

Solvatochromic Shift of Phthalocyanine Q-band Governed by a Single Solvent Parameter

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Position of the main optical absorption band (Q-band) in electronic spectra of some *trans*-[M(Pc)L₂]^k (Pc = substituted or unsubstituted phthalocyaninate, M = Co(III), L = CN⁻, k = -1; M = Sn(IV), L = Cl⁻, k = 0; M = Sb(V), L = Cl⁻, k = +1) complexes depends only on the refractive index of the solvents, indicating that interaction of the transition dipole moment with induced dipole moment generated in the surrounding solvent molecules is predominant.

Optical absorption spectra of phthalocyanines (Pcs) are of great interest to those who work in the field of dyes and pigments, photovoltaic and solar cells, optical disks, infrared cut-filter, photodynamic cancer therapy, and nonlinear optics.^{1,2} Absorption spectra, particularly positions of the most intense absorption band (Q-band³) of Pcs are affected by the nature of central metal in the cavity and its axial ligation, size and symmetry of the π conjugation system, peripheral substitution, etc.² In solution spectroscopy, solvent should play an important role, but this has not yet been systematically investigated not only because of poor solubility of Pcs in common solvents but also occurrence of solvent-induced chemical reactions, such as axial ligation of solvent molecules,^{4a} tautomerization,^{4b} and molecular aggregation.^{4c} Thus, it has been hard to extract contribution of solute-solvent interaction alone in solvatochromism of Pcs. In this paper, we wish to report a simple example of solvatochromism of Pcs, in which the Q-band position is governed by a single solvent parameter.

We have chosen *trans*-[M(Pc)L₂]-type complexes ((ⁿBu₄N⁺)[Co(pc)(CN)₂]⁻,⁵ [Sn(pc)Cl₂]⁶ and [Sb(tbpc)Cl₂]⁺ (ClO₄⁻),⁷ where pc²⁻ and tbpc²⁻ denote unsubstituted and tetra-*t*-butyl-substituted phthalocyaninate, respectively) for the following reasons: i) There is little space for solvent molecules to coordinate to the metal as the additional ligand because these complexes have octahedral, six-coordinate geometry around the metal as mentioned below, ii) inert M-L bonds would minimize the effects of axial ligand substitution by solvent molecules, iii) the presence of the axial ligands would prevent molecular aggregation between Pc macrocycles that is a common phenomenon in phthalocyanine chemistry,^{4c,8} iv) there is no functional group that contributes to specific chemical interaction like hydrogen bonding. These three complexes and that of antimony(III), [Sb(tbpc)]⁺(I₃⁻),⁸ were prepared according to the literature methods. Commercially available 1-chloronaphthalene (CLN⁹) was used after treated with activated alumina. The others were of reagent grade and used as received. Spectra were measured at room temperature below 10⁻⁵ M (1 M = 1 mol dm⁻³), where effects of molecular aggregation were negligible.¹⁰ The spectra of [Co(pc)(CN)₂]⁻, [Sn(pc)Cl₂], and [Sb(tbpc)Cl₂]⁺ in DCM⁹ are shown in Figure 1. These spectra are typical of metal complexes of Pcs² and characterized by the appearance of a single, distinctive Q-band in 650–750 nm region. Spectra in the other

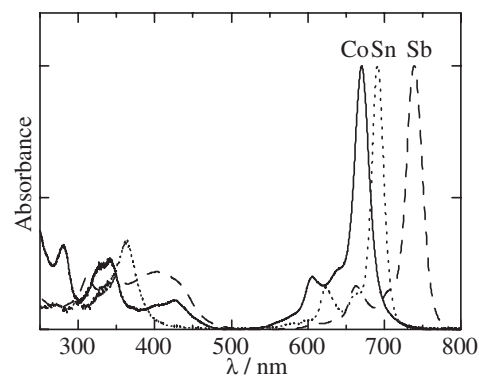


Figure 1. Optical absorption spectra of [Co(pc)(CN)₂]⁻, [Sn(pc)Cl₂], and [Sb(tbpc)Cl₂]⁺ in DCM solution. The spectra are normalized so that their maximum intensities are to be unity.

solvents were essentially the same, but only absorption maxima shifted depending on the solvent used.

Figure 2 shows plots of the Q-band maximum energy in a specific solvent as a function of refractive index of the solvent in the form of Onsager's solvent polarity function.¹¹ A fairly good linear correlation is observed in each case and the respective Q-band shifts to lower energy in solvent with a larger refractive index. Any attempts to correlate the shift with the other solvent parameters like donor number, acceptor number, E_T value, etc, which are conventionally used to rationalize solvatochromism of organic dyes, were unsuccessful. This indicates that the Franck-Condon excited state in the Q-transition is stabilized by interaction of the transition dipole moment with induced dipole moment temporarily generated in the surrounding solvent molecules by $-(1/2)\mu_j^2 a^{-3} f(n^2)$,¹¹ where μ_j , a , and $f(n^2)$ denote, transition dipole moment, the radius of the solute cavity, and Onsager's solvent polarity function, respectively. Therefore, it is reasonable that this solvatochromism is not governed by the other (above-mentioned) solvent parameters because reorientation or rearrangement of the surrounding solvent molecules upon the light-absorption on a time scale of ca. 10⁻¹⁵ s is essentially impossible. The value of the slope for [Co(pc)(CN)₂]⁻ is smaller than those for the others, but this is unlikely to be due to the difference in the magnitude of μ_j because the molar extinction coefficient at Q-band for [Co(pc)(CN)₂]⁻ ($\epsilon = 1.6 \times 10^5$ M⁻¹cm⁻¹ in AN) is close to that for [Sb(tbpc)Cl₂]⁺ ($\epsilon = 2.0 \times 10^5$ M⁻¹cm⁻¹ in DCM), but larger than that for [Sn(pc)Cl₂] ($\epsilon = 7.0 \times 10^4$ M⁻¹cm⁻¹ in CLN).¹² The other factor, such as the size of solute cavity, can affect the solvent sensitivity. By extrapolating these plots to the limit of $f(n^2) = 0$, the Q-band maximum wavelength of each complex in vacuum ($n = 1$) can be estimated; 649 nm for [Co(pc)(CN)₂]⁻, 651 nm for [Sn(pc)Cl₂], 695 nm for [Sb(tbpc)Cl₂]⁺.¹³ Interestingly, the estimated wavelengths for [Co(pc)(CN)₂]⁻ and [Sn(pc)Cl₂] in

vacuum are essentially the same though these differ considerably (by ca. 500 cm^{-1}) in common solvents. However, unlike the three complexes, the Q-band of $[\text{Sb}(\text{tbpc})]^+$ shows another type of solvatochromism in which its position seems to depend on whether the solvent used is donor or non-donor (e.g., 762 nm in BZ and DCM while 746 nm in AN and 742 nm in DMSO). No linear correlation was seen between the Q-band energy and $f(n^2)$.

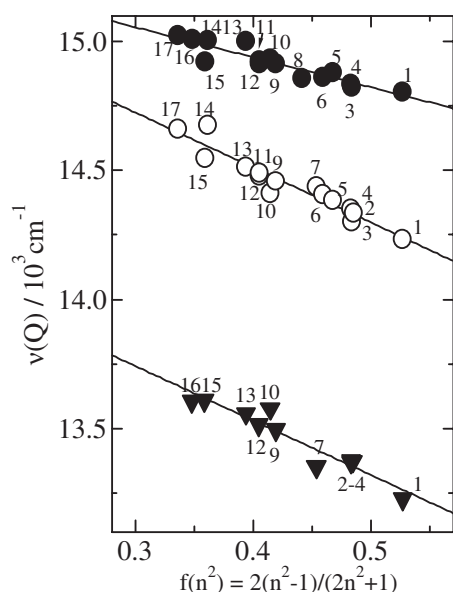


Figure 2. Plots of solvatochromic shifts of Q-band against solvent refractive index in a form of Onsager's solvent polarity function; ●: $[\text{Co}(\text{pc})(\text{CN})_2]^-$, ○: $[\text{Sn}(\text{pc})\text{Cl}_2]$, ▼: $[\text{Sb}(\text{tbpc})\text{Cl}_2]^+$; 1. CLN, 2. TCB, 3. NB, 4. DCB, 5. CB, 6. PY, 7. BZ, 8. DMSO, 9. CLF, 10. DMA, 11. DMF, 12. DCM, 13. THF, 14. EtOH, 15. AC, 16. AN, 17. MeOH.

Molecular structures of $[\text{Co}(\text{pc})(\text{CN})_2]^-$ and $[\text{Sn}(\text{pc})\text{Cl}_2]$ are known.^{14,15} Although that of $[\text{Sb}(\text{tbpc})\text{Cl}_2]^+$ is unknown, it may be assumed to be similar to those of porphyrin analogues.¹⁶ Thus, these complexes, in which the central metal is surrounded by four pyrrole nitrogen atoms and two axial ligands in a six-coordinate and octahedral coordination manner, show similar solvatochromic behavior, irrespective of cationic, neutral, or anionic species. As solvent-induced reactions are unlikely to occur for the above-mentioned reasons, it is reasonable that the solute-solvent dipole-dipole interaction should be predominant in this solvatochromism. On the other hand, antimony(III) ion in $[\text{Sb}(\text{pc})]^+$ is located above the pc plane by ca. 1 \AA ,¹⁷ and hence a large open space should be created around the metal ion also for $[\text{Sb}(\text{tbpc})]^+$, allowing solvent molecules to solvate.

We have shown that the solvatochromic shift of Pcs' Q-band can be interpreted in terms of a simple dipole-dipole interaction between Pc and solvent molecules unless effects of any solvent-induced chemical reaction are significant. This work also suggests that when comparing spectral properties of Pcs, only measuring in the same solvent can be insufficient and their solvent-sensitivities need to be considered and hence estimated Q-band energies in vacuum can be useful. Thus, the result of this work should be intriguing not only to experimental chemists who

work with dyes, but also to theoreticians who study molecular designing of dyes.

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- 9 Abbreviations for solvents used in this work are as follows; AC = acetone, AN = acetonitrile, BZ = benzene, CB = chlorobenzene, CLF = chloroform, CLN = 1-chloronaphthalene, DCB = *o*-dichlorobenzene, DCM = dichloromethane, DMA = *N,N*-dimethyl acetoamide, DMF = *N,N*-dimethyl formamide, DMSO = dimethyl sulfoxide, EtOH = ethanol, MeOH = methanol, NB = nitrobenzene, PY = pyridine, TCB = 1,2,4-trichlorobenzene, THF = tetrahydrofuran.
- 10 In some solvents, $[\text{Sn}(\text{pc})\text{Cl}_2]$ showed an additional band at the red flank of its Q-band that diminished upon dilution and hence aggregation is likely to occur even below 10^{-5} M . However, this band is well isolated and does not affect position of the monomer Q-band.
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