Carbazole-Based Organogel as a Scaffold To Construct Energy Transfer Arrays with Controllable Fluorescence Emission

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A diaryldiketopyrrolopyrrole derivative functionalized with phenothiazine moieties (**DPPP**) was synthesized and introduced into the ordered 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzamide (**TBCB**) organogel system. It was found that **TBCB**-based gel became a scaffold to make **DPPP** molecules line up along the gel fibers, resulting in new self-assembled arrays, whose XRD patterns were quite different from those of the neat **TBCB** gel and **DPPP** crystal. In the composite gel, the occurrence of a partial energy transfer from the excited light-harvesting antenna of **TBCB** to the **DPPP** acceptor was confirmed on the basis of time-dependent and time-resolved fluorescence investigations. Remarkably, the composite gel could emit intense red light or purplish white light by tuning the excitation wavelength. Such ordered soft materials with color-tunable emission may possess potential applications in sensor and photonic devices.

Introduction

Photosynthetic light-harvesting antennae play an important role in the conversion of light energy to chemical energy that can be used by biological systems.[1] Photosynthesis starts by the absorption of a photon by light-harvesting antenna, comprising a great deal of pigments, which are organized in a specific geometry and embedded in protein matrices. It is found that the well-ordered assemblies of photofunctional chromophores are responsible for the highly efficient excitation energy transfer in the following step.[2] In the past decades, tremendous efforts have been made to mimic the natural photosynthetic system for exploring photochemical solar energy conversion and other optoelectronic devices operating at the molecular level.[3] As one of the strategies in the preparation of artificial light-harvesting antennae, the design of supramolecular multichromophoric arrays displaying directional energy transfer is fascinating. Recently, low molecular weight gels (LMWGs) have attracted particular attention due to their unique supramolecular architectures and potential applications in optoelectronic devices, template syntheses, drug delivery, and biomimetics systems.[4,5] LMWGs prefer to form 1D assemblies driven by multiple weak interactions (including dipole−dipole, van der Waals, hydrogen-bonding, π-stacking, etc.) in the original process of the gel formation. Thus, it provides an opportunity to fabricate novel 1D arrays with photoelectric functionality from π-conjugated organogelators.[6,7] Moreover, π-gel can be used as a scaffold or guider to

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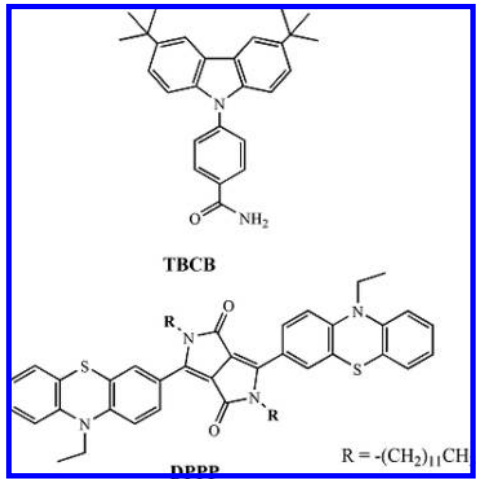
Scheme 1. Molecular Structures of TBCB and DPPP



arrange other chromophores for understanding energy transport processes, in which the organogelator molecules are good candidates for energy donors.[8]

Recently, we have designed a carbazole-based organogelator **TBCB** (Scheme 1) bearing two *tert*-butyl groups, which could form stable nanofibers of several micrometers in length in cyclohexane.[9] It is well-known that carbazole can transfer its excitation energy to the acceptor.[10] Therefore, if a π-conjugated energy acceptor, whose absorption may overlap the emssion of the **TBCB**-based gel, can arrange along the gel fiber and the distance between the donor and the acceptor may be in the range of the radius of Förster energy transfer, suparmolecular functional arrays with efficient photoinduced energy transfer can be generated. On the other hand, diaryldiketopyrrolopyrrole (**DPP**) is one of the important pigments with fascinating properties, such as strong red emission, extraordinary stability toward light and heat, high performance, and exceptionally fade-proof nature.[11] Notably, **DPP** is an electron-poor molecule, whose absorption can overlap the emission of the **TBCB** gel. Herein, we synthesized a **DPP** derivative functionalized with phenothiazine moieties (**DPPP**; Scheme 1), which was subsequently introduced into the ordered **TBCB**-based gel. Significantly, **TBCB**-based gel became a scaffold to make **DPPP** molecules line up along the gel fibers, which leads to the excitation energy transfer from **TBCB** to **DPPP** partly; thus, the fluorescence emission could be tuned by the excited wavelength.

Results and Discussion

As shown in Figure 1, we could find that the emission band of the cyclohexane gel of **TBCB** was located at 420 nm, which

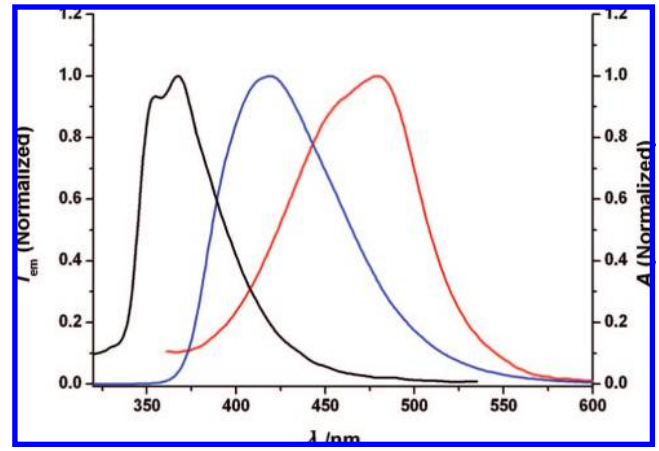


Figure 1. Normalized emission spectra of **TBCB** in solution (black) and gel (blue) and the absorption spectrum of **DPPP** (red) in cyclohexane.

showed larger overlapping with the absorption band of **DPPP** (480 nm) compared with the emission of **TBCB** in dilute solution (370 nm). In other words, the red-shift of the emission band of the gel compared with that of the corresponding solution would be in favor of the occurrence of the excitation energy transfer from **TBCB** to **DPPP**. We also calculated the spectral overlap integral $J(\lambda)$ of the emission band of the **TBCB**-based gel and the absorption band of **DPPP**, which was 9.24×10^{14} M^{-1} cm^{-1} nm^4 and almost 5-fold that of the **TBCB** solution (1.90×10^{14} M^{-1} cm^{-1} nm^4).

Because the well-ordered assemblies of the chromophores favor efficient excitation energy transfer, and the **TBCB** donor tended to self-assemble into ordered 1D nanostructures in the gel phase, we tried to use **TBCB**-based gel as a scaffold to arrange the **DPPP** acceptor to construct a novel photoinduced energy transfer system. The composite gels based on **TBCB** (1.9×10^{-3} M) and **DPPP** (1.9×10^{-4} M) were gained after the hot cyclohexane solution of **DPPP** and **TBCB** was cooled naturally to room temperature. From the SEM images as shown in Figure 2a,b, we could find that the composite gel gave some longer fibers, which preferred to be parallel, compared with many dense and random 1D fibers to interlink with each other in the neat **TBCB**-based gel. The TEM image (Figure 2c) revealed that the fibers in the composite gel were straight with several micrometers in length and 120−140 nm in width, and each fiber bundle was composed of several fine fibers juxtaposed with each other, which was very clear in the AFM phase image (Figure 2d). The morphologic difference between the composite gel and the neat gel of **TBCB** suggested that **DPPP** molecules might interact with the **TBCB** organogelator in the composite gel. This would be further affirmed on the basis of XRD, FT-IR, and electronic spectral investigations. As reported in our previous work, **TBCB** molecules could form bimolecular lamellar packing with a long period of 2.41 nm in the gel phase.[9] Figure 3 showed the XRD pattern of the **DPPP** crystal obtained from cyclohexane, and a sharp peak corresponding to a period of 2.44 nm appeared. It was notable that the composite gel gave three legible peaks corresponding to the periods of 5.84, 2.90, and 1.48 nm, respectively, according with the ratio 1:1/2:1/4. It illustrated that the lamellar structure with an interlayer distance of 5.84 nm formed in the composite gel.[12] Thus, we could deduce that **DPPP** molecules were embedded into the self-assemblies of **TBCB** to

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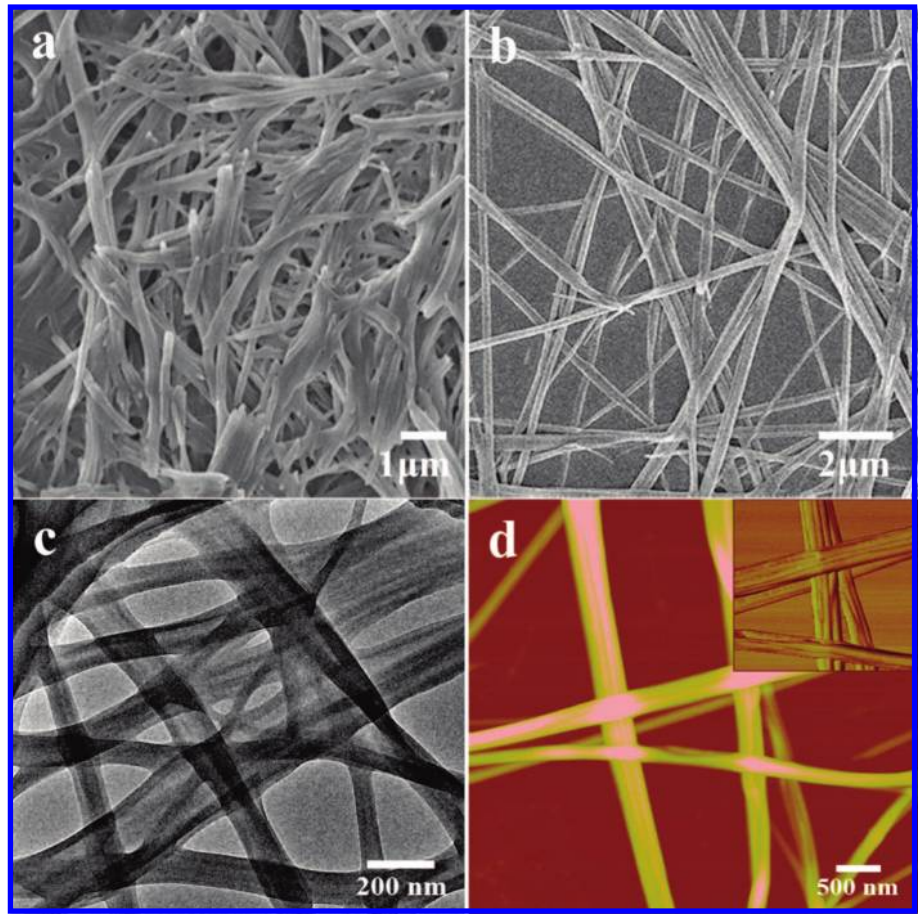

Figure 2. SEM images of (a) **TBCB** gel and (b) the composite gel based on **TBCB** and **DPPP** (the molar ratio is 10:1). (c) TEM and (d) AFM height images of the composite gel. Inset is AFM phase image.

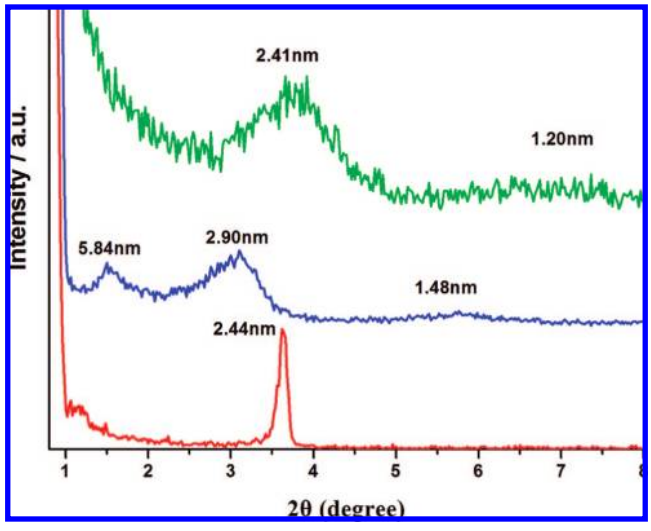

Figure 3. XRD patterns of the dried **TBCB** gel (green), the dried composite gel based on **TBCB** and **DPPP** (blue, the molar ratio is 10:1), and the **DPPP** crystal (red) obtained from cyclohexane.

lead to new self-assembled arrays, rather than simply deposited on the surface of the **TBCB** gel fibers on account of the absence of XRD patterns attributed to the neat **TBCB** gel and **DPPP** crystal.

The FT-IR spectra of the neat **TBCB** gel and the composite gel based on **TBCB** and **DPPP** are given in Supporting Information Figure S1. In the neat **TBCB** gel, two peaks located at 3379 and 3209 cm^{-1} with equivalent intensity, ascribing to the vibration of N−H moieties, were detected, suggesting the formation of hydrogen bonding between amides.[9] However, in the composite gel the peak at 3220 cm^{-1} was much weaker than that at 3370 cm^{-1}, and a new peak at 3540 cm^{-1} arising from the free N−H units was observed. It suggested that the **DPPP** molecules have inserted into the self-assemblies of **TBCB**, and parts of the hydrogen bonds between amides in **TBCB** were cleaved. As a result, **DPPP** were integrated into the self-assembled organogel, and new well-ordered supramolecular arrays based on the energy donor and acceptor were generated. The absorption spectrum of the composite gel based on **TBCB** (1.9×10^{-3} M) and **DPPP** (1.9×10^{-4} M) in cyclohexane revealed no electronic interaction in the ground state between the two components, because it was a simple combination of the absorption of **TBCB** and **DPPP** except for a slight hypsochromic shift of **DPPP** from 527 to 524 nm (Supporting Information Figure S2).

Figure 4 showed the fluorescence microscopy (FM) images of the neat **TBCB** gel, **DPPP** crystal, and the composite gel. It was found that many gel fibers based on **TBCB** emitting bright blue light (Figure 4a) could be observed when excited by the light at 330−385 nm, while the **DPPP** crystal could give intense red emission under excitaion by either UV (330−385 nm; Figure 4b) or visible (510−550 nm, not shown) light. Meanwhile, different excitation wavelengths were employed to excite the composite gel. It was clear as shown in Figure 4c that many nanofibers emitting red light appeared when excited by the light of 510−550 nm, which could only excite **DPPP** instead of **TBCB**, so the red emission was ascribed to the fluorescence of **DPPP**. When the same sample was excited by the light of 330−385 nm, all the gel fibers turned to emit strong purplish white light (Figure

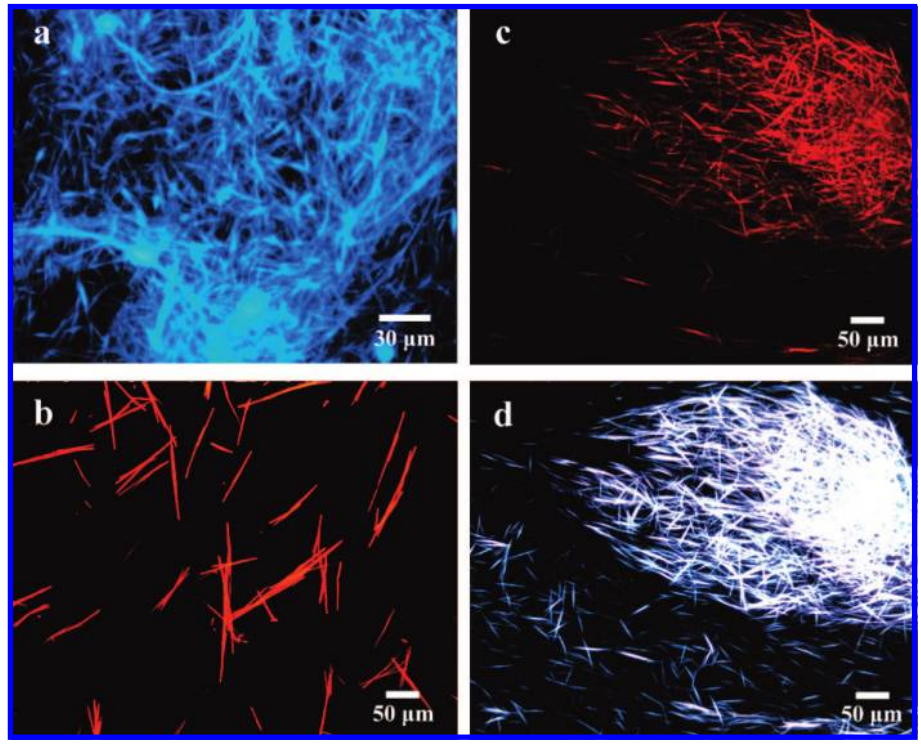

Figure 4. Fluorescence microscopy images of (a) the **TBCB** gel, (b) **DPPP** crystal, and (c,d) the composite gel based on **TBCB** and **DPPP** (the molar ratio is 10:1). The excitated wavelengths for (a,b,d) are 330−385 nm and (c) 510−550 nm.

4d). It further illustrated that **DPPP** molecules with red emssion were embedded in the **TBCB** gel fibers emitting blue light uniformly, and the purplish white light resulted from the mixed colors of red and blue in a certain percentage.

The time-dependent fluorescence emission spectra of **TBCB**, **DPPP**, and the mixture of **TBCB** and **DPPP** in cyclohexane were obtained via natural cooling of the solutions from 80 to 20 °C and aging at room temperature (Figure 5). Upon excitation at 297 nm, **TBCB** (1.9×10^{-3} M) gave an emission at 371 nm at 80 °C. With decreasing temperature, the emission band notably shifted bathochromically, accompanied by a sharp enhancement of the emission intensity (Figure 5a). After cooling the **TBCB** solution for 3 min, the stable organogel was formed, and the emission band shifted to 400 nm. After more than 38 min, it reached 419 nm. On the contrary, the emission intensity at 607 nm decreased rapidly with cooling of the hot solution of **DPPP** when excited at 297 nm (Figure 5b), owing to the aggregation, which could be approved by the fact that the emssion intensity of **DPPP** gradually decreased with increasing concentration in cyclohexane (Supporting Information Figure S3). When **DPPP** was added into the hot solution of **TBCB**, the emission bands of the mixture seemed to be a simple combination of the two components, suggesting no interaction between the donor and the acceptor in the case of absence of self-assemblies. Significantly, the emission intensity of **DPPP** at ca. 600 nm started to increase obviously when the hot solution of the mixture was cooled down as shown in Figure 5c. Notably, it ran counter to the decrease of the emission of **DPPP** during cooling of its individual hot solution. It was also found that the emission intensity at ca. 400 nm ascribed to **TBCB** in the composite gel was restricted compared with that in the neat **TBCB** gel (the PL measurement was taken under the same conditions, and the width of the slit was 5 nm), which revealed that the excitation energy of **TBCB** might partly transfer to the acceptor. It was responsible for the color-tunable emission of the composite gel observed in the FM images.

Further evidence for the excitation energy transfer was obtained from the fluorescence decay profiles of the neat **TBCB** gel and the composite gel based on **TBCB** containing a different amount of **DPPP** as shown in Figure 6 (monitored at 402 nm). The neat **TBCB** gel exhibited a monoexponential decay with time constant $\tau = 6.86$ ns, whereas the emission decay of **TBCB** became faster with an increasing amount of **DPPP** in the composite gel. For example, the lifetime of **TBCB** decreased to 5.26, 5.19, and 4.97 ns when the molar ratio of **DPPP** to **TBCB** was 1:100, 1:20, and 1:10, respectively. We deduced that the decrease of the lifetime of **TBCB** was due to the migration of the excitation energy of **TBCB** to **DPPP**.[8a,13]

Conclusions

In conclusion, we generated well-ordered 1D arrays based on carbazole and diaryldiketopyrrolopyrrole derivatives, in which **TBCB** organogel was used as a scaffold to make **DPPP** line up along the gel fibers. In the composite gel, partial excitation energy transfer from **TBCB**, the light-harvesting antenna, to the **DPPP** acceptor occurred. Notably, the composite gel could emit intense red light or purplish white light by tuning the excitation wavelength. It provided a simple way to fabricate functional supramolecular arrays. Such ordered soft materials with various colors may have potential applications in sensor and photonic devices.

Experimental Section

General Information. ^{1}H NMR spectra were recorded on Mercury plus 500 MHz using $CDCl_3$ and DMSO-d_6 as solvents. Mass spectra were performed on Agilent 1100 MS series and AXIMA CFR MALDI/TOF (Matrix assisted laser desorption ionization/time-of-

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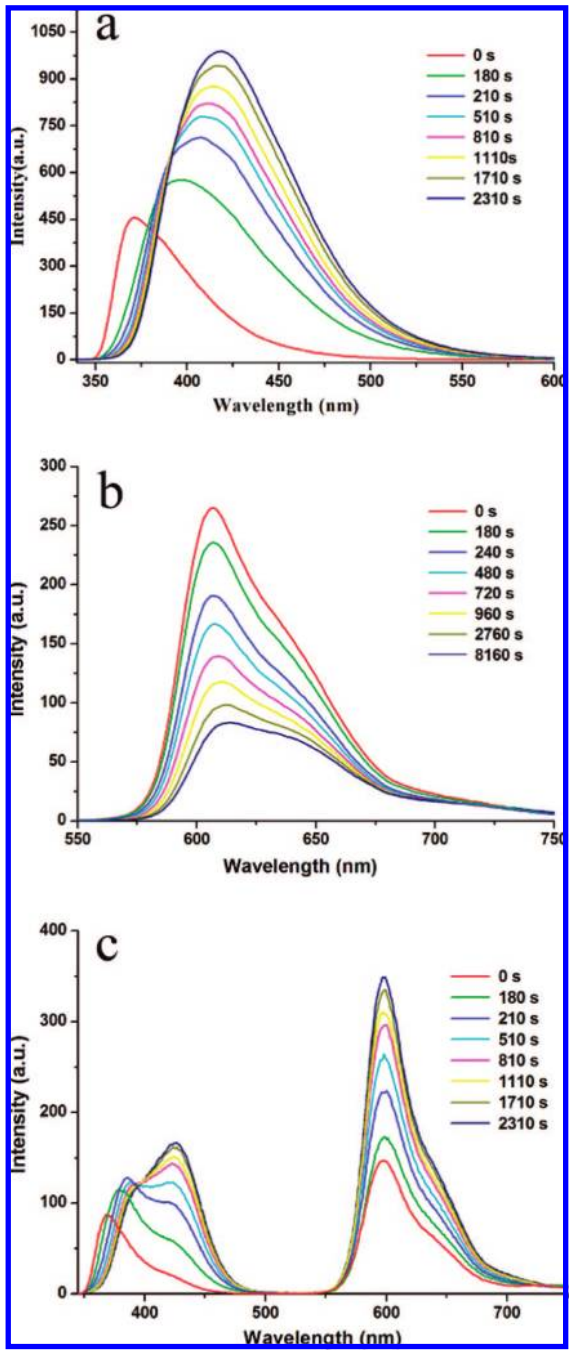


Figure 5. Time-dependent PL spectra excited at 297 nm: (a) **TBCB** (1.90 mM), (b) **DPPP** (0.19 mM), and (c) the mixture of **TBCB** (1.90 mM) and **DPPP** (0.19 mM) in cyclohexane, cooling the hot solutions at 80 to 20 °C naturally.

flight) MS (COMPACT). UV−vis absorption spectra were determined on a Shimadzu UV-1601PC spectrophotometer. Fluorescence spectra were carried out on a Shimadzu RF-5301 luminescence spectrometer. Fluorescence lifetimes were measured using the time-correlated single photon counting technique with FL920 fluorescence lifetime spectrometer. The excitation source was a nF900 ns flashlamp. Lifetimes were obtained by deconvolution of the decay curves. Fluorescence microscopy images were taken on fluorescence microscope (Olympus Reflected Fluorescence System BX51, Olympus, Japan). FT-IR spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating samples in KBr pellet. X-ray diffraction (XRD) patterns were carried out on a Japan Rigaku D/max-γA instrument. XRD was equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å), employing a scanning rate of 0.02 s^{-1} in the 2θ range from 0.7 to 10. Scanning electron microscopy

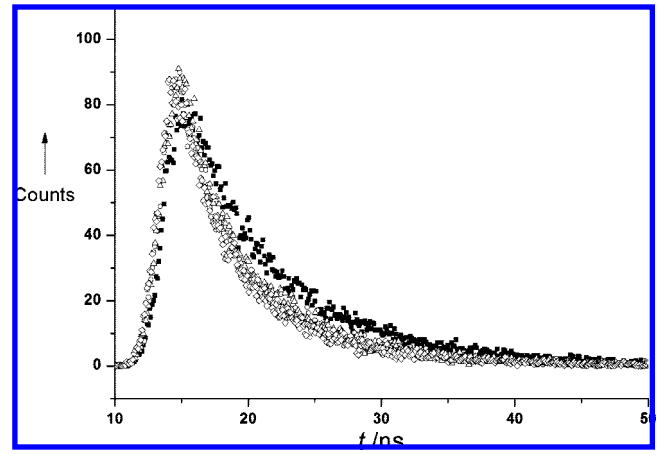


Figure 6. Fluorescence decay profiles of the neat **TBCB** gel (■) and the composite gel based on **DPPP** and **TBCB**; the molar ratios are 1:100 (○), 1:20 (△), and 1:10 (◇), monitored at 402 nm, $\lambda_{ex} = 297$ nm.

(SEM) observations were carried out on a Japan Hitachi model X-650 San electron microscope. The samples for these measurements were prepared by casting the organogel on silicon wafers and drying at room temperature, and then coating with gold. Transmission electron microscopy (TEM) was taken with a Hitachi mode H600A-2 apparatus by wiping the samples onto a 200-mesh copper grid followed by naturally evaporating the solvent. Atomic force microscopy (AFM) images were taken with a Nanoscope IIIa AFM Multimode (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si cantilevers.

Synthesis and Characterizations. The organogelator **TBCB** was synthesized as per literature procedure.[9] 10-Ethyl-10*H*-phenothiazine (**1**) was prepared according to the literature.[14]

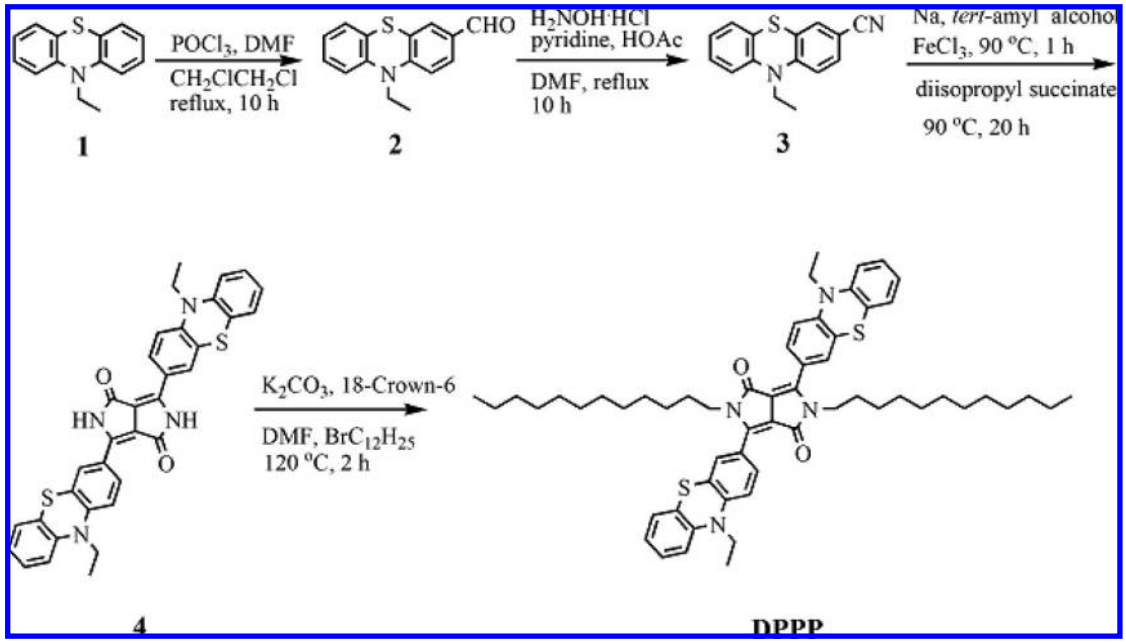
*10-Ethyl-10H-phenothiazine-3-carbaldehyde (**2**).* $POCl_3$ (6.7 g, 43.1 mmol) was added slowly in DMF (6 mL) at 0 °C, and the mixture was stirred for 1 h at 25 °C. Then, the 1,2-dichloroethane solution (15 mL) containing 10-ethyl-10*H*-phenothiazine **1** (5.0 g, 22.0 mmol) was added slowly into the above mixture at 0 °C. After refluxed for 10 h, the mixture was cooled to room temperature and poured into 150 mL H_2O. The product was extracted with dichloromethane. After concentrating, the solid was recrystallized from petroleum ether to give 3.0 g (54%) of a light yellow solid. mp: 128.0−130.0 °C. IR (KBr, cm^{-1}): 2980, 1670, 1600, 1580. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 9.79 (1 H, s, CHO), 7.64 (1 H, d, Ar−H), 7.58 (1 H, d, Ar−H), 7.18−7.15 (1 H, t, Ar−H), 7.10 (1 H, d, Ar−H), 6.98−6.95 (1 H, t, Ar−H), 6.92−6.89 (2 H, t, Ar−H), 4.00−3.96 (2 H, m, -CH_2), 1.47−1.44 (3 H, t, -CH_3). MS, *m/z*: calcd 255.3, found 256.0 [$M^+ + H$].

*10-Ethyl-10H-phenothiazine-3-carbonitrile (**3**).* A mixture of 10-ethyl-10*H*-phenothiazine-3-carbaldehyde **2** (4.0 g, 17.6 mmol), $H_2NOH \cdot HCl$ (1.3 g, 18.7 mL), pyridine (2.3 g, 34.3 mmol), HOAc (2.5 g, 41.6 mL), and DMF (10 mL) was stirred and refluxed for 5 h. After cooling to room temperature, the mixture was poured into 150 mL H_2O and stirred for 20 min. The solid was collected by filtration and purified by chromatography (silica gel, petroleum ether/ethyl acetate = 8:1 v/v) to give 4.1 g (92%) of a white solid. mp: 100.0−102.0 °C. IR (KBr, cm^{-1}): 2920, 2870, 2220, 1600, 1570. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.40 (1 H, d, Ar−H), 7.32 (1 H, d, Ar−H), 7.19−7.16 (1 H, t, Ar−H), 7.09 (1 H, d, Ar−H), 6.97 (1 H, s, Ar−H), 6.90 (1 H, d, Ar−H), 6.84 (1 H, d, Ar−H), 3.94 (2 H, s, -CH_2), 1.44−1.41 (3 H, t, -CH_3). MS, *m/z*: calcd 252.1, found 253.0 [$M^+ + H$].

*3,6-Bis(10-ethyl-10H-phenothiazin-3-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**4**):* Sodium (2.3 g, 0.1 mol) was dissolved in 50 mL of *tert*-amyl alcohol at 90 °C for 1 h catalyzed by trace of $FeCl_3$.

(14) Danilevicius, A.; Ostrauskaite, J.; Grazulevicius, J. V.; Gaidelis, V.; Jankauskas, V.; Tokarski, Z. *J. Photochem. Photobiol. A: Chem.* **2004**, *163*, 523.

Scheme 2. Synthesis of DPPP



After the solution was cooled to 50 °C, 10-ethyl-10*H*-phenothiazine-3-carbonitrile **3** (2.5 g, 10 mmol) was added, and the mixture was heated to 90 °C. Then, diisopropyl succinate (0.8 g, 4 mmol) in 5 mL of *tert*-amyl alcohol was added dropwise over 2 h. Subsequently, the resulting suspension was kept at 90 °C for 20 h. After the mixture was cooled to 50 °C, 20 mL of glacial acetic acid was slowly added. The solid was collected by filteration, washed with hot methanol and water for several times, and dried in vacuo at 80 °C. 4.2 g (72%) of purplish red solid was obtained. Since the product was insoluble, it was not further purified for the following step.

*2,5-Didodecyl-3,6-bis(10-ethyl-10H-phenothiazin-3-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**DPPP**).* A mixture of 3,6-bis(10-ethyl-10*H*-phenothiazin-3-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **4** (3.4 g, 3 mmol), K_2CO_3 (1.4 g, 10 mmol), and 70 mL DMF was heated to 120 °C using a trace of 18-crown-6 as the catalyst. 1-Bromododecane (2.5 g, 10 mmol) in 10 mL DMF was slowly added, and the mixture was kept at 120 °C for another 2 h. After cooling to room temperature, the mixture was poured into 200 mL H_2O and stirred for 20 min, and the solid was collected by filtration and purified by chromatography (silica gel, petroleum ether/ethyl acetate = 15:1 v/v) to give 1.2 g (42%) of a purplish red solid. mp: 128.0−130.0 °C. IR (KBr, cm^{-1}): 3060, 2920, 2850, 1670, 1590. ^1H NMR (DMSO-d_6, 500 MHz, ppm): δ 7.70 (4 H, d, Ar−H), 7.25−7.22 (2 H, t, Ar−H), 7.15 (4 H, d, Ar−H), 7.08 (2 H, d, Ar−H), 7.01−6.98 (2 H, t, Ar−H), 4.02−3.98 (4 H, m, $-CH_2$), 3.77−3.74 (4 H, t, $-CH_2$), 1.46−1.42 (4 H, t, $-CH_2$), 1.35−1.33 (6 H, t, $-CH_3$), 1.23−1.14 (36 H, m, $-CH_2$), 0.83−0.80 (6 H, t, $-CH_3$) (Supporting Information Figures S5 and S6). MS, *m*/*z*: calcd 922.5, found 922.6 [$M^+ + H$] (Supporting Information Figure S7).

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Supporting Information Available: Additional images (Figures S1−S4), ^1H NMR spectra, and MALDI-TOF mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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