Observation of a Novel Fluorescent Dimer of Zinc Tetrasulphonatophthalocyanine

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Zinc(II) tetrasulphonatophthalocyanine (ZnPcS^{4-}) exhibited a new absorption band (λ_{max} 699 nm) at the longer wavelength side of the monomer absorption band in 1:49 aqueous acetonitrile. Irradiation of the new band exerted an emission (690–730 nm, λ_{max} 710 nm) different from the monomer fluorescence. The new absorption and emission were ascribed to a novel type of ZnPcS^{4-} dimer.

We have recently reported excitation light wavelength dependence of electron transfer of zinc(II) tetrasulphonatophthalocyanine (ZnPcS^{4-}) in the presence of triethanolamine in water[1] or aqueous acetonitrile;[2] irradiation with 366-nm light resulted in the formation of ZnPcS$^{5-\cdot}$, while irradiation at 656 nm led to no reduction of ZnPcS^{4-}. During the course of this work we also studied dimer formation of ZnPcS^{4-} in water-acetonitrile mixtures of varying compositions to clarify the roles of dimeric species in the photoreduction. We have found that the ZnPcS^{4-} dimer formed in water plays no roles in the photoreduction but that a novel type of dimer is formed in "wet" organic solvents such as acetonitrile and ethanol. We now wish to report spectral features, particularly, an emissive property of the novel dimer.

As previously reported,[2] the absorption spectrum of ZnPcS^{4-} is changed in profile with the ratio of solvent components in water-acetonitrile mixtures. Figure 1 shows the absorption spectra observed in mixtures of water and acetonitrile in varying compositions. In pure water the absorption maxima (λ_{max}) of Q band appear at 667 and 635 nm due to the monomer and dimer, respectively,[3] while, with increasing content of acetonitrile, the apparent absorbance of the former increased with a concomitant decrease of that of the latter, and the 667-nm band (λ_{max} 672 nm) was exclusively observed with a small peak at 605 nm in a 1:1 mixture of acetonitrile and water. We determined the equilibrium constant for dimer formation to be 4.7×10^5 mol^{-1} dm^3 in water at room temperature.[2,4]

The spectral profile of ZnPcS^{4-} (tetrasodium salt, 1×10^{-5} mol dm^{-3}) in a 1:49 (by volume) water-acetonitrile mixture was different from that in a 1:1 mixture; the new absorption band appeared at wavelengths (λ_{max} 699 nm) longer than those of the monomer band (λ_{max} 675 nm), as shown in Figure 1. The increase of water content decreased the absorbance at 699 nm with a concomitant increase of that at 675 nm, and finally in the 1:1 mixture the absorption maxima shifted to 672 and 605 nm to give the monomer absorption.

The relative intensity of the 699-nm band was dependent upon ZnPcS^{4-} concentration (4×10^{-8}–4×10^{-5} mol dm^{-3}) in 1:49 aqueous acetonitrile; with decreasing concentration of ZnPcS^{4-} the intensity at 699 nm decreased and in concentrations of lower than 10^{-6} mol dm^{-3} this band was scarcely detected. These results indicate that ZnPcS^{4-} forms a novel type of dimer in wet acetonitrile and the increase of water content decreases the dimer composition. The equilibrium constant for dimer formation was determined in 1:49 aqueous acetonitrile to be 2.0×10^5 mol^{-1} dm^3.

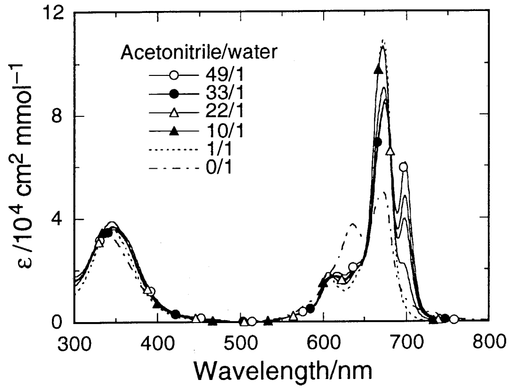

Figure 1. Absorption spectra of ZnPcS^{4-} in acetonitrile-water mixtures of varying compositions ([dye]=1×10^{-5} mol dm^{-3}).

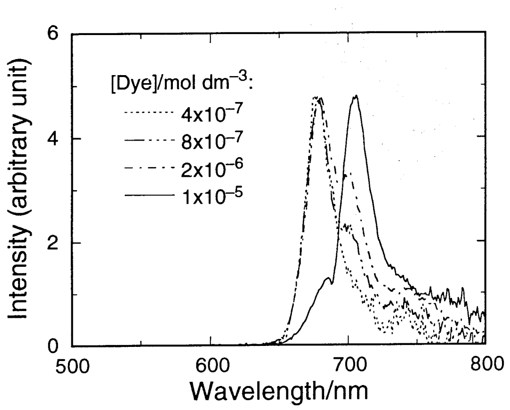

Figure 2. Fluorescence spectra of ZnPcS^{4-} observed on excitation at 690 nm in 1:49 aqueous acetonitrile.

Appearance of an absorption band at the red side of the monomer band was reported for dimer formation of chloroaluminum(III) tetrasulphonatophthalocyanine (AlPcS^{4-}) in aqueous alcohol.[5]

The dimer formation usually provides excited dye molecules with a decay channel and no emissions have been detected from the dimers except the above AlPcS^{4-} case.[5–7] This is the case for the ZnPcS^{4-} dimer formed in water.[8] In the case of the present dimer, however, its excitation resulted in a characteristic fluorescence emission. The fluorescence profile was dependent upon the solvent composition, dye concentration, and excitation wavelength; the fluorescence spectrum in 1:49 aqueous acetonitrile exhibited two peaks at 684 and 706 nm on Soret-band excitation or on excitation at 608 nm,[9] and these peaks were located immediately at the red side of the absorption peaks of monomer and dimer of ZnPcS^{4-}, respectively. The intensity of the emis-

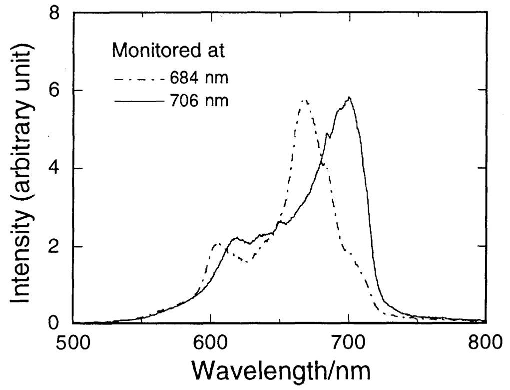

Figure 3. Fluorescence excitation spectra of ZnPcS^{4-} observed in 1:49 aqueous acetonitrile ([dye]=1×10^{-5} mol dm^{-3}).

sion peak at 706 nm decreased and that at 684 nm increased with increasing water content (H_2O:CH_3CN=1:49–5.5:44.5).

The excitation of ZnPcS^{4-} in 1:49 aqueous acetonitrile at 710 nm, where only the dimer species absorbed the light, gave exclusively the band at 706 nm (ϕ_{fl} = ca. 0.18), while on excitation at 690 nm, where both the dimeric and monomeric species absorbed the light, both bands at 706 and 684 nm were observed. Figure 2 shows fluorescence spectra observed on 690-nm excitation of ZnPcS^{4-} in different concentrations. In parallel to the absorption spectrum, the fluorescence spectrum depends upon the concentration of ZnPcS^{4-}.

These observations indicate that the 706- and 684-nm bands can be ascribed to the dimer and monomer of ZnPcS^{4-}, respectively. This was confirmed by the fluorescence excitation spectra (Figure 3); the spectra monitored at 706 and 684 nm are very similar to the absorption spectra of the dimer and monomer, respectively, in the same solvent. The possibility that the dimer fluorescence might be due to a reabsorption effect[5,7] can be ruled out since the excitation spectra observed were independent of the ZnPcS^{4-} concentration ($\leq1\times10^{-5}$ mol dm^{-3}). The fluorescence decay curves monitored at 705–710 (dimer fluorescence) and 680–685 nm (monomer fluorescence) on excitation of ZnPcS^{4-} at 655 nm in 1:49 aqueous acetonitrile obeyed one-component analysis, which gave the fluorescence lifetimes of the dimer and monomer as 3.24±0.03 and 3.15±0.02 ns, respectively.[10]

The conformation of the dimer in pure water absorbing light of wavelengths shorter than those of the monomer and emitting no fluorescence is assumed to be a face-to-face stacking dimer.[11] The lack of fluorescence is explained by a facile relaxation from the spectroscopically observed lowest singlet excited state to the dipole forbidden low-lying charge resonance state.[12] As mentioned above, the dimer in pure water exhibited an absorption maximum at 635 nm; however, the dimer formed in wet acetonitrile exhibits an absorption maximum at 699 nm and a rather intense fluorescence at 706 nm. Therefore, the dimer in wet acetonitrile should take a different structure from that in pure water, such as a face-to-face slipped or tilted conformation as proposed for AlPcS^{4-} in aqueous alcohol.[5,13]

Phthalocyanine dimers have been believed to be non-fluorescent.[7] However, the present observations clearly show that the different dimers are formed with change of the solvent compositions of acetonitrile-water mixture, and that only the dimer formed in solutions of higher acetonitrile compositions emits fluorescence.

References and Notes

1 Y. Nishimura, Y. Kaneko, T. Arai, H. Sakuragi, K. Tokumaru, M. Kiten, S. Yamamura, and D. Matsunaga, *Chem. Lett.*, **1990**, 1935.

2 Y. Kaneko, Y. Nishimura, T. Arai, H. Sakuragi, K. Tokumaru, and D. Matsunaga, *J. Photochem. Photobiol.*, **89**, 37 (1995).

3 A. Harriman and M.-C. Richoux, *J. Photochem.*, **14**, 253 (1980); P. C. Martin, M. Gouterman, B. V. Pepich, G. E. Renzoni, and D. C. Schindele, *Inorg. Chem.*, **30**, 3305 (1991).

4 For a Co(II) complex, an equilibrium constant of 1.21×10^{-5} mol dm^{-3} was reported; Y. C. Yang, J. R. Ward, and R. P. Seiders, *Inorg. Chem.*, **24**, 1765 (1985).

5 M. Yoon, Y. Cheon, and D. Kim, *Photochem. Photobiol.*, **58**, 31 (1993).

6 The dimer of AlPcS^{4-} was reported to be emissive;[5] however, this report might be erroneous and the observed emission might be due to a reabsorption effect.[7] If so, the present work is the first observation of the dimer fluorescence emission from phthalocyanine dyes.

7 S. Dhami, A. J. de Mello, G. Rumbles, S. M. Bishop, D. Phillips, and A. Beeby, *Photochem. Photobiol.*, **61**, 341 (1995).

8 J. R. Darwent, P. Douglas, A. Harriman, G. Porter, and M.-C. Richoux, *Coord. Chem. Rev.*, **44**, 83 (1982); J. D. Spikes and J. C. Bommer, *Int. J. Radiat. Biol.*, **50**, 41 (1986).

9 An isosbestic point was observed at this wavelength in different solvent compositions of water and acetonitrile.

10 The lifetimes of emission were determined under argon on excitation with 655-nm laser pulses (fwhm<40 ps) from a semiconductor laser (Hamamatsu PLP-02). The emission was passed through a grating monochromator (Jobin Yvon CP200) and detected with a streak scope (Hamamatsu C4334) and transferred to a personal computer (Apple Macintosh IIfx). The system was computer-controlled and the data were analyzed by the personal computer.

11 R. M. Negri, A. Zalts, E. A. San Roman, R. F. Aramendia, and S. E. Braslavsky, *Photochem. Photobiol.*, **53**, 317 (1991).

12 N. Ishikawa, O. Ohno, Y. Kaizu, and H. Kobayashi, *J. Phys. Chem.*, **96**, 8832 (1992).

13 The absorption and fluorescence spectra from bisporphynate complexes, appearing immediately at the red side of those from the corresponding monomers were ascribed to a substantial porphyrin-porphyrin π-orbital overlap; O. Bilsel, J. Rodriguez, D. Holten, G. S. Girolani, S. N. Milam, and K. S. Suslick, *J. Am. Chem. Soc.*, **112**, 4075 (1990).