On the nature of supramolecular colour phenomenon

Bansi L. Kaul (✉ kaul@mcatechnologies.com)

MCA Technologies GmbH,

Research Article

Keywords: monomolecular colour phenomenon (MMCP), supramolecular colour phenomenon (SMCP), and rationale for their differentiation, Colour beyond

Posted Date: January 18th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1265065/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Colour is of special interest in chemistry, physics, biology, medicine and of course for culture and life style. The relation between colour and constitution of organic materials at molecular level, to be called mono molecular colour phenomenon (MMCP), is well understood based on PPP-MO calculations of energy levels of excited states upon light absorption. However, such a relation cannot always be extrapolated to supramolecular state in which colorants normally exist both in nature and for their actual functionality. The present study provides examples of both mono molecular colour phenomenon (MMCP) and supramolecular colour phenomenon (SMCP), and a rationale of their differentiation.

Summary

Colour, a multifaceted phenomenon associated with light, is certainly instrumental for the creation and existence of vegetation and life on this planet, particularly by virtue of colorants such as chlorophyll and hemin. Colour is of special interest in chemistry, physics, biology, medicine and of course for culture and lifestyle. Colour is being increasingly exploited in digital technology for the storage and reproduction of information and in medicine for photodynamic therapy (PDT). Colorants are basically the materials responsible for the creation of one of the fifteen known colour phenomena. The relation between the colour and constitution of organic materials at the molecular level, called the monomolecular colour phenomenon (MMCP), is well understood based on PPP-MO calculations of the energy levels of excited states upon light absorption. However, such a relation cannot always be extrapolated to the supramolecular state in which colorants normally exist both in nature and for their actual functionality. The present study provides examples of both monomolecular colour phenomena (MMCPs) and supramolecular colour phenomena (SMCPs) and a rationale for their differentiation.

Discussion

Colour is one of the most important phenomena of nature^{1,2}. There are fifteen causes of colour known³. Thus, the colour of organic compounds is attributed to electron transitions between orbitals of the individual molecules provoked by light absorption. The principle of excitation by light absorption, valid for all molecules and not only for the colorants, is well understood based on molecular orbital concepts⁴ and the extensive work of the 1998 Nobel Laureate John Pople on quantum chemical models^{5,6}. This phenomenon is coined the monomolecular colour phenomenon (MMCP). However, the phenomenon of colour in the solid state of substances and their certain naturally occurring and/or artificially created surroundings is still not well understood^{7,8}. This understanding can facilitate further exploitation of colour for hitherto unknown applications. For this understanding, we have compared the light absorption characteristics of certain organic colorants (Fig 1) in solution and as microdispersions in their realistic surroundings. This letter presents our surprising findings and their interpretation.

[Figure 1 (Kaul_fig1.doc)]

THI pigments⁹ are a novel class of environmentally benign colorants¹⁰ recently developed for commercial exploitation. THI pigments are related to naturally occurring trichosiderins contained in human and animal keratinic materials¹¹. Although THI pigments provide only yellow solutions when dissolved, their colours vary between yellow and deep red in their solid states. Thus the absorption spectra (Fig. 2) of C.I. Pigment Red 279 (I), as a microdispersion in toluene or hexane, with a particle size of $< 1\ \mu\text{m}$ of $> 95\%$ population, represents a paint or a printing ink formulation and shows absorption bands between 350 and 500 nm in the visible region due to its inherent electronic structure, coined the monomolecular colour phenomenon (MMCP), and between 500 and 600 nm due to the so-called supramolecular colour phenomenon (SMCP), accounting for its red colour. As a dispersion in polyethylene, a similar SMCP spectrum is obtained¹². However, when totally dissolved in N-methylpyrrolidone, a yellow solution showing only the absorption bands between 350 and 500 nm, representing its inherent electronic structure or molecular conjugation, was discernible.

[Figure2 (Kaul_fig2.doc)]

Absorption bands responsible for its red colour in its solid state are completely absent. However, upon dilution with water to cause precipitation, red absorption bands appear. The slightly hypsochromic appearance of these bands compared to those of the dispersions in polyethylene, toluene or hexane is attributed to the less densely packed, almost amorphous metastable nature of such a precipitate .

[Figure 3 (Kaul_fig3.doc)]

Diketopyrrolopyrrole pigments such as C.I. Pigment Red 254 (II)¹³ displays a similar behaviour as dispersions against solutions (Fig. 3). Thus, the longest wavelength absorption band between 586 and 568 nm as a dispersion in N-methylpyrrolidone and polyethylene, accounting for the red colour of pigment red 254(II) as a solid, totally disappears in solution in N-methylpyrrolidone, providing only a yellow colour. In solution only the absorption between approx. 400 – 550 nm, which is also discernible in microdispersions due to its inherent electronic structure. Again, upon dilution of the N-methylpyrrolidone solution with water to cause precipitation, a red absorption band appears. Notably, the red absorption band of the resulting almost colloidal metastable precipitate is also hypsochromically shifted, as is to be expected based on the results of THI studies. However, to be particularly noted is a somewhat hypsochromic shift of the red band in polyethylene compared to the appearance of this band as dispersions in N-methylpyrrolidone, toluene and hexane. This is perhaps due to the tendency of the DPP Red, C.I. Pigment Red 254 to form colloidal dispersions or to go into solution in polyethylene. In the case of THI Red, no such pronounced shift of the red band between the polyethylene dispersion and microdispersions in various solvents is observed.

[Figure 4 (Kaul_fig4.doc)]

Quinacridone pigments such as Pigment Violet 19 (III)¹⁴ now also display supramolecular colour phenomenon (SMCP) in the solid state and show a similar difference between their absorption spectra in

solution and in the solid state (Fig. 4).

However, the supramolecular colour phenomenon is not confused with other types of aggregation effects frequently encountered in the solid state. Not all types of aggregations lead to supramolecular colour phenomena. For the supramolecular colour phenomenon, the aggregation needs to be at the chromophoric sites, enabling conjugation across the chromophores of the individual molecules.

Thus Phthalocyanine pigments, such as C.I. Pigment Blue 15¹³ (IV), a synthetic analogue of naturally occurring chlorophyll and hemin¹⁵, does not show such a dual absorption pattern in solution or as microdispersions. Additionally, most of the azo, anthraquinone, quinophtalone and perinone colorants investigated by us are devoid of such a behaviour¹⁶. We believe that the colour of certain materials in the solid state is not only due to the excitation of the p-electron system of their individual molecules but also due to the cross conjugation across the molecules enabled by the light-induced hybridization in the excited state of the lone pair electron orbitals of their heteroatoms, following Heisenberg's uncertain principle. Thus, a supramolecule behaves like an extended p-electron system of an individual molecule.

[Figure 5 (Kaul_fig5.doc)]

The supramolecular colour phenomenon (SMCP) of THI pigments in the excited state is attributed to conjugation across the molecules, enabled by the hybridisation of the lone pair electron orbitals of the sulfur atom of one molecule with those of the oxygen atom of the neighbouring molecule placed above and/or under it, although interactions even with neighbouring nitrogen lone pair orbitals cannot be completely ruled out. X-ray structural study of THI pigments further confirms the probability of such supramolecular hybridisation in the solid state¹⁷. Thus in the crystal structure of C.I. Pigment Red 279 (Fig. 5) sulfur atom of one of the THI molecules in a particular layer is located next to the oxygen and the nitrogen atom of the molecule in the layer above (or underneath) at a distance of 4.3 Å in the ground state, enabling the required hybridisation for supramolecular colour phenomenon (SMCP) upon excitation. That supramolecular colour phenomenon is indeed due to the three-dimensional crystal structure is also evidenced by the absorption spectrum of the vapour deposited film of Pigment Red 254 (II). Being only a monolayered assembly of molecules, the absorption spectrum pattern is identical to that of its solution, with bands only slightly shifted bathochromically¹⁸. There seems to be no evidence of SMCP.

Implications of the supramolecular colour phenomenon reported herein are relevant not only for the colour appearance but also for a deeper understanding of the formation and nature of supramolecular structures both in chemistry and biology. Such an understanding can even be a tool in drug discovery programmes¹⁹. For example, lycopene, the red carotenoid of tomatoes and other coloured carotenoids, has been shown to have chemopreventive properties only as constituents of fresh food, i.e. as supramolecules and not when used as isolated food additive²⁰.

Methods

All colorants investigated were commercially available [C.I. Pigment Red 279 = THI Novoperm® Red 4G70 (Clariant). C.I. Pigment Red 254 = Irgazin® DPP Red BO (Ciba). Pigment Violet 19 = PV Fast® Red E3B (Clariant)]. UV-visible spectroscopy was performed using a UV-2401-PC (SCHIMADZU) apparatus. The solutions and suspensions were prepared as described in the corresponding figures and then measured in quartz cells with an optical trajet of 1 cm.

In 2008, the Nobel Prize in Chemistry was jointly awarded to Martin Chalfie, Osamu Shimomura and Roger Y. Tsien for the discovery and development of the green fluorescent protein **gfp**. “Scientists have used three fluorescent proteins in cyan, yellow and red colours similar to those used by a computer printer to colour the brain of a mouse. Different neurons randomly produce different amounts of the proteins”. The different colour appearances of these proteins are attributed to supramolecular colour phenomena.

Declarations

Competing interests: The author declares no conflicting interests.

Acknowledgements

My research team at Clariant, Huningue ; France (2000).

References

1. Nassau, K. (Ed.) *Color for Science, Art and Technology* (Elsevier Science, Amsterdam, 1998).
2. Ball, P. Chemistry, psychology, art and alchemy casting light on a multifaceted topic. *Nature* **404**, 703–704 (2000).
3. Nassau, K. The Fifteen Causes of Color. *Color Research and Application* **12**, 4–26 (1987).
4. Försterling, H.D. & Kuhn, H. *Principles of Physical Chemistry*, (Wiley, New-York, 1999).
5. Pople, John A. Quantum chemical models (Nobel lecture). *Angew. Chem., Int. Ed.* **38**, 1894–1902 (1999).
6. Pople, John A. *Quantum chemical models* (Book of Abstracts, 218th ACS National Meeting, New Orleans, Aug. 22-26, 1999).
7. Martin, H.-D. The Function of Natural Colorants: The Biochromes. *Chimia* **49**, 48–68 (1995).
8. Ball, P. Why grass is green, or why our blood is red, Are mysteries which none have reach'd int. *Nature* **400**, 229–230 (1999).
9. Kaul, B.L. & Piastra, B. Thiazine indigo pigments, their preparation, their solid solutions and their application, *PCT Int. Appl. WO 9832800 A1*, Priority: GB 97-1784 19970129.
10. Jansen, M. & Letschert H.P. Inorganic Yellow-red Pigments Without Toxic Metals. *Nature* **408**, 980–982 (2000)

11. Thomson, R.H. The Pigments of Reddish Hair and Feathers, *Angew. Chem. Internat. Edit.* **13**, 305 (1974).
12. Although not identical to naturally occurring trichosiderins, such a dispersion represents a state of the occurrence of such a chromogen even in nature as colorants of feathers, fur and hair.
13. Hunger K. & Herbst W. *Industrial Organic Pigments* (VCH, Weinheim, 1997).
14. Zollinger H. *Color Chemistry: syntheses, properties and application of organic dyes and pigments* (2nd, revised edition, VCH, Weinheim, 1991)
15. Zollinger H. *Color: A Multidisciplinary Approach* (HVCA Zürich & Wiley-VCH Weinheim, 1999).
16. Kaul, B. L. *Unpublished results*
17. Schmidt, M.U. *Crystal Structures of Organic Pigments Determined from X-Ray Powder Data* (Abstract, Colour Science'98, Harrogate, UK, March 30 – April 1st, 1998).
18. Iqbal, A., Jost, M., Kirchmayr R., Pfenninger J., Rochat A. & Wallquist O. The Synthesis and properties of 1,4-Diketo-Pyrrolo[3,4-C]Pyrroles. Physical Properties and Crystal Structure. *Bull. Soc. Chim. Belg.* **97**, 636 (1988).
19. Pelton, J. *Science* **291**, 2175–2176 (2001).
20. Hennekens, C.H. *et al.*, Omenn, G.S. *et al.*, Kushi, L.H. *et al.*, Long-term Supplementation with carotene (etc.). *New England Journal of Medicine* **334**, 1145–1162 (1996).

Figures

Figure1 Chemical structures: (I) C.I. Pigment Red 279. (II) C.I. Pigment Red 254. (III) C.I. Pigment Violet 19. (IV) C.I. Pigment Blue 15.

Figure 1

See image above for figure legend.

Figure 2 Absorption spectra of C.I. Pigment Red 279 (THI Red): (1) micro dispersion in toluene. (2) micro dispersion in hexane. (3) 0.1 % pigment dispersion in polyethylene. (4) solution in N-methylpyrrolidone. (5) precipitation in N-methylpyrrolidone with 50 % water.

Figure 2

See image above for figure legend.

Figure 3 Absorption spectra of C.I. Pigment Red 254 : (1) micro dispersion 5mg/100ml of toluene. (2) micro dispersion 5 mg/100 ml of hexane. (3) 0.1 % dispersion in polyethylene. (4) solution in N-methylpyrrolidone. (5) solution + micro dispersion in N-methylpyrrolidone. (6) precipitation in N-methylpyrrolidone with 50 % water.

Figure 3

See image above for figure legend.

Figure 4 Absorption spectra of C.I. Pigment Violet 19(PV Fast Red E3B) :
 (1) micro dispersion in toluene. (2) micro dispersion in hexane. (3) 0.1 % dispersion in polyethylene. (4) Solution in N-methylpyrrolidone. (5) precipitation in N-methylpyrrolidone with 50 % water. (6) precipitation in N-methylpyrrolidone with 75 % water. (7) precipitation in N-methylpyrrolidone with 85 % water.

Figure 4

See image above for figure legend.

Figure 5 Part crystal structure of C.I. Pigment Red 279

Figure 5

See image above for figure legend.