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Spectral properties of a novel antimony(III)-phthalocyanine complex that behaves like J-aggregates in non-aqueous media†

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An unusual red-shift of phthalocyanine Q-band upon aggregation in non-aqueous media has been observed for antimony(III) derivative and has been studied by using optical absorption and magnetic circular dichroism spectroscopy.

Aggregates of dye molecules play an important role in photobiological systems, such as energy and/or electron transfer and light harvesting processes.[1] J-aggregates of organic dye ions, which show optical absorption band at a longer wavelength than the corresponding monomer band, have recently attracted much attention in the field of non-linear optics as well as photosensitizers in photographic process.[1] Phthalocyanines, which are typical functional dyes being used in variety of industrial fields,[2] are well known to aggregate in solution.[3] However, their most prominent absorption band (Q-band) generally blue-shifts upon aggregation. Red-shifts of Q-band have been observed mostly in solid state[4] or in only few cases for water-soluble ionic porphyrins[5] and phthalocyanines[6] in aqueous media. Quite recently J-aggregates of water-insoluble porphyrins have been reported, but even in this case the presence of water seems to be essential.[7] This paper reports a novel example of red-shift of Q-band upon aggregation in non-aqueous media observed for antimony(III) derivative (Fig. 1). Not only antimony(III) but also the whole Group-15 elements had been ignored in phthalocyanine chemistry until our first reports,[8] and are still uncommon even today. Antimony(III) derivatives have mostly been investigated crystallographically[9] whereas the spectroscopic work has been limited to one species that has not yet been isolated.[10]

Fusion of a mixture of commercially available 4-*tert*-butylphthalonitrile (1.5 g; 7.96 mmol) and anhydrous SbI₃ (1.0 g; 1.99 mmol) at 165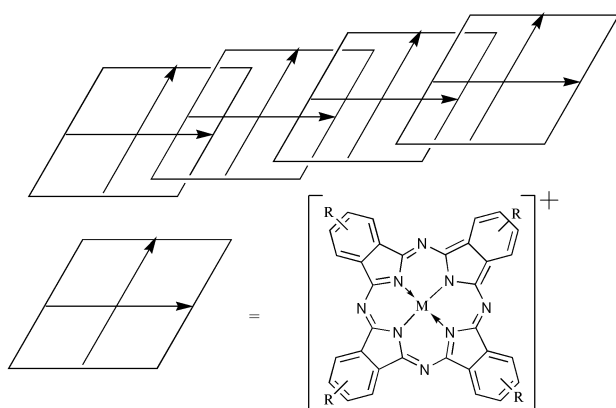 °C for 20 h with vigorous stirring yielded viscous green syrup. This was dissolved into 200 ml of dichloromethane and, after removal of insoluble yellow solids by filtration, the green solution was evaporated to dryness. The green solid was washed with benzene/hexane (1/3 in volume) three times and then with CH₂Cl₂/hexane (1/3) twice, respectively, until the washings turned essentially colorless. Collection of this solid and drying at 60 °C for 1 h gave green powder (1.17 g). Repetitive recrystallization (twice) of 210 mg of the crude material from CH₂Cl₂/hexane (1/3) and drying at 80 °C for 2 h yielded 155 mg of [Sb(tbpc)]I₃ (tbpc = tetra-*tert*-butylated phthalocyaninate; C₄₈H₄₈N₈²⁻) as a mixture of four regioisomers. Yield; 35% vs. *tert*-butylphthalonitrile. Anal. Found: C, 46.69; H, 3.77; N, 8.74%. Calcd for C₄₈H₄₈N₈I₃Sb: C, 46.52; H, 3.77; N, 9.04%. The presence of triiodide (I₃⁻ ion) has been evidenced by the appearance of a prominent Raman scattering peak at 112 cm⁻¹ (for tablet).†

The ESI-TOF mass spectrum of this compound in CH₂Cl₂ is in good agreement with the theoretical pattern based on natural isotope abundance (Fig. 2), indicating that the chromophore is cationic species. This is consistent with the results of crystallographic studies on unsubstituted phthalocyanine analogues, [Sb(pc)]⁺X⁻ (pc = phthalocyaninate ligand, C₃₂H₁₆N₈²⁻; X⁻ = Cl⁻, I⁻, I₃⁻).[9b–d] The optical absorption spectrum of [Sb(tbpc)]⁺I₃⁻ in CH₂Cl₂ are shown in Fig. 3 with those of [Zn(tbpc)] and [Sb(tbpc)Cl₂]⁺ for comparison. Surprisingly, the Q-band (an electronic transition from HOMO to LUMO of the phthalocyanine ligand in character[11]) is significantly red-shifted by *ca.* 1600 cm⁻¹ (762 nm) when compared to the normal
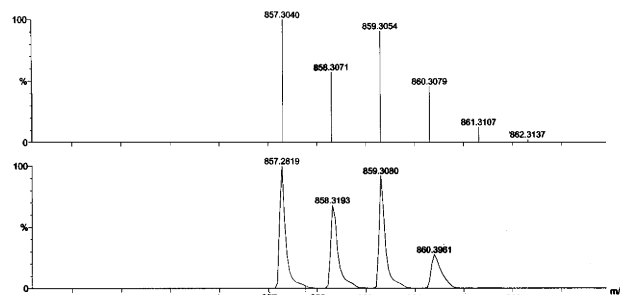

Fig. 1 A schematic representation of phthalocyanine J-aggregation and a structural presentation of phthalocyanine complex cation studied in this work, where R = *tert*-butyl, M = Sb(III), and the arrows mean transition dipole moments of the phthalocyanine monomers.

Fig. 2 The theoretical (top) and experimental (bottom) ESI-TOF mass spectra of [Sb(tbpc)]⁺.
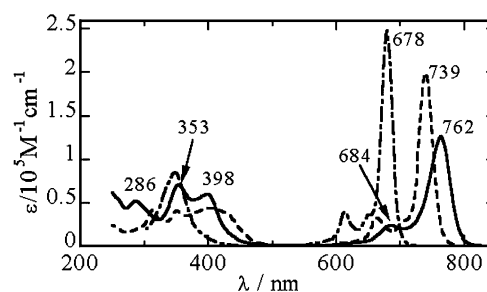

Fig. 3 Optical absorption spectra of [Sb(tbpc)]⁺ (solid line), [Sb(tbpc)Cl₂]⁺ (dashed line), and [Zn(tbpc)] (dot-dash line) in CH₂Cl₂.

position for the zinc analogue ($\lambda_{max} = 678$ nm), and even to the Q-band of antimony(V) analogue ($\lambda_{max} = 739$ nm). The band width (65 cm^{-1}) is considerably larger than that of antimony(V) derivative (48 cm^{-1}). The broadness both in optical absorption and mcd (magnetic circular dichroism) spectra is similar to those for bismuth(III) complexes, [Bi(pc)X] (X$^-$ = Cl$^-$and Br$^-$).[8a,8b,12] Unlike the known antimony(V) analogues,[8f,10] no emission was observed around the Q-band for [Sb(tbpc)]$^+$, as is the case for porphyrin and phthalocyanine complexes of low-valent main group elements.[11,13] The I$_3^-$ counter ion does not contribute to the absorption in the Q-region although it does in the Soret region ($\varepsilon = 3.66 \times 10^4$ and 2.94×10^4 M^{-1}cm^{-1} (1 M = 1 mol dm^{-3}) at 294 and 364 nm, respectively, for tetrabutylammonium salt in CH$_2$Cl$_2$).

Molecular aggregation of [Sb(tbpc)]$^+$ has been observed in concentrated solutions (above $ca.$ 10^{-4} mol dm^{-3}), like most phthalocyanines[3] (but unlike its antimony(V) analogue[8f]). Concentration dependence of optical spectra of [Sb(tbpc)]$^+$ in CH$_2$Cl$_2$ is shown in Fig. 4. With an increase in concentration, the apparent molecular extinction coefficient at the Q-band became smaller while in turn a new absorption band formed around 870 nm that disappeared upon dilution. In order to study absorption spectra in condensed phase, solvent-cast films of [Sb(tbpc)]$^+$ have been prepared from CH$_2$Cl$_2$ solution ($ca.$ 2 $\times$ 10^{-4} mol dm^{-3}) by deposition onto quartz plate and evaporation of the solvent. The films show intense absorption in 600–1000 nm region due to the appearance of two broad bands at 770 and 890 nm (Fig. 4). Unlike the solution spectra, the relative intensity of the lower energy band is comparable to that of the higher energy counterpart. Therefore, the bands at higher and lower energy sides are attributable to absorption by monomer and dimer (or higher aggregates), respectively. Although it is well known for the Q-band of most phthalocyanines in solution to show significant blue shift upon aggregation when compared to the respective monomers, observations of red shift have been limited to water-soluble derivatives.[6] According to Kasha's exciton coupling theory,[14] the dimer absorption band will be blue-shifted with respect to the monomer band when the angle, θ, which is made by the polarization axes of the monomer with the line of molecular center, is larger than 54.7° (in a face-to-face manner in a particular case when $\theta = 90°$) while red-shifted when $\theta < 54.7°$ (in a head-to-tail manner when $\theta = 0°$). The red-shifts observed for J-aggregates are rationalized by assuming the latter conformation (Fig. 1).[1,7] Hence, it is likely that [Sb(tbpc)]$^+$ aggregates in a similar fashion[14] although the red-shifted band

is rather broadened than those for the known J-aggregates.[5,6] Like most porphyrins and pthalocyanines possessing a four-fold axis, the Q-band of [Sb(tbpc)]$^+$ monomer is an orbitally doubly degenerate transition (x,y-polarized if the four-fold axis is taken as the z-axis), as is evidenced by the appearance of distinctive Faraday A-term (the s-shaped curve) in the Q-region in the mcd spectrum (Fig. 4). The degeneracy, however, is lifted upon J-aggregation.[15] A typical mcd spectrum of the aggregated species in 800–1000 nm region (Fig. 4) shows a trough at essentially the same wavelength as the absorption maximum ($i.e.$, Faraday B-term), indicating that the transition is orbitally non-degenerate. Therefore the aggregated species has no longer C_4 symmetry, supporting the above proposed conformation between the macrocycles.

This work has revealed that phthalocyanine derivatives can form J-aggregates in non-aqueous media and hence will serve for further understanding of the driving force of J-aggregation. It should be also noted that the solvent-cast films absorbing near-infrared light (600–1000 nm) should be intriguing from the view point of potential application as infrared cut-filter for plasma display and silicon photodiodes in addition to as photosensitizers for semiconductor-lasers.

Notes and references

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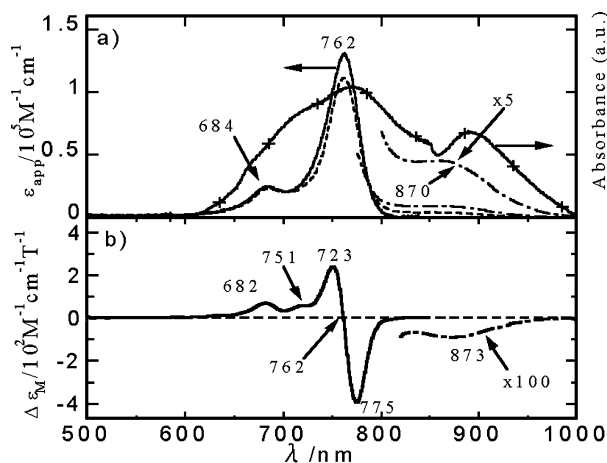
Fig. 4 Optical absorption (a) and mcd (b) spectra (in Q-region) of [Sb(tbpc)]$^+$ in CH$_2$Cl$_2$ at various concentrations; 1.34×10^{-6} (solid line), 1.68×10^{-4} (dashed line), 8.34×10^{-4} mol dm^{-3} (dot-dash line) and solvent cast film (solid line with crosses).