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A series of 4-nitrophenylacrylonitrile and phenylacrylonitrile derivatives consisting of carbazole moiety was synthesized. Some of these derivatives with longer alkyl chains and nitro group could gelatinize some organic solvents, such as ethanol, n-butanol, ethyl acetate, and DMSO. By contrast, phenylacrylonitrile derivatives did not form gels in measured solvents. This result proved that the electron-withdrawing nitro moiety was important for gel formation because it conferred the molecules with large dipole moments, which enhanced intermolecular interaction. Analyses by UV–vis absorption, X-ray diffraction, and scanning electron microscopy showed that the gelator molecules could self-assemble into one-dimensional nanofibers with layer packing, which further twisted into thicker fibers and formed three-dimensional networks in gel phase. The single crystal structure of C4CNPA implied that the gelators might adopt an anti-parallel molecular stacking because of their larger ground-state dipole moment. Interestingly, the organogels had enhanced fluorescence relative to solutions at the same concentration.

Introduction

Researchers and engineers have significantly focused on stimulus-active functional materials because these materials can change their physical or chemical properties upon exposure to particular stimuli, such as heat, electricity, light, magnetic, solvent, and pH value. These unique characteristics enable stimulus-active materials to be used in many fields, such as smart textiles and apparels, intelligent medical instruments and auxiliaries, artificial muscles, biomimetic devices, heat shrinkable materials, self-deployable sun sails in spacecrafts, miniature manipulators, actuators, and molecular motors and sensors. In particular, smart functional organogels, formed by a large amount of organic solvents and a small amount of low-molecular mass compound with low concentration, have been widely developed in recent years. Their bulk shape and properties can be either switched or tuned by an external chemical or physical stimulus, such as metal ions, anions, small organic compounds, protons, light irradiation, oxidation or reduction reaction, and sound and temperature by introducing functional units. Thus, such supramolecular gels are considered as smart and versatile functional materials for applications in solar cells, ion and molecular recognition, light switches, logic gates, biomimetic systems, and electronics. Among various supramolecular gels, fluorescent organogels have attracted intense interest and are extensively studied because of their promising applications in optoelectronics and fluorescence sensors.

In this study, we designed and synthesized a series of 4-nitrophenylacrylonitrile and phenylacrylonitrile derivatives to obtain temperature-controlled fluorescent switches. Some derivatives with longer alkyl chains and nitro group could form gels in some organic solvents. However, phenylacrylonitrile derivatives without the nitro group were not gelator. This result suggests that the electron withdrawing nitro moiety is important for gel formation because the nitro group increases the molecular dipole moment and then enhances the intermolecular interaction, which was confirmed by the single crystal structure of C4CNPA. Interestingly, the organogels formed by C4CNPA could be used as fluorescent switches controlled by temperature because gels have stronger fluorescence relative to solutions.

Experimental Section

Instruments. Infrared spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating the samples in KBr disks. The UV-vis absorption spectra were determined on a Mapada UV-1800pc spectrophotometer. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Photoluminescence measurements were taken on a Shimadzu RF-5301 Luminescence Spectrometer. The fluorescence spectra of gels were measured in a 1mm cell by right angle observation. NMR spectra were carried out on Mercury plus 500 MHz. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR MALDI-TOF (Compact) mass spectrometers. SEM images were carried out on a Japan Hitachi model X-650 Scan electron microscope. The samples for SEM observation were prepared by a method of drop-cast film. The samples were then kept overnight in a vacuum oven at room temperature followed by coating of gold. Small angle X-ray diffraction (XRD) patterns were obtained on a (λ=1.5418 Å), by employing a scanning rate of 0.02° s⁻¹ in the 2θ from 1.1 to 10°.
The samples were prepared by casting the wet gels on glass slides and drying at room temperature. The fluorescence quantum yields (Φ) of CnCNPA in toluene were measured by comparing to a standard, 10-diphenylanthracene in benzene with a Φ of 0.85.
The excitation wavelength was 390 nm. The optimal molecular configurations of C1CNPA and C1CPA were obtained by density functional theory (DFT) calculation at B3LYP/6-31G level with the Gaussian 09W program package.10

Single crystal was obtained in the toluene solution by slow solvent vaporization. Single crystal of C4CNPA was selected for X-ray diffraction analysis on a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystals were kept at room temperature during data collection. The structures were solved by the direct methods and refined on F2 by full matrix least square using the SHELXTL-97 program.10 The C, N, O and H atoms were easily placed from the subsequent Fourier difference maps and refined anisotropically. CCDC 993696 contains the supplementary crystallographic data for this paper.

Gelation Test. The solution containing weighed compound in organic solvent was heated in a sealed test tube with 1 cm diameter in an oil bath until the solid were 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.

Synthetic procedures and characterizations. The synthesis route of compounds CnCNPA and CnCPA was shown in Scheme 1. 4-nitrophenylacetonitrile, 2a-c and 3a-d were synthesized by the procedures reported previously.11

Scheme 1 Synthesis route of CnCNPA and CnCPA.

(Z)-3-(9-octylcarbazolyl)-2-(4-nitrophenyl)acrylonitrile (C8CNPA): By following the synthetic procedure for C4CNPA. C8CNPA was synthesized with compound 3b (1.7 g, 5.6 mmol), 4-nitrophenylacetonitrile (1.0 g, 6.2 mmol), and diethylamine (1 mL). Yield: 85 %. mp: 131.5 °C. Element analysis (%): calculated for C39H30N2O2: C, 85.99; H, 6.87; N, 6.14; Found: C, 85.97; H, 6.89; N, 6.15. 1H NMR (CDCl3, 500 MHz, ppm), δ = 8.74 (d, J = 1.6 Hz, 1H), 8.37 – 8.31 (m, 2H), 8.22 (d, J = 8.7, 1.7 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.93 – 7.87 (m, 3H), 7.56 (t, J = 7.2 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 4.37 (t, J = 7.3 Hz, 2H), 1.97 – 1.90 (m, 2H), 1.46 – 1.23 (m, 12H), 0.90 (t, J = 7.0 Hz, 3H). MS (MALDI-TOF), m/z: cal: 563.35, found: 563.30.

(Z)-3-(9-octylcarbazolyl)-2-Phenyl-acrylonitrile (C8CPA): After 3b (1.2 g, 3.9 mmol) and phenacylonitrile (0.49 mL, 4.3 mmol) in ethanol was dissolved upon heating, 0.2 mL tetrabutylammonium hydroxide (TBAOH, 40% in water) was added and the mixture was refluxed for 10h. And then, the solution was cooled to room temperature. The product was obtained by vacuum suction filtration and washing by cooled ethanol. Yield: 85%. mp: 216.5 °C. Element analysis (%): calculated for C52H38N2: C, 85.67; H, 7.44; Found: C, 85.69; H, 7.41; N, 6.86. 1H NMR (CDCl3, 500MHz, ppm), δ = 8.64 (d, J = 1.7 Hz, 1H), 8.15 (dd, J = 13.3, 4.7 Hz, 2H), 7.72 (dd, J = 5.4, 3.2 Hz, 3H), 7.54 – 7.49 (m, 1H), 7.47 (d, J = 7.0 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.29 (dd, J = 11.3, 4.3 Hz, 1H), 4.32 (t, J = 7.3 Hz, 2H), 1.89 (m, 2H), 1.43 – 1.20 (m, 10H), 0.89 – 0.81 (t, J = 7.0 Hz, 3H). MS (MALDI-TOF), m/z: cal: 406.23, found: 406.25.

(Z)-3-(9-dodecylcarbazolyl)-2-(4-nitrophenyl)acrylonitrile (C12CNPA) By following the synthetic procedure for C4CNPA. Yield: 95 %. mp: 192.5 °C. Element analysis (%): calculated for C60H50N2O2: C, 85.67; H, 7.44; N, 6.86; Found: C, 85.69; H, 7.41; N, 6.86. 1H NMR (CDCl3, 500MHz, ppm), δ = 8.64 (d, J = 1.7 Hz, 1H), 8.15 (dd, J = 13.3, 4.7 Hz, 2H), 7.72 (dd, J = 5.4, 3.2 Hz, 3H), 7.54 – 7.49 (m, 1H), 7.47 (d, J = 7.0 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.29 (dd, J = 11.3, 4.3 Hz, 1H), 4.32 (t, J = 7.3 Hz, 2H), 1.89 (m, 2H), 1.43 – 1.20 (m, 10H), 0.89 – 0.81 (t, J = 7.0 Hz, 3H). MS (MALDI-TOF), m/z: cal: 563.35, found: 563.30.
Yield: 86 %. Element analysis (%): calculated for C_{3}H_{7}N_{2}: C, 78.07; H, 7.35; N, 8.28; Found: C, 78.03; H, 7.21; N, 8.22. \textsuperscript{1}H NMR (CDCl_{3}, 500 MHz, ppm), δ = 8.65 (d, J = 1.3 Hz, 1H), 8.15 (dd, J = 13.7, 4.8 Hz, 2H), 7.75 – 7.69 (m, 3H), 7.51 (t, J = 7.2 Hz, 1H), 7.47 (d, J = 6.3 Hz, 2H), 7.45 (dd, J = 10.6, 5.0 Hz, 3H), 7.37 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 4.32 (t, J = 7.2 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.43 – 1.20 (m, 18H), 0.87 (t, J = 7.0 Hz, 3H). MS (MALDI-TOF), m/z: cal: 462.30, found: 462.31.

\textbf{(Z)-3-(9-hexadecylcarbazolyl)-2-Phenyl-acrylonitrile}

\textbf{C16CPA}: By following the synthetic procedure for C8CPA. Yield: 83 %. Element analysis (%): calculated for C_{16}H_{20}N_{2}: C, 85.66; H, 8.94; N, 5.40; Found: C, 85.63; H, 8.89; N, 5.43. \textsuperscript{1}H NMR (CDCl_{3}, 500 MHz, ppm), δ = 8.64 (d, J = 1.3 Hz, 1H), 8.19 – 8.12 (m, 2H), 7.74 – 7.69 (m, 3H), 7.51 (t, J = 7.7 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.44 (t, J = 6.0 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 4.32 (t, J = 7.2 Hz, 2H), 1.93–1.88 (m, 2H), 1.44–1.21 (m, 26H), 0.88 (t, J = 6.9 Hz, 3H). MS (MALDI-TOF), m/z: cal: 518.37, found: 518.30.

\textbf{Photophysical properties in solution}

Because only CnCNPA could form gels in measured solvents, their spectral characteristics rather than those of CnCPA in solutions were studied. We found that CnCNPA with different alkyl chains had the same spectral behavior, but TBAOH as a strong base is necessary for benzyl cyanide because of its weak activity. The products were characterized by \textsuperscript{1}H NMR spectroscopy, MALDI-TOF mass spectrometry, and C, H, N elemental analyses.

\textbf{Gelation ability in organic solvents}

Through the standard heating-and-cooling method,\textsuperscript{12} the gelation abilities of CnCNPA and CnCPA were investigated. We found that the gelation properties were strongly affected by the nitro group and alkyl chain. For example, CnCNPA with C8, C12, and C16 alky chains could form gels in DMSO and some alcohol. However, the CnCPA solutions in these solvents remained in a solution state, or the precipitate was separated from the solutions. Although two types of compounds had large solubility and maintained the solution state in some solvents, such as CH_{2}Cl_{2}, CHCl_{3}, THF, benzene, and DMF, the solubility of CnCPA and CnCNPA were different in n-hexane, cyclohexane, acetone, ethyl acetate, and n-butanol. CnCPA with nitro unit had lower solubility in these solvents. These results suggest that nitro moiety is very important for compounds to form gels in organic solvents.\textsuperscript{13} The gelation ability of CnCNPA in the given solvents is relative to the length of the alkyl chain.\textsuperscript{14} C4CNPA is not the gelator for selected solvents. Only C8CNPA could gelatinize acetone and ethyl acetate at high concentration, whereas C12CNPA and C16CNPA separated as depositions from their solutions in two solvents. C12CPA is formed alone in n-butanol and t- Amyl alcohol. The minimal gelation concentration of C8CPA in gelation solvents except in ethanol was generally lower compared with C12CNPA and C16CNPA.

\textbf{Results and discussion}

\textbf{Synthesis}

Scheme 1 shows the synthesis routes of CnCNPA and CnCPA. Compound 1 was obtained through the nitration reaction of benzyl cyanide in a mixed acid. \textbf{C8CNPA}: By following the synthetic procedure for C8CPA. Gelation properties in different organic solvents.

\textbf{Table I Gelation properties in different organic solvents.}\textsuperscript{a}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>C4CNPA</th>
<th>C8CNPA</th>
<th>C12CNPA</th>
<th>C16CNPA</th>
<th>C8CPA</th>
<th>C12CPA</th>
<th>C16CPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>Cyclohexane</td>
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<td>I</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>S</td>
<td>S</td>
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<tr>
<td>Dichloromethane</td>
<td>S</td>
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<td>S</td>
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<td>S</td>
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<td>S</td>
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<tr>
<td>n-Hexane</td>
<td>I</td>
<td>I</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Petroleum ether</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>P</td>
<td>P</td>
<td>S</td>
<td>S</td>
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<tr>
<td>THF</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Acetone</td>
<td>P</td>
<td>G (18)</td>
<td>P</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>P</td>
<td>G (18)</td>
<td>P</td>
<td>P</td>
<td>S</td>
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<td>S</td>
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<tr>
<td>Toluene</td>
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<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>α-Dichlorobenzene</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>DMF</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>DMSO</td>
<td>G (10)</td>
<td>G (4.1)</td>
<td>G (4.7)</td>
<td>S</td>
<td>S</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Methanol</td>
<td>G (1.2)</td>
<td>G (2.5)</td>
<td>G (5.4)</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
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<tr>
<td>Ethanol</td>
<td>G (2.0)</td>
<td>G (1.8)</td>
<td>G (7.1)</td>
<td>P</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>α-Butanol</td>
<td>P</td>
<td>G (8.8)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>t-Amyl alcohol</td>
<td>P</td>
<td>G (6.7)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>tert-Butanol</td>
<td>P</td>
<td>G (7.9)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
</tbody>
</table>

\textsuperscript{a}G: stable gel formed at room temperature; S: soluble; E: insoluble; P: precipitate. \textsuperscript{b}Minimal gelation concentration (MGC, mM).

The gelation ability of CnCNPA and CnCPA were investigated. We found that the gelation properties were strongly affected by the nitro group and alkyl chain. For example, CnCNPA with C8, C12, and C16 alky chains could form gels in DMSO and some alcohol. However, the CnCPA solutions in these solvents remained in a solution state, or the precipitate was separated from the solutions. Although two types of compounds had large solubility and maintained the solution state in some solvents, such as CH_{2}Cl_{2}, CHCl_{3}, THF, benzene, and DMF, the solubility of CnCPA and CnCNPA were different in n-hexane, cyclohexane, acetone, ethyl acetate, and n-butanol. CnCPA with nitro unit had lower solubility in these solvents. These results suggest that nitro moiety is very important for compounds to form gels in organic solvents.\textsuperscript{13} The gelation ability of CnCNPA in the given solvents is relative to the length of the alkyl chain.\textsuperscript{14} C4CNPA is not the gelator for selected solvents. Only C8CNPA could gelatinize acetone and ethyl acetate at high concentration, whereas C12CNPA and C16CNPA separated as depositions from their solutions in two solvents. C12CPA is formed alone in n-butanol and t-Amyl alcohol. The minimal gelation concentration of C8CPA in gelation solvents except in ethanol was generally lower compared with C12CNPA and C16CNPA.

\textbf{Photophysical properties in solution}

Because only CnCNPA could form gels in measured solvents, their spectral characteristics rather than those of CnCPA in solutions were studied. We found that CnCNPA with different alkyl chains had the same spectral behavior, but the C8CNPA was selected to show the spectral characteristic in solution. As shown in Fig. 1a, C8CNPA has an absorption band with a maximum of 404 nm in cyclohexane, which red-shifted to 408 nm in toluene, to 411 nm in THF and CH_{2}Cl_{2}, to 413 nm in CHCl_{3}, and to 421 in DMF. The red-shifted absorption peaks in polar solvents suggest that C8CNPA has a larger dipole moment in the excited state than in the ground state,\textsuperscript{15} which can be confirmed by solvent-dependent fluorescence spectra. An emission peak at 449 nm for C8CNPA in cyclohexane was found (Fig. 1b), which indicates a Stockes shift of 2480 cm\textsuperscript{-1}. In THF, the emission peak was located at 542 nm, implying green fluorescence and a Stockes shift of 5881 cm\textsuperscript{-1}. With the further increase in the solvent polarity, the fluorescence exhibited a continued red shift, whereas the emission color changed to yellow, orange, and red in CHCl_{3}, CH_{2}Cl_{2} and DMF, respectively.\textsuperscript{16} The largest Stockes shift was observed in DMF (7386 cm\textsuperscript{-1}). Such significant red-shift of emission band in polar solvents indicates an intramolecular charge-transfer (ICT) characteristic for the excited state.\textsuperscript{17} A linear relationship between the emission maximum energy and
the Lippert solvent polarity instead of cyclohexane was found (Fig. 1c), and the emission band in cyclohexane was narrow and had a shoulder peak. It indicates that the emission in cyclohexane is the locally excited one and fluorescence in other solvents is attributed to ICT emission. Therefore, C8CNPA is a typical D-π-A molecule.

![Normalized absorption (a) and emission (b) spectra of C8CNPA in different solvents (1 × 10^{-6} M). λex = 390 nm. Lippert–Mataga plot: (c) Quantum chemical calculations were performed on C1CNPA by density functional theory calculations at the B3LYP/6-31G(d) level to further clarify the ICT transition. Fig. 1d shows that the HOMO state density is distributed at the 4-nitrobenzene and vinyl units. By contrast, the LUMO density is mainly localized on the carbazole and vinyl moieties. The stimulated absorption spectrum of C1CNPA shows an absorption peak at ca. 451 nm (Fig. S1) ascribing to the HOMO→LUMO transition. Therefore, light excitation clearly induces a charge distribution change from donor to acceptor. This result further proves that the maximum absorption and emission are due to the ICT transition. We also obtained the optimal conformation of C1CPA and compared their dipole moments to understand the role of the nitro unit on gel formation (Fig. S2). The result suggests that the dipole moment of C1CNPA (10.6269 Debye) is larger than that of C1CPA (4.3811 Debye), implying that the larger dipole moment may be responsible for the gel formation.

We also found that C8CNPA was a weak emissive fluorophore. The fluorescence quantum yield (Φ) in toluene was as low as 0.21%. In other solvents, the Φs were also lower than 1%. Φs of C4CNPA, C12CNPA and C16CNPA in toluene were 0.21%, 0.25%, and 0.25%, respectively. Thus, small Φs are ascribed to the intramolecular rotation of a single bond and the existence of cyano moiety, which induces the twisted conformation in the isolated state because of the steric interaction between the bulky cyano unit and the neighboring hydrogen atoms. This condition could be confirmed by the optimal geometry of C1CNPA (Fig. S2a), in which the dihedral angles of the vinyl group with carbazole and 4-nitrobenzene units are 5.8° and 24.4°.

![Frontier orbital plots of the HOMO and LUMO of C1CNPA. The long alkyl chain was replaced by the methyl group to simplify the calculation.]

**Fig. 1**

**Self-assembly in gel state**

First, the morphologies of the gelators in gel phases were observed and compared. Fig. 2 shows the scanning electron microscope (SEM) images of C8CNPA, C12CNPA, and C16CNPA in ethanol and DMSO. Three compounds had similar morphologies in DMSO gels and self-assembled into a one-dimensional (1D) nanoribbon with a large aspect ratio (Figs. 2b, 2d, and 2f). However, the self-assemblies in ethanol gels were different. Larger ribbons with larger widths were observed for C8CNPA (Fig. 2a). Some ribbons were more than 10 µm in width. C12CNPA and C16CNPA could form thinner and longer ribbons in ethanol gels, whereas right-handed and left-handed twisted ribbons were found in C16CNPA ethanol gel. Because longer alkyl chain will increase the disordering of molecular packing, so gelator with long chain can self-assemble into thin and soft fiber. This result suggests that the length of the alkyl chain strongly affect the gelator morphologies in solvents.

![SEM images of C8CNPA (a, b), C12CNPA (c, d) and C16CNPA (e, f) gels in ethanol and DMSO. Insets are the enlarged images.]

**Fig. 2**
ethanol and DMSO, respectively) relative to those of gels (Fig. S5). These spectral changes illustrate the J-aggregate formation during gelation.\textsuperscript{23} The absorption spectra of C12CNPA and C16CNPA during the gel process were also measured. As shown in Fig. S6, maximal absorption peaks for C12CNPA and C16CNPA had blue-shifts of 7 nm and 10 nm relative to those of hot sols. Moreover, the gels in ethanol possessed blue-shifted absorption bands relative to those of dilute solutions (Fig. S7). This observation suggests that the packing models of C12CNPA and C16CNPA in gels are different from that of C8CNPA, although the absorption band at 500 nm also appeared in their gels. In the C12CNPA and C16CNPA gels, the H-aggregate formation is responsible for the blue-shifted absorption.\textsuperscript{24}

Fig. 3 Absorption spectra of C8CNPA in ethanol and DMSO during gelation, C = 3.2 mM in ethanol, and 19 mM in DMSO. The interval time is 1 min.

Fig. 4 XRD patterns of C8CNPA, C12CNPA, and C16CNPA xerogels from ethanol.

Considering that X-ray diffraction (XRD) always shows the stack model of gelator in gels, small-angle XRD patterns of the three gelators in ethanol gels were investigated (Fig. 4). C8CNPA, C12CNPA, and C16CNPA clearly adopts a lamellar packing structure with packing periods evaluated to be 1.75, 2.30, and 2.78 nm, respectively.\textsuperscript{25} The XRD patterns of the DMSO xerogels were also obtained. C8CNPA and C16CNPA DMSO xerogels possessed similar lamellar structures and stacking periods to corresponding ethanol xerogels (Fig. S8). However, two types of layer period in the DMSO xerogel of C12CNPA were observed. One layer was similar to that of ethanol xerogel, whereas another one had a longer period of 2.13 nm, indicating that two types of molecular packing models. These results show that three gelators self-assembled into ribbons with a layer packing structure in gel phases.

Fig. 5 (a) 1D packing of C4CNPA in crystal, and (b) top view of one dimer.

We attempted to obtain single crystals of three gelators to further understand the detailed stacking model in gels. However, only thin and longer orange fibers were grown from their solutions. Fortunately, enough large orange single crystals of C4CNPA from toluene solution were obtained, and its single-crystal structure and crystal data are shown in Fig. 5 and Table S1. In the crystal, the dihedral angles between the vinyl and two benzene rings were very small at 2.9° and 9.9°, respectively, indicating that the planarity of the molecule is good. The molecules were also arranged into 1D stacking, in which one anti-parallel dimer appeared repeatedly. Molecules adopt anti-parallel packing rather than parallel ones in crystal because of the inherent large dipole moment of C4CNPA. Anti-parallel stacking permits sufficient electrostatic attraction force between molecules. The distance between two molecules in the dimer was 3.48 Å, suggesting a strong intermolecular interaction between molecules.

We found a new peak at 500 nm and a blue-shifted absorption band at 383 nm in the absorption spectrum of the crystal (Fig. S9) relative to its solution. The crystal absorption spectrum could be explained by the crystal structure. Two molecules in the dimer were stacked together face-to-face, producing an H-aggregate and then inducing blue-shifted absorption peak. The sliding angle between the two dimers is larger than that in the dimer itself, so a red-shifted absorption band appears that indicates a J-aggregate (Fig. 5a). This spectral change is similar to those in C12CNPA and C16CNPA gels, so C12CNPA and C16CNPA in gels have similar intermolecular packing models (Fig. 6).

Considering that C8CNPA had red-shifted absorption during gelation, a large dipole moment, and the existence of an absorption peak at 500 nm, C8CNPA reasonably stacked together in the anti-parallel model. A different dimer structure from C4CNPA also exists. As shown in Fig. 6, the sliding angles between two molecules in the dimer and between two dimers are
large enough to induce two red-shifted absorption bands. The difference of van der Waals interaction between alkyl chains should be in charge of different molecular stacking in gels because aromatic moieties of three compounds are same, and the length of alkyl chain is only different.

Fig. 6 Packing models in gels for (a) C12CNPA and C16CNPA, and for (b) C8CNPA.

The fluorescence of the sol was very weak before gelation. When the sol started to become turbid and form a gel, the emission intensity of system increased swiftly. This result suggests that the emission enhancement originated from the molecular aggregate.\(^{26}\) Fig. 7 shows the fluorescence spectral change for C8CNPA in ethanol and DMSO during gelation. The hot ethanol sol of C8CNPA emitted weak green fluorescence with a maximum of 539 nm. After 2 min, the emission band at approximately 600 nm appeared and gradually enhanced. After 15 min, the system changed into a gel and had an orange red emission with more than 6-fold intensity compared with the sol. In DMSO, the system also exhibited similar emission enhancement during gel formation. Weak and red fluorescence for the hot DMSO sol was observed, but the corresponding gel emitted blue-shifted orange fluorescence with a maximum at 594 nm and 4-fold increase in the emission intensity. Temperature-dependent fluorescence spectra showed the same result (Fig. S10). At low temperature the system had strong emission, and fluorescence intensity decrease at higher temperature. Through comparison of the optimal configuration from theory calculation and molecular structure in crystal state, the enhanced emission of the gel is attributed to the synergetic effect of the restricted molecular motion and the formation of more coplanar conformations.\(^{27}\) In addition, the similar emission wavelengths of gels in ethanol and DMSO should attribute to the same molecular stacking in two solvents.

As shown above, the gels with enhanced emission were obtained when the hot sols were cooled. Therefore, when the gels were heated to form the sol, the obvious fluorescent change was anticipated. As expected, when the temperature was higher than the sol-gel phase transition temperatures (T\(_{gel}\)) of gels and gels transferred into sols, the emission intensity sharply decreased, showing temperature-controlled fluorescence switches. Given that T\(_{gel}\) could simply be adjusted by the gelator concentration, the sensing temperatures of these switches could also be decided by gelator concentration. As shown in Fig. S6, the T\(_{gel}\) values rise nonlinearly with the increasing gelator concentration. For example, the C8CNPA gel (11 mM) changed into a sol at 45 °C, accompanied by fluorescence decrease. As the concentration increased to 16 mM and 22 mM, the T\(_{gel}\) also increased to 59 °C and 70 °C, respectively. The solvent is also important for the fluorescent color change. In ethanol, the fluorescence color changed from orange red to green, whereas the DMSO gel with stronger orange emission transformed into a red solution with weak red fluorescence.

**Conclusion**

A series of 4-nitrophenylacrylonitrile and phenylacrylonitrile derivatives consisting of carbazole moiety was synthesized. Some of these derivatives with longer alkyl chains and nitro group
could gelatimize some organic solvents. However, phenylacrylonitrile derivatives were not gelators. This result suggests that the electron withdrawing nitro moiety is important for gel formation because it makes molecules with large dipole moments, which was proven by theory calculation and the single-crystal structure. The single crystal structure of C4CNPA implies that gelators might adopt an anti-parallel molecular stacking given the larger ground-state dipole moment. The organogels also exhibited enhanced fluorescence relative to solutions. This result indicates that the gels can be used as temperature-sensitized fluorescent switches. The switch temperature can be easily adjusted by gelator concentration.

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Notes and references

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5. Electronic Supplementary Information (ESI) available: [Calculated absorption spectrum and optical structure, Photos of gels, the absorption spectra of C4CNPA in solution and crystal, XRD patterns of DMSO gels, crystal data of C4CNPA, plots of Tgel vs concentration, and CCDC 993696]. See DOI: 10.1039/b000000x/


