CHEMISTRY LETTERS, pp. 583-586, 1994.

Anomalous Behavior of Triplet-Excited Zinc(II) Tetraphenylporphyrin Moieties Compartmentalized in the Hydrophobic Cluster of Pendant Cyclododecyl Groups in an Amphiphilic Polyelectrolyte

Yotaro MORISHIMA,* Kazunori SAEGUSA, and Mikiharu KAMACHI*
Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560

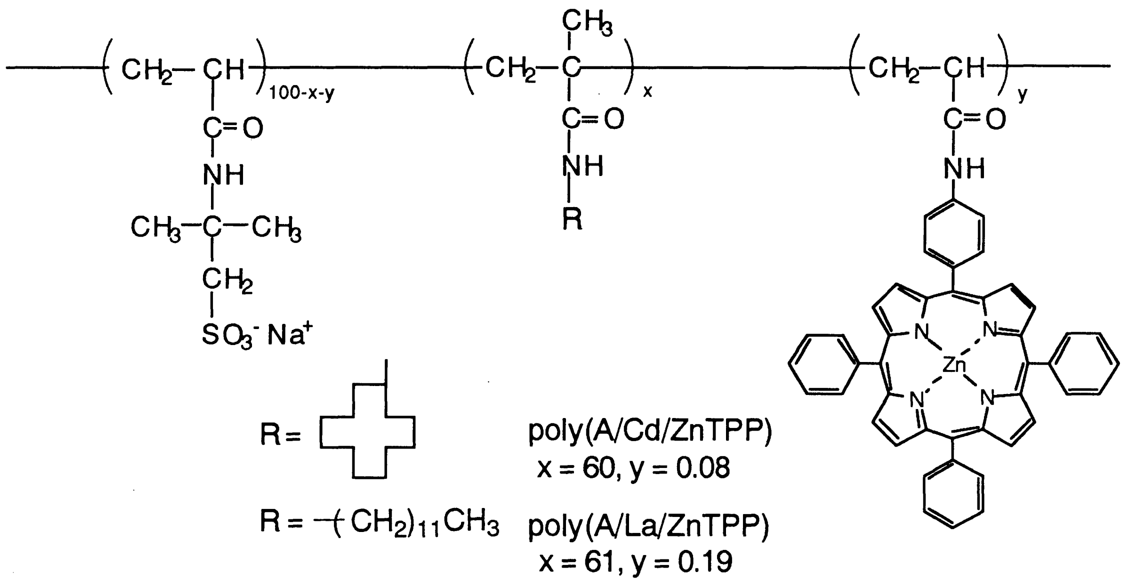
A small quantity of zinc(II) tetraphenylporphyrin (ZnTPP) moicites were covalently incorporated into an amphiphilic copolymer of sodium 2-acrylamido-2-methylpropanesulfonate and *N*-cyclododecylmethacrylamide. The ZnTPP moieties were compartmentalized in the hydrophobic cluster of the cyclododecyl pendants in the polymer in aqueous solution, and showed a unusual blue-shifted phosphorescence due to a high energy triplet-excited (T_1) state. The lifetime of the high energy T_1 state was extraordinarily long: ca. 56 ms at 20 °C in aqueous solution.

Amphiphilic copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) with comonomers bearing bulky hydrophobic side-chain groups adopt unimolecular micelles (unimers).1) Recently, we have recognized that zinc(II) tetraphenylporphyrin (ZnTPP) moieties compartmentalized in the cluster of the hydrophobic groups in the unimer in aqueous solution show room-temperature phosphorescence, E-type delayed fluorescence due to thermal repopulation from the triplet-excited (T_1) state, and long T_1 lifetime.2)

In the course of our previous work, we came across the fact that the photophysical behavior of the ZnTPP moieties compartmentalized in the hydrophobic cluster of cyclododecyl (Cd) pendant groups was quite different from that in the clusters of other hydrophobic pendant groups in the amphiphilic polyelectrolytes. For example, in aqueous solution at room temperature, the ZnTPP moieties in the Cd cluster showed phosphorescence with a peak blue-shifted by ca. 40 nm as compared with the phosphorescence of the ZnTPP moieties in the clusters of lauryl (La), adamantyl, and naphthyl groups.2) These unexpected observations prompted us to investigate the behavior of the triplet-excited ZnTPP moieties compartmentalized in the Cd cluster by focusing on the delayed emissions and transient T-T absorption as a function of delay time and temperature.

In the present study, we prepared a terpolymer of 0.08 mol% zinc(II) 5-(4-acrylamidophenyl)-10,15,20-triphenylporphynate (ZnAATPP), 60 mol% *N*-cyclododecylmethacrylamide (CdMAm), and AMPS. The terpolymer of 0.19 mol% ZnAATPP, 61 mol% *N*-laurylmethacrylamide, and AMPS, which had been prepared in the previous work,2) was used for comparison. The Cd- and La-containing terpolymers are abbreviated as poly(A/Cd/ZnTPP) and poly(A/La/ZnTPP), respectively (Scheme 1).

Delayed emission spectra were obtained with a Shimadzu RF-502A spectrofluorometer equipped with a light chopper operated at varying frequencies. Concentrations of the ZnTPP residues were adjusted to 1 μ*M*. Laser photolysis was performed by using a Q-switched Nd:YAG laser (Quantaray DCR-2) operated at the second harmonics (7-ns fwhm at 532 nm). The laser power was attenuated to 1.9 mJ/pulse. To avoid the effect of a trace of oxygen, the sample solutions were outgassed by several pump-and-thaw cycles on a high vacuum line.



Scheme 1.

Figure 1 compares phosphorescence spectra of poly(A/Cd/ZnTPP) and poly(A/La/ZnTPP) in aqueous rigid solution at 77 K. Phosphorescence of ZnTPP itself is known to have a peak near 780 nm in rigid glasses at 77 K.3) Poly(A/La/ZnTPP) showed a normal phosphorescence spectrum peaking at 793 nm. In contrast, poly(A/Cd/ZnTPP) showed blue-shifted phosphorescence with a peak at 746 nm and a shoulder at ca. 785 nm, the shoulder being attributable to normal phosphorescence. Even in aqueous fluid solution at high temperatures, the Cd- and La-containing terpolymers exhibited phosphorescence together with E-type delayed fluorescence.2)

Figure 2 shows the delayed fluorescence and phosphorescence spectra of poly(A/Cd/ZnTPP) in aqueous solution at 20 and 90 °C. Importantly, the blue-shifted phosphorescence peak disappeared at 90 °C, while the normal phosphorescence band remained although the intensity became weak. It should be noted here that poly(A/La/ZnTPP) showed normal phosphorescence in aqueous fluid solution.2) The spectral pattern of the delayed fluorescence of poly(A/Cd/ZnTPP) at 20 °C was significantly different from that of poly(A/La/ZnTPP): the band was significantly broad and distorted such that the intensity of the 0-0 emission band (601 nm) was weaker than that of the 0-1 band (645 nm), while the La-containing terpolymer exhibited a normal fluorescence pattern.2) At 90 °C, however, the delayed fluo-rescence spectrum of the Cd-containing terpolymer showed a normal pattern, and its intensity became very strong because of the thermal repopulation from the

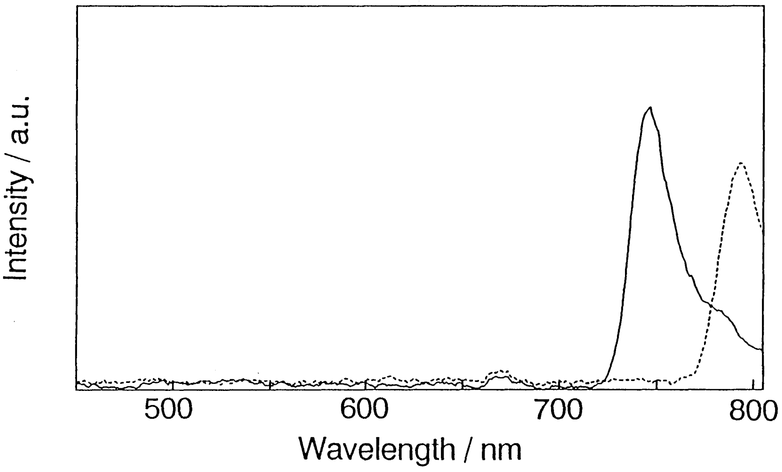


Fig. 1. Phosphorescence spectra for poly(A/Cd/ZnTPP) (solid line) and poly(A/La/ZnTPP) (dotted line) in aqueous rigid solution at 77 K recorded at a delay time of 2.5 ms.

T_1 state. These observations may suggest that in the Cd-containing terpolymer a fraction of the ZnTPP moieties are sterically distorted in the Cd cluster giving rise to a high energy T_1 state which is responsible for the blue-shifted phosphorescence. At 90 °C, a temperature at which hydrophobic interactions are essentially nil, the Cd cluster becomes loosened and the compartmentalized ZnTPP moiëties can adopt relaxed conformations for the T_1 and ground states, respectively. In fact, we have revealed that the Cd cluster is more rigidly packed than the La cluster, and molecular motions of a compartmentalized chromophore in the Cd cluster are much more restricted than in the La cluster.[1e] Figure 3 compares delayed emission spectra of poly(A/Cd/ZnTPP) in aqueous solution at 30 °C observed at different delay times. Of importance is the fact that, at a longer delay time, the normal phosphorescence diminished relative to the blue-shifted phosphorescence. This implies that the lifetime for the high energy T_1 state is longer than that for the normal T_1 state.

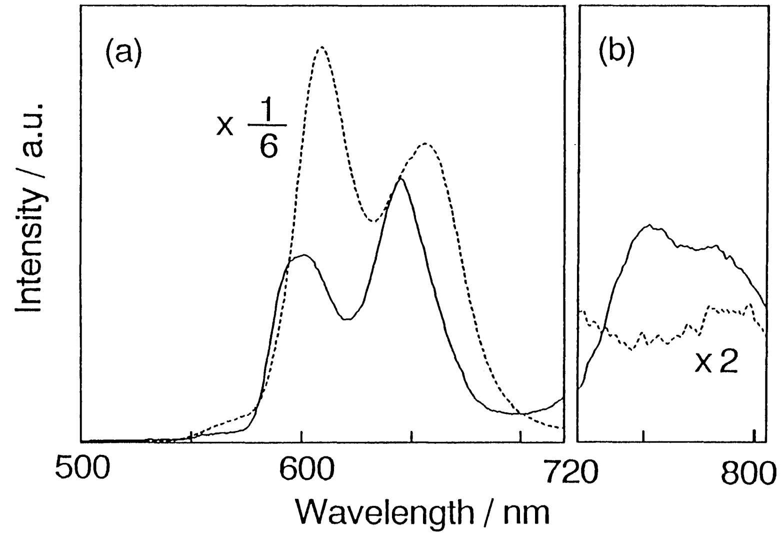


Fig. 2. Delayed fluorescence (a) and phosphorescence (b) spectra for poly(A/Cd/ZnTPP) in aqueous solution at 20 °C (solid line) and 90 °C (dotted line): delay time, 2.5 ms; excitation, at 426 nm for delayed fluorescence and at 430 nm for phosphorescence measurements.

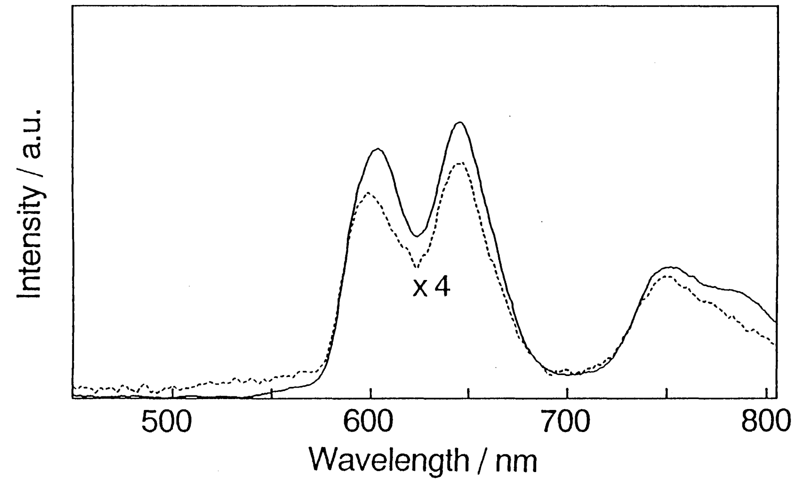


Fig. 3. Delayed fluorescence and phosphorescence spectra for poly(A/Cd/ZnTPP) in aqueous solution at 30 °C: delay times, 2.5 ms (solid line) and 30 ms (dotted line); excitation; at 430 nm.

These unusual observations of the phosphorescence and thermally activated delayed fluorescence at high temperatures are primarily due to an extremely long-lived T_1 state of the compartmentalized ZnTPP moieties. As reported previously,[2] the triplet lifetime of poly(A/Cd/ZnTPP) in aqueous solution at room temperature was much longer than that of poly(A/La/ZnTPP). Figure 4 compares the first-order plots of the triplet absorption decays over a time region of 180 ms for poly(A/Cd/ZnTPP) in aqueous solution at 20 and 95 °C. It is apparent from Fig. 4 that at 20 °C there is an extremely longer-lived T_1 component. The decay profiles were able to be fitted to a double-exponential decay function.[4] Triplet lifetimes ($\tau_{T,1}$ and $\tau_{T,2}$ for shorter and longer lifetime, respectively) and their fractions which yielded the best fits were indicated in the figure. The main decay component at 20 °C was found to be extraordinarily long-lived ($\tau_{T,2}$=56.2 ms). At 95 °C, however, the triplet absorption decayed mostly with a lifetime of the shorter component (12.3 ms) and the fraction of the longer-lived component became much lower than that at 20 °C. From the fact that the Cd-containing terpolymer shows mainly normal phosphorescence at 90 °C (Fig. 2), the decay profile at 95 °C may be mostly attributed to the decay of the normal T_1 state. Considering the observations shown in Figs. 2 and 3, the longer-lived decay component at 20°C can be attributed to the high energy T_1 state.

The lifetimes of ZnTPP itself have been reported to be 1.19 and 1.25 ms in ethanol and toluene solutions at 300 K, respectively,[5] while its phosphorescence lifetimes have been reported to be 25 and 26 ms in ethanol and toluene rigid glasses at 77 K, respectively.[5] The high energy triplet-excited state with unusually long lifetime observed for the ZnTPP moieties in the Cd cluster in aqueous solution at room temperature may be attributed to the fact that the Cd cluster serves as a rigid matrix in which the ZnTPP residues are in a distorted conformation.

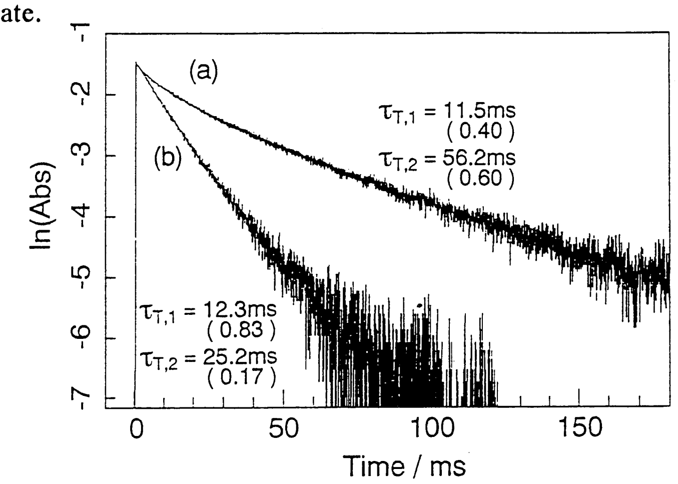


Fig. 4. Decay profiles of the T-T absorption monitored at 480 nm for poly(A/Cd/ZnTPP) in aqueous solution at 20 °C (a) and 95 °C (b). Triplet lifetimes and fractions of their components (in parentheses) for the best-fits are indicated in the figure.

In summary, the ZnTPP moieties compartmentalized in the Cd cluster in poly(A/Cd/ZnTPP) in aqueous solution showed a blue-shifted phosphorescence due to the high energy T_1 state. The lifetime of the high energy T_1 was estimated to be ca. 56 ms at 20 °C in aqueous solution. This extraordinarily long-lived T_1 state of the compartmentalized ZnTPP may be of great advantage in use for sensitization and electron transfer reactions.

This work was supported in part by the Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Science, and Culture, Japan.

References

1) a) Y. Morishima, Y. Tominaga, M. Kamachi, T. Okada, Y. Hirata, and N. Mataga, *J. Phys. Chem.*, **95**, 6027 (1991); b) Y. Morishima, M. Tsuji, M. Kamachi, and K. Hatada, *Macromolecules*, **25**, 4406 (1990); c) Y. Morishima, M. Seki, Y. Tominaga, and M. Kamachi, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 2099 (1991); d) M. Seki, Y. Morishima, and M. Kamachi, *Macromolecules*, **25**, 6540 (1992); e) Y. Morishima, M. Tsuji, M. Seki, and M. Kamachi, *ibid.*, **26**, 3299 (1993).

2) H. Aota, Y. Morishima, and M. Kamachi, *Photochem. Photobiol.*, **57**, 989 (1993).

3) K. Kalyanasundaram and M. Neumann-Spallart, *J. Phys. Chem.*, **86**, 5153 (1982).

4) The decays were fitted to a double-exponential function $A(t)/A(0)=\alpha\exp(-t/\tau_{T,1}) + (1-\alpha)\exp(-t/\tau_{T,2})$, where $A(t)$ and $A(0)$ are the 480-nm absorbances at time t and t=0, respectively, and α is the fraction of the faster decay component. For the fitting computation, the damping Gauss-Newton algorithm for the nonlinear least-squares method was used.

5) A. G. Harriman, G. Porter, and N. Searle, *J. Chem. Soc., Faraday Trans. 2*, **75**, 1515 (1979).

(Received December 13, 1993)