Supramolecular Complexation of Porphyrin and Quinone with Two Coordination Bonds and Intramolecular Electron Transfer

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ABSTRACT: V-shaped zinc porphyrin dimer and quinone with two pyridyl groups have been rationally designed and synthesized to assemble a porphyrin–quinone supramolecule with two coordination bonds. Selective formation of the 1:1 bridging structure between the host–guest molecules was seen by 1H NMR and UV-Vis absorption spectroscopy. Molecular mechanics calculation suggests that the bridging structure has rigidity as well as flexibility in geometry between the redox pair, which supports the interpretation of 1H NMR studies. Intramolecular photoinduced electron transfer from the excited singlet state of the porphyrin to the quinone was observed by steady-state fluorescence spectra and picosecond fluorescence lifetime measurements. © 1997 by John Wiley & Sons, Ltd.


KEYWORDS: porphyrin; quinone; supramolecule; electron transfer; coordination bond

1. INTRODUCTION

Since advocacy of supramolecular chemistry by Lehn [1, 2], supramolecular chemistry has been rapidly developed by interaction with many fields, such as chemistry, physics and biology. The resulting crossover has provided new principles and concepts in chemistry involving molecular recognition, catalysis, molecular device and so on. One elegant example of biological supramolecular structure is the reaction centre from a photosynthetic bacterium [3–5]. Primary processes in photosynthetic bacteria involve light-driven electron transfer (ET) across a bilayer lipid membrane which converts the light energy into chemical energy. In the supramolecular machinery, photoinitiated ET cascade is achieved by arranging related chromophores precisely in protein matrix. A number of donor (D)–spacer (S)–acceptor (A) molecules have been synthesized to mimic supramolecular charge separation (CS) and ET relay in photosynthesis [6–9]. Some of them, triads, tetrads and pentads consisting of porphyrins, quinones, pyromellitimides and carotenoids as building blocks have achieved long-lived CS with a high quantum yield [10–13]. However, much synthetic effort must be focused on the construction of such multichromophore arrays to control separation distance, free energy change, linking mode and relative orientation between these chromophores. Considering that in natural systems pigments are well arranged in protein by weak molecular interactions, such as hydrogen bonds and electrostatic interactions, a non-bonding strategy for the assembly of D and A systems seems to be an alternative. Since separately prepared D and A units can be combined to assemble supramolecular D–A systems in a non-covalent fashion, it is generally easy to access synthetically. Although there have been many
reports about photosynthetic D–A systems using hydrogen bonds [14–24], electrostatic interactions [25–31], and so on [32–36], less attention has been paid to those using coordination bonds [37–41]. We rationally designed a porphyrin–quinone supramolecule where a host molecule, zinc porphyrin dimer with phenanthrene spacer, and a guest molecule, two pyridine-linked quinone, can be assembled with two coordination bonds [42–46]. Within the host molecule there is a flexibility in relative orientation and separation distance between the two porphyrins via the linker, while the guest molecule has similar flexibility in the linker connecting the aromatic moiety and pyridyl groups. The chelate effect, where the first binding greatly facilitates the second binding, allows selective formation of the bridge involving quinone across the two porphyrin chromophores schematically as shown in Fig. 1. Therefore, the redox pair in the supramolecule is expected to adopt a relatively fixed geometry using two point bindings. In this paper we describe the structure and photophysical properties of the supramolecule. Molecular mechanics calculations, as well as spectroscopic studies including 1H NMR, UV-Vis absorption, electrochemistry, steady-state fluorescence, and fluorescence lifetime measurements, have demonstrated that the porphyrin–quinone supramolecule has function with intramolecular photoinduced ET. Preliminary results have already been reported [47].

2 EXPERIMENTAL

2.1 General

Melting points were recorded on a Yanagimoto micro-melting point apparatus and were not corrected. 1H NMR spectra were measured on a JEOL EX-270. Mass spectra were obtained on a JEOL JMS-DX 300. IR and UV-Vis spectra were measured on a Hitachi 330, respectively. Redox potentials were recorded on a Bioanalytical System, Inc. CV-50W. Elemental analyses were performed on a Perkin-Elmer Model 240C elemental analyser. Fluorescence lifetimes were measured by a picosecond time-correlated single-photon counting method using a synchronously pumped cavity-dumped dye laser [48]. SALS at Osaka University Computation Center was used for the non-linear least-squares analysis of the observed decay curves.

2.2 Starting Materials

All solvents and chemicals were of reagent grade quality, purchased commercially and used without further purification except as noted below. Tetrahydrofuran was pre-dried over potassium hydroxide and distilled from benzophenone ketyl. Dimethylformamide was distilled from calcium hydride and stored over molecular sieves. Dichloromethane was refluxed and distilled from P2O5.

2.2.1 5-(4-Hydroxyphenyl)-10,15,20-tris(4-isopropylphenyl)porphyrin (1) [49] In a 5 L round-bottomed flask were placed 3 l of propionic acid, 11.6 g (95 mmol) of 4-hydroxybenzaldehyde, 42.0 g (43 ml, 284 mmol) of 4-isopropylbenzaldehyde, and 27 ml (380 mmol) of pyrrole. The mixture was refluxed for 2 h and cooled to room temperature. The acid solvent was removed in vacuo. The remaining tarry mixture was neutralized with aqueous sodium bicarbonate and extracted with several portions of chloroform. The organic extracts were combined and dried over anhydrous sodium sulphate. The solution was filtered through a short column of silica gel with chloroform to remove tar. Purification was accomplished by chromatography on silica gel with chloroform to remove tar. Purification was accomplished by chromatography on silica gel with chloroform. A filter recrystallization from chloroform–hexane, 7.0 g (9.3 mmol, 9.8%) of pure 1 was isolated as red crystals. mp > 300°C; fast atom bombardment mass spectroscopy (FA B-M S) m/z 757 (M+); 1H NMR (270 MHz, CDCl3) δ 7.57 (2 H br s, NH), 1.52 (18 H, m, Pr-i-Me), 3.25 (3 H, septet, Pr-i-H), 3.74 (1 H, br s, OH), 7.19 (2 H, d, J = 8 Hz, C6H4OH), 7.60 (8 H, d, J = 8 Hz, C6H4Pr-i-H), 8.07 (2 H, d, J = 8 Hz, C6H4OH), 8.13 (4 H, d, J = 8 Hz, C6H4Pr-i-H), 8.86 (8 H, s, β-H).

![Fig. 1. Schematic illustration of the supramolecular complex between the zinc porphyrin dimer and bidentate acceptor.](https://example.com/f1.png)
2.2.2 3,6-Bis(5,10,15-tris(4-isopropylphenyl)porphyrinato)-20-yl)-4-phenoxymethyl)phenanthrene (2) [50] In a flask equipped with a reflux condenser were placed 115 mg (0.152 mmol) of 1, 25 mg (0.069 mmol) of 3,6-bis(bromomethyl)phenanthrene [51, 52], 25 mg of potassium carbonate and 6 ml of dimethylformamide. The contents were kept at 80-90°C for 24 h. The reaction mixture was diluted with water, extracted with chloroform and then dried over sodium sulphate. A fter removal of the solvent, the residue was chromatographed on silica gel with chloroform to give 51 mg (0.030 mmol, 43%) of 2.

Recrystallization from hexane-chloroform gave the pure free base as red crystals. mp 285-287°C; FAB-MS m/z 1715 (M + H+); 1H NMR (270 MHz, CDCl3) δ -2.76 (4 H, br s, NH), 1.47-1.52 (36 H, m, Pr1-Me), 3.20 (6 H, m, Pr1-Me), 5.65 (4 H, s, -OCH2-), 7.46-7.60 (16 H, m, phenyl-H), 7.89 (2 H, s, 9,10-phenanthrene (pht)-H), 7.94 (2 H, m, 2,7-pht-H), 8.06-8.18 (18 H, m, 1,8-pht-H), 8.85 (16 H, m, β-H), 9.07 (2 H, s, 4,5-pht-H).

The zinc complex 3 was prepared by refluxing 1:1 methanol:chloroform (33 ml) solution of 2 (39 mg, 23 μmol) with an excess of zinc acetate for 40 min. The mixture was poured onto water, extracted with chloroform and dried. A fter removal of the solvent, the residue was chromatographed on alumina with chloroform to give 42 mg (100%) of 3. Recrystallization from chloroform-methanol gave pure 3 as purple crystals. mp > 300°C; FAB-MS m/z 1842 (M + H+); 1H NMR (270 MHz, CDCl3) δ 1.48-1.55 (36 H, m, Pr1-Me), 3.20 (6 H, m, Pr1-Me), 5.65 (4 H, s, -OCH2-), 7.44-7.59 (16 H, m, phenyl-H), 7.86 (2 H, s, 9,10-pht-H), 7.90 (2 H, m, 2,7-pht-H), 8.06-8.17 (18 H, m, 1,8-pht-H), 8.94 (16 H, m, β-H), 9.04 (2 H, s, 4,5-pht-H); U V-Vis (CH2Cl2) λ max (log ε) 420 (6.00), 548 (4.61), 588 (4.01) nm.

2.2.3 5,10,15,20-Tetakis(4-isopropylphenyl)porphyrinate zinc (II) (4) Porphyrin monomer 4 was synthesized according to the procedure in the literature [49], mp > 300°C; FAB-MS m/z 847 (M + H+); 1H NMR (270 MHz, CDCl3) δ 1.49-1.55 (24 H, m, Pr1-Me), 3.26 (4 H, m, Pr1-Me), 7.60 (8 H, d, J = 8 Hz, phenyl-H), 8.14 (8 H, d, J = 8 Hz, phenyl-H), 8.97 (8 H, s, β-H); U V-Vis (CH2Cl2) λ max (log ε) 420 (5.72), 549 (4.29), 588 (3.69) nm.

2.2.4 2,6-Bis-(4-pyridoxymethyl)-1,4-dimethoxybenzene (6) [53] Compound 5 [54] (0.55 g, 3.5 mmol), chloropyridine hydrochloride (0.75 g, 5 mmol), and TDA -1 (0.16 g, 0.16 ml, 0.5 mmol) were added to a suspension of powdered potassium hydroxide (1.4 g, 25 mmol) and potassium carbonate (0.69 g, 5 mmol) in dry toluene (25 ml). Reaction mixture was refluxed with stirring for 20 h, filtered, concentrated and the residue was purified by column chromatography using chloroform/methanol/triethylamine (100/5/1) as an eluent. Recrystallization from hexane-chloroform gave 6 (0.52 g. 42%) as white crystals. mp 127-128°C; electron ionization mass spectrometry (EI-MS) m/z 352 (M+); Found: C, 68.27; H, 5.74; N, 7.79%: Calculated for C20H18N2O4: C, 68.17; H, 5.72; N, 7.95%.

2.2.5 2-(4-Pyridoxymethyl)-1,4-dimethoxybenzene (9) Compound 9 was prepared from 8 by the similar method described for 5 [53]. Recrystallization from hexane gave 9 (60%) as white crystals. mp 54-55°C; EI-MS m/z 245 (M+); Found: C, 68.35; H, 6.06; N, 5.65%. Calculated for C14H12NO3: C, 68.56; H, 6.16; N, 5.71%; 1H NMR (270 MHz, CDCl3) δ 3.76 (3 H, s, -OMe), 3.83 (3 H, s, -OMe), 5.13 (2 H, s, -OCH2-), 6.84 (2 H, s, -OCH2-), 6.89 (2 H, dd, J = 5 and 1 Hz, pyridyl-H), 6.99 (1 H, s, 3-phenyl-H), 8.43 (2 H, dd, J = 5 and 1 Hz, pyridyl-H).

2.2.6 2,6-Bis-(4-pyridoxymethyl)-1,4-benzoquinone (7) [55] A stirred solution of ceric ammonium nitrate (CAN) (620 mg) in 2 ml of H2O was added portionwise to a solution of 6 (115 mg, 0.325 mmol) in 9 ml of acetonitrile over 10 min. A fter the addition was over, stirring was continued at 70°C for 30 min and then the mixture was cooled to room temperature. The precipitates were collected by filtration and dried in vacuo. The solid was dissolved in chloroform, washed with sodium hydrogen carbonate, and then dried over anhydrous sodium sulphate. A fter removal of the solvent, pure 7 (24 mg, 23%) was isolated as yellow crystals. mp 103-105°C (decomp.); EI-MS m/z 324 (M + 2H+); IR (KBr) 1650 cm –1; 1H NMR (270 MHz, CDCl3) δ 5.00 (4 H, s, -OCH2-), 6.70 (4 H, dd, J = 5 and 1 Hz, pyridyl-H), 6.97 (2 H, s, quinone-H), 8.51 (4 H, dd, J = 5 and 1 Hz, pyridyl-H).

2.2.7 2,6-Bis-(phenoxymethyl)-1,4-dimethoxybenzene (12) [54] Sodium hydride (60%, 890 mg, 22.3 mmol) was washed with dry hexane and 11 [54, 56] (580 mg, 1.8 mmol) and phenol (440 mg, 4.7 mmol) in dry tetrahydrofuran (THF) (10 ml) was added to the flask. The solution was refluxed for 2 h and then cooled to room temperature. The reaction mixture was poured onto iced-water, extracted with
ethyl acetate, washed with water, and dried over anhydrous sodium sulphate. After removal of the solvent, the residue was chromatographed on silica gel with benzene–hexane (1:1) as an eluent to give 12 (280 mg, 45%). Recrystallization from hexane afforded pure 12 as colourless crystals. mp 48–50°C; El·M S m/z 350 (M+); Found: C, 75.40; H, 6.24%; Calculated for C22H22O4: C, 74.99; H, 5.03%; IR (KBr) 1655 cm–1; 1H NMR (270 MHz, CDCl3)

2.2.8 2,6-Bis(phenoxymethyl)-1,4-benzoquinone (13) [55] Compound 12 (102 mg, 0.29 mmol) was dissolved in acetonitrile (2 ml), and an aqueous solution (1 ml) of CAN (340 mg, 0.66 mmol) was added portionwise over 5 min. After stirring for 30 min at room temperature, the reaction mixture was extracted with chloroform, washed with water, and then dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the crude product was recrystallized from hexane–chloroform to provide 45 mg (42%) of 13 as yellow crystals, mp 140–141°C; EI-MS m/z 350 (M+); Found: C, 74.76; H, 5.06%; Calculated for C20H16O4: C, 75.40; H, 6.24%; 1H NMR (270 MHz, CDCl3)

3.1 Synthesis
Zinc porphyrin dimer 3 was prepared by the coupling of hydroxyporphyrin 1 and 3,6-bis(bromomethyl)phenanthrene in the presence of potassium carbonate in DMF followed by the treatment with zinc acetate in CHCl3 as shown in Scheme 1. Zinc porphyrin monomer 4, was synthesized by the Adler method and subsequent metallation with zinc acetate. Bi- and monodentate with dimethoxybenzene subunits, 6 and 9, respectively, were obtained by the coupling reaction of alcohols 5 and 8 with 4-chloropyridine hydrochloride (Scheme 2). Oxidation of 6 with CAN in MeCN-H2O gave bidentate quinone 7, while monodentate quinone 10 was not obtained in the reaction of 9 under the same conditions for 6, probably due to the instability of the corresponding quinone. Reference 13 was prepared by the coupling reaction of 11 and phenol followed by the oxidation with CAN.

3.2 UV-Vis Absorption Spectroscopy
Before discussing the equilibria between the zinc porphyrin dimer and bidentate ligand, we consider the equilibria of a more simple system. Zinc porphyrins generally bind only single ligands such as pyridine to give five-coordinate species. Therefore, a zinc porphyrin monomer and a monodentate ligand give a 1:1 complex with binding constant K. When the corresponding bidentate ligand is employed, the equation K1 ≈ 2K is set up. However, with a bidentate ligand there is a second equilibrium, which leads to the formation of a 2:1 complex with binding

\[
\ln \frac{[A - A_0]}{(A - A)} = x \ln [\text{free ligand}] + \ln K
\]

where A is the absorption at a given wavelength, \( \lambda \); A0 is the initial absorption at \( \lambda \); A is the final absorption at wavelength \( \lambda \); K is the binding constant and x is a Hill coefficient which defines the number of ligands bound per site. A plot of \( \ln[A - A_0]/(A - A) \) vs ln [free ligand] yields a straight line of slope 1 for independent, identical binding at the two sites. Cooperative binding, where the second binding is facilitated by the first binding, gives \( x > 1 \), while negative cooperativity gives \( x < 1 \).
constant $K_2$. The relation between $K_1$ and $K_2$ is expressed by the equation $4K_2 = \alpha K_1$ where $\alpha$ is an interaction parameter between the two ends of the ligand. The parameter takes the following value: in a negative cooperative system, $0 < \alpha < 1$; in a non-cooperative system, $\alpha = 1$; in a positive cooperative system, $\alpha > 1$. Similar arguments can be applied when monodentate ligands bind to zinc porphyrin dimer. Although there are several equilibria between the zinc porphyrin dimer and bidentate ligand as shown in Fig. 2, either one-point binding of the bidentate ligand on the two porphyrin rings within the zinc porphyrin dimer ($C_2$), or 1:1 complex formation of the bridging structure across the two porphyrins ($C_1$), tends to dominate in most cases. Therefore, it is reasonable to consider only one of the two pathways involving $C_1$ and $C_2$. By using ligands designed to fit into the cleft, we expect that the two-point binding of the bidentate ligand inside the dimer cavity (lower equilibrium) is overwhelming because of the large chelate effect.

On addition of ligands, the Soret peak of 3 shifted from 420 to 428 nm and sharpened with isosbestic points as shown in Fig. 3. Binding constants in dichloromethane were obtained from UV-Vis spectroscopic titration of the porphyrins for various

\textbf{Scheme 1.}

\textbf{Scheme 2.}

concentrations of the ligands by using the shift of the Soret band on ligation [43–46]. The binding constants for single equilibria systems were obtained from the titration data by using Benesi–Hildebrand plots [57], while the data for multi-equilibria systems were obtained by computer-assisted non-linear curve-fitting methods. In addition, Hill coefficients were obtained from Hill plots [58].

Owing to the instability of quinone ligands 7 and 10, the analogous compounds 6 and 9 were employed in the titration experiments. The results are summarized in Table 1. The binding constant of 3 and 6 is $1.1 \times 10^7$ M$^{-1}$, which is three orders of magnitude larger than that for the binding of 3 and 9. The larger binding constant for the coordination of the bidentate ligand to the porphyrin dimer suggests that 3 and 6 form the bridging structure predominantly. However, no exciton coupling of the two porphyrins in this complex was seen, indicating distal disposition or flexible geometry of the two porphyrins [43–46]. Binding of 6 to monomer 4 as well as that of 9 to dimer 3 gave Hill coefficients of about 1.00, indicating the formation of simple 1:1 and 1:2 complexes. On the other hand, the 3 and 6 system showed strong allosteric behaviour with a Hill coefficient of 1.46, showing that the first binding accelerates the second binding because of the chelate effect.

3.3 1H NMR studies

$^1$H NMR titrations of 3 were carried out with various concentrations of 6 and 9 in CDCl$_3$. The results are shown in Fig. 4 and 5. In the absence of added ligand, the $^1$H NMR signals of 3 and 4 in CDCl$_3$ were sharp. Addition of 0.6 equivalent of 6 to a CDCl$_3$ solution of 3 induced large upfield shift of signals in 6 because these protons feel the ring currents of the two porphyrins [43–46]. On the other hand, we can see only small shifts of the protons assigned to phenanthrene and porphyrin moieties around the aromatic regions. As up to 1.8 equivalent of 6 was added to 3, all signals of 6 were shifted downfield and became broad due to the existence of various species. A similar tendency was observed in the 3–9 system as shown in Fig. 5. The $^1$H NMR spectrum of 3 and 0.6 equivalent of 6 in CDCl$_3$ clearly shows the bridging

![Fig. 2](image-url). Binding equilibria for reactions between the porphyrin dimer and bidentate ligand.

structure. Thus, the characteristic pyridyl aromatic signals at 2.22 and 4.86 ppm shifted upfield by ca. 6.6 and 2 ppm, respectively, compared with those of 6 alone, due to the ring current effect of zinc porphyrins. The methoxy signals of 6 appeared at 2.79 and 3.26 ppm. The chemical shift difference (0.47 ppm) between them is unusually large in contrast to the lack of apparent splitting of the methoxy signals of 9 in the 3–9 system, showing the rigid structure of the complex 3–6. However, no nuclear Overhauser effect (NOE) was observed for the complex 3–6 where some of the protons are expected to be in close proximity within the complex. In addition, no apparent change of spectrum in the 3–6 system was seen even as the temperature was decreased down to -50°C.

3.4 Molecular Mechanics Calculation
Various attempts failed to isolate the supramolecule 3–6 by crystallization. Therefore, a molecular mechanics calculation was employed to get information about the structure. The conformation of porphyrin–dimethoxybenzene supramolecule in vacuum was derived using the Insight II/Discover program from Molecular Simulations Inc. To hold the five-coordinated structure of the porphyrin ring, the structure of the porphyrin moiety observed by X-ray crystallography was used and retained throughout the calculation [59]. The porphyrin dimer and the dimethoxybenzene bidentate are linked together via two coordination bonds, and eight single bonds in the four methyleneoxy groups are rotated individually by 30°. Two hundred of the different conformations generated are chosen in energy and minimized. During all procedures the usual Discover parameters were retained to calculate the optimized structure for the supramolecule. The result is illustrated in Fig. 6. The population of the conformations are divided into three groups; folded and extended conformations, and the intermediates depending upon the energies. Compared with the extended supramolecule with the highest energy in the population (total potential energy, \( E_t = \) internal energy, \( E_i \) + non-bonded energy, \( E_n \) + restraint energy, \( E_r = 333 + (-173) + 2 = 162 \text{ kcal mol}^{-1} \)), shown in Fig. 6b, the folded supramolecular structure as the lowest energy conformation (\( E_t = E_i + E_n + E_r = 337 + (-208) + 2 = 131 \text{ kcal mol}^{-1} \)), shown in Fig. 6a, is found to be more stable in energy by 31 kcal mol⁻¹. The difference is mainly ascribed to that of the non-bonded energy consisting of van der Waals' and electrostatic interactions.

3.5 Electrochemical Measurements
In order to investigate the redox properties of the quinone and the porphyrin moieties within the supramolecule, redox potentials were measured by differential pulse voltammetry in dichloromethane containing 0.1 M tetra-n-butylhexafluorophosphate using the reference electrode Ag/AgCl. Attempts to measure redox peaks using cyclic voltammography were unsuccessful because of the irreversible wave. The values of the first reduction potential of 7 and the first oxidation potential of 3 are -0.34 and +0.74 V, respectively. When the complex 3–7 is formed, no apparent change of the reduction potential (-0.31 V) of 7 was observed, while the oxidation potential of 3 was shifted to negative (+0.64 V) by 100 mV in the complex.

3.6 Fluorescence Spectroscopy
The fluorescence quenching of 3 (8.0 \times 10^{-7} M) in CH₂Cl₂ with excitation at 428 nm was investigated by the addition of 100 equivalent of 6 or 7 (Fig. 7). A prominent change for the fluorescence spectra of 3 was seen in shape as well as in peak position after the addition of the ligands [43–46]. Thus, the peak positions of \( \alpha \)- and \( \beta \)-emission bands are red-shifted by about 20 nm after the addition of the ligands. The relative intensity for the fluorescence of 3–7 versus 3–6 is 0.06 when the Soret band is excited with the
Table 1. Binding constants of dimer 3 and monomer 4 with bidentate 6 and monodentate 9

<table>
<thead>
<tr>
<th>Porphyrins</th>
<th>Ligands</th>
<th>$K_1$(M$^{-1}$)</th>
<th>$K_2$(M$^{-1}$)</th>
<th>Hill Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>6</td>
<td>1.1 x 10(^7)</td>
<td>negligible</td>
<td>1.46</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>2.4 x 10(^7)</td>
<td>6.4 x 10(^7)</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>2.4 x 10(^7)</td>
<td>6.0 x 10(^7)</td>
<td>0.99</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>1.4 x 10(^7)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$K_1 = [\text{mono-adduct}/([\text{ligand}][\text{porphyrin}])].$

$K_2 = [\text{bis-adduct}/([\text{ligand or porphyrin}][\text{mono-adduct}])].$

same concentration of the samples. On the other hand, no fluorescence quenching of 3 occurred in the presence of 13 instead of 7. Therefore, the quenching can be ascribed to intramolecular ET from the excited singlet state of the porphyrin to the quinone. Time-resolved, single-photon counting fluorescence studies were carried out for 3 (2.2 x 10$^{-6}$ M) and 100 equivalent of 6 in CH$_2$Cl$_2$ with excitation at 405 nm to give mono-exponential decay kinetics with a lifetime of 1.2 ns ($\tau_0$) monitoring at 610 nm. The fluorescence decay of 3, with excitation at 405 nm, was single exponential with a lifetime of 1.6 ns, which is consistent with that of 4. Therefore, the somewhat shorter lifetime in the presence of ligand are due to the coordination of the pyridine moiety to the zinc porphyrin. When 100 equivalent of 7 instead of 6 was

Fig. 4. 270 MHz $^1$H NMR spectra of 3 (5.9 x 10$^{-4}$ M) in CDCl$_3$ after the addition of (a) 0, (b) 0.6, (c) 1.0 and (d) 1.8 equivalent of 6. The $^1$H NMR spectrum of 6 in CDCl$_3$ is shown in (e) for the comparison.

Fig. 5. 270 MHz $^1$H NMR spectra of 3 (5.9 x 10$^{-4}$ M) in CDCl$_3$ after the addition of (a) 0, (b) 0.6, (c) 1.6 and (d) 4.0 equivalent of 9. The $^1$H NMR spectrum of 9 in CDCl$_3$ is shown in (e) for the comparison.

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added, the decay profiles at 610 nm could be analysed in terms of three exponential components: one major component (98%) with a lifetime of 60 ps ($\tau_1$) and two minor components (1%) with lifetimes of 1.2 ns ($\tau_2$) and 4.0 ns ($\tau_3$). The short-lived component is assigned to the fluorescence of the porphyrin moieties quenched by the quinone within the 3–7 complex, while the long-lived components are considered to the porphyrin fluorescences which are not quenched by the quinone. Based on the above results, the ET rate for CS was obtained to be $1.6 \times 10^{10}$ s$^{-1}$ ($\tau_1^{-1} - \tau_0^{-1}$).

### 3.7 Relationship between Structure and Photoinduced ET

We have investigated the geometries of the porphyrin–quinone supramolecule by UV-Vis absorption and $^1$H NMR spectroscopy and molecular mechanics calculations. In all the cases described here, selective formation of the 1:1 bridging structure in the complex 3–6 and 3–7 was seen, as we expected. The value of the Hill plot, 1.46, is larger, compared with those in flexible cyclic zinc porphyrin dimer-bis-amine ligand complexes reported by Sanders et al. [43–46], and smaller compared with those in rigid gable porphyrin-bis-zinc-dipyridylmethane (or dimidazolylmethane) reported by Tabushi et al. [42]. This comparison suggests two characteristics in our supramolecule; rigidity and flexibility in the host–guest interaction. $^1$H NMR titration indicates that the relative environments of the two methoxy groups are different magnetically within the bridging complex 3–6 due to the ring currents of the two porphyrin $\pi$-systems. Although this observation supports the relatively rigid structure of the complex, we could not observe NOE signals for protons which are expected to be quite close to each other. In addition, no apparent splitting and shift of the $^1$H NMR signals due to the rigid structure of the complex were seen even under the conditions at low temperature. The NMR time scale is very slow compared with the usual rates of rotation about single bonds. Free rotations are possible around the spacers across the two porphyrins in 3, and across the dimethoxybenzene unit and the pyridyl groups in 6 when 3

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**Fig. 6.** Stereo views of the conformations for 3–6 derived from molecular mechanics calculations using the Insight II/Discover program. The total energy of the most stable conformation, the folded conformer shown in (a), is lower by about 30 kcal mol$^{-1}$, compared with that of the extended conformer with the highest energy in the population shown in (b).

and 6 are combined to produce the complex 3–6. As a result, the NMR chemical shifts observed above may represent time averages of rapidly inter-exchanging conformations.

Conformational analysis using the molecular mechanics methods is complementary to the NMR study. The molecular mechanics calculation on the complex shows that the most stable conformation is the folded structure shown in Fig. 6a. There is an energy barrier between the folded conformers and the extended conformers shown in Fig. 6b by about 30 kcal mol$^{-1}$. Several conformers with a similar energy to the folded structure are found to have somewhat different geometry compared with the folded conformer. These supports the interpretation of 1H NMR studies. This behaviour seems to be comparable to protein–ligand interaction. In protein, global conformational change occurs in the quaternary structure upon the binding of ligands at specific sites to give activated or inactivated species. In addition, local conformation is still moving in the protein–ligand complex. In our system host–guest interaction may also be specific to lead the folded structure globally as well as flexibly to produce a mobile structure locally.

From the UV-Vis absorption and the emission spectra it is clear that the two pyridine ligands in the quinone remain coordinated to both zinc porphyrins throughout the lifetime of the excited singlet state, as supported by the emission spectra as well as the absorption behaviour. Fluorescence behaviour in the porphyrin–quinone supramolecule clearly demonstrates the photoinduced CS within the complex. Free energy change ($\Delta G_{CS}$) for CS can be calculated as follows [60–62]:

$$\Delta G_{CS} = \Delta E_{0-0} - E_{ox} + E_{red} - \Delta G_s$$

$$\Delta G_s = \frac{e^2}{4\pi\varepsilon_0} \left\{ \frac{1}{2(R_+ +)} + \frac{1}{2(R_- -)} - \frac{1}{R_{cc}} \left( \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_r} \right) \right\}$$

where $\Delta E_{0-0}$ (2.04 eV) is the energy of the 0–0 transition between the S$_1$ and the S$_0$ state of porphyrin, $E_{ox}$ and $E_{red}$ are the half-wave potentials of one-electron oxidation of porphyrins and one-electron reduction of quinone in CH$_2$Cl$_2$, respectively, $R_+$ and $R_-$ are radii of D and A, respectively, and $\varepsilon_s$ and $\varepsilon_r$ are static dielectric constants of the solvent used and when measured the redox potentials, respectively. $R_+ = 5.0$ Å for porphyrin, $R_- = 3.0$ Å for quinone, $R_{cc} = 8.3$ Å and $\varepsilon_s = \varepsilon_r = 8.9$ in CH$_2$Cl$_2$ are used for the calculation. The calculated value for $\Delta G_{CS}$ is 1.28 eV, showing that CS is possible in the complex 3–7.

Basically coordination of the pyridine ligand on the zinc porphyrin could affect the ET rates [63, 64]. The size, shape and energy of each of the zinc porphyrin molecular orbitals will change upon coordination, and such change will affect the D–A properties and orbital overlap. Gust and his coworkers reported that coordination of the electron-donating pyridine helps stabilize a positive charge on the zinc porphyrin moiety and thus lowers the energy of the charge-separated state on the basis of the Hammett study and the cyclic voltammetry [64]. The results of the Hammett study indicate that the magnitude of the effect correlates with the electron-donating ability of the substituent. Electrochemical experiments with a poorly-coordinating electrolyte, tetra-n-butylhexafluorophosphate, show that coordination of the pyridine ligand to zinc tetraphenylporphyrin lowers the first oxidation potential by 0.11 V, while a strongly coordinating electrolyte, tetra-n-butylammoniumperchlorate, masks this effect, which is consistent with our results of the electrochemical measurements [64–66]. Values of the first reduction potential of 7 in CH$_2$Cl$_2$ containing 0.1 M tetra-n-butylhexafluorophosphate are −0.34 and −0.31 V in the presence of 3. This small difference would suggest that there is no significant interaction between D and A in the ground state.

Sanders et al. reported photoinduced ET in the zinc porphyrin monomer–pyromellitimide system using a coordination bond [37]. The CS rate in our

![Fluorescence spectra of 3 (8.0 × 10$^{-7}$ M) in the presence of 100 equivalent of 6 (solid line) and 7 (dashed line) in CH$_2$Cl$_2$ exciting at the Soret band.](image)

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system is comparable to that in Sanders’ system with similar $\Delta G_{\text{CS}}$ values. A single decay component of the fluorescence due to the ET process was observed in the complex 3–7 in spite of the asymmetrical structure, i.e. $R_{cc} = 7.0$ and 9.5 Å. We could not observe the conformational-fluorescence lifetime in the complex 3–7. Owing to the fast exchange of several conformations with the lowest energy, the fluorescence decay due to the intramolecular ET might be averaged. There are two possible mechanisms for the ET process via, through-bond and through-space. If the ET is ascribed to the through-bond mechanism, it may be supported by the fact that the CS rate is similar to those in other porphyrin–quinone linked molecules with a similar separation distance as well as similar $\Delta G_{\text{CS}}$ [67, 68]. It is reasonable to suppose that in natural protein systems coordination of an amino acid residue such as histidine to metallated porphyrins can (i) perform a structural role, (ii) tune redox potentials to control the rates of various ET events and (iii) become an ET pathway. This indicates that the coordination bond is also effective in ET like the covalent bond. Alternatively, it may be interpreted that photoinduced CS occurs via through-space due to the close proximity of the quinone ligand onto the porphyrin plane. If this is the case, the geometry is similar to those in porphyrin–quinone cyclophane where ET takes place via through-space mechanism. Therefore, the ET rate might be similar compared with those in model compounds [69].

4. CONCLUSIONS

The porphyrin–quinone supramolecule has been designed and assembled using two coordination bonds. The supramolecule is selectively formed in solution and has two features in structure; it takes folded conformation to minimize non-bonding energy related to van der Waals’ and electrostatic interactions. Although the global structure is the folded conformation, it seems to be flexible and mobile within the complex. Intramolecular photoinduced ET takes place from the excited singlet state of the porphyrin to the quinone in the complex, showing that the supramolecule has a function of photoinduced CS. The present work shows that the porphyrin–quinone supramolecule is elegant nanoscale photoactive machinery where coordination chemistry and photoinduced ET chemistry are combined well. The results will provide a next step in the design of artificial photosynthetic models and the photoactive switch.

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REFERENCES

