Light-Triggered Self-Assembly of a Spiropyran-Functionalized Dendron into Nano-/Micrometer-Sized Particles and Photoresponsive Organogel with Switchable Fluorescence

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The synthesis, self-assembly, and spectroscopic investigations of spiropyran (SP)-functionalized dendron 1 are reported. Under UV light irradiation, assembly of 1 into nano-/microparticles occurs due to the transformation of the closed form of SP into the open merocyanine (MC) form. The formation of these nano-/microparticles is confirmed by transmission electron microscopy (TEM) and dynamic light scattering (DLS) experiments in addition to the confocal laser scanning microscopy (CLSM) measurements. These nano-/microparticles exhibit relatively strong red emission. It is interesting to note that the direct cooling of the toluene/benzene solution of 1 to 0 °C leads to gel formation. Multivalent π–π interactions due to the dendron in 1 may be the driving-force for the gelation. The UV light irradiation cannot destroy the gel phase, and in fact, the gel–gel transition is successfully realized. The purple-blue gel exhibits relatively strong red fluorescence; moreover, the fluorescence can be reversibly switched by alternating UV and visible light irradiation. The results clearly indicate that the MC form after aggregation becomes more stable and fluorescent.

1. Introduction

Spiropyran (SP) molecules constitute an important class of photochromic compounds. It is well known that the closed form of SP can be transformed into the open (merocyanine, MC) form under UV light irradiation, and the MC form can revert to the closed form under visible light irradiation or heating.[1] Because of their photochromic behavior, SP molecules have been investigated extensively for optical memories, switches, and displays.[2,3] A number of molecular switches and logic gates based on SP derivatives are reported.[4–10]

Meanwhile, assemblies of SP compounds and relevant photomodulation have also attracted attention. In the 1970's, Krongauz et al. reported the formation of MC aggregates (referred to as "quasicrystals") upon UV irradiation of SP molecules in aliphatic hydrocarbons.[11] They also concluded that the crystalline cores were composed of J-aggregate-like stacks of the MC form based on spectral studies. Sato et al. reported recently the observation of micrometer-sized long-lived crystals generated by prolonged UV irradiation of the solutions of SP molecules.[12] The aggregation of the MC form was also observed for the polymer with SP-containing side chains.[13] These results indicate that the MC form tends to aggregate, probably due to its zwitterionic nature, unlike the closed form of SP. Additionally, the reversible interconversion between the closed and MC forms can also influence the assembly of certain polymers.[14] Recent studies from Li et al. show that the MC aggregates in the hydrophobic cavities of polymer nanoparticles exhibit strong red emission.[15]

Self-assembly of certain organic molecules, referred to as low-molecular-weight gelators (LMWGs), through weak intermolecular interactions (such as H-bonding, π–π stacking and van der Waals interactions) can lead to gelation of organic solvents and form organogels.[16] Organogels based on LMWGs with functional groups have been the target of increasing attention in recent years because of various potential applications as soft materials.[17–30] For instance, photochromic organogels featuring bisthienylethene with intriguing optical properties have been studied.[31–33] Some SP-functionalized macromolecular gels have also been reported.[34] However, to the best of our knowledge, LMWGs with the SP moiety still remain rare.[35,36]

In this paper, we will describe the synthesis and self-assembly of a SP-functionalized dendron **1** (Scheme 1). The results show that i) UV light irradiation of toluene solutions of **1** leads to its self-assembly into nano-/micrometer-sized particles exhibiting strong red emission; ii) a photoresponsive organogel can be obtained with

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DOI: 10.1002/adfm.200901358

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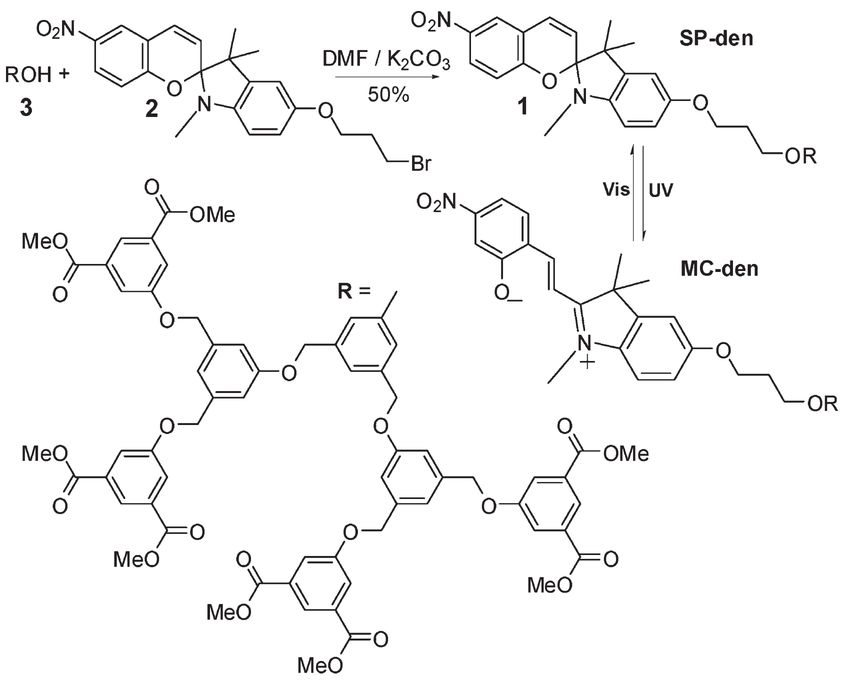

Scheme 1. The synthetic approach to SP-functionalized dendron **1** and the photochromic reactions under UV and visible light irradiation.

SP-functionalized dendron **1** with switchable fluorescence. Moreover, it is found that the MC form in the gel phase is strongly emissive and more stable compared to that in solution, and accordingly, the organogel based on **1** may be useful for information storage.

2. Results and Discussion

2.1. Synthesis and Light-Triggered Self-Assembly of SP-Functionalized Dendron 1

The synthesis of SP-functionalized dendron **1** is shown in Scheme 1. Compounds **2** and **3** were prepared according to reported procedures.[37] Reaction of compound **2** with compound **3** in the presence of K$_2$CO$_3$ led to SP-functionalized dendron **1** in 50% yield. The synthesis and characterization data are provided in the Experimental section.

The solution of **1**, prepared by dissolving 20 mg of **1** in 1.0 mL of toluene and then cooled down to 30 °C, was subjected to confocal laser scanning microscopy (CLSM) measurements. At the beginning, no apparent particles were observed in both fluorescence and bright-field images. However, particles with nearly spherical shape appeared after exposure to UV light (365 nm) as shown in Figure 1. The particle size increased by prolonging the UV light irradiation time, and nanoparticles grew gradually into micrometer-sized particles. For instance, the particle size was ~500 nm after the sample was exposed to UV light for 10 s, and it became ~5.0 μm when the irradiation time was extended to 120 s. Moreover, these particles generated from **1** after UV light irradiation exhibit strong red emission, as clearly displayed in Figure 1. It has to be noted that only where the area was irradiated by UV light did the particles appear.

We also studied the UV-light-triggered assembly of **1** with different concentrations. It was interesting to note that the particle size was also dependent on the concentration of **1**. When the concentration of **1** in toluene was 0.2 mg mL^{-1}, only dots were observed after irradiating the sample with UV light even for 10 min. Under similar conditions particles with sizes around 500 nm were detected for the solution of **1** (2.0 mg mL^{-1}) after exposure to UV light for 10 min, as shown in Figure S1 in the Supporting Information (SI). This was understandable: the reduction of the concentration of **1** would lead to the reduction of the concentration of the corresponding MC form (self-assembly blocks as to be discussed below) in solution; accordingly, the decrease of the feed concentration of the self-assembly blocks would decrease the particle size.

Both transmission electron microscopy (TEM) and dynamic light scattering (DLS) experiments also indicated the formation of spherical nano-/microparticles after UV light irradiation. Figure 2 shows the TEM images for the solution of **1** (20 mg mL^{-1}) after exposure to UV light (365 nm) for 30 and 60 s. The sizes (based on TEM images) of the formed spherical particles were approximately 1000 and 3000 nm after UV light irradiation for 30 and 60 s, respectively. Similarly, spherical particles with sizes around 250 nm were also generated for the solution of **1** (2.0 mg mL^{-1}) after exposure to UV light (365 nm) for

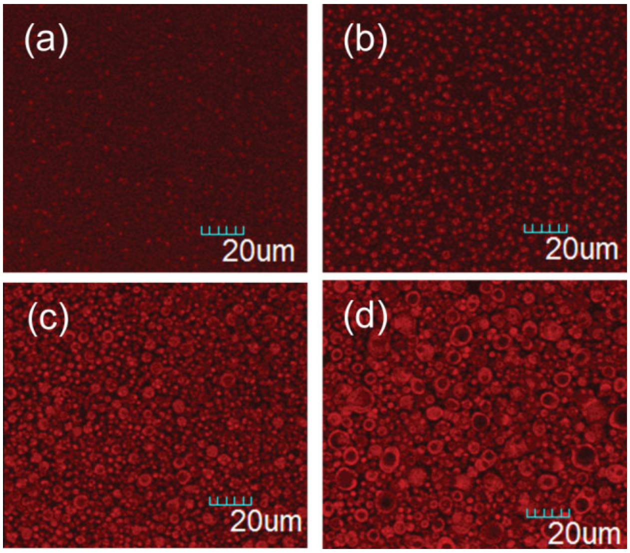

Figure 1. CLSM fluorescence images for the toluene solution of **1** (20 mg mL^{-1}) observed under 559 nm laser light excitation immediately after UV light (365 nm) irradiation for a) 10, b) 30, c) 120, and d) 480 s, respectively; for UV light irradiation, a mercury lamp with a excitation filter (BP330-385, Olympus) was used.

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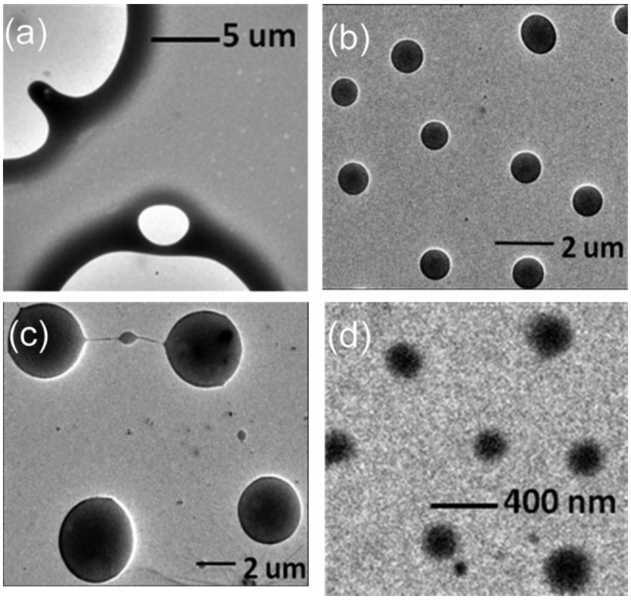


Figure 2. TEM images of the self-assembly aggregates generated from the toluene solution of **1** (20 mg mL^{-1}) before (a) and after exposure to UV light (365 nm) for 30 (b) and 60 s (c) respectively. d) TEM image of the self-assembled aggregates generated from the toluene solution of **1** (2 mg mL^{-1}) after exposure to UV light for 60 s; samples were prepared by dropping the respective solutions onto the copper grid and the solvents were allowed to evaporate at room temperature.

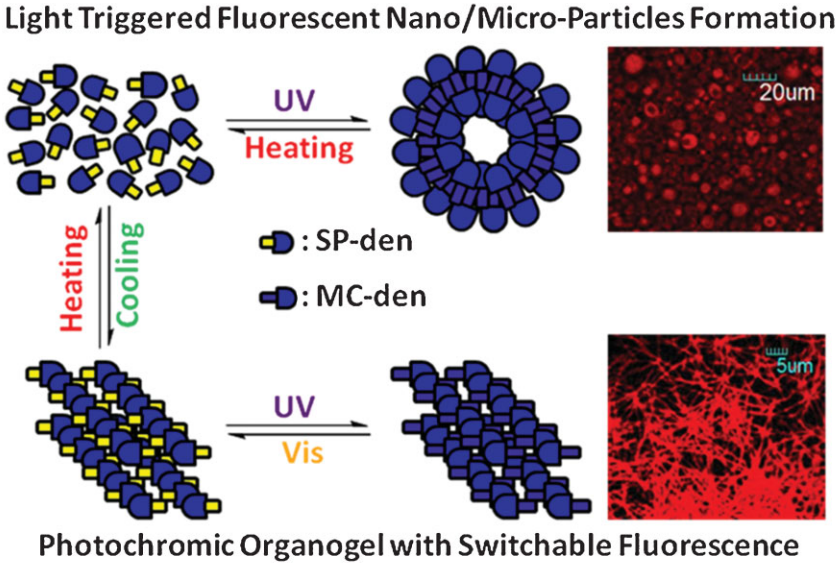
60 s (see Fig. 2). It should be mentioned that no particles were detected for the solution of **1** before UV irradiation. For the toluene solution of **1** (2.0 mg mL^{-1}), no DLS signals corresponding to particles larger than 5.0 nm were detected. After UV irradiation however, DLS signals due to particles with sizes over 200 nm were observed (see Fig. S2, SI), indicating the formation of self-assembled aggregates.[38] All the investigations with CLSM, TEM, and DLS indicate the UV-light-triggered self-assembly of SP-functionalized dendron **1** into spherical nano-/microparticles and the increase of particle size with increasing concentrations of **1** and UV irradiation time. It should be noted that such nano-/microparticles with spherical shape generated from SP compounds in situ after exposure to UV light were not previously reported, although formation of aggregates of SP compounds induced by UV light has been described.[12,13]

The UV-light-triggered self-assembly of **1** into particles can be understood as follows: i) the SP unit in **1** will transform into the corresponding MC form under UV light irradiation; ii) the polar MC form is solvophobic towards toluene, and thus the intermolecular MC forms tend to aggregate as previously reported;[12,13] iii) the formation of spherical particles may be related to the structure of the dendron in **1** as schematically shown in Scheme 2. The self-assembly propensity of dendron **1** into particles may further minimize the contact among toluene molecules and polar MC groups, thus lowering the energy of the system.

Although the MC form can convert into the closed SP form under visible light irradiation (for spectral investigations, see below), the particles formed in the toluene solution of **1** after exposure to UV light cannot be totally disassembled by further visible light irradiation. As shown in Figure 3, where the CLSM images for the solution of **1** (20 mg mL^{-1} in toluene) are displayed, the particle morphology in the bright field remains, even after the solution that was exposed to UV light for 2.0 min was further irradiated with a 559 nm laser light for 30 min. This implies that these particle aggregates are relatively stable. However, disassembly occurred in these particle aggregates when the solution was heated to 80 °C, and complete disappearance of these particles was observed when the solution was kept at 80 °C for only 1.0 min. This is understandable since the self-assembly process is usually enthalpy-favored and entropy-disfavored, and thus heating will facilitate the disassembly process.

Figure 4a shows the absorption spectra of the solution of **1** (0.2 mg mL^{-1}, 0.127 mM) before and after UV light irradiation for 2.0 min. The new broad absorption band in the range of 500–700 nm that appeared after UV light irradiation should be due to the corresponding MC form. Normally, MC forms exhibit maximum absorption around 570 nm. The fact that the maximum absorption of **1** after UV light irradiation appears at 608 nm together with a shoulder band around 570 nm indicates the formation of MC aggregates, according to previous studies.[12] Similar absorption spectra were obtained for the solutions of **1** with concentrations of 2 mg mL^{-1} (1.27 mM), 0.02 mg mL^{-1} (12.7 μM), and 0.002 mg mL^{-1} (1.27 μM).

It is known that the MC forms of SP compounds usually exhibit rather weak fluorescence in the range of 580–800 nm in solution. However, the particles generated in the solution of **1** after UV light



Scheme 2. Schematic representation of the self-assembly of SP-functionalized dendron **1** into particles and network structure within the organogel, and the corresponding transformations under UV and visible irradiation as well as the corresponding CLSM images.

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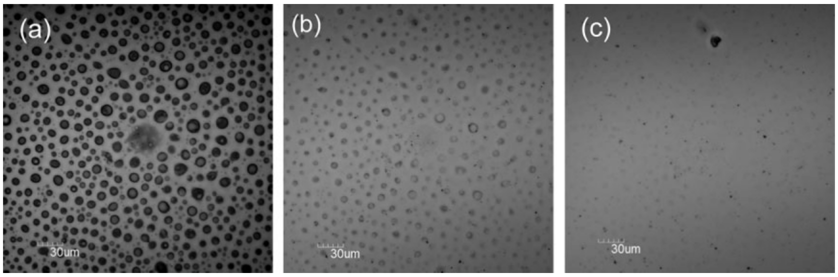

Figure 3. a) CLSM bright-field images for the toluene solution of **1** (20 mg mL^{-1}) after UV light (365 nm) irradiation for 2 min. b) Further visible light (559 nm) irradiation for 30 min, and c) incubation at 80 °C for 1.0 min.

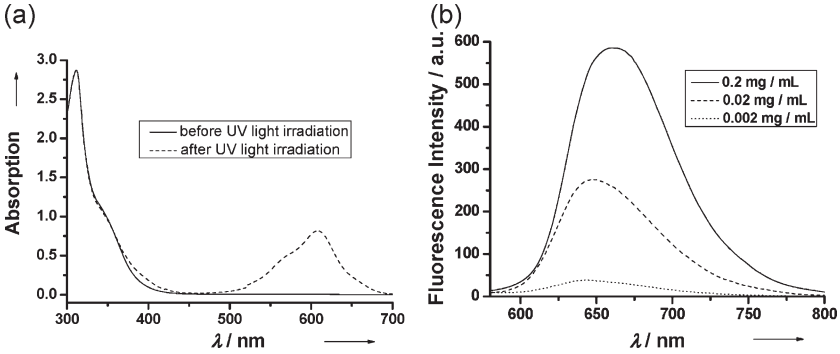

Figure 4. a) Absorption spectra of the toluene solution of **1** (0.2 mg mL^{-1}) before and after UV light (365 nm) irradiation for 2 min. b) Fluorescent spectra of **1** with three different concentrations (0.002, 0.02, and 0.2 mg mL^{-1} in toluene) after UV light (365 nm) irradiation for 2 min; $\lambda_{\text{exc.}} = 560$ nm.

irradiation show red emission, as clearly shown in Figure 1, where the corresponding CLSM images are displayed. Figure 4b shows the fluorescence spectra of the solutions of **1** with different concentrations after UV light irradiation for 2.0 min. Obviously, the fluorescence intensity of **1** after UV light irradiation increases significantly as the concentration increases from 0.002 to 0.02 mg mL^{-1} and 0.02 mg mL^{-1}, along with the red-shift of the emission peak from 643 to 650 nm and 661 nm. The fluorescence quantum yields of solutions of **1**, however, with three respective concentrations after UV light irradiation for 2.0 min were similar, that is, 0.05 with respect to rhodamine B. The red-shift of the fluorescence spectrum by increasing the concentration of **1** again indicates the formation of MC aggregates. Two factors may contribute to the relatively strong fluorescence of the particles: i) the aggregation of MC forms may restrict the conformational flexibility, which may minimize nonradioactive relaxation through internal motions of the excited molecules; ii) the dendron in **1** may function as protective shells for the MC aggregates (see Scheme 2), and as a result the MC form may be isolated from nonradioactive decay pathways involving solvents.

2.2. Gel Formation, Switchable Fluorescence, and Application

When the hot toluene solution of **1** (20 mg mL^{-1}, 12.7 mM) was directly cooled by ice water to 0 °C, a transparent light yellow gel resulted, as shown in Figure 5. SEM and TEM images (Fig. 6) of the xerogel of **1** show that molecules within have self-assembled into long fibers with widths of about 50 nm, which are further interconnected to generate a 3D network. Molecules of **1** in the gel phase are relatively orderly, as indicated by X-ray diffraction (XRD) analysis (Fig. S3, SI), in which a signal around 0.77° was detected, corresponding to *d*-spacings of 11.5 nm. The *d* value is relatively large compared to those of normal organogels, and this may be related to the bulky dendron group in **1**. Other solvents were also tested to examine the gelation ability of **1**. Besides toluene, dendron **1** can also gel benzene (20 mg to 0.02 mg mL^{-1}). However, dendron **1** cannot gel acetonitrile, methanol, ethanol, dichloromethane, tetrahydrofuran, and ethyl acetate. Dendron-based gelators were reported, but intermolecular H-bonds were believed to be responsible for the gelation processes.[39,40] Although the gelation mechanism with **1** in toluene and benzene is not fully clarified at this stage, multivalent π–π interactions due to the dendron in **1** may be the driving-force for the gelation.

The SP unit in **1** can be converted to the polar MC form under UV light irradiation, and such structural alteration may destabilize the self-assembled structure and induce a gel–solution phase transition. However, when the gel was exposed to UV light for 2.0 min, the gel phase was not destroyed and the light yellow gel was transformed into the purple-blue gel as illustrated in Figure 5. This result further suggests that the driving force for the gelation of toluene (and benzene) with **1** may be the multivalent π–π interactions due to the dendron in **1**. Further visible light irradiation of the purple-blue gel led to the yellow gel again (see Fig. 5). Figure 5 also illustrates the transition of the purple-blue gel into the corresponding solution after heating, which can be converted to the light yellow gel again after further cooling to 0 °C.

The purple-blue gel shows a broad absorption in the range of 500–700 nm due to the MC aggregates. After exposure to visible

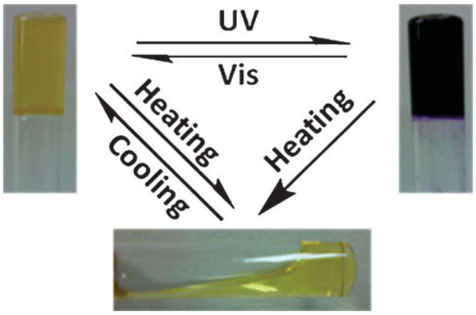

Figure 5. Illustration of the gel–gel transformation under alternating UV (365 nm) and visible light irradiation, and the gel–solution–gel transition under heating and cooling for the toluene solution of **1** (20 mg mL^{-1}).

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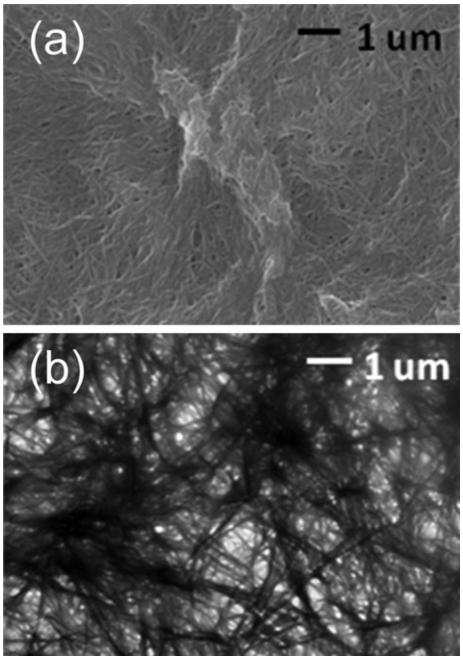

Figure 6. a) SEM and b) TEM images of the corresponding xerogel of **1** formed in toluene.

light irradiation for a few minutes, this broad absorption disappeared because of the transformation of MC into the closed SP form as expected. The corresponding solution of **1**[41] also exhibits a broad absorption in the range of 500–700 nm after UV light irradiation. Of particular interest is the fact that the MC form in the gel phase becomes more stable compared to that in solution as indicated in Figure 7a, where the plot of the transmittance at 580 nm for the gel and solution versus the decay time is displayed (the sample was kept under dark conditions after recording each spectrum). The stable MC form may enable this organogel of **1** to be used as soft materials for information storage. As illustrated in Figure 7b, the light yellow gel was covered with a photomask containing the characters "ICCAS 2008," and these characters became apparent from the blue-colored background after exposure to UV light for 1.0 min. Such a photopattern can last (i.e., still be distinguished with the naked eye) for at least 12 h. Two pathways are applicable for erasing the written data and generating the original gel state. One is to illuminate the gel with visible light, and the other is to heat the gel, resulting in the solution, followed by rapid cooling to generate the gel again.

The purple-blue gel exhibits relatively strong red fluorescence as illustrated in Figure 8. Also, the xerogel shows strong red fluorescence as indicated by the CLSM image (Fig. 8b). The strong red fluorescence of the gel can be switched off by additional visible light irradiation. This is simply because of the conversion of the MC form into the closed form of SP that emits no intrinsic fluorescence. Furthermore, the fluorescence of the gel can be restored. In this way, the fluorescence of the gel can be reversibly tuned by alternating UV and visible light irradiation as shown in the inset of Figure 8, where reversible changes of the fluorescence intensity of the gel at 667 nm is displayed. Therefore, this organogel can function as a fluorescence switch.

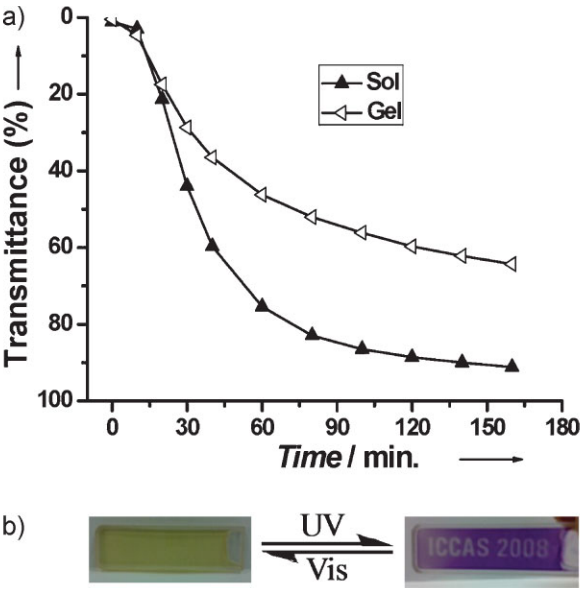

Figure 7. a) Variation of the transmittance at 580 nm versus the decay time for the corresponding gel and solution of **1** (20 mg mL^{-1} in toluene); the samples were firstly exposed to UV light (365 nm) for 5 min and were kept under dark conditions after recording each spectrum. b) Illustration of the recording of "ICCAS 2008" characters on the gel of **1** (20 mg mL^{-1} in toluene) by exposure to UV light (365 nm) for 1.0 min, and erasing the recorded pattern by exposure to visible light for 5.0 min.

3. Conclusion

In summary, we have described the synthesis, self-assembly, and spectroscopic studies of the SP-functionalized dendron **1**. The results show that by manipulating the cooling process, the toluene solution of **1** can lead to different self-assembled structures: spherical nano-/microparticles in solution by cooling the hot solution to 30 °C and additional UV light irradiation, and 3D interconnected fiber-network within an organogel by cooling the hot solution to 0 °C as schematically shown in Scheme 2. Multivalent π–π interactions due to the dendron in **1** may be the driving force for the gelation. These self-assembled structures were successfully characterized by CLSM, SEM, TEM, and DLS. The UV light irradiation cannot destroy the gel phase, and in fact gel–gel transition is successfully realized. The purple-blue gel exhibits relatively strong red fluorescence; moreover, the fluorescence can be reversibly switched by alternating UV and visible light irradiation. The results clearly indicate that the MC form after aggregation becomes more stable and strongly fluorescent. These results provide insights into the design of new MC aggregates, which may have potential applications in fluorescence imaging, particularly in biological systems.

4. Experimental

General Procedures: Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. The solvents used were dried and purified by standard methods prior to use. ^{1}H and ^{13}C NMR spectra were recorded with Bruker

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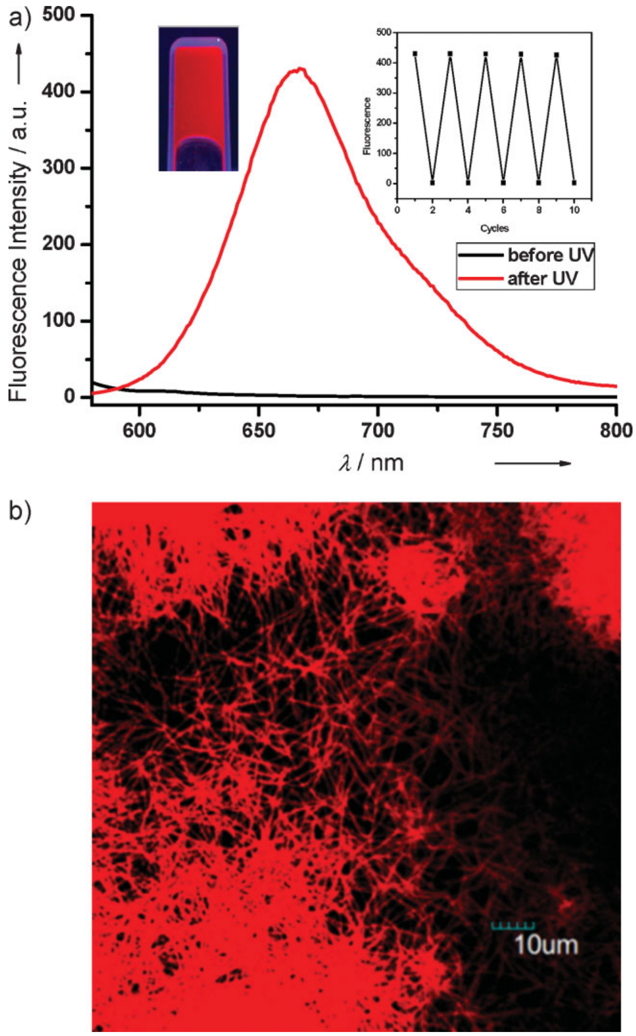

Figure 8. a) Fluorescence spectra of the gel of **1** (20 mg mL^{-1} in toluene) before and after UV light (365 nm) irradiation for 5.0 min, $\lambda_{exc.} = 560$ nm. The insets show the photo of the gel under UV (365 nm) light illumination (left), and the reversible change of the fluorescence intensity of the gel at 667 nm by alternating UV and visible light irradiation (right). b) CLSM image of the corresponding xerogel.

400MHz spectrometers. Mass spectrometry (MS) were determined with a BEFLEX III for time-of-flight (TOF) MS. Elemental analysis was performed on a Carlo-Erba-1106 instrument. The CLSM system, FV-1000-IX81 Olympus (Japan), was employed. XRD data were collected on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation. For SEM experiments, a JEOL JSM 6700F field-emission scanning electron microscope was used, and the freeze-dried xerogel was sputtered with platinum. TEM measurements were conducted with JEOL 2010 transmission electron microscopes using an accelerating rate voltage of 120 keV. DLS experiments were carried out with an ALV5000 Laser Light Scattering Instrument. Absorption spectra were recorded on a JASCO V-570 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer.

*Synthesis of Compound **1***: Compound **2** was prepared according to the reported procedure [37]. The synthesis and characterization of compound **3** is published elsewhere [37]. A solution of **2** (250 mg, 0.545 mmol), **3** (650 mg, 0.544 mmol), and K_2CO_3 (700 mg, 5 mmol) in dimethylformamide (DMF, 20 mL) was stirred at room temperature for three days. The resulting reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried over anhydrous Na_2SO_4. The solvents were removed under vacuum, and the residue was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (30/1, v/v) to give compound **1** as a white solid powder (424 mg, 50%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, tetramethylsilane: TMS): $\delta = 1.16$ (s, 3H), 1.25 (s, 3H), 2.26 (m, 2H), 2.66 (s, 3H), 3.93 (s, 24H), 4.13 (t, $J = 6$ Hz, 2H), 4.21(t, $J = 6$ Hz, 2H), 5.08–5.13 (12H), 5.82 (d, $J = 10$ Hz, 1H), 6.42 (d, $J = 9$ Hz, 1H), 6.72 (3H), 6.89 (d, $J = 10$ Hz, 1H), 7.07 (m, 9H), 7.82 (d, $J = 1$ Hz, 8H), 7.98 (d, $J = 8$ Hz, 2H), 8.29 (t, $J = 1$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 166.2$, 160.0, 159.7, 159.5, 158.8, 153.6, 142.15, 141.07, 138.8, 138.4, 137.8, 132.1, 128.3, 126.0, 123.5, 122.8, 121.7, 120.4, 120.3, 119.0, 118.8, 118.6, 115.6, 113.7, 113.3, 112.6, 110.3, 107.4, 107.0, 70.3, 70.25, 70.1, 65.4, 64.9, 52.57, 52.53, 29.8, 29.7, 29.3, 25.9, 20.0; MALDI(matrix-assisted laser desorption/ionization)-TOF-MS (*m/z*): 1574.2 $[M + H]^+$, 1596.3 $[M + Na]^+$; Anal. calcd. for $C_{86}H_{80}N_2O_{27}$: C, 65.64; H, 5.12; N, 1.78; Found: C, 65.72; H, 5.37; N, 1.99.

Gel Formation: In a typical gelation experiment, a weighed amount of **1** and 1.0 mL of the solvent were placed in a test tube, which was sealed and then heated until the compound was dissolved. The solution was then cooled down with ice water.

Acknowledgements

The present research was financially supported by NSFC, the State Basic Program and Chinese Academy of Sciences. This work was partially supported by the NSFC-DFG joint project (TRR61). We thank the anonymous reviewers for their suggestions and comments which enabled us to significantly improve the manuscript. Supporting Information is available online from Wiley InterScience or from the authors.

Received: July 22, 2009
Published online: October 26, 2009

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[38] For the DLS experiments, a red light (632 nm) was used for signal detection. Also, it takes a relatively long time to finish each DLS measurement. In order to reduce the influence of disaggregation during the measurement, the solution of **1** was exposed to UV light for a relatively long period.

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[41] As mentioned above, if the hot toluene solution of **1** is not cooled to 0 °C, gelation cannot occur.

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