

Rapid Exciton Migration and Fluorescent Energy Transfer in Helical Polyisocyanides with Regularly Arranged Porphyrin Pendants

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Photophysical properties of a series of polyisocyanides possessing porphyrin pendants (porphyrin polymers) were investigated by steady state and transient spectroscopic methods. The B (Soret)-band of the free base porphyrin polymers showed splitting indicating substantial exciton coupling in the porphyrin polymers due to a face-to-face stacking conformation. On the other hand, the B-band of the zinc porphyrin polymers split into four peaks indicating deviation from the strict face-to-face stacking conformation. The fluorescence quantum yields of the porphyrin polymers were small compared with those of the corresponding monomers and dimers. Furthermore, the fluorescence decay profiles of the porphyrin polymers deviated from single-exponential decay due to the structural heterogeneity of the polymers. It was revealed that the porphyrin polymers showed transient absorption changes attributable to the exciton–exciton annihilation accompanying structural change with the rate constant of $(2-4) \times 10^{10} \text{ s}^{-1}$ regardless of the length of the polymer chain. The quantum yields of the intersystem crossing of the polymers were smaller than those of monomers due to the efficient exciton–exciton annihilation process in the singlet excited states. In the block copolymers of zinc and free base porphyrins, energy transfer processes from zinc to free base porphyrin moieties were confirmed by time-resolved fluorescence spectral and transient absorption spectral measurements. It became clear that the energy transfer rates were almost independent of the sequence of the block copolymers, suggesting that the rate-determining step of the energy transfer in the present block copolymers is the process at the interface of zinc and free base porphyrins because of the sufficiently fast exciton migration in each block.

Introduction

Recently, various porphyrin arrays mimicking the light harvesting systems of the natural photosynthetic systems have attracted considerable attention^{1–10} because of their potential applicability to the molecular wire conducting the excitonic energy. Artificial porphyrin arrays have been realized by various methods. Many kinds of porphyrin arrays have been synthesized by connecting porphyrin units with an adequate covalent linkage.^{1,2} By connecting the meso-positions of porphyrin units, considerably long porphyrin arrays, in which porphyrins are arranged in a side-by-side configuration, have been synthesized.² A coordinate bond to the central metal of the porphyrin unit affords various architectures, including linear, circular, and box-like porphyrin arrays.^{3–5} Formation of aggregates, such as J-aggregates, is also important for formation of porphyrin arrays.⁶ Dendrimers composed of porphyrin dendrons have been reported recently.⁷ In these porphyrin arrays, excitonic interaction between porphyrin units governs various properties of porphyrin arrays such as absorption, fluorescence, and exciton migration processes. For construction of relatively large nanoarchitecture with these porphyrin arrays, polymerization of monomers possessing a porphyrin unit is also beneficial. Several porphyrin polymers in which porphyrin pigments are aligned in a linear or face-to-face manner have been synthesized.^{8–10} Precise control of the polymer chain length, geometry, and sequence will afford porphyrin arrays favorable to excitonic migration.

We have reported that the living polymerization of aryl isocyanides initiated by the Pd–Pt μ -ethynediyl complex generates polyisocyanides with well-defined polymer structure.⁸ These polyisocyanides exhibit a stable 4_1 helical structure when bulky substitutes are introduced. Actually, by employing porphyrin as a pendant group, syntheses of the helical porphyrin polymers have been attained. The molecular weight distributions of these polymers are rather small: For example, the M_w/M_n value of the 100-mer of isocyanide possessing a free base porphyrin unit is as small as 1.08. The present living polymerization method also afforded block copolymers including blocks of zinc porphyrin and free base porphyrin.^{8d} Since this polymerization method generates well-defined homopolymers and block copolymers, in which porphyrin units are stacked in a face-to-face manner, photophysical properties of these porphyrin polymers will be important information on the excitonic behavior in these sufficiently long and stacked porphyrin arrays.

In the present paper, we estimated several photophysical properties of the porphyrin polymers with a polymerization degree of 2 to 200 using steady state and transient absorption and fluorescence spectroscopy. Exciton migration and energy transfer processes in the homopolymers and block copolymers of zinc porphyrin and free base porphyrin were elucidated (Figure 1).

Experimental Section

Materials. Porphyrin polymers were synthesized according to the procedure reported previously.⁸ Other chemicals are of the best commercial grades available. In the present study, all

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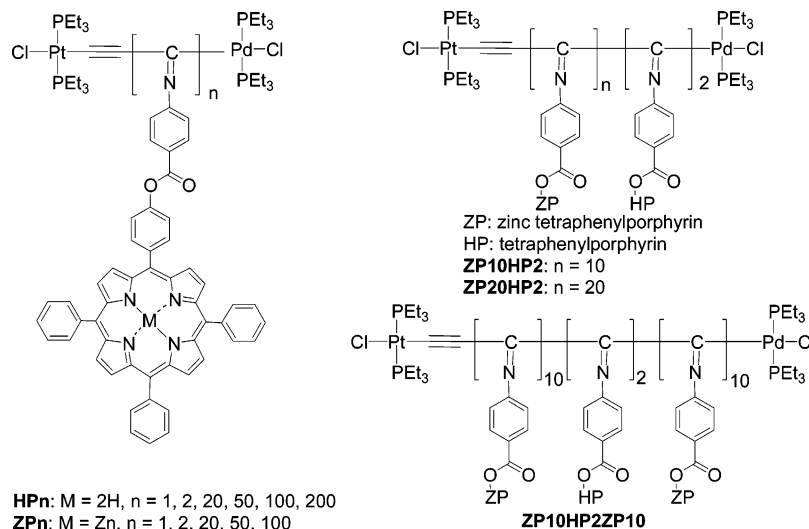


Figure 1. Molecular structures of **ZPn**, **HPn**, **ZPnHP2**, and **ZP10HP2ZP10**.

properties of the porphyrin polymers were estimated with use of THF as a solvent.

Apparatus. Transient absorption spectra in the picosecond region were measured by the pump and probe method employing the second harmonic generation (SHG, 532 nm) of a picosecond Nd:YAG laser (Continuum, RGA69-10LD, fwhm 30 ps, 20 mJ pulse⁻¹) as an excitation source. Probe pulse generated by focusing the fundamental light of the Nd:YAG laser on a D₂O: H₂O cell was detected with a MOS linear image sensor (Hamamatsu Photonics, M2493-40) equipped with a polychromator (Hamamatsu Photonics, C5094) after passing through the sample (Optical path: 2.0 mm).

Nanosecond laser flash photolysis was carried out with SHG (532 nm, fwhm 5 ns) of a nanosecond Nd:YAG laser (Continuum, Surelite II-10) as the excitation source. A Si avalanche photodiode detector (Hamamatsu Photonics, S5343) equipped with a monochromator (Nikon, G250) was used to detect probe light from a Xe lamp (150 W).

Time-resolved fluorescence spectra were measured by the single photon counting method, using a streakscope (Hamamatsu Photonics, C4334-01) equipped with a polychromator (Acton Research, SpectraPro150). Ultrashort laser pulse was generated with a Ti:sapphire laser (Spectra-Physics, Tsunami 3941-M1BB, fwhm 100 fs) pumped with a diode-pumped solid-state laser (Spectra-Physics, Millennia VIIIs). For excitation of the sample, the output of the Ti:sapphire laser was converted to SHG (430 nm) with a harmonic generator (Spectra-Physics, GWU-23FL).

Steady-state absorption and fluorescence spectra were measured on a Shimadzu UV-3100PC and a Hitachi 850, respectively. Emission spectra in the near-IR region were measured with use of a CW Nd:YAG laser (532 nm, 120 mW) as an excitation source. The emission from the sample was focused onto a monochromator (Koken Kogyo, SG-100) equipped with an InGaAs-PIN photodiode (New Focus, 2153). The output signal was recorded with a lock-in amplifier (NF Electronic Instruments, LI 5640).

Results and Discussion

Absorption Spectra of Porphyrin Polymers. Figure 2 shows absorption spectra of the porphyrin polymers as well as the corresponding monomers. The absorption spectra of the dimers are almost the same as those of the corresponding monomers, indicating quite small excitonic interaction between two porphyrin units. This finding indicates that the porphyrin units in the dimer take a conformation where the excitonic interaction

becomes minimal. Such conformation seems to be advantageous to minimize possible steric interaction between the porphyrin units. In the cases of the polymers, the B (Soret)-band showed splitting and substantial broadening with an increase in the number of repeating units as summarized in Table 1. In detail, the B-band of **HP1** showed a peak at 416.8 nm, while that of **HP20** showed peaks at 403.4 and 416.2 nm. As shown in Table 1, the absorption band at the higher energy side shifted to the blue side with an increase in the number of repeating units, although the peak position of the absorption band at the lower energy side was independent of the number of repeating units. The splitting of the B-band can be attributed to the exciton coupling between the porphyrin units.¹⁻¹⁰ The shift to the higher energy side with an increase in relative intensity indicates that porphyrin units are stacked in a face-to-face conformation in which the transition dipole moments are aligned in a parallel form.^{1a,b} It has been reported that polyisocyanides with a bulky group on the nitrogen atom form a 4₁ helical structure with a pitch of ca. 4 Å,⁸ which is a sufficiently close distance to induce the excitonic interaction between the porphyrin units. Thus, the face-to-face stacking conformation seems to be an adequate structure for the free base porphyrin polymers. Assuming that the splitting of the B-band of **HP200** is generated from the exciton coupling of 50 porphyrin units, the splitting energy (ΔE_0) of the neighboring porphyrin units was estimated to be 2210 cm⁻¹ from the relation, $\Delta E = \Delta E_0 \cos[\pi/(N + 1)]$, where ΔE and N are the splitting energy of the array and the number of chromophores participating in the splitting, respectively.^{2d} It is interesting to note that the splitting energy in **HP20** was estimated to be 1760 cm⁻¹, which is smaller than that of **HP200**. It was revealed that the splitting energy became larger for the longer porphyrin polymers. The larger splitting energy in the longer polymers indicates stiff and regular structures of the longer porphyrin polymers. The estimated splitting energies of the present porphyrin polymers are larger than those of the previously reported face-to-face stacked porphyrin arrays probably due to the shorter distance between the porphyrin units.^{1a,b} In the case of the Q-bands of free base porphyrins in the polymers, the spectral shift is rather small due to smaller extinction coefficients compared with the B-bands (Table 1).

The proposed structure of the porphyrin polymer was obtained by using an MM calculation as shown in Figure 3.¹¹ As seen in the top view, **HP50** takes the 4₁ helical structure, which affords the face-to-face geometry to the porphyrin pendants. In the side

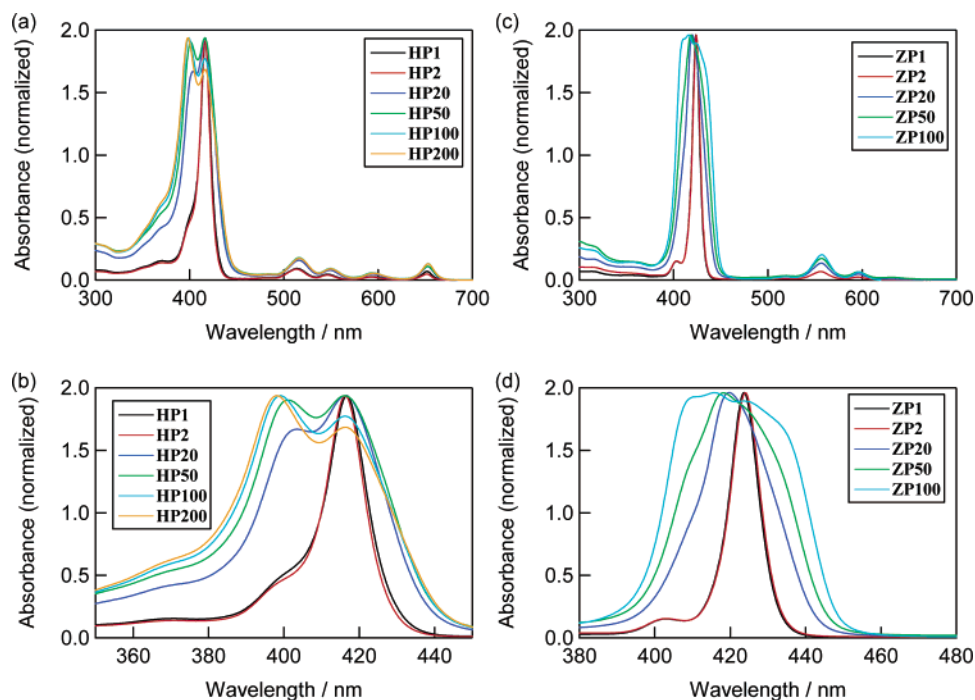


Figure 2. Absorption spectra of (a, b) **HPn** and (c, d) **ZPn** in THF. Absorbance was normalized at the maxima in the B-band region.

TABLE 1: Steady State Absorption Peaks of HPn and ZPn in THF

	$\lambda_{\text{abs}}/\text{nm}^a$	
	B-band ^b (fwhm/cm ⁻¹)	Q-band
HP1	416.8 (761)	513.8, 546.4, 594.0, 651.9
HP2	416.2 (728)	513.4, 546.6, 592.7, 651.6
HP20	403.4, 416.2 (2189)	515.8, 548.9, 594.7, 652.5
HP50	401.2, 416.2 (2467)	516.1, 549.5, 594.4, 652.8
HP100	399.1, 416.2 (2618)	516.4, 549.2, 594.6, 653.0
HP200	398.0, 416.2 (2713)	516.5, 549.7, 595.4, 653.0
ZP1	423.6 (501)	555.8, 595.1
ZP2	424.0 (511)	556.1, 595.2
ZP20	410 (sh), 419.7, 424 (sh) (1294)	556.6, 595.5
ZP50	410 (sh), 418.2, 424 (sh), 431 (sh) (1796)	556.7, 596.1
ZP100	410.8, 415.8, 423.6, 432 (sh) (2212)	557.2, 596.6

^a λ_{max} denotes absorption peak. ^b (sh) denotes a shoulder peak that was estimated by differentiation.

view, the polyisocyanide backbone shows a zigzag structure. The normal axes of porphyrin rings tilted against the direction of the polymer chain are probably due to the steric hindrance of the peripheral phenyl groups. Although the porphyrin units at both ends of the polymer chain seem apart from the stacking structure, another part holds the face-to-face stacking conformation with slight heterogeneity.

The B-bands of the zinc porphyrin polymers do not show clear splitting of the band, although they show substantial broadening with an increase in the number of repeating units (Table 1). It is worth mentioning that the B-band of **ZP100** shows 4 peaks (Figure 2(d)), indicating that the zinc porphyrins in the polymer do not form a strict face-to-face conformation. Since the peak-to-peak energies of the B-band are almost equivalent, the transition dipole moments of the porphyrin units seem to take the angle of ca. 60°. The deviation from the face-to-face conformation possibly results from the deviation from the 4_i symmetry and/or rotation around the ester group connecting the porphyrin pendant and the polyisocyanide backbone. The result indicates that some steric factors of the zinc porphyrin unit including a ring-distortion and/or repulsion of the central metal ions induce the structural difference from the free base porphyrin polymers.

Fluorescence Properties of Porphyrin Polymers. Figure 4 shows fluorescence spectra of the porphyrin polymers in THF.

Fluorescence spectra of the dimers were almost the same as those of the corresponding monomers, indicating negligible interaction between the porphyrin units in the dimers, as observed in the absorption spectra. Quite weak interaction between the porphyrin units in the dimer was also indicated by the fluorescence lifetime (τ_f) and quantum yield (Φ_f). The dimers exhibited essentially the same values as those of the corresponding monomers (Table 2).¹² On the other hand, the polymers showed substantial changes from the monomers. In the cases of the free base porphyrin polymers, fluorescence quantum yields became small. The Φ_f value of **HP200** was almost half that of the monomer. Fluorescence decay profiles of the polymers deviated from the single exponential function, probably due to the structural heterogeneity of the polymers. In the present study, the decay profiles of the polymers were analyzed by employing two exponential functions as summarized in Table 2. The structural heterogeneity in the polymers was supported by the fact that the relative amplitude of the longer lifetime component decreased by 3–10% at 273 K: At low temperature, the heterogeneity of the polymeric structure became small as evidenced by absorption spectra at 273 K. It is worth mentioning that the fluorescence lifetime tends to become shorter for the longer polymers. Shorter fluorescence lifetimes for the longer porphyrin arrays are reported by Kim et al.^{2d}

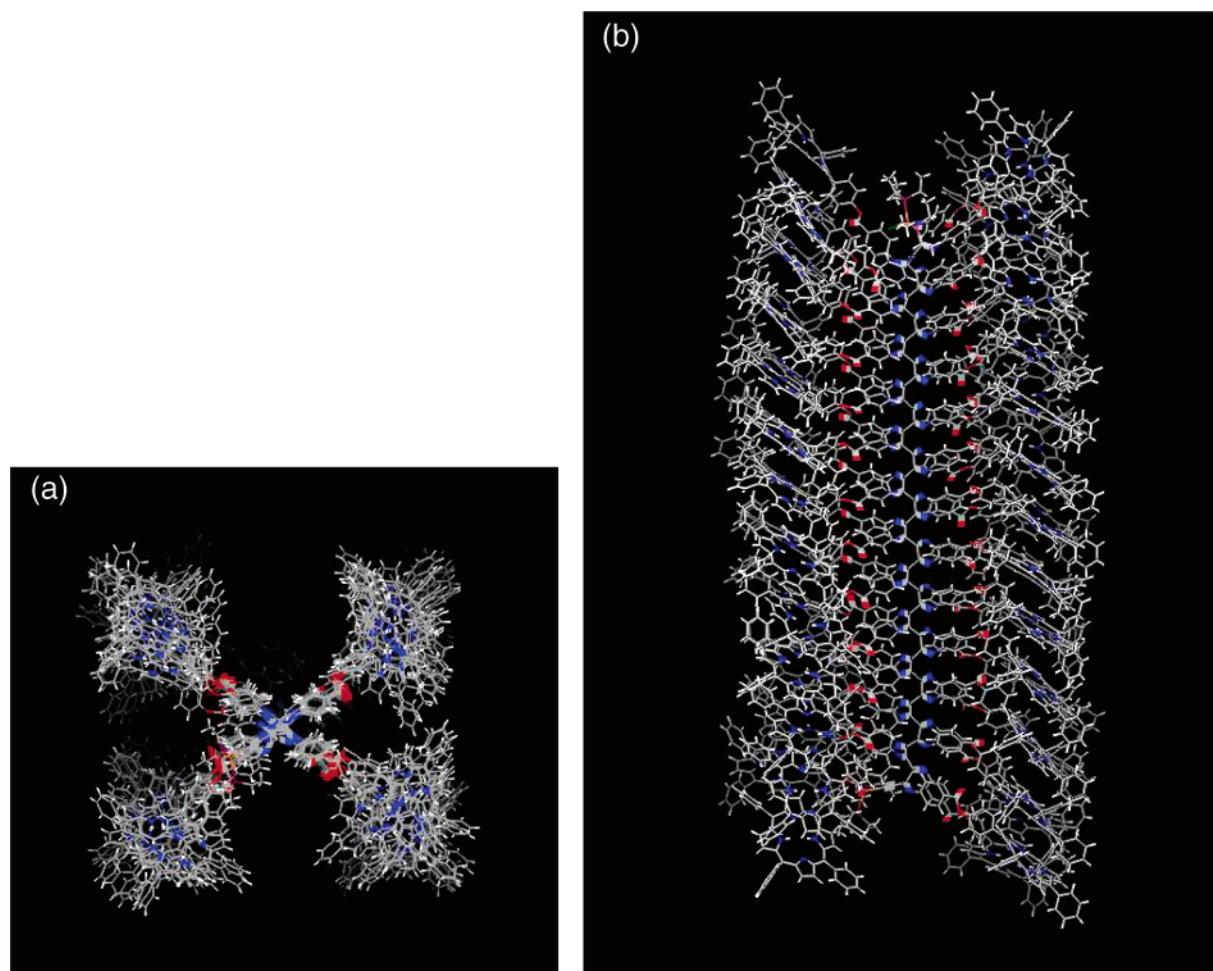


Figure 3. (a) Top and (b) side views of the energy-minimized structure of **HP50**.

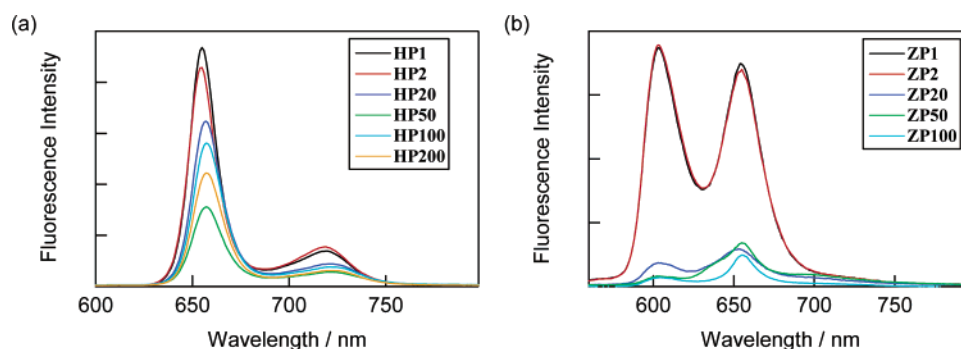


Figure 4. Fluorescence spectra of (a) **HPn** and (b) **ZPn** in THF. Absorbance of the sample was matched at the excitation wavelength (0.010 at 550 nm).

The Φ_F value of **ZP100** was approximately one-seventh that of the monomer. Furthermore, the relative amplitude of the longer lifetime component was smaller than that of the free base porphyrin polymers. These findings indicate that the pendant groups of the zinc porphyrin polymers have rather homogeneous conformation other than the strict face-to-face stacking conformation. Reduction of structural heterogeneity at lower temperature was also confirmed for the zinc porphyrin polymers.

Porphyrin Polymers in the Singlet Excited States. Further fast excitonic processes in the polymers were investigated by using the picosecond transient absorption spectroscopy. Figure 5 shows transient absorption spectra of **HP200** in THF during the laser flash photolysis employing the picosecond Nd:YAG laser (532 nm, fwhm 30 ps) as an excitation source. The spectrum observed at 20 ps after the laser flash exhibited

characteristic features of porphyrin derivatives in the singlet excited state, i.e., a large absorption band around 470 nm and bleaching due to Q-bands (500–650 nm).¹³ It should be pointed out that the transient absorption bands of the porphyrin polymers in the singlet excited state decayed according to the two-step decay in the picosecond region as shown in the inset of Figure 5. The decay rate of the slowly decaying component was evaluated to be $(1.1 \pm 0.2) \times 10^9 \text{ s}^{-1}$, which is the same as the fluorescence decay rate listed in Table 2, indicating that the slowly decaying part is deactivation of the singlet excited state. On the other hand, the decay rate constant of the fast decaying part was $(3.9 \pm 0.4) \times 10^{10} \text{ s}^{-1}$. It is interesting to note that for all free base porphyrin polymers the rate constants of the fast decaying components were $(2.7\text{--}3.9) \times 10^{10} \text{ s}^{-1}$, almost independent of the number of repeating units. In the cases of

TABLE 2: Fluorescence and Triplet Properties of HPn and ZPn in THF^a

	λ_f/nm	τ_f/ns	Φ_f	$\tau_T/\mu\text{s}$	Φ_{ISC}^b
HP1	655, 719	9.7 (100%)	0.12	760	0.84
HP2	654, 718	9.9 (100%)	0.11	640	0.82
HP20	657, 722	8.7 (100%)	0.083	670	0.56
HP50	657, 721	1.4 (58%), 8.1 (42%)	0.040	970	0.38
HP100	657, 721	1.5 (27%), 8.5 (73%)	0.072	660	0.32
HP200	657, 721	1.0 (53%), 7.8 (47%)	0.057	750	0.51
ZP1	603, 654	2.0 (100%)	0.041	560	0.66
ZP2	603, 655	1.9 (100%)	0.041	540	0.66
ZP20	603, 654	0.18 (87%), 1.2 (13%)	0.0069	900	0.14
ZP50	603, 655	0.13 (94%), 1.5 (6%)	0.0080	980	0.06
ZP100	604, 655	0.15 (88%), 1.9 (12%)	0.0058	710	0.11

^a λ_f , τ_f , Φ_f , τ_T , and Φ_{ISC} denote fluorescence peak, fluorescence lifetime, fluorescence quantum yield, triplet lifetime, and intersystem crossing yield at room temperature (296 K), respectively. ^b Φ_{ISC} values were estimated by employing the Φ_{ISC} values of free base tetraphenylporphyrin and zinc tetraphenylporphyrin as standards.

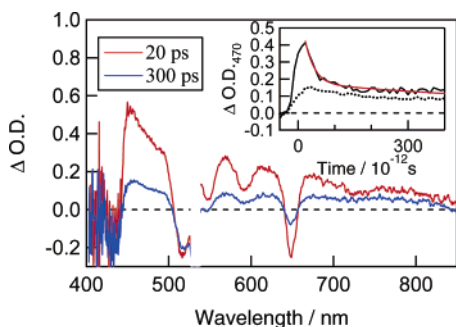


Figure 5. Transient absorption spectra observed at 20 and 300 ps after the laser flash (532 nm, fwhm 30 ps, 20 mJ pulse⁻¹) during the laser flash photolysis of **HP200** in THF (1×10^{-4} M). Inset: Kinetic trace of $\Delta\text{O.D.}$ at 470 nm (laser fluence: (solid line) 20 mJ pulse⁻¹, (dotted line) 5 mJ pulse⁻¹). The red line is a fitted curve.

the zinc porphyrin polymers, the fast decaying components were also confirmed. The rate constants of the fast components were $(2.4\text{--}3.6) \times 10^{10} \text{ s}^{-1}$, almost the same values as those of the free base porphyrin polymers. It should be stressed that the monomers and dimers did not show two-component decay. Thus, the fast deactivation process is a characteristic of the porphyrin polymers.

Photoexcitation dynamics of porphyrin arrays have been investigated by several groups using ultrafast laser experiments.^{1–7} Cho et al. reported that the energy migration rate constants of Q states in the cyclic porphyrin dimer, trimer, and hexamer are $(60 \text{ ps})^{-1}$, $(70 \text{ ps})^{-1}$, and $(180 \text{ ps})^{-1}$, respectively, based on the anisotropy decay.¹⁸ In the cases of the present polymers, anisotropy change was not observed in a few tens of picoseconds region, indicating that the exciton migration rate in the porphyrin polymers should be faster than the picosecond region, probably due to short distance between the porphyrin units (ca. 4 Å) in the helical polymers. For the phthalocyanine polymer in which phthalocyanines are stacked at a distance of 3.3 Å, Ern et al. reported that the exciton population became half that of the initial value at 80 fs by the exciton–exciton annihilation.¹⁴ Thus, a similar fast annihilation process is expected for the present polymers, while the deactivation of the singlet excited state was observed in the range of a few tens of picoseconds. This finding indicates that the rate-determining step of the annihilation is not the energy migration but another process such as a structural change. Rubtsov et al. reported that the porphyrin dimer with a meso-to-meso ethyne bridge showed a hole burning shift that is attributable to the conformational relaxation related to the bridge with the rate constant of ca. $(30 \text{ ps})^{-1}$,^{1h} which is similar

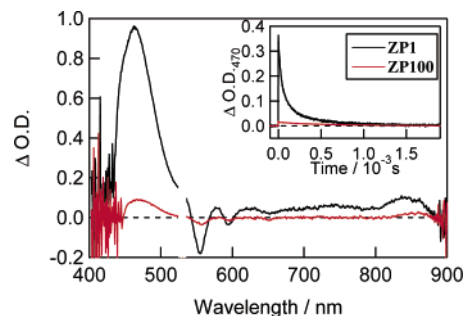


Figure 6. Transient absorption spectra observed at 3 ns after the laser flash (532 nm, fwhm 30 ps, 8.5 mJ pulse⁻¹) during laser flash photolysis of **ZP1** and **ZP100** in THF. Absorbance was matched at the excitation wavelength (0.20 at 532 nm). Inset: Kinetic traces of $\Delta\text{O.D.}$ at 470 nm during the laser flash photolysis upon the nanosecond laser excitation (532 nm, fwhm 5 ns, 10 mJ pulse⁻¹).

to the decay rate of the present porphyrin polymers. Therefore, it seems possible that the fast decay of the present porphyrin polymers indicates the exciton–exciton annihilation in the polymer chain accompanying the polymeric structural change after the fast exciton migration. The exciton–exciton annihilation process is also supported by the fact that the contribution of the fast decaying part became small at low laser fluence (inset of Figure 5). Assuming that the single excited state remains on each polymer chain after the exciton–exciton annihilation, 1.5–2.5 of the singlet excited states were generated on each polymer chain immediately after the laser irradiation under the condition of Figure 5. The exciton–exciton annihilation process in the polymers also explains the absence of the fast decay component within a few tens of picoseconds in the transient absorption spectra of the monomers and dimers.

Porphyrin Polymers in the Triplet Excited States. As indicated by the fluorescence lifetime measurements, the porphyrin polymers in the triplet excited states were generated at several nanoseconds after a laser flash. In the case of **ZP1**, the transient absorption spectrum at 3 ns after the laser flash showed absorption peaks at 740 and 840 nm (Figure 6), which are characteristic of the triplet excited state.¹⁵ Similarly, a transient absorption spectrum due to the triplet excited **ZP100** was also observed as shown in Figure 6. It is worth mentioning that the intensities of the transient absorption bands of the zinc porphyrin polymers were quite small compared with those of the monomer and dimer by a factor of 6–10, even when the absorbance was matched at the excitation wavelength (532 nm). Furthermore, although the kinetic trace of $\Delta\text{O.D.}$ at 470 nm of **ZP1** showed a substantial contribution of the intermolecular triplet–triplet annihilation process, **ZP100** showed the single-exponential decay (inset of Figure 6). The small transient absorption bands and the absence of the triplet–triplet annihilation process indicate the quite small intersystem crossing yields of the porphyrin polymers compared with those of the monomer and dimer. Smaller intersystem crossing yields are also suggested for the free base porphyrin polymers.

In the presence of molecular oxygen, transient absorption bands due to the triplet excited states were quenched completely, indicating the triplet energy transfer generating singlet oxygen ($^1\Delta_g$). In the present case, electron transfer from the triplet excited porphyrin polymers can be ruled out, since the absorption band attributable to the radical cation of the porphyrin was not observed in the transient absorption spectra. The energy transfer process with molecular oxygen was also confirmed by the observation of the emission spectrum of the singlet oxygen at 1270 nm (Figure 7).¹⁶ Since the bimolecular rate constants of the present energy transfer process were the diffusion-limited

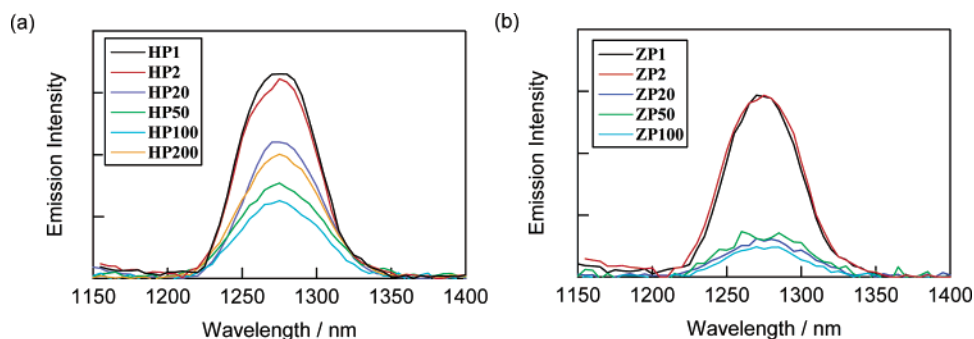


Figure 7. Emission spectra of (a) **HPn** and (b) **ZPn** in THF saturated with molecular oxygen upon excitation with the cw 532-nm laser (120 mW). Absorbance of the sample was matched at the excitation wavelength (0.050 at 532 nm).

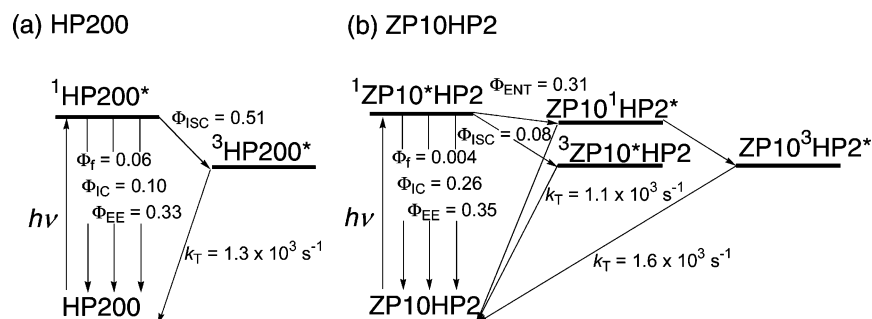


Figure 8. Schematic energy diagrams of (a) **HP200** and (b) **ZP10HP2** in THF. Φ_F , Φ_{IC} , Φ_{EE} , and Φ_{ISC} indicate the quantum yields of fluorescence, internal conversion, exciton–exciton annihilation, and intersystem crossing, respectively. k_T is the triplet decay rate.

rate for all compounds, the emission intensity can be related to the quantum yields of the intersystem crossing process (Φ_{ISC}). The estimated Φ_{ISC} values are summarized in Table 2. It should be noted that the Φ_{ISC} values of the free base porphyrin polymers are smaller than those of monomer and dimer by 0.3–0.5. In the cases of the zinc porphyrin polymers, the Φ_{ISC} decreased by 0.5–0.6. From the kinetic traces obtained by the picosecond laser flash photolysis, the yields of the fast decaying part attributable to the intrachain exciton–exciton annihilation process were estimated to be 0.3–0.6, which are almost the same as the decrease in the Φ_{ISC} values. Thus, the decrease in the Φ_{ISC} values can be attributed to the contribution of the intrachain exciton–exciton annihilation mainly. The rate constants of the unimolecular internal conversion and radiative processes seem not to be altered in these porphyrin polymers. Furthermore, the triplet lifetimes of the polymers (Table 2) did not deviate from those of monomers,¹² indicating that the deactivation process in the triplet state does not change much in the polymers, probably because structural change occurs in the picosecond region rather than in the microsecond region.

In Figure 8a, the deactivation pathways of **HP200** were summarized as representative. From the quantum yields of processes, the main deactivation pathways of the free base porphyrin polymers are intersystem crossing and exciton–exciton annihilation while those of zinc porphyrin polymers are internal conversion and exciton–exciton annihilation. The deactivation through the exciton–exciton annihilation should be a major pathway when the polymer is excited at large excitation fluence.

Energy Transfer Processes in the Block Copolymers. Zinc porphyrins exhibit fluorescence in the wavelength region where free base porphyrins absorb. Thus, an efficient energy migration and transfer system can be produced by connecting the zinc porphyrin wire and free base porphyrin as building blocks of a block copolymer (Figure 1). Figure 9 shows time-resolved fluorescence spectra of **ZP10HP2** in THF. Since the selective excitation of the zinc porphyrin moiety, the energy donor, is

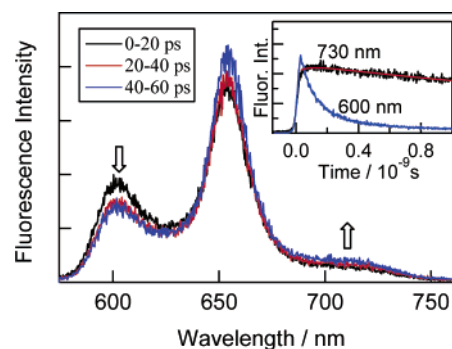


Figure 9. Time-resolved fluorescence spectra of **ZP10HP2** in THF upon excitation at 430 nm. Inset: Fluorescence time profiles at 600 and 730 nm. The red line is a fitted curve.

difficult under the present experimental conditions, the fluorescence spectrum immediately after the laser excitation can be explained as a superposition of the fluorescence spectra of the zinc and free base porphyrin moieties. As seen in the fluorescence decay profile at 600 nm (inset of Figure 9), the fluorescence band due to the zinc porphyrin moiety decreased with a rate constant of $9.3 \times 10^9 \text{ s}^{-1}$. On the other hand, the fluorescence profile at 730 nm, where the free base porphyrin solely emits fluorescence, showed a rise, of which the rate is almost the same as the decay rate of the zinc porphyrin fluorescence. The agreement of the rate constants strongly indicates the energy transfer from the zinc porphyrin to the free base porphyrin moiety. Further evidence for the excitation energy transfer was obtained from the transient absorption spectrum. In the transient absorption spectra, the bleaching due to the free porphyrin moiety (650 nm) increased with the decrease in that of the zinc porphyrin (550 nm) (Figure 10 and inset). Furthermore, the kinetic trace of $\Delta\text{O.D.}$ at 450 nm needs a decay component of $9.3 \times 10^9 \text{ s}^{-1}$ for adequate fit in addition to the components of 3.0×10^{10} and $1.0 \times 10^8 \text{ s}^{-1}$, which are the rate constant of the exciton–exciton annihilation of the zinc porphyrin polymers and the fluorescence decay rate of **HP2**,

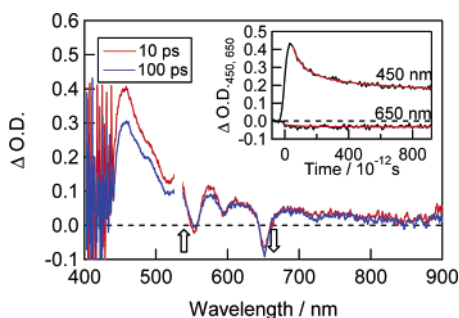


Figure 10. Transient absorption spectra observed at 10 and 100 ps after the laser flash (532 nm, fwhm 30 ps) during the laser flash photolysis of **ZP10HP2** (1×10^{-4} M) in THF. Inset: Kinetic traces of $\Delta O.D.$ at 450 and 650 nm. The red lines are fitted curves.

respectively, indicating the energy transfer from the zinc porphyrin moiety to the free base porphyrin moiety.

It is interesting to note that the rate constants of the excitation energy transfer processes in other block copolymers, **ZP20HP2** and **ZP10HP2ZP10**, were estimated to be 9.3×10^9 and 9.1×10^9 s $^{-1}$, respectively. The essentially same rate constants indicate that the exciton migration process is too fast to affect the energy transfer rate at the interface between the zinc porphyrin and the free base porphyrin units, i.e., energy transfer is the rate-determining step in the present block copolymers.

The deactivation processes of **ZP10HP2** were summarized in the schematic energy diagram (Figure 8b). As indicated by the picosecond transient absorption spectra, the fast exciton–exciton annihilation process decreases the population of the singlet excited state of the zinc porphyrin moiety. Therefore, the quantum yield of the energy transfer process is 0.35. As indicated above, the yield of the exciton–exciton annihilation depends on the excitation fluence. In the limit of low excitation fluence, where the annihilation process can be neglected, the yield of the energy transfer increases to 0.48.

Conclusions

It was revealed that photophysical properties of the porphyrin polymers, in which porphyrin units are stacked in a face-to-face manner, are much different from those of the corresponding monomers and dimers. The excitonic interaction among the porphyrin units governs the properties to a great degree. It is interesting to note that the exciton–exciton annihilation rate constants were almost identical regardless of the length of polymer chain, indicating that the exciton migration is quite fast in the polymer chain. This finding accords with the fact that the energy transfer rates in the block copolymers do not depend on the sequence in the polymer chain. The fast exciton migration in the porphyrin polymers indicates that these polymers are useful as molecular wires connecting photofunctional molecules.

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