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Color-Tunable White-Light Emitting Materials Based on Liquid-Filled Capsules and Thermally-Responsive Dyes

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ABSTRACT: Color-tunable white-light emitting materials are currently attracting much attention because of their potential applications in artificial lighting, sensing and imaging. However, preparation of these systems from organic emitters is often cumbersome due to the interchromophoric interactions occurring upon solvent drying in the final solid materials, which can be hardly predicted and may lead to detrimental effects. To circumvent these obstacles, we have developed a new fabrication methodology that relies on dye encapsulation within liquid-filled capsules, thus enabling direct transfer of the luminescent properties from solution to the solid state and, as such, rational design of miniaturized white-light emitting materials. By introducing a temperature-responsive chromophore into the capsules, these materials are further endowed with color tunability, which does not only allow ample modulation of the emitted color, but also facilitates external fine control of the system so as to ensure precise realization of white light.

INTRODUCTION

Artificial white lighting has been the subject of intensive research in the past decades, especially with the aim of developing new light sources providing energy savings and environmental benefits.¹⁻⁷ Owing to their potential advantages over inorganic lighting materials (e.g. lower toxicity and density, larger flexibility, and better processability), organic white-light emitting systems are receiving special attention in this area.¹⁻⁵ To generate white light in these materials, the additive color mixing principle is normally followed, which requires concurrent emission of the three primary colors (red, green and blue) or two complementary colors (e.g. blue and orange) from distinct or multichromophoric organic compounds.¹⁻⁵

A number of different aspects are currently attracting the interest of researchers in the field of organic white-light emitting materials. Since single layer devices are preferred over multilayer structures to simplify manufacturing processes and improve operation conditions,¹ a plethora of strategies are being described to achieve white-light emission upon incorporation of emitters into individual solid matrices¹⁻⁵ (e.g. polymer hosts,^{2,8} gels,^{9,10} mesoporous materials^{11,12}). In all these systems, however, white-light production does not only require simultaneous emission from the different dyes in the material, but also good control over the energy transfer processes that could take place among them, which are almost unavoidable due to the occurrence of spectral overlaps and short

interchromophoric distances.^{4,13} Unfortunately, mutual chromophore arrangement and, as such, energy transfer efficiencies are difficult to be predicted, and they often vary when transferring a mixture of emitters from solution to the solid state during the processing of the system. As a result, screening through repetitive and time-consuming experiments is demanded to find the optimal conditions that lead to the target white-light emission in the final solid material (i.e. emitters ratio, separations and concentrations).¹³ Therefore, efforts are also underway to overcome this obstacle and facilitate the rational realization of white light in single layer devices, which can be accomplished by: (a) inhibiting energy transfer between emitters;¹³⁻¹⁵ (b) designing white-light emitting single molecules where different chromophores are arranged at controlled distances regardless of the surrounding medium;¹⁶⁻¹⁸ or (c) introducing stimuli-responsive dyes in the system to externally fine tune the emitted color so as to obtain white light irrespective of the energy transfer processes occurring.¹⁹⁻²² By additionally enabling spectral variation of the emission, the latter approach is of particular relevance for artificial lighting, since color tunability can be used to define brands or modify environments and moods.³ This, together with their use in other areas such as imaging, labeling and sensing,^{20,23-25} has recently driven attention toward color-tunable white-light emitting materials. Finally, miniaturization of these materials down to the micro- and nanoscale is further pursued in

view of the interest for their implementation over a wide range of applications.^{5,19,20,26-29}

In this work we report a new methodology to prepare organic white-light emitting materials that addresses all these challenges at once (i.e. ease of experimental design, color tunability, and miniaturization). Our approach relies on two fundamental principles. First, liquid-filled polymeric microcapsules are selected as vehicles for the encapsulation of the organic dyes of interest; in our case, turquoise-emitting 9,10-bis(phenylethynyl)anthracene (BPEA) and a thermochromic orange-emitting spirocyclic Meisenheimer complex (SMC),^{30,31} whose concurrent fluorescence should result in white light generation (Figure 1a). Several advantages derive from this strategy, which we have already exploited for the preparation of photochromic^{32,33} and thermochromic capsules.³⁴ On the one

solutions of BPEA and of the tautomeric mixture SMC-AR, which becomes enriched in the colored and fluorescent isomer SMC as temperature decreases.

hand, a solid microstructured material is obtained, which can be easily manipulated and processed for the ulterior fabrication of miniaturized devices. On the other hand, direct transfer of the luminescent behavior of the emitters from solution to the solid state is warranted owing to the liquid nature of the capsules core. This allows preventing most of the problems encountered when preparing solid-state organic white-light emitting materials by solvent drying (e.g. dye aggregation, uncontrolled dye separation distances, dye-matrix segregation), which critically affect chromophore interaction and, therefore, color emission in the final system with respect to the initial solution.^{13,35}

The second underlying basis of our methodology is the use of the thermally-responsive dye SMC, a compound that tautomerizes to its noncolored and nonfluorescent aromatic isomer AR.^{30,31} Since the equilibrium constant of this process depends on temperature, gradual and reversible disappearance of SMC and, as such, of its orange emission can be achieved upon heating (Figure 1b).^{30,31} Consequently, this should allow thermal fine adjustment of the intensity ratio between BPEA and SMC fluorescence so as to precisely obtain white light. Furthermore, in this way the system will also be provided with temperature-controlled wide-range color-tunability' a property that has been seldom reported for organic white-light emitting materials despite its potential range of applications (e.g. in lightning, sensing and imaging).^{25,36-38} Actually, our molecular approach toward this goal is completely novel, since previous works mainly relied on the thermal properties of the solid matrix and its interactions with the dyes entrapped to achieve temperature-controlled color variation of white-light emitting materials.^{25,37,38}

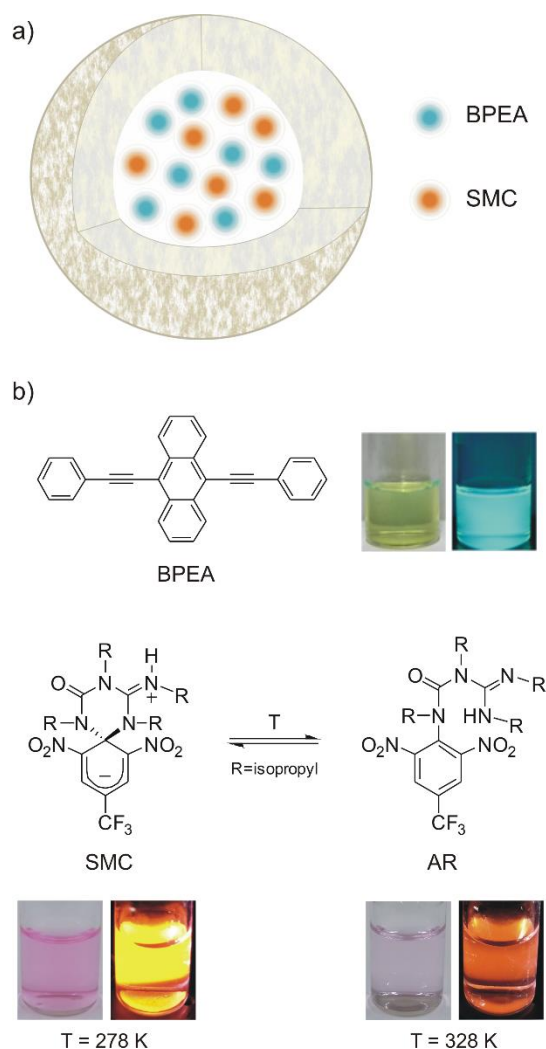


Figure 1. (a) Schematic representation of our strategy toward color-tunable white-light emitting materials, which relies on the preparation of polymer capsules loaded with liquid solutions of a turquoise-emitting dye (BPEA) and a thermally-responsive orange-emitting chromophore (SMC). (b) Structures of BPEA and SMC, which tautomerizes toward nonfluorescent compound AR. The photographs show acetonitrile

RESULTS AND DISCUSSION

Selection of the materials for the preparation of liquid-filled capsules. Prior to the synthesis of the target dye-loaded liquid-filled capsules, careful selection of their constituting materials was needed to warrant: (a) preservation of the optical properties of the encapsulated emitters over the range of temperatures tested; (b) mechanical, chemical and thermal stability of the capsules. To fulfill the latter requirements and based on our previous experience on the synthesis of robust liquid-filled capsules,³⁴ we chose their shell to be made of cross-linked polyurea polymers (PU). This selection was further supported by the fact that both BPEA and SMC dyes proved to be resistant to the reagents and conditions involved in the preparation of PU capsules, in contrast to what was observed when assaying the synthesis of other types of polymer shells (e.g. cross-linked polyamides using acyl chlorides).

After exploring a number of different solvents, dioctyl terephthalate (DOTP, Scheme S1) was selected for the preparation of the liquid interior of the capsules. This

choice was motivated by several factors. First, DOTP is a colorless oil that melts at 225 K and does not boil up to 673 K,³⁹ thereby ensuring that the liquid core of the capsules is maintained over a large thermal range. In addition, it dissolves the two dyes of interest and, according to preliminary experiments in bulk solution, it preserves the thermofluorochromic behavior of SMC, as clearly illustrated in Figure 2. Thus, a dramatic decrease of the intensity of the visible-region absorption and emission bands of SMC in DOTP was observed upon heating from 248 to 358 K (ca. 85%), a process that was found to be fully reversible when cooling down the sample (Figure S1). Based on our previous results in other solvents,^{30,31} we attributed the spectral changes observed in DOTP to the thermal variation of the equilibrium constant for the SMC-AR tautomerization process, which should lead to an increase of the noncolored and nonfluorescent isomer AR with temperature. Actually, by comparison with the data previously obtained in acetonitrile and neglecting solvent-induced absorptivity changes,³⁰ the molar content of the fluorescent SMC compound in the tautomeric mixture was estimated to be 4.3, 2.0 and 0.6% at 248, 300 and 358 K in DOTP, respectively. In spite of this low molar fraction, DOTP solutions of SMC displayed strong luminescence owing to the large fluorescence quantum yield (Φ_f) of this compound ($\Phi_f = 0.78$ in DOTP at 298 K).

In the case of BPEA, absorption spectra showed small variations within the 248–358 K temperature range (Figure 2). Since this behavior was observed to be reversible (Figure S1), we ascribed it to the nonnegligible thermal dependence of the molar absorptivity of the chromophore. Nevertheless, minimal spectral changes were encountered around $\lambda = 400\text{--}430$ nm, the reason for which we decided to measure the emission spectra of BPEA and BPEA-SMC mixtures upon excitation in this spectral range. This, together with the temperature independent Φ_f values found for BPEA in DOTP ($\Phi_f \sim 1.0$), allowed minimal differences to be observed in the emission intensity registered for this compound upon heating from 248 to 358 K (Figure 2).

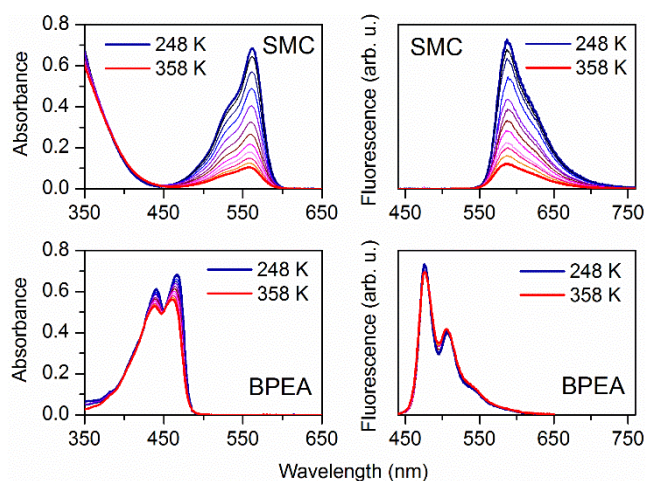


Figure 2. Temperature dependence of the absorption and fluorescence spectra of SMC and BPEA in DOTP ($\lambda_{exc} = 473$ and 405 nm for SMC and BPEA, respectively). Spectra were measured every 10 K.

Aside from changes in fluorescence intensity, we also analyzed the effect of temperature on the color emitted by each of the dyes in DOTP separately. As shown in Figure S2, the shape and position of the emission spectra of BPEA and SMC barely varied from 248 to 358 K, which led to very small changes in color with temperature according to the Commission Internationale de l'Éclairage (CIE) 1931 chromaticity coordinates determined. The latter, in combination with the substantial thermal effect found for the fluorescence intensity of SMC and the complementary colors measured for the two dyes of choice, prompted us to prepare color-tunable white-light emitting materials composed of polymer capsules filled with DOTP solutions of BPEA and SMC. Actually, based on the CIE 1931 chromaticity coordinates calculated for BPEA in DOTP at 358 K (i.e. the temperature at which SMC fluorescence will be minimized) and for SMC in DOTP at 248 K (i.e. the temperature at which SMC fluorescence will be maximized), white-light emission with coordinates of (0.333, 0.377) should be expected from the capsules loaded with BPEA-SMC mixtures, which lie very close to those corresponding to pure white color ((0.333, 0.333)).

This was confirmed by monitoring the fluorescence of a DOTP solution of BPEA ($1 \cdot 10^{-6}$ M) upon addition of increasing amounts of SMC at 298 K and $\lambda_{exc} = 428$ nm (Figure S3). Eventually, white light was generated with coordinates of (0.336, 0.365) ($c_{SMC} = 3.6 \cdot 10^{-5}$ M), which nearly matched the expected values. Importantly, very minor changes in the emission intensity of BPEA with the content of SMC were observed in this experiment, thus suggesting that energy transfer effects were insignificant in DOTP solution at the concentrations used. Therefore, under these conditions, a good estimate of the final color emitted by BPEA-SMC mixtures in solution could be simply obtained from the separate spectra of the dyes and their concentration ratio, a behavior that should also be preserved in our target liquid-filled capsules.

Synthesis of color-tunable white-light emitting liquid-filled capsules. For the synthesis of liquid-filled polyurea capsules (PU_DOTP), we applied an emulsion interfacial polymerization procedure previously developed by us (Figure 3a). Briefly, an oil-in-water emulsion was prepared by stirring a mixture of: (a) a DOTP solution of the dyes of interest and an oil-soluble commercial triisocyanate monomer (Desmodur® N 3300, Scheme S1); (b) an aqueous solution of a surfactant (sodium dodecylsulfate, SDS) and diethylenetriamine (DETA). Upon heating (333 K), the polymerization process initiated at the interface of the oil droplets, thus leading to the formation of the polyurea shell as well as the *in situ* encapsulation of the DOTP solution of the emitters. In this way, liquid-filled capsules bearing BPEA (BPEA@PU_DOTP), SMC (SMC@PU_DOTP) and a mixture of both dyes (BPEA-SMC@PU_DOTP) were

synthesized and then isolated by decantation and lyophilization as colored powder solids (Figure 3b and Figure S4a-b).

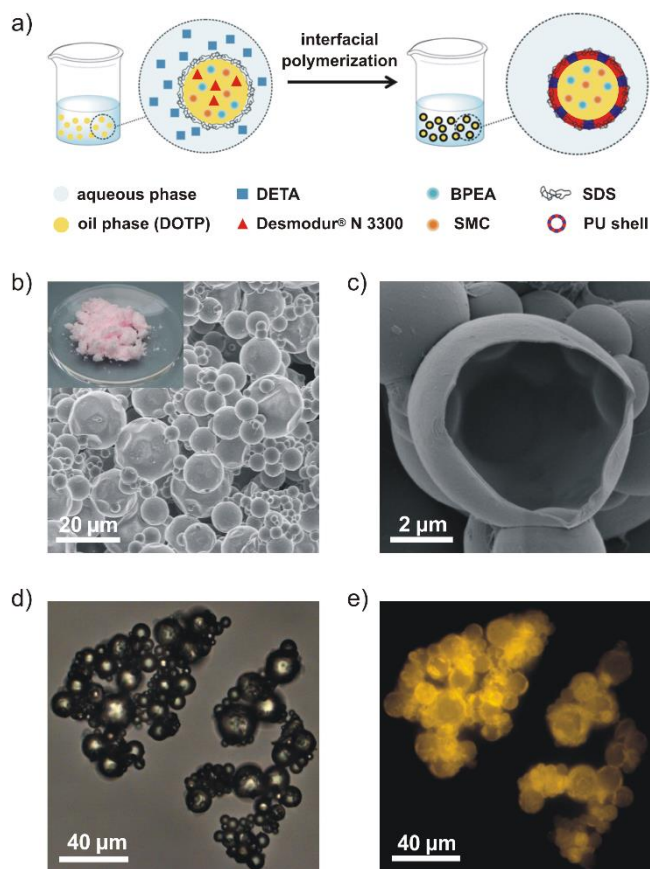


Figure 3. (a) Procedure used for the preparation of polyurea capsules loaded with DOTP solutions of BPEA and/or SMC via emulsion interfacial polymerization. (b-c) SEM images of BPEA-SMC@PU_DOTP capsules. The inset in (b) shows the pink powder solid obtained from the synthesis after lyophilization. A broken capsule exhibiting its hollow interior is observed in (c). (d-e) Optical (d) and fluorescence (e) microscopy images at room temperature of BPEA-SMC@PU_DOTP capsules stored for 6 months under ambient conditions ($\lambda_{exc} = 450\text{-}490\text{ nm}$, $\lambda_{det} > 500\text{ nm}$ in (e)).

Figure 3b-d and Figure S4c-f depict SEM and optical microscopy images of the capsules obtained, which presented spherical shapes and micrometer dimensions (14 ± 9 , 11 ± 10 and $8 \pm 5\ \mu\text{m}$ for BPEA@PU_DOTP, SMC@PU_DOTP and BPEA-SMC@PU_DOTP, respectively). The presence of some broken capsules enabled direct visualization of their hollow core (Figure 3c) and the liquid-filled core-shell structure was unambiguously ascertained from SEM and optical microscopy after mechanical crushing (Figure S5). In addition, this also allowed determination of the thickness of the polyurea shell (*ca.* 180-250 nm) and of the oil content of the capsules (*ca.* 88% of the total weight). In the absence of strong mechanical forces, however, PU_DOTP capsules preserved their morphology and com-

position, even when subjected to large temperature variations or stored under ambient conditions for long periods (Figure 3d and Figure S4c-d).

By analyzing the absorption spectrum of the liquid ejected upon mechanical crushing of the capsules, the dye encapsulation efficiencies could also be estimated. In general, significantly lower values were encountered for SMC (41%) than for BPEA (70%), probably due to the nonnegligible solubility of the former in the aqueous phase of the emulsion. In spite of this, successful encapsulation of both dyes was demonstrated by fluorescence microscopy. While selective fluorescence in the turquoise (BPEA@PU_DOTP) and orange-red (SMC@PU_DOTP) regions of the spectrum was registered upon encapsulation of individual chromophores (Figure S4e-f), a combined yellow emission was detected for BPEA-SMC@PU_DOTP (Figure 4e), thus confirming confinement of the two types of emitters within the same capsules. It must be noted, however, that the images registered in all these microscopy experiments were affected by incomplete detection of BPEA fluorescence ($\lambda_{det} > 500\text{ nm}$) and, therefore, they do not accurately illustrate the actual colors emitted by the capsules.

Actually, in the case of BPEA-SMC@PU_DOTP, the concentration of the two dyes in the initial DOTP solution was chosen so as to accomplish white light emission in the final capsules at room temperature ($1.4 \cdot 10^{-6}\text{ M}$ and $8.9 \cdot 10^{-5}\text{ M}$ for BPEA and SMC, respectively). To perform this estimation, an exhaustive experimental screening of PU_DOTP capsules loaded with different dye concentrations was not needed. Instead, owing to the inherent advantages of our approach that allows direct transfer of solution behavior to the solid state, it could be rationally predicted based on the following parameters: the optical properties of the separate chromophores and their diluted mixtures in DOTP, their different encapsulation efficiencies, and the wavelength to be used to simultaneously excite both types of dyes with low thermal variability ($\lambda_{exc} = 428\text{ nm}$). Notably, a different ratio of the dyes could be employed if white-light emission was needed to be achieved at another temperature and/or upon excitation at a distinct λ_{exc} , in which case the chromaticity coordinates could be also easily estimated from the emission spectra of the pure products.

Color-tunable white-light emission from liquid-filled capsules. Temperature-dependent fluorescence measurements were conducted for dye-loaded PU_DOTP capsules in solid powder state. In the case of BPEA@PU_DOTP and SMC@PU_DOTP, the emission spectra measured were equivalent to those already registered for the free dyes in DOTP solution at room temperature (Figure S6). As expected, this indicates that their optical properties in solution are preserved upon encapsulation. Moreover, similar thermal variations were observed, the fluorescence intensity of SMC@PU_DOTP drastically decreasing with temperature (Figure S7). However, smaller changes were detected for the capsules with respect to free solutions. For instance, when heating from 273 to 353

K, a *ca.* 65% emission reduction was determined for SMC@PU_DOTP, while a *ca.* 75% decrement had been measured before encapsulation. Most probably, these discrepancies are the result of inefficient heat diffusion from the temperature-controlled bath surrounding the solid powder samples to the internal core of the capsules

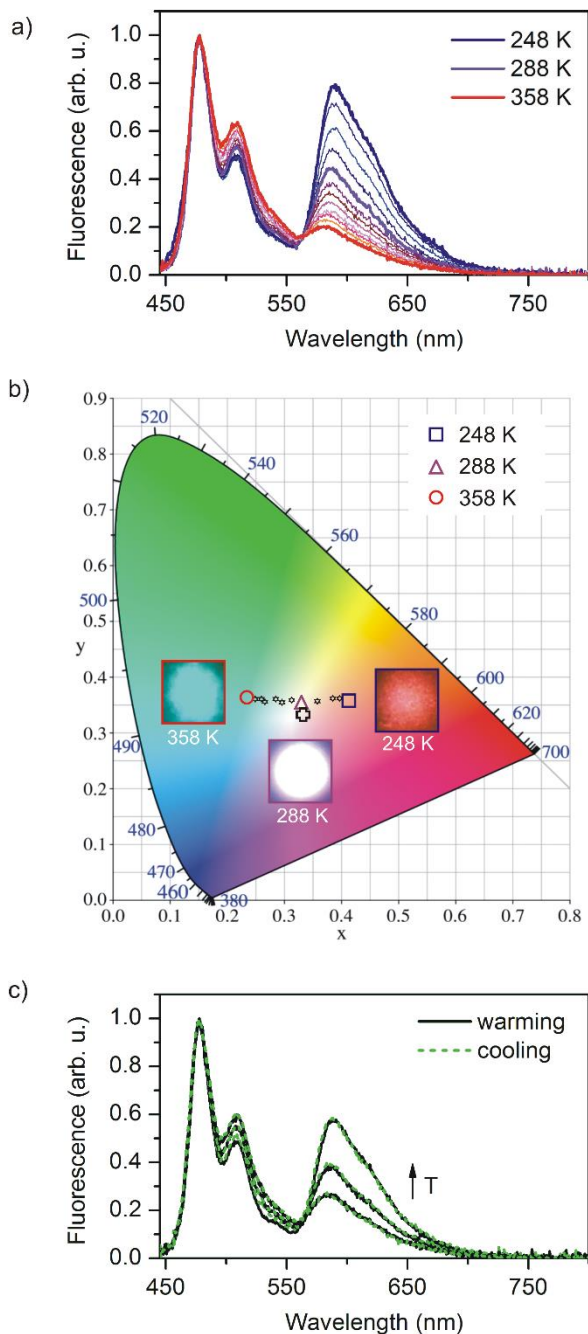


Figure 4. (a) Temperature dependence of the fluorescence emission spectra of BPEA-SMC@PU_DOTP ($\lambda_{\text{exc}} = 428$ nm). Spectra were measured every 10 K. (b) Temperature-dependent chromaticity coordinates of the emission of BPEA-SMC@PU_DOTP ($\lambda_{\text{exc}} = 428$ nm) in the CIE 1931 color space chromaticity diagram. The insets show photographs of the emission arising from the capsules at 248, 288 and 358 K. At 288 K "cool" white light was emitted with chromaticity coordinates of (0.330, 0.353). For comparison purposes, the

chromaticity coordinates for pure white light are also shown in the diagram (cross, (0.333, 0.333)). (c) Fluorescence emission spectra of BPEA-SMC@PU_DOTP ($\lambda_{\text{exc}} = 428$ nm) at 268, 298 and 328 K, which were measured during consecutive warming and cooling cycles along the 248-358 K range to demonstrate the reversibility of the optical changes observed.

where the thermally sensitive dye molecules lie. As a consequence, less extreme temperatures than those externally applied should be achieved in the capsule interior, although this small limitation in the temperature range amplitude is not expected to modify the behavior of our system.

The emission color variation of BPEA-SMC@PU_DOTP was monitored at $\lambda_{\text{exc}} = 428$ nm from 248 to 358 K, the largest temperature interval that could be scanned with our equipment. Figure 4a plots the fluorescence spectra measured under such conditions, while the resulting colors emitted at each temperature are shown in the CIE 1931 chromaticity diagram of Figure 4b. Clearly, dyes fluorescence behavior was not modified when mixed, and SMC emission intensity could be selectively tuned with temperature. As a result, color variation from bright rose to dark turquoise could be achieved within the 248-358 K range, which can be visually observed by the photographs taken to the emission stemming from the solid powder sample at the lowest and highest temperatures applied (Figure 4b). Noticeably, this color tuning process was found to be fully reversible, as demonstrated in Figure 4c showing the fluorescence spectra of the capsules at three different temperatures upon successive cooling-heating cycles.

Figure 4b also shows that, by thermally regulating the fluorescence intensity ratio between the turquoise- and orange-emitting dyes encapsulated, white light could be produced by BPEA-SMC@PU_DOTP. In particular, white-light emission with CIE 1931 chromaticity coordinates of (0.330, 0.353) was obtained at 288 K, which resemble those of pure white color ((0.333, 0.333)). These coordinates correspond to "cool" white light with a correlated color temperature of 5603 K that nearly matches the value of average noon sunlight (~ 5500 K). Remarkably, the precise color of the white emission arising from BPEA-SMC@PU_DOTP and the actual temperature at which it was observed nicely agree with the values anticipated from the preparation conditions of the system (CIE 1931 chromaticity coordinates of (0.336, 0.365) at $T = 298$ K). The minor differences found could be ascribed to several experimental factors, such as the effective temperature inside the capsules, deviations in the estimated dye encapsulation efficiencies, unexpected energy transfer processes in the final solid materials, or partial diffusion of the dyes to the solid polymer shell of the capsules. In spite of this, our results prove that the use of liquid-filled dye-loaded capsules ensures nearly direct transfer of the emission properties of bulk solutions to the solid state, thus providing a novel strategy for the rational design of white-light emitting materials. Moreover, the incorpora-

tion of thermoresponsive chromophores within the capsules further aids the attainment of white light by enabling fine tuning of the ultimate color emitted.

A further advantage of our approach towards tunable white-light emission is the capacity to disperse the liquid-filled capsules prepared in solid matrices without detrimentally modifying their properties. As a result, the designed optical behavior of these capsules could be directly exported to virtually any material of interest, thus allowing white-light emission to be accomplished with no need for additional work to establish the optimal experimental conditions for each system (i.e. emitters ratio and concentrations). To demonstrate this concept, we compared the fluorescence emission at room temperature of BPEA-SMC@PU_DOTP with those of different polymer thin films prepared by drop casting: (a) a poly(vinyl alcohol) (PVA) film loaded with BPEA-SMC@PU_DOTP capsules (BPEA-SMC@PU_DOTP@PVA), which preserved their shape and integrity within the polymeric matrix (Figure 5a); (b) a PVA and a poly(methyl methacrylate) (PMMA) films where BPEA and SMC dyes were directly dispersed at the same concentration as in the capsules (BPEA-SMC@PVA, BPEA-SMC@PMMA, Figure S8). As observed in Figure 5b, fluorescence spectra with variable BPEA/SMC emission ratios were measured for the BPEA-SMC@PVA and BPEA-SMC@PMMA films with respect to BPEA-SMC@PU_DOTP capsules. This can be ascribed to the different nature of the media surrounding the fluorescent molecules in each of these samples, which has an impact on their spectral properties, dye aggregation (i.e. energy transfer processes) and SMC tautomerization, and

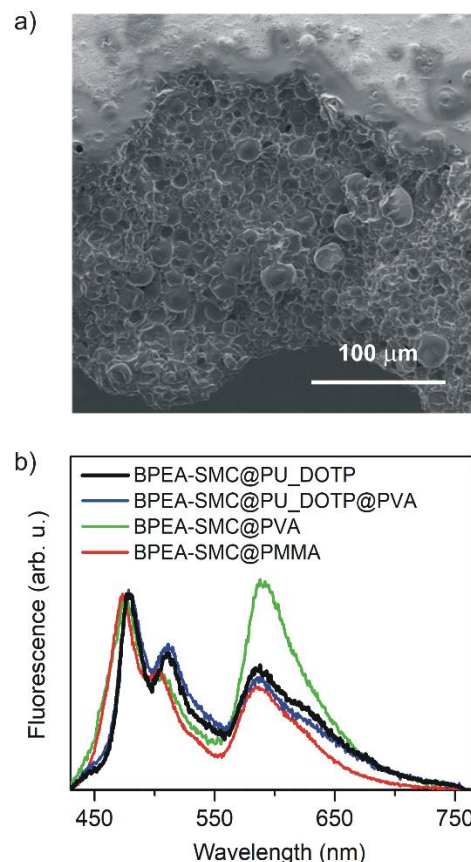


Figure 5. (a) SEM image of a broken edge of a PVA film loaded with BPEA-SMC@PU_DOTP capsules. (b) Fluorescence spectra at 298 K of BPEA-SMC@PU_DOTP capsules and polymer films BPEA-SMC@PU_DOTP@PVA, BPEA-SMC@PVA and BPEA-SMC@PMMA ($\lambda_{exc} = 405$ nm).

therefore critically affects the final emission of the system. By contrast, the fluorescence spectrum of the BPEA-SMC@PU_DOTP@PVA film fairly reproduced the emission from the capsules (Figure 5b), thus demonstrating successful transfer of their optical behavior to the solid matrix where they are embedded.

CONCLUSIONS

A new methodology is reported for the preparation of color-tunable white-light emitting materials that relies on the encapsulation of liquid solutions of two complementary fluorescent dyes, one of which is temperature-responsive. In this way, microstructured, solid state materials were produced, the emission of which: (a) reversibly varies from dark turquoise to bright rose by thermally modulating the fluorescence intensity ratio between the encapsulated dyes, and (b) provides white light at around room temperature. As such, the capsules obtained could not only be of use for lightning applications, but also for temperature sensing and imaging. Other additional advantages derive from the novel fabrication approach described. On the one hand, external fine tuning of the color produced can be accomplished, thus eventually warranting white-light emission. On the other hand, it

allows to directly reproduce the solution behavior of dye mixtures in the final liquid-filled capsules and, if necessary, in any solid matrix where these capsules are eventually dispersed. As a result, most of the drawbacks often encountered when attempting the realization of white-light emission in the solid state are circumvented, such as the need for repetitive and time-consuming experiments to obtain the optimal mixture conditions for each system or the detrimental effects observed on the emitter properties upon solvent drying. Importantly, the benefits resulting from the encapsulation of dye solutions can be easily expanded to other types of emissive molecules, thus providing a simple and general strategy for the fabrication of smart luminescent solid materials.

EXPERIMENTAL SECTION

Materials and methods. BPEA (Sigma-Aldrich), DOTP (Sigma-Aldrich), Desmodur[®] 3300 (Bayer), diethylenetriamine (Sigma-Aldrich), SDS (Sigma-Aldrich), PVA (Kuraray Poval[®] 4-88) and PMMA (Sigma-Aldrich, $M_w = 120000$) were purchased and used without further purification. SMC was synthesized as previously reported by us.³⁰ Distilled water was used in all the procedures. Emulsification was achieved by means of high shear homogenization using an IKA ULTRA-TURRAX[®]. Lyophilization was performed using a TELSTAR CRYODOS -50 freeze dryer with one single stage compressor, giving a refrigerating power of 450 W and a final temperature of 223 K. SEM images were acquired with a FEI Quanta 650F ESEM microscope at 2 kV acceleration voltages. Microcapsules were directly deposited onto SEM metal stubs covered with aluminum tape. Optical and fluorescence microscopy images were obtained using a Zeiss Axio Observer Z1m inverted optical microscope equipped with a motorized XY stage, a halogen lamp (Philips 7724) for bright-field imaging, a Hg lamp excitation source (HBO 103 W/2) for fluorescence imaging, an AxioCam HRc digital camera and standard filters. Images of crushed capsules and liquid ejection were obtained by smashing the capsules of interest between two cover glass slides. Steady-state UV-vis absorption measurements were recorded on a HP 8453 spectrophotometer. Fluorescence emission spectra were acquired using a custom-made spectrofluorometer, where a cw laser ($\lambda = 405$ nm, SciTec; $\lambda = 473$ nm, SDL-BS-300) or a pulsed Nd:YAG-pumped optical parametric oscillator ($\lambda = 428$ nm, Brilliant, Quantel) is used as an excitation source and the emitted photons are detected in transmission or reflection using an Andor ICCD camera coupled to a spectrograph. Temperature-controlled absorption and emission measurements were conducted using a refrigerator circulating bath (Huber MPC-K6) connected to the sample holder. Fluorescence quantum yields in solution were determined using the standard method⁴⁹ and relative to BPEA in toluene ($\Phi_f = 1.0^{49}$) and SMC in acetonitrile ($\Phi_f = 0.76^{30}$). The same excitation wavelength was used for both the sample of interest and the standard, and solutions with absorbance values below 0.05 were measured to prevent inner-filter effects.

Synthesis and characterization of PU_DOTP capsules.

PU_DOTP capsules were synthesized following the procedure previously optimized by us for preparing polyurea thermochromic capsules.³⁴ First, DOTP solutions containing the desired amount of dye molecules were prepared ($2.0 \cdot 10^{-6}$ M for BPEA@PU_DOTP, $1.0 \cdot 10^{-4}$ M for SCM@PU_DOTP, and $1.4 \cdot 10^{-6}$ M and $8.9 \cdot 10^{-5}$ M for BPEA and SMC in BPEA-SMC@PU_DOTP, respectively. Dyes (BPEA or SMC) were dissolved in the minimum volume of chloroform (to help dyes dissolution) and the resulting solutions were added to the appropriate amount of DOTP. For dye mixtures, the convenient volumes of each solution were mixed to attain the desired concentrations. After chloroform evaporation, Desmodur[®] N 3300 (0.29 g) was then dissolved in 3.04 g of the dye-DOTP solution. At the same time, 5.7 mL of SDS in water (2 wt %) were introduced in a 25 mL beaker and vigorously stirred by high shear homogenization (5000 rpm). The DOTP solution was next added dropwise to the stirred aqueous solution and emulsification was performed for 10 minutes. The beaker was then introduced in an oil bath heated at 333 K and the emulsion was magnetically stirred at 1500 rpm. Subsequently, an aqueous solution of DETA (47 μ L of DETA in 885 μ L H₂O) was slowly added to the emulsion (200 μ L/min) with a syringe pump (NE-1000, New Era Pump Systems, Inc) and the polymerization was allowed to proceed for 2 hours at 333 K. Once the reaction was finished, 60 mL of Na₂SO₄ aqueous solution (1 M) were added to the resulting suspension in order to induce the creaming process, since the density of DOTP is very similar to water ($\rho_{\text{DOTP}} = 0.984$ g/mL³⁹). The mother liquor was then removed, the suspension was washed repetitively with water upon centrifugation ($\times 4$, 4 min, 6000 rpm) and the final capsules were lyophilized. To determine capsule liquid loading and encapsulation efficiency, a known amount of capsules was subjected to physical crushing in an agate mortar. The broken capsules were then washed with a controlled volume of chloroform and filtrated to collect separately the solution encapsulated and the broken shells. The liquid content was estimated from the weight loss after capsule crushing, comparing the weight of the isolated shells with that of the intact capsules. Dye concentration in the liquid core was obtained from absorbance measurements performed on the mother liquor collected during filtration. Encapsulation efficiency was finally calculated from dye concentration in the oil core and in the initial solution employed for capsule synthesis.

Preparation of polymer thin films. Polymeric films were prepared through the drop-casting method. The BPEA-SMC@PU_DOTP@PVA film was obtained by first dispersing 164 mg of dry capsules into 3.3 g of a PVA water solution previously prepared (20 wt.%) and then casting the resulting suspension onto a polystyrene Petri plate of 5.5 cm of diameter. Prior to casting the suspension, it was sonicated at 30°C for 1 h to assure homogeneous capsules dispersion. The BPEA-SMC@PVA film was prepared by mixing the suitable amounts of acetonitrile solutions of BPEA ($5.81 \cdot 10^{-4}$ M) and SMC ($1.4 \cdot 10^{-2}$ M) with 3.3 g of a

PVA aqueous solution (20 wt.%) and casting the obtained homogeneous solution onto a polystyrene Petri plate of 5.5 cm of diameter. The BPEA-SMC@PMMA film was obtained by mixing appropriate amounts of acetonitrile solutions of (5.81 10^{-4} M) and SMC (1.4 10^{-2} M) with 3.5 g of a PMMA chloroform solution (20 wt.%) and casting the obtained mixture onto a glass Petri plate of 5.0 cm of diameter. In all cases the solvents were evaporated at room temperature over time. The flexible films could be peeled out from the corresponding containers to be characterized.

ASSOCIATED CONTENT

Supporting Information. Additional data on the synthesis and characterization of liquid-filled capsules loaded with fluorescent dyes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ABBREVIATIONS

BPEA, 9,10-bis(phenylethynyl)anthracene; SMC, spirocyclic Meisenheimer complex; PU, polyurea; DOTP, dioctyl terephthalate; CIE, Commission Internationale de l'Éclairage; PU_DOTP, DOTP-filled polyurea capsules; SDS, sodium dodecyl sulfate; PVA, poly(vinyl alcohol); PMMA, poly(methyl methacrylate).

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