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Anomalously Blue-Shifted Fluorescence and Phosphorescence of Zinc(II) Tetraphenylporphyrin in Highly Constraining Microenvironments in Hydrophobically Modified Polysulfonates

Yotaro Morishima,* Kazunori Saegusa, and Mikiharu Kamachi*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

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ABSTRACT: Zinc(II) tetraphenylporphyrin (ZnTPP) moieties, covalently attached to amphiphilic sodium polysulfonates carrying cyclododecyl (Cd; 60 mol %) or lauryl (La; 61 mol %) groups, are compartmentalized within the clusters of the hydrophobic groups in aqueous solution. Such compartmentalized ZnTPP chromophores exhibit delayed fluorescence and phosphorescence at ordinary temperatures. The spectral patterns of the fluorescence and phosphorescence of the ZnTPP moieties in the Cd cluster strongly depended on the excitation wavelength; anomalously blue-shifted fluorescence (both prompt and delayed) and phosphorescence spectra were observed when excited at wavelengths on the shorter wavelength side of the Soret band maximum, while these emissions showed normal spectra when excited at wavelengths on the red side of the Soret band maximum. No such dependencies of the emission spectra on the excitation wavelength were recognized for the ZnTPP moieties compartmentalized in the La cluster. The spectral data indicate that the microenvironment about the ZnTPP chromophores in the Cd cluster is markedly different from that in the La cluster and that there are ZnTPP species whose electronic energy levels are considerably perturbed in the Cd cluster. These species are ascribed to conformationally distorted ZnTPP species owing to the highly constraining microenvironments in the Cd cluster.

Introduction

In a variety of biological systems, metalloporphyrins are embedded in protein environments[1-3] that play a key role in controlling reactivities and biological functions of the metalloporphyrins. In the reaction center of natural photosynthetic systems, chlorophylls are assembled in protein matrices with the specific alignment and orientation such that quantum efficiencies of photoinduced energy and electron transfers are maximized. Studies of the effects of generic microenvironments on photophysical and photochemical behavior of metalloporphyrins in model systems may provide mechanistic insight into the biological photosynthesis. In addition, such studies may provide a guideline for designing of artificial photosystems such as photon energy conversion (into electronic energy or chemical potential), information processing, and organic photoimaging systems. In recent years, a number of studies have focused on the catalytic, electrochemical, and photochemical behavior of porphyrins in various supramolecular assemblies such as micelles,[4] vesicles,[5-9] monolayers[10,11] and Langmuir–Blodgett films.[12,13]

We have shown that the photophysics and photochemistry of some chromophores can be greatly modified if they are incorporated into self-organized microphases of some amphiphilic polyelectrolytes in aqueous media.[14-16] Amphiphilic copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) and methacrylamides carrying bulky hydrophobic side-chain groups adopt unimolecular micelles or unimers due to intramolecular hydrophobic self-association of the side-chain hydrophobic groups.[16-19] The unimers consist of hydrophobic clusters in which the hydrophobic side-chain groups are so tightly packed that their molecular motions are highly restricted. Thus, the hydrophobic clusters provide highly constraining microenvironments for chromophores incorporated into the clusters.[20,21]

If a small amount of zinc(II) tetraphenylporphyrin (ZnTPP) is covalently incorporated into the amphiphilic AMPS copolymer bearing bulky hydrophobic groups, such as lauryl (La), cyclododecyl (Cd), 1-adamantyl, and 1-naphthylmethyl groups, the ZnTPP moieties are "compartmentalized" in the hydrophobic clusters in aqueous media.[22-24] With these ZnTPP moieties in the constraining microenvironments, we recognized large modifications of their photophysical behavior at ordinary or higher temperatures, including observations of phosphorescence, "E-type" delayed fluorescence due to thermal repopulation from the triplet excited state back to the singlet excited state, and extraordinarily long triplet lifetime.[22,23] These unusual observations arise from the fact that chromophore–chromophore interactions, including triplet–triplet (T–T) annihilation, are prevented because of the chromophore isolation in the confining space, and also from the fact that the triplet quenching by impurities is prevented because of the chromophore protection from the bulk phase.

In the course of the ongoing studies, we encountered rather peculiar observations that the ZnTPP moieties confined in the cluster of the Cd groups exhibited emissions significantly different from those in the clusters of other hydrophobic groups such as La, 1-adamantyl, and 1-naphthylmethyl groups.[22,23] In the preceding paper, we reported on the temperature dependencies of the phosphorescence, delayed fluorescence, and triplet lifetime of the ZnTTP chromophores confined in the cluster of the Cd groups.[24] The ZnTPP species in the Cd cluster showed a blue-shifted phosphorescence with a peak near 750 nm besides a normal phosphorescence with a peak at ca. 780 nm. At temperatures below 30 °C, the blue-shifted phosphorescence was predominant over the normal phosphorescence. As the temperature was raised, however, the intensity of the blue-shifted phosphorescence relative to the normal phosphorescence decreased, and the blue-shifted phosphorescence completely vanished at ca. 90 °C. A significantly blue-shifted excitation spectra were ob-

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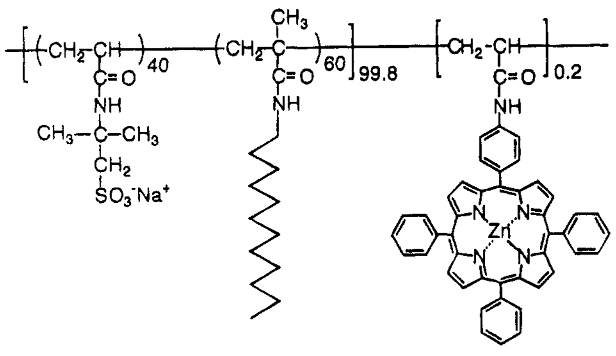
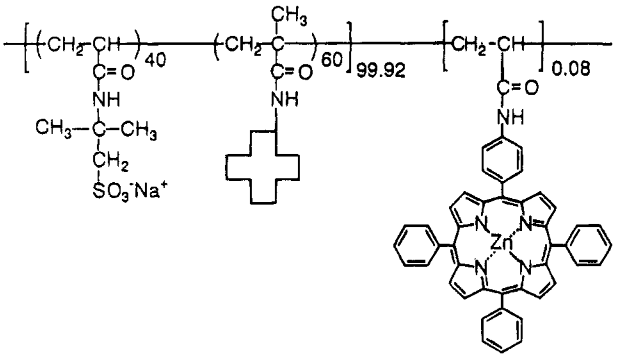
Chart 1



poly(A/La/ZnTPP)



poly(A/Cd/ZnTPP)

served when monitored at the blue-shifted phosphorescence peak. In the delayed fluorescence at room temperature, the spectral pattern was broad and the vibronic 0−0 band was less intensive than the 0−1 band. With increasing temperature, however, the bandwidth gradually narrowed and the emission maxima were steadily red-shifted with a concomitant increase in the intensity of the 0−0 band relative to that of the 0−1 band.

These rather unusual observations[24] prompted us to attempt to clarify the origin of the anomalous spectral patterns of the delayed fluorescence and phosphorescence of the ZnTPP species confined in the cluster of the Cd groups. In the present study, we further characterized fluorescence (both prompt and delayed) and phosphorescence spectra of the ZnTPP chromophores confined in the cluster of the Cd groups in comparison with those of the ZnTPP moieties confined in the cluster of the La groups. Emphasis was placed on the comparison of the excitation spectra monitored at varying wavelengths and of the emission spectra observed with varying excitation wavelengths.

Experimental Section

Polymers. The terpolymer of 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) with 60 mol % *N*-cyclododecylmethacrylamide (CdMAm)[25] and 0.08 mol % zinc(II) 5-(4-acrylamidophenyl)-10,15,20-triphenylporphynate (ZnAATPP)[22] and the terpolymer of AMPS with 61 mol % *N*-laurylmethacrylamide (LaMAm)[26] and 0.19 mol % ZnAATPP were prepared as reported previously.[22] The contents of the ZnAATPP unit in the terpolymers were determined by UV−visible absorption spectroscopy.

Measurements. Absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5000 spectrofluorophotometer. Delayed emission spectra were obtained with a Shimadzu RF-502A spectrofluorometer equipped with a cylindrical chopper operated at varying frequencies. An optical cell containing a sample solution was immersed in temperature-controlled water in a Pyrex vessel. The solutions were deaerated by bubbling with argon for 30 min prior to measurements.

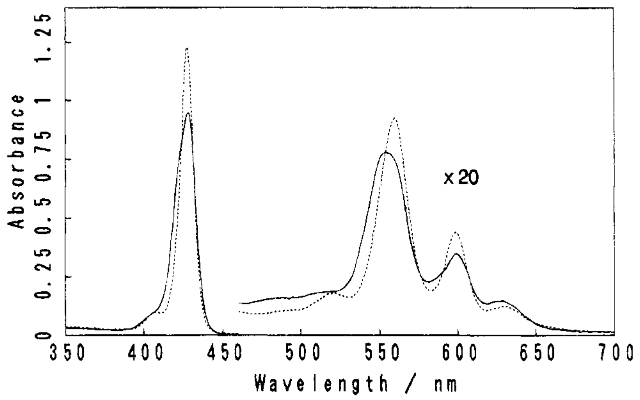


Figure 1. Absorption spectra of poly(A/La/ZnTPP) (dotted line) and poly(A/Cd/ZnTPP) (solid line) in aqueous solution at room temperature.

Results

The contents of the lauryl (La) and cyclododecyl (Cd) residues in the terpolymers are high enough (61 and 60 mol %) for the unimers to be formed due to the self-association of the hydrophobic residues in dilute aqueous solution.[14-16] These La- and Cd-containing terpolymers are abbreviated as poly(A/La/ZnTPP) and poly(A/Cd/ZnTPP), respectively, in the text (Chart 1). The amounts of the ZnTPP chromophores in the terpolymers were limited to 0.08−0.20 mol % to ensure complete encapsulation and isolation of the chromophore species in the hydrophobic clusters in the unimers. We previously confirmed[25,27] that the copolymerization systems of both AMPS−LaMAm and AMPS−CdMAm were "ideal copolymerization" systems giving copolymer compositions equal to compositions in the monomer feed and completely random distributions of the monomer units in the copolymers. Since ZnAATPP is an acrylamido-type monomer with a reactivity similar to those of AMPS, LaMAm, and CdMAm, the ZnTPP units should be randomly distributed along the polymer chains in the terpolymers.

The ZnTPP moieties in poly(A/La/ZnTPP) and poly(A/Cd/ZnTPP) show significantly different UV−visible absorption spectra in dilute aqueous solution (Figure 1). The Soret and Q bands of the ZnTPP species in the Cd-containing terpolymer are broader than those in the La-containing terpolymer. In polar organic solvents such as DMF and methanol, on the other hand, the absorption spectra of these two terpolymers were virtually identical with each other, the terpolymers adopting random coils in organic solvents.[22]

In aqueous solution, poly(A/Cd/ZnTPP) exhibits fluorescence spectra with markedly different spectral patterns depending on the excitation wavelength (Figure 2). When an aqueous solution of the Cd-containing terpolymer is excited at 436 nm, a wavelength on the longer wavelength (red) side of the absorption maximum of the Soret band (429 nm), the intensity of the 0−0 emission band at 608 nm is higher than that of the 0−1 band at 660 nm. This spectral profile of the Cd-containing terpolymer is virtually identical with the fluorescence profile of poly(A/La/ZnTPP) in aqueous solution.[22] As the excitation wavelength is decreased, however, the Cd-containing terpolymer shows a decrease in the intensity of the 0−0 emission band relative

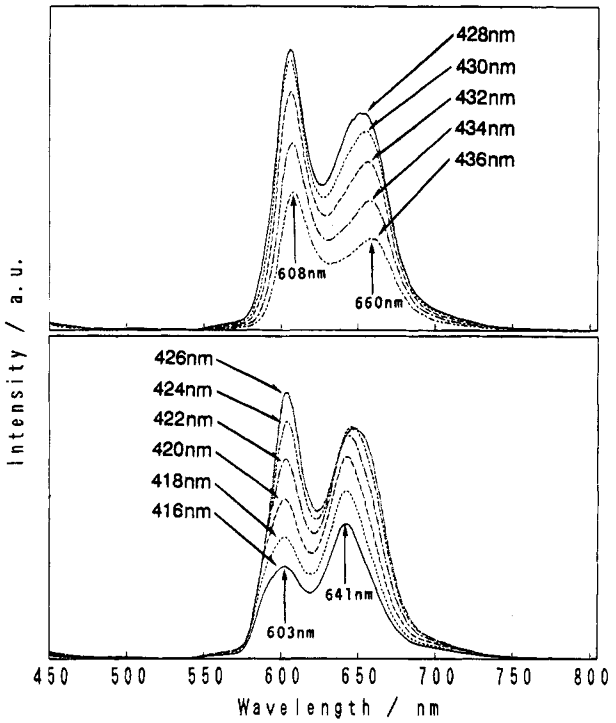


Figure 2. Fluorescence spectra of poly(A/Cd/ZnTPP) in aqueous solution recorded at varying excitation wavelengths at room temperature; [ZnTPP] (residue) = 1 μM. Excitation wavelengths are indicated in the figure.

to that of the 0−1 band, which is accompanied by a blue shift of the emission maxima. A more significant blue shift occurs in the 0−1 band than in the 0−0 band. Upon decreasing the excitation wavelength to 416 nm, a wavelength on the blue side of the Soret band maximum, the emission peak intensity of the 0−0 band becomes considerably lower than that of the 0−1 band, and the emission peaks of the 0−0 and 0−1 bands are blue-shifted to 603 and 641 nm, respectively. In contrast, the fluorescence spectral profiles of the La-containing terpolymer are independent of the excitation wavelength; the emission maxima and relative intensities of the 0−0 and 0−1 emission bands are constant regardless of the excitation wavelength.

In aqueous rigid solution at 77 K, poly(A/Cd/ZnTPP) and poly(A/La/ZnTPP) show remarkably different phosphorescence spectra (Figure 3). The small molecular weight ZnTPP molecule is known to show a phosphorescence peak near 780 nm in rigid glasses at 77 K.[27,28] The La-containing terpolymer exhibits the "normal" phosphorescence spectrum with a peak at 793 nm (Figure 3a). The spectral profile of the phosphorescence of the La-containing terpolymer is independent of the excitation wavelength. In contrast, the Cd-containing terpolymer shows anomalously blue-shifted phosphorescence with a peak at 746 nm, and the phosphorescence profile is strongly dependent on the excitation wavelength. When an aqueous solution of poly(A/Cd/ZnTPP) is excited at 422 nm, a shorter wavelength than the Soret band maximum, the blue-shifted phosphorescence is predominantly emitted. However, when excited at 429 nm (at the Soret band maximum), the normal phosphorescence peaking at 785 nm predominates over the blue-shifted phosphorescence (Figure 3b).

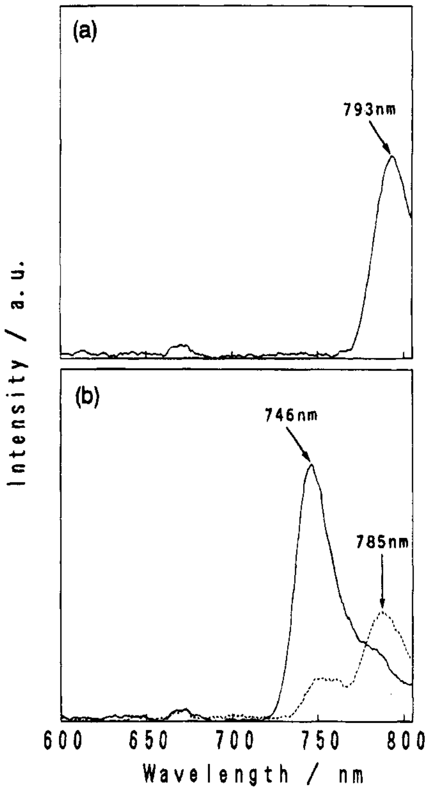


Figure 3. Phosphorescence spectra in aqueous rigid solutions at 77 K observed at a delay time of 2.5 ms: (a) poly(A/La/ZnTPP) with excitation at 429 nm; (b) poly(A/Cd/ZnTPP) with excitations at 422 (solid line) and at 429 nm (dotted line); [ZnTPP] (residue) = 1 μM.

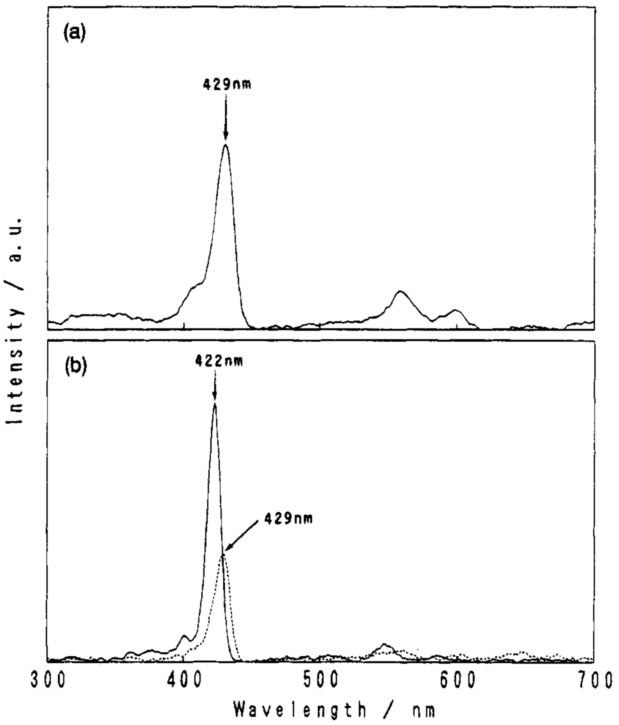


Figure 4. Excitation spectra in aqueous rigid solution at 77 K recorded at a delay time of 2.5 ms: (a) poly(A/La/ZnTPP) monitored at 793 nm; (b) poly(A/Cd/ZnTPP) monitored at 746 (solid line) and at 785 nm (dotted line); [ZnTPP] (residue) = 1 μM.

Figure 4a shows an excitation spectrum of the La-containing terpolymer monitored at the phosphorescence peak (793 nm) at 77 K. The excitation spectra monitored at any wavelengths in the region of 770−805 nm were found to be virtually identical after normalization of the spectra at the peak at 429 nm. In contrast, poly(A/Cd/ZnTPP) shows two distinct excitation spectra depending on the wavelength to monitor. As shown in

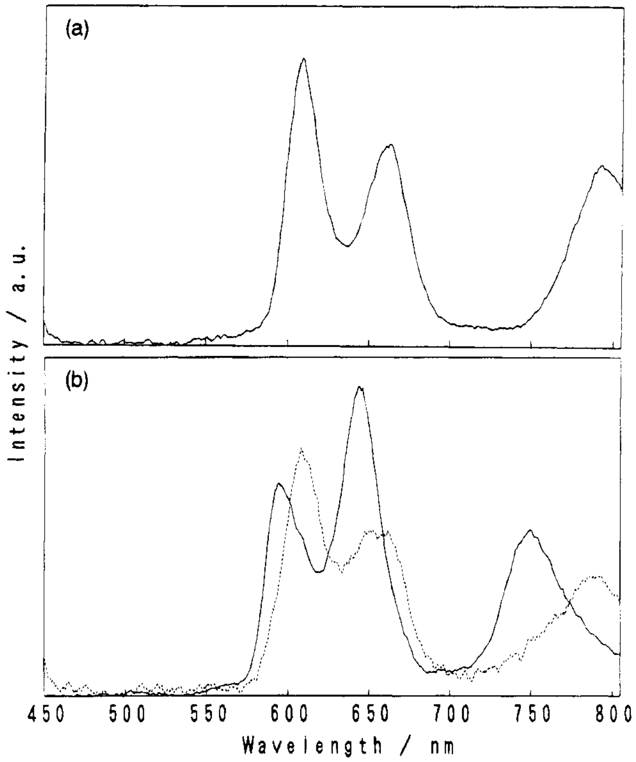


Figure 5. Delayed emission spectra in aqueous solution at 30 °C at a delay time of 2.5 ms: (a) poly(A/La/ZnTPP) with excitation at 433 nm; (b) poly(A/Cd/ZnTPP) with excitations at 420 (solid line) and at 440 nm (dotted line); [ZnTPP] (residue) = 1 μM.

Figure 4b, when monitored at the normal phosphorescence peak at 785 nm, the excitation spectrum of poly(A/Cd/ZnTPP) in the Soret band region coincides with that of poly(A/La/ZnTPP), both the terpolymers showing peaks at 429 nm and practically the same bandwidths. On the other hand, when monitored at the blue-shifted phosphorescence peak at 746 nm, the Cd-containing terpolymer shows a significantly blue-shifted excitation spectrum with a peak at 422 nm in the Soret band region.

The La- and Cd-containing terpolymers exhibit E-type delayed fluorescence along with phosphorescence in fluid aqueous solution at ordinary and higher temperatures.[22,23] Figure 5a displays delayed fluorescence and phosphorescence spectra of poly(A/La/ZnTPP) in aqueous solution at 30 °C with excitation at 433 nm. The delayed fluorescence and phosphorescence spectra observed with excitation at any wavelengths in the Soret band region were essentially identical (after normalization) with the spectrum presented in Figure 5a. In the case of the Cd-containing terpolymer, on the other hand, both the delayed fluorescence and phosphorescence spectra in fluid aqueous solution are strongly dependent on the excitation wavelength (Figure 5b). With excitation at 420 nm, the Cd-containing terpolymer shows an anomalous pattern in the delayed fluorescence with blue-shifted emission peaks, the 0−0 band being less intensive than the 0−1 band. The blue-shifted phosphorescence is predominant at this excitation wavelength. When excited at 440 nm, however, the Cd-containing terpolymer exhibits delayed fluorescence and phosphorescence with the normal profiles (Figure 5b). These spectral profiles and emission maxima are practically the same as those of the La-containing terpolymer (Figure 5a). Excitation spectra of the Cd-containing terpolymer monitored at the blue-shifted phosphorescence peak at 746 nm and the normal phosphorescence peak at 785 nm at 30 °C were practically the same as those observed in rigid aqueous solution at 77 K (Figure 4b), peaks appearing at 422 and 429 nm, respectively, in the Soret band region.

Discussion

All these spectral data for poly(A/Cd/ZnTPP) in aqueous solution indicate that there are two electronically distinctive ZnTPP species in the Cd cluster, electronic energy levels of one species being considerably perturbed. In conjunction with the temperature dependencies of the delayed emissions and T−T absorption that we reported previously,[24] it is clear that the electronically perturbed ZnTPP species are responsible for the blue-shifted fluorescence and phosphorescence. These species have a blue-shifted absorption band in the UV−visible spectrum because the blue-shifted fluorescence and phosphorescence were observed only when poly(A/Cd/ZnTPP) was excited at wavelengths on the blue side of the Soret band.

In our previous studies,[20,21] we incorporated a small mole fraction of azobenzene moieties into amphiphilic copolymers of AMPS containing ca. 50 mol % of La or Cd groups. The mobilities of the azobenzene species compartmentalized in the La and Cd clusters were compared by ^{1}H-NMR relaxation times and by photoisomerization rates. The NMR relaxation times indicated that the motions of the azobenzene species were much more restricted in the Cd cluster than in the La cluster. The photoisomerization of the azobenzene moieties was much more impeded in the Cd cluster than in the La cluster, being consistent with the NMR relaxation data. This is a clear indication that the Cd groups are more tightly packed in the hydrophobic cluster than are the La groups, presumably because the Cd group is conformationally more rigid than the La group; cyclododecane has much less conformational freedom than dodecane because of its cyclic structure. The self-association of the Cd groups should produce a more rigid hydrophobic cluster due to their tighter packing, which should produce a highly constraining microenvironment about chromophore species compartmentalized in the cluster.

In such a highly constraining microenvironment, steric restraints may be imposed on the ZnTPP species to such an extent that conformational relaxation is restricted and attainment of the most appropriate conformation is prevented. Such sterically distorted ZnTPP species may give rise to a high-energy excited state which is responsible for the blue-shifted fluorescence and phosphorescence.

Figure 6 shows absorption spectra of the Soret band on an expanded scale. Clearly, the Soret band of the Cd-containing terpolymer has a shoulder on the blue side of the absorption maximum, whereas the La-containing terpolymer exhibits a nearly symmetrical band pattern. The Soret band of the Cd-containing terpolymer can be resolved into two absorption bands with peaks at 422 and 429 nm as depicted in Figure 6b. These two peaks coincide with the peaks in the excitation spectra shown in Figure 4b.

We may attribute the shorter-wavelength band peaking at 422 nm shown in Figure 6b to the ZnTPP species, which are conformationally constrained and geometrically distorted in the highly constraining space in the Cd cluster, the species responsible for the blue-shifted fluorescence and phosphorescence. The longer-wave-

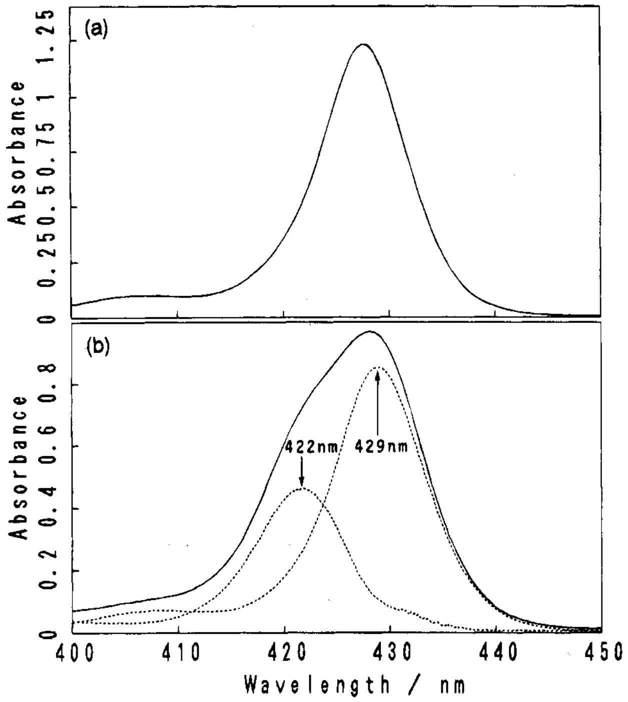


Figure 6. Comparison of the expanded Soret absorption bands for (a) poly(A/La/ZnTPP) and (b) poly(A/Cd/ZnTPP) in aqueous solution at room temperature. The observed spectrum for poly(A/Cd/ZnTPP) (solid line) was resolved into two absorption bands (dotted lines) peaking at 422 and 429 nm.

length band peaking at 429 nm is almost identical with the Soret band of the La-containing terpolymer (Figure 6a). This longer-wavelength band should be attributed to the ZnTPP species whose conformational dynamics are not restricted, the species responsible for the "normal" fluorescence and phosphorescence.

Conclusions

Amphiphilic polysulfonates, consisting of La or Cd groups and a small mole fraction of ZnTPP chromophores, form unimers with the ZnTPP species confined in the hydrophobic clusters in aqueous media. Fluorescence and phosphorescence properties of the ZnTPP chromophores compartmentalized in the Cd cluster were very different from those in the La cluster. The ZnTPP moieties in the Cd cluster showed anomalously blue-shifted fluorescence (both prompt and delayed) and phosphorescence of which spectral patterns strongly depended on excitation wavelength. These unusual emission properties of the ZnTPP moieties confined within the Cd cluster can be attributed to ZnTPP species that are conformationally constrained and geometrically distorted owing to the highly constraining microenvironment.

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