Sandwich Dimer Complexes of Zinc Porphyrins Bearing Three-Dimensionally Oriented Redox-Active π-Conjugated Pendant Groups

Toshikazu Hirao,* Kaori Saito

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan
Fax +81(6)68797415; E-mail: hirao@ap.chem.eng.osaka-u.ac.jp

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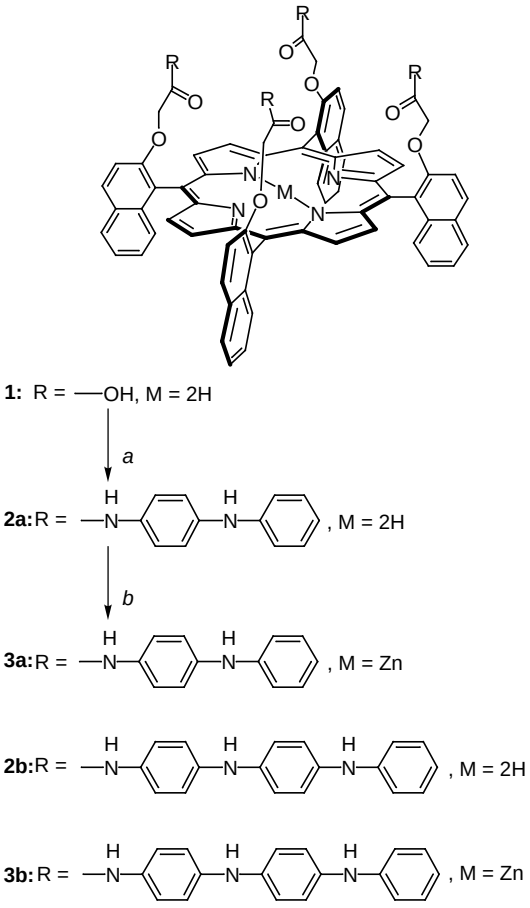
Abstract: Treatment of the zinc porphyrins bearing four dimensionally oriented phenylenediamine strands with a bidentate ligand, DABCO, led to the formation of the sandwich dimer complexes, in which the porphyrin moieties are surrounded by π-conjugated pendant groups.

Key words: zinc porphyrin, π-conjugated pendant group, dimensional control, diazabicyclooctane (DABCO), sandwich dimer complex

Dimensionally controlled arrangement of multiple redox-active sites is essential for an efficient electron transfer device in biological, material, and catalytic systems, as exemplified by linear-[1] and dendrimer-type[2] acceptor-donor systems. The architecturally ordered orientation and/or assembly of redox-active π-conjugated moieties are considered to construct a dimensionally ordered π-conjugated electronic systems. In a previous paper,[3] we demonstrated the synthesis of the porphyrins bearing four oriented phenylenediamine strands as redox-active π-conjugated ones, in which the intramolecular photoinduced electron transfer is performed from the phenylenediamine moiety to the porphyrin. Zinc porphyrins have been utilized in a variety of host-guest systems[4] and electron or energy transfer systems.[5] An additional functionality is allowed to be introduced to the vacant axial coordination site of zinc porphyrins. Use of a bidentate ligand as a secondary bridging spacer is considered to form a sandwich dimer-type zinc porphyrin-ligand complex.[6] According to this type of molecular design, a dimensionally ordered π-conjugated system, in which the central porphyrin-bridging ligand-porphyrin moiety is surrounded by π-conjugated pendant groups, is envisioned to be constructed by using the porphyrins bearing four oriented phenylenediamine strands. We herein report the synthetic aspect of such a triad.

The zinc porphyrin unit for a sandwich dimer complex was synthesized as shown in Scheme 1. The free base porphyrin **2a** was obtained by condensation of **1** and *N*-phenyl-1,4-phenylenediamine using EDCI·HCl {*N*-[3-(dimethylamino)propyl]-*N*'-ethylcarbodiimide hydrochloride} and HOBt (1-hydroxybenzotriazole).[3,7] Zincation of **2a** was performed by treatment with zinc(II) acetate dihydrate to give **3a** in 61% yield from **1**.[8] Zinc(II) species is likely to be introduced selectively from the side opposite to the anilinoanilino strand side because the corresponding αβαβ atropisomer was not metallated efficiently in less than 24% yield from the free base porphyrin. The zinc porphyrin **3a** is soluble in a less polar solvent such as dichloromethane, chloroform, and toluene. The structure of **3a** was determined by ^{1}H NMR, FT-IR, and MS spectrometry. In the ^{1}H NMR spectra of **3a**, the phenylene protons of the anilinoanilino moiety close to the porphyrin ring appeared as broad signals, suggesting conformational restriction of the pendant groups as observed in **2a**.[3]



Scheme 1 *a* EDCI·HCl, HOBt; then *N*-phenyl-1,4-phenylenediamine. *b* $Zn(OAc)_2 \cdot 2H_2O$.

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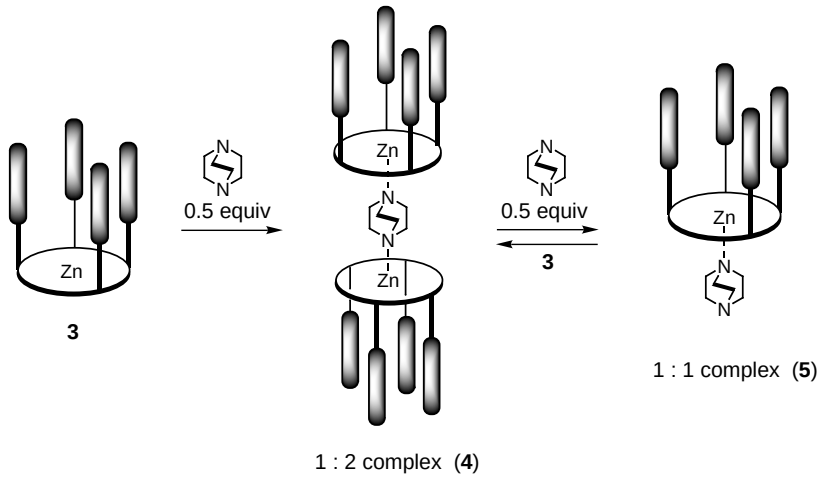


Scheme 2 Complexation of the zinc(II) porphyrin **3** with DABCO.

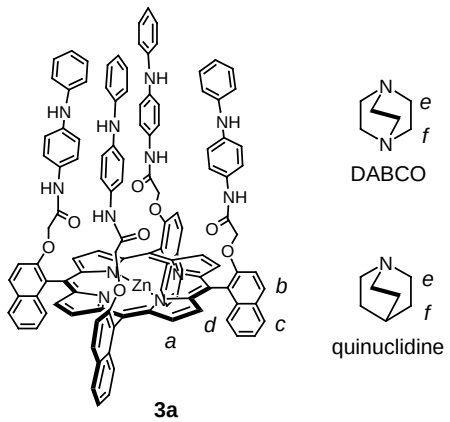
Diazabicyclooctane (DABCO) was used here as a bridging ligand because of its relatively strong basicity. Complexation of the zinc porphyrin **3a** with DABCO was investigated by ^{1}H NMR titration. When a portion of DABCO was added to a CD_2Cl_2 solution (5.0×10^{-4} M) of **3a** (Scheme 2), new signals appeared and grew up until the addition of 0.5 molar equiv of DABCO. These new signals are assigned to be the 2:1 complex **4a** because the methylene protons, H_e and H_f, of DABCO were highly shielded (δ = –3.57 ppm) as shown in the Table and the Figure. Then, the signals decreased with more than 0.5 molar equiv of DABCO, and were replaced by the other new signals at 1.30 ppm and –1.96 ppm on the addition of 1.0 molar equiv of DABCO. This species is considered to be assigned to the 1:1 complex **5a**, which was ascertained by comparison of the spectral data of the 1:1 complex of **3a** with quinuclidine possessing only one coordination site. The shifts of the protons, H_e and H_f, and those of the porphyrin moiety were almost the same in both complexes. DABCO is coordinated to the lower side (the naphthyl side) of the 1: complex, which was confirmed by NOE measurement in CD_2Cl_2 (5.0×10^{-4} M). The β-pyrrole and naphthyl protons of **3a** were shifted to an upper-field in the case of the 2:1 complex **4a** than the 1:1 complex **5a** [δ**4a**-δ**5a** : –0.16 (H_a), –0.06 (H_b), and –0.14 (H_c) ppm]. Thus-observed shift of the β-pyrrole protons is probably accounted for by the proximity of two porphyrin π-planes.[6,9] The 2: 1 complex **4a** was actually isolated almost quantitatively by treatment with 0.5 molar equiv of DABCO at a high concentration and recrystallization from dichloromethane–toluene.[10] It should be noted that the addition of **3a** to the solution of **5a** also led to the reformation of **4a**.

The porphyrin **3b** bearing the longer redox-active π-conjugated chains was similarly synthesized by amidation of **1** with *N*-(4-aminophenyl)-*N'*-phenyl-1,4-phenylenediamine[11] and metallation with zinc(II) acetate dihydrate.[12,13] Complexation of **3b** with DABCO resulted in a dramatic change in the ^{1}H NMR and absorption spectra. The 2:1 complex **4b**, however, is less soluble in dichloromethane to precipitate almost quantitatively on the addition of DABCO to the solution of **3b** at a high concentration. The similar complexation behavior was

Table Chemical Shifts of **3a** and Complexes with DABCO or Quinuclidine in ^{1}H NMR (CD_2Cl_2, 5.0×10^{-4} M, 600 MHz)[a]

Complex					Ligand	
	H_a	H_b	H_c	H_d	$H_e(\Delta\delta^b)$	$H_f(\Delta\delta^b)$
3a	8.71	8.28	8.12	7.41		
4a[c]	8.47	8.21	8.00	[d]	–3.57 (–6.28)	
5a	8.63	8.27	8.14	7.53	–1.96 (–4.67)	1.30 (–1.41)
3a–Quinuclidine	8.62	8.27	8.14	7.53	–1.88 (–4.67)	0.10 (–1.40)
4b[c,e]	8.42	8.12	7.90	[d]	–3.67 (–6.38)	

[a] Chemical shifts in ppm from tetramethylsilane as an internal standard.
[b] $\Delta\delta$ is difference of chemical shift from uncomplexed free DABCO or quinuclidine.
[c] Most of the signals appeared as broadened signals.
[d] Chemical shift was not determined because of overlap with the signals of other protons.
[e] Chemical shifts in $CDCl_3$ solution (5.0×10^{-4} M).



Figure

observed in a chloroform solution without precipitating as observed in the complexation of **3a** (Table).[14]

In summary, the sandwich-type π-conjugated systems were found to be constructed by the complexation of the zinc porphyrins bearing four dimensionally oriented redox-active π-conjugated pendant groups with bidentate bridging ligand, DABCO. Thus-obtained complexes are considered to be a unique electron transfer system composed of the electron acceptor moiety surrounded by electron donating π-conjugated pendant groups. The redox-switchable properties of the π-conjugated pendant groups are presumed to make these systems more promising as a redox-active system. Further investigation including applications as a redox-active system is now in progress.

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(7) EDCI·HCl (22.3 mg, 0.117 mmol) and HOBt (59.4 mg, 0.117 mmol) were added to a THF solution (10 mL) of **1** (21.6 mg, 0.0194 mmol) at room temperature and the solution was stirred for 30 min. Then, a THF solution (15 mL) of *N*-phenyl-1,4-phenylenediamine (21.5 mg, 0.117 mmol) was added to the reaction mixture, which was stirred for 24 h and then evaporated. Purification by column chromatography on silica gel using solvents with gradient from dichloromethane to dichloromethane–ethyl acetate (8:2 v/v) and recrystallization from THF–methanol gave **2a** in 68% yield.

(8) A THF solution (5 mL) of **2a** (20.0 mg, 11 μmol) was added to a methanol solution of zinc(II) acetate dihydrate (10.3 mg, 55 μmol), which refluxed under argon for 12 h and then evaporated. Purification by column chromatography on alumina (acetone–methanol 95:5 v/v) gave **3a** in 90% yield. **3a**: pinkish light brown solid; mp 223–225 °C(uncorrected); R_f = 0.60 (SiO_2, ethyl acetate); IR (KBr) 3380, 3051, 1678, 1593, 1511, 1496, 1323, 1271, 1109, 799 cm^{-1}; ^1H NMR (600 MHz, CD_2Cl_2) δ 8.71 (br s, 8 H), 8.28 (d, 4 H, *J* = 9.2 Hz), 8.12 (d, 4 H, *J* = 8.5 Hz), 7.45 (dd, 4 H, *J* = 8.5, 6.6 Hz), 7.41 (d, 4 H, *J* = 8.7 Hz), 7.35 (d, 4 H, *J* = 9.2 Hz), 7.23 (dd, 4 H, *J* = 8.7, 6.6 Hz), 7.13 (dd, 8 H, *J* = 8.2, 7.3 Hz), 6.80 (t, 4 H, *J* = 7.3 Hz), 6.64 (d, 8 H, *J* = 8.2 Hz), 5.71 (br s, 4 H), 5.67–5.60 (br, 8 H), 5.28 (bs, 4 H), 5.24–5.12 (br, 8 H), 3.60 (br s, 8 H); MS (FAB) *m/z* 1838.8 $(M + 2H)^+$; UV-vis(dichloromethane) λ_{max} (log ε) 549 (4.34), 430 (5.45), 303 (4.95); Anal. Calcd. for $C_{116}H_{84}N_{12}O_8Zn \cdot H_2O$: C, 75.01; H, 4.67; N, 9.05. Found: C, 74.90; H, 4.78; N, 8.91.

(9) The reason for the upper shift of H_b, H_c, and H_d remains obscure, but it may be due to the shield effect of the naphthalene rings.

(10) **4a**: purple solid; mp 235–238 °C(uncorrected); IR (KBr) 3379, 3051, 1679, 1594, 1511, 1495, 1322, 1269, 1229, 1108, 1063, 798 cm^{-1}; ^1H NMR: See Table; MS (TOF) *m/z* 1841.3 [M– **3a** –112(DABCO) + 2]$^+$.

(11) *N*-(4-Aminophenyl)-*N'*-phenyl-1,4-phenylenediamine was prepared in 47% yield by oxidative coupling of phenylenediamine with *N*-phenyl-1,4-phenylenediamine, followed by reduction with hydrazine: Wei, Y.; Yang, C.; Ding, T. *Tetrahedron Lett.* **1996**, *37*, 731.

(12) Purification of **2b** was performed by column chromatography on silica gel eluting with ethyl acetate and further reprecipitation from ether to give **2b** in 68% yield. **2b**: brown solid; mp 204–206 °C(uncorrected); R_f = 0.45 (SiO_2, ethyl acetate); IR (KBr) 3380, 3321, 3044, 1675, 1598, 1505, 1494, 1302, 1108, 802 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 8.56 (bs, 8 H), 8.33 (d, 4 H, *J* = 9.3 Hz), 8.11 (d, 4 H, *J* = 8.4 Hz), 7.87 (bs, 4 H), 7.75 (bs, 4 H), 7.65 (d, 4 H, *J* = 9.3 Hz), 7.48 (bs, 4 H), 7.38 (dd, 4 H, *J* = 8.4, 6.8 Hz), 7.16–7.10 (m, 12 H), 6.94–6.89 (m, 20 H), 6.77 (d, 8 H, *J* = 8.5 Hz), 6.68 (t, 4 H, *J* = 7.3 Hz), 6.20–6.10 (br, 16 H),

4.21 (bs, 8 H), –2.04 (bs, 2 H); MS (TOF) *m/z* 2141.9 (M + H)$^+$; UV-vis ($CHCl_3$) λ_{max} (log ε) 645 (3.32), 590 (3.74), 547 (3.54), 517 (4.23), 428 (5.29), 317 (5.03); Anal. Calcd. for $C_{140}H_{106}N_{16}O_8 \cdot 2H_2O$: C, 77.26; H, 5.09; N, 10.30. Found: C, 77.39; H, 4.96; N,10.16.

(13) **3b**: pinkish light brown solid; mp 214–216 °C(uncorrected); R_f = 0.20 (SiO_2, ethyl acetate); IR (KBr) 3377, 3046, 1678, 1598, 1510, 1496, 1304, 1271, 1109, 801 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (bs, 8 H), 8.19 (d, 4 H, *J* = 9.3 Hz), 8.03 (d, 4 H, *J* = 8.5 Hz), 7.41 (dd, 4 H, *J* = 8.5, 6.6 Hz), 7.37 (d, 4 H, *J* = 8.9 Hz), 7.32 (d, 4 H, *J* = 9.3 Hz), 7.20 (dd, 4 H, *J* = 8.9, 6.6 Hz), 7.16 (dd, 8 H, *J* = 8.3, 7.3 Hz), 6.92–6.79 (m, 16 H), 6.83 (t, 4 H, *J* = 7.3 Hz), 6.58 (d, 8 H, *J* = 8.3 Hz), 5.71 (bs, 4 H), 5.60–5.51 (br, 8 H), 5.43 (bs, 4 H), 5.25–5.15 (br, 8 H), 5.06 (bs, 4 H), 3.66 (bs, 8 H); MS (TOF) *m/z* 2205.1 (M + H)$^+$; UV-vis ($CHCl_3$) λ_{max} (log ε) 549 (4.25), 429 (5.38), 315 (4.99); Anal. Calcd. for $C_{140}H_{104}N_{16}O_8Zn$: C, 76.30; H, 4.76; N, 10.17. Found: C, 76.29; H, 4.93; N, 10.13.

(14) **4b**: purple solid; mp >300 °C; IR (KBr) 3377, 3031, 1684, 1596, 1508, 1464, 1320, 1298, 1252, 1212, 1109, 1070, 798 cm^{-1}; ^{1}H NMR: See Table; MS (TOF) *m/z* 2205.7 [M – **3b** – 112(DABCO) + 2H]$^+$.