



A potent triphenylbenzene-based H-bonding donor to assist formation of two-component organogels with stilbazoles

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ABSTRACT

Two-component organogelators based on a discotic H-bonding donor of 1,3,5-tris(4-amidobutanoic acid)phenyl benzene (**2**), and acceptors of 4-(4-alkoxybenzoyloxy)-4'-stilbazole derivatives were reported. These complexes showed good gelation ability for alcohols, which are known to be unfavorable for H-bonding formation. SEM study revealed that sheet-like network, nanotapes, and nanorods were gained from the self-assembling of the complexes with small difference of the carbon chain length. Based on XRD, IR, temperature-dependent ¹H NMR, and UV-vis absorption investigations, the gel-phase materials were generated from 1D columnar-type packing of complexes facilitated by cooperative H-bonding, π -stacking, and van der Waals interactions.

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The creation of well-defined nanosized architectures using the principles of supramolecular chemistry, the bottom-up approach, is a topic of considerable importance.¹ Since decades, scientists have been passionately applying this approach to develop gel-phase materials based on organogels.² The recent and rapid growth of interest in organogels is motivated not only by the potential applications ranging from cosmetics, templates, catalysis, and controlled release to optoelectronics and related fields but also by the fact that these systems exhibit striking properties with respect to the reversible self-assembly phenomena.^{2a,b,e,f,h,3} With the development of gel phase based on two-component systems by Hanabusa,^{4a} research efforts have been made on multicomponent gelators which rely on the initial interaction of distinct individual components that subsequently self-assemble into a fibrous supramolecular aggregates.^{4,5} It is believed that multicomponent gel systems may assist to introduce the functional groups and obtain organogels with desired functionalities in a facile way avoiding complicated organic synthesis.^{5a,b,6,7} Therefore, self-assembly of two-component systems provides a route to ordered nanomaterials that would be impossible to generate by traditional synthetic approaches.

It is known that stilbazole derivatives are versatile materials for the construction of optically nonlinear systems, pyroelectric Langmuir–Blodgett fabrications, and metallomesogens⁸ and can act as H-bonding acceptor for supramolecular self-assembly.^{7a} As reported previously, 4-(4-alkoxybenzoyloxy)-4'-stilbazole deriva-

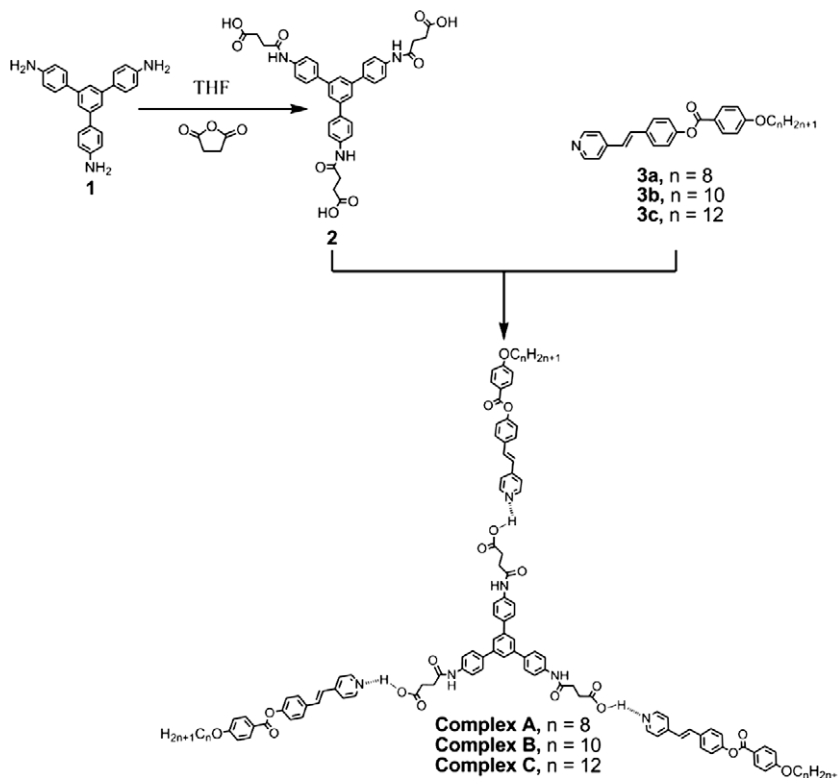
tives cannot gel any solvent themselves^{7a} except that were linked to cholesterol backbone⁹ which is known to favor 1D packing.¹⁰ Moreover, we have found that the alcoholic solvents were unfavorable for gel formation due to the breaking of intermolecular H-bonding between complex units although the H-bonding between COOH group in ι -tartaric acid and pyridine in stilbazole still was reserved in methanol.^{7a} In order to gain two-component gels assisted by H-bonding in alcoholic solvents, we designed a new H-bonding donor based on triphenylbenzene derivative (Scheme 1), which prefers to arrange via π - π interactions.^{7b} Notably, the π -aggregates provide appropriate surroundings for intermolecular H-bonding between amides. Thus, the cooperation of π - π interactions and H-bonding would strengthen the intermolecular interactions, resulting in gelation of alcohols.

Compounds **1** and **3a–3c** were synthesized as reported previously.⁷ The mixture of compound **1** and 3 equiv of succinic anhydride in THF was stirred at room temperature for 24 h to afford compound **2** in a yield of 84% (Scheme 1). Complexes **A**, **B**, and **C** were easily obtained by dissolving triphenylbenzene-based carboxylic acid **2** and 3 equiv of stilbazole derivatives **3a**, **3b**, and **3c**, respectively, in THF followed by solvent evaporation.

Gelation ability of the three complexes was evaluated in various organic solvents, including apolar aliphatic hydrocarbons (hexane and cyclohexane), aromatic ones (benzene, *p*-xylene, and toluene), dichloromethane, chloroform, THF, alcohols (methanol, ethanol, isopropanol and butanol), DMSO, and acetone. It is clear from Table 1 that hydrocarbon and aromatic solvents failed to dissolve the complexes, and the gels could be formed only in alcoholic solvents and DMSO. In addition, the CGC rose with increasing the

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Scheme 1. Synthetic route for compound **2** and complexes **A**, **B**, and **C**.

Table 1
Gelation test for complexes **A**, **B**, and **C**

Solvent	Galators		
	Complex A	Complex B	Complex C
<i>n</i> -Hexane	Is	Is	Is
Cyclohexane	Is	Is	Is
Methanol	OG ^a	OG ^a	OG ^a
Ethanol	OG ^a	OG ^a	OG ^a
Isopropanon	OG ^b	OG ^b	OG ^b
Butanol	OG ^d	OG ^d	OG ^d
1,4-Butane diol	OG ^c	OG ^c	OG ^c
4-Methylbutanol	OG ^d	OG ^d	OG ^d
CH ₂ Cl ₂	Is	Is	Is
CHCl ₃	Is	Is	Is
THF	S	S	S
DMSO	OG ^c	OG ^c	OG ^c
Benzene	Is	Is	Is
Toluene	Is	Is	Is
<i>p</i> -Xylene	Is	Is	Is

OG: opaque gel, S: soluble, Is: insoluble. The low critical gelation concentration (CGC): ^a1.0 wt/v%, ^b1.25 wt/v%, ^c2.0 wt/v%, ^d2.5 wt/v%.

length of alkyl chain in alcohols due to high solubility of the complexes in the alcohols with long carbon chain. However, it took less time for the gel formation of complex **A** than complex **B**, which also could form gel faster than complex **C** when cooling their hot ethanol solutions to room temperature (20 °C). On the other hand, in butanol systems, the time for the gel formation was in the order of complex **C**, complex **B**, and complex **A**. To compare the thermal stability of the gels based on the three complexes in ethanol, we determined the T_{gel} (the thermally reversible gel–sol transition temperature) values. It can be seen from Figure 1 that for each complex the T_{gel} increases with increasing the concentration of the complex. However, under the same concentration, T_{gel} values appear in the order of complex **A** > complex **B** > complex **C** which

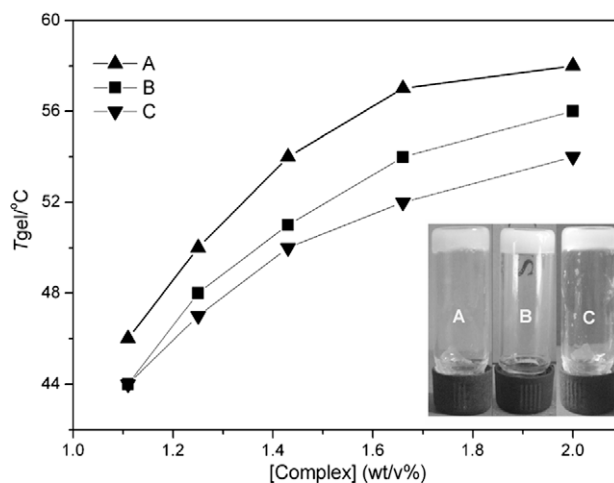


Figure 1. Plots of the T_{gel} versus the concentration of (▲) complex **A**, (■) complex **B**, and (▼) complex **C** in ethanol. Inset shows the ethanol gels of the three complexes (2.0 wt/v%).

means that the complex **A** was the most stable in ethanol. These observations suggested that the alkyl chain in stilbazole had an effect on the gelation process.

The morphological features of the three two-component gel systems were investigated using SEM. As shown in Figure 2, the ethanol gel of complex **A** showed a frizzy sheet-like structure suggesting that complex **A** should aggregate in some two-dimensional morphology (Fig. 2a). Figure 2b illustrated that in the xerogel obtained from ethanol gel, the complex **B** self-assembled into nanotapes with 150–500 nm in width and several micrometers in length, which further entangled into gel network. On the other hand, the arrangement of gelators in the gel of complex **C** led to lots of nanorods (Fig. 2c–e). For instance, the ethanol gel based

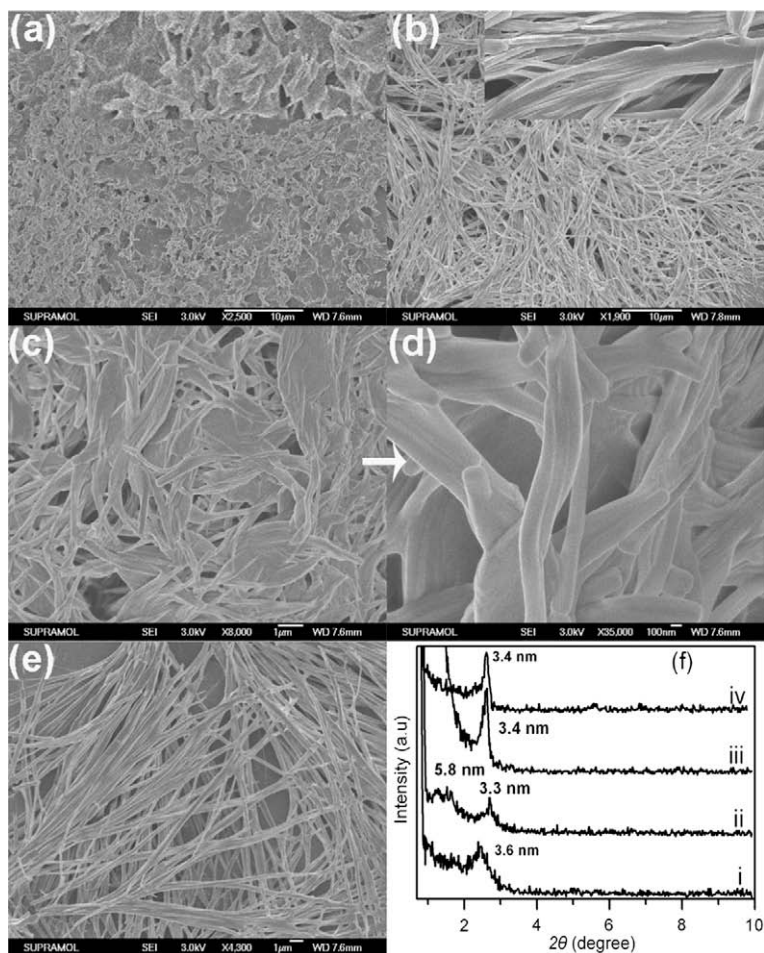


Figure 2. SEM images of ethanol gels (1.0 wt/v%) of (a) complex **A**, (b) complex **B**, (c) and (d) complex **C**; and (e) butanol gel of complex **C** (1.0 wt/v%). (f) Small-angle X-ray diffraction patterns of ethanol gels of (i) complex **A**, (ii) **B**, (iii) **C**, and butanol gel of complex **C** (iv).

on complex **C** exhibited twisted rods with a diameter of 180–200 nm, which intertwined into a spiderweb-like structure (Fig. 2c and d). However, in the case of complex **C**-based butanol gel, the rods are less twisted and the diameters are not very regular as those in ethanol varying from 150 to 500 nm (Fig. 2e). The SEM images illustrated that the alkyl chain length has significant effect on the hierarchical growth of the complexes at the nanoscale and microscopic levels.

XRD is a powerful tool in elucidating long-range structures of supramolecular assemblies. The XRD patterns of the ethanol gels of the three complexes (**A**, **B**, and **C**) and butanol gel of complex **C** are illustrated in Figure 2f. Only one distinct diffraction peak around $2\theta \approx 2.4\text{--}2.6^\circ$ could be observed for xerogels of complexes **A** and **C**, suggesting that the gelators packed into one-dimensional columnar structures with a diameter of ca. 3.6 nm for complex **A** and 3.4 nm for complex **C**.^{11,12a} This is understandable that columnar structure could be generated from discotic compounds.^{7b,11,13} However, complex **B** adopted an hexagonal columnar structure instead of a simple columnar one as shown by the two Bragg reflections at d-spacing of 5.8 and 3.3 nm with a periodicity of close to 1/1 and $1/\sqrt{3}$ (Fig. 2fii).^{7b,c}

In order to evaluate the driving forces behind the gelation process, the UV–vis absorption and FT-IR spectra of complex **C** in gel phase and in dilute solutions are given in Figures 3a–c. We could find that the maximum absorption peak of complex **C** in dilute ethanol appeared at 286 nm and blue-shifted to 281 nm in gel phase. Complexes **A** and **B** showed similar absorption spectral changes (not shown). It suggested that the π – π interaction is one of the

key driving forces for the formation of these two-component gels, and the gelators assembled into H-aggregates in gel phases. As shown in Figure 3b, the NH stretching bands appeared at 3510 cm^{-1} for free amides, and it shifted to 3289 cm^{-1} in ethanol xerogel.^{7b,14} The virtual missing of OH stretching band suggested the strong interaction between COOH and pyridine groups. The amide I band appeared at 1682 cm^{-1} in the monomer state, and shifted to 1663 cm^{-1} in ethanol xerogel, supporting the formation of the H-bonding between the complex entities (Fig. 3c).^{7b,13,14}

In addition, the vibration frequencies for CH_2 antisymmetric $\nu_{\text{as}}(\text{CH}_2)$ and symmetric $\nu_{\text{s}}(\text{CH}_2)$ stretching as well as the CH_2 scissoring deformation $\delta(\text{CH}_2)$ in the xerogel would somewhat reflect the packing conformation of alkyl chains.^{7b,15} For the xerogel of complex **C**, the $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ bands appeared at 2924 and 2852 cm^{-1} , respectively, in a relatively low wavenumber region, which suggested that the alkyl chains adopted all-*trans* conformation (Fig. 3b). The $\delta(\text{CH}_2)$ band was located at 1468 cm^{-1} with full width at half-maximum of 7.5 cm^{-1} , which could be ascribed to a triclinic chain packing of the complex (Fig. 3c).^{7b,15} Moreover, the temperature-dependent FT-IR spectra of the complexes in ethanol gels were shown in Figure 3d–f. From Figure 3d, it is clear that the NH stretching band of complex **A** gave a peak at about 3290 cm^{-1} ascribed to the H-bonded amides at 20°C . At 60°C , besides the former peak we could find a new broad band at 3438 cm^{-1} , which might be explained that H-bonding between amides in a part of complexes was weakened. On the other hand, as shown in Figure 3f, only one broad peak at 3435 cm^{-1} could be observed at 60°C for complex **C**. Moreover, when heating the samples from 20 to

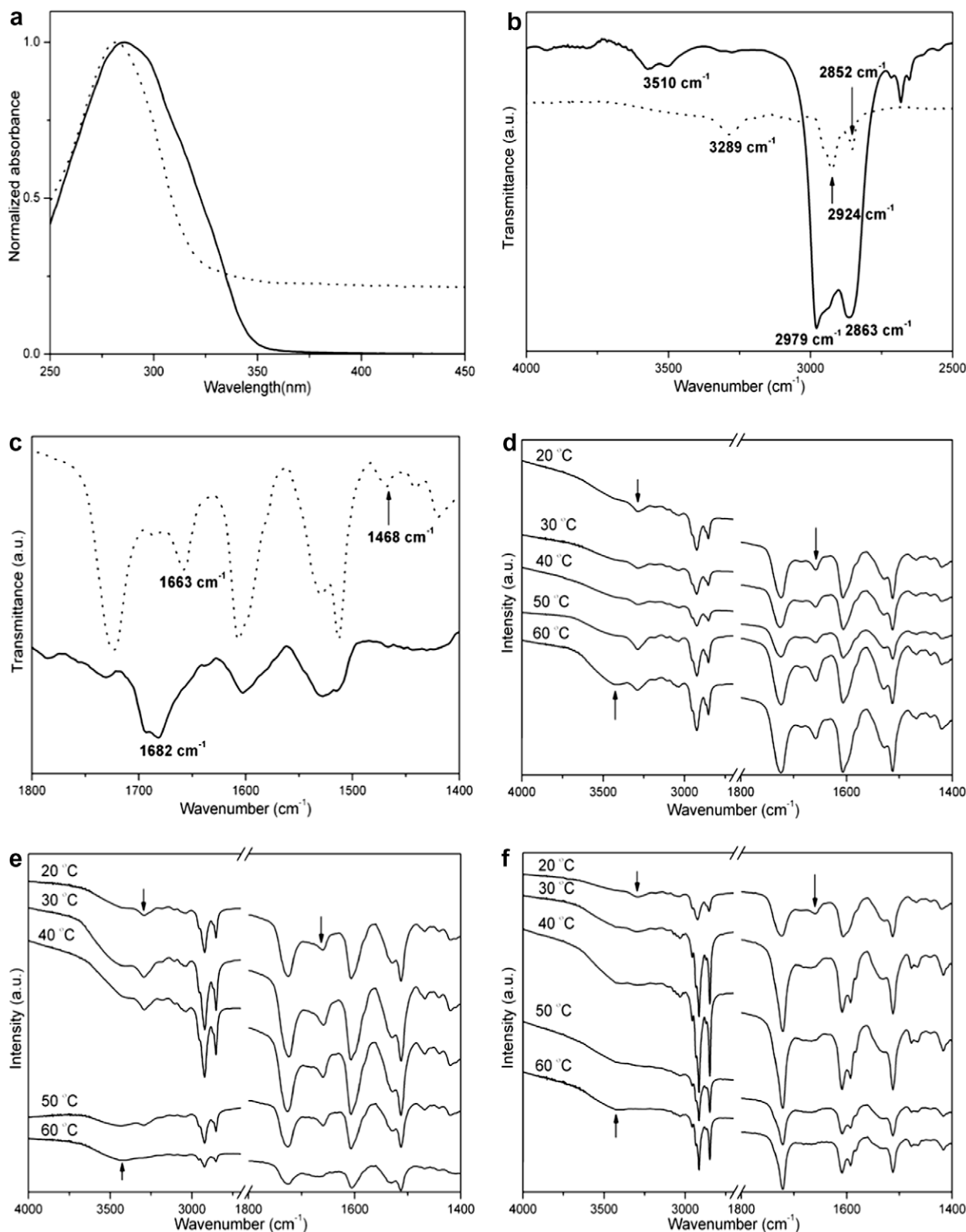


Figure 3. UV-vis absorption spectra of complex **C** (a) in ethanol (5.2×10^{-5} M, solid) and in gel (1.0 wt/v%, dot); FT-IR spectra of complex **C** (b) and (c) in THF (1.0 wt/v%, solid) and in ethanol xerogel (1.0 wt/v%, dot); temperature-dependent FT-IR spectra for ethanol gels (2.0 wt/v%) of complex **A** (d), complex **B** (e), and complex **C** (f).

60 °C, the vibration band of amide I in complex **A** did not shift, while it shifted from 1659 to 1668 cm⁻¹ in the case of complex **C**, meaning that the H-bonding in complex **C** with longer carbon chains was weaker than that in complex **A**. The temperature-dependent FT-IR spectral changes of complex **B** were in the med-

ium between complexes **A** and **C**. This observation further suggested that the gel of complex **A** was the most stable. As a result, the self-assembling of the complexes into fibrous nanostructures is directed not only by van der Waals interaction among alkyl chains but also by the π - π interaction as well as H-bonding.

In general, NMR technique can give a great deal of information on the self-assembling process leading to gel phases.^{2d,h,12b,16} Figure 4 illustrated the ¹H NMR spectra of complex C in DMSO at different temperatures. We must underline that DMSO is sometime said to be a breaking of H-bonding or highly competitive H-bonding solvent.^{17a–c,17f} But some studies have revealed the evidence of H-bonding between functional molecules in DMSO.^{17b,18c} Changes of the resonance signal for the protons in carboxyl and amide groups from 20 to 60 °C are shown in Figure 4a. At 20 °C, the protons in carboxyl and amide appeared at 12.13 and 10.09 ppm, respectively. As the temperature was increased, the peak for protons in COOH became less pronounced and shifted upfield^{19b} (reached 11.81 ppm at 60 °C, $\Delta\delta = 0.32$ ppm), while the one in NH group become slightly sharp and shifted to 9.85 ppm ($\Delta\delta = 0.24$ ppm) at 60 °C.^{17e} At elevated temperatures, the H-bonding between COOH and pyridine is weakened, and protons in COOH are exchanging with traces of H₂O (see Supplementary data), so the average signal is broadened into the baseline.^{18a} In addition, the temperature-induced upfield shift of the NH protons is related to an increase in the electron density of the carbonyl oxygen atoms upon destruction of the H-bonding.^{5d} On increasing the temperature, the H-bonding between amides begin to break apart as entropy begins to dominate, hence resulting in the observed upfield shifts. These changes of chemical shift values suggested the presence of H-bondings between amides in gel state as well as between COOH in triphenylbenzene derivative and pyridine in stilbazole.^{5b–d,15a,18b,19} On the other hand, the signals for protons in aromatic and vinylic units at 20 and 60 °C are also shown in Figure 4b. At high temperature, the resonance signals corresponding to the aromatic and vinylic protons became stronger and distinguishable, further indicating that π - π interactions played a role in the aggregation of the complex.^{2h} Based on ¹H NMR, UV–vis absorption, XRD, and FT-IR data, the packing model for the two-component gelators in the gel phase was suggested as shown in Figure 4c, in which the triphenylbenzene cores stacked into face-to-face aggregates directed by π - π interaction, meanwhile, H-bonding between amides further strengthened the intermolecular interactions, favoring the building of fibrous assemblies.

In summary, two-component gel systems based on the interaction between a new potent triphenylbenzene-based H-bonding donor and stilbazole derivatives (Scheme 1) were reported. Although the alcoholic solvents and DMSO are known to be unfavorable for

H-bonding formation between functional molecules, our complex systems have been revealed to be excellent gelling agents for those solvents. ¹H NMR, UV–vis absorption, XRD, and FT-IR measurements as well as gelation ability monitoring revealed that H-bonding, π - π interaction, and van der Waals forces were the driving forces behind the gelation of these complexes. The morphological study illustrated that the small difference of the carbon chain length has significant effect on the gel materials at the microscopic level. The sheet-like network, nanotapes, and nanorods could be gained from the assembling of complexes with octyloxy, decyloxy, and dodecyloxy, respectively, as side chains. Herein, we provide a strategy to design H-bonding-based two-component gelators with excellent gelling ability for alcohols via strengthening the H-bonding assisted by π - π interactions. The well understanding of the supramolecular interactions and the gelation process would be useful for fabrication of novel well-ordered functional assemblies.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.05.043.

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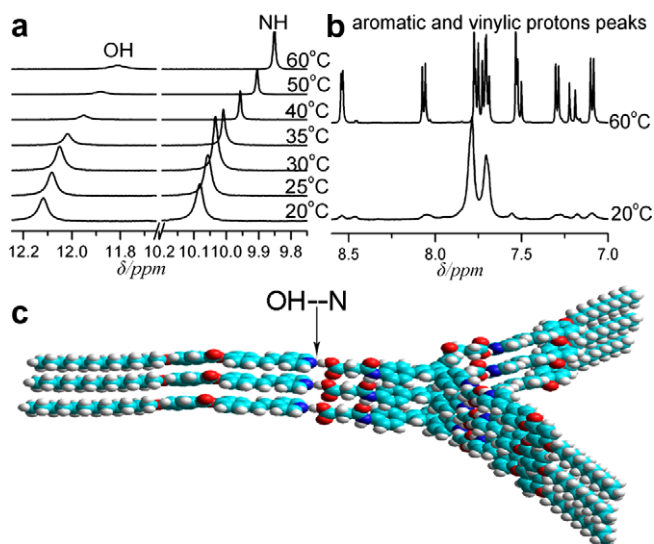


Figure 4. Temperature-dependent ¹H NMR spectra of complex C in DMSO-*d*₆ (2.0 wt/v%) in the range of (a) 9.8–12.2 ppm, (b) 7.0–8.6 ppm; (c) schematic packing model of the complex in gel state on side view.

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