

# Olympian colour chemistry

The performance of photochromic dyes has much in common with that of top-class athletes, in terms of their endurance, speed, strength and teamwork, writes Andy Towns

The summer of 2012 should be a momentous one for the UK whatever the weather. Years of planning will see the focus of the sporting world centre on London and the UK for a few weeks as sportsmen and sportswomen compete in the spirit of the Olympian motto *Citius, Altius, Fortius* to prove they are the fastest,

highest and strongest. This summer will also see 'athletes' of another kind perform in the sunshine on an altogether smaller scale: photochromic dyes that must demonstrate world-class speed, strength, endurance and teamwork. Like their human counterparts, they have to be given the right environment to coax the best out of them – and can even benefit

from performance-enhancing substances! Photochromic colourants are organic compounds that change colour reversibly on exposure to light. In doing so, they must perform an acrobatic change in molecular structure. The light-induced breaking, bending and twisting has been exploited in a commercially successful way over the last

couple of decades. Ophthalmic lenses for spectacles that darken reversibly in sunlight account for most commercial photochromic dyes today. However, photochromism is employed with plastics and surface coatings to create products with striking colour change properties, for example, from toys to clothing and cosmetics to safety visors. They have

also attracted the attention of the security industry, to combat fraud and counterfeiting of passports, travel tickets, and even currency.

For industrially important dyes, the change is between a colourless and a coloured state. The two dominant commercial types, spirooxazines and naphthopyrans, produce colours that span the visible spectrum. Vivimed Labs Europe in Huddersfield, UK, for example, manufactures a *Reversacol* range of both kinds that run the gamut from yellow and orange, to red and purple, through to blue and even green. The appearance of colour with these compounds is usually driven by ultraviolet (UV) light. When the stimulus is removed, they fade back, eventually to their original colourless states. Unfiltered sunlight produces pronounced photochromism because it has a significant UV component. Artificial light sources, such as compact fluorescent lamps and tungsten filament bulbs, are much less effective. Consequently, the dyes colour up well in daylight, but much less so indoors or behind glass, which tends to filter out the wavelengths

**In brief**

- Photochromic colourants are organic compounds that change colour reversibly on exposure to UV light
- The main commercial use is in lenses that darken in sunlight, but the technology is also used to create plastics with striking colour-change properties
- A reversible light-driven reaction, involving coloured and colourless dye forms, is responsible for these colour-change effects
- Achieving the desired photochromic effect depends on balancing the various properties of

needed for activation.

The reverse reaction – from coloured to colourless – is thermally driven, the colourants being said to exhibit T-type photochromism. A key property of this phenomenon is its reversible nature. The different forms of the dyes are in dynamic equilibrium, constantly switching between coloured and colourless isomers. Figure 1 shows the interconversion between colourless ring-closed and coloured ring-opened isomers that occurs with spirooxazines and naphthopyrans. Ring-closed forms consist of two halves that are perpendicular to each other, joined by a central carbon atom. The relatively small  $\pi$ -systems of these moieties are kept separate by this atom so that molecules absorb only in the UV region and are therefore colourless. On absorption of UV light, the bond between the central carbon atom and the adjacent oxygen atom breaks. Following this ring-opening,

molecular twisting and bending via intermediates gives a planar species with an extended conjugated  $\pi$ -system that leads to absorption moving into the visible light region and the generation of colour.

The higher the intensity of UV light, the greater will be the proportion of dye in its coloured state. As an example, irradiating oxazine-based systems with UV favours ring opening of the colourless spiro form, shifting the equilibrium towards the coloured photomercyanine isomers. Removal of the light source has the opposite effect: the concentration of the colourless ring-closed form increases, which is seen as fading. If the illumination level is constant, the system will settle into a 'photostationary' state in which the isomer concentrations hold steady. Thermodynamics dictates the intensity of colour; however, as the equilibrium reached is a dynamic one, dye molecules continue to swap between their colourless and coloured forms, despite their concentrations remaining essentially unchanged.

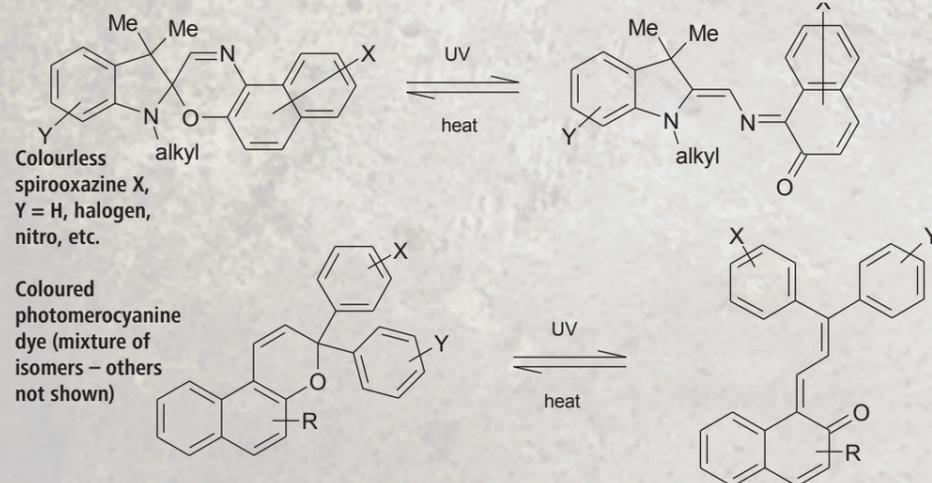
The ideal photochromic athlete for use in lenses would at first glance be a sprinter. Dyes not only need great activation speed, colouring up rapidly on exposure to strong light, but also a very quick fade that races back to colourless as soon as light levels lower to prevent impairment of vision. However, colourants face additional demands. Their ring-opened isomers must show great strength in terms of absorption, because even when activated by brilliant sunshine, only a small proportion of dye is not in the colourless ring-closed form. While they have to reach the heights of intense colouration, photochromic colourants should also possess the stamina to produce the same effect time and again on repeated exposure to light.



Before activation, above, and below, after



Figure 1 Photochromism of important industrial dye types



Just as no sports person can simultaneously be an Olympian sprinter, weightlifter and marathon runner, the design of photochromic dyes involves compromise. Typically, a balance must be struck between rapid speed of fade and high colour strength, since the two properties tend to be mutually exclusive. Making structural changes in order to increase fade rate, often referred to as 'half-life', which is the time taken for absorbance to halve, frequently results in a loss in strength. The chemist must find the middle ground where sufficient depth of shade is achieved while ensuring thermal bleaching is acceptably fast. For lenses, half-lives of the order of tens of seconds are practical.

So that dyes can perform to their potential, they need the right arena. The gymnastic changes in shape and structure associated with their photochromic behaviour require a suitable microenvironment. Colourants must also be dissolved, not dispersed, in the medium in which they are used because they do not exhibit useful photochromism as solids.

Dyes tend to perform best in plastics with relatively flexible chains and low glass transition temperatures, like polyolefins and plasticised polyvinyls. In polymers such as poly(styrene-acrylonitriles), where the matrix is too rigid or affords insufficient free volume, changes to molecular shape are restricted so that only weak photochromic effects will be observed at best. One solution is to apply colourant in microencapsulated form. Provided precautions are taken not to rupture these tiny pigment particles when they are incorporated into polymers, dye performance is unaffected by the choice of plastic. Striking photochromic transitions can be obtained that would not otherwise have been possible.

Just as many athletes struggle under very hot conditions, the performance of photochromic dyes suffers when the temperature rises. Because ring-closure is driven thermally, a temperature increase promotes the formation of the colourless isomer. Dyes that colour up intensely in the mountain sun of the ski slope therefore do so less effectively in hot climates. Naphthopyrans are less susceptible to this temperature dependence than spirooxazines, which is one reason for their commercial dominance.

Another basis for their importance is endurance. When used in ophthalmic lens applications, naphthopyrans are expected to withstand photochemical attack in

both coloured and colourless forms for at least two years so that the wearer does not readily notice the steady loss in performance. In addition, the dyes must resist the tendency to 'fatigue'. This relates to the occurrence of side-reactions that compete with photo-isomerisation during activation. They cause dye to be irreversibly converted to non-photochromic molecules, leading to a decrease in colour intensity on repeated activation. To get to the top and stay there, sportspeople have to be focused on what they do. Photochromic dyes must also be selective in their behaviour. Because of the repeated ring-opening and closing on prolonged exposure, fatigue will be pronounced if side-reactions make up anything other than a tiny proportion of the transformations between the different dye forms.

Rate constants for side-reactions for spirooxazines and naphthopyrans are small, but even here the constant photo-isomerisation that occurs on exposure to light means that formation of non-photochromic byproducts can soon build up over time reducing their useful lifetime. Fortunately, performance-enhancing chemicals can be employed – perfectly legally – to improve their stamina. Several types of additives are routinely exploited, including hindered amine light stabilisers that mop up damaging free radicals and triplet state quenchers that help prevent side reactions. UV absorbers can also usefully shield dyes from destructive radiation.

Unfortunately, just as substances used illicitly by athletes may produce nasty side effects, additives intended to stabilise photochromic dyes can also have undesired consequences, such as altering photocolouration kinetics or generating residual colour in the non-activated state. Absorbers must be chosen carefully so they do not soak up the wavelengths of UV light needed to activate the dye. However, when formulated judiciously, cocktails of additives have been reported to extend the lifetime of photochromic effects by an order of magnitude – without attracting the possibility of a ban! Despite this, current technology is not robust enough for applications that require long-term regular and prolonged exposure to strong sunlight, such as smart windows.

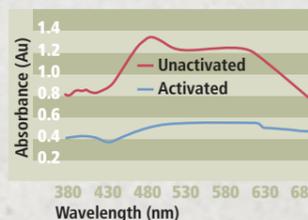
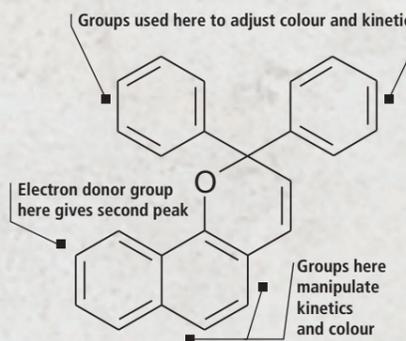
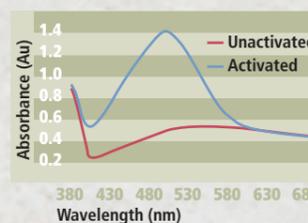
As well as the qualities discussed above, photochromic dyes have to work well as a team. The most commercially important lens shades are neutral colours – greys and browns – which call for the use of dye

**P-type photochromism**

Great strides have been made over the past couple of decades with commercial T-type photochromic dyes in terms of their colour palette, kinetic control and robustness. However, because they fade thermally, they're not suited to some keenly researched uses. These high-tech applications – for example, as optical switches or in data storage – rely on P-type photochromism instead. This phenomenon involves light-driven switching in each direction so that, once activated by UV, a dye remains coloured until it is switched back to its colourless state with visible light rather than by thermal fading.

The dihetarylethene class is one of the most extensively explored classes of P-type photochromic compounds and has been targeted as a source of light-actuated elements in nanotechnology. Compounds from this class switch between coloured and colourless forms even in solid form. The transformation in structure that occurs upon photo-isomerisation alters the dimensions of crystals of these derivatives. Although the changes are small, they have been used to striking effect – dihetarylethene crystals have been observed to bend and then straighten under the influence of light to kick nearby particles away like miniature footballs.

Figure 2 A strategy for creating neutral coloured photochromic dyes



Addition of electron donor group

mixtures. However, when photochromism is involved, formulating blends does not simply involve combining colours in the right proportions to achieve the desired shade. The photochromic properties of the individual components of a mixture must also be closely matched. If rates of activation and half-lives differ too much between dyes, then the hue of the mixture will vary as it colours and fades. To be commercially acceptable, the dyes must activate as well as fade in unison so that the mixture stays on tone.

Team members should also have the same high stamina levels. If components fatigue at different rates, then activated colour will change over the long term. Additionally, the responses of the dyes to changes in environment, such as temperature, must be similar.

Assembling a successful team is no easy task, especially when up to six dyes may be required. One strategy is to formulate mixtures from a single class of dye where possible. Another commercially successful approach has been to develop dyes that are intrinsically neutral in colour. This has been done by incorporating structural features into a dye that convert it from a bright colourant with just a single peak in its visible absorption spectrum when activated to one that has a more complex absorption curve. For example, an electron donor function in the right position will furnish a colourant with more than one broad absorption maximum of similar intensity, conferring on it a duller, more neutral appearance (Figure 2).

Vivimed researchers have designed and marketed single-molecule greys and browns of this kind for use either as self-shades or with just one or two shading components.

The time and effort devoted to nurturing the technologies based on T-type photochromic materials has paid off. Millions of people around the globe routinely take advantage of the acrobatic talents of these dyes.

Come the summer sunshine, while Olympians are performing on track and field, a glance around the stadium crowd will reveal other teams of athletes at work, showing off their speed, strength and stamina, albeit on a much smaller scale! ●

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