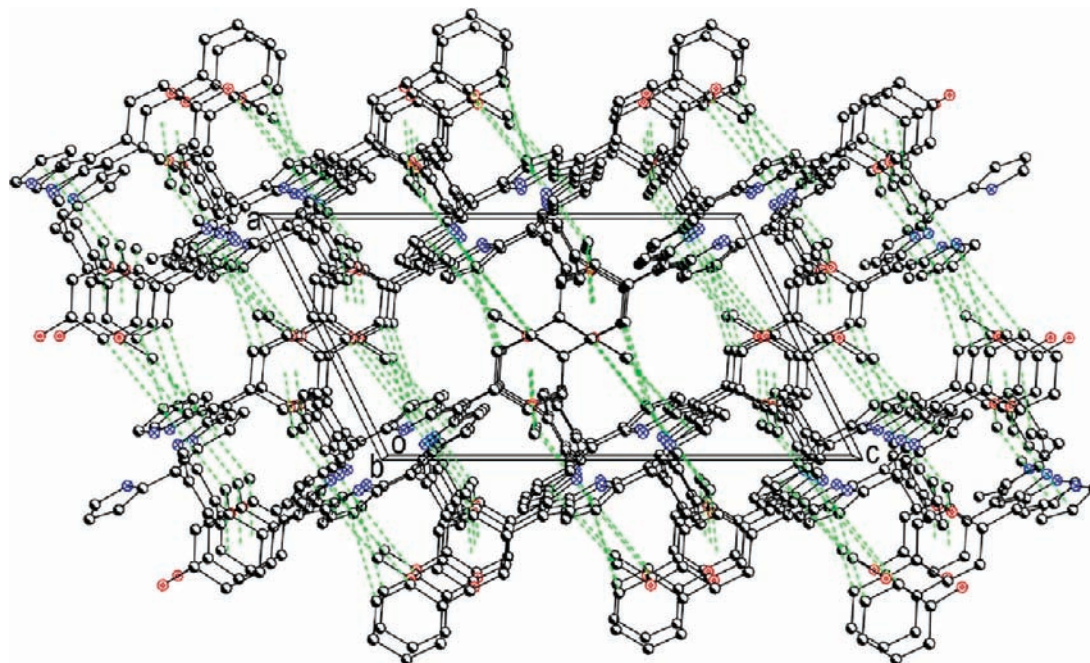


Figure 4. Packing diagram of $\text{H}_2\text{T}(4'\text{-OMePh})\text{P}$ with the dashed lines representing hydrogen bonding interactions. Geometry of represented hydrogen bonding interactions: $\text{C}(17)\text{-H}(17\text{C})\cdots\text{C}_g(1)$ with $d_{\text{C}\cdots\text{C}_g} = 3.551(6)\text{ \AA}$ and $\angle(\text{DHA}) = 108.18^\circ$; $\text{C}(15)\text{-H}(15)\cdots\text{C}_g(2)$ with $d_{\text{C}\cdots\text{C}_g} = 3.697(5)\text{ \AA}$ and $\angle(\text{DHA}) = 126(2)^\circ$; $\text{C}(16)\text{-H}(16)\cdots\text{C}_g(2)$ with $d_{\text{C}\cdots\text{C}_g} = 3.751(5)\text{ \AA}$ and $\angle(\text{DHA}) = 132(2)^\circ$; $\text{C}(24)\text{-H}(24\text{C})\cdots\text{C}_g(2)$ with $d_{\text{C}\cdots\text{C}_g} = 3.80(1)\text{ \AA}$ and $\angle(\text{DHA}) = 122.83^\circ$; $\text{C}(24)\text{-H}(24\text{A})\cdots\text{C}_g(3)$ with $d_{\text{C}\cdots\text{C}_g} = 3.797(9)\text{ \AA}$ and $\angle(\text{DHA}) = 147.92^\circ$ [$\text{C}_g(1)$, $\text{C}_g(2)$ and $\text{C}_g(3)$ stands for the centers of gravity of the rings $\text{N1}(\text{C1}\text{-}\text{C4})$, $\text{N2}(\text{C6}\text{-}\text{C9})$, and $\text{C11}\text{-}\text{C16}$, respectively]. O, red; N, blue; C, gray.

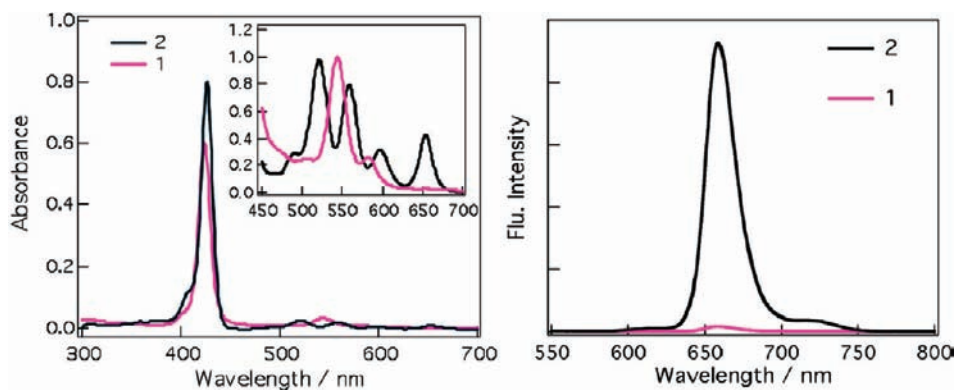


Figure 5. UV-vis absorption (left) and fluorescence (right) spectra of $\text{CuT}(4'\text{-OMePh})\text{P}$ (**1**) and $\text{H}_2\text{T}(4'\text{-OMePh})\text{P}$ (**2**) in benzonitrile at room temperature. The concentrations are kept at $3.3\text{ }\mu\text{M}$.

of **1** and **2** measured in benzonitrile at room temperature are shown in Figure 5. The fluorescence spectrum of **1** shows one emission band at 658 nm. As for nonmetalated $\text{H}_2\text{T}(4'\text{-OMePh})\text{P}$, the fluorescence emission spectrum has a similar feature with a band at 659 nm, which is red-shifted by about 1 nm as compared with that of **1**. The fluorescence quantum yields of **2** and **1** in benzonitrile were determined to be 0.10 and 0.003, respectively. By using a time-correlated single photon counting technique, the fluorescence lifetimes in solution were conducted upon the excitation wavelength of 421 nm. The decays of the singlet-excited states of **1** and **2** were fitted as single exponential, from which the fluorescence lifetimes of the metalated compound **1** and **2** are 2.5 and 9.4 ns, respectively (see Figure S3 in the Supporting Information). The shorter fluorescence lifetime of **1** compared to **2** is attributed to the metalation effect.

Electron-Transfer Reactions from 1 and 2 to the Triplet C_{60} . By the use of a nanosecond laser pulse, the triplet

states of compounds **1** and **2** can be observed in real time. By photoexcitation of $\text{H}_2\text{T}(4'\text{-OMePh})\text{P}$ (**2**) in deaerated benzonitrile using 430 nm laser light (See Figure S4 in the Supporting Information), the transient absorption spectrum immediately after the laser pulse exhibited only an absorption band at 440 and 610 nm, which is assigned to the triplet state of $\text{H}_2\text{T}(4'\text{-OMePh})\text{P}$. Although the steady-state absorption spectra of **1** and **2** are quite similar, the absorption of the triplet states of **1** and **2** are quite different. Excitation of benzonitrile solution of $\text{CuT}(4'\text{-OMePh})\text{P}$ (**1**) by 430 nm showed no absorption bands of the triplet $\text{CuT}(4'\text{-OMePh})\text{P}$ (**1**) (See Figure S5 in the Supporting Information).³⁹ In the case of metalloporphyrins with unpaired d-electrons, it was found that the excited electronic states become complicated because of the interaction of the unpaired d-electrons with the porphyrin π -electron system.⁴⁰ Darwent et al.⁴¹ reported that porphyrins with paramagnetic transition metals have

very short excited-state lifetimes, which essentially precludes their use as sensitizers in fluid solution at room temperatures.

To examine the electron-donating properties of CuT-(4'-OMePh)P **1** vs H₂T(4'-OMePh)P **2**, the nanosecond transient spectra are recorded for a mixture of C₆₀ and **1** or **2** in deaerated benzonitrile (Figure 6 and Supporting Information Figures S6 and S7). By photoexcitation of C₆₀ (0.050 mM) in the presence of H₂T(4'-OMePh)P (0.10 mM) by applying 355 nm laser light, the transient spectra exhibited the characteristic absorption bands of

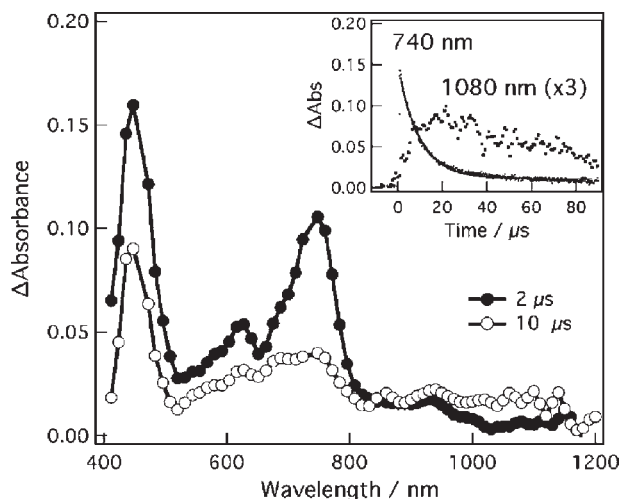


Figure 6. Nanosecond transient spectra of C₆₀ (0.050 mM) in the presence H₂T(4'-OMePh)P (0.05 mM) in deaerated benzonitrile. $\lambda_{\text{exc}} = 355$ nm.

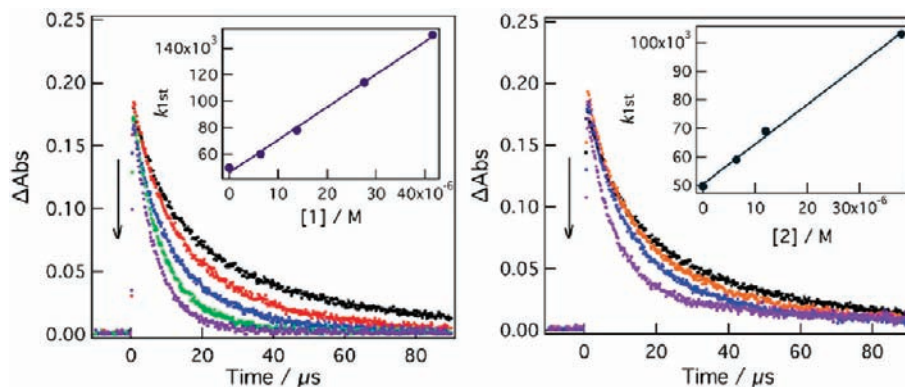


Figure 7. Decay profiles of the triplet C₆₀ at 740 nm with changing the concentrations of **1** (left) and **2** (right) in deaerated benzonitrile. Inset: Pseudo-first-order plot.

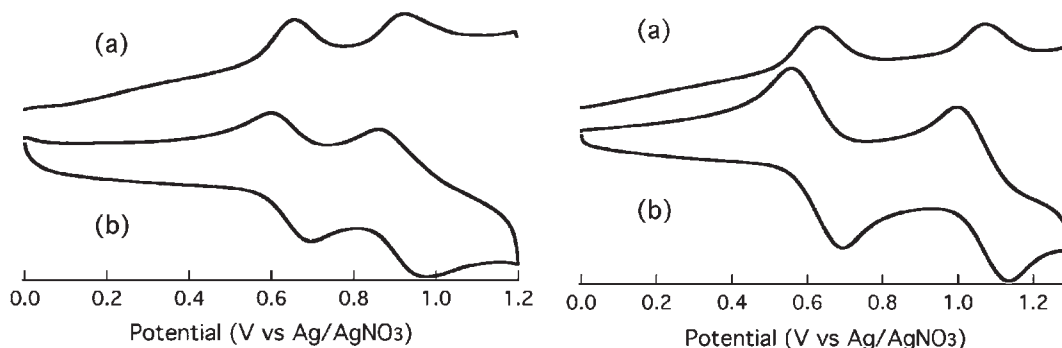


Figure 8. (a) DPV and (b) CV of **1** (right) and **2** (left) in deaerated dichloromethane. Scan rate = 50 mVs⁻¹.

the triplet state of C₆₀ (³C₆₀^{*}) at 740 nm and **2** at 450 and 620 nm. With the decay of the triplet states, the concomitant rises of the characteristic absorption band of the C₆₀ radical anion (C₆₀^{•-}) in the NIR region with a maximum at 1080 nm were observed.⁴² The broad absorption in the visible region with a maximum at 930 nm is likely due to the H₂T(4'-OMePh)P radical cation. The decay of ³C₆₀^{*} and rise of C₆₀^{•-} and H₂T(4'-OMePh)P radical cation seem to match each other. These observations indicate that the electron-transfer process takes place via the triplet excited C₆₀ because of the electron-donating substituents on the porphyrin ring.

The rate constant of the electron transfer (k_{et}) was determined to be $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ under the pseudo-first-order conditions by monitoring the decay of ³C₆₀^{*} or rise of C₆₀^{•-} as a function of the concentration of the H₂T(4'-OMePh)P (Figure 7). Similarly the k_{et} from **1** to the triplet C₆₀ was found **1** to be $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 7), which is slightly larger than the k_{et} value of **2** ($2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Such difference in the k_{et} values can be explained by the difference in the oxidation potentials of the planar **2** and distorted **1**. Electrochemical measurements were carried out by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques at a glassy carbon electrode in carefully dried dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆; 0.10 M) at room temperature (Figure 8). Electrochemistry on several porphyrins was reported previously.⁴³ The first oxidation potential (E_{ox}) of the **1** was located at 632 mV vs Ag/AgNO₃ (0.010 M), compared to 664 mV vs Ag/AgNO₃ (0.010 M) for **2**.

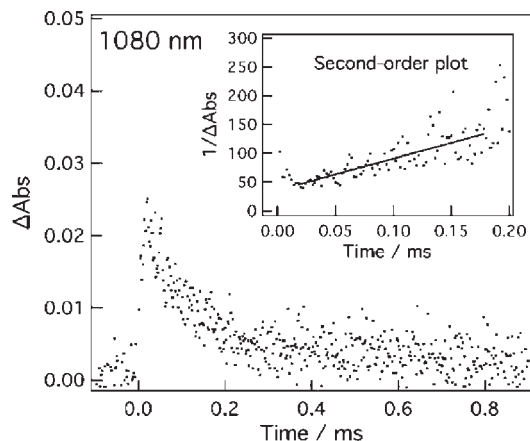


Figure 9. Decay of $C_{60}^{\bullet-}$ on long time scale produced under the same conditions as described in Figure 6. Inset: Second-order plot.

These values are close to those reported for meso-substituted octaethylporphyrins and their copper complexes.^{44–50} Although it has been reported that the distortion of the porphyrin ring results in significant decrease in the electron-transfer reactivity,^{51,52} there is

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no clear indication of the effect of saddled distortion in **1** on the rate of electron-transfer reaction with the triplet excited C_{60} .

In long time-scale (1 ms), the $C_{60}^{\bullet-}$ begins to decay slowly after reaching the maximal absorbance (Figure 9). The decay time profile was fitted with second-order kinetics, suggesting that bimolecular back electron-transfer process between $C_{60}^{\bullet-}$ to $(H_2T(4'-OMePh)P)^{\bullet+}$ takes place. The rate constant of back electron transfer (k_{bet}) between the porphyrin $(H_2T(4'-OMePh)P)^{\bullet+}$ and $C_{60}^{\bullet-}$ was estimated as $6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ from the slope of the second-order plot in the form of k_{bet}/ϵ , where ϵ refers to the molar extinction coefficient of $C_{60}^{\bullet-}$. The obtained k_{bet} for $(H_2T(4'-OMePh)P)^{\bullet+}$ and $C_{60}^{\bullet-}$ is close to the diffusion-controlled limit in benzonitrile.⁵³

Conclusion

In conclusion, we have reported two crystalline porphyrins $CuT(4'-OMePh)P$ (**1**) and $H_2T(4'-OMePh)P$ (**2**) that are crystallized in different crystal systems with different space groups. It is observed that the metalation brings changes in the crystal structures, supramolecular conformations, and photophysical properties. In particular, the porphyrin ring exhibits saddled distortion in the crystal of **1**, whereas the porphyrin ring is planar in the crystal of **2**. With regard to the electron-transfer reactivity, however, there is no clear indication of the effect of saddled distortion in solution.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1** and **2**, fluorescence lifetime measurements, nanosecond transient absorption spectra of **1**, **2** and their interactions with fullerene C_{60} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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