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# 20 Years of DPP Pigments – Future Perspectives

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**Summary:** Diketopyrrolopyrroles (DPP), one of the major innovations in Pigment Chemistry in the last 20 years, have developed to an important class of organic pigments. Chemical transformations have been the door opener for most of the innovations. The insoluble nature of the DPP Pigments allows for solid-state phenomena to be investigated. Crystal modifications and solid solution formation have enhanced the scope of DPP pigments. Specific elaborations of the DPP chemistry have lead to interesting developments also for electronic applications like color filters for liquid crystal displays or for the second generation display technologies like the OLED involving electro luminescent materials.

## Introduction

This paper will provide an overview on DPP (**d**iketo**p**yrrolo**p**yrrole) chemistry. In the last twenty years this new pigment class have been intensely studied by chemists at Ciba resulting in the commercialisation of many excellent products in various application areas. Milestones such as the finding of an efficient and general synthesis for DPPs and the elucidation of relationships between its structure and physical properties will be highlighted. Furthermore, the very interesting crystallographic properties of DPPs, including polymorphism and solid solutions, will be presented including two newly commercialised DPP pigments. Finally, factors controlling important properties in certain applications, such as particle size, heat stability and rheological behaviour, will be discussed and illustrated with typical examples within the DPP family.

## Background

The DPP chromophore was mentioned for the first time in the literature in 1974, when Farnum et al. [1] briefly reported on the attempted synthesis of 2-azetinones via a modified Reformatsky reaction.

However, the proposed reaction failed to produce the target unsaturated β-lactam **1** *(Scheme 1)*. Instead, the authors isolated in unpredictably varying yields of 5-20% the unsubstituted DPP derivative **2**, in addition to other by-products. This unexpected product was described as "a highly insoluble, brilliant red crystalline compound" with a melting point beyond 350°C. These

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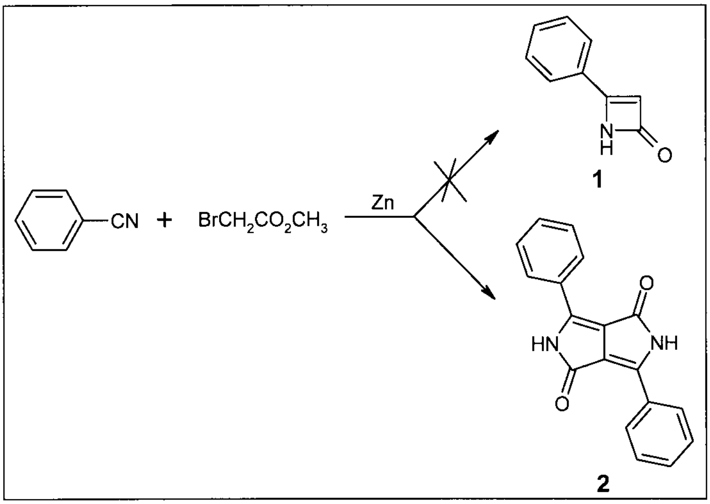
properties together with its structural features similar to many commonly known pigments, such as isoindolinones, indigos, and quinacridones, prompted chemists at Ciba in the early eighties to start an investigation of its performance as a pigment. The observed fastness properties were so encouraging that a series of new DPP derivatives were additionally synthesised for a rapid evaluation of the practical scope of these pigments and, at the same time, to seek appropriate patent protection [2]. A commercial synthesis was developed and the first industrial grade was commercialised in 1986.



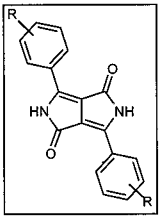
*Scheme 1*

## Structure and Physical Properties

Inspection of several DPPs with varying substituents in the phenyl moiety, led to a few generalisations regarding its properties. First of all, a broad spectrum of shades ranging from orange-yellow via blue-red to violet could be accomplished by simply exchanging the substituents at the *para-* and *meta*-position of the two phenyl rings attached to the DPP chromophore unit. The following table shows the absorption maxima of such compounds measured in solution together with the $\varepsilon_{max}$ values, as well as the absorption maxima in the solid state obtained by reflectance measurement on PVC-white reduction *(Table 1)*.

**Table 1. Influence of substituents on shade and absorption ($\lambda_{max}$) of diaryl-DPP’s**

| R | $\lambda_{max}$ (NMP) | $\varepsilon$ | Shade (PVC) |
|---|---|---|---|
| 3-$CF_3$ | 509 | ~21’500 | Yellowish Orange |
| 3-CN | 515 | ~20’500 | Yellowish Orange |
| 3-Cl | 512 | ~27’000 | Orange |
| 4-t-Bu | 511 | ~42’000 | Orange |
| H | 504 | ~33’000 | Yellowish Red |
| 4-Br | 515 | ~35’000 | Bluish Red |
| 4-Ph | 534 | | Bluish Red |
| 4-$NMe_2$ | 554 | ~81’500 | Violet-Blue |

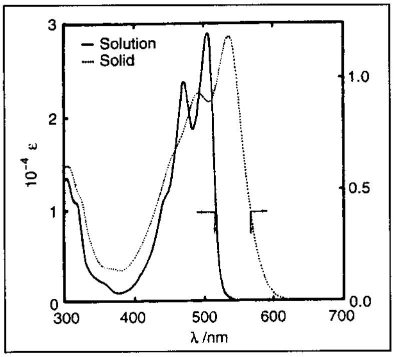


As with many other classes of pigments, all DPP compounds show a bathochromic shift of the maximum absorption in the solid state in comparison to maximum absorption in solution *(Scheme 2)*. This effect is due to strong intermolecular interactions in the crystal lattice such as hydrogen bonding, π-π- and van der Waals interaction. Detailed experimental [3] and theoretical [4] investigations on the influence of the intermolecular hydrogen bonding on the spectral properties of DPP in particular strongly indicate that this type of interaction is actually playing the most important role.

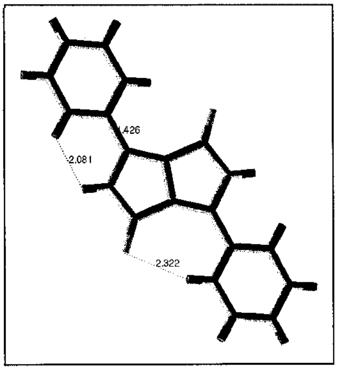
The solid state absorption maxima of DPP vary strongly depending on the nature and position of the substituent. In comparison to the unsubstituted DPP **2**, *meta*-substituted DPPs often show a hypsochromic shift and *para*-substituted DPP a bathochromic shift *(Table 1)*. The DPP pigments generally show bright shades, which are related to the high purity of the compounds and the sharp bands in solution as exemplified in *Scheme 2*. Most of the DPP pigments also display high colour strength, as shown by the relatively high $\varepsilon_{max}$ values of the solution spectra.

The average level of light and weather fastness of DPP pigments is outstanding. Despite their low molecular weights, the diaryl-1,4-diketo-pyrrolo-pyrroles are highly insoluble and remarkably resistant to migration, even when carrying otherwise solubilising alkyl substituents, such as the *tert*-butyl group.

These excellent properties may be attributed, above all, to the presence of strong intermolecular bonding forces in the pigment solid state, as was also corroborated by x-ray structure analyses of individual members of this class of pigments exemplified below for the unsubstituted DPP **2** *(Schemes 3 and 4)*.

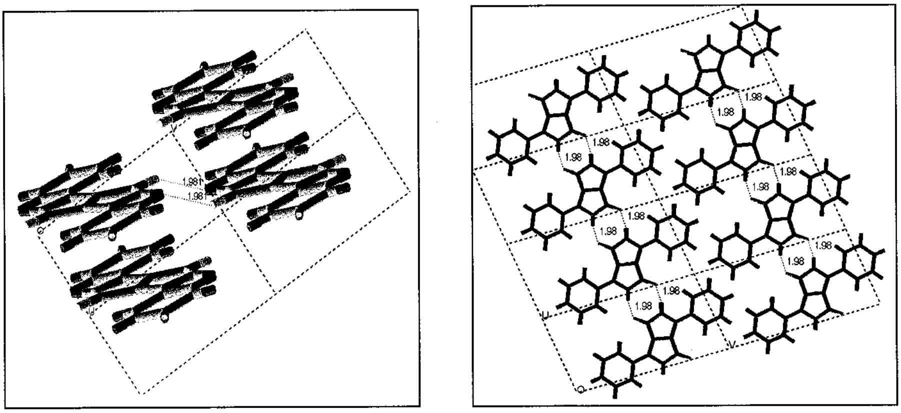


Scheme 2



Scheme 3

The DPP molecule is virtually planar, the two phenyl rings being twisted out of the pyrrolopyrrole plane by merely 7°. The distance between the two hydrogen atoms at $N_2$ and $C_6$ is 2.08Å, while that between the hydrogen atom at $C_{10}$ and $O_{11}$ is 2.32Å *(Scheme 3)*. For both cases, the sum of the corresponding van der Waals radii are substantially larger, 2.4Å and 2.6Å respectively, thus implying resonance interaction between the central unit and the phenyl rings. This appears to be confirmed by a $C_3$–$C_5$ bond length of 1.43Å, which is shorter, and hence possesses even more pronounced double bond character, than the bond (1.496Å) between the two aromatic rings of biphenyl. Such resonance interactions, amongst others, would explain the electronic influence of substituents on the earlier mentioned wavelength shifts of different DPP derivatives in solution *(*see *Table 1)*.

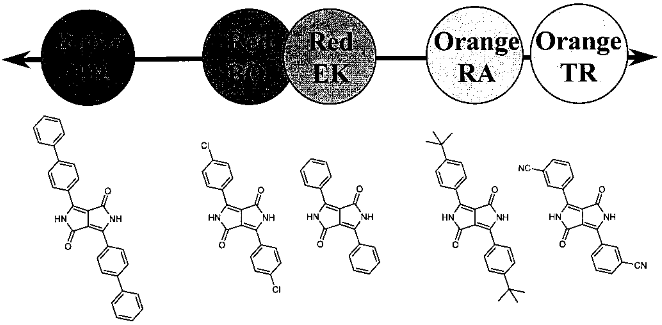


Scheme 4

The crystal packing along the a-axis is determined by π-π interactions between the layer of molecules. The interlayer distances (3.36Å - 3.54Å) are short enough to warrant significant overlap *(Scheme 4, left)*. Along the (a,b)-diagonal hydrogen bonding takes place. These bonds are formed between neighbouring lactam-N and carbonyl-O atoms leading to a one-dimensional tape-like structure *(Scheme 4, right)*. Intermolecular van der Waals contacts between the terminal phenyl groups determine the packing along the crystallographic c-axis.

## Extension of Colour Space - Chemical Structure

The fact, that the absorption spectra of different DPP pigments in the solid state is varying significantly, despite that they have a very similar absorption spectra in solution, has allowed for the development of many new DPP Pigments covering a large colour area (*Scheme 5)*.



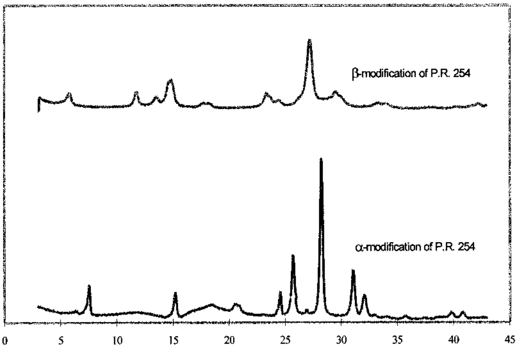
*Scheme 5*

## Crystal Modifications

As with many other classes of pigments, polymorphism is also observed within the DPP family. Such polymorphs have the same chemical constitution but differ in their crystal modification which is usually characterised by powder X-ray diffraction. Some pigment polymorphs are almost indistinguishable in appearance whereas others differ very widely in their colouristics and other properties. A typical example for the latter case is C.I. Pigment Red 254 (p-chloro DPP) where a new crystal modification (β-form) has recently been identified [5] *(Scheme 6)*. In paint applications this β-form is significantly more yellowish compared to the thermodynamically more stable α-form.

## Solid Solutions

Another crystallographic concept has proven to be very fruitful when applied to DPP chemistry: solid solutions [6]. Solid solutions can be obtained by combining two or more pigments of different constitutions by methods other than simple mechanical mixing. The resulting powder X-ray diffraction pattern is either the same as (or very similar to) that of one of the components, the so-called "host". In analogy to liquid solutions, one can therefore say that in solid solutions the "guest" molecules are dissolved into the crystal lattice of the "host". In some cases this can lead to a variation of the colouristic properties compared to a physical mixture of the individual pigments.

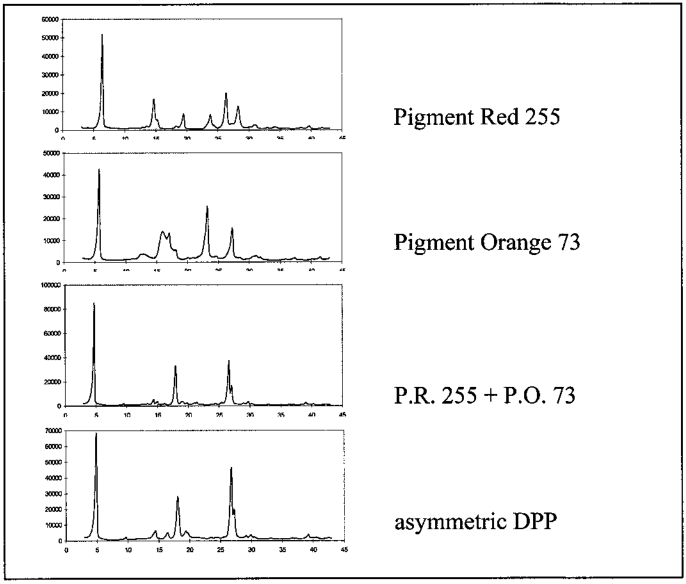


*Scheme 6*

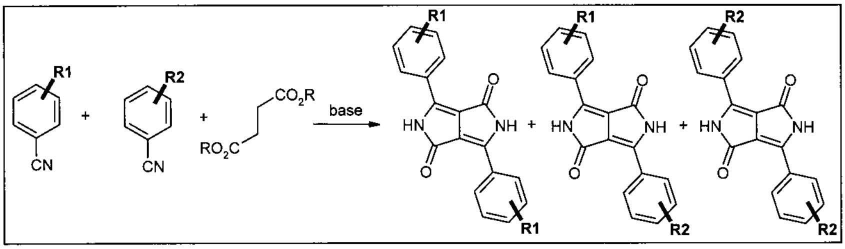
The same is true for mixed crystals. Here, specific compositions of two or more pigments lead to a new unique diffraction pattern, different from either of the component pigments. In this case, loose analogy can be drawn to the formation of azeotropes in the liquid state. An example, where the concept of mixed crystals is advantageously exploited to extend the colouristic scope of DPP chemistry, is shown below *(Scheme 7)*. It has been found that equimolar amounts of the unsubstituted C.I. Pigment Red 255 and the *tert*-butyl substituted DPP C.I. Pigment Orange 73 can be combined and form an entirely new crystal lattice [7]. Compared to the parent pigments which exhibit a pure red and orange shade in paints or plastics, the resulting pigment shows a significant bathochromic shift leading to a bluish red hue. Interestingly, the new crystal lattice formed by the combination of the two DPPs is nearly identical to that of the corresponding asymmetrically substituted DPP derivative.

The very special conditions in a solid solution are illustrated by the fact that equimolar amounts of the unsubstituted C.I. Pigment Red 255 and the p-chloro substituted C.I. Pigment Red 254 form a mixed crystal, which in contrast to the above mentioned example exhibit a hypsochromic shift.

Solid solution formation can also be achieved by a "mixed synthesis" approach [8]. Instead of using just one aromatic nitrile in the DPP synthesis, two (or more) nitriles are used leading to ternary mixtures as depicted in *Scheme 8*. These mixtures consist of the two symmetric DPPs and the corresponding asymmetric derivative. The ratio of the three products strongly depend on the reactivity of the nitriles and the specific reaction conditions.

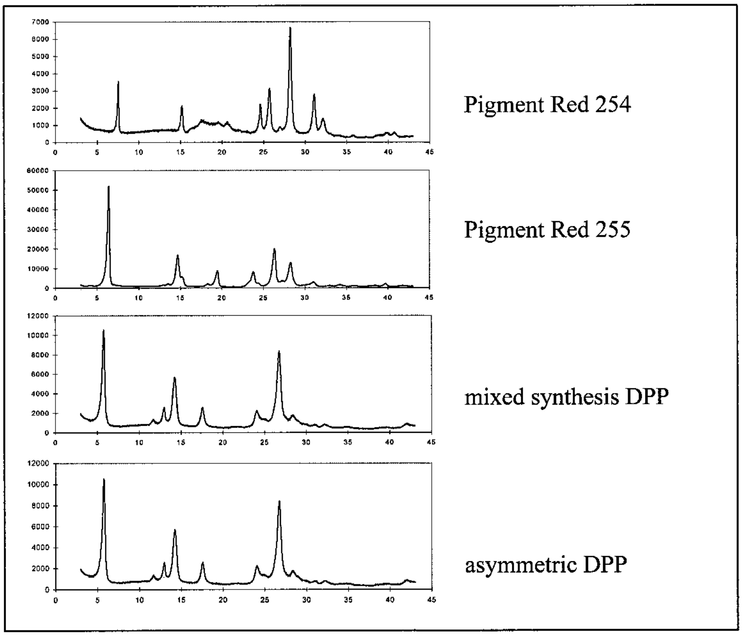


*Scheme 7*



*Scheme 8*

An interesting example is the use of benzonitrile and p-chlorobenzonitrile in the DPP synthesis. As in the example discussed above, the resulting solid solution shows a hypsochromic shift in comparison to the corresponding symmetric DPPs (C.I. Pigment Red 255 and 254) providing evidence that this concept is capable of expanding the colour range in both directions *(Scheme 9)*. Again, the resulting X-ray diffractogram (XRD) is very similar to that of the corresponding asymmetric DPP.



*Scheme 9*

## Extension of Colour Space – C.I. Pigment Orange 81

Through the combination of new DPP chemistry with manipulation of the solid state, a new very opaque and highly saturated orange DPP pigment has been developed and just introduced to the market. The new **C.I. Pigment Orange 81** combines a high opacity with an outstanding full shade colouristics. A comparison of the full shade chroma/hue as well as the opacity[1] is given in *Scheme 10*. The high opacity and the saturated shade consequentially renders the C.I. Pigment Orange 81 a very attractive value in use for coatings applications.

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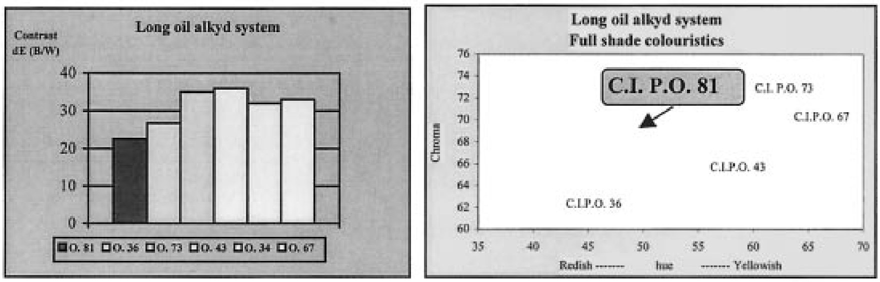
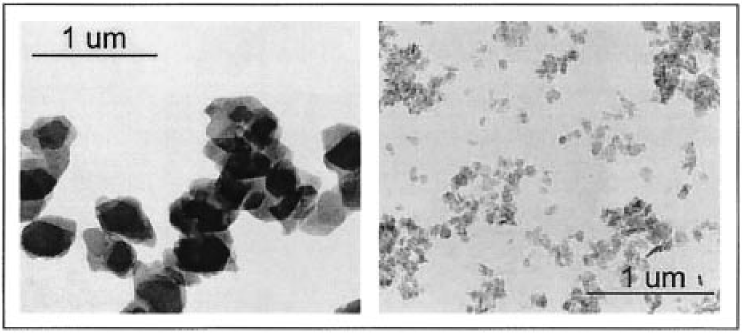
[1] Contrast dE (black over white) as a measure of the opacity – lower dE corresponds to higher opacity



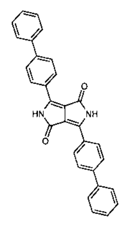
*Scheme 10*

## Particle Size and Distribution Control

The crystal size of a pigment as well as the particle size distribution have an important effect on the tinctorial strength, hiding power, durability and viscosity, and can also affect the shade. It is therefore essential to efficiently control these parameters in order to obtain a pigment with the desired properties. Small particle sized pigments can be achieved by finishing methods such as milling or kneading of large particle sized crude pigments or by a (more economic) direct pigmentary approach. For DPP pigments several methods have been developed in order to condition the pigment particles *in situ*. The most important approach is to vary the conditions during the DPP synthesis by changing solvents, temperature, time or pH. C.I. Pigment Red 254 gives an example, illustrating to what extent the particle size of a pigment can be influenced. Its opaque form is obtained under elevated temperature and basic conditions, whereas by applying lower temperatures and non-basic conditions a very transparent version is formed. Transmission electron micrographs (TEMs) of these two pigment morphologies are shown in *Scheme 11*.



*Scheme 11*



C.I. Pigment Red 264

The manipulation of the particle size towards very small particle size versions of DPP pigments opens up the possibilities of DPP pigments to be used in automotive metallic and effect colorations. One example is the C.I. Pigment Red 264.

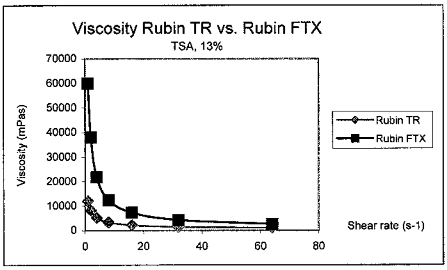
Again the combination of a specific chemistry (constitution) and solid-state manipulations (particle size, size distribution etc.), have lead to the development of a strong medium transparent DPP with outstanding fastness properties in both organic and aqueous binder systems (see further p. 14).

## Particle Surface Manipulations

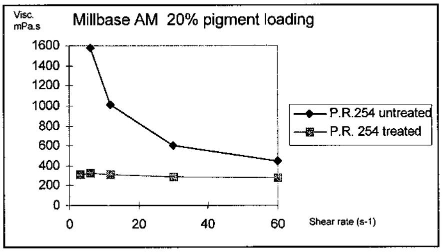
Since the performance of a pigment is not only given by the chemistry and the solid state properties of the pigment itself but to a large extent also by the application in which the pigment is being used, the interaction between a pigment and a specific application media is of utmost importance. This interaction, however, depends to a large part on the surface characteristics of the pigment. In order to fully exploit the potential of a pigment in a given application, the surface of the pigment has to be optimised. Many surface treatment procedures have been developed [9]. Most of them have in common that they promote the formation of an adsorbed layer. Due to the intrinsic differences in the properties of the various application media, e.g. paints or plastics, individual surface treatments of a given pigment have to be found for each application or polymer system.

In paint application there is, for ecological and economical reasons, a trend towards higher pigment loadings. This poses a problem to pigment manufacturers since higher pigment concentrations in the paint inevitably results in higher viscosity of the whole paint system leading to difficulties in processing and inferior properties of the final paint such as reduced gloss. The rheological properties of the pigment have therefore to be improved by an appropriate treatment of the pigment surface. The result of such a treatment on C.I. Pigment Red 254 is shown below *(Scheme 12)*.

Although the untreated P.R. 254 already exhibits a relatively good rheological behaviour, its viscosity in AM-paint under high pigment concentrations could still be strongly reduced by adsorbing a DPP derivative bearing sulfonic acid groups onto its surface [11].



*Scheme 12*



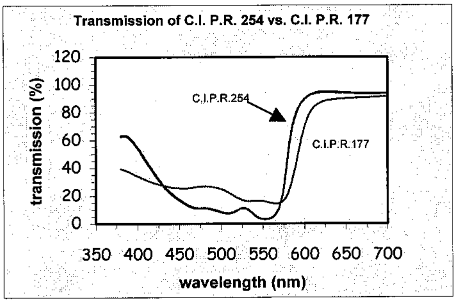
*Scheme 13*

Transparent pigments, having a much larger surface area than opaque pigments, show higher viscosities in different binder systems leading to poor formulations both from a technical as well as from an economical and ecological point of view. Specific modifications of the surface of C.I. Pigment Red 264 have now lead to a new rheology improved version of C.I. Pigment Red 264 with strongly improved viscosity compared to the base pigment (*Scheme 13*).

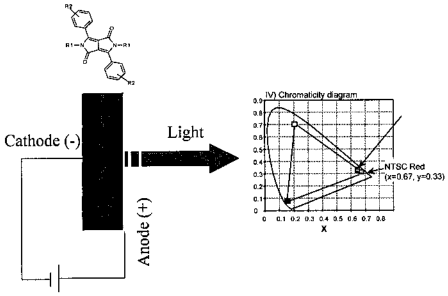
## New Applications

Utilisation of specific DPP chemistry to optimise and improve the physical and applicatory properties of DPP pigments has led to many new commercial products. Major objectives in the past have obviously been to find new and improved products for the coatings, inks and plastics industry. Some of the physical properties of DPP's, however, indicates, that the DPP structure could be of interest also for electronic applications. For example, the high chroma of the DPP pigments as illustrated by the steep transmission curve is not only an advantage for conventional applications but an essential requirement also for Colour Filter applications for LCD screens.

The red colour of the RGB system used for colour filter is not ideally positioned in the chromaticity diagram due to the spectral properties of the state of the art pigment. The steep transmission curve of many DPP pigments in combination with specific optimisations of the transparency, dispersibility and the rheological properties in the photopolymer have led to another new transparent DPP Pigment specifically developed for Colour Filter applications and now developing to the industry standard Red for Colour Filter applications (*Figure 14*).



*Scheme 14*



*Scheme 15*

Another area currently being actively researched in many academic and industrial laboratories is organic light emmitting diodes (OLED). This technology is being viewed as one of the technologies which might partly replace the LCD's. The fact, that specifically substituted DPP's show fluorescence in the solid state makes them interesting for electroluminescence applications. Work on DPP's as elctroluminescent materials has been reported both in the direction of small molecules ([12]) as well as on polymeric DPP ([13]). In both cases, promising chromaticity and efficiencies have been found *(Scheme 15).*

## Conclusion and Outlook

Pigment chemistry is generally regarded to be a rather mature science, where industrial interests are mainly focused on the improvement of known products and on the development of new products within the established pigment classes. However, occasionally novel classes of pigments are discovered leading to new opportunities in many application areas, thus revitalising the pigment industry. Elaboration of the DPP chemistry in many directions has resulted in many innovative products for different conventional applications. Specific properties of this interesting chromophore have lately also allowed to find new applications in the electronic applications like for colour filters for LC display or potentially as electroluminescent materials for OLED applications.

## References

[1] Farnum, D.G, Mehta, G., Moore, G.G.I., and Siegal, F.P., *Tetrahedron Lett.* **1974**, *29*, 2549-52.

[2] Iqbal, A. and Cassar, L. (Ciba-Geigy Ltd.), US Patent 4,415,685 (1983).

[3] Iqbal, A., Kirchmayr, R., Pfenninger, J., Rochat, A.C., and. Wallquist, O., *Bull. Soc. Chim. Belg.* **1988**, *97*, 615-643.

[4] Adashi, A. and Nakamura, S., *J. Phys. Chem.* **1994**, *98*, 1796-1801.

[5] Hao, Z., Schlöder, I., and Iqbal, A. (Ciba-Geigy Ltd.), EP 690,058 (1994).

[6] Whitaker, A. *J. Soc. Dyers Colour.* **1986**, *102*, 66.

[7] Hao, Z., Iqbal, A., Medinger, B., and Wallquist, O., (Ciba-Geigy Ltd.), EP 704,497 (1994).

[8] Iqbal, A., Pfenninger, J., Rochat, A.C., and Bäbler, F., (Ciba-Geigy Ltd.), EP 181,290 (1986).

[9] Hays, B.G., *Am. Ink Maker* **1984**, *30*, 270; *ibid.* **1990**, *10*, 13; *ibid.* **1990**, *11*, 28.

[10] Bugnon, Ph. and Herren, F., (Ciba-Geigy Ltd.), EP 466646 (1990).

[11] Jost, M., Iqbal, A. and Rochat, A., (Ciba-Geigy Ltd.), EP 224445 (1986).

[12] J. Otani et al., (Ciba Specialty Chemicals Inc.), EP 1087006 (2000).

[13] B. Tieke et.al., (Ciba Specialty Chemicals Inc.), EP 1078970 (2001).