Chimia 45 (1991) 304
© Schweiz. Chemiker-Verband; ISSN 0009–4293

Experiments in Color

Herbert W. Roesky*

Chemistry can be defined as the integrated study of the preparation, properties, and reactions of the chemical elements and their compounds and of the systems they form. Therefore, it is quite obvious that chemical demonstrations lead to fundamental knowledge in chemistry. Furthermore people are mainly attracted to chemistry by exciting experiments. However, more than 99% of all speakers in chemistry are not using chemical demonstrations. What are the reasons? From my experience with chemical demonstrations, it takes a long time to optimise an experiment and to be well prepared to ensure success. In the case one experiment fails to react in the proper way, people are enjoying and talking about this one more than about the rest of the well performed ones. In addition, the chemical community has not created awards to encourage scientists to do chemical demonstrations in the public.

In my opinion, the most important purpose of chemical demonstrations is to communicate with the audience and to appreciate the intellectual excitement and challenge of chemistry. I hope that the following 24 demonstrations will contribute to the bright colors of this symposium.

1. Oscillating colors
2. Ice cream and cherry juice
3. Dancing fireball
4. Barking dog
5. Disco colors
6. Bang box
7. Fractal structures
8. Artificial beer
9. Artificial softdrink
10. Chemiluminescence
11. A colored water test of Montreux water
12. Singlet oxygen
13. Start of a rocket
14. Two-color chemiluminescence
15. *Landolt* reaction
16. Red and blue ink
17. Three-color oscillating reaction
18. Love story
19. *Belousov* reaction
20. Chemical garden
21. Blue bottle
22. Colored structures in solution, self-organization
23. Silver mirror
24. Recycling

**Correspondence*: Prof. Dr. H.W. Roesky
Tammannstrasse 4
D–3400 Göttingen

Chimia 45 (1991) 304–307
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The Functional Dyes - Definition, Design, and Development

John Griffiths*

1. What Are Functional Dyes?

For more than a century, new dye research has been driven by the needs of the textile industry, but the 1970's saw a major change in this situation. For economic and (increasingly) ecological reasons a period of rationalisation of the dye making industries took place, which continues today, and the search for new textile dyes is now seen generally to be of low priority. However, from about the same period new technologies arose, stimulated by rapid advances in materials, microelectronics and lasers, and many of these were dependent on highly specialised dyes. The function of these dyes was more than merely aesthetic, and thus the term *functional dye* was coined to distinguish them from conventional colorants. They have presented the dye chemist with many new challenges, and research into these high technology materials continues apace. This intense interest is demonstrated by the success of the first ever international conference on functional dyes which was held in Osaka in 1989 and which attracted around 600 participants. A second is planned for 1992.

It could be argued that any commercial colorant is functional, otherwise it would necessarily be of no commercial interest. However, we can exclude dyes from our definition that are used solely for aesthetic coloration purposes, thus making the term *functional dye* more precise. Other designations encountered in connection with functional dyes are *speciality dyes* and *hi-tech dyes*, but these are much less specific terms. Although such terms embrace all functional dyes, not all speciality and high-technology dyes can be classed as functional dyes. *E.g.*, smoke dyes are clearly 'specialised', and thermal transfer dyes used in electronic photography are 'hi-tech'. However, neither are strictly speaking functional dyes as in both instances the dyes are used solely to impart colour. Many dyes show dual functionality, and *e.g.* fluorescent dyes as used in textiles and inks are simply 'specialised' colorants, but when used as laser dyes are then true 'functional' dyes.

It is also important to consider what we mean exactly by the word *dye* when we talk of these functional colorants, as the traditional concept of a dye can become severely stretched. *E.g.* functional IR dyes with practically no colour are known, and even colourless UV absorbing compounds used as light attentuators in high resolution microphotolithographic resist resins are popularly referred to as 'dyes'. For convenience and generality, therefore, a functional dye may be thought of as an organic molecule whose electronic structure is such that electromagnetic radiation can be absorbed readily by electronic excitation, and whose function is directly or indirectly dependent on the potential of the molecule for such excitation. It follows that the vast majority of functional dyes will contain conjugated π-electron systems.

We can classify functional dyes according to the molecular opto-electronic process that their function is dependent on. These possible mechanisms are summarised in the

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**Correspondence*: Dr. J. Griffiths
Department of Colour Chemistry
University of Leeds
Leeds LS2 9JT, U.K.

Chimia 45 (1991) 304
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Department of Colour Chemistry
University of Leeds
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Figure, together with some examples of their practical application.

2. The Design of Functional Dyes

As with conventional dyes, functional dyes can be dissected into the chromophoric (π-electron) system and various peripheral property-modifying groups. Selection of the latter is dictated by the desired physical properties of the dye, such as solubility, polymer compatibility, volatility, order parameter *etc.*, and is largely based on experience and empiricism. The chromophoric part generally requires a more theoretical approach, particularly if specific characteristics of the π-electron structure are required. As a first approach one can use molecular modelling to optimise geometry, and then follow this with an appropriate molecular orbital calculation. MO programs can range from the sophisticated (*e.g. ab initio*, CNDO/S, INDO/S) to the crude (PPP, *Hückel*), and the choice is very much in the hands of the individual. However, it should be said that the relatively simple *Pariser-Parr-Pople* (PPP) method is the most favoured, as not only can this be used with personal computers [1] [2], but it also produces surprisingly good results for a wide range of dye types. This success is due in no small part to the dependence of the method on semi-empirical parameterisation, whereby many of the approximations of the method (*e.g.* the neglect of sigma-pi interactions) and the uncertainties of electronic absorption spectral data (vibronic structure and band shapes, solvent effects *etc.*) can be compensated for by the parameters [3]. The all-valence-electron methods lack this versatility and often give apparently poorer absolute agreement between calculated spectra and experimental data. However, for the study of subtle structure-spectroscopic relationships, particularly where closely related series of chromophores are being compared, the more sophisticated methods may be more appropriate.

Apart from calculating the λ_{max} value of a dye structure, the PPP MO method can give other information that can be of direct help in the design of a functional dye. Some of the data available and the application areas where they can be applied are summarised in *Table 1*.

3. Recent Developments in Functional Dyes. Near-Infrared Dyes and Their Applications

It would be impossible in a single lecture to review the innumerable developments of the last few years in the field of functional dyes, so I shall confine my overview to that interesting sub-class, the IR dyes. Not only are these informative because of the synthetic challenge that they offer, but they are pertinent because of their major importance

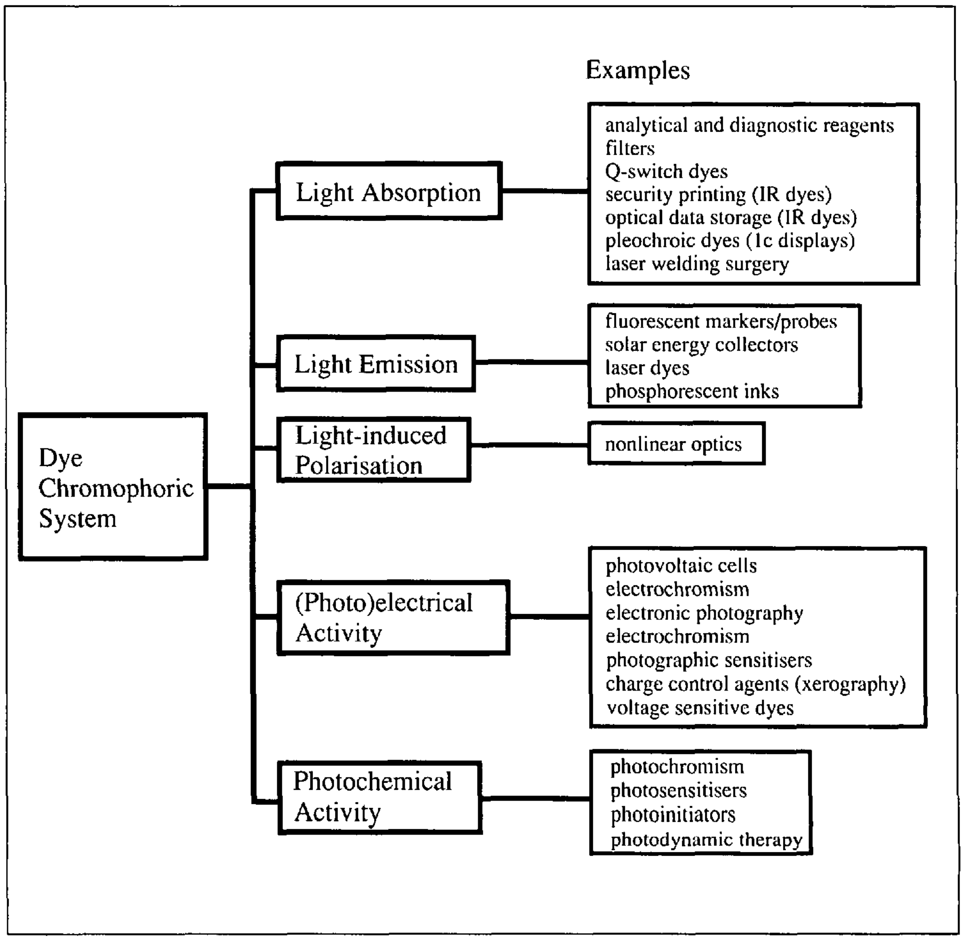


Figure. *Mechanisms for the action of functional dyes*

Table 1. *Data Available from PPP MO Calculations of Value in Functional Dye Design*

Area of application	Calculated data
Ground state	Dipole moment; electron density distribution; total π-energy
Light absorption	λ_{max}; oscillator strength; transition moment direction; bandwidths
Light emission	*Stoke*'s shifts; E_{ST} values
Polarisation	Hyperpolarisabilities; excited-state dipole moments
(Photo)electrical	Ionisation potential; electron affinity; excited-state electron densities and dipole moments

Table 2. *Applications of IR Dyes*

Functional mechanism	Applications
Light absorption	Camouflage materials; security printing; medical diagnostics; protective filters; horticultural plastics; Q-switch dyes; optical data recording based on the photothermal effect; laser welding surgery
Light emission	fluorescent markers and probes; laser dyes
Light-induced polarisation	NLO materials
Photoelectrical effects	silver halide photographic sensitisers for IR photography; electrophotography, laser printers etc.; photopolymerisation initiators; charge control agents in xerography; voltage-sensitive dyes (biomedical probes)
Photochemical activity	photochromic materials; photodynamic therapy

at the present time. This importance is reflected in the recent publication of two new books dealing exclusively with IR dyes [4] [5], as well as the many review articles appearing in other texts.

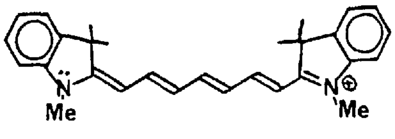
Firstly let us consider the main applications of IR dyes, which are summarised in *Table 2*.

The growth in importance of the IR functional dyes was initiated by the development of lasers, particularly the inexpensive and robust diode lasers emitting near 820 nm. Such light sources when of sufficient power offer a means of recording information by photo-thermal effects, and IR dyes are required to absorb the radiation and to convert this to heat. Lower intensity lasers also mean improved instrumentation, for reading recorded data, and as light sources in various detector systems. Cheap detectors of IR radiation are also available, and so such areas as security printing, and spectrophotometric-based diagnostics have become of significance. The diode lasers also permit other phenomena to be used in imaging systems and imaging processes (*e.g.* laser printers, photopolymerisation, thermal transfer), and for all these applications a suitable IR dye intermediary is needed. In the biomedical area IR fluorescent probes are of great interest because they permit minimisation of background effects. In the photodynamic therapeutic treatment of cancer, IR sensitising dyes are attracting much attention, again because their use minimises the absorption of light by blood and tissue so enables more effective use of the radiation. IR lasers (*e.g.* YAG) are used in transplant surgery for tissue welding, and it has been found that IR dyes can greatly increase the effectiveness of the technique [6].

It should be mentioned that shorter wavelength diode lasers are being developed (*e.g.* emission wavelength *ca.* 680 nm), which will see a shift in interest away from IR dyes to more conventional chromophores. However, for many applications there will always be advantages in having a dye with little colour.

In addition to having an intense absorption band in the near IR (usually near 820 nm), functional IR dyes often have to satisfy many other requirements. In optical data recording materials, which depend on the heating effect of a dye after it absorbs IR radiation, the heat causes sublimation or ablation of the dye layer with a consequent decrease in the reflectivity of the resultant 'pit'. Ideally, the dyes should form layers with good reflectivity, and few satisfy this need. Suitable materials are certain cyanine dyes, *e.g.* **1**.

For some applications, *e.g.* security printing, the dye must have very good photostability. Here the metal complex IR dyes seem to be the best, *e.g.* phthalocyanine and naphthalocyanine complexes and the Ni dithiolenes (*e.g.* **2**). Commercial materials based on these are now available, *e.g.* the Projet dyes of I.C.I.



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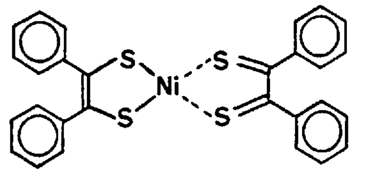


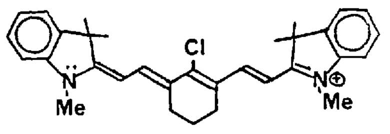
2

For many applications, the IR dye must have good solubility and compatibility with a host material, be it a plastic, liquid crystal, or binder, and it is here that problems are often encountered. Many IR absorbing chromophores are of relatively high molecular weight, and consequently have poor solubility properties. There is particular incentive, therefore, for the chemist to design new IR systems with a small molecular size, and this presents a considerable synthetic challenge.

Some Aspects of Infrared Dye Design

For dye chromophores that can be classified loosely as 'cyanine-type' or 'donor-acceptor' in character there are three simple ways in which the λ_{max} value can be shifted into the near IR:
a) the length of the conjugation pathway between the terminal groups can be increased; *b*) electronically perturbing substituents can be attached to strategic parts of the chromophore; *c*) the effective strength of the electron donor (and in the case of donor-acceptor chromophores, the electron acceptor) terminal groups can be increased. The system **1** can be used to demonstrate some of these effects, and *e.g.* the dye **3** with the same conjugation length as **1** shows a λ_{max} at 782 nm in dichloromethane in comparison with *ca.* 740 nm for **1**. The additional shift is due to the greater rigidity of **3** and also the addition of an electron withdrawing chlorine atom to what is effectively an 'unstarred' position, as predicted by perturbational MO theory [7].

The electronic symmetry of **1** and **3** favours a large 'vinylene shift' in these systems, but this renders the dyes cationic and can cause solubility difficulties. It is possible to retain and even enhance the large shift after converting the dye to a neutral molecule by replacing one of the terminal indoline residues with a powerful neutral electron acceptor group. This is exemplified with **4**, which is electrically neutral, has good solubility in organic solvents, and yet has a λ_{max} at 860 nm in dichloromethane.



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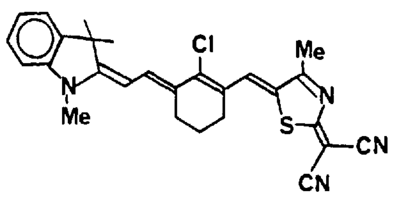
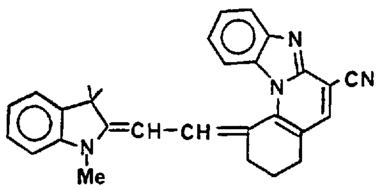


4

The dye **5** is interesting as it is a version of **4** with a benzimidazole electron acceptor terminus, but which has undergone intramolecular cyclisation. The weak acceptor residue makes this compound violet with λ_{max} = 577 nm in dichloromethane. However, addition of acid produces **6**, which now has cyanine character, and absorbs at 760 nm. This is a rare example of an IR dye pH indicator [8].



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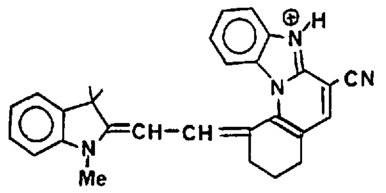
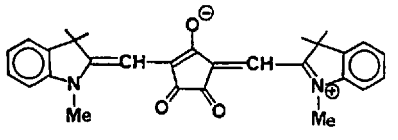


6

Croconium and squarylium dyes provide a useful means of enhancing bathochromic shifts whilst retaining a small molecular size. *Eg.*, dye **7** absorbs at 770 nm in dichloromethane, and yet it contains one fewer vinylene group than **1** or **3**. This can be explained in simple PMO terms [7], since in **7** there is an electron donor $-O^-$ group at a starred position and two (bridged) carbonyl groups at unstarred positions. Similar though less dramatic shifts are observed with the squarylium dyes. The powerful bathochromic effect of the croconium system can be seen with the bis-aryl derivative **8**, with λ_{max} = 822 nm (ε = 214 000 l· mol^{-1} cm^{-1}) in dichloromethane. The analogous squarylium dye absorbs at 648 nm. It is interesting to note that synthetically the hydroxyl group in **8** is an important prerequisite for the preparation of the dye (unlike corresponding squarylium systems), and if it is not present, croconic acid will not condense with the *N*,*N*-dialkylarylamine [9].



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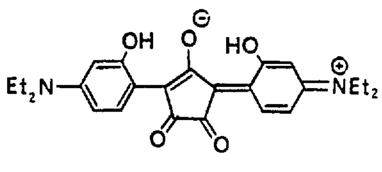
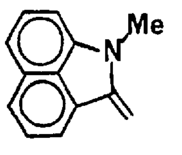


8

Modification of the electron donor terminal residues in systems such as **1** or **3** also provides a powerful means of achieving large bathochromic shifts. Particularly effective donors are **9–11**, and their spectroscopic value can be seen from dye **12**, which absorbs at 760 nm and yet has two fewer vinylene groups in the conjugated chain than dye **1**. The analogous dye with terminal groups **11** absorbs at 818 nm [10]. An extreme example to show how these various effects can be combined is dye **13** which absorbs at 1014 nm with high intensity and yet has only three vinyl groups in the conjugating bridge [9]. To obtain similar absorption in a conventional cyanine dye, five or six vinyl groups would be required, and the absorption band would be very broad and of low extinction coefficient due to conformational mobility.



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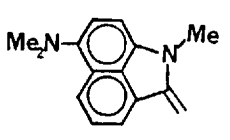

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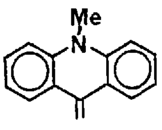

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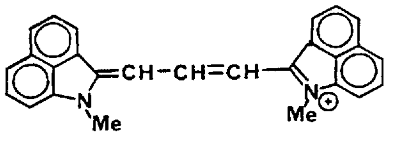

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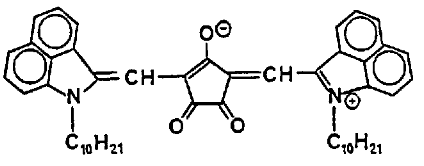
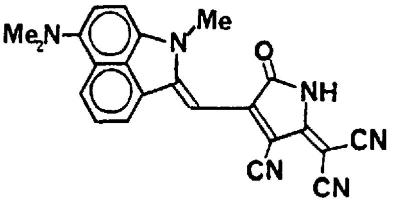


13

Short chain IR dyes can sometimes be achieved by combining a powerful electron donor, such as **9–11**, with a particularly strong electron acceptor moiety, as exemplified by dye **14** (λ_{max} 780 nm) [10].



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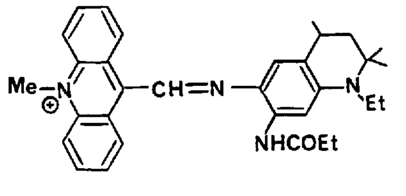

15

A new class of useful IR dyes, exemplified by **15**, makes combined use of *a*) a powerful electron donor residue; *b*) the large vinylene shift of a cationic cyanine-type chromophore, and *c*) the perturbing effect of aza substitution at an 'unstarred' position. The resultant dyes show intense near IR absorption combined with good solubility properties associated with the relatively low molecular weight. Dye **15** thus shows λ_{max} = 823 nm (ε = 73 400 l· mol^{-1} cm^{-1}) in dichloromethane [10].

I would like to acknowledge the invaluable collaboration of *S.N. Corns*, *L. Cheng*, *Z. Li*, *K.A. Bello*, and *V. Millar*, and the financial support of the *SERC*.

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Chimia 45 (1991) 307–310
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Porphyrins, Phthalocyanines, and Naphthalocyanines for Various Processes of Visible Light Driven Conversion Processes

Dieter Wöhrle*

Dedicated to Prof. Dr. *M. Hanack* on the occasion of his 60th birthday

Abstract. Phthalocyanines, naphthalocyanines, tetraphenylporphyrins, and perylenebis(dicarboximides) are interesting compounds for the conversion of visible light. For photon-induced reactions in solution or in thin films of photoelectrochemical or photovoltaic cells some examples are given. It is shown that the position of energy levels or energy bands is a prerequisite for these visible-light-driven processes.

1. Introduction

The high amount of colored organic compounds is a powerful tool to design materials for processes driven by visible light (solar radiation, artificial light) with good efficiency [1–14]. In solutions containing sensitizers – homogeneously dissolved or heterogeneously distributed –, acceptors and donors, charge separation or energy transfer within the very short excitation time of the sensitizer occurs [1][4–8]. Research is focussed to obtain energy-rich fuels such as hydrogen from water or to perform other processes. Irradiation of an organic semiconductor electrode in contact with a liquid phase re-

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**Correspondence*: Prof. Dr. D. Wöhrle
Institut für Organische und Makromolekulare Chemie
Universität Bremen
Leobener Str. NW II
D-2800 Bremen 33