

New Fluorescent Amide-Functionalized Phenylethynylthiophene Low Molecular Weight Gelator

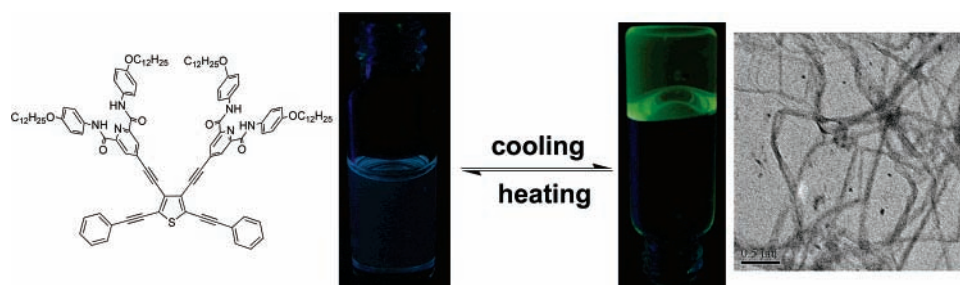
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ABSTRACT



An amide-functionalized phenylethynylthiophene gelator has been synthesized. Self-assembly of this molecule via cooperative hydrogen bonding and π -stacking induced gelation of a variety of organic solvents. The presence of aggregates was confirmed by concentration-dependent absorption and fluorescence properties. SEM and TEM studies reveal the formation of fiberlike nanostructure.

The unique ability of small organic gelators to immobilize organic solvents via the cooperative effect of noncovalent interactions, such as hydrogen bonding, π - π stacking, donor-acceptor, and van der Waals interactions, has received considerable current interest for various potential applications.¹ In order for these assemblies to form, it is crucial to control the intermolecular interactions in such a way that the molecules are able to self-organize into higher order structures but without transformation to a crystalline state. Many structure prototypes of low-molecular-weight organic gelators have been reported in the recent literature.²

In contrast, only scant work has been explored on the structures and properties of organogels based on the rigid

π -conjugated systems.³ Surprisingly, to the best of our knowledge, there is no report of low molecular weight organic gelators based on phenyleneethynylene derivatives although phenylene ethynylene derivatives have played significant roles in the recent advances of optoelectronic applications.⁴ Herein, we report the first example of thermoreversible low molecular weight organic gelator of fluorescent phenyleneethynylene derivative via cooperative hydrogen-bond- and π -stacking-induced supramolecular assembly.

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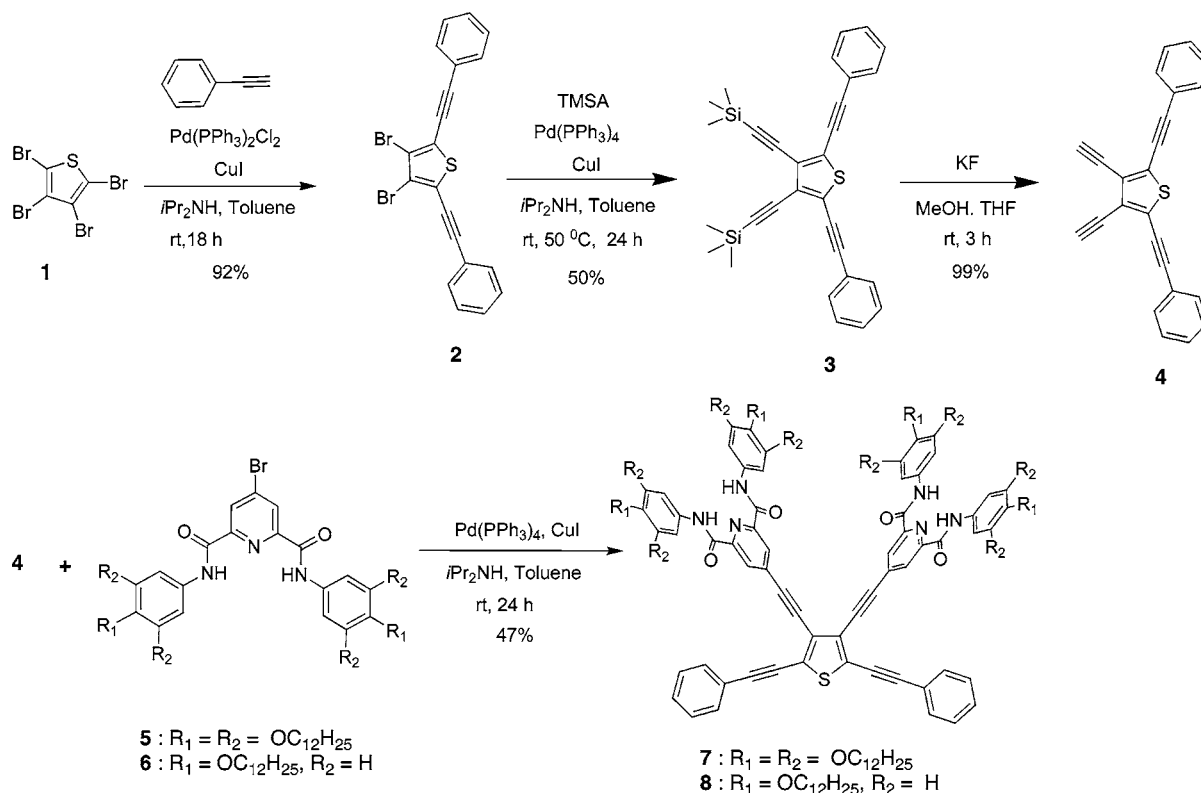
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Scheme 1. Synthesis of Amide-Functionalized Phenylethynylthiophene Derivatives



The amide-functionalized phenylethynylthiophenes **7** and **8** were prepared in four steps starting from 2,3,4,5-tetrabromothiophene according to Scheme 1. Palladium-catalyzed cross-coupling procedures were used extensively in the syntheses.⁵ All new compounds synthesized were characterized by ¹H and ¹³C NMR, mass spectrometry, and elemental analysis.⁶ Compound **7** is soluble in virtually all common organic solvents and forms a clear homogeneous solution at room temperature. In contrast, compound **8** is only soluble in certain organic solvents at elevated temperature. After the solution was cooled, a nonflowing material was formed. The gelation propensity of **8** was assessed in different solvents. It exhibited remarkable capability of gelating a variety of organic solvents including benzene (2 mg/mL), toluene (3 mg/mL), *p*-xylene (5 mg/mL), chloroform (8 mg/mL), dichloromethane (8 mg/mL), 1,2-dichloroethane (5 mg/mL), and 1-heptanol (1 mg/mL).⁷ In the case of 1-heptanol, one molecule of **8** is capable of immobilizing ~12000 molecules of 1-heptanol, and thus, **8** can be considered as a supergelator.^{3f,8} Except for dichloromethane, gels formed from the solvents listed above are highly transparent. The sol–gel interconversion is fully thermoreversible by several cycles of heating and cooling. In addition, the gels from **8**

can be stored for months without showing sign of decomposition. It should be noted that compound **8** is not effective in gelating solvents that strongly compete for hydrogen-bond formation. Addition of MeOH or DMSO into hot toluene solution of **8** resulted in no gel formation after cooling the solution, indicative of the crucial role of self-complementary hydrogen bonding in the gelation process of **8**.

The optical properties of compounds **7** and **8** are summarized in Table 1. Both compounds show very similar photophysical properties in dilute solution. Figure 1 compares the absorption and fluorescent spectra of **8** measured in dilute toluene solution (5×10^{-6} M) at 25 °C and at concentration slightly higher above critical gelation concentration (2 mM). The spectra of freeze-dried film are also included for comparison. In dilute solution **8** displays typical π – π^* transitions in the UV and near UV region. An extra shoulder appears at ~440 nm in gelling solution, and it is even more prominent and tailing into visible region in the absorption spectrum of freeze-dried film. A weak fluorescent band appears at 448 nm in dilute toluene solution with quantum yield of 0.0087. The fluorescent spectra are red-shifted in

Table 1. Photophysical Properties in CH₂Cl₂ Solution at 293 K

compd	absorption		emission	
	λ_{max} , nm ($\epsilon \times 10^{-3}, \text{M}^{-1} \text{cm}^{-1}$)		λ_{em} , nm	Φ_{em}
7	334 (86.8), 390 (sh, 30.7)		458	0.0038
8	335 (94.3), 388 (sh, 32.8)		448	0.0087

(5) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: Orlando, 1985.

(6) The characterization and spectral analyses are included in Supporting Information.

(7) The critical gelation concentration for each solvent is included in parentheses.

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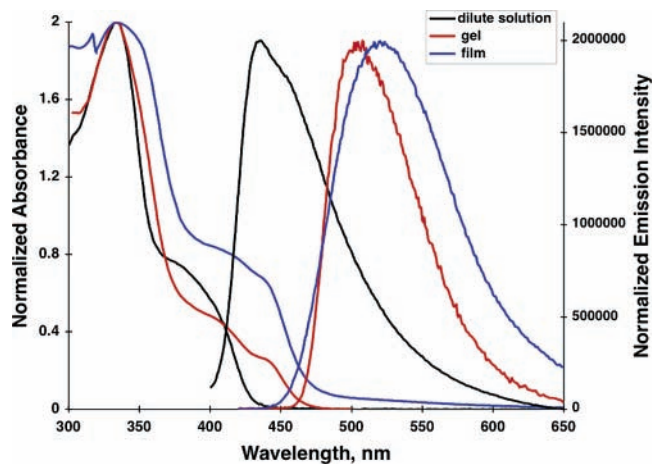


Figure 1. Normalized absorption and emission spectra of **8** in dilute solution, gelling solution, and dried film.

gelling solution and film. The fluorescence maxima exhibit bathochromic shift to 506 and 523 nm in gelling solution and film, respectively. Variable-temperature absorption and fluorescence spectra of **8** in toluene (5×10^{-6} M) also revealed the transition from self-assembly nanostructure to the molecularly isolated molecule as the temperature raised from -10 to $+70$ °C (see Figure 2 for fluorescence spectra).

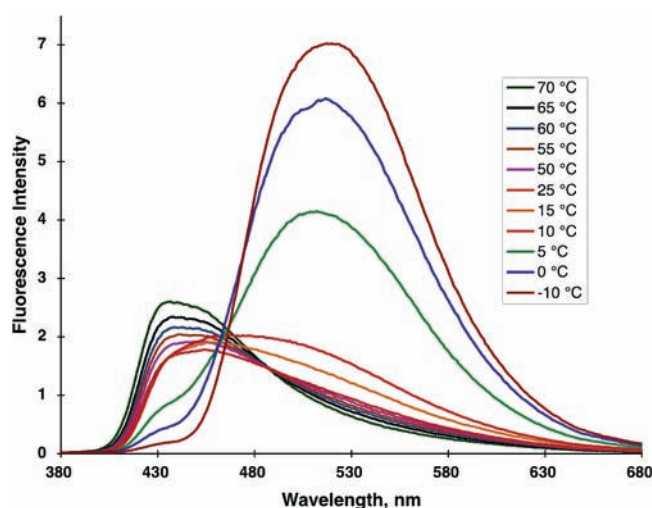


Figure 2. Variable-temperature fluorescence spectra of **8** in toluene (1×10^{-5} M).

The prominent difference of spectra in dilute solution compared to the spectra in gelling solution and freeze-dried film as well as the spectral transition in the variable temperature fluorescence spectra indicate the possibility of molecular aggregation through amide hydrogen bonding and/or π -stacking.⁹ The fluorescence quantum yield also enhances to 0.091 in film. This result is in contrast to the common observation of decreasing fluorescence quantum yield in π -stacking film compared to dilute solution.¹⁰

IR and ^1H NMR measurements were employed to probe the role of amide functional groups play in the assembly process. Figure 3 shows the variable-temperature ^1H NMR

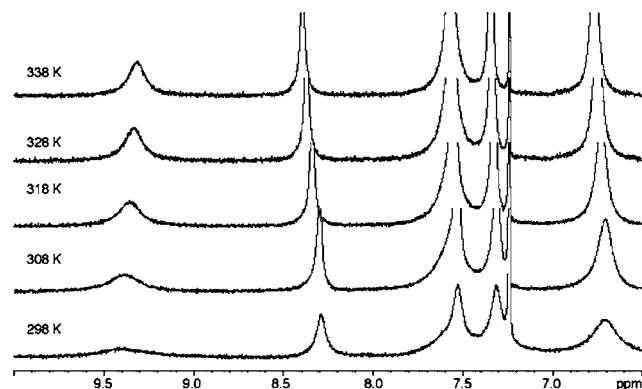


Figure 3. Variable-temperature ^1H NMR of **8** in the aromatic region.

spectra of **8**. As expected, the ^1H NMR spectrum of **8** (2 mM) in CDCl_3 at 298 K shows broad proton signals indicating extensive aggregation in solution. Unlike the chemical shift of “free” N–H peak, the chemical shift of N–H peak downfield shifts to 9.41 ppm that is evidenced of the formation of intermolecular hydrogen bonds¹¹ and confirmed by dilution ^1H NMR experiments.⁶ The proton signals were getting sharper upon heating the solution. Concomitantly, the N–H peak upfield shifts to 9.32 ppm indicating the disruption of intermolecular hydrogen bonds. In addition, the evidence of reducing aromatic π – π interactions is provided by the downfield shift of β protons of pyridines from 8.29 ppm (298 K) to 8.39 ppm (338 K). The IR spectra of **7** and **8** in toluene solution exhibit the same vibrational bands at 3342 cm^{-1} that are assigned to the intramolecular hydrogen-bonded N–H stretching frequency. On the other hand, the N–H vibrational frequency of **8** in toluene gel and in dried film shifts to lower values at 3339 and 3327 cm^{-1} , respectively. All these observations point toward the intermolecular aggregation of **8** in solution with the participation of both hydrogen-bonding and π – π stacking interactions.

The morphology of dried gels of **8** was studied by scanning electron microscopy (SEM) and transmission electron micrograph (TEM). The SEM images of **8** from CHCl_3 display three-dimensional networks of fiber bundles with 200–300 nm in diameter and several micrometers in length (Figure 4a). We believe the gathering of numerous fiber bundles

(9) The formation of excimer in the excited state is ruled out on the basis of closely resemblance between their absorption and excitation spectra for both dilute solution and gelling solution.

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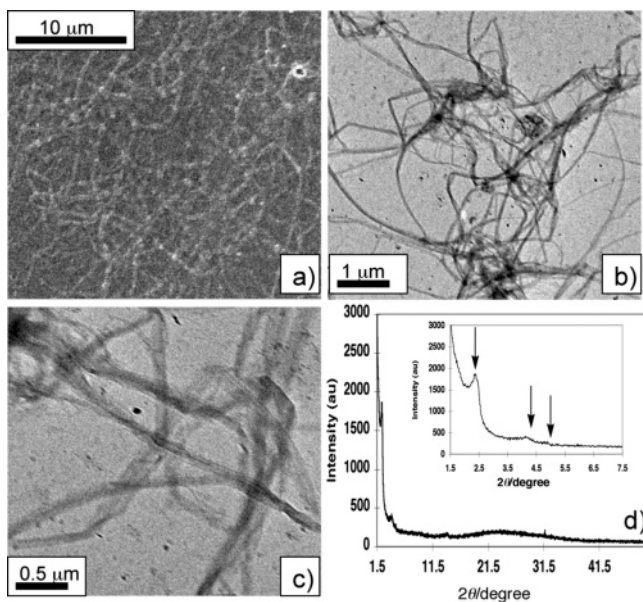


Figure 4. SEM image (a), TEM images (b, c), and XRD pattern (d) of **8**. The inset in (d) shows the expansion of small-angle region of the spectrum.

forms the steric intertwined structure that results in the immobilization of the organic solvents. The TEM images of **8** from 1-heptanol solution display tape-like morphology with 50–80 nm in diameter (Figure 4b,c). Powder X-ray diffraction pattern of toluene film of **8** (Figure 4d) reveals long-range periodic order where three reflection peaks appearing at $d = 36.8$, 21.5 , and 18.0 Å in the small-angle region, which indicates a macroscopic order of hexagonal packing.¹² A diffuse reflection at $d = 3.9$ Å is observed in

wide-angle region. The broad band in the wide-angle region is most likely due to the interdigitated packing of the alkoxy chains or the intermolecular distance within a column.^{3h,12}

In summary, we have synthesized the first example of low molecular weight organic gelator based on phenylene ethynylene derivative that is capable of immobilizing a variety of organic solvents to form stable organogels. The general properties of **8** are similar to many other reported gelators. However, it exhibits very unique optical property. Even though with apparently more ordered π -stacking and intermolecular interactions in the self-assembled three-dimensional architecture, the fluorescence of these gels is greatly enhanced compared to their solution states. We are currently investigating in more detail the role of conjugation and aliphatic chains in controlling the self-assembly and gelation behavior of these amide-functionalized phenylenethynylenes aiming to tune their optical properties and explore the potential applications in optoelectronics.

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Supporting Information Available: Synthetic details, characterization data, and ^1H NMR spectra of dilution experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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