Determination of the aggregation numbers of the red-shift stacks in dispersions of oxovanadium and oxotitanium phthalocyanines

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For dispersions of VOPc-II and α-TiOPc in thf, an aggregation number of eight for the red-shift stacks, in which mutual spectral perturbation occurs, is determined for the first time from absorption spectra.

Phthalocyanine compounds are a very important class of organic materials and have been found to be promising materials as photoconductors,[1] photoreceptors[2] and optical recording media.[3] For phthalocyanine and other dyes aggregation is a well known phenomenon.[4–8] In these aggregates, interactions can occur between adjacent molecules both in solution and in the solid state, resulting in coupling between the electronic states of two or more molecular units. In solution, the blue-shift aggregates with lower aggregation numbers can always be observed. In films or the solid state, the situation becomes very complicated,[4] with the spectral bands being broadened and strongly overlapped. The differences in cyclic ring overlap, separation distance and relative position of transition moment between molecules, and number of molecules that interact can result in a variety of aggregates and polymorphs. Recent research aimed at developing a molecular level understanding of photoconduction in organic solids has shown that this phenomenon is dependent both on the intrinsic molecular properties of the potential photoconductive material and on the intermolecular interactions occurring in the solid state.[1,8,10,11] Clear spectral characterization of aggregates of organic photoconductive dyes and pigments is of practical importance and could provide insights into the effects of intermolecular interaction on the properties of these molecules. In this work, the aggregate numbers of red-shift VOPc-II and α-TiOPc are determined from their absorption spectra for the first time.

VOPc and TiOPc were prepared in this laboratory[12,13] (Anal. for VOPc. Calc.: C, 66.40; H, 2.80; N, 19.40. Found: C, 66.41; H, 2.93; N, 19.34%. Anal. for TiOPc. Calc.: C, 66.67; H, 2.77; N, 19.44. Found: C, 66.73; H, 2.69; N 19.56%). FAB mass spectra show single peaks at 580 (M^+ + 1) and 577 (M^+ + 1) for VOPc and TiOPc, respectively. VOPc-II and α-TiOPc are obtained by acid-pasting of the above products. The X-ray powder diffraction angles (2θ) for VOPc-II occur at 7.35, 10.05, 12.50, 13.05, 16.15, 18.35, 22.35, 24.15, 25.30, 28.20° and for α-TiOPc, at 7.56, 10.32, 12.70, 13.26, 15.12, 16.30, 17.28, 18.38, 21.50, 22.50, 24.32, 25.46, 28.68. (lit.[14] 7.6, 10.3, 12.7, 13.3, 16.3, 18.4, 22.7, 24.3, 25.5 and 28.8). The diffraction angles for VOPc-II and α-TiOPc are almost the same, which implies that they have similar crystal structures. Fig. 1(a) shows the absorption spectra at different concentrations of VOPc-II ultrasonically dispersed in thf. At low concentrations, the absorption spectra show a narrow Q band at 684 nm with a shoulder at 618 nm while the B band is at 336 nm. These absorption bands can be attributed to the monomer state. As the concentration of VOPc is increased, a broadened band associated with light scattering appears, which corresponds to the absorption of the dispersion of VOPc-II. When the concentration of VOPc is increased further, steady enhancement of the broadened absorption band of the dispersion can be observed. For the assignment of the solid spectra, a dimeric structure was successfully modelled by Sharp and Lardon to interpret the

spectra of the X-form of the metal-free phthalocyanine.[15] However, this has been established to be insufficient to clearly account for the spectra of VOPc-II,[16] and single crystal structure analysis confirms that there is no discrete dimer pair in solid VOPc-II.[17] In the present work, for the determination of the effects of the concentration on the absorption of the monomer, the systems in Fig. 1(a) were centrifuged at 12 000 rpm for 10 min and the absorption spectra of the solution layer recorded [Fig. 1(b)]. It is surprising to find that, in accordance with the enhancement of the broadened absorption band of the dipersion, the absorption of the monomer increases gradually and a linearity between the absorbances at 684 and 618 nm is observed. This indicates that for the solutions at the concentrations studied, there is no obvious aggregation. When the precipitated solid was redispersed in its original medium under ultrasonic agitation, a spectrum essentially identical to that of the untreated dispersion was again obtained. More detailed investigation shows that the absorptions of the monomer in the systems of Fig. 1(a) reach their maxima after ca. 40 min. Longer treatment causes no further changes in the relative intensity of the monomer and colloidal VOPc-II. These observations indicate that the equilibrium between the monomer in solution and the colloidal VOPc-II particles is not a simple solubilization equilibrium. Although there are some differences in the particle size and electronic properties for the present phthalocyanine compounds and ionic cyanine dyes, the spectral shift induced by aggregation and the stability in the present phthalocyanines are similar to those of colloidal J-aggregates of some cyanines.[5] For the J-aggregation process of an ionic cyanine, eqn. (1) introduced by West and Pearce[18] was used successfully by Herz to determine the aggregation number.[5] Therefore it is reasonable to use this method in the present system. Based on the assumptions made by Herz for the J-aggregation of an ionic cyanine, we can use eqns. (1)–(3).

$$nM \rightleftharpoons M_n \quad K = [M_n]/[M]^n \tag{1}$$

$$\ln[Mn] = \ln K + n \ln[M] \tag{2}$$

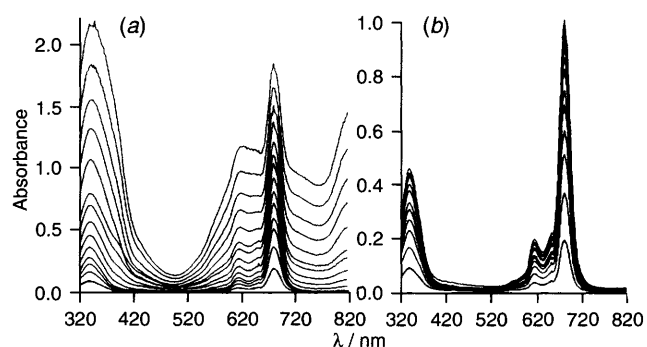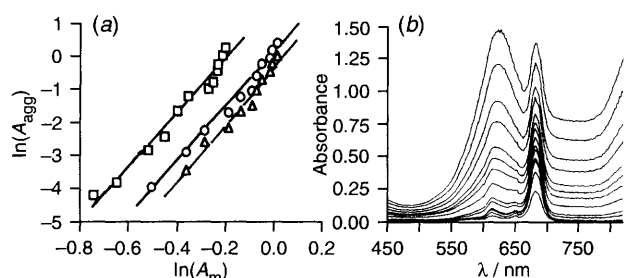$$\ln A_{agg.} = n \ln A_M + \ln K + \ln \varepsilon_{agg.} - n \ln \varepsilon_M \tag{3}$$

Fig. 1(a) Absorption spectra at different concentrations of VOPc-II in thf, [VOPc-II] from bottom to top 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, 12.0, 16.0, 20.0, 24.0, 32.0, 40.0, 50.0, 60.0 × 10⁻⁶ m. (b) Absorption spectra of the solution layers of the above after centrifugation at 12000 rpm for 10 min.

Here M and M_n represent the monomer and aggregate form, respectively, where n is the number of monomer units in the aggregate, K is the aggregation constant. A_{agg}, A_M, ε_{agg} and ε_M are the absorbances and absorption coefficients of the aggregate and monomer, respectively. According to eqn. (3) a plot of $\ln A_{agg}$ vs. $\ln A_M$ should be linear with a slop of n. Fig. 2(a) shows the plots of $\ln A_{agg}$ of VOPc-II at $\lambda = 820$ and 618 nm vs. $\ln A_M$ at 684 nm, which gives aggregate numbers of 8.1 and 8.2, respectively. This result is consistent with the view that the broadened absorption band in the range 500–900 nm arises from a single species. Detail anslysis shows that, in the present system, the error in the determination of absorbance introduced by light scattering is <8% at the wavelength concerned. The most important finding is that the error caused by light scattering may be treated as a systematic error. The effect of the error on the aggregate number obtained is < 0.2. However, an aggregate number of eight cannot be assumed from the light-scattering colloidal measurement of the dispersion. Such a result can be understood in terms of the fact that absorption measurements, and mass action calculations based on them, relate only to the number of participants involved in mutual

spectral perturbation and not necessarally to the total number of molecules per particle. It appears significant, however, that the repeating stack unit consists of just eight VOPc molecules. These can then be considered to constitute the repeating spectroscopic unit cell of the VOPc-II dispersion. For α-TiOPc a similar result (apparent aggregate number of 8.3) has been obtained under similar conditions [Fig. 2(a) and 2(b)].

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Fig. 2(a) Plots of $\ln A_{agg}$ vs. $\ln A_M$. For VOPc-II, A_M at 684 nm, A_{agg} at 820 nm (O), A_{agg} at 618 nm (△); for α-TiOPc, A_M at 684 nm and A_{agg} at 818 nm (□). (b) Absorption spectra at different concentrations of α-TiOPc in thf, [TiOPc] from bottom to top 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, 12.0, 16.0, 20.0, 24.0, 32.0, 40.0, 50.0, 60.0 × 10⁻⁶ M.