Science and Technology of Dyes and Pigments for Imaging Applications

- various colors arising from polymorphs in organic pigments -

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Abstract

Dyes and pigments play a crucial role as the colorants in the imaging areas. In the period of black & white copies, organic pigments have extensively been studied as photoconductors for electrophotographic photoreceptors. However, nowadays, pigments have more and more attracted attention as colorants, not only for color copies based upon the electrophotographic process, but also for inkjet printers. The color of the dyestuff is mostly determined by its molecular structure; whereas that of pigments arises from the molecular structure as well as intermolecular interactions in the solid states. Therefore, the color of pigments can be influenced by molecular arrangement, i.e., crystal structure. In present keynote, I begin with a brief introduction about the difference between dyes and pigments in general and then talk about the intermolecular interactions in the solid state from the standpoint of the crystal structure. I will also introduce you a variety of polymorphs in pigments that are isolated as single crystals and discuss some representative factors which induce phase transition, leading to different colors.

1. Introduction

Polymorph is often observed in organic pigments, causing a variety of colors to appear in the solid state.[1, 2] On the other side, polymorph is also related to the emission phenomenon as well as photoconduction. Existence of local energy-minima in addition to the global one is prerequisite for the appearance of the polymorph. A phase which is stable at one set of values of pressure and temperature may change to a different phase if either or both of these variables are changed. The present phase change is common to both organic and inorganic compounds. However, there is another influencing parameter which is specific of organic pigments: *i.e.* solvent effect. The phase change due to solvent or solvent vapor occurs with ease even at room temperature.

Table1 Polymorphs in organic pigments isolated as single crystals

	Compound	Crystal form	Literature
DPP and its related pigments	3,6–Di–4–pyridylpyrrolo[3,4–*c*]pyrrole–1,4(2*H*,5*H*)–dione	I & II	5, 7
	3,6– diphenylpyrrolo[3,4–*c*]pyrrole–1,4–dithione	I, II & III	7, 8
	1,4–dioxo– 3,6– diphenylpyrrolo– [3,4–*c*]pyrrole–2,5(1*H*,4*H*)– dicarboxylic acid bis (1,1–dimethylethyl) ester	α & β	9, 10
QA and related pigments	5,7,12,14–Tetrahydro[2,3–*b*]quinolinoacridine	β & γ	11, 12
	2,9–Dichloro–5,12–dihydroquino[2,3-b]acridine–7,14–dione	red & black	13, 14
	2,9–dihydroquino[2,3–*b*]acridine–7,14–dithione dimethylacetamide disolvate	monoclinic & triclinic	15, 16
Perylene–imide and related pigments	*N,N'* –bis(2–phenylethyl)perylene–3,4:9,10–bis(dicarboxyimide)	amorphous, I & II	17, 18, 19
	N,N' –di–*n*–butylperylene–3,4:9,10–bis(dicarboximide)	I & II	20, 21
	3,4:9,10– perylene–tetracarbocylic dianhydride	α & β	22, 23
	N,N' –Bis[2–(4–pyridyl)ethyl]perylene–3,4:9,10–bis (dicarboximide)	*cis/trans* forms	24, 25, 26
TiOPc	Titanylphthalocyanine	I & II	27
Indigo	Indigo	A & B	28, 29

Although a number of polymorphs have been reported in pigment industries, these are not in the form of single crystals but mostly in powdered forms. This is also the case in near-IR active photoconductors for the laser printer, where a variety of organic pigments have extensively been characterized as photoconductors. In the meantime, the issue of the near-IR-active photoconductor has been settled. Instead, organic pigments have more and more attracted attention as colorants for toners and inkjet inks because of their stability against temperature and light irradiation. The color matching and the color reproduction space are now the central issue in color copies as well as the stability of the color prints.

The author has been involved in the research and development on the correlation between electronic structure of organic pigments (*i.e.* color generation mechanism) and their crystal structure with special attention to the polymorph. In the present keynote, to start with, I will introduce a variety of polymorphs which are isolated in our laboratory as single crystals and whose structures have been analyzed. Then, the basic exciton theory of the color generation mechanism generation will briefly be introduced. After that, I will discuss some parameters that induce phase change in organic pigments to yield different colors.

2. Polymorphs in organic pigments analyzed on the basis of single crystals

Table 1 lists a number of polymorphs studied in our laboratory which also includes some important modifications such as in TiOPc (I & II) and indigo (A & B).

3. Different colors arising from different polymorphs: excitonic interactions

When we deal with intermolecular interactions, it is imperative to differentiate the interactions in the ground state from that in the excited state. The interactions which occur in the ground state is associated with the stabilization of the material in dark. Therefore, the interaction is related to the thermal stability (melting and sublimation points), mechanical property (hard or soft), solubility in organic solvents. On the contrary, the interactions in the excited state (*i.e.* interactions between excited molecules) involve optical properties such as absorption and emission. Especially, the latter interaction is extremely important in systems of dyestuffs and pigments, as far as the color in the solid state is concerned. The present interactions is called excitonic interactions between transition dipoles which prevail when the molecules with high absorption coefficient are periodically arranged. That is, the interaction is remarkable in crystals and aggregates, but not in amorphous states. The present interaction induces bathochromic or hypsochromic shifts, band splitting, appearance of a new band etc., depending on the molecular arrangement.

When an excitation induces a transition dipole in the molecule, the excited state in crystals involves wavefunctions with significant probabilities on nearest neighbors. Therefore, the exciton coupling may well involve energy contributions from interactions with all of these nearest neighbor molecules acting in concert in the lattice. This may lead to a band splitting of the

excited state or spectral displacement toward longer wavelengths or shorter wavelengths. The interaction energy ($\Delta E_{\text{exciton}}$) is given by the dipole-dipole equation[3, 4]: $\Delta E_{\text{exciton}} = |\mu_T|^2 (1-3\cos^2\theta) / r^3$, where the transition dipole is denoted by μ_T, the distance and angle between two transition dipoles by r and θ, respectively. As evident from the present equation, the overall spread or shift energy is determined by the strength of the interneighbor coupling ($|\mu_T|^2$) which directly depends on the absorption coefficient of the molecule as well as the mutual relative orientation of the transition dipoles in molecular assemblies. That is, the term $(1-3\cos^2\theta)$ determines the geometrical relationship of transition dipoles correlated with the crystal structure. The bathochromic or hypsochromic shift depends on the critical angle of $\theta=54.7°$, below which the former will result and above which the latter will be the case. The maximum bathochromic or hypsochromic shift is achieved by "head-to-tail"-arrangement or "parallel" arrangement, respectively.

4. Factors which induce color changes in the solid state

4.1 Phase change due to thermal energy
A phase which is stable at one set of values of pressure and the temperature may change to a different phase if either or both of these variables are changed. Thermal vibration of the molecules around their equilibrium positions is essential for the phase change due to thermal energies. Thermal phase transition is quite common in inorganic compounds, but relatively rare in organic pigments. Some examples will be given in presentation.[13, 14, 17-19]

4.2 Solvent or solvent vapor effect
Solvent effect has been used for a long time in pigment industries in order to prepare uniform colored particles. The phase change due to solvent vapor occurs quite often in organic pigments.[7,8,17-19] Solvent or solvent vapor may loosen the crystal lattice, thus allowing the molecules to slide and/or rotate to find a more stable arrangement. Because of the polar nature of both the solvent and the molecules, the phase change due to solvent vapor is selective and the molecules cannot slide and/or freely, but they can only move under certain constraints.

4.3 Mechanical shearing to induce molecular arrangement
This phenomenon is typical of the low density pigments.[17-19, 28] Mechanical shearing is known to induce molecular arrangement, for example, when the powders were ground in a mortar with a pestle. This effect is sometimes called tribo or piezochromism".

4.4 Color change due to protonation
In pyridylring-containing pigments, protonation at the N-site often brings about a drastic color change. In pigment dispersed polymer layers, even a trace of protons liberated gradually from the polymer matrix is found to exert a profound influence in color as well as electrical resistivity and photoconduction.[5, 7]

4.5 Strength of the intermolecular hydrogen bond
In hydrogen-bonded pigments such as

diketopyrrolopyrroles[5-10] and quinacridones[11-16], the color change occurs, depending on the strength of the intermolecular hydrogen bond between the NH group of one molecule and the O atom of the carbonyl group of the neighboring one. In these pigments, There are two functions in intermolecular hydrogen bonds. One is to align the transition dipole in a fashion "head to tail" to displace the absorption band toward longer wavelengths. Another function of the hydrogen bond is to bridge small molecules of pigments together to impart a polymer-like stability. Therefore, the hydrogen bond determines the color as well as the stability of the pigments.

4.6 Water moisture

Metal-containing phthalocyanine (*e.g.* MgPc) is easily hydrated at the central metal to induce a different molecular arrangement, thus giving rise to an intense near-IR absorption.[31] The amorphous state (red) of ethylphenylperylene-imide[19] is exceptionally stable in the absence of moisture, but the color changes gradually its color from red to black in the presence of water moisture.

5. Conclusions

A variety of polymorphs of organic pigments have been presented which give different colors. The basic theory of the color generation mechanism has been outlined in terms of excitonic interactions. The present interactions prevail in dyestuffs and pigments where the molecules with high absorption coefficient are periodically arranged. Crystals as well as clusters and aggregates of organic dyestuffs or pigments are in a position to basically give different colors, depending on the molecular arrangement. Some influential factors to induce molecular rearrangement have been discussed.

References

1) W. Herbst and K. Hunger: Industrial Organic Pigments: Production, Properties, Applications, 3rd ed.; VCH: Weinheim, 2004.

2) H. Zollinger: Color Chemistry, synthesis, properties and applications of organic dyes and pigments, Second, revised edition, VCH: Weinheim, 1991.

3) M. Kasha: Molecular Excitons in Small Aggregates. In NATO Advanced Study Institute Series, Series B; Bartolo, B. D., Ed.; Plenum Press: New York, 1976; Vol. 12; pp 337–363.

4) D. P. Craig and S. H. Walmsley: Excitons in Molecular Crystals: theory and applications; W. A. Benjamin, Inc.: New York, 1968.

5) J. Mizuguchi, T. Imoda and H. Takahashi: 3,6-Di-4-pyridylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione, Acta Cryst. E61, o500-o502 (2005).

6) J. Mizuguchi, H. Takahashi and H. Yamakami: Crystal structure of 3,6-bis(4'-pyridyl)-pyrrolo[3,4-c]pyrrole-1,4-dione, Z. Krist. NCS 217, 519-520 (2002).

7) J. Mizuguchi, A. C. Rochat and G. Rihs: Structure of 3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4-dithione, Acta Cryst. C 46, 1899-1903 (1990).

8) J. Mizuguchi, M. Arita and G. Rihs: A new crystal structure of 3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4-dithione, Acta Cryst. C 47, 1952-1956 (1991).

9) J. Mizuguchi: Refinement of the crystal structure of α-1,4-dioxo- 3,6-diphenylpyrrolo- [3,4-c]pyrrole-2,5(1H,4H)-dicarboxylic acid bis (1,1-dimethylethyl) ester, Z. Krist. NCS 218, 134-136 (2003).

10) J. Mizuguchi: The β-form of di-tert-butyl-1,4-dioxo-3,6-diphenyl-1,2,4,5-tetrahydropyrrolo-[3,4-c] pyrrole-2,5-dicarboxylate, Acta Cryst. E 59, o469-o471 (2003).

11) N. Nishimura, T. Senju and J. Mizuguchi: 5,7,12,14-Tetrahydro[2,3-b]quinolinoacridine (β form), Acta Cryst. E62, o4683-o4685 (2006).

12) J. Mizuguchi, T. Sasaki and K. Tojo: Refinement of the crystal structure of 5,7,12,14-tetrahydro[2,3-b]-quinolinoacridine (γ-form), Z. Krist. NCS 217, 249-250 (2002).

13) T. Senju, N. Nishimura, T. Hoki and J. Mizuguchi: 2,9-Dichloro-5,12-dihydroquino[2,3-b]acridine-7,14-dione (red phase), Acta Cryst. E61, o2596-o2598 (2005).

14) T. Senju, T. Hoki and J. Mizuguchi: 3,10-Dichloro-5,12-dihydroquino[2,3-b]acridine-7,14-dione, Acta Cryst. E62, o261-o263 (2006).

15) T. Hoki, T. Senju and J. Mizuguchi: The monoclinic form of 2,9-dihydroquino[2,3-b]acridine-7,14-dithione-dimethyl-acetamide disolvate, Acta Cryst. E61, o1927-o1929 (2005).

16) T. Senju, T. Hoki and J. Mizuguchi: The triclinic form of 2,9-dichloro-5,12-dihydroquino[2,3-b]acridine-7,14-dithione dimethylacetamide disolvate, Acta Cryst. E61, o1930-o1932 (2005).

17) J. Mizuguchi: Electronic characterization of N,N'-bis(2-phenylethyl)perylene-3,4:9,10-bis-(dicarboxyimide) and its application to optical disks, J. Appl. Phys. 84, 4479-4486 (1998).

18) E. Hädicke and F. Graser: Structures of eleven perylene-3,4:9,10-bis(dicarboximide) pigments, Acta Cryst. C42, 189-195 (1986).

19) J. Mizuguchi: N,N'-bis(2-phenylethyl)perylene-3,4:9,10-bis (dicarboxyimide), Acta Cryst. C 54, 1479-1481 (1998).

20) E. Hädicke and F. Graser: Acta Cryst. C42, 189-195 (1986).

21) J. Mizuguchi: Crystal structure of a second modification of N,N'-di-n-butylperylene-3,4:9,10-bis(dicarboximide), Z. Krist. NCS 218, 131-133 (2003).

22) K. Tojo and J. Mizuguchi: Refinement of the crystal structure of α-3,4:9,10- perylene-tetracarbocylic dianhydride at 223 K, Z. Krist. NCS 217, 253-254 (2002).

23) K. Tojo and J. Mizuguchi: Refinement of the crystal structure of β-3,4:9,10- perylene-tetracarbocylic dianhydride at 223 K, Z. Krist. NCS 21 , 255-256 (2002).

24) J. Mizuguchi and K. Hino: N,N'-Bis[2-(4-pyridyl)ethyl]perylene-3,4:9,10-bis(dicarboximide)phenol disolvate, Acta Cryst. E61, o669-o671 (2005).

25) K. Hino and J. Mizuguchi: N,N'-Bis[2-(4-pyridyl)ethyl]-perylene-3,4:9,10-bis (dicarboximide)m-cresol disolvate, Acta Cryst. E61, o672-o674 (2005).

26) J. Mizuguchi and K. Tojo: Crystal structure of N,N'-bis(2-(4-pyridyl)ethyl)-perylene-3,4:9,10-bis-(dicarboximide), Z. Krist. NCS 217, 247-248 (2002).

27) W. Hiller, J. Strähle, W. Kobel and M. Hanack: Solid-State Spectra of Titanylphthalocyanine, Z. Kristallogr 159, 173-183 (1982).

28) P. Süsse, M. Steins and V. Kupcik: Crystal structure refinement based on synchrotron data, Z. Kristallogr. 184, 269-273 (1988).

29) P. Süsse and A. Wolf: A new crystalline phase of indigo, Naturwissenschaften 67, 453, (1980).

30) J. Mizuguchi, N. Tanifuji and K. Kobayashi: Electronic and structural

characterization of a piezochromic indigoid:
11-(3'-oxodihydrobenzothiophen-2'-ylidene)cyclopenta[1,2-b:4,3-b']

31) -dibenzothiophene, J. Phys. Chem. B 107, 12635-12638 (2003).

32) A. Endo, S. Matsumoto and J. Mizuguchi: Interpretation of the near-IR absorption of magnesium phthalocyanine comlexes in terms of molecular distortion and exciton coupling effects, J. Phys. Chem. A 103, 8193-8199 (1999).

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