Additions and corrections

Unusual UV (λ_{exc} = 303 nm) and visible (λ_{exc} = 574 nm) activated photochromism of an indeno-fused naphthopyran

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In 2003 we reported[1] that a chromene-type photochromic compound, benzo[3,4]fluoreno[2,1-*b*]pyran-13-ol,3,13-dihydro-3,3-bis(4-methoxyphenyl)-6,11,13-trimethyl (BFP), compared with other chromenes, exhibited peculiar properties, which were also potentially interesting for applications. This photochromic system exhibited a red shift of the absorption spectra of both the coloured and colourless forms, as well as thermochromism and positive solvatochromism of the coloured form. We have also reported that photocolouration could be activated by two distinct stimulations: UV-irradiation (λ_{exc} = 303 nm), as normally used for photochromic chromene activation, and "monochromatic" visible light (λ_{exc} = 574 nm) activation of the thermally equilibrated solution. Photocolouration by visible light could be reasonably explained since two spectrally distinguishable coloured species were detected: one of them, P (λ_{max} = 582 nm), is photochemically produced by UV irradiation of the colourless form, while the other, T (λ_{max} = 557 nm), is present in thermal equilibrium with the closed form. This latter species was considered to be responsible for photocolouration under visible light irradiation, since it could be continuously supplied by the BFP ↔ T thermo-equilibrium. The peculiarity of this system was that it seemed to exhibit a doubly activated photochromism: a normal one, excited by UV light, and an anomalous one, promoted by irradiation with visible light.

Since this property appeared quite unusual and worthy of further investigation, particularly in view of possible technological applications, one of us (F. B.) wanted to gain more insights into this aspect and therefore reproduced the experiments (which had been previously performed in the laboratory at Perugia) at the PPG Industries Laboratories by using a slightly different experimental set-up. In particular, for activation, interference filters were used instead of the monochromator used in the previously performed experiments. However, the re-activation was unsuccessful.

This made us all suspicious about the previous findings and we wanted to shed light on the BFP photobehaviour and ascertain whether it was real or "virtual". The only possibility that reactivation was not due to visible light absorption was that a higher-order UV beam was passing through the monochromator to activate the colourless form. To verify this hypothesis, a UV cut-on filter (Oriel CS 51292), which excludes all light at $\lambda < 475$ nm, was positioned between the fibre optic used for irradiation and the cryostat containing the sample. No colour reactivation was observed after the same irradiation time with 574 nm light. This confirmed our suspicion that the visible light used in the previous experiments was not really "monochromatic". In the absence of the sample, we determined the output from the monochromator when it was set at 574 nm: in addition to the primary wavelength, λ_1 = 574 nm, a maximum of consistent intensity appeared at λ_2 = 287 nm ($\lambda_2 = 1/2\ \lambda_1$). This light could well be responsible for the colouration, considering that the photoprocess is very efficient and the absorbance of BFP is high at this irradiation wavelength. These experimental findings eliminate any ambiguities about the photobehaviour of BFP, which can still be considered as a very interesting photochromic, thermochromic and solvatochromic system, but not as unusual as we previously thought.

In Fig. 1 the scheme that we previously presented[1] is shown with the necessary correction: the photochemical path T → P, which has been proven not to be real, has been removed.

However, problems of wider significance arise from these experiments. Have other systems been photochemically investigated using the visible light output from a monochromator? What could be the effect of spurious light output on quantum yield determinations? These questions are here asked based on our experience, but they obviously have implications as well for what the literature reports as facts. Of course, these concerns refer to molecular species that have an absorption spectrum that extends over a broad wavelength range and when excitation is performed using $\lambda > 450$ nm. When shorter wavelengths are used for irradiation no problem should arise due to the air and solvent inner filter effect on higher harmonics of the grating. Typically, in photochromic systems, photocolouration is studied under UV irradiation, whereas photobleaching is obviously studied using visible light. Therefore, we have reviewed some results that we obtained previously on the photobleaching quantum yields of photochromic compounds.[2–7] Our conclusion is that our published results are all reliable, since in most cases[2–5,7] excitation with visible light was performed by using wavelengths in the 400–436 nm range; in a few other cases[6,7] excitation was carried out at longer wavelengths but the solvent itself (toluene) worked as an inner filter for the higher harmonics.

All the aforementioned observations give us confidence in the previously reported results, but also show that an awareness of possibly misleading experimental findings is necessary to arrive at a correct interpretation. Considering that most coloured substances also absorb in the UV region, it can be concluded that literature results on chemical processes activated by visible light should be cautiously considered since the effect of spurious light can affect their reliability. This incon-

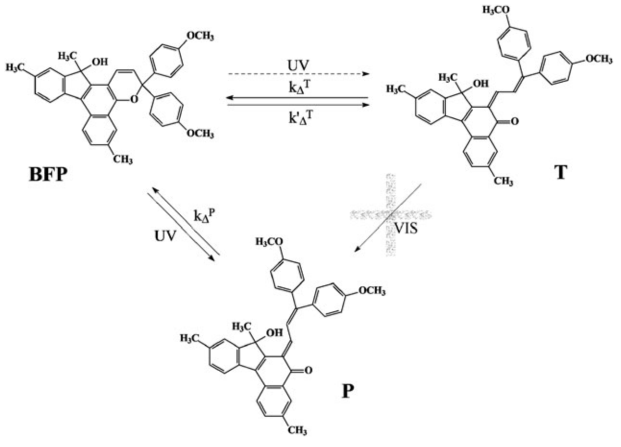

Fig. 1 Corrected reaction mechanism: the T → P photochemical path has been removed from the previously proposed scheme.

venience can be bypassed if cut-on filters are positioned at the exit of the monochromator.

References

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The unusual solid state structure of heroin hydrochloride monohydrate and its selective detection using NQR spectroscopy

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Eqn. (2) in this article should read

$$\nu_{\pm} = \frac{3}{4}\left(\frac{e^2qQ}{h}\right)\left(1 \pm \frac{\eta}{3}\right)$$

All calculations of quadrupole parameters have been performed with this equation.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.
Additions and corrections can be viewed online by accessing the original article to which they apply.