NOTE

Surface Modification of a Hydrogen-Bonded Pigment: A Fluorescence Spectroscopy Study

The effect of hydrogen-bonding additives on the surface modification of a hydrogen-bonded organic pigment is studied using absorption and fluorescence spectroscopy. Evidence for surface dissolution that occurs during the mixing of solids is presented. The spectral signatures of monomers and hydrogen-bonded aggregates of the pigment that are present on the surface of crystallites of the pigment are quite distinct, as revealed by fluorescence excitation and emission spectra.   © 1999 Academic Press

Key Words: hydrogen bonding; organic pigments; surface dissolution.

1.0. INTRODUCTION

3,6-Diphenylpyrrolo[3,4-c]pyrrole-1,4-dione (DPP) belongs to a new class of heterocyclics called *diketopyrrolopyrroles,* which are finding increasing use in a variety of industrial applications, especially as high performance pigments (1). The crystal structure of DPP indicates that these molecules form infinite chains of hydrogen bonds in the solid state (2). Also, there are significant interactions between the heterocyclic ring systems in the solid state, causing strong π–π interactions along the stacking axis. Substitution at nitrogen with alkyl groups removes hydrogen bonding but stacking interactions are still present albeit weaker than in the parent system. Consequently, some of these derivatives are quite intensely fluorescent in the solid state and have found useful applications, including optical data storage (3). Theoretical calculations have been performed to evaluate the role of hydrogen bonding and stacking interactions for DPP in the solid state (4). The photochemistry of singlet and triplet excited states of an *N,N*-dimethyl derivative of DPP (NMDPP) is reported (5). Recently, rotational dynamics of DPP and NMDPP have been studied in hydrogen-bonding solvents (6).

In the present work, we studied the *m*-CN derivative of DPP (MCD). We investigated the interaction of the MCD pigment and an additive (HA) that has similar hydrogen-bonding functional groups. The structures of HA, DPP, and MCD are shown in Scheme 1.

2.0. EXPERIMENTAL

The *m*-CN derivative of DPP (MCD) and the hydrogen bonding additive (HA) were supplied by Ciba Specialty Chemicals Inc., Switzerland, and were used as received. The MCD pigment and the additive were homogeneously dispersed in a polyvinylchloride (PVC) matrix. Preparation of the PVC film is briefly described below. The MCD pigment, additive (HA), and PVC powder were mixed thoroughly, and a transparent PVC film of thickness ca. 0.5 mm was prepared using a commercial instrument at Ciba. The film was drawn using a mechanical process. This differs from the normal polymer casting method for preparing thin films that uses suitable solvents for dissolving the polymer. The concentration of the pigment in the PVC film was ca. 0.02% w/w PVC. Two concentrations of the additive (HA), 0.1 and 0.3% w/w PVC, were used. The absorbance of pigments in these films was ca. 0.2 at 450 nm. Optical

absorption spectra of the pigment in PVC films were recorded using a Cary-5 UV–Vis spectrometer with an integrating sphere accessory. Corrected emission and excitation spectra were recorded using a SPEX Flourolog instrument. For the fluorescence measurements a front-face geometry was used to minimize the effects of self-absorption.

3.0. RESULTS AND DISCUSSION

When crystalline organic solids are mixed mechanically, they interact during mixing. Surface dissolution and surface modification takes place at the crystal surfaces. The extent to which these changes occur depends on the nature of the solid surface and the reaction conditions. Pigments of *diketopyrrolopyrroles* form strong intermolecular hydrogen bonds in the solid state. Interaction of the surfaces of these H-bonded pigments with additives containing suitable functional groups can produce changes in the structure of the surface. Detection of such changes is usually difficult since the fraction of material that is modified constitutes only a small portion of the total sample. On the other hand, if there are specific signatures that are characteristic of the surface species and if they are well distinguished from the features of the bulk material, then one can characterize these surface species.

In the present study, we have chosen a surface-perturbing additive (HA) containing hydrogen-bonding functional groups that are also present in MCD. This additive is expected to form strong intermolecular hydrogen bonds with molecules of MCD, can disrupt the hydrogen-bonding patterns of MCD in its crystalline state, and therefore can induce surface dissolution under suitable conditions. Also, the additive HA has only one amide group instead of the two found in MCD and therefore can disrupt the chains of H-bonds of MCD in the solid state.

Interaction of the additive (HA) and the pigment (MCD) takes place during mixing in the presence of the inert PVC matrix. In our experiments, the concentration of the pigment and other conditions were kept constant and only the concentration of the additive was varied. A PVC film with MCD pigment was used as a reference for comparison. In the present work, characterization of the surface species was accomplished by optical spectroscopy. Optical absorption, fluorescence excitation, and emission spectra were used for this purpose.

MCD shows moderate solubility in hydrogen-bonding solvents but is nearly insoluble in nonpolar and non-hydrogen-bonding solvents. The solubility of MCD in PVC, a nonpolar matrix, is negligible. Figure 1 shows the optical absorption spectrum of MCD dissolved in dioxane. The spectrum shows a well-defined vibrational structure, characteristic of this class of molecules in organic solvents, with an absorption max at 508 nm. The same figure shows the absorption spectrum for the pigment of MCD in the solid state dispersed in a PVC film. The absorption spectrum in the solid state differs vastly from that of the monomer. The average size of crystallites of MCD is ca. 100 nm as determined by SEM. The spectrum is broad with a peak at 450 nm and a shoulder at 530 nm. The absorption maximum is blue-shifted by 60 nm compared to that of the monomer in organic solvents. The relative intensities of the main peak and the shoulder are 1.0 and 0.44, respectively. Stacking interactions are known to be very important in addition to hydrogen bonding for DPP and its derivatives (7). Pigment particles of the *m*-chloro derivative of
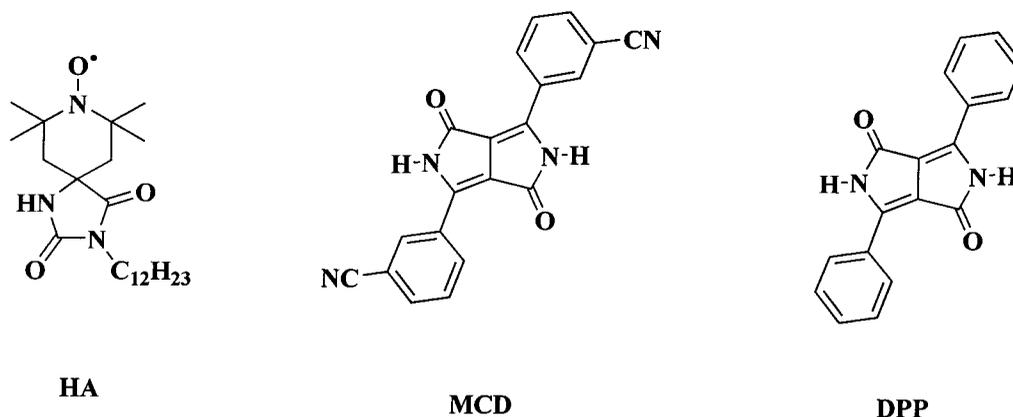
SCHEME 1.   Structures of HA, MCD and DPP.

DPP (Cl atom in the meta position of the phenyl ring) exhibit an absorption spectrum that is nearly identical to that of MCD in a PVC matrix (8). It has been observed for this class of systems that even for structural isomers, changes of the substitution pattern on the phenyl ring result in significant changes in crystal packing. Consequently, the optical signatures of these materials in the solid state tend to be very different, whereas the properties in organic solvents are similar. For example the *p*-Cl derivative of DPP (the Cl is on the para position of the phenyl ring) shows significantly less stacking than the *m*-Cl derivative. Their absorption spectra are vastly different in the solid state but are nearly identical in organic solvents (8). The absorption maxima for *m*-Cl and *p*-Cl derivatives in the solid state are 450 and 561 nm, respectively. A similar trend has been observed when Cl atoms are replaced by CN groups (8).

Interestingly, thin films of DPP and its derivatives reveal optical properties that tend be very different compared to their respective monomers and particles in the crystalline state. Figure 2 shows the optical absorption spectrum of a thin film of MCD (ca. 125 nm thick). The spectrum shows a well-defined structure with two peaks at 530 and 490 nm and a shoulder at about 460 nm. In the case of MCD we find an absorption maximum for pigment particles in the crystalline state at 450 nm (see Fig. 1) indicating a significant blue shift compared with the film. Strong intermolecular interactions in the crystalline state are responsible for the observed changes. The optical spectrum of a thin film of DPP is similar to that of MCD with peaks at 538 and 490 nm and a shoulder at 460 nm. Treatment of this film with vapors of hydrogen-bonding solvents, like acetone, has increased the degree of crystallinity which is confirmed by XRD findings. Vapor treatment promoted crystal growth which resulted in an
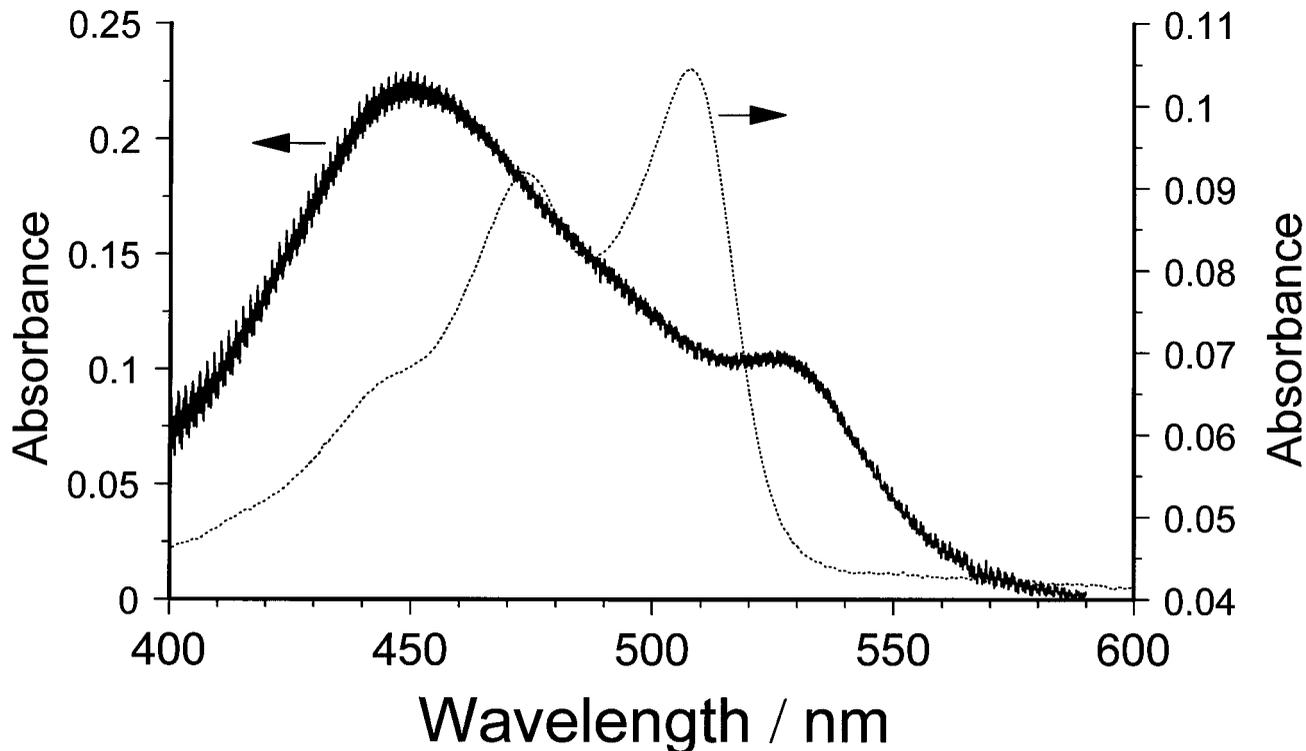

FIG. 1.   Spectrum of the monomer of *m*-CN DPP (MCD) in dioxane (dotted line) and the absorption spectrum of 100 nm particles of MCD in a transparent PVC film (solid line).
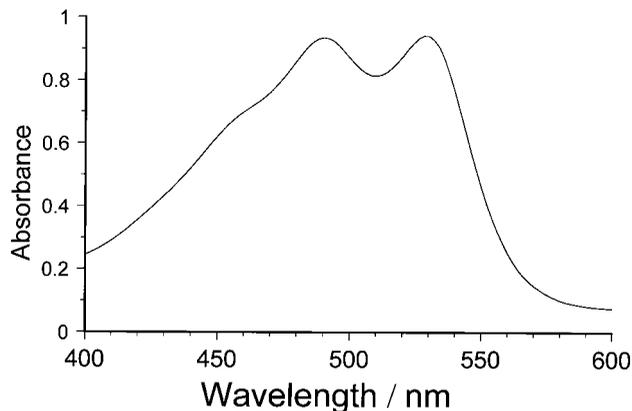
FIG. 2. Optical absorption spectrum of a thin film of MCD. Film thickness is ca. 120 nm.

increase in the observed domain size (9) compared to a freshly prepared film. Also, there is a loss of structure in the optical spectrum resulting in a blue-shifted spectrum with a peak at 450 nm. It was also observed for two other derivatives of DPP (m- and p-Cl derivatives) that the XRD patterns of the phases in thin films after the vapor treatment were similar to those seen in single crystals of these derivatives. The optical spectra for the thin films after vapor treatment resembled the spectra of crystallites dispersed in polymer films. In a way the vapor treatment of the thin films enables a controlled increase in the degree of crystallinity.

To quantify the emission quantum yield for MCD in PVC, we used the N, N-dimethyl derivative of DPP (NMDPP) in the PVC film as a reference. This molecule has a fluorescence quantum yield (Φ_f) of 0.93 in ethanol (5). The absorption and emission spectra of the dye in a PVC film are similar to the spectra in ethanol. Assuming a fluorescence quantum yield of unity for this dye in PVC, the relative quantum yield for the total emission of MCD in the solid state was determined to be $\sim 10^{-3}$ in a PVC film.

Fluorescence excitation spectra of MCD in PVC films are shown in Fig. 3. The spectrum of "pure MCD" without any additive is shown in curve B. The spectra of MCD pigment in the presence of additive (HA) concentrations of 0.1 and 0.3 wt% are shown by curves A and C, respectively. The pigment concentration for all the samples was 0.02 wt%. In the absence of any additive, the observed excitation spectrum is quite broad with a maximum at 500 nm and a shoulder at 530 nm, which appears to represent more than one species. After the addition of 0.1% of HA, there is a dramatic change in the shape of the spectrum as well as in intensity. One observes a well-defined spectrum with two well-resolved peaks with a maximum at 535 nm. This spectrum is very similar to the spectrum of the thin film of MCD shown in Fig. 2. With further addition of the additive, at 0.3% HA, there is a distinctly different spectrum compared to that seen for 0.1% w/w HA.

Fluorescence emission spectra of MCD in PVC films are shown in Fig. 4. For these systems, selection of a suitable exciting wavelength is very important. The choice of 540 nm, as excitation wavelength, was to eliminate all the possible contributions of monomers to the emission. As can be seen from Fig. 1, MCD monomer has no absorption beyond 520 nm. Therefore, for excitation at 540 nm, one expects to see emission only from the solid crystallites of the MCD pigment, from the bulk phase, and also from the surface. The emission spectrum for "pure MCD" without any additive (curve A) and for MCD with different concentrations of the additive are shown in Fig. 4 (curves B and C). The nature of the emission spectra remains the same, but only the relative intensities are affected as a function of additive concentration reflecting the relative changes in the concentration of the emitting species. On the other hand, the excitation spectra show very distinct changes, indicating the presence of different species on the surface of the MCD pigment that contribute to the emission observed at 590 nm.
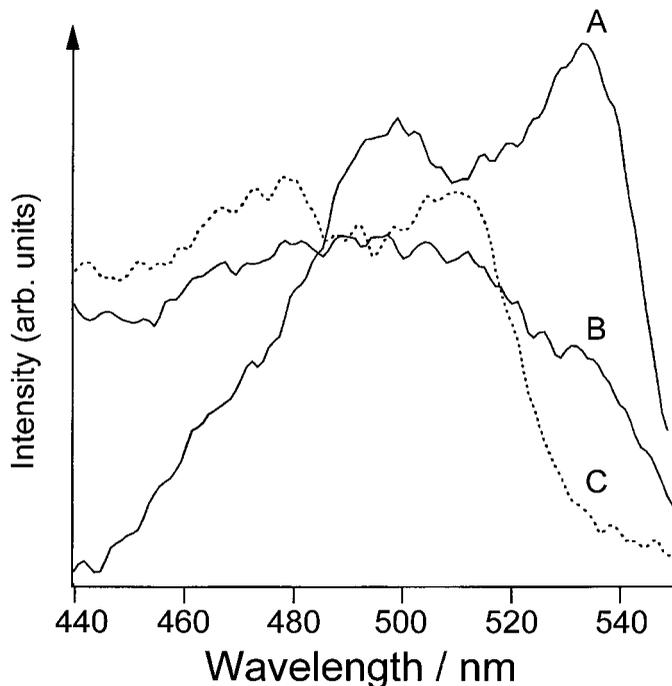

FIG. 3. Fluorescence excitation spectra of MCD in a PVC film without any additive (curve B) and for different concentrations of the additive (HA), 0.1 wt% (curve A) and 0.3 wt% (curve C). The pigment concentration in all the samples is 0.02 wt%. Emission is monitored at 600 nm.

From these results it is apparent that the changes observed are quite dramatic for the addition of 0.1 wt% of additive. For this concentration the excitation spectrum observed is very similar to the absorption spectrum of the thin film of MCD but different from that of the optical absorption spectrum of MCD particles in PVC which remains unchanged. This implies that most of the bulk material remains unperturbed. Fluorescence emission and excitation have
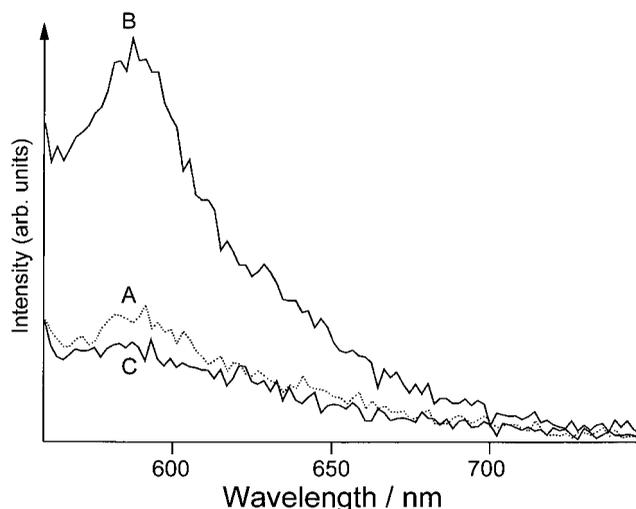

FIG. 4. Fluorescence emission spectra of MCD in a PVC film without any additive (curve A) and for different concentrations of the additive (HA), 0.1 wt% (curve B) and 0.3 wt% (curve C). The pigment concentration in all the samples is 0.02 wt%. Excitation wavelength is 540 nm.

revealed clearly that most of the observed emission does not originate from the bulk phase. Whenever a single species is responsible for emission, fluorescence excitation spectrum would be identical to the absorption spectrum. From a molecular viewpoint, at this concentration of additive, the surface is perturbed only moderately. This results in partial dissolution of the surface of the crystallites forming regions of low crystallinity. The surface of the particles is subjected to changes in the microenvironment and will interact with additives. We also find that the relative intensity of the emission goes up at this level of additive concentration. The fluorescence intensity of a given species is governed by the quantum yield and concentration of the emitting species. If the quantum yield is high, then one can detect even minute concentrations, and using the excitation spectra it is possible to determine the absorption characteristics of the emitting species.

Based on the results, we propose the following physical picture. The additive HA can form strong hydrogen bonds, involving C═O and NH groups, with the molecule of MCD. As a result, the additive can disrupt the hydrogen-bonding patterns of MCD in the crystalline state. During the mixing process, the additive interacts with pigment particles, causing partial dissolution of the surface and forming domains of low crystallinity which we refer to as hydrogen-bonded aggregates. Since these aggregates exhibit strong emission characteristics, we could see intense emission from these species. The excitation spectrum, therefore, is similar to the thin film which consists of domains of low crystallinity. As the concentration of additive increases, smaller domains on the surface of the pigment are broken further forming a mixture of aggregates and monomers. As a result, the emission intensity for excitation at 540 nm, where only aggregates absorb, decreases. The interaction of the surface of pigment crystallites of MCD and the hydrogen-bonding additive HA can be treated like a reaction. These sequential changes are summarized below:

Step 1. MCD with No Additive

Crystallites reveal slight disorder on the surface. The excitation spectrum is broad indicating multiple species (monomers, aggregates, and bulk). Emission seen at 590 nm is quite weak.

Step 2. MCD + 0.1% Additive

The crystalline bulk phase dissolves slightly on the surface forming large concentration of domains of low crystallinity (H-bonding aggregates) on the surface. The excitation spectrum is well resolved with two peaks and bears a resemblance to the absorption spectrum of the thin film. There is also a large increase in the emission intensity. For the excitation wavelength of 540 nm, since no monomer is directly excited, the 590-nm emission arises from the newly formed surface species with small contributions from the bulk phase.

Step 3. MCD + 0.3% Additive

For this case, the excitation spectrum is broad and shows peaks at 510 nm and 470 nm. These are signatures of the monomer (see Fig. 1). But this spectrum is not as well defined indicating possible contributions from other species to the emission. Since the absorption spectrum of the bulk is broad with a maximum at 450 nm, sharper peaks of monomer could be easily identified based on their position. Also the emission intensity has decreased dramatically, compared to step 2, which implies a decrease in the concentration of the surface species that are excited at 540 nm. These results clearly demonstrate that the surface species, formed in step 2, are disrupted by the H-bonding additive.

These results provide clear evidence for the process of surface dissolution in a solid–solid mixing process. It is apparent that the interaction between the additive and the MCD crystallites that takes place during the process of mixing is quite dramatic. This phenomenon certainly depends on the hardness of the surface. In crystallites where the binding energy is very high, one can expect less dramatic variations. The hardness of the crystalline solids depend upon packing considerations and the strength of hydrogen bonding. Since the strength of hydrogen bonding is not expected to vary very significantly with a series of derivatives, the stacking interactions in the crystallite are possibly very important. This is clearly reflected in the optical absorption spectra as well as in the X-ray structures of some of the derivatives of DPP. A more detailed investigation involving a series of derivatives of varying binding strength is underway.

REFERENCES

1. Iqbal, A., Cassar, L., Rochat, A. C., Pfenninger, J., and Wallquist, O., *J. Coat. Tech.* **60,** 37 (1988).
2. Mizuguchi, J., Grubenmann, A., Wooden, G., and Rihs, G., *Acta. Crystallogr. B* **48,** 696 (1992).
3. Langhals, H., *J. Inf. Rec. Mat.* **19,** 449 (1991).
4. Adachi, M., and Nakamura, S., *J. Phys. Chem.* **98,** 1796 (1994).
5. Srivatsavoy, V. J. P., Eschle, M., Moser, J. -E., and Grätzel, M., *J. Chem. Soc. Chem. Commun.* 303 (1995).
6. Dutt, G. B., Srivatsavoy, V. J. P., and Sapre, A. V., *J. Chem. Phys.* **110,** 9623 (1999).
7. Mizuguchi, J., Grubenmann, A., and Rihs, G., *Acta Crystallogr. B* **49,** 1056 (1993).
8. Srivatsavoy, V. J. P., unpublished results.
9. Mizuguchi, J., and Wooden, G., *Ber. Bunsenges. Phys. Chem.* **96,** 597 (1992).

V. J. P. Srivatsavoy*[,1]
J.-E. Moser*
M. Grätzel*
L. Chassot†[,2]

Institut de chimie physique 2
Ecole Polytechnique Fédérale de Lausanne
CH-1015 Lausanne, Switzerland
†*Ciba Specialty Chemicals Inc.*
Research Centre
CH-1723 Marly 1, Switzerland

[1] To whom correspondence should be addressed. Present Address: Unilever Research India, 64 Main Road, Whitefield, Bangalore - 560 066, India. E-mail: velagapudi.srivatsavoy@unilever.com. Fax: +91 80 845 3086.

[2] Present address: Cosmital, Rte de Chésalles 21, CH-1723, Marly 1, Switzerland.