

Exciton interactions in a self-assembled phthalocyanine dimer

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Photophysical properties of tri-*tert*-butylpyridinotribenzotetraazaporphinatozinc (ZnPcPy) complexes, a self-assembled dimer ((ZnPcPy)₂) and a monomer (ZnPcPy-Py) in a non-polar solvent and with pyridine, respectively, have been studied. The lowest excited singlet (S₁) state is investigated by the combined use of electronic absorption, magnetic circular dichroism and fluorescence spectroscopy and the S₁ properties are analyzed by configuration interaction calculations including exciton interactions between ZnPcPy constituents. The lowest excited triplet state is investigated by time-resolved electron paramagnetic resonance (TREPR). TREPR spectra of (ZnPcPy)₂ exhibit a dramatic temperature dependence at 10–220 K, in contrast to a negligible change for ZnPcPy-Py. The spectral changes are reasonably attributed to triplet energy transfer between two ZnPcPy constituents, and are well reproduced using energy transfer rates, $k = 3 \times 10^8 \text{ s}^{-1}$ (100 K), $7 \times 10^8 \text{ s}^{-1}$ (140 K), and $2 \times 10^9 \text{ s}^{-1}$ (180 K), respectively. The activation energy of the energy transfer process is evaluated as $2.7 \times 10^2 \text{ cm}^{-1}$ from the Arrhenius plot. This study demonstrates the utility of TREPR for investigating energy transfer processes among these macrocycles.

Introduction

In relation to photosynthesis and photonic wires, photophysical properties of porphyrin oligomers are of interest, and therefore self-assembled porphyrin oligomers have been intensively studied.^{1–8} In these oligomeric compounds, the location of excitation energy *i.e.* localization, delocalization, or transfer of excitation energy, is the most important property in the excited states. While phthalocyanines (Pcs), which are useful compounds in terms of functional dyes, are analogous to porphyrins, characteristic photophysical properties are expected for Pc oligomers, because of the large oscillator strength of the Q band, resulting in strong exciton interactions.⁹ However, there have been few studies focusing on the excited states of self-assembled Pc oligomers.^{10,11}

In this report, we have investigated photophysical properties of tri-*tert*-butylpyridinotribenzotetraazaporphinatozinc (ZnPcPy) complexes (Fig. 1). It is known that ZnPcPy forms a self-assembled dimer ((ZnPcPy)₂) in a non-polar solvent, while it becomes a monomer (ZnPcPy-Py) when pyridine is added.¹¹ Since photophysical properties have been reported only for cofacial or coplanar Pc dimers,^{9–13} it is important to clarify how the conformation of (ZnPcPy)₂ influences the excited state properties. Therefore, the lowest excited singlet (S₁) state of the ZnPcPy complexes is investigated by the combined use of electronic absorption, magnetic circular dichroism (MCD) and fluorescence spectroscopy. The S₁ properties are analyzed by configuration interaction (CI) calculations including exciton interactions between ZnPcPy constituents. The lowest excited triplet (T₁) state is examined by means of a time-resolved

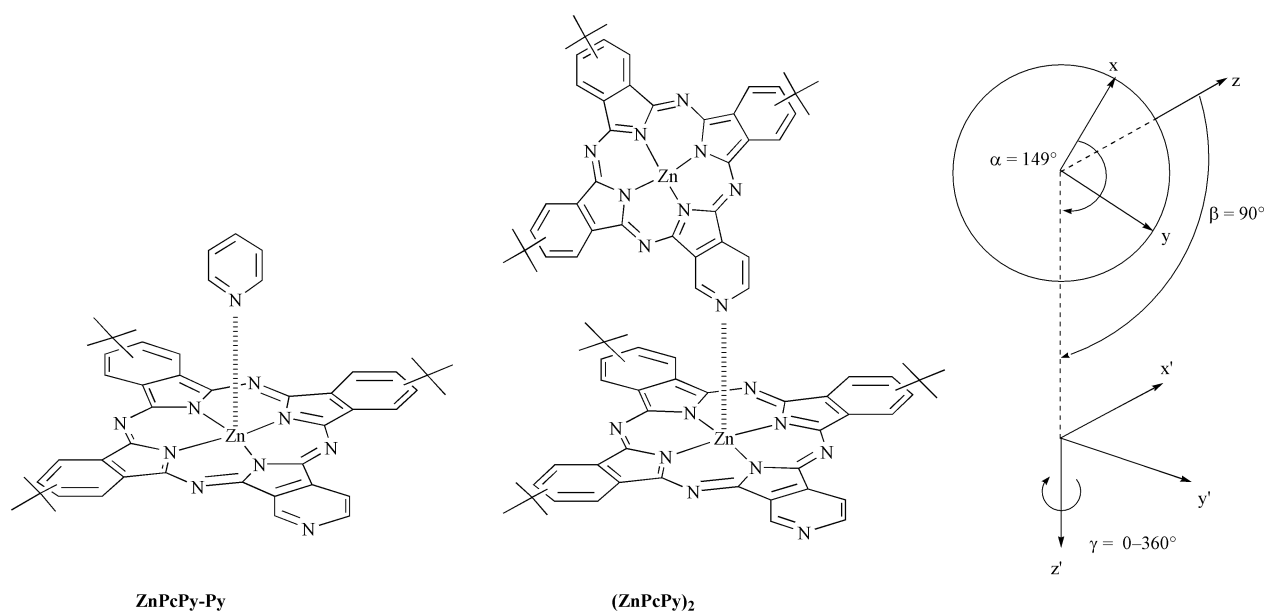


Fig. 1 Molecular structures of ZnPcPy complexes.

electron paramagnetic resonance (TREPR) method, which is useful for investigating the T_1 dimers.^{13–20} The triplet energy transfer process is analyzed quantitatively, which demonstrates the utility of TREPR for investigating energy transfer processes among these macrocycles.

Experimental

Materials

ZnPcPy was obtained by fusing 4-*tert*-butylphthalonitrile (1.2 mmol) and 3,4-pyridinedicarbonitrile (0.4 mmol) in the presence of zinc acetate (0.4 mmol) and hydroquinone (0.4 mmol) at 270 °C for *ca.* 20 min, followed by purification by silica gel and gel-permeation (Bio-Beads S-X1, Bio-Rad) chromatography in a 3.8% yield. *m/e*: 746 (M^+). Anal. Calcd for $C_{43}H_{39}N_3Zn$: C, 69.12; H, 5.26; N, 16.87. Found: C, 68.434; H, 5.770; N, 15.797. Formation of $(ZnPcPy)_2$ and ZnPcPy-Py was checked by electronic absorption, MCD, and ESI-TOF mass spectroscopy.²¹ *n*-Decane was used as the solvent for all measurements.

Measurements

UV-vis absorption spectra were measured with a Hitachi U3410 spectrometer. MCD measurements were made with a JASCO J-720 spectrodichromometer equipped with a JASCO electromagnet that produced magnetic fields of up to 1.1 T with parallel and then antiparallel fields. Steady-state emission spectra were recorded with a Hitachi F-4500 fluorescence spectrometer. Fluorescence quantum yields were determined by the use of H_2Pc ($\phi = 0.60$). Time-resolved fluorescence emissions were measured by a single-photon counting method using an argon ion laser (Spectra-Physics, BeamLok 2060–10-SA), a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps fwhm) with a pulse selector (Spectra-Physics, Model 3980), a second harmonic generator (GWU-23PS), and a streak-scope (Hamamatsu Photonics, C4334-01).²² For the time-resolved fluorescence measurements, samples were excited at 365 nm. TREPR measurements were carried out at 10–220 K on a Bruker ESP 300E spectrometer.²³ An Oxford ESR 900 cold gas flow system was used for controlling temperature. The concentrations of samples were *ca.* 10^{-4} – 10^{-3} M, and samples were excited at 585 nm by a Lumonics HD 350 dye laser pumped with a Lumonics EX 600 excimer laser. The TREPR signals from the EPR unit were integrated by a LeCroy 9450A oscilloscope.

TREPR line shape analyses

TREPR line shape analyses including dynamic processes were calculated following the method previously reported.¹⁹ When the energy transfer between A and B units occurs with an exchange rate, k , the TREPR line shape is expressed as in eqn. 1 and Q^\pm , Δ and C^i ($i = A$ or B) are given in eqns. 2–4.

$$I(\Delta) \propto \int_0^\pi \int_0^{\pi/2} [P_{21} \times Q^+ + P_{32} \times Q^-] \sin\theta \, d\theta \, d\varphi \quad (1)$$

$$C^i = -D(1 - 3n_i^2)/2 + 3E(l_i^2 - m_i^2)/2$$

$$\begin{pmatrix} l_A \\ m_A \\ n_A \end{pmatrix} = \begin{pmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{pmatrix}$$

$$\begin{pmatrix} l_B \\ m_B \\ n_B \end{pmatrix} = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix} \begin{pmatrix} l_A \\ m_A \\ n_A \end{pmatrix} \quad (4)$$

$$Q^\pm = [(C^A + C^B \pm 2\Delta)^2 (k + 1/T_2) - 2(2k + 1/T_2)\{(C^A \pm \Delta)(C^B \pm \Delta) - (k + 1/T_2)^2 + k^2\}]/\{(C^A \pm \Delta)(C^B \pm \Delta) - (k + 1/T_2)^2 + k^2\}^2 + \{(k + 1/T_2)(C^A + C^B \pm 2\Delta)\}^2] \quad (2)$$

$$\Delta = B_0 - \omega/g\beta \quad (3)$$

The term Δ represents the magnetic field shift from the resonance magnetic field of the unperturbed Zeeman transition ($g\beta B_0$), P_{ij} ($ij = 21$ or 32) denotes the population difference between the i and j levels, $1/T_2$ is the effective line width, θ and φ are the angles between the external magnetic field, B_0 , and the principal axes of the A unit, and structural relationships between the A and B units are represented by the Euler angles (α , β , and γ as shown in Fig. 1).

Results and discussion

Electronic absorption, MCD and fluorescence

Electronic absorption and MCD spectra of ZnPcPy-Py and $(ZnPcPy)_2$ are shown in Fig. 2. The electronic absorption spec-

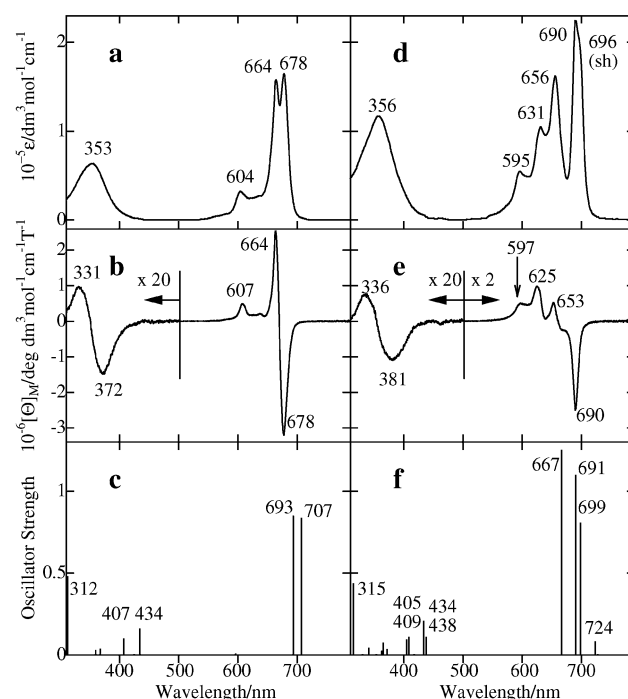


Fig. 2 Electronic absorption (a, d), MCD (b, e), CI calculation (c, f) spectra of ZnPcPy-Py (a, b, c) and $(ZnPcPy)_2$ (d, e, f) in *n*-decane. The concentration of the samples was 10^{-4} M.

trum of ZnPcPy-Py exhibits two intense peaks (664 and 678 nm) in the Q band region. These two absorption peaks coincide with positive and negative MCD peaks (664 and 678 nm), which indicates the Faraday B terms, originating from non-degenerate transitions. These are characteristic of symmetry-

lowered Pc derivatives composed of two kinds of isoindoles.²⁴ On the other hand, the electronic absorption and MCD spectra of (ZnPcPy)₂ are obviously different from those of ZnPcPy-Py, reflecting the formation of a self-assembled dimer.¹¹ This spectral change is reasonably interpreted by exciton interactions between the large transition electric dipole moments of the Q bands in the two ZnPcPy constituents, which indicates a delocalization of excitation over two ZnPcPys in the S₁ state. To evaluate quantitatively, CI calculations of ZnPcPy-Py and (ZnPcPy)₂ were carried out using ZINDO/S Hamiltonian (Fig. 2).²⁵ For ZnPcPy-Py, two intense transitions (707 and 693 nm) are seen, which mainly consist of the HOMO → LUMO + 1 or HOMO → LUMO configuration (> 85%). For (ZnPcPy)₂, four transitions originating from the exciton interactions are observed in the Q band region (724, 699, 691, and 667 nm), and the transitions at 667, 691, and 699 nm reproduce well the observed Q band splitting (656 and 690 nm) and shoulder (696 nm). While these transitions constitute several configurations, we tried to offer plausible explanations. The transitions calculated at 691 and 699 nm mainly consist of the HOMO → LUMO configurations of the coordinated and coordinating ZnPcPys (~ 77%), respectively, resulting from the relatively weak exciton interactions. In contrast, the configurations of the coordinating and coordinated ZnPcPys are heavily admixed (60/30) in the transitions at 667 and 724 nm, originating from the strong exciton interactions. Since transition dipole moments of the coordinated and coordinating ZnPcPys are parallel and anti-parallel for the transitions at 667 and 724 nm, respectively, the transition at 667 nm is more intense than the transition at 724 nm, similarly to cofacial dimers.^{9,12}

In contrast to several cofacial Pc dimers,^{9,12} relatively intense fluorescence is seen for (ZnPcPy)₂ (Fig. 3). The fluorescence of

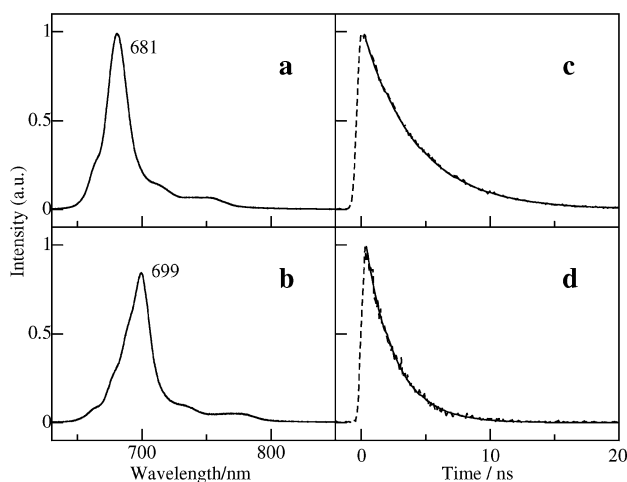


Fig. 3 Fluorescence spectra (a, b) and decay-profiles (c, d; broken lines) of ZnPcPy-Py (a, c) and (ZnPcPy)₂ (b, d) in *n*-decane. Fitting curves (c, d; solid lines) were calculated by a least-square method.

(ZnPcPy)₂ is shifted to lower energy compared with that of ZnPcPy-Py, similarly to the electronic absorption spectra. The fluorescence quantum yield (= Φ_F) and lifetime (= τ_F) of (ZnPcPy)₂ (Φ_F = 0.16, τ_F = 2.3 ns) are smaller than those of ZnPcPy-Py (Φ_F = 0.36, τ_F = 4.2 ns). In order to discuss this fluorescence quenching quantitatively, the radiative ($k_r = \Phi_F/\tau_F$) and non-radiative ($k_{nr} = (1 - \Phi_F)/\tau_F$) decay rates were evaluated from the Φ_F and τ_F values. It is found that the k_{nr} value ($3.7 \times 10^8 \text{ s}^{-1}$) of (ZnPcPy)₂ is larger than that ($1.5 \times 10^8 \text{ s}^{-1}$) of ZnPcPy-Py, while the k_r value ($7.0 \times 10^7 \text{ s}^{-1}$) of (ZnPcPy)₂ is similar to that ($8.6 \times 10^7 \text{ s}^{-1}$) of ZnPcPy-Py.²⁶ The enhancement in k_{nr} is interpreted by the fact that the lower exciton state is close to the T₁ and singlet ground (S₀) states, as a result of the exciton splitting. In addition, the relatively flexible structure of the self-assembled dimer may also contribute to the non-radiative decay.

Time-resolved EPR

TREPR spectra of (ZnPcPy)₂ (20, 100, 140, and 180 K) and ZnPcPy-Py (20 and 180 K) are shown in Fig. 4. The TREPR

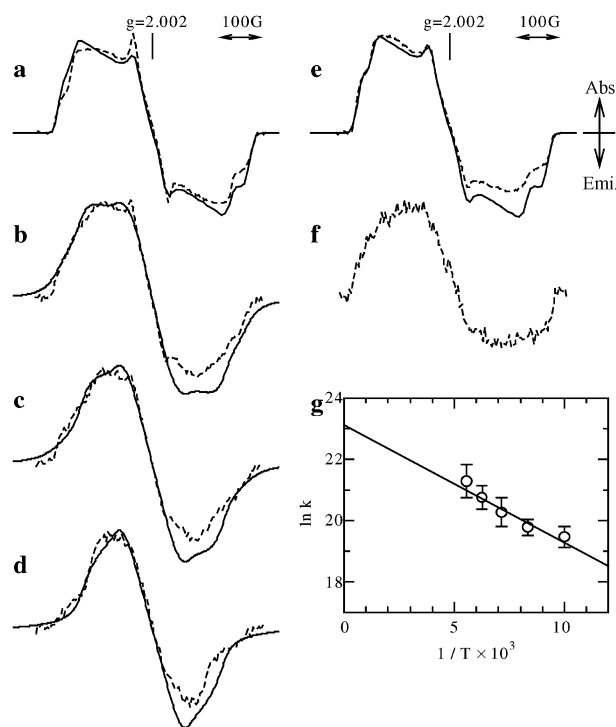


Fig. 4 TREPR spectra (broken lines) of (ZnPcPy)₂ at 20 K (a), 100 K (b), 140 K (c), and 180 K (d) and of ZnPcPy-Py at 20 K (e) and 180 K (f) with their simulations (a–e: solid lines). The Arrhenius plot of $\ln k$ vs. $1/T$ is also shown in g. Simulated spectra of (ZnPcPy)₂ at 100 K, 140 K, and 180 K were calculated using $k = 3 \times 10^8$, 7×10^8 , and $2 \times 10^9 \text{ s}^{-1}$, respectively.

spectrum of ZnPcPy-Py at 20 K was reproduced using zero field splitting (zfs) parameters $D = 0.705 \text{ GHz}$, $E = 0.145 \text{ GHz}$, and selective intersystem crossing (ISC) from the S₁ state to the z sublevel of the T₁ state ($P_x : P_y : P_z = 0 : 0 : 1$, P_i denotes the population of the i sublevel), and therefore the T₁ state of ZnPcPy is assigned to a typical $\pi\pi^*$ configuration.²⁷ The TREPR spectrum of (ZnPcPy)₂ at 20 K was reproduced using similar parameters ($D = 0.705 \text{ GHz}$, $E = 0.155 \text{ GHz}$, and $P_x : P_y : P_z = 0 : 0 : 1$). This similarity shows that the T₁ excitation energy localizes on one constituent unit in the EPR time scale, and that the charge transfer character is negligibly small. The exciton interaction in the T₁ state is much smaller than that in the S₁ state, which is rationalized by a spin-forbidden transition between the T₁ and S₀ states. In addition, it is found that the charge transfer character of (ZnPcPy)₂ is much smaller than those of the sandwich-type porphyrin dimers.^{13,20} This results from the conformation of (ZnPcPy)₂, where out-of-plane axes of the ZnPcPy constituents are perpendicular to one another and resonance integrals between two ZnPcPys, which promote a mixing between the exciton and charge transfer configurations, are small.^{5,28}

For (ZnPcPy)₂, a dramatic temperature dependence is seen in the TREPR spectra, where the zfs decreases with increasing temperature. Since the TREPR spectrum of ZnPcPy-Py at 180 K is almost similar to that at 20 K, the change in the TREPR spectrum of (ZnPcPy)₂ must not be due to the dynamics of the monomer unit, and is, therefore, attributed to energy transfer between the two ZnPcPy constituents.²⁹ In order to evaluate quantitatively, spectral simulations taking the energy transfer process into account were carried out. Euler angles (α , β , and γ as shown in Fig. 1) were employed to represent relationships between the fine structure axes (fsa) of the constituting units. The fsa of ZnPcPy were calculated under a half-point charge

approximation.^{30,31} The α and β values were determined as 149° and 90°, respectively.²⁵ For the γ value, since various conformations are possible, all γ values (= 0°–360°, step 10°) were calculated and integrated. Simulated spectra are shown in Fig. 4b–d. The TREPR spectra of (ZnPcPy)₂ at 100, 140 and 180 K were well reproduced using energy transfer rates, $k = 3 \times 10^8 \text{ s}^{-1}$, $7 \times 10^8 \text{ s}^{-1}$ and $2 \times 10^9 \text{ s}^{-1}$, respectively. The activation energy of the energy transfer process was evaluated as $2.7 \times 10^2 \text{ cm}^{-1}$ by the Arrhenius plot (Fig. 4g).

Conclusions

In this report, ZnPcPy complexes have been investigated using electronic absorption, MCD, fluorescence, and TREPR spectroscopy. The electronic absorption spectra are well analyzed by the CI calculations including the exciton interactions. In the S₁ state, the excitation delocalizes over the two ZnPcPy constituents, and the non-radiative decay is enhanced by dimerization.

In contrast to the S₁ state, the exciton interaction is very weak in the T₁ state. Using TREPR, the triplet energy transfer process is quantitatively analyzed. This is the first TREPR study on the triplet exciton state of a porphyrin dimer, satisfying the following three conditions. (1) The fsas of constituent units are fixed and not parallel to one another. (2) At low temperature, the zfs of the dimer is similar to that of the corresponding monomer, indicating that the charge transfer character is negligibly small. (3) The EPR spectra of the dimer show a dramatic temperature dependence due to a decrease in the zfs in the temperature range where the EPR spectra of the corresponding monomer are unchanged.

In general, it is very difficult to evaluate the T₁ energy transfer in oligomers consisting of identical units, while the energy transfer process of porphyrinic complexes is important in relation to photosynthesis and photonic wires. This study is important in exemplifying the utility of TREPR for investigating energy transfer processes in these macrocycles.

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