Bull. Chem. Soc. Jpn., ***72***, *1263—1271 (1999)* 1263

Aggregation, Complexation with Guest Molecules, and Mesomorphism of Amphiphilic Phthalocyanines Having Four- or Eight Tri(ethylene oxide) Chains

Nagao Kobayashi,* Ryuji Higashi, Kazuyuki Ishii, Kazuaki Hatsusaka,† and Kazuchika Ohta†

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578

†Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567

(Received November 30, 1998)

Zinc and metal-free amphiphilic phthalocyanines (pcs) substituted by four or eight tri(ethylene oxide) chains (3,6,9-trioxadecyloxy groups) {(H_2(4EGpc), [Zn(4EGpc)], H_2(8EGpc), and [Zn(8EGpc)] in Fig. 1)} have been prepared in order to study their aggregation in water, dioxane, and dioxane/water mixtures, their complexation phenomena with guest molecules in benzene, and mesomorphism in the neat state. In particular, tetra-substituted pcs have C_{4h} symmetry and do not contain other positional isomers. [Zn(8EGpc)] forms aggregates in water and water–organic solvent mixtures; the extent of this was examined by electronic absorption and fluorescence spectroscopy. ^{1}H NMR and fluorescence spectroscopy indicated that H_2- and [Zn(8EGpc)] form inclusion complexes with quinones in benzene via hydrogen bonding. Benzoquinones with more hydroxy groups form complexes more effectively, plausibly laterally outside of the pc plane. From the higher field shift of the ^{1}H singals of 2,2′-dihydroxy-1,1′-binaphthyl (BINAP) in the presence of [Zn(8EGpc)], BINAP molecules were suggested to lie above or below the pc plane. The mesomorphism of H_2(8EGpc), [Zn(4EGpc)], and H_2(4EGpc) was studied. In the case of H_2(8EGpc), the discotic hexagonal ordered columnar (D_{ho}) phase was seen in the range of from room temperature to 265 °C. However, liquid-crystalline phases were not observed for H_2(4EGpc) and [Zn(4EGpc)].

Phthalocyanines (pcs) have been the subject of intensive study in many fields, such as dyes, pigments, deodorants, charge-generation materials in photocopiers, non-linear optics, optical disks, removal of sulfur from oil, sensors, synthetic metals, photodyamic therapy of cancer, and liquid crystals.[1)] In particular, pcs substituted with linear or cyclic oligo(oxyethylene) units are interesting, because this unit endows amphiphilicity,[2)] lowered melting points, and occasionally cation complexation ability, as seen in crown ether-substituted pcs.[3)] However, many properties of these molecules have so far remained unelucidated. For example, complexation with organic guest molecules is not known. In addition, although the liquid-crystalline properties of pcs substituted by eight[4)] or six[5)] long chains have been examined by several groups, those of single isomers of pcs substituted by four long chains have not been reported,[6)] probably because they are mixtures of several positional isomers (tetra-substituted metallophthalocyanines are generally mixtures of four isomers, and if a compound is a mixture of isomers,[7)] it will not give a sharp phase transition temperatures). Accordingly, in this context, we decided to prepare single isomers of octakis- and tetrakis {*linear*-oligo(oxyethylene)}pcs, as shown in Fig. 1, and examined their aggregation properties in water, dioxane, and water/dioxane mixtures, as well as their complexation properties with benzoquinones (BQs) and optically active 2,2′-dihydroxy-1,1′-binaphthyls (BINAP) in benzene, as well as their mesomorphism at various temperatures. The use of benzoquinone and optically active molecules is appropriate in studying complexation phenomina, since the former quench the flourescence of pcs and the latter produce induced circular dichroism (ICD) upon complexation.

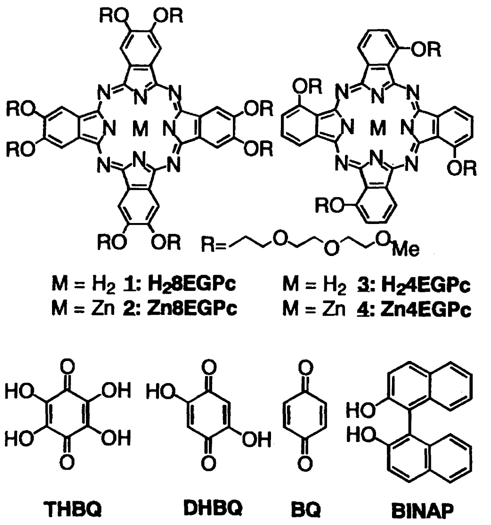

Fig. 1. Structures and abbreviations of compounds in this study. Names of some of the compounds are introduced in the text.

Experimental

Measurement. Electronic absorption spectra were recorded with a Hitach 330LC spectrophotometer, and magnetic circular dichroism (MCD) measurements were made with a JASCO J-400X spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields up to 1.53 T (T = tesra) with parallel and then antiparallel fields. The magnitude was expressed in terms of the molar ellipticity per tesla, $[\Theta]_M/10^4 \mathrm{deg\,mol^{-1}\,dm^3\,cm^{-1}\,T^{-1}}$. Fluorescence spectra were recorded with a Hitachi F-4500 spectrofluorimeter. Fluorescence quantum yields (Φ_f) were determined by the use of H_2(pc) and [Zn(pc)], (Φ_f = 0.60 and 0.30, respectively)[8a] and quinine sulfate in 1 equiv H_2SO_4 (Φ_f = 0.55 at 296 K)[8b,8c] as standards. Data were obtained by a comparative calibration method using the same excitation wavelength and absorbance for H_2(8EGpc), [Zn(8EGpc)], H_2(4EGpc), and [Zn(4EGpc)] and the calibrants as well as the same emission energy. Fluorescence decay curves were obtained by a Horiba NAES-550 series, using combinations of glass filters and a monochromator for monitoring the emission. The lifetimes were determined from the decay curves by using a least-squares method. All sample solutions for fluorescence measurements were purged with nitrogen before measurements. The 400 MHz ^{1}H NMR spectra were recorded with a JEOL GSX-400 spectrometer using $CDCl_3$ and C_6D_6 as solvents. FTIR spectra were recorded on a Shimadzu FTIR-8100M spectrometer using KBr discs. The phase-transition behaviors of these compounds were observed using a polarizing microscope equipped with a heating plate controlled by a thermoregulator (Mettler FP80 and FP82) and measured with Shimadzu DSC-50 differential scanning calorimeters. To establish the mesophases, powder X-ray patterns were measured with Cu *Kα* radiation using a Rigaku Geigerflex equipped with a hand-made heating plate controlled by a thermoregulator.[9]

Materials. 3-(1,4,7,10-Tetraoxaundecyl)phthalonitrile. 3-Nitrophthalonitrile (3.0 g, 17.3 mmol), triethyleneglycol monomethylether (3.67 g, 22.4 mmol), and dry potassium carbonate (2.4 g 17.4 mmol) were stirred in dry dimethylformamide under a slow stream of nitrogen for 24 h at room temperature. The solvent was removed under reduced pressure and the residue was purified on a silica-gel column using chloroform as an eluent. Evaporation of the solvent, followed by recrystallization from methylene chloride–hexane, gave 3.41 g (68%) of white powder of the desired nitrile. Mp = 58—59 °C. Found: C, 61.85; H, 6.21; N, 9.68%. Calcd for $C_{15}H_{18}O_4$: C, 62.06; H, 6.25; N, 9.65%. IR (KBr) 2899 (ϕ), 2228 cm^{-1} (CN). ^{1}H NMR ($CDCl_3$,TMS) δ = 3.37—4.33 (m, 15H), 7.30—7.65 (m, 3H).

2,3,9,10,16,17,23,24-Octakis(1,4,7,10-tetraoxaundecyl) phthalocyanine, H_2(8EGpc), 1. After 4,5-bis(1,4,7,10-tetraoxaundecyl)phthalonitrile[3a] (0.5 g, 1.11mmol) and lithium (1.88 mg, 0.27 mmol) were refluxed in hexanol (3 ml) for 2 h, the solvent was removed by an evaporator. The residue was imposed on an alumina column (activity III) using chloroform : methanol = 20 : 1 v/v as an eluent and further on a gel permeation column (BIO-BEADS S-X1) using chloroform as an eluent to give a dark-green compound. Further, this was reprecipitated from chloroform–hexane six times to give pure H_2(8EGpc) (0.18 g, 36% yield). Found: C, 58.27; H, 7.75; N, 6.15%. Calcd for $C_{88}H_{130}O_{32}N_8$: C, 58.33; H, 7.23; N, 6.18%. ^{1}H NMR (C_6D_6): δ = 3.26 (s, 24H), 3.56 (t, 16H), 3.75 (t, 16H), 3.87 (t, 16H), 4.02 (t, 16H), 4.19 (t, 16H), 4.46 (t, 16H), 8.38 (s, 8H).

2,3,9,10,16,17,23,24-Octakis(1,4,7,10-tetraoxaundecyl) phthalocyaninatozinc(II), [Zn(8EGpc)], 2. H_2(8EGpc) (0.04 g, 0.022 mmol) and zinc chloride (0.04 g, 0.29 mmol) were refluxed in a mixed solution of ethanol (0.5 ml) and 1,2-dichloroethane (0.5 ml) for 10 h. The solvent was removed under reduced pressure, and the resultant solid was passed through an alumina column (activity III) using chloroform : methanol = 20 : 1 v/v and gel permeation column (BIO-BEADS S-X1) using chloroform as the eluent. Evaporation of the solvent, followed by reprecipitation from chloroform-hexane eight times, afforded 0.03 g (73%) of green [Zn(8EGpc)]. Found: C, 55.72; H, 7.31; N, 6.11%. Calcd for $C_{88}H_{128}O_{32}N_8Zn$: C, 56.36; H, 6.88; N, 5.97%. ^{1}H NMR (C_6D_6) δ = 3.22 (s, 24H), 3.47 (t, 16H), 3.62 (t, 16H), 3.68 (t, 16H), 3.76 (t, 16H), 3.91 (t, 16H), 4.24 (t, 16H), 8.44 (s, 8H).

1,8,15,22-Tetrakis(1,4,7,10-tetraoxaundecyl)phthalocyanine, H_2(4EGpc), 3. 3-(1,4,7,10-Tetraoxaundecyl)phthalonitrile, (0.5 g, 1.72 mmol) and lithium (0.6 g, 86.5 mmol) were stirred in hexanol (50 ml) for 1 week at room temperature under a nitrogen atmosphere. The solvent was removed using an evaporator and the residue was purified on an alumina column (activity III) using toluene : methanol = 10 : 1 v/v and preparative thin layers of alumina and a gel permeation column (BIO-BEADS S-X1) using chloroform as the common eluent. Evaporation of the solvent, followed by recrystallization from toluene–hexane six times, gave 0.38 g (76%) of a blue powder of H_2(4EGpc). The following ^{1}H NMR data indicate that the long alkyl chains are indeed linked in a single-handed manner.[11] Found: C, 62.32; H, 6.60; N, 9.66%. Calcd for $C_{60}H_{74}O_{16}N_8$: C, 61.95; H, 6.41; N, 9.63%. ^{1}H NMR ($CHCl_3$) δ = -0.33 (s, 2H), 3.32 (s, 12H), 3.51 (t, 8H), 3.69 (t, 8H), 3.85 (t, 8H), 4.19 (t, 8H), 4.56 (t, 8H), 4.95 (t, 8H), 7.66 (d, 4H), 8.12 (t, 4H), 9.10 (d, 4H).

1,8,15,22-Tetrakis(1,4,7,10-tetraoxaundecyl)phthalocyaninatozinc(II), [Zn(4EGpc)], 3. H_2(4EGpc) (0.2 g, 0.17 mmol) and zinc chloride (0.2 g, 1.47 mmol) were refluxed in a mixed solvent of ethanol (1 ml) and 1,2-dichloroethane (1 ml) for 10 h. The solvent was evaporated and the resultant solid was purified using an alumina column (activity III), an alumina preparative thin layer and a gel permeation column (BIO-BEADS S-X1) using toluene : methanol = 10 : 1 v/v as the common eluent. After evaporation of the solvent under a reduced pressure, the residue was recrystallized from toluene-hexane six times to give 0.17 g (82%) of blue [Zn(4EGpc)]. The following NMR data clearly indicate that the resultant ZnEGpc has C_{4h} symmetry.[11] Found: C, 58.22; H, 6.50; N, 8.92%. Calcd for $C_{60}H_{72}O_{16}N_8Zn$: C, 58.75; H, 5.92; N, 9.13%. ^{1}H NMR (C_6D_6) δ = 3.00 (s, 12H), 3.26 (t, 8H), 3.43 (t, 8H), 3.55 (t, 8H), 3.82 (t, 8H), 4.09 (t, 8H), 4.51 (t, 8H), 7.81 (s, 4H), 8.89 (s, 4H).

Results and Discussion

1. Spectra and Aggregation of [Zn(8EGpc)] and H_2(8EGpc). The electronic absorption, magnetic circular dichroism (MCD), and fluorescence spectra of [Zn(8EGpc)] and H_2(8EGpc), recorded in dioxane and water, are shown in Figs. 2 and 3, respectively. Judging from the shape of the electronic absorption and MCD spectra,[10] both [Zn(8EGpc)] and H_2(8EGpc) clearly exist as monomeric species in dioxane. However, in water the spectra, particularly the Q-band region, become broader and weak, which are the characteristics of aggregated species.[10,12—14] From the Q-band position in water, which appears at both the shorter (629 nm) and the longer wavelength (679 nm) sides of the Q band in dioxane (670 nm), the existence of mainly a cofacial-type aggregation, mixed with some amount of slipped-stack type species, are conjectured. The broad, weak peak at around 425 nm appears to correspond to an n–π transition of ether oxygen, since this band is seen for pcs containing alkoxy groups, and

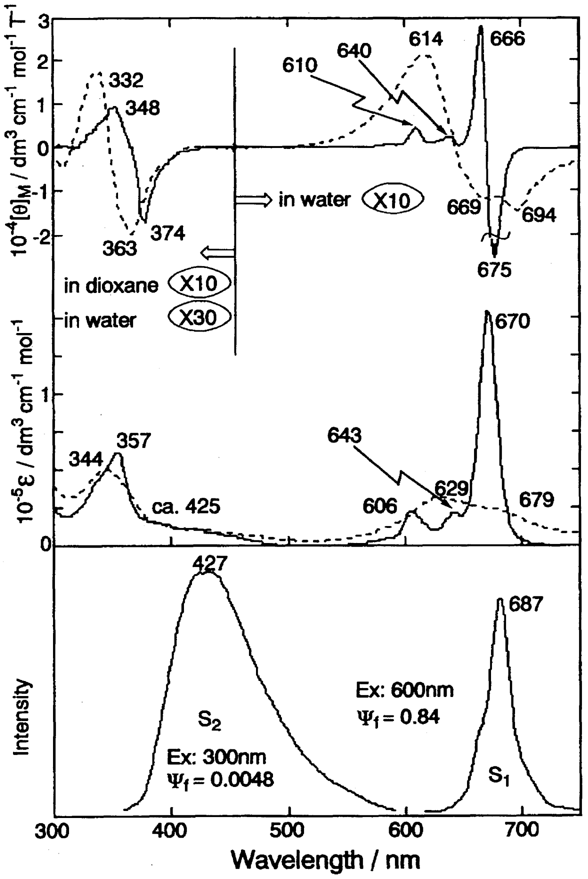

Fig. 2. Magnetic circular dichroism (MCD) (top), electronic absorption (middle), and emission (bottom) spectra of [Zn-(8EGpc)] in dioxane (solid lines) and water (broken lines). Emission spectra were recorded in dioxane, although they are drawn by solid lines. Excitation wavelengths and quantum yields are shown. There is no intensity relationship between S_1 and S_2 emissions.

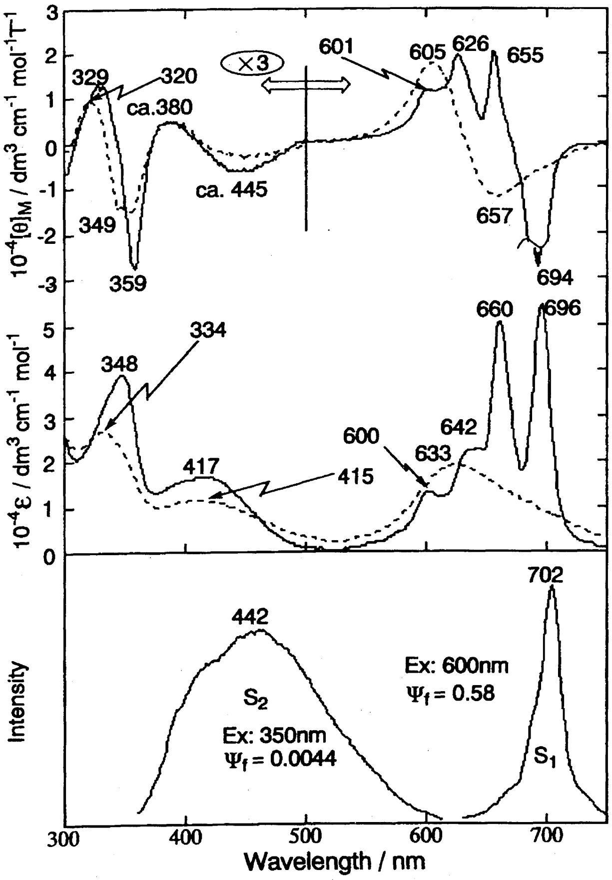

Fig. 3. Magnetic circular dichroism (MCD) (top), electronic absorption (middle), and emission (bottom) spectra of H_2(8EGpc) in dioxane (solid lines) and water (broken lines). Emission spectra were recorded in dioxane, although they are drawn by solid lines. Excitation wavelengths and quantum yields are shown. There is no intensity relationship between S_1 and S_2 emissions.

becomes stronger with increasing number of alkoxy groups.[3)] For some reason, the corresponding band in H_2(8EGpc) (with a peak at 417 nm) is fairly strong. The MCD spectrum of [Zn(8EGpc)] contains Faraday *A*-terms corresponding to the Q_{0-0} and Soret bands.[10,12)] However, the *A*-terms in the Soret region are not symmetrical with respect to the peak at 357 nm due to the superimposition of several transitions present in this region.[15,16)] In the case of H_2(8EGpc), all transitions are contributions of Faraday *B*-terms.[10)] Thus, MCD peaks and troughs appear corresponding roughly to the absorption peaks and shoulders. Theoretically, unsymmetrical dispersion curves in the Q_{0-0} and Soret regions are attributed to the mutually interacting Faraday *B*-terms.[17)] The MCD spectra of aggregates were observed, shifted to the blue compared with those of monomers. In contast to the case of the monomer, both the metal-free and Zn complexes show Faraday *A*-term-like spectra corresponding to the Q_{0-0} absorption peak. Previously, it was pointed out, using low-symmetrical pc and pc analogs,[18)] that the band shape of the Q band MCD of cofacial dimers is insensitive to the molecular symmetry of the constituent monomers. Accordingly, this curve also seems to have appeared for the same reason, although theoretically it is caused by the superimposition of Faraday *B*-terms.[10,19)] A negative MCD trough observed at 694 nm of the [Zn-(8EGpc)] aggregates is a contribution from a Faraday *B*-term attributable to slipped stack species.[12a)]

The emission spectra from both the S_1 and S_2 states were observed in dioxane, but no emission was detected in water due to aggregation of the species.[3,18,20)] Although S_2 emision is relatively rare in general pcs, pcs containing alkoxyl groups often show not only S_1, but also S_2, emissions.[21)] The quantum yields (Φ_f) of S_2 fluorescence are 0.0048 and 0.0044 for [Zn(8EGpc)] and H_2(8EGpc), respectively, which are similar in order to those reported to date.[18,21,22)] The Φ_f values of S_1 fluorescence are 0.84 and 0.58 for [Zn(8EGpc)] and H_2(8EGpc), respectively.

In order to elucidate the aggregated structures more quantitatively, the electronic absorption in the Q band region and S_1 fluorescence emission spectra were recorded in a mixed solvent of water and dioxane, and analysed. The results for [Zn(8EGpc)] are displayed in Fig. 4. As can be inferred from the data in Figs. 2 and 3, the electronic absorption spectra are

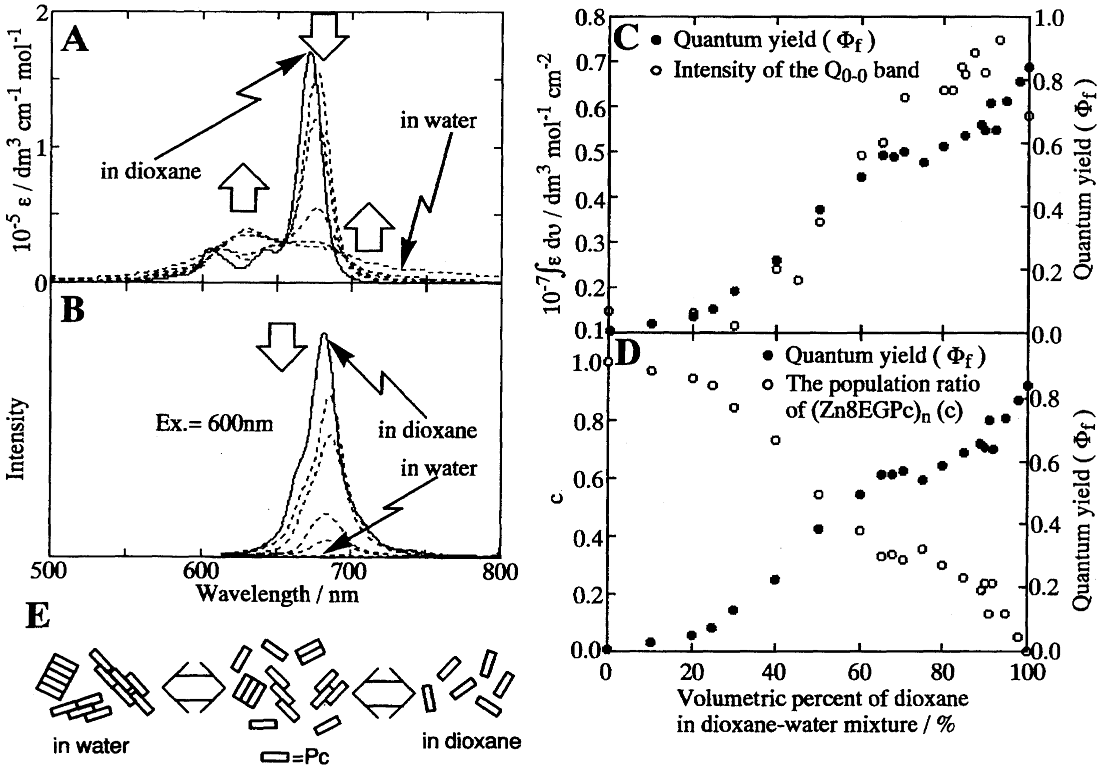

Fig. 4. (A) Electronic absorption in the Q band region and (B) S$_1$ emission spectra of [Zn(8EGpc)] in dioxane (solid lines), water (broken lines), and their mixtures (broken lines). (C) Quantum yields (Φ_F; filled circles) and the intensity of the Q$_{0-0}$ band (empty circles) of [Zn(8EGpc)] in dioxane, water, and their mixtures. $\int \varepsilon \mathrm{d}\nu$ is the area of the Q$_{0-0}$ absorption band. (D) Quantum yields (Φ_F; filled circles) and the population ratio of ([Zn(8EGpc)])$_n$, obtained using Eqs. 6 and 7. (E) Proposed structures of pc in dioxane, water, and their mixtures.

remarkably broadened by increasing the proportion of water (Fig. 4A). On the other hand, the change in the shape of the S$_1$ emission spectrum is relatively small (Fig. 4B), although the Φ_f of the S$_1$ emission decreased along with an increase in the ratio of water (Fig. 4C). The observed Φ_f values ($\Phi_{f(obs)}$) in our system is expressed as follows.

$$\Phi_{f(obs)} = a\Phi_{f([Zn(8EGpc)])} + b\Phi_{f([Zn(8EGpc)])+H_2O} + c\Phi_{f([Zn(8EGpc)])n}, \quad (1a)$$

$$\Phi_{f(i)} = k_{r(i)}/(k_{nr(i)} + k_{r(i)}), \quad (1b)$$

where $\Phi_{f([Zn(8EGpc)])}$, $\Phi_{f([Zn(8EGpc)]+H_2O)}$, and $\Phi_{f([Zn(8EGpc)])n}$ are the Φ_f values of [Zn(8EGpc)] in dioxane, hydrated [Zn(8EGpc)], and aggregated [Zn(8EGpc)], respectively, and a, b, and c are the population ratios for [Zn(8EGpc)], hydrated [Zn(8EGpc)], and aggregated [Zn(8EGpc)], respectively (a+b+c = 1). $k_{r(i)}$ and $k_{nr(i)}$ are the radiative and nonradiative decay rate constants of species i, respectively. Since the line shapes of the emission spectra do not change significantly, we can postulate that the emission from the aggregated [Zn(8EGpc)] is absent, or at least negligebly small. Then, assuming $\Phi_{f([Zn(8EGpc)])n} = 0$, Eq. 1a is rewritten as

$$\Phi_{f(obs)} = a\Phi_{f([Zn(8EGpc)])} + b\Phi_{f([Zn(8EGpc)])+H_2O}. \quad (2)$$

In order to clarify the difference between $\Phi_{f([Zn(8EGpc)])}$ and $\Phi_{f([Zn(8EGpc)]+H_2O)}$, the effect of hydration was examined. In general, the radiative decay rate constant, (k_{ri}), is represented as[23)]

$$k_{ri} = 3 \times 10^{-9} \times \nu^2 \int \varepsilon \mathrm{d}\nu, \quad (3)$$

where ν is the wave number of the absorption peak and ε is the extinction coefficient. The integration values, ($\int \varepsilon \mathrm{d}\nu$), are given in Fig. 4D. The $\int \varepsilon \mathrm{d}\nu$ of the Q$_{0-0}$ band for a 20 (and also 30) % aqueous solution is almost the same as that for a dioxane solution. Therefore, we can deduce that $k_{r([Zn(8EGpc)])}$ nearly equals $k_{r([Zn(8EGpc)]+H_2O)}$. In order to obtain the k_{nr} value experimentally, the fluorescence lifetime (τ) was measured. The estimated lifetimes were 4.68, 4.91, 4.90, and 4.78 ns for 100, 80, 60, and 40 volumetric % solutions of dioxane. Therefore, we can conclude that the lifetimes are not influenced by the ratio between water and dioxane, i.e. $\tau_{([Zn(8EGpc)])} \cong \tau_{([Zn(8EGpc)]+H_2O)}$. τ is generally expressed using k_{ri} and k_{nri} as follows:[24)]

$$\tau_i = 1/(k_{ri} + k_{nri}). \quad (4)$$

From the absorption spectroscopic data in Fig. 4C (i.e. by comparison with the Q$_{0-0}$ intensity in 0, 20, and 30% aqueous solutions), $k_{r([Zn(8EGpc)])} \cong k_{r([Zn(8EGpc)]+H_2O)}$. Since $\tau_{([Zn(8EGpc)])} \cong \tau_{([Zn(8EGpc)]+H_2O)}$; therefore, $k_{nr([Zn(8EGpc)])} \cong k_{nr([Zn(8EGpc)]+H_2O)}$. Hence, we come to the conclusion that $\Phi_{f([Zn(8EGpc)])} \cong \Phi_{f([Zn(8EGpc)]+H_2O)}$. Using this relationship, Eq. 2 is reevaluated as

$$\Phi_f = (a+b)\,\Phi_{f([Zn(8EGpc)])}. \qquad (5)$$

Therefore, using $a+b = 1-c$, the population ratio of $([Zn(8EGpc)])_n$ among the excited species (c) is expressed as

$$c = 1-(\Phi_f/\Phi_{f([Zn(8EGpc)])}). \qquad (6)$$

Further, the absorbance at 600 nm, at which samples were excited, has little dependence on the proportion of water ($<15\%$) (Fig. 4B). Consequently, the following important equation is derived:

$$c = [([Zn(8EGpc)])n]/([[Zn(8EGpc)]] + [[Zn(8EGpc)] + H_2O] + [([Zn(8EGpc)])_n]). \qquad (7)$$

The values of c, obtained by using Eqs. 6 and 7, are shown in Fig. 4D (empty circles). This figure shows that the degree of aggregation is dependent on the proportion of water.

2. Complexation with Benzoquinone Derivatives. To investigate the possibility of complexation between tri(ethylene oxide) chain-substituted pcs and benzoquinone derivatives, the extent of quenching of the S_1 fluorescence of [Zn(8EGpc)] and the chemical shift of protons of [Zn(8EGpc)] and H_2(8EGpc) were examined in the presence of benzoquinone (BQ), 2,5-dihydroxybenzoquinone (DHBQ), or 2, 3, 5, 6-tetrahydroxybenzoquinone (THBQ) in benzene. The dependence of the fluorescence intensity on the quinone concentration is shown in Fig. 5A. In the case of BQ, which has no hydroxyl group, the fluorescence of [Zn(8EGpc)] is quenched only slightly with increasing [BQ]. In the presence of DHBQ, which has two hydroxyl groups, the Φ_f changes to a moderate extent with increasing [DHBQ]. However, when THBQ, which has four hydroxyl groups, is added to the system, the Φ_f decreases markedly with increasing [THBQ].[25] Consequently, it is found that the BQ derivatives substituted with many hydroxyl groups can quench the S_1 state of [Zn(8EGpc)] effectively.[26] Effective quenching of fluorescence emission is observed when quencher molecules (in this case BQ) approach or are particularly linked to the pc skeleton. Thus, for example, pcs substituted by four benzoquinone units do not show fluorescence emission because of intensitive intramolecular quenching.[26] The quenching phenomenon in this study is interpreted as being due to photo-induced electron transfer from [Zn(8EGpc)] to the BQ derivatives.[26] The difference of the Φ_f values in the presence of BQ, DHBQ, and THBQ is attributable to differences in the electron-transfer rate. Two possibilities are considered for the origin of the difference in the electron-transfer rate. Firstly, the reduction potential: Edward et al.[27] reported on the reduction potentials of BQ, DHBQ, and THBQ in DMF at $E_{1/2} = -0.15$ V, -0.01V, and -0.32 V, respectively. If we consider only the values of the reduction potential, the electron-transfer rate in the presence of THBQ must be the slowest among the BQ derivatives. The other possibility is the formation of complexes between [Zn(8EGpc)] and the BQ derivatives substituted by hydroxyl groups. If hydrogen bonding is important, THBQ would be the best quencher of the exited singlet pc. In fact, since the experimentally obtained Φ_f values in the presence of THBQ are the smallest among the BQ derivatives used, the effective fluorescence quenching of [Zn(8EGpc)] by DHBQ or THBQ is assigned to the complex formation between them.

The following observations, furthermore, lend support to complexation between [Zn(8EGpc)] and THBQ: In the absence of [Zn(8EGpc)], THBQ is sparingly soluble in benzene. Thus, a 10^{-5} M benzene solution ($1\ \text{M} = 1\ \text{mol dm}^{-3}$) of THBQ is already not transparent due to the formation of fine particules of THBQ. This situation is practically held even in the presence of tetra-*t*-butylated [Zn(pc)], which may have little complexation ability with benzoquinones. However, the addition of [Zn(8EGpc)], [10^{-5} M], to the 10^{-5} M benzene solution of THBQ makes the solution visually transparent. Thus, these observations strongly suggest that complexation mainly occurs between the tri(ethylene oxide) chains of [Zn(8EGpc)] and the BQ molecules.

In order to obtain direct evidence of complex formation,

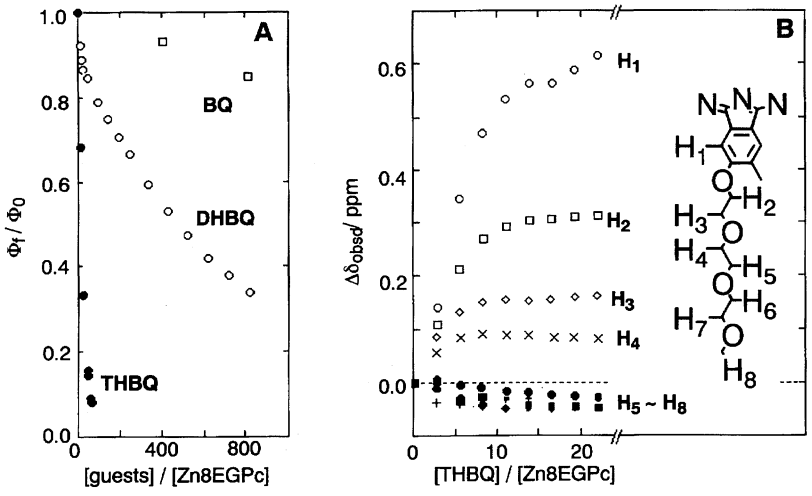

Fig. 5. (A) The decrease of the quantum yield of [Zn(8EGpc)] with increasing concentration of BQ (empty squares), DHBQ (empty circles), and THBQ (filled circles) in benzene. (B) Complexation induced shift of the protons of [Zn(8EGpc)] with THBQ in benzene ($\Delta\delta_{obsd} = \delta_{obsd}(CH) - \delta_{[Zn(8EGpc)]}(OH)$).

the ^{1}H NMR spectra were recorded in d_6-benzene. Figure 5B shows the resonance magnetic field of protons of [Zn(8EGpc)] in the presence of THBQ. At a fixed concentration of [Zn(8EGpc)], the resonance magnetic fields of protons of the pc ring (H_1) and the protons of the tri(ethylene oxide) chains which are close to the pc ring (i.e. H_2, H_3, H_4) shift to lower fields by increasing the [THBQ]. The shift is larger the closer are the positions of the protons to the pc plane. The change of the resonance magnetic field of all protons almost saturates until the [THBQ]/[[Zn(8EGpc)]] value reaches about 10, suggesting that a [Zn(8EGpc)] molecule forms a complex with about ten or less THBQ molecules (∵ the complex formation constant cannot be infinitely large).

The complexation-induced-shift (CIS) of the hydroxyl groups of THBQ by [Zn(8EGpc)] and H_2(8EGpc) were also measured in an attempt to find evidence of hydrogen bonding. At a fixed concentration of [Zn(8EGpc)], the resonance magnetic field of the hydroxyl groups shifted to lower fields by increasing [THBQ] (for example, when [THBQ]/[[Zn(8EGpc)]] = 5.3 and 9.75, the values of CIS were 0.54 and 1.17 ppm, respectively). For this phenomenon, we may have to consider two possibilities. Firstly, the ring-current effect of the pc ring, which is known to be very strong, and secondly, the hydrogen-bonding effect. Taking the ring-current effect into account, the resonance magnetic field is expected to shift markedly to higher fields ($\Delta\delta_{\max} \approx 7$ ppm) when molecules are above or below the pc plane, while it shifts to lower fields ($\Delta\delta_{\max} \approx 3$ ppm) when molecules are on the lateral direction of the pc plane.[28] On the other hand, hydrogen bonding shifts the resonance magnetic field to a higher field ($\Delta\delta_{\max} \approx 4$ ppm).[29] Accordingly, when THBQ forms hydrogen bonding above the pc plane, the resonance magnetic field is shifted to higher fields by the amount of ring-current effect plus the hydrogen-bonding effect. In contrast, when the complexation occurs at a lateral position of the pc ring via hydrogen bonding, the shift depends on the balance between the ring-current effect and hydrogen-bonding effects. However, since complexation of above or below the pc plane always shifts the resonance magnetic field to higher fields, the experimentally observed lower field shift is explained only by complexation at the lateral position. Hence, it is concluded that complexation between THBQ and [Zn(8EGpc)] occurs on the lateral direction of the pc ring. The possibility of the coordination of THBQ to the central zinc ion of [Zn(8EGpc)] appears small, since the shift of the resonance magnetic field of the hydroxyl groups of THBQ by [Zn(8EGpc)] is comparable to that by H_2(8EGpc) (for example, when [THBQ]/[H_2(8EGpc)] = 10.90, the values of CIS was 0.96 ppm). From these results, the hydrogen bonding is considered to be formed near to the pc ring and on the lateral position of the [Zn(8EGpc)] plane (Fig. 6A).

Complexation experiments between [Zn(4EGpc)] and BQ molecules could not be performed due to the instability of [Zn(4EGpc)] and low solubility of [Zn(4EGpc)]-BQ complexes.

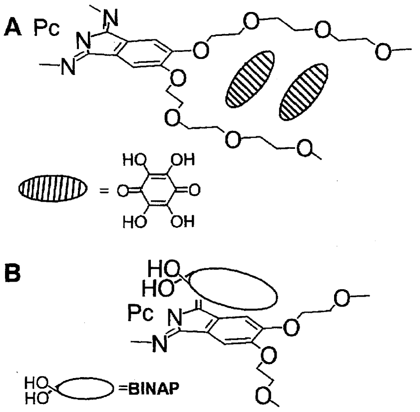

Fig. 6. Proposed structures for (A) the Zn- or H_2(8EGpc)- THBQ complex and (B) the Zn- or H_2(8EGpc)–BINAP complex.

3. Complexation with BINAP. With the aim of investigating the complexation of [Zn(8EGpc)] and [Zn(4EGpc)] with optically active BINAP, their circular dichroism (CD) spectra were measured in benzene. In the case of [Zn(8EGpc)], positive and negative CD signs were observed in the Q-band region with *S*- and *R*-optically active BINAP, respectively (apart from the sign, their magnitude was 3.5×10^3 degree dm^3 mol^{-3} cm^{-1} at about 680 nm), while in the other region, CD signals were too weak to read. On the other hand, CD signals too weak, and therefore meaningless, were recorded in the whole region in the [Zn(4EGpc)]–BINAP system ([BINAP]/[[Zn(4EGpc)]] = 50). These results suggest that [Zn(8EGpc)] binds more strongly than [Zn(4EGpc)] does with BINAP. However, since the CD intensity in even the [Zn(8EGpc)]–BINAP system is very weak, it appears that there are not many BINAPs fixed around the [Zn(8EGpc)] molecule.[30] Accordingly, in order to detect the interaction between [Zn(8EGpc)] and BINAP molecules more directly, the ^{1}H NMR spectra of BINAP were measured in both the presence and absence of [Zn(8EGpc)] (Fig. 7). The resonance magnetic fields of all protons of BINAP shift to a higher field in the presence of [Zn(8EGpc)]. In particular, the shift of protons, indicated by H_1–H_4 in Fig. 7, is much larger than that of the H_5 and H_6 protons. If we consider that the ring-current effect, which causes higher-field shifts, is the strongest near to the center of a pc molecule,[28] the H_1–H_4 protons may be near to the center of the pc molecule above the pc plane, while the H_5 and H_6 protons may lie close to the rim of the pc molecules, as depicted in Fig. 6B. If this is the case, the weaker CD intensity in the [Zn(4EGpc)] system compared to the [Zn(8EGpc)] system is reasonably explained, since four tri(ethylene oxide) chains attached to the carbons closest to the pc core in the [Zn(4EGpc)] may sterically prevent taking this kind of conformation. At least, in the case of [Zn(8EGpc)], such a possibility appears to be small, since eight tri(ethylene oxide) chains are stretching outward from the carbons furthest from the center of the pc core.

4. Mesomorphism. (a) [Zn(4EGpc)] and H_2(4EGpc). Several kinds of organic transition-metal complexes substituted by four long chains are known to show liquid-crystalline (L.C.) phases.[31] However, as mentioned in the intro-

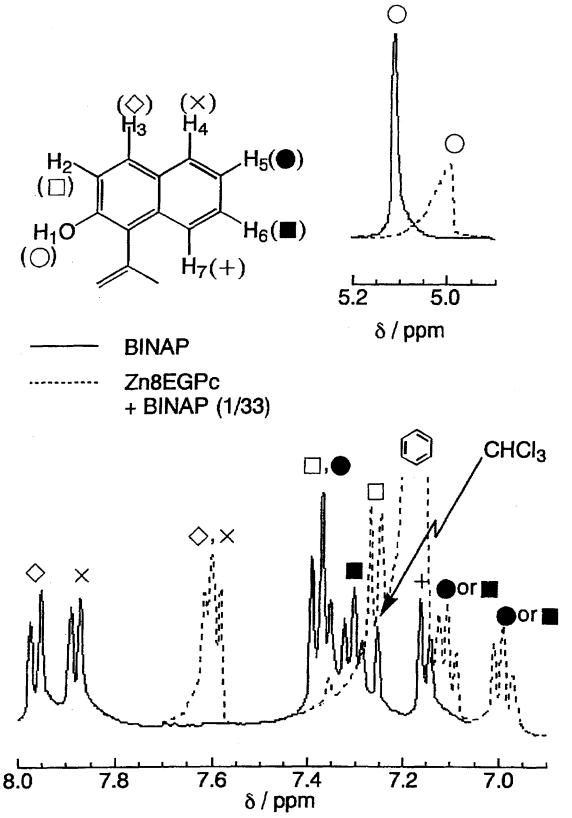

Fig. 7. 400 MHz ^{1}H NMR spectrum of BINAP in the absence (solid lines) and presence (broken lines) of [Zn(8EGpc)] in deuterated benzene. [BINAP]/[[Zn(8EGpc)]] = 33.

ductory section, tetra-substituted pcs are generally mixtures of at least four positional isomers, and to date no single isomers exhibiting mesomorphism have been reported for pcs substituted with four long chains.$^{6)}$ If mixtures are used in L.C. experiments, their transition temperatures should be lower than those of single isomers, as occurs with melting points in normal compounds. We, accordingly, prepared single isomers of pcs substituted with four long-chains (i.e. H_2(4EGpc) and [Zn(4EGpc)]) by the method of Leznoff et al.$^{32a)}$ and Kasuga et al.$^{32b)}$ (for details, see experimental section), in order to study their mesomorphic behavior. Unfortunately, the virgin states of both H_2(4EGpc) and [Zn(4EGpc)] are crystalline phases at room temperature, and when they are heated up, very complicated phase transitions and relaxations are observed. For example, the virgin state of [Zn(4EGpc)] is a dark-green crystalline phase (K_1) at room temperature (Fig. 8(a)), which clears into an isotropic liquid (I.L.) at 62.6—63.0 °C. When this I.L. is maintained at 65 °C, it slowly relaxes and crystallizes into a new crystalline phase (K_2). However, upon slow heating, the K_2 phase relaxes into a new crystalline phase (K_3) and further heating transforms the K_3 phase into an I.L. at 120.5—121.0 °C. On the other hand, when the K_2 phase is rapidly heated up, it clears into an I.L. at 93.1 °C, and when this I.L. phase is maintained at 100 °C, it slowly relaxes and crystallizes into the K_3 phase. These complicated phase transitions and relaxation behaviors can be reasonably explained by using a schematic free-energy versus temperature (G–T) diagram.$^{33)}$ In the case of the corresponding metal-free derivative, i.e. H_2(4EGpc), phase transitions and relaxation behaviors are more complicated, giving six crystalline phases. Hence, it is too complicated to establish the phase-transition sequence, such as in the upper part of Fig. 8(a). Accordingly, Fig. 8(b) shows only a G–T diagram of H_2(4EGpc). From a temperature-dependent polarizing microscope observation, both H_2(4EGpc) and [Zn(4EGpc)] are found not to show any L.C. phases. Therefore, it is deduced that four tri(ethylene oxide) chains are not enough to show a L.C. phase in pc derivatives.

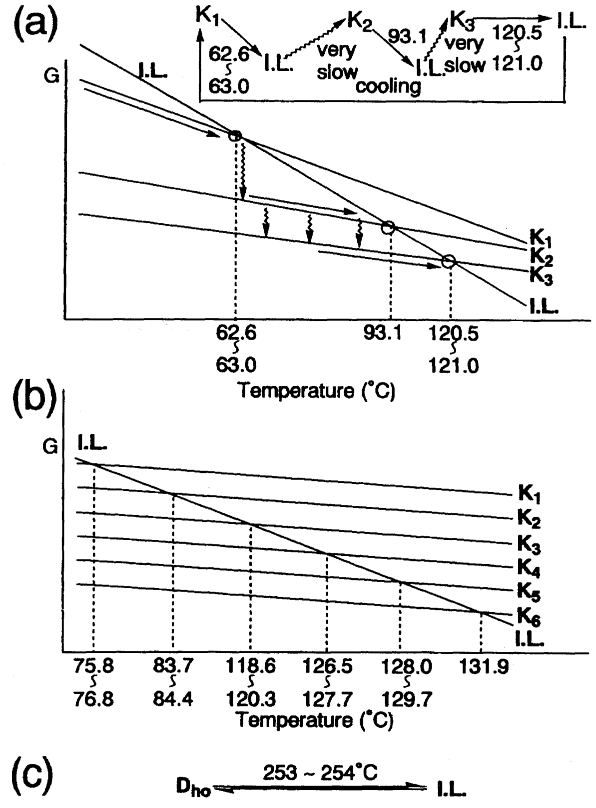

Fig. 8. Phase transition behaviour of H_2(8EGpc), H_2(4EGpc), and [Zn(4EGpc)]. (a) Phase transition sequence (upper) and the schematic free energy vs. temperature (G–T) diagram (bottom) of [Zn(4EGpc)]. (b) The G–T diagram of H_2(4EGpc). (c) Phase transition sequence of H_2(8EGpc). ○: transition temperature; →: heating; ⇝: relaxation.

(b) H_2(8EGpc). The virgin state of this derivative is a dark-green L.C. at room temperature. When it is heated up, it clears into an I.L. at 253—254 °C. (Fig. 8(c)), while when this L.C. is slowly cooled, it gives some homeotropic parts and a snowflake-like texture having a six-fold axis of symmetry. Therefore, this mesophase should be a D_h phase. Further, X-ray diffraction study carried out at room temperature establishes the mesophase structures as shown in Table 1. However, since it gives only one sharp reflection line in the low-angle region, it is impossible to determine the 2D-lattice. In addition, from the texture mentioned above, it should have a 2D-hexagonal lattice, so that the sharp reflection is identified as (100). In addition, the mesophase gives

Table 1. X-Ray Diffraction Data of $H_2(8EGpc)$

Mesophase	Lattice constant (Å)	Spacing (Å)		Miller indices
		d_{obsd}	d_{calcd}	(*hkl*)
D_{ho}	$a = 27.2$	23.5	23.5	(100)
	h_1 = ca. 3.5	ca. 7.0	—	(001)$^{b)}$
	h_2 = ca. 7.0	ca. 4.1	—	a)
		ca. 3.5	—	(100)$^{c)}$

a) Melt of the chains, b) interdimer distance = h_2, c) intermonomer distance = h_1.

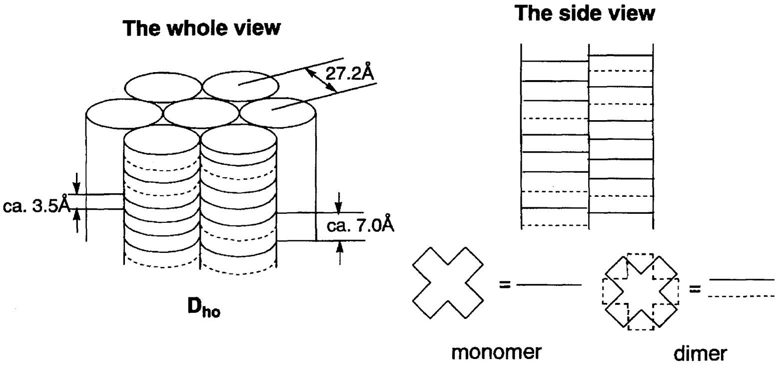

Fig. 9. A structural model of the discotic hexagonal ordered columnar (D_{ho}) phase of $H_2(8EGpc)$.

three broad peaks in the middle-angle region. The reflection at around $d = 4.1$ Å is identified as the halo related to the melting of long chains.[34] The refraction at around $d = 3.5$ Å is identified as (001), corresponding to the ordered stacking distance of a face-to-face structure between the monomeric pcs in the column.[34] Since the reflection at around $d = 7.0$ Å is double that of 3.5 Å, it is identified as (001), corresponding to the ordered stacking distance between the dimerized pcs in the column. Consequently, the present mesophases can be identified as being a discotic hexagonal ordered columnar (D_{ho}) phase. It is noteworthy that the column in this D_{ho} phase is made up of a mixture of monomers and dimers (Fig. 9), because both distances between the monomers and dimers can be observed at the same time.

Generally speaking, discotic liquid-crystalline compounds are known to dramatically change their supramolecular structure upon slightly changing the molecular structure; particularly, the number and the length of the chains are important.[31c)] In the case of tri(ethylene oxide) chain-substituted pcs, the number of chains appears not to be enough to show the discotic liquid-crystalline phase.[31c)]

Conclusion

The aggregation behavior of pcs having four or eight tri(ethylene oxide) chains in water, dioxane, and water–dioxane mixtures have been studied, mainly by electronic absorption and fluorescence spectroscopy. They form aggregates in water and water–dioxane mixtures. ^{1}H NMR and fluorescence or circular dichroism spectroscopy indicate that they form complexes with benzoquinones and BINAPs in benzene, and their supramolecular model structures are proposed on the bases of experiments: benzoquinones with more hydroxy groups form complexes at laterally outside of the pc plane, while BINAP molecules are suggested to lie above or below the pc plane. The mesomorphism of three amphiphilic pcs have been studied in the neat state. Of these, an H_2pc having eight tri(ethylene oxide) chains are found to form the discotic hexagonal columnar ordered (D_{ho}) phase in the range of from room temperature to 265 °C.

This research has been partially supported by a Grant-in-Aid for Scientific Research on Priority Area "Metal-Assembled Complexes" No. 10149203 from the Ministry of Education, Science, Sports and Culture, and the Mitsubishi and Asahi Glass Foundations.

References

1) a) "Phthalocyanines - Properties and Applications," ed by C. C. Leznoff and A. B. P. Lever, VHC Publications, New York (1989); b) Vol. 2 (1993); c) Vol. 3 (1993); d) Vol. 4 (1996); e) "Phthalocyanines - Chemistry and Applications," ed by H. Shirai and N. Kobayashi, IPC, Tokyo (1997).

2) a) J. M. Kroon, R. B. M. Koehorst, M. van Dijk, G. M. Sanders, and E. J. Sundholter, *J. Mater. Chem.*, **7**, 615 (1997); b) S. F. Foley, G. Jones, R. Liuzzi, D. J. McGarvey, M. H. Perry, and T. G. Truscott, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 1725.

3) a) N. Kobayashi and A. B. P. Lever, *J. Am. Chem. Soc.*, **109**, 7433 (1987); b) T. Toupance, V. Ahsen, and J. Simon, *J. Am. Chem. Soc.*, **116**, 5352 (1994).

4) a) C. Piechochi, J. Simon, A. Skoulious, D. Guillan, and P. Weber, *J. Am. Chem. Soc.*, **119**, 7281 (1997); b) M. J. Cook, N. B. McKeown, A. J. Thomson, K. J. Harrison, R. M. Richardson, A. N. Davies, and S. J. Roser, *Chem. Mater.*, **1**, 287 (1989); c) T. Toupance, P. Bassoul, L. Mineau, and J. Simon, *J. Phys. Chem.*, **100**, 11704 (1996).

5) D. Guillon, P. Weber, A. Skoulionus, C. Piechocki, and J. Simon, *Mol. Cryst. Liq. Cryst.*, **130**, 223 (1985); C. Piechocki and J. Simon, *J. Chem. Soc., Chem. Commun.*, **1985**, 259.

6) a) N. B. McKeown and J. Painter, *J. Mater. Chem.*, **4**, 1153

(1994); b) H. Eichorn, D. Wöhrle, and D. Pressner, *Liq. Cryst.*, **22**, 643 (1997); c) N. B. McKeown, C. C. Leznoff, R. M. Richardson, and A. S. Cherodian, *Mol. Cryst. Liq. Cryst.*, **213**, 91 (1992); d) G. J. Clarkson, B. M. Hassan, D. R. Maloney, and N. B. McKeown, *Macromolecules*, **29**, 1854 (1996).

7) N. Kobayashi, T. Ohya, M. Sato, and S. Nakajima, *Inorg. Chem.*, **32**, 1803 (1993).

8) a) P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.*, **31**, 1 (1969); b) W. Melhuish, *J. Phys. Chem.*, **64**, 762 (1960); c) J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 991 (1971).

9) H. Ema, Master Thesis, Shinsyu University, Ueda, Japan, 1988; H. Hasebe, Master Thesis, Shinsyu University, Ueda, Japan, 1991.

10) M. J. Stillman and T. Nyokong, "Phthalocyanines - Properties and Applications," ed by C. C. Leznoff and A. B. P. Lever, VCH Publications, New York (1989), pp. 135—289.

11) M. Hanack, G. Schmid, and M. Sommerauer, *Angew. Chem., Int. Ed. Engl.*, **32**, 1422 (1993); M. Sommerauer, C. Rager, and M. Hanack, *J. Am. Chem. Soc.*, **118**, 10085 (1996).

12) a) N. Kobayashi, Y. Yanagisawa, T. Osa, H. Lam, and C. C. Leznoff, *Anal. Sci.*, **6**, 813 (1990); b) N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, and A. B. P. Lever, *Inorg. Chem.*, **29**, 3415 (1990).

13) E. S. Dodsworth and A. B. P. Lever, *J. Phys. Chem.*, **89**, 5698 (1985).

14) N. J. Turro, "Modern Molecular Photochemistry," University Science Books, California (1991).

15) N. Kobayashi and H. Konami, "Phthalocyanines - Properties and Applications," ed by C. C. Leznoff and A. B. P. Lever, VCH Publications, New York (1996), Vol. 4, pp. 343—404.

16) K. Toyota, J. Hasegawa, and H. Nakatsuji, *J. Phys. Chem.*, **101**, 446 (1997); N. Ishikawa, O. Ohno, and Y. Kaizu, *J. Phys. Chem.*, **97**, 1004 (1993); A. Rosa and E. Baerends, *Inorg. Chem.*, **31**, 4717 (1992); E. Orti, J. L. Bredas, and C. Clarisse, *J. Chem. Phys.*, **92**, 1228 (1990); L. K. Lee, N. H. Sabelli, and P. R. LeBreton, *J. Phys. Chem.*, **86**, 3926 (1982); A. M. Schaffer, M. Gouterman, and E. Davidson, *Theor. Chim. Acta*, **30**, 9 (1973); A. M. Schaffer and M. Gouterman, *Theor. Chim. Acta*, **25**, 62 (1972).

17) A. Tajiri and J. Winkler, *Z. Naturforsh., A*, **38a**, 1263 (1983).

18) N. Kobayashi, M. Togashi, T. Osa, K. Ishii, S. Yamauchi, and H. Hino, *J. Am. Chem. Soc.*, **118**, 1073 (1996).

19) S. B. Piepho and P. N. Schatz, "Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism," Wiley, New York (1983).

20) Emission from dimer is generally very weak, if any: N. E. Kagan, D. Mauzerall, and R. B. Merrifield, *J. Am. Chem. Soc.*, **99**, 5486 (1977). However, an exceptional emission from tetra-sulfonated [Zn(pc)] dimer was reported recently; Y. Kaneko, T. Arai, K. Tokumaru, D. Matsunaga, and H. Sakuragi, *Chem. Lett.*, **1996**, 345.

21) Y. Kaneko, Y. Nishimura, N. Takane, T. Arai, H. Sakuragi, N. Kobayashi, D. Matsunaga, C. Pac, and K. Tokumaru, *J. Photochem. Photobiol. A: Chem.*, **106**, 177 (1977).

22) N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, T. Koyama, A. Monden, and H. Shirai, *J. Am. Chem. Soc.*, **116**, 879 (1994).

23) F. Perrin, *J. Phys. Radium.*, **7**, 390 (1962); I. B. Berlman, *Mol. Cryst.*, **4**, 157 (1968).

24) a) K. Sauer, J. R. L. Smith, and A. J. Schultz, *J. Am. Chem. Soc.*, **88**, 2681 (1966); b) J. A. Shelnutt, M. M. Dobry, and J. D. Satterlee, *J. Phys. Chem.*, **88**, 4980 (1984).

25) In chloroform, the change of Φ_f/Φ_{f0} of [Zn(8EGpc)] with increasing [BQ] is similar to that in benzene. However in methanol, the Φ_f/Φ_{f0} value changes slightly and to the same extent by the presence of either THBQ or BQ: (i.e. for example, when [BQ]/[[Zn(8EGpc)]] = 129, $\Phi_f/\Phi_{f0} = 0.95$ and when [THBQ]/[[Zn(8EGpc)]] = 114, $\Phi_f/\Phi_{f0} = 0.90$).

26) Benzoquinone derivatives can generally quench the fluorescence of phthalocyanines; see for example: Ref. 7 and N. Kobayashi, Y. Nishiyama, T. Ohya, and M. Sato, *J. Chem. Soc., Chem. Commun.*, **1987**, 390.

27) T. G. Edward and R. Grinter, *Trans. Faraday Soc.*, **64**, 1070 (1968).

28) T. Koyama, T. Suzuki, K. Hanabusa, H. Shirai, and N. Kobayashi, *Inorg. Chim. Acta*, **218**, 41 (1994); T. Sauer and G. Wegner, *Mol. Cryst. Liq. Cryst.*, **162**, 97 (1988); E. A. Cuellar and T. J. Marks, *Inorg. Chem.*, **20**, 3766 (1981); J. E. Maskasy, J. R. Mooney, and M. E. Kenney, *J. Am. Chem. Soc.*, **94**, 2132 (1972); T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Am. Chem. Soc.*, **91**, 5210 (1969).

29) J. T. Arnold and M. E. Packard, *J. Phys. Chem.*, **19**, 1680 (1951); A. D. Chohen and C. Reid, *J. Phys. Chem.*, **25**, 790 (1956).

30) If many BINAP molecules are fixed around pc molecules, strong induced CD signal will be recorded as shown in: N. Kobayashi, Y. Kobayashi, and T. Osa, *J. Am. Chem. Soc.*, **115**, 10994 (1993).

31) a) J. Billard, *C. R. Acad. Sci. Paris*, **299**, 905 (1984); b) H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta, and I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, **163**, 211 (1988); c) K. Ohta, R. Higashi, M. Ikejima, I. Yamamoto, and N. Kobayashi, *J. Mater. Chem.*, **8**, 1979 (1998); Y. Shimizu, A. Ishikawa, and S. Kusabayashi, *Chem. Lett.*, **1986**, 1041; d) M. Veber, R. Fugnitto, and H. Strzelecka, *Mol. Cryst. Liq. Cryst.*, **96**, 211 (1983); e) K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, K. Matsuzaki, T. Inabe, and Y. Maruyama, *J. Chem. Soc., Chem. Commn.*, **1986**, 883; f) X.-Q. Wang, C.-S. Cao, S. Gao, T.-S. Shi, T.-S.L.-X. Yu, and X. Z. Cao, *Chem. J. Chin. Univ.*, **17**, 684 (1996).

32) a) C. C. Leznoff, M. Hu, C. R. McArther, Y. Qin, and J. E. van Lier, *Can. J. Chem.*, **72**, 1990 (1994); b) K. Kasuga, K. Asano, L. Lin, T. Sugimori, M. Hanada, K. Abe, T. Kikkawa, and T. Fujiwara, *Bull. Chem. Soc. Jpn.*, **70**, 1859 (1997).

33) W. C. MacCrone,"Physics and Chemistry of the Organic Solid State," ed by D. Fox, M. Labess, and A. Weissberger, John Wiley & Sons, New York (1965), Vol. II, pp. 725—766.

34) "The Nature of Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry," 3rd ed, ed by L. Pauling, Cornell Univ. Press, New York (1960).