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Wavelength-dependent Photofading of Zinc Phthalocyanin in the Presence of an Electron Donor

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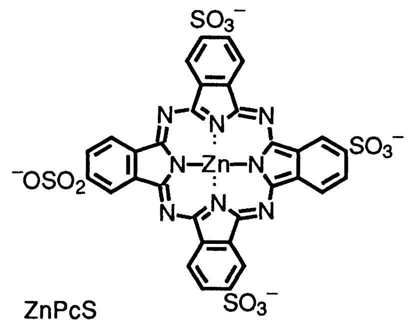
Zinc(II) phthalocyanintetrasulfonate exhibits a remarkable wavelength effect in its photoreduction with triethanolamine. This compound is durable to visible light but reduced on irradiation with near-UV light.

Phthalocyanins are widely used as dye-pigments because of their brightness and durability towards sunlight and various reagents. However, our recent finding that tetrasodium zinc(II) phthalocyanintetrasulfonate (ZnPcS) is faded in polymer matrices on exposure to light has led us to investigate its photochemical behavior in the presence of amines as electron donors in solution.1) We now wish to report a remarkable effect of wavelength of the irradiating light on the fading of ZnPcS in deaerated aqueous solutions containing triethanolamine (TEOA).

ZnPcS (8×10^{-6} mol dm^{-3}) was irradiated in degassed (freeze-thaw cycles) aqueous solutions [water, water-acetonitrile (1:1 by volume), and water-ethanol (1:1)] in the presence of TEOA (0.8 mol dm^{-3}) with a high-pressure mercury lamp through appropriate filters. As a typical example, irradiation in water with 365-nm light resulted in a decrease of the absorption at 670 nm accompanied with an increase of an absorption around 580 nm, as shown in Fig. 1. Contact of the irradiated solution with air recovered the original spectrum.2) The 580-band is assigned to the one-electron reduced species of ZnPcS, ZnPcS$^{-\cdot}$, by comparison with the spectrum obtained by reduction of ZnPcS with aqueous sodium hydrosulfite. The quantum yield for fading of ZnPcS determined under similar conditions is 0.5%. On the contrary, the irradiation with 656-nm light led to no detectable change of the spectrum.



ZnPcS

Figure 2 depicts transient absorption spectra obtained on laser flash photolysis of ZnPcS (8×10^{-6} mol dm^{-3}) in water containing TEOA (0.8 mol dm^{-3}) with 308-nm laser pulses. A broad absorption around 500 nm observed immediately after excitation decays with first-order kinetics (lifetime≈100 μs), and a new absorption grows quickly around 580 nm. The former absorption is assigned to the lowest triplet state of ZnPcS,3,4) and the latter absorption to the one-electron reduced form of the phthalocyanin, ZnPcS$^{-\cdot}$. Essentially the same phenomena were observed in aqueous acetonitrile and aqueous ethanol. On the other hand, laser flash photolysis with 670-nm pulses from an excimer laser-pumped dye laser (Rhodamine 101) exhibited solely the absorption due to the triplet but none of the radical anion.

On 308-nm laser excitation, the increase in TEOA concentration from 0.01 to 0.8 mol dm^{-3} increased the yield of ZnPcS$^{-\cdot}$, but did not affect essentially the decay rate of the triplet state. These facts indicate that the excited state to react with TEOA is not the observed lowest triplet state but other excited states. Lack of the reactivity of the lowest triplet state with TEOA may arise from an endothermic nature of the electron transfer process, nearly +0.34 V, as estimated from electrochemical potentials, $E°$(ZnPcS/ZnPcS$^{-\cdot}$) = −0.65 V and $E°$(TEOA$^{+\cdot}$/TEOA) = +0.82 V vs. NHE, and the triplet excitation energy of ZnPcS, 1.13 eV.[1)]

At present, nature of the reactive excited state is not clear, although an undetectable n,π* excited state could be a candidate. Several phthalocyanins containing other metals are known to exhibit fluorescence at 670-680 nm accompanied by a weak emission around 420 nm which is supposed to arise from the higher triplet states.[4)] ZnPcS actually exhibits fluorescence at 688 nm and a weak emission at 440 nm in aqueous acetonitrile (1:1) on excitation at 365 nm. In the presence of TEOA in 5×10^{-3} mol dm^{-3}, the weak emission with a lifetime of 5.4 ns was shifted to 450 nm and slightly increased in intensity. Further addition of TEOA did not change the emission maximum but gradually reduced its intensity as well as its lifetime. The apparent quenching of the emission lifetime affords a quenching rate constant of 1.0×10^{8} mol^{-1} dm^{3} s^{-1}.

Finally, it should be pointed out that phthalocyanin ZnPcS is mostly stable under visible light as often believed; however, near-UV light makes it reactive with an electron donor. This is attributed to the participation of the higher excited state produced only by the excitation with near-UV light.

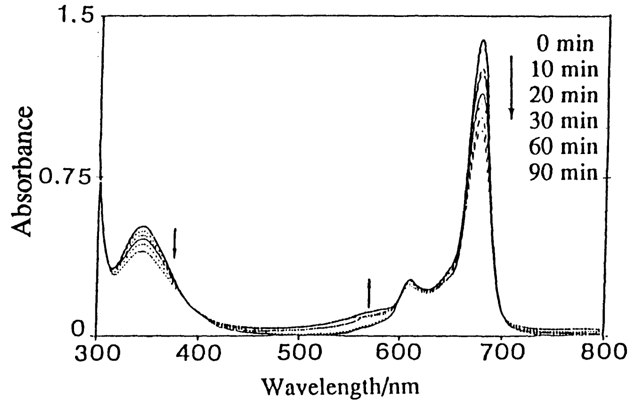


Fig. 1. A spectral change of ZnPcS on 365-nm light irradiation in water in the presence of TEOA (0.8 mol dm^{-3}).

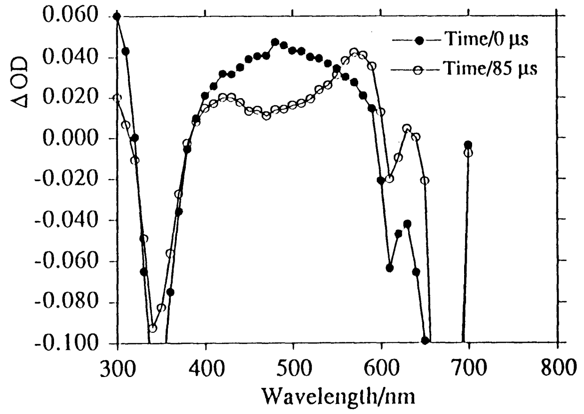


Fig. 2. Transient absorption spectra on 308-nm laser excitation of ZnPcS in water in the presence of TEOA (0.8 mol dm^{-3}).

References

1) Photochemistry of phthalocyanins, particularly with electron acceptors, is briefly reviewed in: D. Woehrle and M. Kaneko, *Yuki Gosei Kagaku Kyokaishi*, **45**, 837 (1987).

2) Water-soluble phthalocyanins exhibit generally two absorption bands at 600-700 nm. In water ZnPcS shows the absorption bands of nearly equal intensity at 672 and 635 nm ascribable to monomeric and dimeric or associated species, respectively. However, addition of TEOA (Fig. 1) or organic solvents like acetonitrile and ethanol reduced remarkably the 635-nm absorption and increased the 672-nm one, indicating that ZnPcS exists mostly as the monomeric species in these solutions.

3) T. Ohno, S. Kato, and N. Lichtin, *Bull. Chem. Soc. Jpn.*, **55**, 2753 (1982).

4) K. Schmatz, S. Muralidharan, and G. Ferraudi, *Inorg. Chem.*, **21**, 2961 (1982); J. R. Darwent, I. McCubbin, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **78**, 903 (1982).

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