Fast Exciton Migration in Porphyrin-Functionalized Polypeptides

Mamoru Fujitsuka,[†] **Michihiro Hara,**[†] **Sachiko Tojo,**[†] **Ayumi Okada,**[†] **Vincent Troiani,**[‡]
Nathalie Solladié,[‡] **and Tetsuro Majima*,**[†]

*The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1,
Ibaraki, Osaka 567-0047, Japan, and Groupe de Synthèse de Systèmes Porphyriniques,
Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Université Louis Pasteur et CNRS,
4 rue Blaise Pascal, 67000 Strasbourg, France*

Received: November 9, 2004; In Final Form: November 28, 2004

The photophysical properties of L-lysine-based polypeptides bearing porphyrin pendants were investigated.
The intramolecular exciton−exciton annihilation resulting from the exciton migration among the porphyrin
units deactivates the singlet excited state efficiently. It was revealed that the rate of the exciton migration
depends on the polymerization degree.

Introduction

Porphyrin arrays attract quite wide attention in light of their importance in artificial photosynthesis and molecular devices, in which excitation energy transport is an important factor. Inspired by the natural light-harvesting system, various kinds of porphyrin arrays have been demonstrated.[1−6] One of the important methods for constructing the large arrays should be the polymerization of a monomer bearing a porphyrin unit. Nowadays, there are several examples of polymers bearing porphyrin, in which porphyrins are aligned in a linear or face-to-face conformation.[4−6] For construction of the porphyrin arrays useful to the light-harvesting system, the polymerization method that controls the polymerization degree and sequence precisely is beneficial.

Recently, some of the present authors and their co-workers synthesized L-lysine-based polypeptides bearing porphyrin pendants (porphyrin polypeptides **P1**, **P2**, **P4**, and **P8**, Figure 1).[5] The porphyrin polypeptides are expected to form a helical structure such as an α-helix, in which the porphyrin units are aligned in a favorable conformation for the exciton migration. Herein, we report the photophysical properties of the porphyrin polypeptides based on transient spectroscopic measurements. Excitonic processes due to the exciton migration are observed.

Experimental Section

Materials. Porphyrin polypeptides were synthesized according to the procedure reported previously.[1]

Apparatus. The excitation dynamics of porphyrin polypeptides were examined using transient absorption and time-resolved fluorescence spectroscopy. The details are described in a previous report.[4b]

Results and Discussion

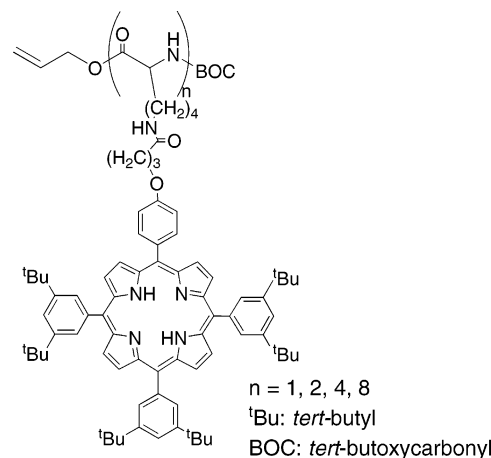In Table 1, the peak position and bandwidth (full width at half-maximum (fwhm)) of the B (Soret)-band of the porphyrin

---
* Corresponding author. E-mail: majima@sanken.osaka-u.ac.jp.
† Osaka University.
‡ Université Louis Pasteur et CNRS.

Figure 1. Molecular structure of porphyrin polypeptides (**P***n*, where *n* = 1, 2, 4, or 8).

TABLE 1: Absorption, Fluorescence, and Triplet Properties of Porphyrin Polypeptides in Toluene

	$\lambda_{abs}{}^{a}$/nm (fwhm)^{c}	$\lambda_{f}{}^{a}$/nm	$\tau_{f}{}^{a}$/ns	$\Phi_{f}{}^{a,b}$	$\Phi_{ISC}{}^{a,b}$	$\tau_{T}{}^{a}$/μs	$k_{TT}{}^{a}$/10^{9} M^{-1} s^{-1}
P1	422.6 (672)	655, 722	11.9	0.12	0.82	740	4.4
P2	422.6 (706)	655, 722	11.4	0.081	0.80	680	3.7
P4	422.8 (828)	654, 723	11.4	0.086	0.83	720	1.9
P8	422.6 (841)	656, 722	11.5	0.095	0.83	890	1.7

^{a} λ_{abs}, λ_{f}, τ_{f}, Φ_{f}, Φ_{ISC}, τ_{T}, and k_{TT} refer to the absorption peak of the B-band, fluorescence peak, fluorescence lifetime, fluorescence quantum yield, intersystem crossing yield, triplet lifetime, and rate constant for the triplet−triplet annihilation, respectively. ^{b} The value was estimated under the conditions where the exciton−exciton migration can be ignored. ^{c} In cm^{-1}.

polypeptides are listed. The peak position was almost independent of the degree of polymerization. The increase of the bandwidth was rather small compared with those of other porphyrin arrays in which porphyrin units take a face-to-face stacking conformation.[1−6] These results show that the interaction between the porphyrins in the present polypeptides is rather weak, suggesting that the distance between the porphyrin units
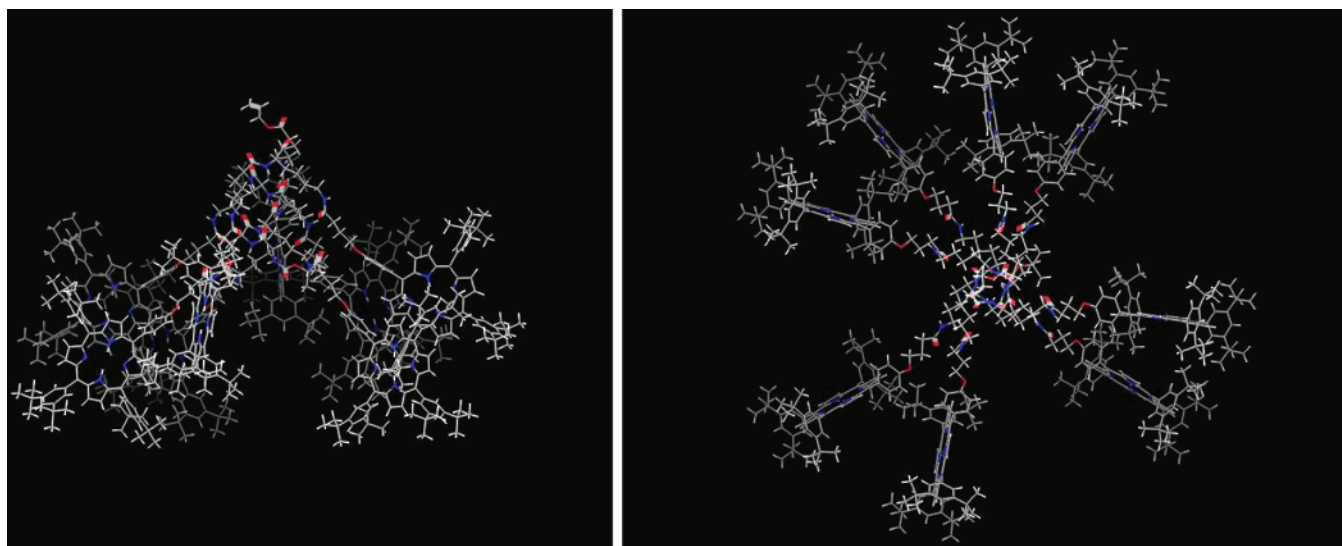
Figure 2. Energy minimized structure of **P8**: (left) side view; (right) top view.

is large even in the longest porphyrin polypeptide, **P8**. The possible structure of **P8** was obtained by MM calculation (Figure 2).[7] As shown in the side view, in such a conformation, the polypeptide holds the α-helix, in which porphyrins are almost parallel to the long axis of the polypeptide. Although the porphyrin units are aligned in a face-to-face manner, the distance between the porphyrin units is rather large, as seen in the top view. The center-to-center distance between the porphyrin units ranges from 9.8 to 20.6 Å, and the averaged distance is 14.9 Å, from which only a few hundred cm^{-1} of exciton coupling is expected in accordance with the observed bandwidth.[8] The distance between the porphyrins will be larger for the shorter polypeptides. Actually, the averaged distance of the porphyrin units of **P4** was estimated to be 20.8 Å. This finding is consistent with the fact that shorter porphyrin polypeptides exhibit a narrower bandwidth in the absorption spectra.

In Table 1, fluorescence properties, such as fluorescence peak position, lifetime, and yield, are also summarized. Fluorescence peak positions and lifetimes were almost identical, while quantum yields show slight decrease with increasing polymerization degree. From the relative long distance between the porphyrin units, negligible interaction in the singlet excited state seems to be adequate.

The excitonic processes in the porphyrin polypeptides were investigated using picosecond laser flash photolysis. The transient absorption spectrum of **P8** at 20 ps after the laser flash (532 nm, fwhm 30 ps) exhibited characteristic features of the porphyrin units in the singlet excited state, that is, a large absorption band around 445 nm and bleaching due to Q-bands (500−650 nm). It should be pointed out that the singlet excited state of **P8** decayed according to the two-step decay in the picosecond region (inset of Figure 3a). The slowly decaying component can be attributed to the decay of the singlet excited state ($\tau_f = 11.5$ ns), which does not show substantial decay in the 0−500 ps time region. On the other hand, the decay rate constant of the fast decaying part was $(1.1 \pm 0.1) \times 10^{10}$ s^{-1}. It is noteworthy that the fast decaying component almost vanished when the excitation laser fluence was low (inset of Figure 3a). From these findings, the fast decaying component can be attributed to the deactivation of the singlet excited state by the intramolecular exciton−exciton annihilation process resulting from the exciton migration among the porphyrin units.[9] This assignment is supported by the fact that the fast decaying component was not observed in the kinetic trace of ΔOD at
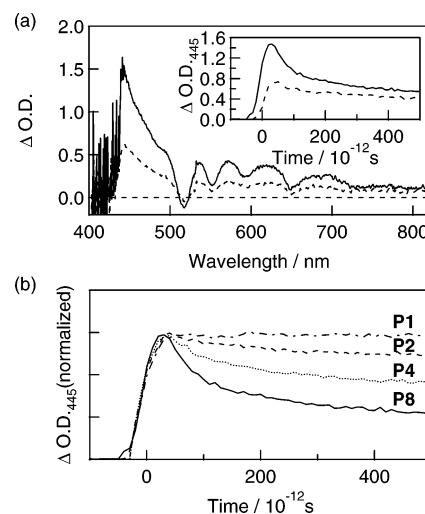

Figure 3. (a) Transient absorption spectra observed at 20 (solid line) and 400 (dashed line) ps after the laser flash (532 nm, fwhm 30 ps, 20 mJ pulse^{-1}) during the laser flash photolysis of **P8** in toluene. The inset shows kinetic traces of ΔOD at 445 nm (laser fluence: (solid line) 20 mJ pulse^{-1}; (broken line) 3 mJ pulse^{-1}). (b) Kinetic traces of **P1**, **P2**, **P4**, and **P8** at 445 nm. The absorbance of the samples was matched at the excitation wavelength (532 nm).

445 nm of **P1** (Figure 3b). It is interesting to note that **P4** also showed the two-step decay due to the exciton−exciton annihilation (Figure 3b), although the decay rate ($(7.3 \pm 0.4) \times 10^9$ s^{-1}) was slower than that of **P8**. This finding indicates that the exciton−exciton annihilation becomes less efficient when the distance between the porphyrin units become large. Furthermore, the rate-determining step of the present deactivation can be attributed to the exciton migration, because the rate depends on the distance between the chromophores.

Cho et al. reported that the energy migration rate constants in the cyclic porphyrin dimer, trimer, and hexamer are (60 ps)$^{-1}$, (70 ps)$^{-1}$, and (180 ps)$^{-1}$, respectively.[1d] They evaluated the distance between the porphyrin units to be ∼10.6 Å for the dimer and hexamer and ∼18.3 Å for the trimer. The results on the present porphyrin polypeptides are comparable to the results by Cho et al., supporting the consideration that the rate-determining step of the exciton−exciton annihilation is the exciton migration among the porphyrin units.

After substantial delay time, generation of the triplet excited states was confirmed for the porphyrin polypeptides. The
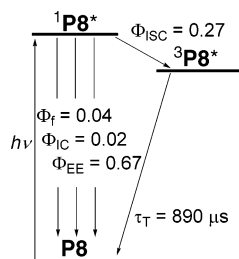
Letters

J. Phys. Chem. B, Vol. 109, No. 1, 2005 **35**

Figure 4. Schematic energy diagram of the photoinduced processes of **P8** under the conditions where exciton−exciton annihilation is included. Φ_{EE} and Φ_{IC} denote the yields of the exciton−exciton annihilation and internal conversion, respectively. For other symbols, see footnote *a* of Table 1.

quantum yields of the intersystem crossing (Table 1) were estimated from the emission intensity of the singlet oxygen (1270 nm), which was generated by triplet energy transfer from the triplet excited porphyrin polypeptides to molecular oxygen. In the experiments, the excitation power was adjusted as low as possible in order to avoid intramolecular exciton−exciton annihilation in the singlet manifold. The estimated yields were identical, indicating that the rate constants of the deactivation processes in the singlet manifold are not varied, except for the exciton−exciton annihilation process. Negligible change of the deactivation processes was also confirmed for the triplet excited state, as evidenced by the lifetime of the triplet state (Table 1). It is interesting to note that the rate constant of intermolecular triplet−triplet annihilation decreased with increasing polymerization degree. The smaller rate constant of longer porphyrin polypeptides can be reasonably attributed to the lower mobility of the longer polypeptides in solution.

The photoinduced processes of **P8**, as a representative, including the exciton−exciton migration are summarized in Figure 4. As indicated in the diagram, the exciton−exciton annihilation efficiently deactivates the excited state of the porphyrin polypeptide, although its contribution depends on the laser fluence.

Conclusion

In the porphyrin polypeptides, fast intramolecular exciton−exciton annihilation resulting from exciton migration was confirmed, although the interaction between the porphyrin units is rather weak. The present results indicate that further artificial molecular systems are possible by employing various functional molecules including porphyrin in the polypeptides.

References and Notes

(1) (a) Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054. (b) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759. (c) Kumble, R.; Palese, S.; Lin, V. S. Y.; Therien, M. J.; Hochstrasser, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11489. (d) Cho, H. S.; Rhee, H.; Song, J. K.; Min, C. K.; Takase, M.; Aratani, N.; Cho, S.; Osuka, A.; Joo, T.; Kim, D. *J. Am. Chem. Soc.* **2003**, *125*, 5849.

(2) (a) Aratani, N.; Osuka, A.; Kim, Y. H.; Jeoung, D. H.; Kim, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1458. (b) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79. (c) Kim, D.; Osuka, A. *J. Phys. Chem. A* **2003**, *107*, 8791.

(3) (a) Choi, M. S.; Aida, T.; Yamazaki, T.; Yamazaki, I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3194. (b) Yeow, E. K. L.; Ghiggio, K. P.; Reek, J. N. H.; Crossley, M. J.; Bosman, A. W.; Schenning, A. P. H. J.; Meijer, E. W. *J. Phys. Chem. B* **2000**, *104*, 2596.

(4) (a) Takei, F.; Hayashi, H.; Onitsuka, K.; Kobayashi, N.; Takahashi, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4092. (b) Fujitsuka, M.; Okada, A.; Tojo, S.; Takei, F.; Onitsuka, K.; Takahashi, S.; Majima, T. *J. Phys. Chem. B* **2004**, *108*, 11935. (c) de Witte, P. A. J.; Castriciano, M.; Cornelissen, J. J. L. M.; Scolaro, L. M.; Nolte, R. J. M.; Rowan, A. E. *Chem.−Eur. J.* **2003**, *9*, 1775.

(5) (a) Solladié, N.; Hamel, A.; Gross, M. *Tetrahedron Lett.* **2000**, *41*, 6075. (b) Solladié, N.; Hamel, A.; Gross, M. *Chirality* **2001**, *13*, 736.

(6) (a) Jiang, B.; Yang, S.; Jones, W. E., Jr. *Chem. Mater.* **1997**, *9*, 2031. (b) Ferri, A.; Polzonetti, G.; Licoccia, S.; Paolesse, R.; Favretto, D.; Traldi, P.; Russo, M. V. *J. Chem. Soc., Dalton Trans.* **1998**, 4063.

(7) MM calculation was performed using Spartan02, Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612.

(8) From the optimized **P8** structure (Figure 2), 320 cm^{-1} of the coupling energy was estimated for **P8** assuming 7.9 D of the transition dipole moment (Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1988**, *110*, 4454.).

(9) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*, 2nd ed.; Oxford University Press: New York, 1999.