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

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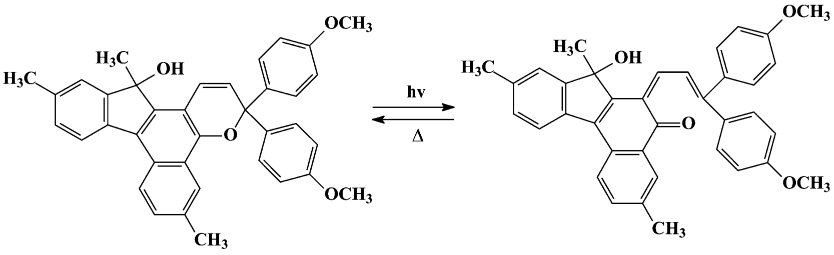
In this work a completely novel photochromic mechanism exhibited by an indeno-fused naphthopyran (chromene) is presented. The studied molecule is the first case of a chromene-type compound exhibiting both photochromism and thermochromism. These phenomena were investigated in ethanol. Thermochromism was detected by monitoring absorption spectra in the 285–320 K temperature range: the enthalpy of the thermocoloration reaction was determined ($\Delta H = 25$ kJ mol^{-1}) and the equilibrium constant was estimated ($K_{eq} \approx 10^{-3}$). For the photochemical investigation, carried out in the 200–270 K temperature range, continuous monochromatic light was used for excitation. The photocoloration was observed under two distinct stimulations: UV-irradiation ($\lambda_{exc} = 303$ nm), which is normally used for photochromic chromene activation, and visible-irradiation ($\lambda_{exc} = 574$ nm) of the thermally equilibrated solution. Two coloured species are involved in the photochemical and thermal processes. One of them, P, is photochemically produced by UV irradiation of the colourless form, while the other, T, is present in thermal equilibrium with the closed form. When the thermally equilibrated solution is irradiated with visible light, T is converted to P. This system not only results in a cyclic on–off chromogenic device, which can be switched-on by UV radiation, but it also exhibits on–off functionality using lower energy visible light. Such behaviour makes this photochromic system exceptionally efficient upon exposure to sunlight.

Introduction

The molecule under investigation, 3,3-bis(4-methoxyphenyl)-6,11,13-trimethyl-3,13-dihydrobenzo[3,4]fluoreno[2,1-*b*]pyran-13-ol (BFP), belongs to the class of photochromic chromenes. Following the chromene numbering, it bears an indeno-group fused into the 5,6-positions and a toluenic moiety condensed in the 7,8-positions. These types of structures were recently synthesized by PPG Industries and, because of their photochromic properties, they have been proposed as useful components for ophthalmic lenses or other plastic materals.[1,2] Their photochromism is due to the ring-opening reaction which is typical of naphthopyrans (Scheme 1).[3–5]

The photochromic behaviour of BFP has already been investigated in different solvents[6,7] as well as in micro-heterogeneous media (inverted micelles and gels) and in a nematic liquid crystal.[6] Activation of the coloured form was accomplished at room temperature. In the 285–320 K temperature range, the BFP apparently behaved as a classical thermoreversible photochromic molecule. Its solutions were colourless in the dark, became coloured under UV irradiation and reverted to colourless when the exciting light source was discontinued. However, the reversibility was not complete. A small residual absorption in the visible spectral region, detected after thermal bleaching in all media, increased in intensity upon irradiation with visible light, except in liquid crystals where it decreased. This anomalous behaviour, never before found for chromene-type molecules, merited an in-depth investigation. In this paper the photochemistry of BFP is studied in ethanol, which was the solvent where the colorability was higher. A wide temperature range was explored, in order to change, and even remove, the contribution of thermal processes to the overall photoreaction. The net result expected was a deeper basic understanding of the photochemistry of this molecule and the mechanisms governing the activation and fading processes. The reaction dynamics scheme that emerges from this study is far more complex than any presented so far. The peculiarity of this system was that it exhibited doubly activated photochromism: a normal one, excited by UV light, and an anomalous one, promoted by irradiation with low energy visible light.



Scheme 1

Experimental

The compound here investigated, BFP, was synthesised in the Laboratories of PPG Industries (Monroeville, PA, USA) and was kindly supplied by F. Blackburn. After checking its purity ($>99\%$) by HPLC, the BFP was utilized without further purification.

The photochemistry of BFP was investigated in ethanol (Carlo Erba, anhydrous) solution, using for irradiation the light emitted by a 75 W Xe lamp, filtered through a Jobin-Yvon H10 UV monochromator and directed by means of a silica fiber optic onto a 1 cm path cell containing the sample solution (1 cm^3). Ferrioxalate actinometry was used to determine the intensity of the irradiating source. The colour-forming and colour-bleaching kinetics were followed from the absorbance changes, using a HP 8453 diode array spectrophotometer. To investigate thermochromism, absorption spectra were also recorded on a Perkin Elmer Lambda 800 spectrophotometer. Temperature was controlled using an Oxford Instruments cryostat.

More details on the experimental conditions have been reported in previous papers.[6,8]

Results and discussion

Photochromism

Ethanol was chosen as the most suitable solvent because the solubility of BFP in ethanol is better than in other solvents, which allowed working in a large concentration range (4×10^{-5} to 2×10^{-4} mol dm^{-3}) even at low temperatures (270–200 K). Moreover, previous studies aimed at investigating the effect of the medium on the BFP photochromism, indicated that the colorability is higher in this solvent compared with hydrocarbons and acetonitrile, since the thermal bleaching process is slower.[6] In ethanol, the activation energy for the bleaching process, determined in the 320–285 K temperature range, was 71 kJ mol^{-1}. By lowering the temperature (270–250 K), the colorability increased, thus improving the accuracy of the absorbance measurements, while at the lowest temperature explored, 200 K, the thermally activated processes were practically absent and this resulted in simpler photokinetic behaviour (irreversible formation of a unique photoproduct).

An experimental run of photocoloration–decoloration in ethanol at 270 K is illustrated in Fig. 1. The closed form (spectrum 1) under UV irradiation ($\lambda_{exc} = 303$ nm) undergoes photocoloration up to the attainment of the photostationary state ($A_{577} = 0.754$, spectrum 2). When the irradiation is discontinued, thermal bleaching occurs ($k_\Delta = 0.00059 \pm 0.00001$ s^{-1}), leaving a residual absorption ($A_{577} = 0.081$, spectrum 3), that is, a thermostationary state is reached. In other chromene photochromic systems, the residual absorption left after thermal decoloration was bleached by irradiation with visible light.[8,9] Surprisingly, in the case of BFP, irradiating the thermally equilibrated solution with monochromatic visible light (574 nm), which was not absorbed by the closed form, increased the colour intensity until a new photostationary state ($A_{577} = 0.137$, spectrum 4) was achieved. This means that visible light is capable of inducing photocoloration of the system after a UV-photocoloration–thermal bleaching cycle. By increasing the total number of photons absorbed by the sample (using a larger, *ca.* 60 nm, band-pass for irradiation) the system was enriched in the coloured form up to a new photostationary state ($A_{577} = 0.385$, spectrum 5). During all of these changes, three definite isosbestic points were maintained (265, 282 and 303 nm). This could suggest that all the transformations only involve two chemical species. However, more than two species could also be involved if they had similar absorption patterns or were present in negligible amounts.

When a BFP solution was irradiated at 200 K with UV light, it became coloured and remained stable in the dark, as well as upon successive visible irradiation (Fig. 2). This means that the photoproduct, P, is photo- and thermo-stable at 200 K. The kinetic evolution of the system at this temperature is shown in Fig. 2(a) where it is compared with the behaviour observed at 270 K. At 200 K, the reaction was considered to be complete at the photostationary state, due to inefficiency of the thermal back process. Thus, the molar absorption coefficients of the coloured form (ε_P) could be obtained from the final spectrum and the known initial concentration (see Table 1). Once the ε_P values were measured, the photochemical yield was determined.[8] The molar absorption coefficients of P at the maximum wavelengths are reported in Table 1. The quantum

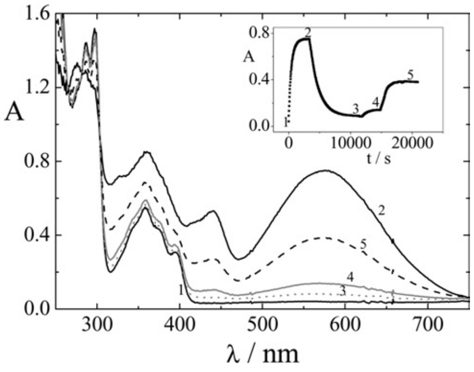


Fig. 1 Spectral evolution of BFP in ethanol at 270 K, $c = 4.44 \times 10^{-5}$ mol dm^{-3}. 1: Before irradiation (closed form); 2: photostationary state (75% photoconversion) under irradiation with UV light ($\lambda_{exc} = 303$ nm); 3: thermostationary state after thermal bleaching; 4: photostationary state under irradiation with visible monochromatic light, $\lambda_{exc} = 574$ nm; 5: photostationary state under irradiation with visible light (large band-pass). Insert: kinetics of the coloration and decoloration processes followed at 574 nm.

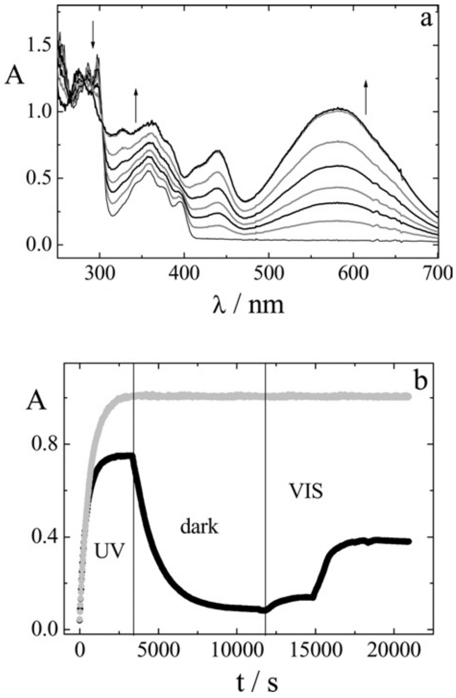


Fig. 2 a) Time evolution of the absorption spectrum of BFP in ethanol at 200 K, $c = 4.44 \times 10^{-5}$ M, under continuous irradiation ($\lambda_{exc} = 303$ nm). b) Absorbance trends followed at the maximum of the coloured form under UV irradiation ($\lambda_{exc} = 303$ nm), in the dark and under visible irradiation ($\lambda_{exc} = 574$ nm), at 200 K (grey) and 270 K (black).

Table 1 Spectral characteristics of the BFP photoproduct (P) in ethanol at 200 K

λ_{max}/nm	ε_P/dm^3 mol^{-1} cm^{-1}
577	23 200
440	15 900
364	20 600
290	25 400
275	29 700

yield, averaged over three analysis wavelengths, was 0.25 ± 0.03.

Quantum yield and ε_P values determined at low temperature (200 K) in the absence of thermal processes are in excellent agreement with those previously obtained by applying photokinetic methods at ambient temperature.[6]

Thermochromism

Serendipitously, we discovered that the BFP solution, while not apparently showing any absorption in the visible spectral region before irradiation, could be coloured using low energy visible light ($\lambda_{exc} = 574$ nm), not absorbed by the closed form. In reality, see Fig. 3, a very weak absorption band ($\lambda_{max} = 557$ nm, $A_{max} = 0.0056$) was only detected by zooming in on the visible region of the spectrum.

To the best of our knowledge, this behaviour has never been observed for chromenes and it seemed unusual enough to merit further investigation.

The first question we addressed was whether the visible-stimulated photocoloration was due to excitation of a small amount of coloured form (T) present in thermal equilibrium with the colourless one. To investigate this aspect, absorption spectra of a concentrated (2×10^{-4} mol dm^{-3}) BFP ethanol solution were recorded at increasing temperatures from 285 to 320 K. The absorbance increase of the colour band (0.019 to 0.057, Fig. 4) on increasing temperature indicated the occurrence of the endothermal ring-opening reaction. The enthalpy of the reaction, 25 kJ mol^{-1}, was determined according to the van't Hoff equation, expressed in terms of the absorbance (A_T) of the coloured form (eqn. 1), by measuring A_T at various temperatures (285–320 K). The linear ln A_T *vs.* T^{-1} plot is shown in the insert of Fig. 4.

$$\frac{\mathrm{d}\ln K}{\mathrm{d}(T^{-1})} = \frac{\mathrm{d}\ln A_T}{\mathrm{d}(T^{-1})} = \frac{\Delta H}{R} \tag{1}$$

The equilibrium constant can be calculated from the absorbance of T in the visible region if ε_T is known, by means of eqn. (2).[10,11] In this equation the denominator, $(C_0 - A_T/\varepsilon_T)$, can be approximated to C_0 considering the very low concentration of T in thermal equilibrium with BFP. Assuming that the spectrum of the thermally equilibrated coloured form T is similar to that of the photoproduced coloured form P, a K value on the order of 10^{-3} was estimated at 298 K.

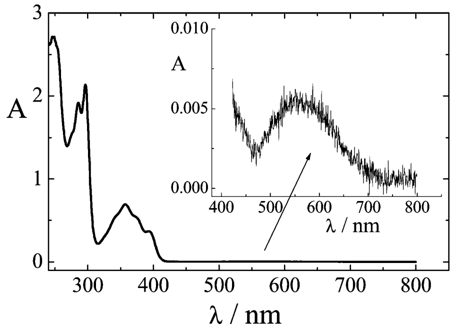


Fig. 3 Absorption spectrum of BFP in ethanol ($c = 6 \times 10^{-5}$ mol dm^{-3}) at room temperature. Insert: zoom on the visible spectral region.

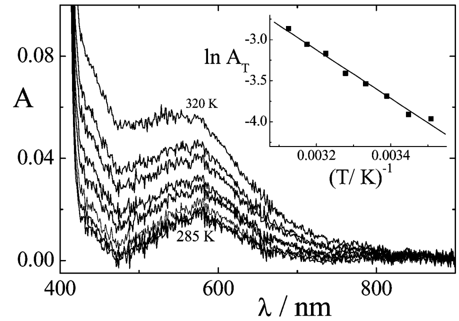


Fig. 4 Absorption spectra of a concentrated BFP ethanol solution (2×10^{-4} mol dm^{-3}) with increasing temperature (285–320 K). Insert: data treated according to eqn. 2.

$$K = \frac{[\mathrm{T}]}{[\mathrm{BFP}]} = \frac{A_T/\varepsilon_T}{C_0 - A_T/\varepsilon_T} \cong A_T/(\varepsilon_T \times C_0) \tag{2}$$

Thermochromism is a well known phenomenon in photochromic compounds[12] and in particular in the spirooxazine class,[10–12] where the percentage of coloured form, present in a thermally equilibrated solution, significantly depends on the contribution of zwitterionic structures to the resonance hybrid, which are favoured by electron-withdrawing substituents in the oxazine moiety. The equilibrium constants for the thermal coloration of the spirooxazines ranged from 10^{-2} to 10^{-4} and were strongly structure- and solvent-dependent.[10,11] In the present case, the phenomenon is less evident due to a somewhat higher ΔH^0 value and lower molar absorption coefficient of the coloured form than those of spirooxazines, for which the forward reaction is endothermal by 10–20 kJ mol^{-1}, , while ε (50 000–70 000 dm^3 mol^{-1} cm^{-1}) of the open coloured form is about 2–3 times larger.

A second point to establish was whether the coloured forms photoproduced by visible light irradiation and UV irradiation were the same molecular species. To this aim, a solution, that had been UV-photocoloured and then thermally bleached, was irradiated twice with visible light and then bleached in the dark. The kinetics are shown in Fig. 5. It can be observed that, at the experimental temperature (270 K), UV-photocoloration is apparently more efficient than visible-photocoloration, but this may largely depend on the different experimental conditions of irradiation and therefore different amounts of absorbed light ($A_{303} = 1.04$, 16 nm band pass and $A_{574} = 0.0285$, ~60 nm band pass). A very rough evaluation of the

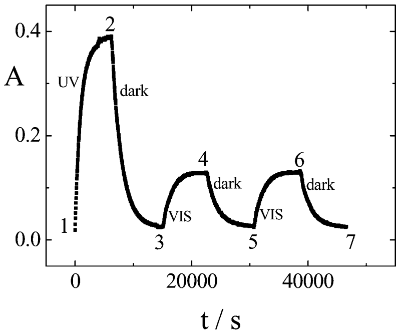


Fig. 5 Time evolution of the maximum absorbance of a BFP ethanol solution (5.1×10^{-5} mol dm^{-3}) at 270 K: $1 \rightarrow 2$ photocoloration ($\lambda_{exc} = 303$ nm); $2 \rightarrow 3$ thermal bleaching ($k_\Delta = 0.00060$ s^{-1}); $3 \rightarrow 4$ photocoloration ($\lambda_{exc} = 574$ nm, large slit); $4 \rightarrow 5$ thermal bleaching ($k_\Delta = 0.00058$ s^{-1}) $5 \rightarrow 6$ photocoloration ($\lambda_{exc} = 574$ nm, large slit); $6 \rightarrow 7$ thermal bleaching ($k_\Delta = 0.00059$ s^{-1}).

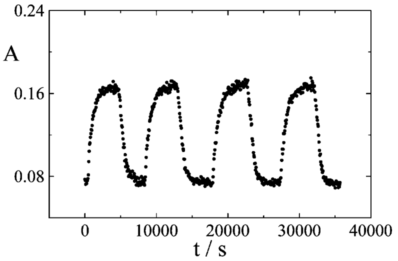


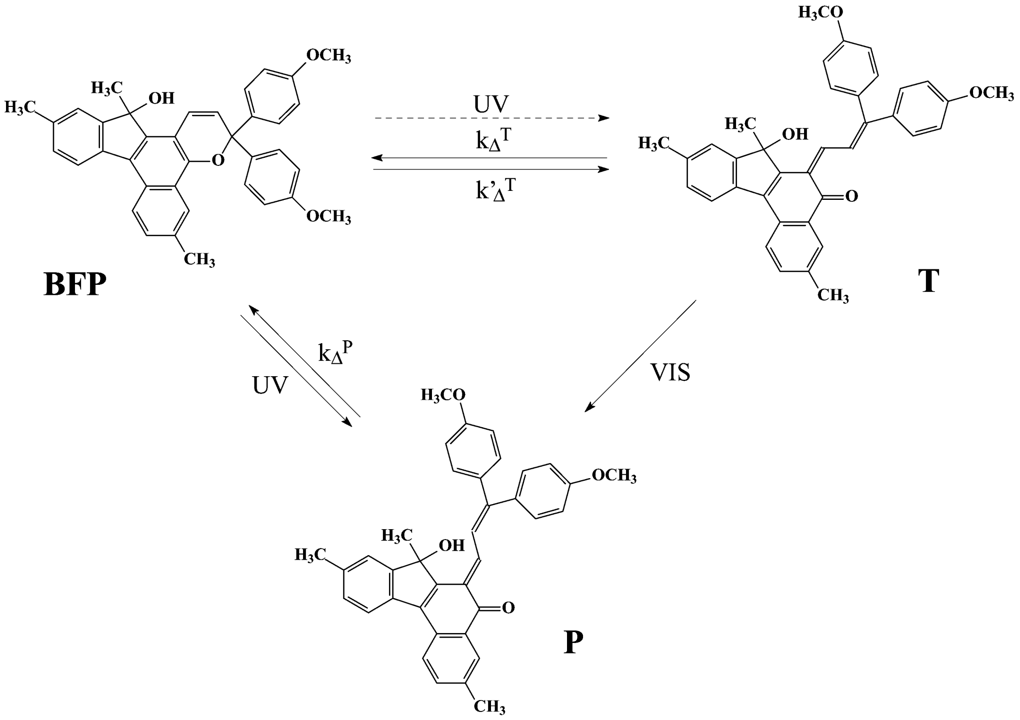
Fig. 6 Time evolution of the maximum absorbance of a BFP ethanol solution (2×10^{-4} mol dm^{-3}) upon cyclic irradiation with visible light ($\lambda_{exc} = 574$ nm, large slit) followed by thermal bleaching at 280 K.

quantum yield for the T → BFP photoreaction can be done knowing the light absorbed by T ($I_T = 4.5 \times 10^{-8}$ Einstein dm^{-3} s^{-1}): the resulting $\Phi_{T \rightarrow P}$ is about 0.1. Bleaching rate constants determined in the dark (2 → 3; 4 → 5 and 6 → 7) and spectra at the thermostationary states (corresponding to 3, 5 and 7 positions in Fig. 5) were compared.

Apart from intensity, the spectrum recorded after each visible-photocoloration (4 and 6 in Fig. 5) was identical to that registered after the first UV-photocoloration (point 2 in Fig. 5) and the values of thermal relaxation constant of the photocoloured form were the same for all three thermal bleachings ($k_\Delta = 0.00059 \pm 0.00001$ s^{-1}). The same experiment was repeated at different temperatures (280 and 285 K) and the results were analogous ($k_\Delta = 0.0015 \pm 0.0001$ and 0.0020 ± 0.0002 s^{-1}, respectively, in agreement with the temperature effect). Thus, it can be concluded that UV-irradiation of the closed form, BFP, and visible-irradiation of the thermally equilibrated open form, T, yield the same coloured species.

A final point to clarify was why the thermal bleaching apparently did not restore the system to the initial equilibrium position (the absorbance in the visible was slightly higher) when the irradiation was performed with UV light and why this effect was greater at low temperature, when the amount of thermally equilibrated species should be smaller. In contrast, when the system was only irradiated with visible light, it was perfectly reversible (Fig. 6). We hypothesize that this was due to the presence of thermally non-equilibrated T (possibly formed by poorly efficient BFP → T UV-stimulated photoconversion). The lower the temperature the greater the amounts of T, because the rate of the thermal T → BFP back process was slow. It was proved that the thermal T → BFP process occurs over a very slow time scale: at 295 K, $k_\Delta^T \approx 2 \times 10^{-4}$ s^{-1}. Using this value and the above estimated equilibrium constant, the rate parameter of the forward thermal process ($k'^T_\Delta \approx 2 \times 10^{-7}$ s^{-1}) could be evaluated.

The reaction Scheme 2 describes the experimental findings. In the dark, the BFP is in thermal equilibrium with the coloured form T; at room temperature, the amount of T equilibrated is about 0.1%. The coloured photoproduct, P, can be formed either by UV-irradiation of the BFP closed form, or by visible-irradiation of the thermal product T, and completely bleaches when irradiation is discontinued. If coloration is accomplished by visible light the thermal bleaching is completely reversible over several on–off cycles (Fig. 6). If coloration is accomplished by UV irradiation, a certain amount of T is photochemically produced that leaves a coloured residue after the faster bleaching of P, and only fades over a longer time scale to restore the BFP ⇄ T thermal equilibrium. At low temperature ($T = 200$ K), when the thermal equilibrium is virtually shifted towards the closed form and all thermal processes are slowed down, UV irradiation generates P and this is the unique species present in the photostationary state. At 200 K, P is thermally and photochemically stable. As previously proposed for other chromenes,[8,9] a primarily formed *cis–cis* open structure may stabilise itself by twisting around different C–C bonds, giving rise to *trans–cis* and/or *trans–trans* isomers. We believe that the *trans–cis* isomer formation (T in the present case), which requires rotation around a C–C single bond, is more likely to occur thermally, while the *trans–trans* isomer formation (P in the present case),



Scheme 2

that requires rotation around a double C=C bond, is promoted by light. The assignment of P to the *trans–trans* structure is in contrast with its assignment to the *trans–cis* structure proposed before the thermal equilibrating species, T, was discovered.[6,7]

Conclusions

The photobehaviour of BFP, which apparently gives rise to a unique photoproduct,[6] seemed simpler than that of other chromenes, for which two photoproducts, one thermally and the other photochemically reversible, were detected. However, even in this case, a second coloured open form (T) was discovered, which is in thermal equilibrium with the BFP closed form. The amount of T, which is very low at room temperature, increases with increasing temperature, that is, BFP is a thermochromic molecule. This is the first case of thermochromic behaviour reported in the literature for chromenes, while thermochromism has often been detected for other classes of photochromic compounds.[12]

The most unusual aspect in the photobehaviour of this molecule is a consequence of its thermochromism. Irradiating the thermo-equilibrated, apparently colourless, solution with low-energy visible light switches-on coloration. The effect is easily detectable, even if the absorbed light intensity is small, due to the small concentration of T equilibrated with BFP. However, to re-establish the thermochromic equilibrium, BFP continuously supplies T, which is erased in the T → P photoconversion. The possibility of activating the photochromism using both UV and visible light (also considering that the UV absorption of the colourless form extends into the first visible region, at about 405 nm) allows a large part of solar emission to be used for photocoloration. Therefore, this photochrome could be very useful for ophthalmic lenses or other plastic transparencies[2] to be switched under sunlight.

Acknowledgements

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