Liquid-Filled Valence Tautomeric Microcapsules: A Solid Material with Solution-Like Behavior

Nuria Alexandra Vázquez-Mera, Claudio Roscini, Jordi Hernando, and Daniel Ruiz-Molina**

The integration of stimuli-responsive valence tautomeric (VT) molecular systems into solid materials without compromising their functionality is a major bottleneck for the use of these compounds in high-added value applications. In this work, an innovative, simple, and universal approach is described to tackle this challenge based on the confinement of the active species into liquid-filled polymeric capsules. A microstructured solid with optimized solution-like behavior is obtained in this way, whose VT properties can be rationally tuned upon variation of the encapsulated solvent. Incorporation of the resulting capsules into thin films or other matrices of interest allows successful transfer of valence tautomerism from the liquid phase to solid materials, thus paving the way to the fabrication of functional devices based on spin transition compounds.

1. Introduction

Valence tautomeric (VT) complexes combining transition metal ions and electroactive ligands are coordination compounds with at least two nearly degenerated electronic states.[1] As such, they present different electronic isomers or valence tautomers, which reversibly interconvert via a metal-ligand intramolecular electron transfer promoted by an external perturbation (e.g., temperature, light, or pressure).[2] This, together with the different structural, optical, and magnetic properties that their electronic isomers exhibit, makes VT complexes excellent candidates for the fabrication of molecular memories and spintronic devices.[3] An enormous interest has therefore been drawn toward this field since the first report on valence tautomerism back in the 1980s,[4] which has led to the development of a large variety of VT systems and the identification of the main factors governing their electronic interconversion.[1,5]

Although most of these factors are related to the composition and structure of the compound of choice (e.g., metal and ligand characteristics,[1,5] steric hindrance,[6] donor/acceptor abilities of the counter ligand,[7] and/or the volume and Coulombic interactions of the counterion),[8] the properties of valence tautomers also show a critical dependence on the surrounding medium,[9] which is often hard to systematize.[10] For instance, whereas most VT complexes undergo thermally induced interconversion in solution, the number of examples preserving this behavior in the solid state is rather limited.[10] In those cases, the occurrence of valence tautomerism and, if so, the temperature at which it takes place have been found to be very sensitive to a variety of parameters, such as the crystallinity of the solid state complexes,[11] the intercalation of solvent molecules within the crystalline network,[12] or the properties of the surrounding matrix when they are dispersed in thin films[13] or as liquid crystals.[14] This leads to an overwhelming lack of reproducibility in valence tautomeric behavior when transferring VT complexes between different media (e.g., from solution to the solid state), which has become one of the greatest roadblocks to their use in high added-value applications. Despite the great improvements made toward this aim, the promise of solid VT functional devices working at room temperature has not completely materialized yet, as their activity strongly depends on the fabrication methodology, the concentration of the active molecular system and the material in which they are finally integrated.

To achieve robust VT-based devices that could be easily handled and integrated in solid materials, the main approach so far followed is the micro-/nanostructuring of VT complexes. With this aim, Schultz et al. described the preparation of 2 nm gold nanoparticles decorated with a cobalt VT compound, which had to be previously functionalized with a mercapto linker.[15] Alternatively, our group has reported amorphous spherical coordination polymer nanoparticles composed of cobalt-based monomeric VT complexes with a broad range of applications,[16] and we have also achieved the encapsulation of VT molecules within polymeric solid micro/nanoparticles.[13] More recently, the control of the charge distribution in a gold monolayer of switchable cobalt–catechol valence tautomers has been attained by means of thermal and optical stimuli.[17] Although VT in

N. A. Vázquez-Mera, Dr. J. Hernando
Departament de Química
Universitat Autònoma de Barcelona
08193 Cerdanyola del Vallès, Spain
E-mail: jordi.hernando@uab.cat

N. A. Vázquez-Mera, Dr. C. Roscini, Dr. D. Ruiz-Molina
Consejo Superior de Investigaciones Científicas (CSIC)
Campus UAB, 08193 Bellaterra, Spain
E-mail: druiz@cin2.es

N. A. Vázquez-Mera, Dr. C. Roscini, Dr. D. Ruiz-Molina
Institut Català de Nanociència i Nanotecnologia (ICN2)
Edifici ICN2
Campus UAB, 08193 Bellaterra, Spain

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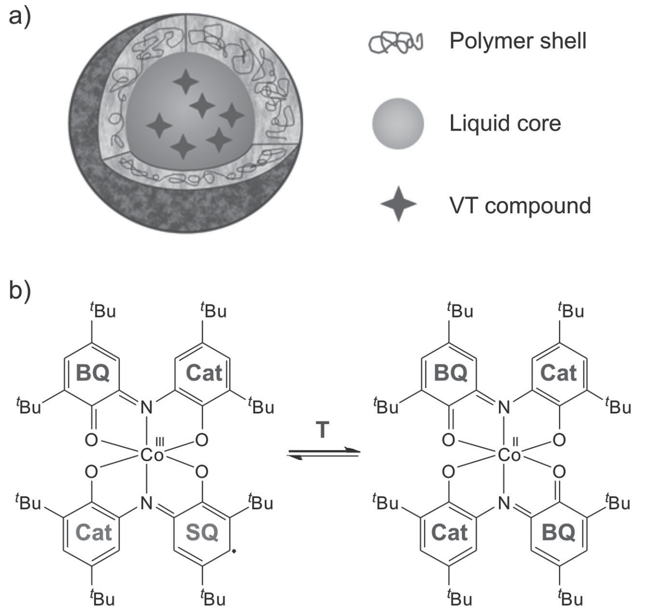

Scheme 1. a) Schematic structure showing the different components of a liquid-filled VT microcapsule. b) Structure and thermally induced tautomerization of the VT system selected (**1**).

the solid state could be successfully observed in all these examples, the approaches applied were rather specific in terms of the metal complex, concentrations, and/or surrounding matrix used and they could hardly be expanded to other compounds and structured media.

To overcome these limitations, in this work we report a universal methodology for the development of VT solid materials, which relies on the encapsulation of the active molecular systems into liquid-filled polymeric capsules (**Scheme 1**a). The resulting solid material should therefore exhibit optimized solution-like responses and, more importantly, enable the original VT behavior to be maintained even after dispersion of the capsules in any matrix of interest. To achieve this goal, a general, simple, and versatile procedure is presented, which i) uses commercially available reactants for the preparation of the target liquid-filled capsules, ii) does not require chemical modification of the VT complex of choice, and iii) allows fine tuning of its VT properties by directly replacing the encapsulated solvent.

As a proof of concept, in this work we focused on compound [Co^{III}(Cat-N-BQ)(Cat-N-SQ)] (**1**, Scheme 1b), where a cobalt ion is coordinated to two units of the O,N,O′-tridentate Schiff base ligand 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine. This complex shows VT behavior and thermally interconverts between its Co(III) and Co(II) isomers by intramolecular oxidation of the radical dianionic form of one of its ligands ((Cat-N-SQ)$^{\bullet 2-}$) into the corresponding monoanionic species ((Cat-N-BQ)$^{-}$).[18] Aside from this, compound **1** was selected for our study because of two additional properties:[2,10] i) high chemical stability and resistance to atmospheric oxygen and ii) remarkably different VT behavior when directly transferred from solution to the solid state, a situation aimed to be overcome by the novel approach presented herein.

2. Results and Discussion

2.1. Preparation of Liquid-Filled Microcapsules

Liquid-filled capsules of **1** were obtained via interfacial polymerization, a method previously used by us to synthesize photochromic polyamide microcapsules.[19] In this case, however, their shells were made of polyurea (PU) to prevent chemical degradation of **1** during the polymerization reaction. Thus, PU microcapsules filled with a 5×10^{-4} M toluene solution of complex **1** (**1**@PUtol) were obtained through interfacial polymerization in an oil-in-water emulsion (**Figure 1**a) composed of i) a toluene solution of **1** and an oil-soluble commercial triisocyanate monomer (Desmodur N 100) and ii) an aqueous solution of a stabilizer (polyvinylalcohol, PVA) and a water-soluble triamine monomer (diethylenetriamine, DETA). The addition of DETA to the emulsion and heating at 333 K triggered the polymerization process 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 toluene solution of the VT complex. After decantantion and lyophilization, a purple brown solid was obtained preserving the color of the initial solution of **1**, which suggested the successful incorporation of the VT complex into the microstructured material.

Figure 1b,c shows scanning electron microscopy (SEM) images of the obtained capsules, which had spherical shape and average diameters ranging between 17 and 63 μm depending on the reaction conditions (Table S1 and Figure S1, Supporting Information). Different experimental observations confirmed the presence of toluene solutions of **1** in the interior of the impermeable capsules: i) their density was found to be lower than water ($\rho_{\text{toluene}} = 0.8669$ g mL^{-1}) since they moved toward the air–liquid interface in aqueous suspension (Figure S2a, Supporting Information); ii) liquid ejection was observed when mechanically crushing the capsules (Figure 1c and Figure S2b,c, Supporting Information), the UV–vis spectrum of the collected liquid showing the typical absorption bands of **1**; and iii) SEM images of broken capsules revealed their hollow interior and the thickness of the polyurea shell, which varied according to the capsule size between ≈100 and 850 nm (Figure 1d and Figure S3, Supporting Information). From the liquid liberated upon capsule crushing, we estimated that the liquid content represented ≈81 wt% of **1**@PUtol total mass. Encapsulation efficiencies of ≈88% and loadings of VT compound **1** of 0.04 wt% were finally determined by UV–vis absorption spectroscopy.

2.2. Valence Tautomeric Behavior of Liquid-Filled Microcapsules

Once prepared, the thermally induced valence tautomeric behavior of **1**@PUtol was investigated and compared to that of a bulk toluene solution of the same complex. For this, variable-temperature UV–vis absorption experiments were performed, which required the use of an integrating sphere-based spectrometer in the case of **1**@PUtol. The diffuse reflectance measurements registered for this solid sample were plotted as the corresponding Kubelka–Munk functions (F(R)), which give a good estimate of light absorption by opaque materials.[20]

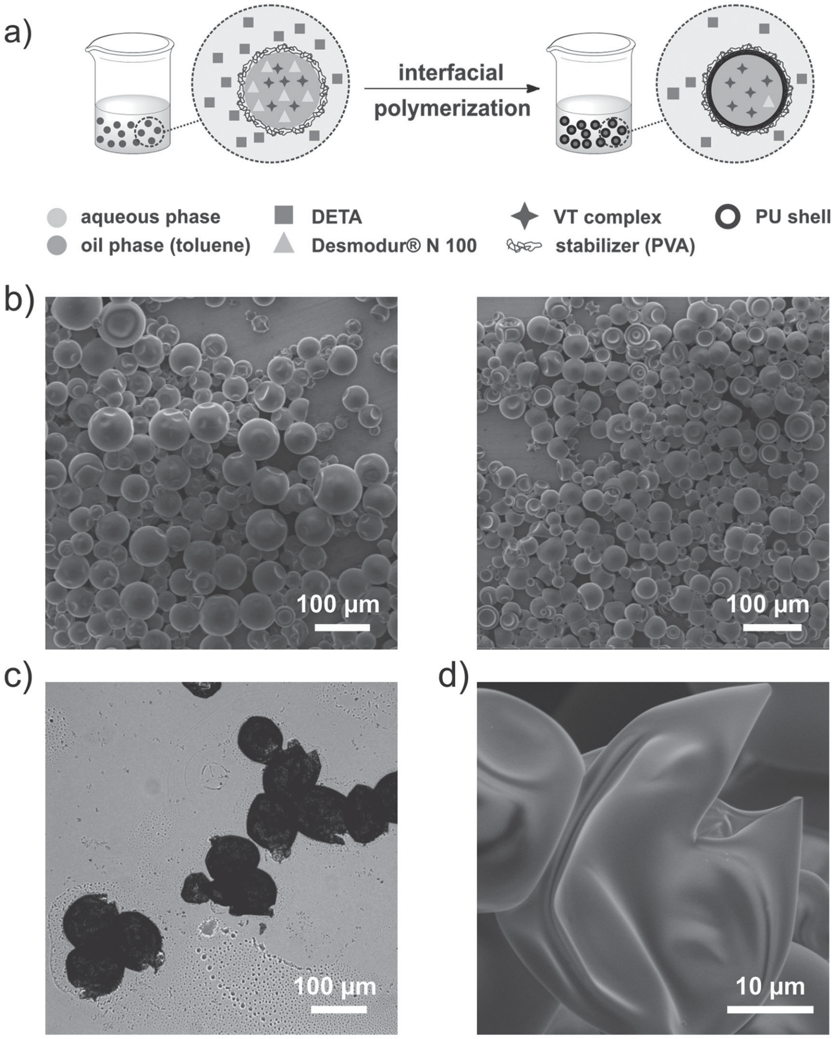

Figure 1. a) General procedure used to prepare polyurea toluene-filled capsules of **1** by interfacial polymerization. b) SEM images of **1**@PUtol. c) Optical microscopy image of the capsules after mechanical crushing, where broken PU shells lying flat onto the substrate and ejected toluene droplets can be observed. d) SEM image of crushed capsules of **1**@PUtol.

Figure 2a,b plots the results obtained within the integrating sphere spectral range (400–800 nm), which allowed large and clear changes to be observed for both samples that are indicative of the interconversion between the two tautomers of the complex. At low temperatures (<300 K), free and encapsulated toluene solutions of **1** exhibited the typical absorption bands attributed to the low spin isomer *ls*-Co(III), with maxima at 436, 530, 720 (shoulder), and 801 nm (for other absorption bands outside the 400–800 nm range see Figure S4a, Supporting Information).[18d] Upon heating, the isomerization to the high spin tautomer *hs*-Co(II) occurred and the intensity of the *ls*-Co(III) absorption bands decreased, while new bands between 600 and 750 nm, a maximum centered at 796 nm and an isosbestic point at 570 nm appeared (Figure 2b and Figure S5a,b, Supporting Information). To plot the progress of the tautomeric equilibrium with temperature, our spectral data were used to estimate the thermal dependence of the molar fraction of the *hs*-Co(II) isomer of **1** in free toluene solution and inside PUtol capsules, which proved that both samples present very similar interconversion behavior (Figure S5c, Supporting Information). Actually, this could be further corroborated by naked eye owing to the color difference between the two electronic isomers of **1**, which is preserved in the interior of the capsules. Thus, while **1**@PUtol displayed the typical blue gray color of *hs*-Co(II) at high temperatures, the capsules turned purple brown at room temperature where both tautomers coexist with similar concentrations in toluene solution[13] (Figures 2c and S4b, Supporting Information). Altogether, these results unambiguously demonstrate the potential of our approach to allow direct transfer of VT behavior from solution to the solid state.

To fully ascribe the solution-like VT properties of **1**@PUtol to its liquid interior, further experiments were performed. First, the optical behavior of the capsules was studied after mechanical crushing and toluene evaporation. The resulting solid material did not show significant temperature dependence of its diffuse reflectance spectrum and the *ls*-Co(III) isomer of **1** was observed to dominate over the whole temperature range studied (Figure S6, Supporting Information). Partial crystallization of **1** upon solvent evaporation should account for this result, since this process is known to shift its electronic interconversion to much higher temperatures[18b] and, therefore, hampers the direct use of this compound in the solid state for the preparation of thermo-responsive functional materials. In a second step, the valence tautomerism of **1** was evaluated upon dispersion into solid PU particles of the same composition as the shell of the liquid-filled capsules (see the Supporting Information, Figure S7, Supporting Information). For the resulting sample, we did not observe either any relevant temperature dependence of its diffuse reflectance spectrum and only the bands related to the *ls*-Co(III) isomer of the complex were detected over the whole temperature range (Figure 2d). This shows that direct dispersion of **1** into a PU matrix also negatively affects its VT properties, whose reversible interconversion could only be preserved by means of the approach introduced herein based on the use of liquid-filled capsules.

2.3. Tailoring the Valence Tautomeric Behavior of Liquid-Filled Microcapsules

A further advantage of our strategy is to allow facile variation of the encapsulated solvent, thus enabling the thermal response of the valence tautomer of choice to be modified in a controlled manner. To demonstrate this concept, Miglyol 812 was selected

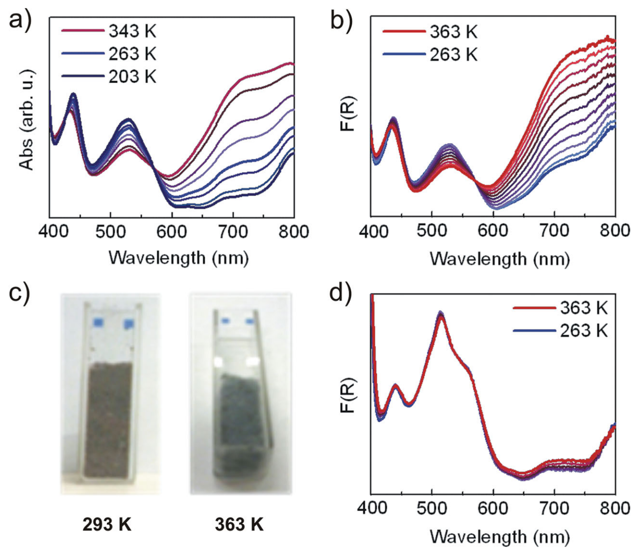

Figure 2. a,b) Temperature dependence of the absorption and diffuse reflectance spectra of a bulk toluene solution of **1** (5.7×10^{-4} M) and **1**@PUtol, respectively. c) Photographs of **1**@PUtol capsules at 293 and 363 K, which displayed different colors due to the electronic interconversion of **1**. d) Temperature dependence of the diffuse reflectance spectrum of **1** encapsulated within solid PU particles.

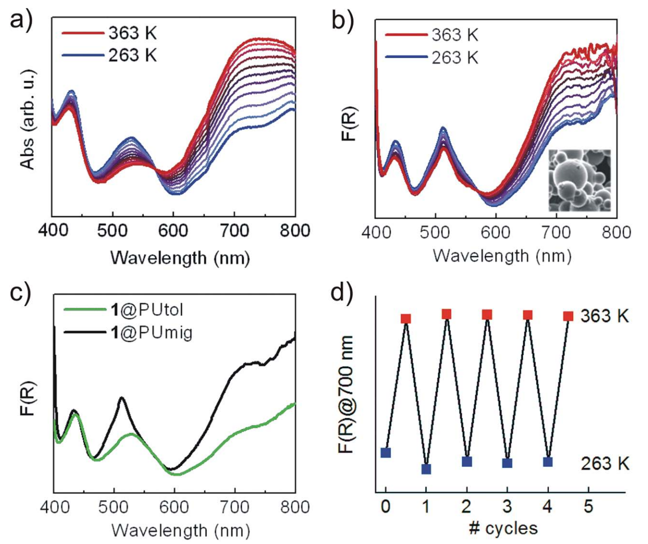

Figure 3. a,b) Temperature dependence of the absorption and diffuse reflectance spectra of a Miglyiol 812 solution of **1** (2.2×10^{-5} M) and **1**@PUmig, respectively. The inset in (b) shows a SEM image of **1**@PUmig capsules. c) Diffuse reflectance spectra of **1**@PUtol and **1**@PUmig at room temperature (293 K). While **1**@PUtol shows spectral features from both isomers of the complex, the spectrum of **1**@PUmig mainly arises from the *hs*-Co(III) tautomer. d) Variation of the F(R) function at 700 nm for **1**@PUmig upon application of several cooling–heating cycles from 263 to 363 K.

as an alternative solvent to toluene. Miglyol 812 is a commercially available oil based on a mixture of caprilic and capric triglycerides, whose higher boiling point and larger viscosity enhances the stability of liquid-filled capsules against solvent evaporation and diffusion through the shell even at high temperatures.[19] More importantly, Miglyol 812 has a different solvation effect on the electronic interconversion of **1** and, as such, it allows variation of its thermochomic response. When measuring the UV–vis spectra of a bulk Miglyol 812 solution of **1**, the same types of bands and thermally induced changes as those previously registered in toluene were measured (**Figure 3**a and Figure S11, Supporting Information). However, the spectral features arising from the *hs*-Co(II) isomer of **1** in Miglyol 812 were found to expand over a larger temperature range, thus indicating that the tautomerization process of this complex had been shifted to lower temperatures. Actually, we estimated that the temperature at which both tautomers of **1** exist in a 1:1 ratio (critical temperature, T_c) was around 60 K lower for Miglyol 812 than toluene, for which a T_c value of 300 K had been determined by ^{1}H NMR.[21]

Prompted by this solvent dependence, we prepared PU microcapsules (**1**@PUmig) filled with Miglyol 812 solutions of **1** (4.6×10^{-5} M) and using a similar strategy to that previously described for **1**@PUtol. Spherical particles with average diameters ranging from 3 to 66 µm were obtained by varying the experimental conditions, whose liquid interior was confirmed by different characterization techniques (Table S2 and Figures S8–S10, Supporting Information). From the liquid liberated by the capsules upon mechanical crushing, we determined that the liquid content represented about 90 wt% of capsule total mass, while the encapsulation efficiency and VT complex loading were estimated to be ≈90% and 0.004 wt%, respectively. Subsequent diffuse reflectance spectroscopy studies showed that **1**@PUmig fairly reproduced the behavior of free Miglyol 812 solutions, both in terms of the absorption bands registered and their thermal dependence arising from electronic interconversion of **1** (Figure 3b and Figure S12, Supporting Information). This does not only prove the general applicability of our methodology to prepare solid materials displaying solution-like VT properties, but also demonstrates its simplicity for enabling systematic variation of their thermal response. Indeed, replacement of toluene by Miglyol 812 as the liquid core of the capsules made the resulting materials present different colors at room temperature (Figure 3c) and interconvert at distinct T_c values.

The use of a nonvolatile oil as encapsulating solvent notably increased the thermal stability of **1**@PUmig, which enabled this microstructured material to retain its morphology upon standing at ambient conditions for at least one year and even after being subjected to temperatures as high as 370 K. In addition, it allowed us to perform successive cooling-heating cycles to investigate the fatigue resistance of the material prepared. As shown in Figure 3d, the amplitude of the thermal modulation between 263 and 363 K of the F(R) function at 700 nm did not significantly vary along several of these cycles, which confirms the robustness of the capsules and the reversibility of the incorporated VT system.

2.4. Thin Films Loaded with Liquid-Filled Microcapsules

To fully explore the potential of our strategy to generate solid devices showing VT properties, we finally considered the preparation of thin films and coatings. With this aim, **1**@PUmig capsules were embedded in film-forming PVA matrices by simply drop casting a water suspension of this polymer and the

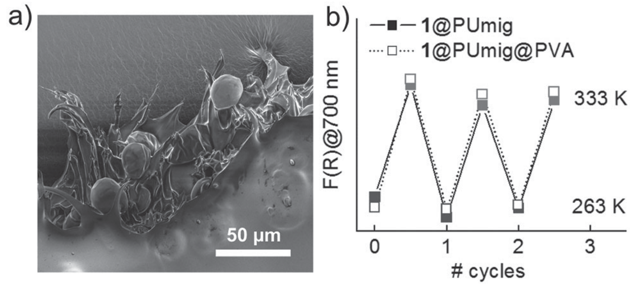

Figure 4. a) SEM image of a broken edge of a PVA film loaded with **1**@PUmig capsules. b) Variation of the F(R) function at 700 nm for **1**@PUmig and **1**@PUmig@PVA upon application of several cooling–heating cycles from 263 to 333 K.

liquid-filled particles (**1**@PUmig@PVA, Figure S13, Supporting Information). Rather uniform dispersion of the capsules was achieved in these films, where they preserved their morphology (**Figure 4**a) and, accordingly, their solution-like behavior. As a proof of that, Figure 4b plots the diffuse reflectance at 700 nm of **1**@PUmig and **1**@PUmig@PVA upon consecutive cooling-heating cycles. In this case, however, a narrower thermal range was scanned (263–333 K) due to the limited T_g value of the PVA matrix ($T_g \approx 358$ K). In spite of this, the spectral variations and the reversible VT behavior obtained for isolated capsules was clearly maintained in the PVA film, as demonstrated by the similar relative changes in F(R)@700 nm determined over the 263–333 K range (36% and 38% for **1**@PUmig and **1**@PUmig@PVA, respectively). Similar results were obtained for other polymeric films assayed (e.g., polyvinylpyrrolidone) and they should be extrapolable to any matrix of choice compatible with the VT complex-loaded liquid-filled capsules. Therefore, this uncovers the capability of our approach to undergo the whole process of transferring valence tautomerism from solution to solid functional materials.

3. Conclusion

Liquid-filled polymeric capsules containing a cobalt-based VT complex have been successfully prepared in this work. These particles as well as the materials resulting from their dispersion into solid matrices exhibit solution-like thermochromic behavior, thus demonstrating the development of a universal platform for the future fabrication of VT devices that can be handled and integrated without compromising its functionality. Moreover, fine tuning of the VT response was demonstrated by directly replacing the solvent used in the encapsulation process. This, together with its simplicity and the lack of synthetic modification of the active molecular complex, makes this methodology very appealing for the fabrication of solid functional materials based on spin transition materials.

4. Experimental Section

*Preparation of **1**@PUtol*: Toluene-filled polyurea capsules were prepared using a synthetic experimental procedure adapted from previous work.[22] Desmodur N 100 (1 g) was dissolved in 5.32 g of a toluene solution containing VT complex **1** (0.51 mg mL^{-1}). The resulting solution was added to a 50 mL beaker containing 20 mL of PVA in water (2 wt%) and was emulsified for 5 min using magnetic stirring (1500 rpm) or high shear homogenization (5000 rpm) according to the desired capsule size. Then, an aqueous solution of DETA (189 µL of DETA in 3.54 mL H_2O) was added dropwise and the emulsification rate was kept for 5 min more. Afterward, the beaker was introduced in an oil bath heated at 333 K and the polymerization reaction was allowed to proceed for 2 h under magnetic stirring (1500 rpm). Once the stirring was stopped, the capsules moved toward the top of the water suspension. The mother liquor was then removed (centrifugation was employed if needed: 5 min, 6000 rpm) and capsules were washed repetitively with water (×3) and lyophilized.

*Preparation of **1**@PUmig*: A similar procedure was used to prepare polyurea capsules filled with Miglyol 812 oil. In this case, however, the commercially available triisocyanate Desmodur N 3300 was used instead. Desmodur N 3300 (1 g) was dissolved in 10.64 g of a miglyol solution containing VT complex **1** (0.04 mg mL^{-1}). The resulting solution was added to a 50 mL beaker containing 20 mL of sodium dodecyl sulfate (SDS) in water (2 wt%) and was emulsified for 5 min using magnetic stirring (1500 rpm) or high shear homogenization (5000 or 20 000 rpm) according to the desired capsule size. Then, an aqueous solution of DETA (189 µL of DETA in 3.54 mL H_2O) was added dropwise and the emulsification rate was kept for 5 additional min. Afterward, the beaker was introduced in an oil bath heated at 333 K and the polymerization reaction was allowed to proceed for 2 h under magnetic stirring (1500 rpm). Once the stirring was stopped the capsules moved toward the liquid–air interface. The mother liquor was then removed and the suspension was washed repetitively with water upon centrifugation (×3: 5 min, 6000 rpm). Finally, capsules were lyophilized.

*Preparation of **1**@PUmig@PVA*: 164 mg of microcapsules were dispersed in 6 mL of a PVA water solution (6 wt%). The mixture was sonicated at room temperature for a few minutes (5 min) to obtain a homogeneous suspension. The suspension was then poured into a plastic petri plate (5 cm of diameter) and the water was left to evaporate over time (48 h) at room temperature to obtain a homogenous opaque PVA film.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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