

Functional Organogel Based on Salicylideneaniline Derivative with Enhanced Fluorescence Emission and Photochromism

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Abstract: A new organogelator based on salicylideneaniline derivative with cholesterol moieties was synthesized, and it was proposed combining with of gelation test that it could gel various organic solvents, such as 1-butanol, 1-octanol, butyl acetate, tetrachloromethane, benzene, and toluene etc. From the results of UV-vis absorption and CD spectra, XRD pattern, SEM and TEM measurements, and the semi-empirical (AM1) calculations, we believed that the

gelator molecules could self-assemble into left-handed helical nanofibers through unimolecular layer packing, which further twisted into the thicker fibers and constructed 3-D networks in the gel phase. Interestingly, the organogel exhibited strong fluorescence enhancement compared with the solution under the same concentration because of the formation of J-aggregation. Meanwhile, the photochromism of the organogel could take place under UV light irradiation.

Both strong fluorescence emission and photochromism properties were concurrent in one system based on salicylideneaniline derivative. It was suggested that the self-assembly of the functional organogelator could lead to unique photophysical properties.

Keywords: enhanced fluorescence · helical structure · photochromism · self-assembly

Introduction

Recently, low molecular mass gelators (LMMG), especially with functional and chiral moieties have attracted substantial attention in supramolecular chemistry and material science,^[1] because some of their physical properties can be sharply

modulated during the formation of the gels, in which the gelator molecules self-assemble into nanoscale superstructures, such as fibers, rods, and ribbons, through weak non-covalent interactions (hydrogen bonding, π - π interaction, van der Waals, coordination, and charge-transfer interaction). So far many functional modules have been successfully integrated into LMMG, which possess specific applications in light harvesting,^[2] energy transfer and charge transfer,^[3] photo, enzyme and other switches,^[4] and chiral or molecular shape selection.^[5] It is well known that salicylideneaniline derivatives could exhibit unusual functionalities, such as tunable fluorescence,^[6] photochromism,^[7] thermochromism,^[8] solvatochromism,^[9] liquid crystal,^[10] and nonlinear optics^[11] etc. Up to date, no example of an organogelator consisting of salicylideneaniline moiety ever was reported.

As suggested by van Esch et al,^[1b] if an organic compound is expected to be a gelator for organic solvent, three important guidelines must be followed: 1) presence of strong self-complementary and unidirectional intermolecular interactions to induce one-dimensional (1-D) packing of the molecules; 2) control of the interfacial energy between the aggregation and the solvent to adjust the solubility of the gelator and to prevent crystallization; and 3) some factors favoring the 1-D fibers to cross-link into three-dimensional (3-D) networks. Recently, Birkedal et al reported the crystal structure of compound **1'** (bis[4-(salicylideneamino)phenyl]-methane),^[12] which is in V-shaped conformation and packed into 1-D J-aggregations along with b axis via strong π - π interaction among the aromatic rings, as shown in Figure 1. Such close

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Supporting information for this article is available on the WWW under <http://www.chemed.org/> or from the author: **The UV-vis spectra of molecule 1'** in dilute solution and crystal state. The FT-IR spectra of xerogel before and after irradiation. TEM image of benzene/cyclohexane gel.

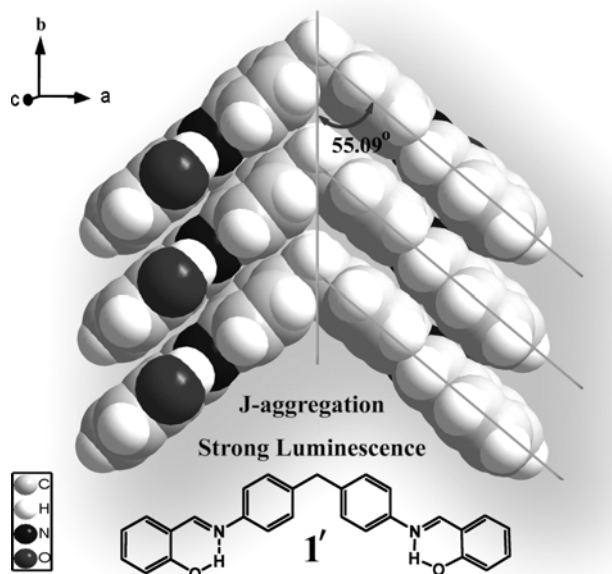
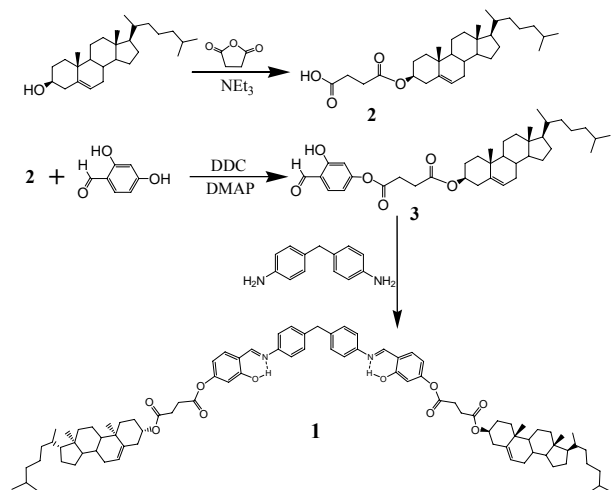


Figure 1. One-dimensional packing of **1'** along with b axis in crystal state.



Scheme 1. The synthetic route for organogelator **1**.

stacking (distance between the two adjacent parallel aromatic rings is 3.6 Å) of the salicylideneaniline groups leads to enhanced photoluminescence and non-photochromism under UV light irradiation.^[7e,13] Therefore, if such Schiff base dimer is integrated into the designed molecule, it would possibly self-assemble and be arranged into 1-D aggregations via unidirectional π - π interaction between aromatic rings. On the other hand, the chiral group in the gelator is usually considered as an important factor to prevent the crystallization from the solvent,^[1c] so lots of gelators with cholesterol units have been reported.^[14] Herein, we present the synthesis and characterization of molecule **1**, which, consisting of cholesterol and salicylideneaniline moieties (See Scheme 1), is found to be a good gelator in various organic solvents. The investigation on the self-assembling property of the gelator revealed that the molecules **1** could form left-handed helical nanofibers through unimolecular layer packing, which further constructed 3-D networks in the

organogel. Interestingly, the fluorescence emission intensity of the organogel was more than 1000 times higher than that of the solution under the same concentration due to the formation of J-aggregation in the gel state. Meanwhile, under UV light irradiation the photochromism of the organogel could be observed. The appearance of both strong fluorescence emission and photochromism in salicylideneaniline derivative system has rarely been reported because the strong photoluminescence proposes the dense stacking of molecules, which strongly suppresses the photo induced isomerization. It suggests that the introduction of certain aliphatic moieties into the functional organogelators may result in unusual optical properties due to their adjusting the intermolecular weak interactions and leading to the supramolecular self-assemblies with special superstructures.

Results and Discussion

Gelation Behavior: To reveal the gelation behavior of compound **1**, a series of organic solvents were employed and the results are listed in Table 1. Compound **1** can be easily dissolved in CHCl_3 , CH_2Cl_2 and THF at room temperature, but insoluble in lower alcohol and ester, such as ethanol and ethyl acetate, and aliphatic hydrocarbon solvents, such as cyclohexane, n-hexane, and n-decane, even under heating. It can gelatinize some higher alcohols and ester, and some non-polar aromatic solvents, including 1-butanol, 1-octanol, butyl acetate, tetrachloromethane, benzene, and toluene. However, the minimum gelation concentrations (MGC) necessary for the gel formation in benzene and toluene are relative large (> 0.5 wt/vol%) compared with that in 1-butanol, 1-octanol, butyl acetate and tetrachloromethane (< 0.2 wt/vol%). The addition of cyclohexane or n-hexane, which has poor solubility for compound **1**, into the benzene or toluene system could decrease the MGC. For example, the system may maintain the gel state below 0.1 wt/vol % in the mixture of benzene and cyclohexane ($v/v = 1/4$). In this case, the solvents with poor solubility for organogelator are deemed as the trapped one in order to decrease the MGC.^[15] As a result, molecule **1** is an effective gelator for various organic solvents.

Table 1. Gelation properties of **1** in organic solvents.

Solvent	1 ^a	Solvent	1 ^a
CHCl_3	S	Benzene ^b	G
CH_2Cl_2	S	Toluene ^b	G
THF	S	cyclohexane	I
ethanol	I	n-hexane	I
1-butanol	G	n-decane	I
1-octanol	G	benzene/cyclohexane ^c	G
ethyl acetate	I	benzene/n-hexane ^c	G
butyl acetate	G	tetrachloromethane	G

G: stable gel formed at room temperature; S: soluble; I: insoluble; ^a gelator = 1.0 wt/vol%; ^b minimum gelation concentration (MGC) is above 0.5 wt/vol%; ^c $v/v = 1:4$, MGC < 0.1 wt/vol%.

UV-vis Absorption and CD Spectra: To monitor the interaction between the chromophores, salicylideneaniline moieties, during the formation of the gels, variable-temperature absorption spectra of compound **1** in benzene/cyclohexane and 1-butanol systems were investigated as shown in Figure 2. It promotes the interaction between the chromophores that the absorption intensities of gels at lower temperature are weaker than those at higher temperature.^[16] Moreover, compared with the sols, red shift of 2 nm can be detected for the two gels, which indicates the formation of J-aggregations of

salicylideneaniline in the gel states.^[17] However, the maximal absorption peak of molecule **1** at 346 nm in dilute solution shifts to 360 nm in crystal state, and such large red shift ($\Delta\lambda = 14$ nm, see Figure S1) shows one strong exciton coupling owing to close distance between the chromophores in the crystal. The small red-shift phenomenon in the gel phase suggests that the exciton coupling of chromophores is weaker and the distance between the chromophores is larger than that of molecule **1** in crystal state.^[18] It is believed that the large cholesterol group actually inhibits the nearness of the chromophores, which will be further discussed in the later section. From the Figure 2e-f, the “melting” temperatures

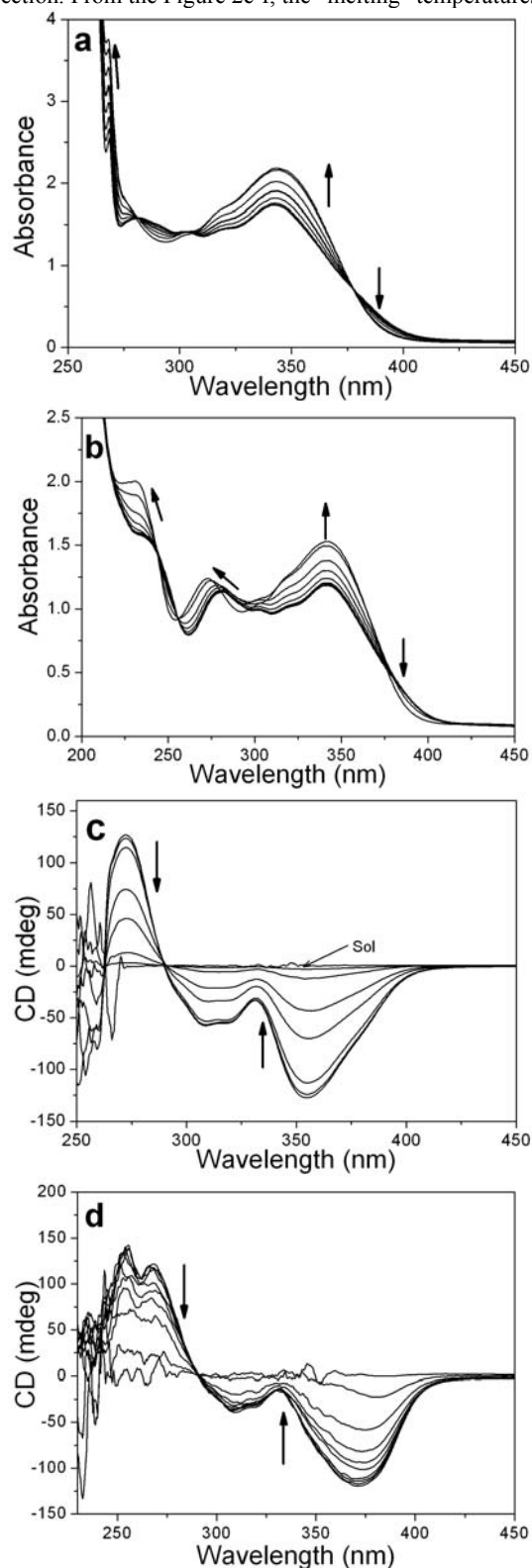


Figure 2. Temperature-dependence of the UV-vis (a and b) and CD spectra (c and d) of benzene/cyclohexane and 1-butanol organogels, respectively. The solution of benzene at 0.1 wt/vol% doesn't give CD response (see the curve of the center one labeled as “sol 20 °C” in the Figure 2c). (e) The plot of the absorbance and intensity of CD at 343 and 354 nm, respectively, in benzene/cyclohexane gel as a function of the temperature. (f) The plot of the absorbance and intensity of CD at 343 nm and 370 nm in 1-butanol gel, respectively. The concentrations in all cases are 0.1 wt/vol%.

are calculated for the phase transitions from aggregation to molecularly dissolved species, not from gel to sol.^[19] There is a clear dependence of the aggregation melting transition on the solvent, for example, the melting transition increases from 55 °C for the benzene/cyclohexane gel to 77 °C for the 1-butanol one at the same concentration.

CD spectroscopy has been considered a power tool in the research of the assembling processes leading to the helical superstructures. In the CD spectra, both gels give similar signals and non-bisignate exciton couplets with the opposite signals, indicating no center helical overlay between the dipole moments of two gelators in the gels^[20] as shown in Figure 2c-d. And the measurement of molar ellipticity [θ] (-175000 and -164144 for benzene/cyclohexane and 1-butanol, respectively) reveals the similar intensity of exciton coupling for both gels. Combining the result of UV-vis absorption spectra, it is rational that molecule **1** is packed in an anti-clockwise helical direction in both gel phases.^[21] In addition, the melting transitions obtained from temperature-dependent CD spectra were the same as those from UV observation (Figure 2e-f).

Variable-temperature ¹H NMR Spectra: NMR spectra can provide the interaction not only between the chromophores but also between the cholesterol moieties. The temperature-dependent ¹H NMR spectral change of **1** in [D₆]benzene/cyclohexane-d₁₂ gel was shown in Figure 3 along with the assignments of the key peaks for aromatic and aliphatic (cholesterol and succinic ester) subunits. The peaks ascribed to aliphatic moieties are consistently visible within the temperature range from 30 to 90 °C, and become sharper and stronger gradually with the increasing temperature.^[22] On the other hand, weak and broad NMR resonance peaks for the aromatic units

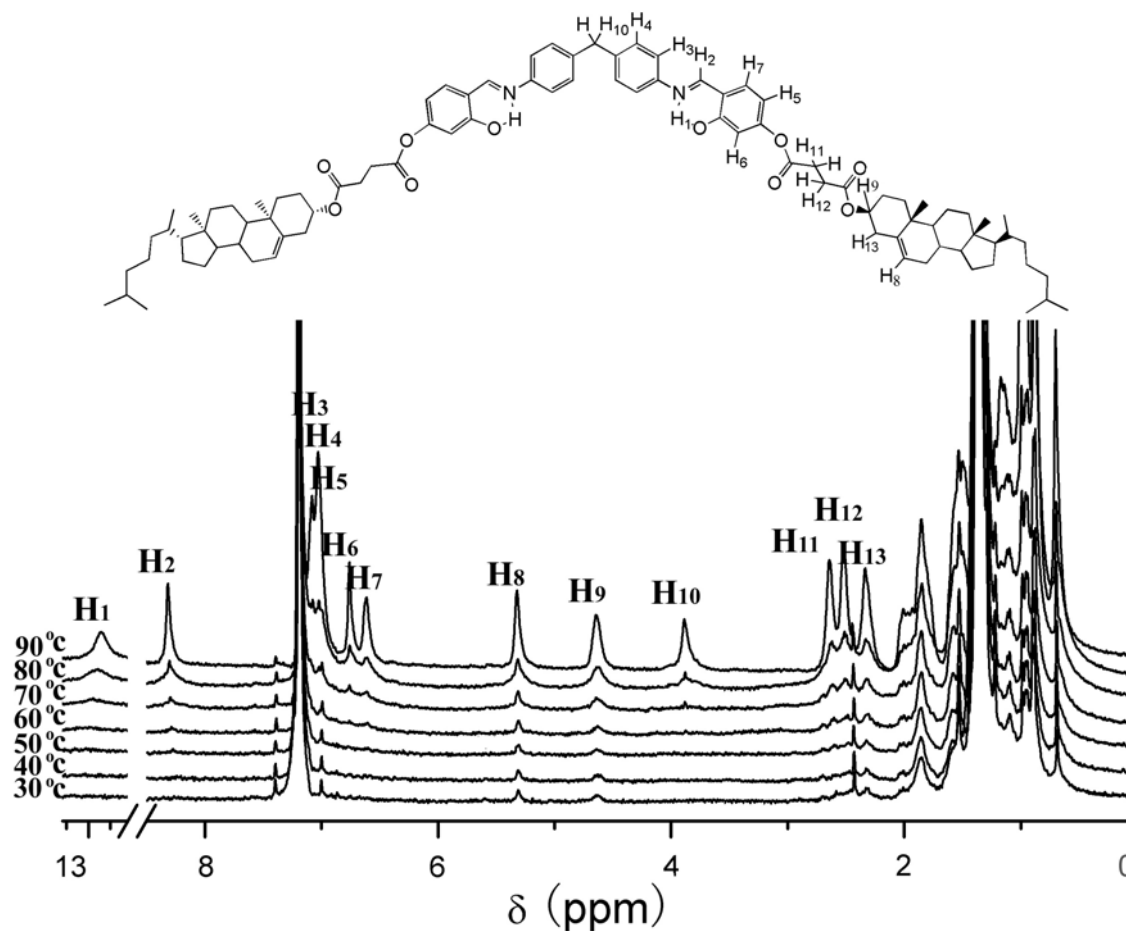


Figure 3. Temperature-dependent ^1H NMR spectra of $[\text{D}_6]$ benzene /cyclohexane- d_{12} organogel **1** at 0.2 wt/vol%.

can only be found when the temperature is over 50 °C. It is well known that the broadening and decrease of resonance intensity of NMR peak can be interpreted as an indication of restricted freedom of the motion, like the behaviors in the solid state. Therefore, the aromatic moieties behave as the “solid-like”, and exhibit relative rigid structure compared to the aliphatic units. It also suggests that the salicylideneaniline moiety has a poorer solubility than the cholesterol groups in the gel phase.^[23] Moreover, the peak at 12.9 ppm illustrates the molecule **1** exists as a *trans*-enol form (E-OH form) even at high temperature,^[24] which can be further confirmed by the FT-IR spectrum since no N-H vibration band around 3310 cm^{-1} is found and the strong C=N band at 1622 cm^{-1} appears.

Small-angle X-ray Diffraction Investigation: The measurement of the small-angle X-ray diffraction (SAXD) of the gel can provide the information of the long range regulation of the molecular self-assembly, thereby the packing model of molecules in the gel phase can be supposed. Figure 4 shows the SAXR spectrum of the xerogel obtained from benzene/cyclohexane gel. The good diffraction pattern was characterized by three reflection peaks of 5.81, 2.91 and 1.93 nm, which was exactly in the ratio of 1: 1/2: 1/3, indicating a lamellar organization within the aggregates of gel **1** with an interlayer distance of 5.81nm.^[25]

TEM and SEM Investigation: To obtain the microstructure of the organogels and molecular self-assembled property, SEM and TEM images of 1-butanol (polar solvent) gel and benzene/cyclohexane (non-polar solvent) gel were obtained. SEM image of

benzene/cyclohexane gel shows that many nanofibers with 30-70 nm width and tens micrometer length construct the 3-D networks so that the flow of the solvent can be prevented to induce the formation of solid-like gel (see Figure 5a). Moreover, TEM image of the benzene/cyclohexane gel shows lots of helical nanofibers. By careful examination, we find that these fibers are all left-handed helix and the diameter of the thinnest fibers is about 5.8 nm, which is in agreement with the periodicity of the structure (5.81 nm) suggested by XRD (Figure 5b). Furthermore, we also find that two or more fibers with 5.8 nm diameter twist each other to form larger ones with the diameters of 11.6, 17.4 and 24.8 nm et al, which further confirms the evidence of the layer structure. Moreover, the helical pitch of the twisted fiber is independent of the diameter of the fiber, and all the fibers have similar helical pitch of 45 nm. Similar to the benzene/cyclohexane gel, in 1-butanol gel some left-handed helical fibers with diameter of 5.8 nm and helical pitch of ca. 50 nm are observed in Figure 5c. It is deemed that the microstructures of molecular self-assemblies in both gels are similar. **Molecular Packing Model:** To reveal the molecular packing model, semi-empirical (AM1) calculations were performed to optimize the ground state geometry of molecule **1**. The result shows that molecule **1** is in a V-shaped conformation as shown in Figure 6a, which coincides with that of the molecule **1'**. And the molecular length for extended form is estimated to be 5.78 nm, which is in accordance with the long period of lamellar structure in the

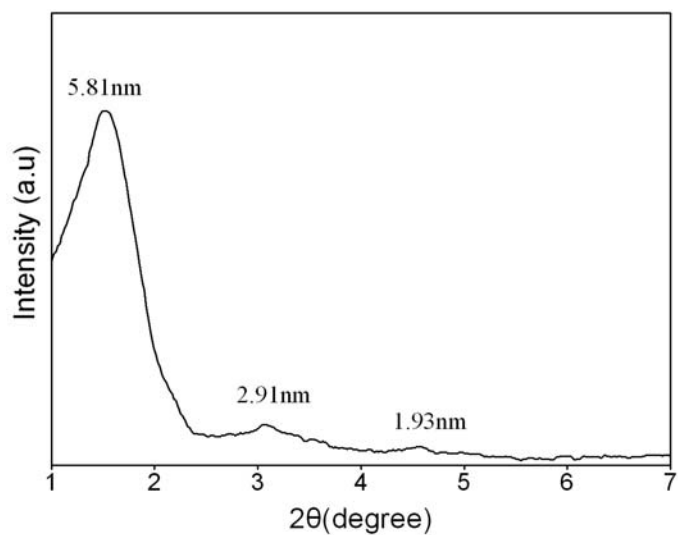


Figure 4. The small angle XRD diagram of the xerogel **1** obtained from benzene/cyclohexane gel.

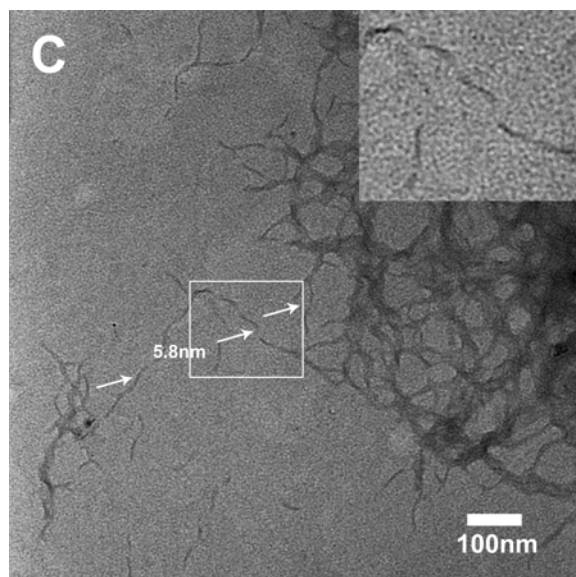


Figure 5. SEM image of benzene/cyclohexane gel (a), and TEM images of benzene/cyclohexane (b) and 1-butanol (c) gels.

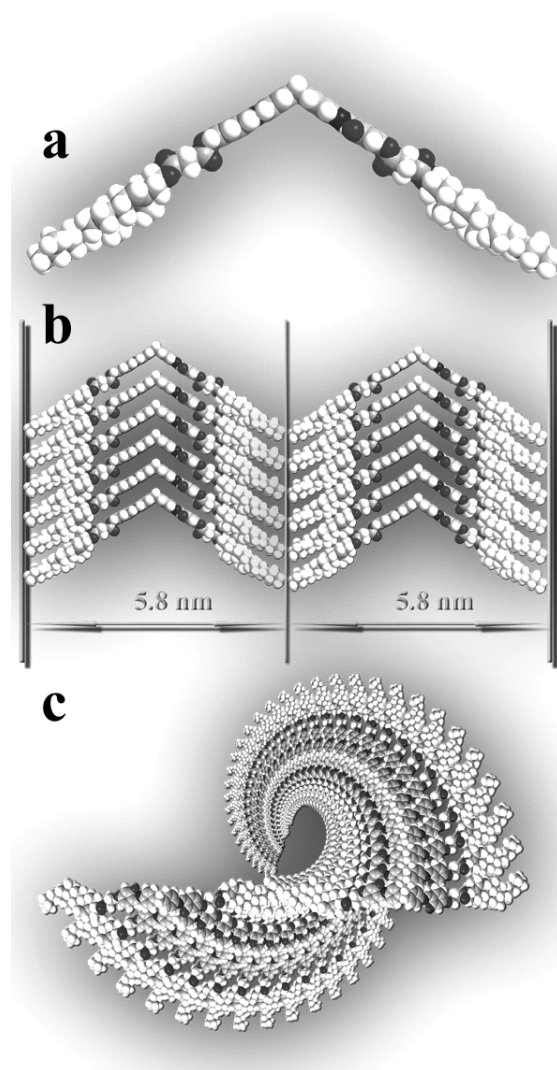
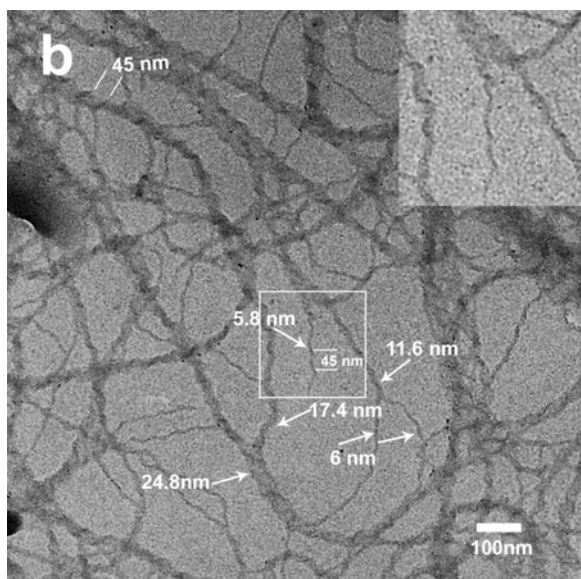
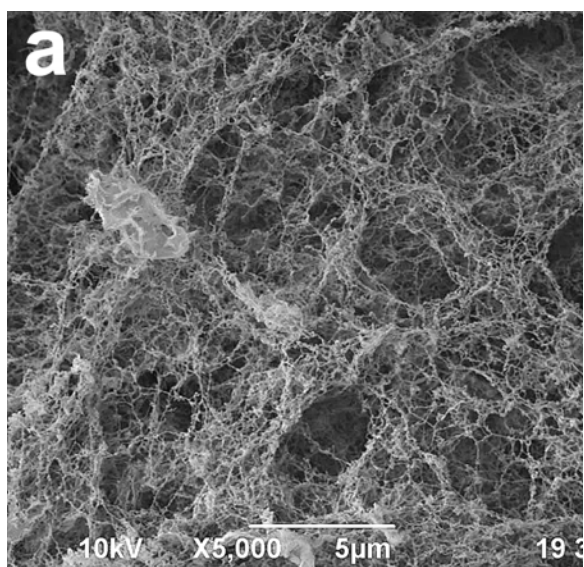
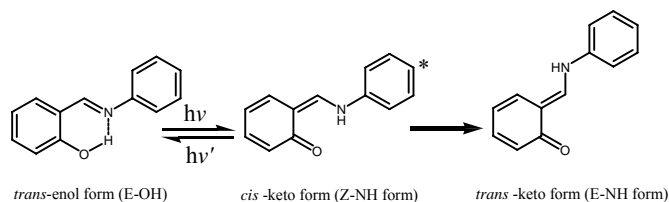


Figure 6. (a) The optimized structure of **1** via the AM1 quantum mechanical calculation. (b) Schematic illumination of monomolecular layer structure with 5.8 nm period distance in gel state. (c) Dimolecular helical packing along with the direction of long axis.

gel phase. In the view of the result of UV-vis spectra indicating that the aromatic moieties formed J-aggregation with weak exciton coupling, it can be confirmed that the gelator molecules are arranged parallel along with the growth direction of the fiber and further extended to form 1-D fibrous structure. In this model, the distance between two parallel salicylideneaniline moieties is up to 5.0 Å, obviously longer than that of **1'** (3.6 Å) in crystal state because of the effect of spatial hindrance of cholesterol group, as shown in Figure 6b. In addition, the CD spectra and TEM observations suggest molecules are packed in an anti-clockwise direction. Therefore, the molecular packing model in the gel phase can be illustrated as shown in Figure 6c. Considering the helical pitch, 450 and 500 Å for benzene/cyclohexane and 1-butanol gels, respectively, it can be deduced that the fiber within a helical pitch includes approximate 90 molecules in benzene/cyclohexane gel and 100 ones in 1-butanol gel, and the torsion angles of adjacent two molecules in both gels are 4° and 3.6°, respectively.

Enhanced Fluorescence Emission from Sol to Gel: In general, after the salicylideneaniline in E-OH form at ground state absorbs one photon, the excited-state intramolecular rapid proton transfer process from oxygen atom to nitrogen atom will happen and yield excited-state Z-NH form owing to the lower potential energy.^[26] Moreover, the Z-NH form can undergo a torsion and transform to a photochromic product, E-NH form, if there is enough space to permit the molecule to rotate as reported by Kawato T. et al.^[7d] or a transition from the excited state to its ground state accompanying with a longer emission wavelength^[6a] and then retune to E-OH ground state rapidly. Therefore, it can lead to a large Stokes shift compared with the absorption peak in E-OH form. The detailed photoinduced isomerization and photoluminescence process are shown in Scheme 2.



Scheme 2. Photoinduced isomerization and photoluminescence process of a typical salicylideneaniline.

Under UV light irradiation, benzene/cyclohexane and 1-butanol gels emit strong green fluorescence, which gradually decreases as the temperature increases (Figure 7). The maximum emission peaks of both gels are located at 520 nm, and the large Stokes-shift (177 nm) is observed compared with the absorption of the gels. Interestingly, it can be found that at the same concentration as that of the benzene/cyclohexane gel, the benzene solution of **1**, in which the molecules are confirmed to exist as unimolecular isolated state because no CD signal is detected as shown Figure 2c, gives very weak fluorescence emission ($\Phi_f = 2.31 \times 10^{-5}$), and the fluorescence intensity increases gradually when cyclohexane is continually added into the benzene solution to induce the formation of the self-assembly of **1**. When the volume ratio of cyclohexane to benzene is up to 4:1, the fluorescence quantum yield of the system reaches 0.0241, which is the same as that of the gel, and is more than 1000 times higher than that of the benzene solution. It suggests that the enhanced fluorescence emission of gel is caused by the formation of the molecular aggregations.

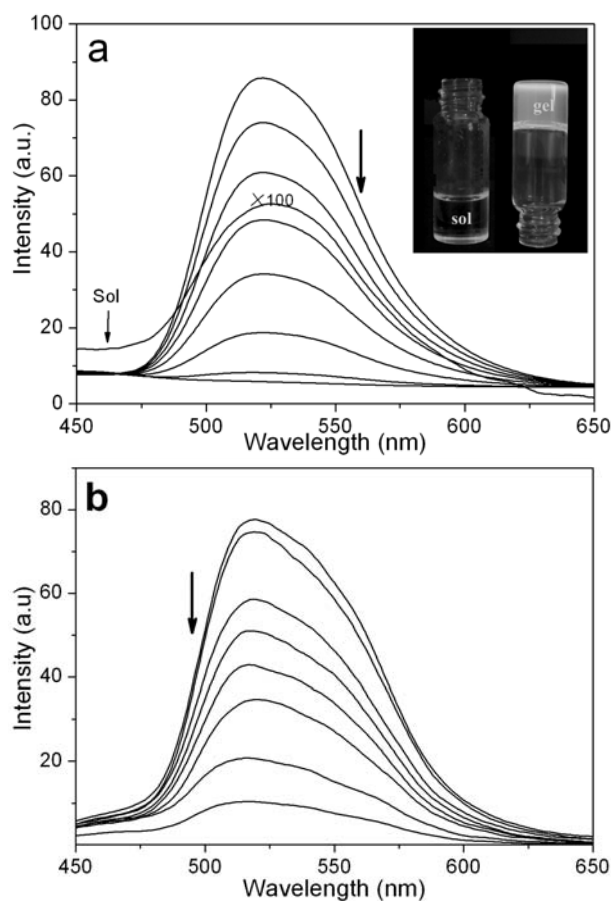


Figure 7. Temperature-dependence of fluorescence emission of benzene/cyclohexane (a) and 1-butanol (b) gels. Inset shows the photograph of benzene/cyclohexane gel and benzene sol at 0.1 wt/vol% irradiated by 365 nm light.

In recent years, a few samples with enhanced emission induced by molecular aggregation have been reported. For example, Tang et al reported a pentaphenylsilole derivative with enhanced emission after aggregation^[27] and suggested that the enhanced fluorescence can be explained by the planar conformation in the solid state, which can activate the radiation process.^[28] Herein, in respect to the absorption band of the gel with only a small red-shift of 2 nm compared with that in solution, the contribution of the molecular planarization to the enhanced emission is not taken into account. It is well known that the increase of the rigidity of a molecule can decrease the molecular vibration and probably suppress the internal conversion of excited molecule, and may increase the fluorescence quantum yield.^[29] In addition, the fluorescence intensity of the π -conjugated chromophores is correlated with the π -aggregation, such as H- and J-aggregations.^[30] H-aggregates, in which the molecules are aligned parallel to each other in a head-to-head form, tend to increase the internal conversion from a higher electronic state to a lower one so that the fluorescence emission is effectively quenched. In contrast, molecules are arranged into a head-to-tail stack as J-aggregation, in which the transition from the lower couple excited state of molecule to ground state is allowed, as a result, the absorption peak will red-shift and the fluorescence emission will be stronger than that of the monomer.^[31] In our case, the gelator molecules form J-aggregation and cross-link into solid-like 3-D network in gel phase, so the enhanced emission of the gel is attributed to the synergetic effect of the restricted molecular motion and the formation of J-aggregation. To obtain further information on the excited state of molecule **1**, time-resolved fluorescence spectra were measured. As shown in

Figure 8, both the monomer solution and the gel gave double-exponential decay with average lifetime of 6.98 and 5.78 ns, respectively. According to the equation of $\tau^{-1} = k_r + k_{nr}$ and $k_r = \Phi_f/\tau$, the radiative rate constant k_r and total nonradiative rate constant k_{nr} of **1** in monomer and J-aggregation state were calculated and listed in Table 2. Although k_{nr} increases slightly due to the formation of gel, which suppresses the fluorescence emission, efficient radiative transition increased more than 1000 times. Therefore, the aggregation-induced fluorescence enhancement is mainly ascribed to the increase of k_r .

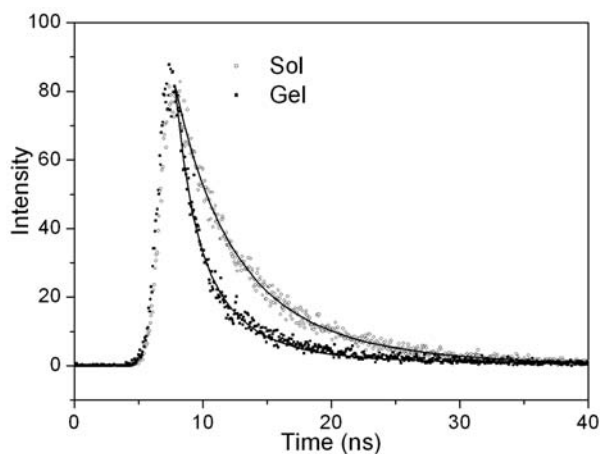


Figure 8. Fluorescence decays of benzene/cyclohexane gel and the benzene sol at 20 °C and $\lambda_{em} = 520$ nm.

Table 2. The fluorescence quantum yields, radiative and total nonradiative rates of the benzene sol and the benzene/cyclohexane gel.

	$\Phi_f (10^{-2})$	τ_1 (ns)	τ_2 (ns)	$\langle \tau \rangle$	$k_r (10^6$ $s^{-1})$	$k_{nr} (10^8$ $s^{-1})$
Benzene Sol	0.0023	3.43	8.65	6.98	0.0033	1.43
Benzene/cyclohexane Gel	2.41	1.92	9.44	5.78	4.15	1.69

Photochromism and Photoinduced Transition from Gel to Sol:

On the basis of three dimensional X-ray structures, the crystals based on salicylideneaniline can exhibit two mutually exclusive properties, either thermochromism or photochromism.^[7e,32] In the thermochromic crystal, the molecules are planar and close-packed via π - π interaction so that strong fluorescence emission can be detected, such as molecule **1'**. On the contrary, in the photochromic crystals, there is large dihedral angle between the planar salicylaldimine group and the aniline ring, which induces an open crystal structure with incompact molecular packing.

From the above discussion, molecule **1** can form regular aggregation and emit strong fluorescence in gel phase, whose property is similar to that of thermochromic crystal. However, the UV-vis absorption spectra and molecular packing model illustrated that the packing of the Schiff base group was not very tight, and the temperature-dependent ¹H NMR spectra suggested that cholesterol groups possessed significant freedom of motion. Therefore, it is worthy to investigate whether the photochromism of the organogel can take place under UV irradiation. Figure 9 shows the absorption spectral

change of the benzene/cyclohexane gel with the irradiation time. After irradiation with 365 nm light, the band at 343 nm decreased and a new peak at 450 nm appeared, which could be intensified when the irradiation time was prolonged.^[33] On the other hand, the FT-IR spectrum of the sample after irradiation revealed two new peaks at 3326 and 1660 cm^{-1} , ascribed to NH and α,β -unsaturated ketone vibration absorption, respectively (see Figure S2). It suggests that compound **1** in gel phase shows significant photochromic property although it also exhibits emission enhancement as thermochromic crystal, which is quite different from the traditional photochromic salicylideneaniline with non-fluorescence. Moreover, after being irradiated for 110 min, the gel state transformed into a solution although not all molecules existed in keto form.

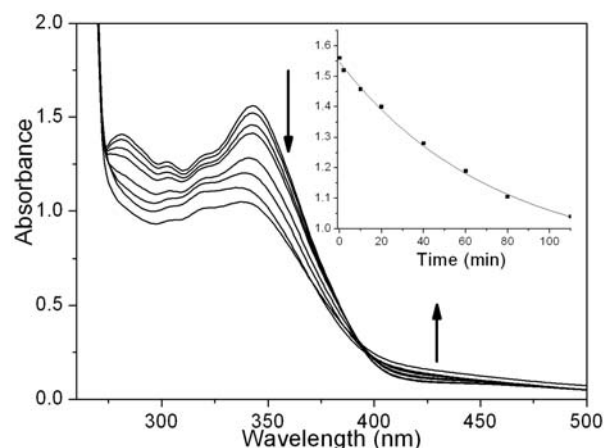


Figure 9. UV-vis absorption spectral changes of the benzene/cyclohexane gel with irradiation time under 365 nm light from a high-pressure mercury lamp. Inset: the plot of absorbance at 343 nm as a function of the irradiation time.

Conclusion

In summary, a new organogelator based on salicylideneaniline derivative with cholesterol moieties was synthesized, and it could gel various organic solvents. SEM and TEM observations revealed that the gelator molecules self-assembled into 1-D helical fibers with diameter of ca. 5.8 nm in an anti-clockwise direction, which further twisted into thicker fibers and constructed 3-D networks. Combining with the UV-vis, CD spectra and the semi-empirical (AM1) calculations, the molecular packing model in the gel phase was illustrated. Interestingly, the fluorescence emission intensity of the organogel was more than 1000 times higher than that of the solution under the same concentration due to the formation of J-aggregation as well as the restricted molecular motion in the gel state. Meanwhile, the UV irradiation could induce the isomerization of salicylideneaniline in the organogel because of the large cholesterol group resulting in an untight packing of the molecules and permitting the molecule to rotate. The strong fluorescence emission and photochromism could be involved into such gel system based on salicylideneaniline derivative, which indicated that the expected optical properties might be realized through tuning the self-assembling process of the functional gelator.

Experimental Section

Instruments: Infrared spectra were measured on a Nicolet-360 FT-IR spectrometer by incorporating the samples in KBr disks. ¹H NMR spectra were taken using a Varian-300 EX spectrometer. Temperature-dependent ¹H NMR spectra were measured on JEOL FX-400, and the NMR tube containing compound **1** in solvent was sealed before measurement. SEM images were obtained using a JEOL JEM-5310LV. Circular dichroism spectra were recorded on JACSO J-725 spectropolarimeter. The UV-vis spectra were determined on a Shimadzu-1601 spectrophotometer. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Photoluminescence measurements were taken on a JACSO PL-5600 spectrofluorometer.

TEM Investigation: A piece of the neat gel **1** was placed on a carbon-coated copper grid (400 mesh) followed by naturally evaporating the solvent. TEM specimens were examined with a Hitachi mode H600A-2 apparatus with an accelerating voltage of 100 kV.

Gelation Test of Organic Fluids: The solution containing certain weighed gelator **1** in organic solvent was heated in a sealed test tube with 1 cm diameter in an oil bath until the solid was dissolved. After the solution was allowed to stand at room temperature for 6 h, the state of the mixture was evaluated by the "stable to inversion of a test tube" method.

X-ray Diffraction (XRD): Diffraction patterns were carried out on a Rigaku D/max-rA X-ray diffractometer with graphite monochromatized Cu KR radiation ($\lambda = 1.5418 \text{ \AA}$). The accelerating voltage was set at 50 kV, with 100mA fluxes at a scanning rate of 0.02 deg/s in the 2θ range of 1-10°. The XRD patterns of xerogel were obtained by casting wet gel samples in a glass flask followed by evaporation of the solvent naturally.

Photochromism: Weighted compound **1** was added into a quartz cell, then the mixture solvent of benzene and cyclohexane ($v/v = 1:4$) was injected into the cell. After the solid was dissolved by heating, the system was cooled to room temperature and the gel formed. A high-pressure mercury lamp was used as irradiation light source with a filter plate ($\lambda_{\text{max}} = 365 \text{ nm}$). After irradiated for expected time, the absorption peak was recorded on a Shimadzu-1601 spectrophotometer. The cell was thermostatted at 20 °C during the irradiation.

Synthesis of Organogelator:

3-cholesteryloxypropionic acid (2): Compound **2** was synthesized according to the method described in the literature.^[34] A solution of cholesterol (3.87 g, 10 mmol), succinic anhydride (1.00 g, 10 mmol), and triethylamine (1.10 g, 10 mmol) in dry acetone (60 mL) was heated to reflux for 24 h. After acetone was then evaporated, the resulting precipitate was recrystallized twice from glacial acetic acid. Yield is of 65%. mp. 177.0-179.0 °C (177.0-179.0 °C in reference^[34]). IR: 1728 cm⁻¹ (ester carbonyl), 1709cm⁻¹ (acid carbonyl), 3440cm⁻¹ (hydroxyl). Elemental analysis (%): calculated for C₃₁H₅₀O₄: C, 76.50; H, 10.27. Found: C, 76.01; H, 10.10.

2-hydroxy-4-(3-cholesteryloxypropionyloxy)benzaldehyde (3): Compound **2** (2.50 g, 5.1 mmol) and 2,4-dihydropyridylbenzaldehyde (0.9 g, 6.5 mmol) were dissolved in 30 mL dry CH₂Cl₂ containing pyridine (1.8 mL). After the solution was cooled to 0 °C, a small amount of DMAP and DCC (2.50 g, 10 mmol) was added. The mixture was stirred for 4 h at 0-5 °C and further aged for 24 h at room temperature. White precipitate was removed by filtration. After the solvent was evaporated under reduced pressure, the resultant residue was purified by silica gel column chromatography (cyclohexane/ethyl acetate = 5:1). Yield: 38 %. mp. 99.0-100.0 °C, IR: 3327 cm⁻¹ (-OH), 1770 cm⁻¹ and 1737 cm⁻¹ (ester carbonyl), 1661 cm⁻¹ (aldehyde carbonyl). Elemental analysis (%): calculated for C₃₈H₅₄O₆: C, 75.21; H, 8.97; Found: C, 75.10; H, 8.86. ¹H NMR (300 MHz, TMS, CDCl₃): 10.24 (s, 1 H), 7.60 (d, J = 2.2 Hz, 1 H), 6.81 (d, J = 2.2 Hz, 1 H), 6.74 (s, 1 H), 5.37 (d, J = 4.2 Hz, 1 H), 4.68 (m, 1 H), 2.87 (t, J = 7.2 Hz, 2 H), 2.72 (t, J = 7.2 Hz, 2 H), 2.33 (t, J = 7.2 Hz, 2 H), 2.20-1.5 (m, 41 H).

4,4'-di[2-hydroxy-4-(3-cholesteryloxypropionyloxy)benzylideneamino]

diphenyl methane (1): The solution of compound **3** (0.606 g, 1.0 mmol) and 4,4'-diamino-diphenyl-methane (0.099 g, 0.5 mmol) in ethanol (10 mL) was refluxed for 2 h and then cooled to room temperature. The precipitates were filtered and washed by cyclohexane repeatedly. Yield: 35%. mp. 217.0-219.0 °C, IR: 3318 cm⁻¹ (OH), 1763 cm⁻¹ and 1732 cm⁻¹ (ester carbonyl), 1622 cm⁻¹ (C=N). Elemental analysis (%): calculated for C₈₉H₁₁₈N₂O₁₀: C, 77.69; H, 8.64; N, 2.04; Found: C, 77.07; H, 8.50; N, 1.93. ¹H NMR (300 MHz, TMS, CDCl₃): 8.60 (s, 2 H), 7.36 (s, 2 H), 7.23 (d, J = 2.4 Hz, 4 H), 6.77 (d, J = 2.4 Hz, 4 H), 6.72 (d, J = 2.1 Hz, 2 H), 6.70 (d, J = 2.1 Hz, 2 H), 5.38 (d, J = 4.2 Hz, 2 H), 4.68 (m, 2 H), 4.04 (s, 2 H), 2.87 (t, J = 7.2 Hz, 4 H), 2.73 (t, J = 7.2 Hz, 4 H), 2.33 (t, J = 7.2 Hz, 4 H), 2.20-1.5 (m, 82 H).

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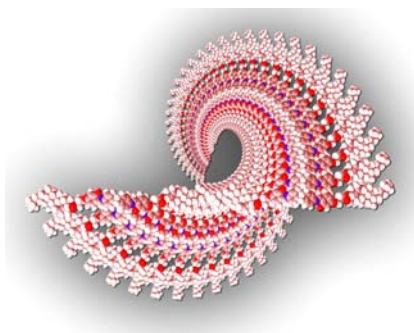
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Self-assembly

P. C. Xue, R. Lu, G. J. Chen, Y. Zhang, H. Nomoto, M. Takafuji, H. Ihara**

Functional Organogel Based on Salicylideneaniline Derivative with Enhanced Fluorescence Emission and Photochromism



Salicylideneaniline derivative with cholesterol moiety can self assemble into 1-D helical superstructure in its gel phase, accompanying with enhanced fluorescence emission because of molecular aggregation. Moreover, the spatial effect of large cholesterol group makes the organogel exhibit photochromism.

Supporting Information

Functional Organogel Based on Salicylideneaniline Derivative with Enhanced Fluorescence Emission and Photochromism

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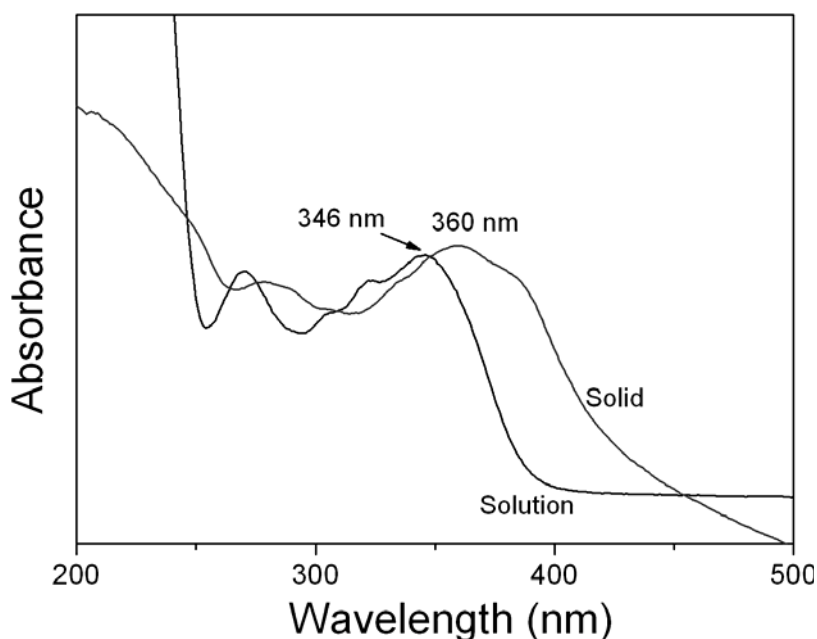


Figure S1. The UV-vis spectra of molecule **1'** in dilute solution and crystal.

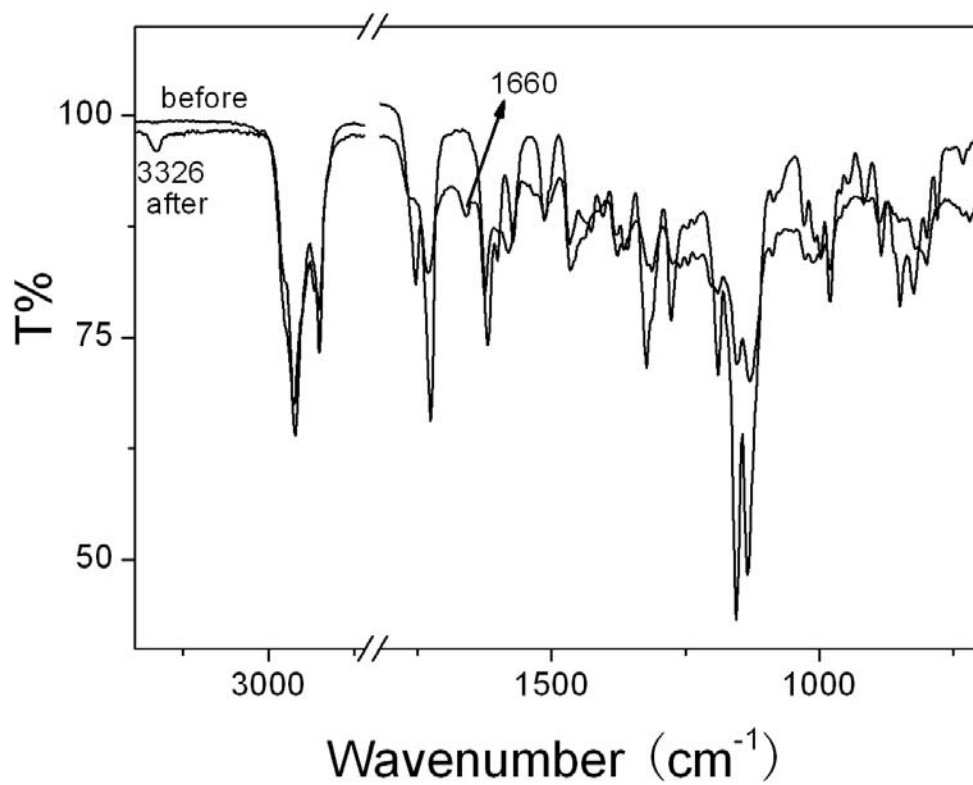


Figure S2. The FT-IR spectra of benzene/cyclohexane gel 1 before and after irradiation.

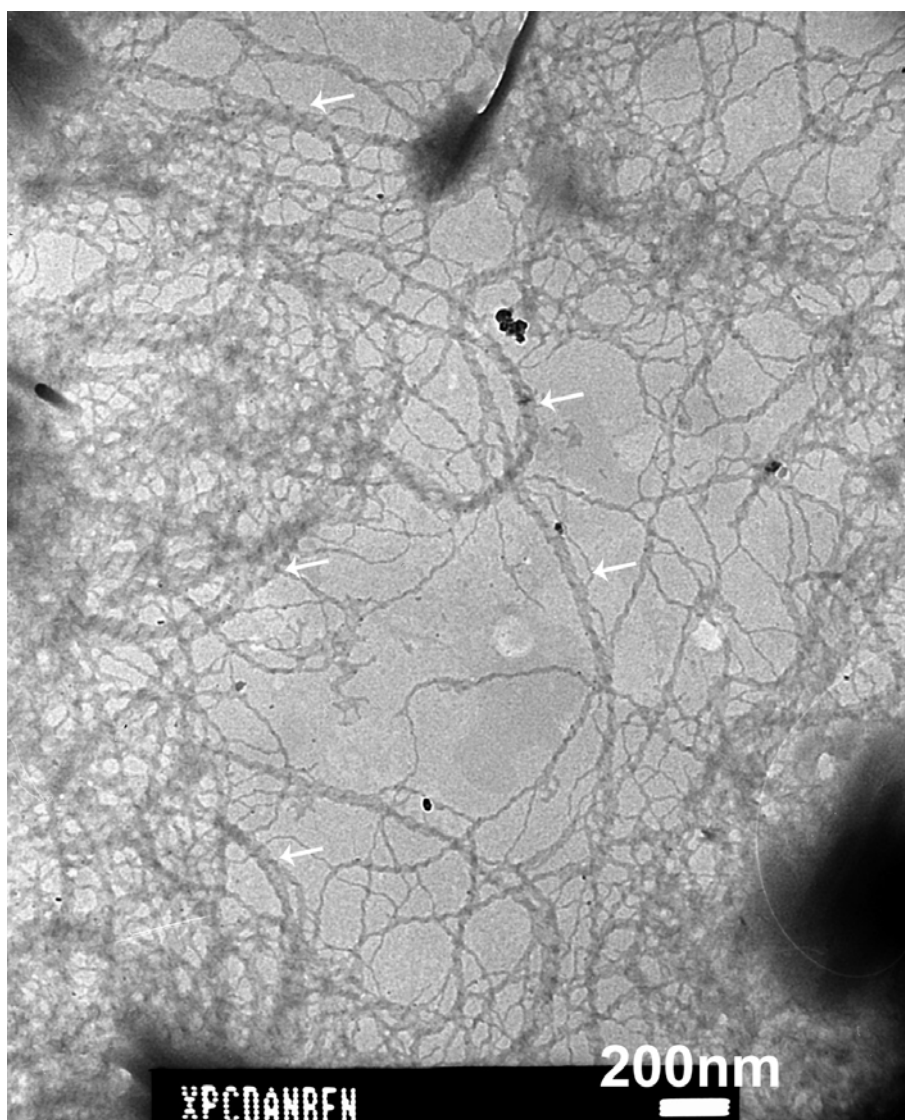


Figure S3. TEM image of benzene/cyclohexane of gel 1.