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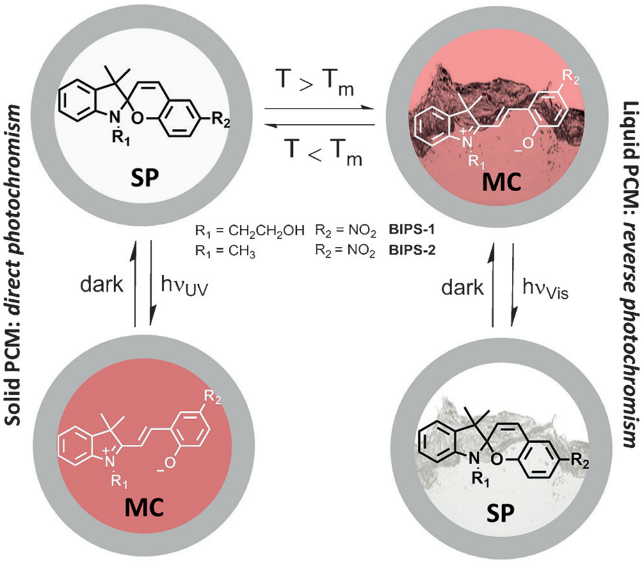
Temperature-Controlled Switchable Photochromism in Solid Materials

*Alex Julià-López, Jordi Hernando, Daniel Ruiz-Molina, Pablo González-Monje, Josep Sedó, and Claudio Roscini**

Abstract: *A novel strategy to achieve thermally switchable photochromism in solid materials is reported, which relies on the preparation of polymeric core–shell capsules containing solutions of photochromic dyes in acidic phase-change materials. Upon changing the phase (solid or liquid) of the encapsulated medium, one of the two photochromic states of the system is selectively stabilized on demand, allowing for reversible interconversion between direct and reverse photochromism when thermally scanning through the melting temperature of the phase-change material. This strategy, which does not require the addition of external agents or chemical modification of the dyes, proved to be general for different spiropyran photochromes and to be applicable to the fabrication of a variety of functional materials by simply embedding the capsules obtained into a solid matrix of choice.*

The reversible color changes of photochromic compounds induced by electromagnetic radiation are attractive properties for a variety of applications.[1] In particular, T-type photochromes thermally reverting back to the initial state after irradiation are currently used in ophthalmic lens coatings and some novelty products (e.g., textile materials, paints),[2] and are explored for other potential applications, for example, as optical switches and holographic materials.[3] Among all photochrome families, organic T-type photochromes (e.g., spirooxazines and spiropyrans) are the most promising for commercial applications owing to their good solubility in plastic materials, their synthetic accessibility, and the tunability of their functional properties either by chemical modification or by changing the surrounding medium.[1,2]

Upon UV irradiation in non-polar organic solvents, spiropyrans and spirooxazines interconvert between the non-colored spiro isomer (SP) and the colored merocyanine state (MC), which thermally reverts back to the stable SP in the dark (Scheme 1, direct or positive photochromism).[1,3c] The rate of this back-isomerization process is strongly related to the thermodynamic stability of the more polar MC isomer, whose electronic distribution varies from the zwitterionic form shown in Scheme 1 to a non-ionic *ortho*-quinoidal structure depending on the nature of the substituents[4] and the medium.[5] In particular, MCs can be stabilized by a) highly polar solvents[6] and solid matrices (e.g., silica),[7] b) chemical modification of the dyes,[8] c) coordination to metal ions,[9] or d) the presence of acids, forming salt-like structures with the protonated MCH^+ form or hydrogen-bonding interactions with MC.[8e,10] Noticeably, stabilization can reach such an extent that the colored MC isomer becomes predominant in the dark at room temperature. In this case, fading and conversion into SP can be photoinduced by UV/Vis irradiation whereas the color is regenerated in the dark (Scheme 1, reverse or negative photochromism).[5a,7c]



Scheme 1. Direct and reverse photochromism of capsules filled with acidic PCMs and BIPS-type spiropyran dyes.

Recently, the development of spiropyran and spirooxazine systems that can reversibly switch between positive and negative photochromism has raised much interest as they can be used to generate frequency-dependent photoinduced optical effects exploitable for controlling input/output optical signals in logic gates, information recording/processing, and rewritable printing devices.[3] To date, most of the reported examples showing switchable photochromism were developed as proof-of-concept liquid solutions where chemicals had to be sequentially added to alter the relative stability of the SP and MC isomers: acids[10a,c,11] or metal ions[9e–h] to stabilize the colored form as MCH^+ or metal–MC complexes and bases to compete with coordinating ligands or complexing metals to reestablish the non-colored SP isomer.

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[*] A. Julià-López, Dr. D. Ruiz-Molina, P. González-Monje, Dr. J. Sedó, Dr. C. Roscini
Nanostructured Functional Materials
Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology
Campus UAB, Bellaterra, 08193 Barcelona (Spain)
E-mail: Claudio.roscini@icn2.cat

Dr. J. Hernando
Departament de Química
Universitat Autònoma de Barcelona
Edifici C/n, Campus UAB, 08193 Cerdanyola del Vallès (Spain)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: http://dx.doi.org/10.1002/anie.201608408.

An alternative approach to selectively stabilize one of the isomeric forms of color-changing dyes (e.g., spirolactones[12,13] and spirooxazines)[14] is based on using acidic phase change materials (PCMs). Upon melting, these materials interact with the contained dyes and induce isomerization to the colored isomer in the dark through hydrogen-bonding interactions, dipole–dipole forces, or acid–base reactions. Although these PCM-based systems may undergo reversible temperature-controlled color changes (i.e., thermochromism) and, in some cases, display direct photochromism,[14] they have not been used for switchable photochromism yet, possibly owing to the lack of photochromic activity of one or both dye isomers when dispersed in these materials.

To overcome these limitations, we herein present a new approach to accomplish switchable photochromism, which relies on a) dispersion of the dyes of interest in acidic PCMs, such that the relative stability of their SP and MC forms can be controlled by melting/solidifying the surrounding medium, enabling direct or reverse photochromism depending on the applied temperature and without the need for chemical additives, and b) confinement of the dye–PCM mixtures in solid shell capsules, which will guarantee that all components are maintained in the same environment during the melting/solidification process and, therefore, the reversibility of the system (Scheme 1). Importantly, this encapsulation strategy enables the direct synthesis of functional solid materials in a straightforward, tunable, and universal approach that does not involve chemical modification of the dyes, as previously done for other stimuli-responsive systems.[15]

To explore the viability of our approach, we first evaluated the preparation of reverse photochromic systems based on PCM-filled capsules. We encapsulated a photochromic solution of the common spiropyran dye 1′-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[1(2*H*)-benzopyran-2,2′-indoline] (BIPS-1; Scheme 1) in nonanoic acid (NA), a weakly acidic ($pK_a = 4.96$),[16] non-volatile PCM that is liquid at room temperature (melting point, $T_m = 12.4\,°C$).[16] Poly(methyl methacrylate) (PMMA) capsules containing NA photochromic solutions were prepared through the reaction-free emulsion–solvent evaporation method,[17] which avoided dye degradation during the synthesis (see the Supporting Information, Scheme S1). The formation of BIPS-1/NA@PMMA capsules (2–5 μm in diameter) was corroborated by SEM (Figure 1 a) whereas the presence of NA inside the capsules was confirmed and quantified through DSC and ^{1}H NMR spectroscopy (Figures S1 and S2).

The red color and the visible absorption band of BIPS-1/NA bulk solutions ($\lambda_{max} = 525$ nm; Figure S3a, b) and capsules ($\lambda_{max} = 525$ nm; Figure 1 b, c) at room temperature indicated that the colored MC isomer of the dye was stabilized by liquid NA. In particular, comparison with the spectral properties reported for the non-protonated ($\lambda^{MC}{}_{max} = 510$–$560$ nm)[5b,7e,18] and protonated ($\lambda^{MCH}{}_{max} = 401$ nm)[11b,c,19] forms of this species suggested stabilization of the free MC base. Color fading of BIPS-1/NA solutions and capsules was photoinduced upon exposure to visible light ($\lambda_{ex} = 532$ nm or ambient light), while this process was reverted in the dark. These findings confirmed that the reverse photochromism of the bulk solution (Figure S3 a–c) was maintained in the capsules (Figure 1 c). Moreover, the very little color increase of the BIPS-1/NA@PMMA capsules under strong UV or blue-light irradiation (Figure S4) and the color fading induced by sunlight indicated that competitive direct photochromism was practically inhibited in this system.

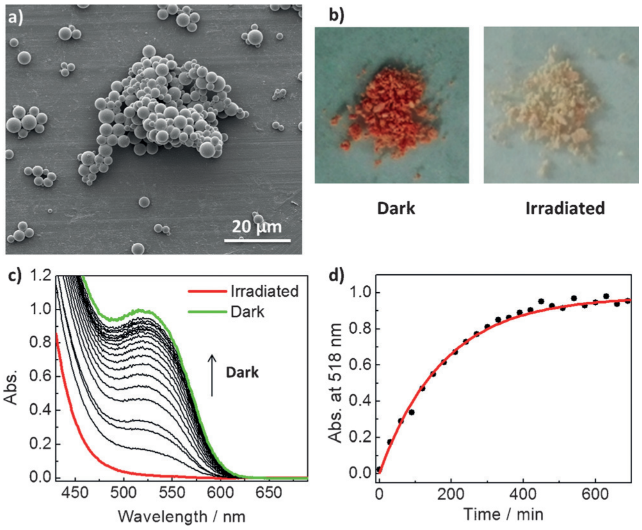

Figure 1. a) SEM image of BIPS-1/NA@PMMA capsules. b) Digital photographs of irradiated and non-irradiated ($\lambda_{max} = 525$ nm) capsules. c) Absorption spectra of irradiated (red) and non-irradiated (green) capsules ($\lambda_{ex} = 532$ nm, 570 mW cm^{-2}, 60 s), and growth of their visible absorption band in the dark after irradiation (time lapse between spectra: 30 min). d) Coloration kinetics of the irradiated capsules in the dark followed at λ_{max} and room temperature.

This system is a clear improvement with respect to other solid materials where reverse photochromism has been attempted, such as silica matrices. High polymerization degrees[5b,7a,b] or low hydrophobic/hydrophilic ratios[4a,7a,e,f] are required in these materials to ensure reverse photochromism; however, this often leads to loss of the dye activity owing to degradation, excessive matrix rigidity, or too much MC stabilization.[7a,d,20] Although these drawbacks can be prevented by lowering the silica matrix polarity, they normally result in mixed reverse/direct photochromism.

Absorption measurements were used to monitor the room-temperature kinetics of the thermal coloration process of BIPS-1/NA@PMMA capsules in the dark after irradiation; these could be fitted to a monoexponential growth function (Figure 1 c, d). This is indicative of a homogeneous solution-like behavior of the photochromic molecules inside the capsules although the rate constant ($k = 9.4 \times 10^{-5}\,s^{-1}$) was slightly lower than that of BIPS-1 bulk NA solutions ($k = 1.5 \times 10^{-4}\,s^{-1}$; Figures S3 c and S5), which is probably due to PMMA matrix effects[15] in some not purely core–shell capsules.

After demonstrating the negative photochromism of spiropyrans in capsules filled with NA, we pursued switchable photochromism by replacing this solvent with an acidic PCM that is solid at room temperature. Owing to the different interactions of the dyes with the solid and liquid states of this PCM, we expected their SP and MC isomers to be differently stabilized in each phase, thus interconverting between direct and reverse photochromism upon thermally scanning through the melting point of the material. To illustrate this and explore the generality of our strategy, we used the emulsion–solvent evaporation method to prepare PMMA microcapsules containing a) dodecanoic acid as the solvent (DA, Scheme S1), a twelve-carbon weak acid with $T_m = 43.8\,°C$,[16] and b) two different photochromic spiropyran dyes, BIPS-1 and 1′,3′,3′-trimethyl-6-nitrospiro[1(2*H*)-benzopyran-2,2′-indoline (BIPS-2; Scheme 1). SEM confirmed the formation of BIPS-1/DA@PMMA and BIPS-2/DA@PMMA capsules (0.5–10 μm in diameter; Figures 2 a and S6) whereas ^1H NMR spectroscopy and DSC proved the presence of DA inside (Figures S7–S10). Variable-temperature SEM showed that no melting or liquid ejection from the capsules was observed until temperatures above the PMMA glass transition temperature (105 °C) were reached,[16] confirming their thermal stability around the DA melting point and the absence of non-encapsulated PCM (Figures S11 and S12).

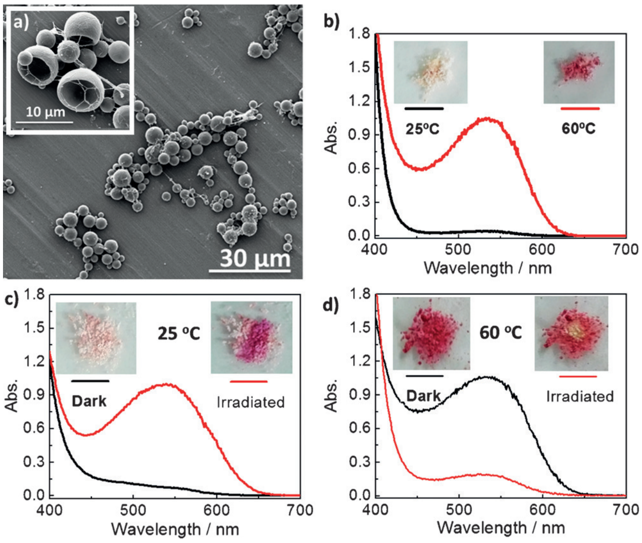

Figure 2. a) SEM image of BIPS-1/DA@PMMA microcapsules (2–10 μm). Inset: Enlarged view of incomplete capsules showing their hollow core. b) Absorption spectra of capsule powder before (25 °C, black) and after (60 °C, red, $\lambda_{max} = 532$ nm) heating. c) Absorption spectra ($\lambda_{max} = 535$ nm) of capsule powder at room temperature (25 °C) before (black) and after (red) blue-light irradiation ($\lambda_{ex} = 405$ nm, 1.3 W c^{-2}, 30 s). d) Absorption spectra of capsule powder at 60 °C before (black, $\lambda_{max} = 532$ nm) and after (red) visible-light irradiation ($\lambda_{ex} = 532$ nm, 570 mW cm^{-2}, 60 s).

At room temperature, both BIPS-1/DA@PMMA and BIPS-2/DA@PMMA capsules were white (or very faintly pink) with only residual absorption around 530–540 nm (Figures 2 b and S13). This indicated the stabilization of the photochrome molecules in their non-colored SP form under these conditions, probably owing to the weak interactions between solid DA and BIPS molecules. By contrast, when the materials were heated above the DA melting point (60 °C), they became red, and an absorption band appeared in the visible region at $\lambda_{max} \approx 530$–$540$ nm, a phenomenon related to the acid-induced stabilization of the MC isomer in the liquid state (Figures 2 b and S13). Consequently, BIPS-1/DA@PMMA and BIPS-2/DA@PMMA capsules show the expected thermochromism in the absence of irradiation as they undergo white–red color interconversion in the dark simply upon varying the temperature around the DA melting point.

Even more interestingly, BIPS dyes were observed to preserve their photochromic behavior both in liquid- and solid-filled DA capsules. On the one hand, upon exposure to UV or blue-light irradiation at room temperature, they underwent rapid coloration owing to light-induced SP→MC conversion, as demonstrated by absorption measurements (Figures 2 c, S14, and S15). The color fading subsequently observed in the dark confirmed the occurrence of direct photochromism at 25 °C for these materials (Figures S14 and S15), with no relevant degradation after three irradiation cycles (Figure S16). In both cases, the decoloration kinetics of the solid-filled capsules were enhanced with temperature (Figure S17), as expected for a thermal isomerization reaction. However, lower rates were measured at room temperature ($k = 3.2 \times 10^{-5}\,s^{-1}$ (BIPS-1) and $k = 6.7 \times 10^{-5}\,s^{-1}$ (BIPS-2)) than those reported in less polar liquid solvents ($k = 5.2 \times 10^{-3}\,s^{-1}$ (BIPS-1)[11c] and $k > 7.9 \times 10^{-5}\,s^{-1}$ (BIPS-2)), which was ascribed to both the higher polarity and rigidity of the solid DA matrix.[15] Furthermore, the formation of MC aggregates could also contribute to delayed thermal photochrome back-isomerization.[3a,21] Actually, when studying the effect of dye concentration on the photochromic activity of BIPS-1 and BIPS-2 in DA bulk solid solutions, spectral changes were observed at high dye loadings (>1 %) that suggested partial MC aggregation: a) higher residual colors in the dark, possibly related to partial stabilization of the MC form in the aggregates (Figures S18 and S19) and b) bathochromic shifts of the MC absorption band, indicating the formation of J-stacks (Figures S20).[3a] Some of these features were also observed when monitoring the thermal MC→SP back-isomerization of the capsules (Figure S21), thus indicating non-negligible photochrome aggregation. Nevertheless, this did not detrimentally affected the photochromic behavior of our materials.

On the other hand, capsule irradiation with visible light at 60 °C induced SP formation and the consequent loss of the red color and of the visible absorption band initially observed at this temperature (Figures 2 d, S22, and S23). This process was reverted in the dark at higher rates ($k = 5.7 \times 10^{-3}\,s^{-1}$ (BIPS-1) and $k = 1.4 \times 10^{-2}\,s^{-1}$ (BIPS-2)) than for analogous capsules filled with liquid NA at 25 °C, probably owing to the temperature effect on the thermal recovery of the most stable MC species (Figures S22 and S23). Therefore, BIPS-1/DA@PMMA and BIPS-2/DA@PMMA capsules display negative photochromism upon melting of their solid interior, and their performance was not affected by thermal degradation of the material (Figure S24). By comparing this behavior to that observed at 25 °C, it can be concluded that BIPS-1 and BIPS-2 DA-based capsules can interconvert between positive and negative photochromism upon temperature variation. In all of these cases, thermal switching between these two scenarios was found to be reversible, though further irradiation with visible light was required to fully reestablish the colorless state of the capsules at 25 °C once the temperature had been reduced below the DA melting point.[22] It must be noted that the intrinsic photochromic properties of the dyes are essentially not altered upon encapsulation as the surrounding medium (i.e., the selected solvent) remains the same as in bulk solution.

To further exploit the potential of our system, we aimed to transfer the behavior of the acid-filled capsules to solid, non-rigid polymeric materials. Poly(vinyl alcohol) (PVA) films loaded with BIPS-1/NA@PMMA and BIPS-1/DA@PMMA capsules were thus prepared by drop-casting a water suspension of the polymer and the capsules (see the Supporting Information). In both cases, the microcapsules preserved their morphology within the films (Figure 3). As expected, when the red BIPS-1/NA@PMMA@PVA polymeric matrix was irradiated with non-coherent visible light (e.g., ambient light or sunlight) or a laser beam at 532 nm at room temperature, negative photochromism was observed (Figures 3 a and S25). The liquid-like behavior of the NA solution was thus transferred to the solid PVA matrix.

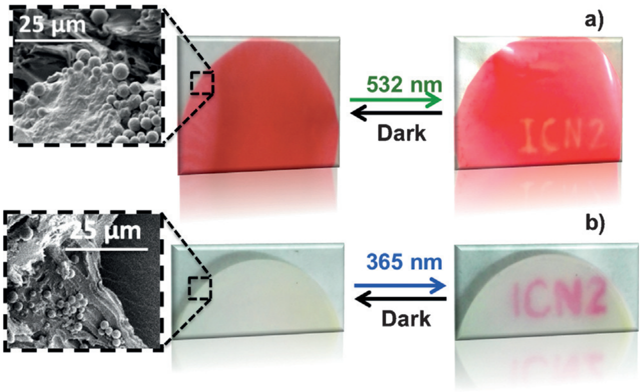

Figure 3. a) Digital photographs of non-irradiated (left) and irradiated (right) BIPS-1/NA@PMMA@PVA films at 25 °C and using a laser pointer at 532 nm ($\lambda_{ex} = 532$ nm, 570 mW cm^{-2}, 60 s). Left: SEM image of a broken edge of the film. b) Digital photographs of non-irradiated (left) and irradiated (right) BIPS-1/DA@PMMA@PVA films at 25 °C and under UV irradiation ($\lambda_{ex} = 365$ nm, 2.7 mW cm^{-2}, 90 s) and an ICN2-shaped mask. Left: SEM image of a broken edge of the film.

On the other hand, the BIPS-1/DA@PMMA@PVA film showed the opposite behavior at room temperature when illuminated with UV light (i.e., positive photochromism) as the loaded capsules had a solid interior that stabilized the colorless SP isomer, and their properties were maintained when dispersed in the PVA polymer matrix (Figures 3 b and S26 a–c). Equivalent color fading kinetics were measured for the film and the free capsules under these conditions (Figure S26 b). After heating at 60 °C, coloration of the film in the dark and light-induced fading were instead observed, as a result of the reverse photochromism shown by the capsules upon DA melting (Figure S26 d–f). This thermal switch of the photochromic behavior was found to be completely reversible as the film recovered the initial non-colored state observed at room temperature after reducing the temperature and irradiation with visible light.[21]

In summary, we have described a straightforward and universal method to control the photochromic behavior (direct vs. reverse) of spiropyrans, which is based on the use of dye-loaded polymer capsules filled with a non-volatile acidic phase-change material. By thermally controlling the state of this material (liquid vs. solid), reversible interconversion between direct and reverse photochromism was achieved for the first time in solid matrices and without requiring the addition of external additives or chemical modification of the photochromic dyes and the surrounding matrix. These properties, in combination with the tunability of the optical properties of the system and the fact that the switching behavior can be transferred to any material of interest, make our approach highly relevant for the fabrication of different functional devices from optical memories to writing/erasing displays and photoprotective coatings. The application of this approach to other photochrome families is currently under investigation.

Acknowledgements

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[22] Visible-light irradiation was required to completely restore the spiro form because upon freezing of the DA, some of the SP molecules remained trapped in an aggregated and zwitterionic colored form.

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