

Spectral Properties of Nonaggregative Antimony(V) Phthalocyanine and Its Film as a Novel Near-Infrared Absorber

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Preparation and spectral properties of antimony complexation ligating tetra-*tert*-butylated phthalocyanine and its film having intense optical absorption in the near-infrared region without significant molecular aggregation even in condensed phase are reported.

Phthalocyanine and their derivatives showing intense absorption in the near-infrared (NIR) region have a wide variety of current and potential applications in many fields using semiconductor-lasers, such as optical disks, charge-generating materials for photocopiers, and photodynamic therapy of tumors.¹ As normal phthalocyanines have their most intense absorption (Q-band) in 660–690 nm,² a lot of efforts have so far been made to let the absorption coincide well with the wavelengths of laser light, e.g., by introducing appropriate substituents to the periphery of the macrocycles,³ distorting the molecular plane,⁴ or by expanding the π -system (i.e., using naphthalocyanines⁵). These in general need multi-step chemical reactions and hence are costly and time-consuming. We have synthesized antimony(V)^{6,7} and bismuth(III)⁸ derivatives that absorb NIR light by a one-step reaction, although these are insufficiently soluble in common solvents to make solvent-cast films. Even though highly soluble, molecular aggregation of phthalocyanines can significantly reduce their optical intensity in the desired spectral region in condensed phase as mentioned below. Therefore, from the viewpoint of application to devices, phthalocyanines that are not only more highly soluble but also less prone to aggregate are more favored. In this communication, we report a new very soluble and nonaggregative antimony-phthalocyanine compound and its film as a new NIR absorber.

A mixture of commercially available 4-*tert*-butylphthalonitrile (3.1 g; 16.7 mmol) and anhydrous SbCl_3 (1.9 g; 8.33 mmol) was fused at 165 °C for 8 h with vigorous stirring.⁹ The crude product, after being washed with benzene/hexane (1/4), was recrystallized from CH_2Cl_2 /hexane (1/4). Collection of this solid and drying at 60 °C for 1 h gave green powder (535 mg) as a mixture of salts of unidentified counter anions.¹¹ Upon the dropwise addition of 20 ml of perchloric acid to a solution (150 ml) of freshly distilled acetonitrile (over P_2O_5) containing 101 mg of the green material, very fine powder of green perchlorate salt began to precipitate. After the addition of ca. 20 ml of water and standing over night, the solid was collected by centrifugation and then was dissolved into CH_2Cl_2 . The solution was washed with water, dried over anhydrous Na_2SO_4 , and was evaporated to dryness. The solid was recrystallized from CH_2Cl_2 /hexane (1/4) and dried at 60 °C under vacuum to yield 54 mg of $[\text{Sb}(\text{tbpc})\text{Cl}_2]\text{ClO}_4$ (tbpc = tetra-*tert*-butylated phthalocyaninate; $\text{C}_{48}\text{H}_{48}\text{N}_8^{2-}$) as a mixture of four regioisomers. Yield; 3.2% vs

tert-butylphthalonitrile. Anal. Found: C, 55.99; H, 4.73; N, 10.65%. Calcd for $\text{C}_{48}\text{H}_{48}\text{N}_8\text{O}_4\text{Cl}_3\text{Sb}$: C, 56.02; H, 4.70; N, 10.89%. This salt is highly soluble in CH_2Cl_2 (solubility $> 2 \times 10^{-2}$ M; more than 200 times as soluble as its unsubstituted analogue) and chloroform (not determined), and is also well soluble even in benzene and acetonitrile (ca. 10^{-3} M) in which its unsubstituted analogue (perchlorate) is insoluble, but is insoluble in hexane and water.

The optical absorption and magnetic circular dichroism (mcd) spectra of $[\text{Sb}(\text{tbpc})\text{Cl}_2]^+$ in CH_2Cl_2 are shown in Figure 1. Optical emission spectrum of $[\text{Sb}(\text{tbpc})\text{Cl}_2]^+$ in CH_2Cl_2 are shown in Figure 2. The most intense absorption band appeared at 739 nm, which was related to a distinctive Faraday A-term in the mcd spectrum and an optical emission at 752 nm with a small Stokes shift (230 cm^{-1}). Therefore, this absorption band is easily assigned as the Q-band (an electronic transition from HOMO to LUMO of the phthalocyanine ligand in character²). When compared to the Q-band of zinc analogue, which appears in normal region (Figure 1), that of $[\text{Sb}(\text{tbpc})\text{Cl}_2]^+$ is significantly red-shifted by ca. 1000 cm^{-1} . These spectral properties are very similar to those of its unsubstituted analogue^{6,7} although the Q-band is more red-shifted by 240 cm^{-1} due to the presence of four *tert*-butyl groups.¹² And hence the corresponding S_1 emission peak also is likewise shifted by 320 cm^{-1} (730 nm for unsubstituted analogue¹³) with almost the same intensity (the ϕ_F values for the *tert*-butylated and unsubstituted analogues are 0.007 and 0.009, respectively¹⁴). The molar extinction coefficient of

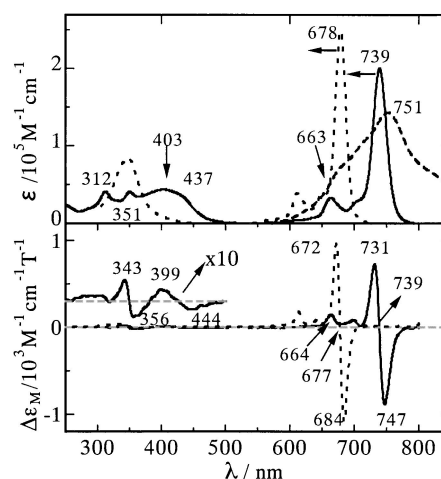


Figure 1. Optical absorption (top) and mcd (bottom) spectra of $[\text{Sb}(\text{tbpc})\text{Cl}_2]\text{ClO}_4$ (solid line) and zinc analogue (dotted line) in CH_2Cl_2 . A typical absorption spectrum of solvent-cast film of $[\text{Sb}(\text{tbpc})\text{Cl}_2]\text{ClO}_4$ is shown as dashed line.

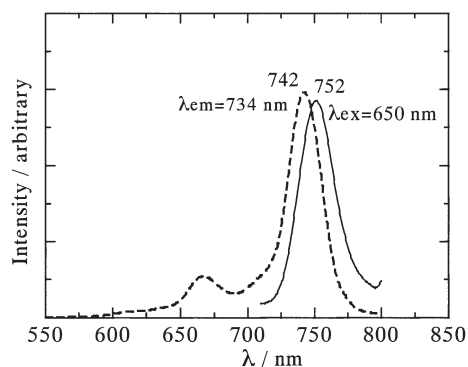


Figure 2. Optical emission (solid line) and excitation (dashed line) spectra of $[\text{Sb}(\text{tbpc})\text{Cl}_2]\text{ClO}_4$ in CH_2Cl_2 .

$[\text{Sb}(\text{tbpc})\text{Cl}_2]^+$ is little dependent of concentration up to ca. 1.5×10^{-4} M (above this concentration, the optical density was too intense to monitor). This indicates that unaggregated species of this complex is the dominant species. Intense optical emission at the red flank of the Q-band was also observed in this concentration range (the corresponding excitation spectra were close to the absorption spectrum of unaggregated species) although the spectra were more significantly distorted in stronger solutions due to reabsorption by the dye. This is rather surprising because molecular aggregation phenomena of phthalocyanines are common in the field of phthalocyanine chemistry and their Q-bands generally broaden, weaken, and blue-shift¹⁶ and fluorescence is quenched¹⁷ upon aggregation. We have also prepared solvent-cast films of this compound onto quartz plate by deposition from dichloromethane solution ($2 - 3 \times 10^{-4}$ M) and evaporation of the solvent. A typical optical absorption spectrum of the film in the Q region is shown in Figure 1 as a broken line. The optical absorption maximum appeared at 751 nm, which is close to that of monomer spectrum although the spectrum is rather broadened as compared to that of solution. This indicates that molecular aggregation of this compound is hindered even in the condensed phase.

In summary, the tetra-*tert*-butylated antimony(V)-phthalocyanine does not lose intense NIR absorption even in condensed phase due to the absence of significant molecular aggregation. In addition, this compound is easy to be prepared and easy to be made to films. The present result provides an important suggestion for developing a new NIR absorber in industrial fields utilizing semiconductor laser lights.

References and Notes

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