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Multicolor Tunable Emission from Organogels Containing Tetraphenylethene, Perylenediimide, and Spiropyran Derivatives

By *Qun Chen, Deqing Zhang,* Guanxin Zhang, Xingyuan Yang, Yu Feng, Qinghua Fan,* and *Daoben Zhu*

A dendron-substituted tetraphenylethene low molecular weight gelator (LMWG)compound, LMWG1, is designed and investigated. Gelation-induced fluorescence enhancement is observed for the gel based on LMWG1 and its fluorescence can be reversibly tuned by varying the temperature of the ensemble. The photoinduced energy-transfer can occur between LMWG1 and PI2 (perylene diimide) in the gel phase, but it cannot occur in the corresponding solution. The emission color of the gel of LMWG1 and PI2 can be tuned from cyan, yellow, to red by varying the concentration of PI2. By taking advantage of the photochromic transformation of spiropyran, the emission color of the organogels based on LMWG1 and SP3 can be switched by alternating UV and visible-light irradiations. The emission color can also be tuned by varying the irradiation time. In this way, organogels based on LMWG1 with multiemission color can be achieved in the presence of SP3 after light irradiations.

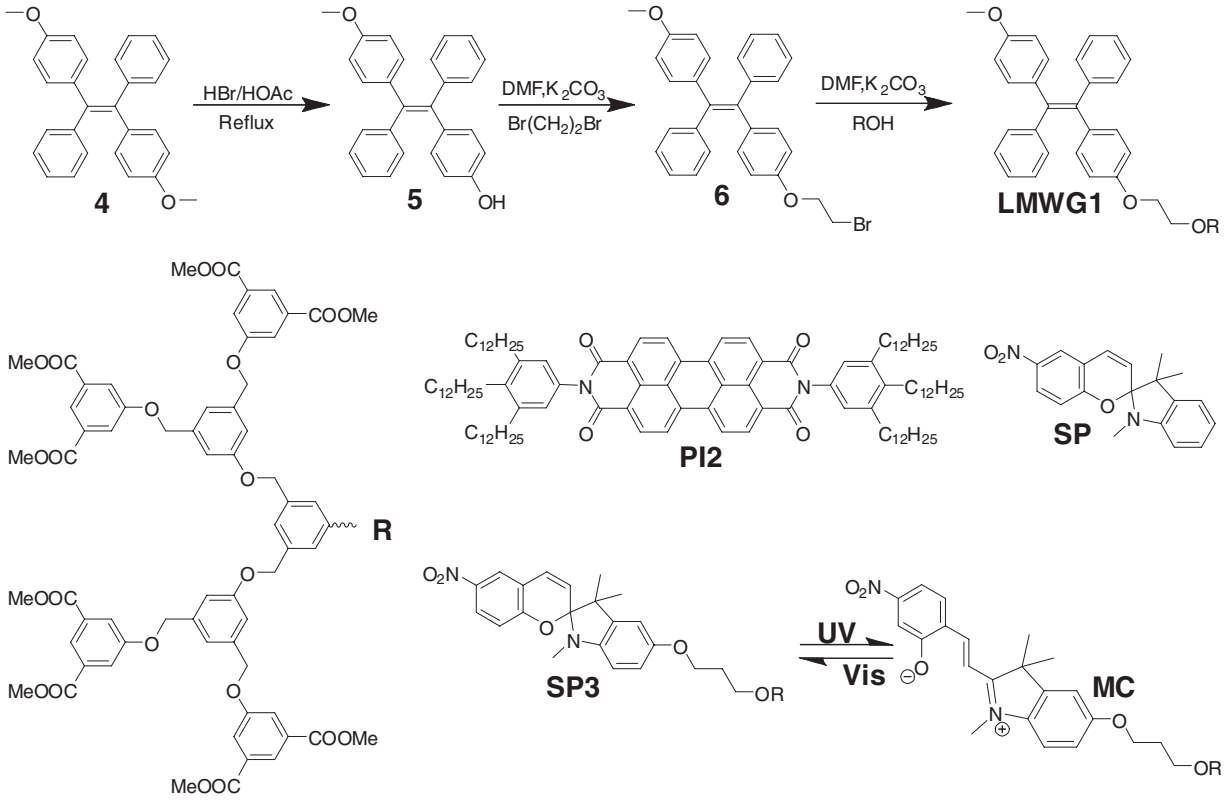
1. Introduction

Low-molecular weight gelators (LMWGs), which form three-dimensional (3D) networks through weak intermolecular interactions such as H-bonding, π–π stacking and van der Waals forces, are capable of immobilizing solvent molecules and forming organogels.[1,2] Because of the weak intermolecular interactions, the gel-solution (sol) transitions for these organogels are thermally reversible. It is interesting to note that some physical properties can be tuned in accompanying the corresponding gel-sol transitions for LMWGs.[3] For instances, Ajayaghosh and co-workers reported a series of oligo (*p*-pheylenevinylene)-derived LMWGs with tunable emission, utilizing the absorption spectral shifts after gelation and effective fluorescence resonance energy transfer process in the organogel scaffold.[4] In a few cases, gelation-induced-fluorescence-enhancement was observed. Park and co-workers reported the fluorescence increase after gelation with 1-cyano-*trans*-1,2-bis-(3′5′-bis-trifluoromethyl-biphenyl) ethylene(CN-TFMBE).[5] Similar phenomena were described for gelators with oxadiazole,[6a] benzoxazole,[6b] naphthalene[6c] and salicylideneaniline[6d] moieties. A significant fluorescence enhancement was observed for gelation with a gelator containing anthracene and urea moieties as reported by us recently.[7] Park and co-workers have very recently described the emission tuning for the organogels by light irradiations apart from heating through incorporating the photochromic compound into the gels.[8] Shinkai and co-workers found that formation of assemblies of chromophores such as perylenediimide after gelation could facilitate the energy-transfer processes and thus the organogels are potentially useful for light harvesting.[9] In addition, it was found that the spectral features of the "doping" compounds in the organogels can also be modulated after gelation. We and others successfully achieved the thermal modulation of the pyrene monomer/excimer fluorescence by making use of the physical difference between gel and solution phases.[10]

Silole and tetraphenylethene derivatives show abnormal fluorescent behaviors; namely, they are weakly fluorescent in solution, but they become strongly emissive after aggregation.[11] A few silole and tetraphenylethene compounds were able to gel organic solvents and gelation-induced fluorescence enhancement was observed.[5,12] In this paper, we describe a new dendron-substituted tetraphenylethene LMWG**1** (**Scheme 1**). As anticipated, the fluorescence intensity of LMWG**1** increases significantly after gelation and the fluorescence of LMWG**1** can be reversibly modulated by alternating heating and cooling. LMWG**1** and PI**2** (perylene diimide, see Scheme 1) can form energy donor–acceptor pair as there is a good spectral overlap between the fluorescence spectrum of LMWG**1** and the absorption spectrum of PI**2**. It is expected that the photoinduced energy-transfer from LMWG**1** to PI**2** can be tuned by taking advantage of AIE behavior of tetraphenylethene compounds; in solution the energy transfer is not efficient

[*] Q. Chen, Prof. D. Q. Zhang, Dr. G. X. Zhang, X. Y. Yang, Y. Feng, Prof. Q. H. Fan, Prof. D. B. Zhu
Beijing National Laboratory for Molecular Sciences
CAS Key Laboratories of Organic Solids
and Molecular Recognition and Function
Institute of Chemistry
Chinese Academy of Sciences
Beijing 100190 (China)
E-mail: dqzhang@iccas.ac.cn
Q. Chen, X. Y. Yang, Y. Feng
Graduate School of Chinese Academy of Sciences
Beijing, 100190 (China)

DOI: 10.1002/adfm.201000590



Scheme 1. The molecular structures of LMWG**1**, PI**2** and SP**3**; the synthetic route of LMWG**1** and photochromic reaction of SP**3**.

because LMWG**1** is non-fluorescent in solution, but in the gel phase the energy transfer can occur efficiently. Moreover, it is known that the absorption and fluorescence spectra of perylene diimide are varied upon aggregation and thus they are dependent on their concentrations.[13] Therefore, the emission color of the ensemble of LMWG**1** and PI**2** can be tuned by varying the temperature and the concentration of PI**2** as shown in **Scheme** 2. Alternatively, the merocyanine form (MC) of spiropyran that can be easily generated by UV-light irradiation[14] shows absorption in the range of 480–700 nm, and thus the MC form of spiropyran is a good energy acceptor of LMWG**1**. Accordingly, the emission of LMWG**1** can be further tuned by light irradiation in the presence of spiropyran (e.g., SP**3** in Scheme 1), as schematically shown in Scheme 2. In this way, the emission of LMWG**1** can be successfully tuned by adjusting the temperature, concentration, and light irradiation and multicolor emission can be achieved for organogels containing LMWG**1**, PI**2** and SP**3** as to be discussed below.

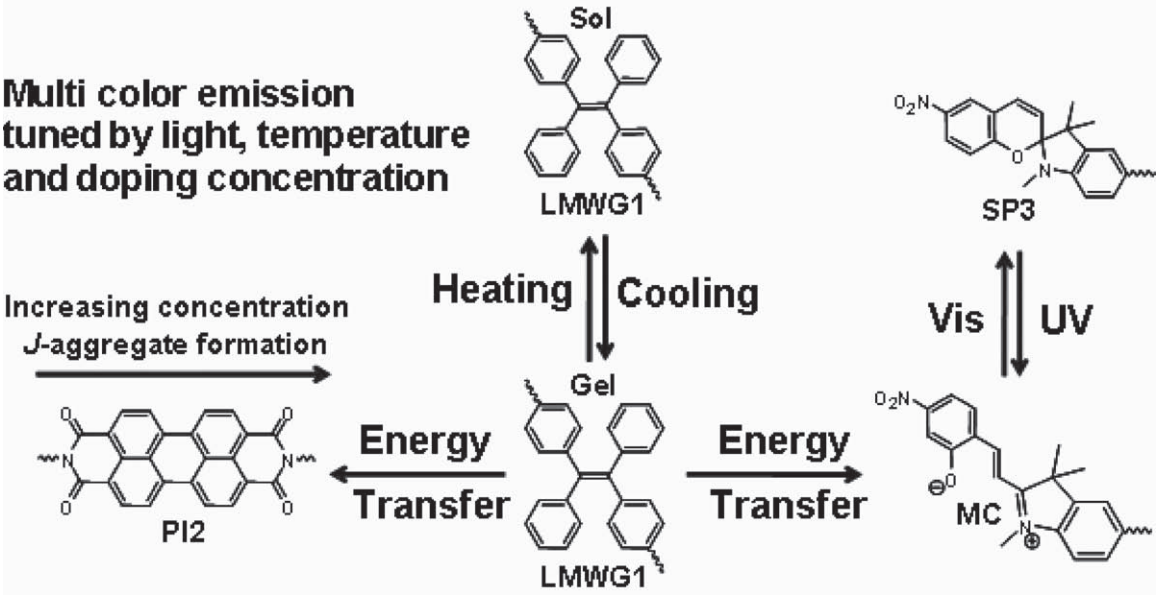
2. Results and Discussion

2.1. Gel Formation, Characterization and Emission Modulation for LMWG1

The synthesis of LMWG**1** started from compound **4** which was transformed into compound **5** after removal of one methyl group. Compound **5** reacted with 1, 2-dibromoethane leading to compound **6** in 80% yield. Further reaction of compound **6** with the dendron compound led to LMWG **1** in 80% yield. The synthetic details and characterization were provided in Experimental section.

The gelation ability of LMWG**1** was examined. The results show that LMWG**1** can gel benzene (>20 mg mL^{-1}) and toluene (>20 mg mL^{-1}). For example, a white translucent organogel was formed by cooling the hot toluene solution of LMWG**1** (20 mg mL^{-1}) at 0 °C for 15.0 min. But, it cannot gel hexane, cyclohexane, dichloromethane, acetonitrile, ethyl acetate, tetrahydrofuran, methanol and ethanol. As reported previously, the multivalent π–π interactions due to the dendron group in LMWG**1** may be the driving-force for the gelation.[15] The xerogels of LMWG**1** were characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). **Figure 1** shows the SEM and TEM images of the xerogel formed with LMWG**1** in toluene. Molecules of LMWG**1** are self-assembled into a 3D entangled network of long thin nano-fibers with an average width of ca. 100 nm. The SEM and TEM images also show that big fibrous nanostructures are composed of several twisted small nanofibers. Confocal laser scanning microscopy (CLSM) image (Figure S1 in the Supporting Information) of the xerogel also shows the same entangled fiber network. Only a broad peak at 0.305° (Figure S2), corresponding a *d*-spacing of 29 nm, was detected in the XRD pattern. The relatively large *d*-spacing may be related to the bulky dendron group in LMWG**1**.

The solution of LMWG**1** (20 mg mL^{-1} in toluene) was almost non-fluorescent as shown in **Figure 2**. But, the fluorescence of



Scheme 2. Multicolor emission tuning for organogels formed with the ensemble of LMWG**1**, PI**2** and SP**3** by varying the temperature, concentration, and light irradiation.

LMWG**1** turned on after gelation; the fluorescence intensity at 490 nm was enhanced by 30 times after gelation. Such fluorescence enhancement is likely due to the fact that the intramolecular rotations are restricted for the tetraphenylethene group in LMWG**1** in the gel phase, thus resulting in fluorescence enhancement according to previous studies.[11] When the gel was converted to solution after heating, the fluorescence of LMWG**1** became weak again. In this way, the fluorescence intensity of LMWG**1** can be reversibly modulated by alternating cooling (transformation of the solution into organogel) and heating (transformation of the gel into solution) as shown in the inset of Figure 2.

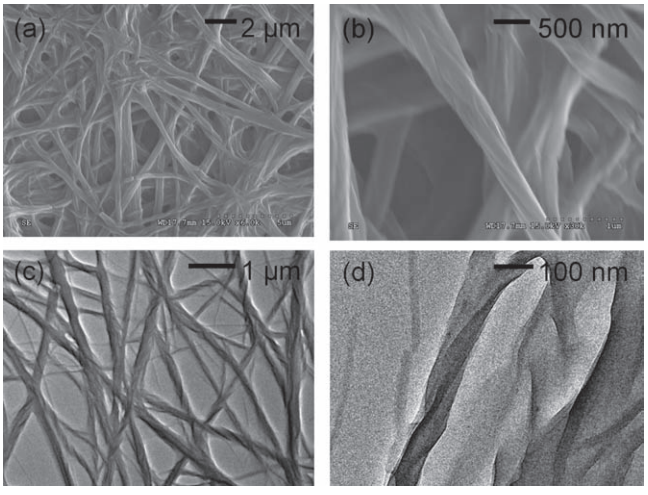


Figure 1. SEM (a,b) and TEM (c,d) images of the xerogel prepared from the organogel formed with LMWG**1** (20 mg mL^{-1} in toluene).

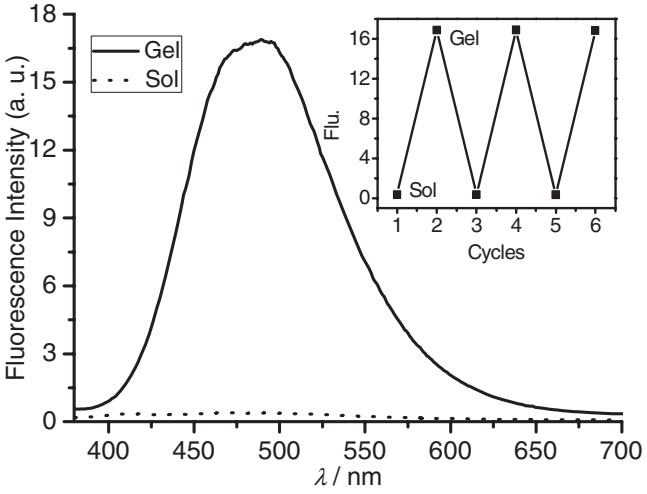


Figure 2. Fluorescence spectra of the solution and the corresponding organogel formed with LMWG**1** (20 mg mL^{-1}) in toluene, $\lambda_{exc.}$ = 365 nm; inset shows the reversible fluorescence tuning by alternating heating and cooling.

In addition, the fluorescence lifetimes of LMWG**1** (20 mg mL^{-1} in toluene) in the gel phase were estimated to be τ_1 = 1.09 ns (47.2%) and τ_2 = 4.33 ns (52.8%) by fitting the fluorescence decay curve (see Figure S3). Similarly, the fluorescence lifetimes of the corresponding solution of LMWG**1** were estimated to be τ_1 = 0.18 ns (88.2%) and τ_2 = 5.78 ns (11.8%) by fitting the fluorescence decay curve (see Figure S4). Although τ_2 of LMWG**1** in the gel phase was slightly shorter than that in the solution, τ_1 of LMWG**1** in the gel phase was longer than that in the solution. This is consistent with the significant fluorescence enhancement of LMWG**1** after gelation.[16]

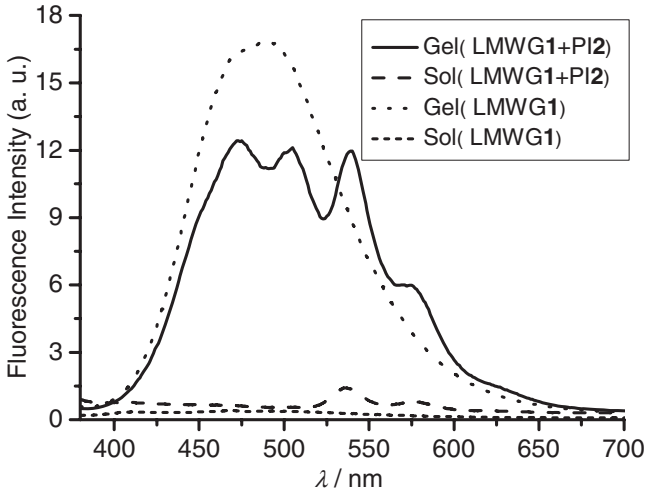


Figure 3. Fluorescence spectra of organogels formed with LMWG**1** (20 mg mL^{-1} in toluene) and PI**2** (0.1 mM) and the corresponding solutions; $\lambda_{exc.}$ = 365 nm.

2.2. Emission Color Tuning for the Ensemble of LMWG 1 and PI2

PI**2** was synthesized according to the reported procedure.[13b] LMWG**1** absorbs strongly at 365 nm while PI**2** shows weak absorption around 365 nm (Figures S5 and S6). Consequently, it is possible to excite LMWG**1** selectively in the presence of PI**2**. As discussed above, PI**2** is a good energy acceptor for LMWG**1** as the fluorescence spectrum of LMWG**1** overlaps well with the absorption spectrum of PI**2** in the range of 400–600 nm. However, the toluene solution composed of LMWG**1** (20 mg mL^{-1}) and PI**2** (0.1 mM) was almost non-fluorescent after excitation at 365 nm (see **Figure 3**). This is understandable by considering the fact that LMWG**1** is weakly emissive in solution; thus, the photoinduced energy-transfer from LMWG**1** to PI**2** cannot take place efficiently in solution. In fact, the fluorescence lifetimes of LMWG**1** in the presence of PI**2** were also measured in solution. Based on the fluorescence decay profile at 490 nm for the solution of LMWG**1** (20 mg mL^{-1}) and PI**2** (0.1 mM) (see Figure S11), the fluorescence lifetimes of LMWG**1** were estimated to be 0.29 ns (90.2%) and 6.11 ns (9.8%). These lifetimes of LMWG**1** in the presence of PI2 are rather close to those of LMWG**1** in the absence of PI2 (see Figure S4). This result also implies that the photoinduced energy-transfer from LMWG**1** to PI**2** in solution does not occur.

The solution of LMWG**1** and PI**2** can be transformed into the gel after cooling. As shown in Figure S8, where the SEM and TEM images for the xerogel from LMWG**1** (20 mg mL^{-1} in toluene) and PI**2** (10 mM) were shown, interconnected nanofibers of widths ranging from ca. 100 nm to ca. 500 nm exist in the xerogel. The big fibrous structures contain entangled thin-nanofibers. The fluorescence spectrum ($\lambda_{ex.}$ = 365 nm) of the gel was displayed in Figure 3. Both the fluorescence band in the range 400–550 nm due to LMWG**1** and that in the range 550–700 nm due to PI**2** were observed after gelation; the fluorescence intensity of organogel formed by LMWG**1** at 485 nm decreased by 31% after "doping" with PI**2**. By considering the difference between the solution and gel phases of LMWG**1** and PI**2** in fluorescence spectrum, it can be concluded that the photoinduced energy transfer between LMWG**1** and PI**2** is governed by the physical phase which is dependent on the temperature of the ensemble.

The energy transfer efficiency between LMWG**1** and PI**2** can be enhanced by increasing the concentration of PI**2** in the gel phase. The organogels based on LMWG**1** with PI**2** as "dopant" can be easily prepared. By increasing the concentration of PI**2** from 0.1 mM to 1.0 mM and 10 mM in the gel, the fluorescence intensity (from 400 to 550 nm) due to LMWG**1** decreased gradually as shown in **Figure 4**. The corresponding energy transfer efficiencies increased from 31% to 52% and 90%. Moreover, the emission of the organogel containing LMWG**1** and PI**2** was red-shifted by increasing the concentration of PI**2** from 0.1 mM to 1.0 mM and 10 mM in the gel, and the emission color was changed from cyan to yellow and red, respectively (see Figure 4). The variation of the emission color for the gel is attributed to the fact that the emission spectrum of PI**2** can be changed

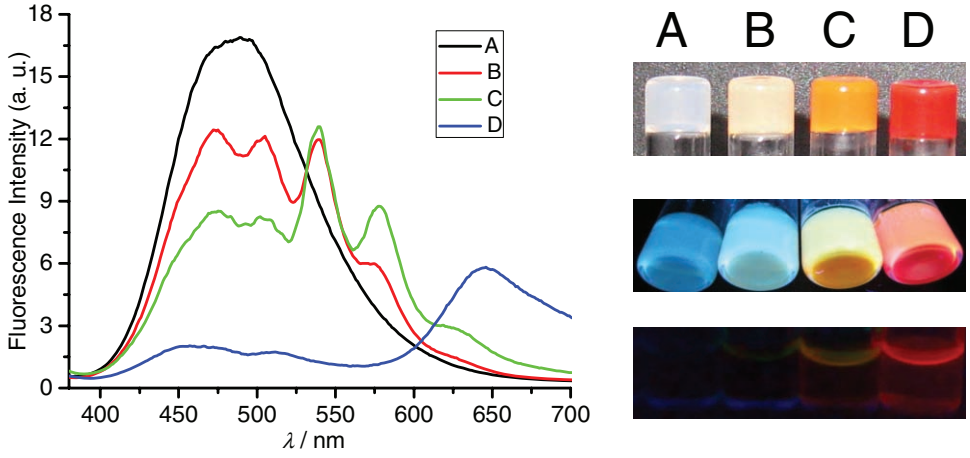


Figure 4. Fluorescence spectra of organogels formed with LMWG**1** (20 mg mL^{-1}) in toluene (A), and those of gels with LMWG**1** (20 mg mL^{-1}) in toluene with different amounts of PI**2** [0.1 mM (B), 1.0 mM (C) and 10 mM (*D*)], $\lambda_{exc.}$ = 365 nm; photos of the organogels under daylight (top right) and UV light (middle right), and the corresponding solutions under UV light (bottom right).

upon aggregation by increasing its concentration. As shown in Figure S6, the emission spectrum of PI**2** was red-shifted by 100 nm when the concentration of PI**2** increased from 0.1 mM to 10 mM. These results clearly indicate that the emission color of the gel based on LMWG**1** and PI**2** as "dopant" can be tuned by varying the concentration of the "dopant".

The photoinduced energy transfer process between LMWG**1** and PI**2** in the gel phase was investigated by measuring the fluorescence life-times of LMWG**1**. The fluorescence decay profiles of organogels at 490 nm were recorded with the excitation wavelength of 365 nm. By fitting the fluorescence decay profiles (see Figures S9–S13), the corresponding fluorescence life-times were obtained for organogels of LMWG**1** containing different concentrations of PI**2**. As listed in **Table 1**, compared to those of the gel in the absence of PI**2** the fluorescence life-times of gels of LMWG**1** and PI**2** are shortened just slightly when the concentration of PI**2** in the gels was not higher than 1.0 mM. In these cases, the photoinduced energy transfer between LMWG**1** and PI**2** proceeds probably with emission-reabsorption mechanism (a trivial radiative mechanism). However, when the concentration of PI**2** reached 10 mM, the corresponding life-times were obviously reduced. When more PI**2** was present in the gel phase, co-assembly of LMWG**1** and PI**2** may occur; accordingly, molecules of LMWG**1** and PI**2** may locate within a distance for effective fluorescence resonance energy transfer through nonradiative dipole-dipole coupling. Alternatively, the fluorescence life-times of PI**2** in the organogels based on LMWG**1** and PI**2** were measured by recording the corresponding fluorescence decay profiles of organogels at either 580 nm or 650 nm[17] with the excitation wavelength of 365 nm. The decay curves shown in Figures S14–16 were fitted with a biexponential function and the lifetimes were listed in Table S1. It is obvious that the fluorescence intensity at either 580 nm or 650 nm (mainly due to PI2) decays more slowly and excited states with long lifetimes emerged gradually by increasing the concentration of PI**2** in the gels. This may be ascribed to the formation of self-assembly aggregates of PI**2** at high concentration and as a result long-lived excited states can be generated according to previous report.[13b]

2.3. Emission Color Tuning for the Ensemble of LMWG1 and SP3

It is known that the photochromic SP compound can be reversibly transformed into the corresponding MC (merocyanine) form which exhibits absorption in the range of 480–700 nm.[14] Therefore, the MC form can function as the energy acceptor for LMWG**1** as mentioned above. The organogels of LMWG**1** containing simple SP compound (1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran, Scheme 1) can be prepared similarly by cooling the corresponding hot solutions. As an example, **Figure 5** shows the fluorescence spectrum of the organogel formed with a hot toluene solution composed of LMWG**1** (20 mg mL^{-1}) and SP (4.0 mg mL^{-1}). Compared to the corresponding solution, the organogel exhibited strong emission around 490 nm.[18] But, the emission intensity of the organogel was reduced by 75% after UV light (365 nm) irradiation for 10 min. This is likely due to the formation of MC form of SP after UV light irradiation and consequently the photoinduced energy transfer between MC form and LMWG**1** can occur, leading to the decrease of the emission intensity of LMWG**1**. The emission intensity of the organogel can be recovered after further visible light (550 nm) irradiation as shown in Figure 5. In this manner, the emission intensity of the organogel of LMWG**1** can be switched off and on by alternating UV and visible light irradiations.

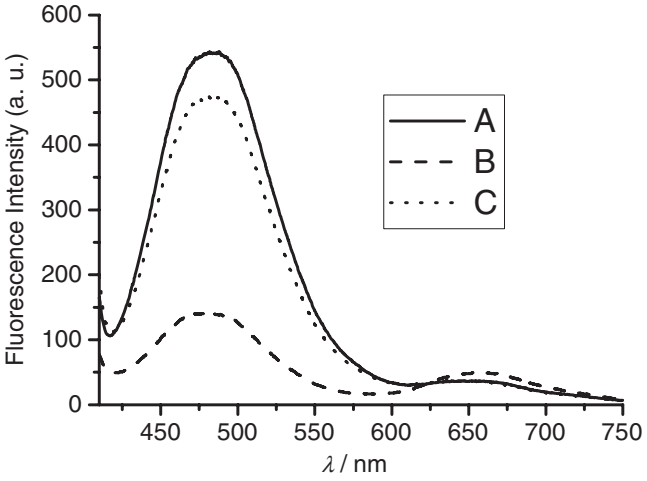


Figure 5. Fluorescence spectra of the organogels formed with LMWG **1** (20 mg mL^{-1}) and SP (4.0 mg mL^{-1}) in toluene (A), after UV light (365 nm) irradiation for 10 min (B) and further visible light (550 nm) irradiation for 10 min (C); $\lambda_{exc.}$ = 400 nm.

SP**3**, a dendron-substituted spiropyran (see Scheme 1), was synthesized and purified with the reported procedure.[15b] We have very recently described the gelation based on SP**3** and it is interesting to note that (i) the gel-phase was kept after the transformation of the open form of SP into the MC form induced by UV light irradiation, (ii) the gel absorbed strongly in the range of 480–700 nm after UV light irradiation, and (iii) the gel based on the MC form of SP**3** exhibited strong red emission.[15b] Therefore, it is appealing to examine the emission color tuning for the organogels based on LMWG**1** and SP**3**. Similarly, the organogel formed by LMWG**1** (10mM) and SP**3** (10 mM) was prepared by cooling the corresponding toluene solution. The xerogel was also characterized with SEM and TEM (see Figure S17). The SEM image shows that the xerogel contains densely-packed entangled nanofibers with the average width of ca. 200 nm. Small nanofibers of different widths are bound together to form

Table 1. Fluorescence lifetimes of organogels formed with LMWG**1** (20 mg mL^{-1}) in toluene (A), and those of gels with LMWG**1** (20 mg mL^{-1}) in toluene with different doping concentrations of PI**2** [0.1 mM (B), 1.0 mM (C) and 10mM (D)]; the fluorescence intensity at 490 nm was monitored; $\lambda_{exc.}$ = 365 nm.

Organogels	τ_1 (ns)	τ_2 (ns)
A	1.091 ± 0.020(47.24%)	4.334 ± 0.034(52.76%)
B	1.082 ± 0.019(47.91%)	4.270 ± 0.032(52.09%)
C	0.939 ± 0.018(45.28%)	4.274 ± 0.030(54.72%)
D	0.541 ± 0.013(52.09%)	3.431 ± 0.025(47.91%)

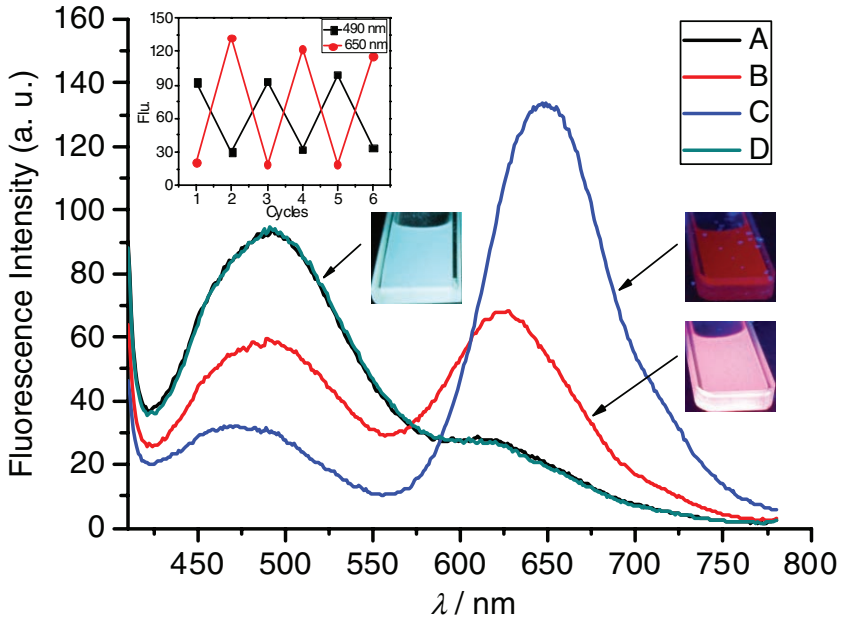


Figure 6. Fluorescence spectra of the organogel formed with LMWG**1** (10 mM) and SP**3** (10 mM) in toluene (A), after UV light (365 nm) irradiation for 30 s (B) and 10 min (C), and further visible light (550 nm) irradiation for 10 min (D), $\lambda_{exc.}$ = 400 nm; the inset shows the reversible variation of fluorescence intensities at 490 nm and 650 nm upon alternating UV and visible light irradiations, and photos of the organogels irradiated under UV light immediately (blue), after 30 s (pink) and 10 min (red), respectively.

large fibers based on the TEM image. As expected, the emission was switched on after gelation, but the emission intensity of gel with LMWG**1** and SP**3** decreased compared to that of the gel with pure LMWG**1** (see Figure S18).[19]

Figure 6 shows the emission spectrum of the gel based on LMWG**1**/SP**3** and those after UV light (365 nm) irradiation for 30 s, 10 min, and further visible light irradiation for 10.0 min. The emission in the range of 425–575 nm due to LMWG**1** became weak after UV light irradiation and simultaneously the emission in the range of 575–750 nm, due to the MC form of SP**3** according to previous report,[15b] emerged. Such emission spectral change is owing to the photoinduced energy transfer between LMWG**1** and the corresponding MC form of SP**3**. The photoinduced energy transfer between LMWG**1** and the MC form of SP**3** should be responsible for emission spectral change for the gel based on LMWG**1**/SP**3** after UV light irradiation. The fluorescence life-times (Figure S19) of the gel at 490 nm based on LMWG**1**/SP**3** after UV light irradiation for 10.0 min were estimated to be 0.25 ns (78.9%) and 1.64 ns (21.1%). Compared to those of the gel with pure LMWG**1** listed in Table 1, the fluorescence life-times of the gel based on LMWG**1**/SP**3** were obviously shortened. This is in agreement with the emission spectral change. Moreover, the emission spectrum could be resumed after further visible light irradiation. Accordingly, the emission intensities at 490 nm and 650 nm of the gel based on LMWG**1**/SP**3** can be reversibly tuned by UV–visible light irradiations as depicted in the inset of Figure 6. Additionally, the emission color of the gel of LMWG**1**/SP**3** was also dependent on the UV light irradiation time and the emission color changed from initial blue to pink and red after UV light (365 nm) irradiation for 30 s and 10.0 min, respectively (see Figure 6). It was also found that the fluorescence intensity at 650 nm decreased and that at 490 nm increased gradually when the gel of LMWG**1**/SP**3** that was exposed to UV light for 10 min was left in dark for different times as depicted in Figure S20. This is understandable by considering the fact that the MC form of SP**3** can be transformed into the closed form in the dark gradually; as a result the photoinduced energy transfer between LMWG**1** and the MC form of SP**3** cannot occur efficiently. The fluorescence decay at 650 nm was also measured for the gel based on LMWG**1**/SP**3** that was exposed to UV light for 10 min (see Figure S21). But, the fluorescence intensity at 650 nm decays very quickly.

Similar emission spectral change was also observed for the organogels based on LMWG**1**/SP**3** in different molar ratios (see Figures S22–S24); the more amount of SP**3** in the gel, the weaker is the emission intensity in the range of 425–575 nm and the stronger is the emission intensity in the range of 575–650 nm after UV light irradiation. This is because more MC form of SP**3** is generated after UV light irradiation if more SP**3** is present in gel and consequently the corresponding photoinduced energy transfer will take place more efficiently.

3. Conclusion

By making use of the AIE behavior of tetraphenylethene derivatives, a dendron-substituted tetraphenylethene compound as a new organogelator (LMWG**1**) was designed and investigated. Gelation-induced fluorescence enhancement was observed for the gel based on LMWG**1** and its fluorescence can be reversibly tuned by varying the temperature of the ensemble. The photoinduced energy-transfer can occur between LMWG**1** and PI**2** in the gel phase, but it cannot occur in the corresponding solution. Furthermore, the emission life-times of the gel of LMWG**1** and PI**2** as a "dopant" indicate that the photoinduced energy transfer occur more efficiently by increasing the concentration of PI**2**. As a result, the emission color of the gel of LMWG**1** and PI**2** can be tuned by varying the concentration of PI**2**. By taking the advantage of the photochromic transformation of spiropyran, the emission color of the organogels based on LMWG**1** and SP**3** can be switched by alternating UV and visible light irradiations. The emission color can be also tuned by varying the irradiation time. In this way, organogels based on LMWG**1** with multiemission color can be achieved in the presence of SP**3** after light irradiations. Such organogels with tunable emission colors may find applications in various areas such as data recording.

4. Experimental Section

General: 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 NMR and ^{13}C NMR spectra were recorded with Bruker 400 MHz spectrometers. Mass spectra were determined with BEFLEX III for TOF-MS and SHIMADZU GCMS-QP2010 for EI-MS. Elemental analysis was performed on a Carlo-Erba-1106 instrument. A confocal laser scanning microscopy system (CLSM, 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 frozen dried xerogel was sputtered with platinum. TEM measurements were conducted with a JEOL 2010 transmission electron microscopes using an accelerating rate voltage of 120 keV. Absorption spectra were recorded on a JASCO V-570 spectrophotometer. Fluorescent spectra were measured with a Hitachi F-4500 spectrophotometer. Fluorescence lifetimes were measured by using an Edinburgh Analytical Instruments (FLS920) and evaluated with the software designed for the equipment. The fluorescence decay were fitted by deconvoluting the instrument response with biexponential decay: Fit = $A + B_1\exp(-t/\tau_1) + B_2\exp(-t/\tau_2)$. The quality of fit was judged by the value of χ^2 and visual inspection of the residuals.

Synthesis of Compound 5: Compound **4** was synthesized according to the literature.[11f] To a 100 mL flask was added **4** (2.36 g, 6.0 mmol) and acetic acid (40 mL). Then, HBr (12 mL, 33% in HOAc w/w) was added and the mixture was refluxed at 120 °C for 12 hours. After cooling to room temperature, it was poured into water (500 mL). The precipitate was filtered and purified by column chromatography on silica with petroleum ether (60–90 °C)/ethyl acetate (6/1, v/v) as eluent. Compound **5** (680 mg) was obtained as light yellow solid powder in 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.08 (m, 10H), 6.92 (m, 4H), 6.64 (m, 2H), 6.56 (m, 2H), 4.71 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.1, 154.0, 144.4, 144.3, 139.9, 139.7, 136.8, 136.6, 136.5, 132.9, 132.7, 131.5, 127.8, 127.7, 126.4, 114.8, 114.7, 113.4, 113.2, 55.3; EI-MS (*m*/*z*): 378 $[M]^+$; Anal. calcd. for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 85.70; H, 6.10.

Synthesis of Compound 6: To a flask (50 mL) were added compound **5** (567 mg, 1.5 mmol), dimethylformamide (DMF, 20 mL), 1, 2-dibromoethane (1.3 mL, 15 mmol) and K_2CO_3 (1.38 g, 10 mmol). The mixture was stirred at room temperature for 3 days. Then it was poured into water (80 mL) and extracted with dichloromethane. The organic layer was washed with water (80 mL) for five times and dried over Na_2SO_4. The solution was purified by column chromatography on silica gel with petroleum ether (60–90 °C)/ethyl acetate (10/1, v/v) as eluent. Compound **6** (582 mg) was obtained as light yellow solid powder in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.10 (m, 10H), 6.99 (m, 4H), 6.67 (m, 4H), 4.24 (m, 2H), 3.75 (s, 3H), 3.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.2, 156.6, 144.4, 144.3, 140.1, 139.6, 137.4, 136.5, 132.8, 132.7, 131.6, 127.9,127.8, 126.4, 114.1, 114.0,113.3, 113.2, 67.9, 55.3, 29.3; EI-MS (*m*/*z*): 484 and 486 $[M]^+$; Anal. calcd. for $C_{29}H_{25}BrO_2$: C, 71.76; H, 5.19; Br, 16.46. Found: C, 71.72; H, 5.20; Br, 16.35.

*Synthesis of LMWG***1**: To a flask (50 mL) were added compound **6** (484 mg, 1.0 mmol), DMF (20 mL), ROH (R = dendron group, Scheme 1) (1.19 g, 1.0 mmol) and K_2CO_3 (1.38 g, 1.0 mmol). The mixture was stirred at room temperature for 3 days. Then it was poured into water (80 mL) and extracted with dichloromethane. The organic layer was washed with water (80 mL) for five times and dried over Na_2SO_4. The solution was purified by column chromatography on silica gel with dichloromethane/ethyl acetate (30/1, v/v) as eluent. LMWG**1** (1.28 g) was obtained as light yellow solid powder in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.29 (s, 4H), 7.82 (s, 8H), 7.12–6.89 (m, 23H), 6.68–6.63 (m, 4H), 5.12–5.09 (s, 12H), 4.31–4.25 (m, 4H), 3.93 (s, 24H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.2, 159.5, 159.4, 158.8, 158.1, 157.1, 144.4, 144.3, 140.0, 139.7, 138.9, 138.4, 137.0, 136.5, 132.8, 132.7, 132.0, 131.5, 127.8, 127.7, 126.4, 126.2, 123.5, 120.3, 119.0, 118.9, 114.0,113.9, 113.7, 113.3, 113.2, 70.2, 70.0, 66.8, 66.4, 55.2, 52.6; MALDI-TOF-MS (*m*/*z*): 1598.4 $[M]^+$, 1621.4 $[M + Na]^+$; Anal. calcd. for $C_{93}H_{82}O_{25}$: C, 69.83; H, 5.17. Found: C, 69.79; H, 5.21.

Gel Formation: In a typical gelation experiment, a weighed amount of LMWG**1** and 1.0 mL of the solvent were placed in a test tube, which was sealed and then heated until the sample was dissolved. Then, the hot solution was slowly cooled in ice water. The gels containing either PI**2** or SP**3** were prepared similarly.

CLSM images, XRD data, SEM images, TEM images, absorption and fluorescence spectra, fluorescence lifetime, and 1H-NMR and 13C-NMR spectra are available in the Supporting Information.

Supporting Information

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

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). The kind help from Prof. A. Xia is appreciated with regard to the fluorescence lifetimes measurements. The authors thank the anonymous reviewers for the comments and suggestions, which enable us to improve the manuscript.

Received: March 27, 2010
Revised: May 21, 2010
Published online: August 4, 2010

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[16] It should be noted that the fluorescence decay curves of LMWG**1** cannot be fitted with a single-exponential function, but they can be well fitted with a bi-exponential function. Therefore, two lifetimes were deduced for LMWG**1** in the gel phase and solution. Such two lifetimes may be ascribed to different conformations of LMWG**1** in the excited states by considering bulky dendron group in LMWG**1** and the intermolecular interactions in the gel phase.

[17] When the concentration of PI**2** in the gel was not higher than 10 mM, the emission intensity at 650 nm was very weak. For this reason the fluorescence decay was measured by monitoring the fluorescence intensity at 580 nm, at which LMWG**1** also exhibits emission. But, the fluorescence intensity at 580 nm should be mainly due to PI**2**.

[18] A weak emission around 660 nm was detected. This may be due to the fact that small amount of MC form of SP was formed during the measurement.

[19] This may be understood by considering the fact the SP**3** is a typical electron donor and as a result photoinduced electron transfer may occur between SP**3** and LMWG**1**.