NJC

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c4nj01131g

Self-assembly of azobenzene-based two-component gels†

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Received (in Montpellier, France)
8th July 2014,
Accepted 7th August 2014

DOI: 10.1039/c4nj01131g

www.rsc.org/njc

An azobenzene derivative was found to form a two-component gelator with lauroyl or stearoyl phenylalanine although phenylalanine units failed to gel the solvent. During gelation, the yellow sols turned into red gels, implying a sharp color change in the system. In gel, molecules self-assembled into one-dimensional nanofibers. Circular dichroism spectral results indicated that the chirality of phenylalanine was passed on to the azobenzene moiety, which formed a right-handed helical stacking in the gel phase. UV-vis experiments and NMR spectra revealed that the azobenzene derivative and lauroyl phenylalanine formed a complex with a ratio of 1 : 4. The critical gelation concentrations and gel-to-sol phase transition temperatures were dependent on the ratio of the two compounds. Moreover, the response of two-component gels to mechanical stimulus could result in a gel-to-sol transition. The gels can again self-heal after resting, which is a process that can be reversed numerous times.

Introduction

Non-covalent interactions are effective tools for constructing well-defined supramolecular structures driven by molecular self-assembly, which generally determine material properties.[1] Considerable interest has been directed toward these interactions for the development of novel gel-phase materials on the basis of low-molecular-mass gelators.[2] The self-assembly process facilitates the formation of supramolecular polymer-like structures through intermolecular non-covalent interactions (*i.e.*, van der Waals, π–π, hydrogen bonding, electrostatic, coordination, and charge-transfer interactions). Organogels are jelly-like soft materials that are generally composed of a one-component gelator and a large amount of solvent. To achieve unique properties in the gel phase, a simple method is to introduce functional moieties into the molecular structure through a covalent bond. So far, one-component gels have been useful in photovoltaics,[3] field-effect transistors,[4] sensors,[5] and various stimuli-responsive materials,[6] and so on.

Two-component gels composed of two compounds have recently been developed.[7] A functional moiety can be easily introduced by non-covalent bonds, and the properties of two-component gels can be controlled by adjusting the ratio of two components. Smith discovered numerous two-component dendritic gels, the properties and morphologies of which can be controlled by components.[8] Shinkai found that fullerene can form a one-dimensional multicapsular structure with a tetraphenylporphyrin derivative, after which a gel phase was observed.[9] Yi, Fang, Ajayaghosh, and Meijer *et al.* also developed numerous functional two-component organogels.[10] Some useful two-component gels have recently been investigated by our group, and have been used in temperature-controlled fluorescence switches, chemosensors for volatile acids, and organic amines and for photocurrent generation in electronic donor–acceptor gels.[11]

In this study, we found that an azobenzene derivative (**PDNA**) can aid lauroyl or stearoyl phenylalanine (**C12Ph** and **C18Ph**) to gel hexane, octane, and cyclohexane even when phenylalanine units fail to gel these solvents. In gel, molecules self-assembled into one-dimensional nanofibers. Results of the circular dichroism (CD) spectra indicated that the chirality of phenylalanine was passed on to the azobenzene moiety, which formed a right-handed helical stacking in the gel phase. Moreover, the critical gelation concentration (CGC) and gel-to-sol phase transition temperatures (T_{gel}) depended on the ratio of these two components. The response of these gels to mechanical stimulus could result in a gel-to-sol transition. The gels could self-heal after resting, which is a process that can be reversed numerous times.

Results and discussion

Three compounds were easily synthesized by classical methods (Scheme 1) and characterized by NMR, IR, MS and elemental analysis. For detailed procedures see Experimental section.

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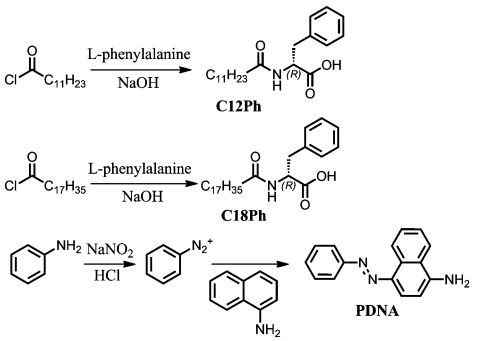
† Electronic supplementary information (ESI) available: ^{1}H NMR spectra, rheometry data, IR spectra and SEM images of complexes, and absorption spectra of complexes (3 : 1) at different concentrations. See DOI: 10.1039/c4nj01131g



Scheme 1 Synthesis routes of **C12Ph**, **C18Ph**, and **PDNA**.

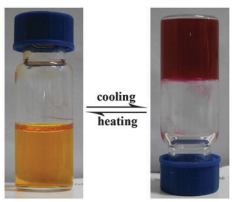


Fig. 1 Mixtures of **PDNA** and **C12Ph** in a ratio of 1 : 1 in cyclohexane.

First, the mixture of **PDNA** and **C12Ph** in a 1 : 1 molar ratio was prepared by mixing the two compounds in CH_2Cl_2 and then removing the solvent. The CH_2Cl_2 solution was yellow, whereas the solid changed to dark red, indicating that **PDNA** formed aggregates in the solid state.[12] This red mixture was dissolved in cyclohexane, hexane, and octane to form a clear yellow solution upon heating, and then transformed into red gels upon cooling (Fig. 1). Under the same conditions, **C12Ph** formed white precipitation in these solvents despite containing amide and the long alkyl chain.[11b] The mixture of **PDNA** and **C18Ph** (1 : 1) can also form a red gel in these solvents. Therefore, **PDNA** can help **C12ph** to gel the solvent.

The light microscopy image (Fig. 2a) of the cyclohexane gel illustrates that the mixture of **PDNA** and **C12Ph** (1 : 1) prefers to self-assemble and form long and thin fibers. A fibrous network structure is also formed by intertwining fibers. A scanning electron microscope (SEM) was used further to study the microscopic structure of the gels. An extended fibrillar network was observed (Fig. 2b). Thus, the mixture is likely to self-assemble into a one-dimensional fiber. The gel stability was studied by rheological measurements. The strength (storage modulus, G') of the gel is more than 6500 pa with a small strain of 0.01% when the concentration was 1.0 mg mL^{-1}. G' and the loss modulus (G'') remained nearly constant up to 3% and G' was greater than G'' of the gel (Fig. S4, ESI†). This result suggests that cyclohexane is stable because of the presence of a 3D fibrous network.

A sharp color change was observed during gelation. UV-vis spectra were used to monitor the gelation process. The absorption peak at 415 nm in the hot cyclohexane solution gradually decreased when the solution was cooled (Fig. 3a). Meanwhile, a

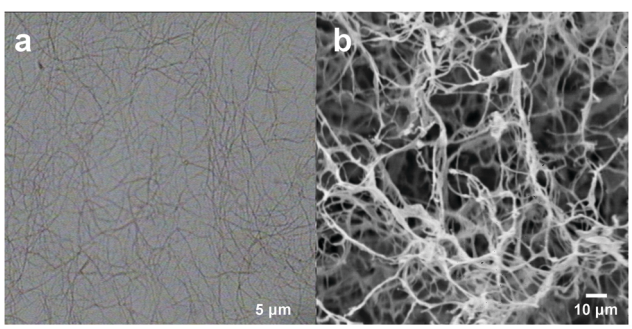


Fig. 2 (a) Optical microscopy images and (b) SEM images of the cyclohexane gel formed by **C12Ph** and **PNDA** (1 : 1).

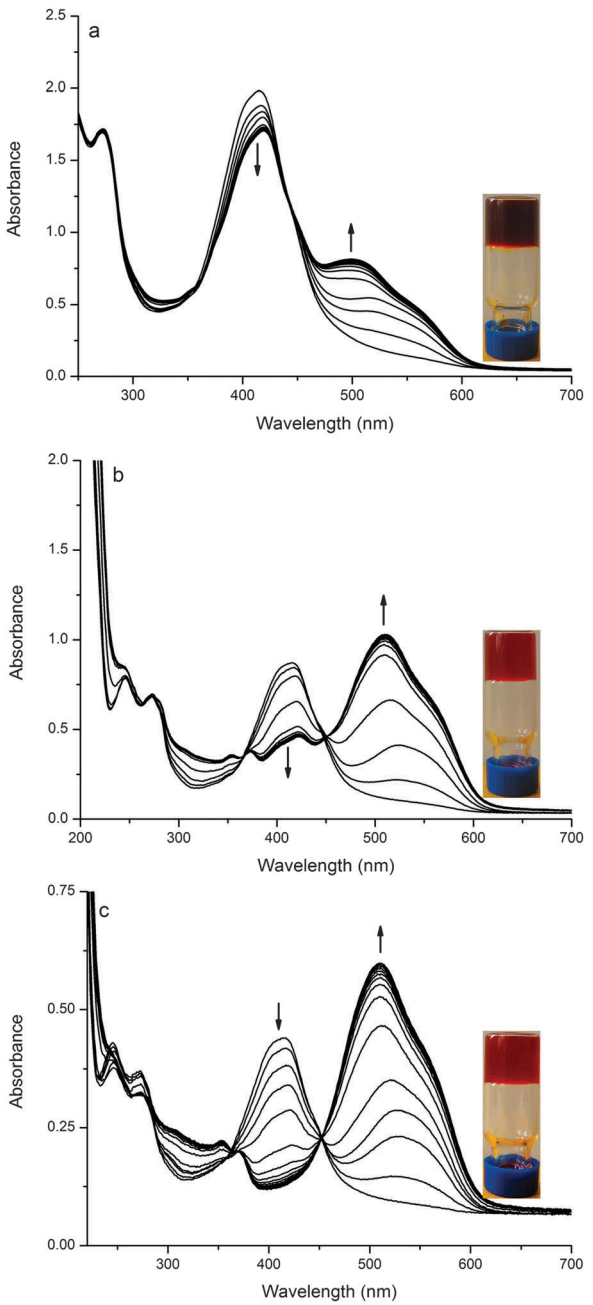


Fig. 3 UV-vis spectral change of **C12Ph** and **PDNA** with different molar ratios of 1 : 1 (a), 3 : 1 (b), and 4 : 1 (c) during gelation (from 80 to 10 °C, at an interval of temperature is 5 °C) in cyclohexane. Concentration of three samples is 1.8 mg mL^{-1}. The optical path is 0.2 mm.

new peak at 500 nm with a shoulder peak at 555 nm appeared and gradually increased. The appearance of two new peaks suggests why the gel is red and implies that **PDNA** self-assembled into J-aggregates.[13] Thus, the exciton coupling exists between **PDNA** molecules.

The 415 nm absorption peak did not disappear and was stronger than that at 500 nm, thus indicating that many **PDNA** molecules exist in the monomeric state in the gel of the mixture (1 : 1). Such a result can be confirmed by the following experiment. The gel was first destroyed through mechanical stirring. Clear yellow solution and red solid were obtained by centrifugation, and their absorption spectra were recorded. The clear yellow solution has an absorption band with a maximal peak of 415 nm, and its absorbance is almost the same as that of the wet gel (Fig. 4). The absorption band of the red solid is similar to that of the new peak at 500 nm in the wet gel. This result affirms that a large amount of **PDNA** did not aggregate in the gel mixture (1 : 1). The ^{1}H NMR spectrum of red solid obtained in the wet gel suggests that the molar ratio of **C12Ph** and **PDNA** is 4 : 1 in red solid (Fig. S5, ESI†). That is, **C12Ph** and **PDNA** formed a complex with a molar ratio of 4 : 1, not 1 : 1, which differs from that of hydrogen-bonded two-component gels previously reported.[14] Small shifts of **PDNA** protons in the ^{1}H NMR spectrum of the red solid may imply the hydrogen-bonded complex formed by **C12Ph** and **PDNA** rather than a hydrogen-bonded ion pair. The infrared (IR) spectra also suggest the same result. **C12Ph** in the solid state has a strong IR absorption peak at 1707 cm^{-1}, indicating a dimer structure of carboxylic acid groups.[15] The red solid possessed a weak and wide peak at 1705 cm^{-1} with a shoulder peak at 1715 cm^{-1} (Fig. S6, ESI†). These results suggest a hydrogen-bonded complex.[16] Moreover, the vibration absorption peaks of NH and amide I appeared at 3306 and 1646 cm, respectively, indicating the formation of intermolecular hydrogen bonds between amide units in the gel.[17] As suggested by NMR spectra, the hydrogen bonded complex in $CDCl_3$ solution existed and its color was yellow, indicating that the color change during gelation is ascribed to π–π interaction between **PDNA** molecules, rather than the charge transfer complex.[18]

Accordingly, **C12Ph** and **PDNA** form the hydrogen bond complex in a ratio of 4 : 1. The gel properties are possibly dependent on the components of the two compounds. It was found that the microstructures of gels with different molar ratios were similar. For example, the gels (3 : 1 and 4 : 1) were comprised of thin and long fibers (Fig. S7, ESI†). This result suggests that microstructures of gels are independent of the components of gels. This case is different from that reported by Smith, in which morphologies of gels are strongly affected by the ratio of two components.[8e] When the ratio of **C12Ph** and **PDNA** was 3 : 1, the absorption peak at 415 nm decreased, and the peak at 500 nm was enhanced (Fig. 3b). In the complex gel with a 4 : 1 ratio, the monomeric absorption band disappeared (Fig. 3c), thus indicating that all **PDNA** molecules formed aggregates. The concentration-dependent UV-vis spectra of the complex (4 : 1) are shown in Fig. S8 (ESI†). At high concentrations, the absorption band of the monomeric state cannot be found. When concentration decreases, the absorbance at around 400 nm gradually increases, and the absorption band at 500 nm becomes weaker. When the concentration reaches 0.003 mg mL^{-1}, the peak at 500 nm vanishes, and only an absorption band at 415 nm remains. Hence, the aggregation degree of **PDNA** is correlated with concentration.

The component of the two compounds determined their CGCs, as shown in Fig. 5. The equimolar mixture of **PDNA** and **C12Ph** in cyclohexane had a CGC of 1.4 mg mL^{-1}. When the molar ratio of **C12Ph** and **PDNA** increased to 3 : 1, CGC decreased to 0.8 mg mL^{-1}. The complex of 4 : 1 had the smallest CGC (0.74 mg mL^{-1}). The excess **PDNA** molecules existing in the solution of equimolar mixture may be responsible for the high CGC. Moreover, the CGCs of **C18Ph** and **PDNA** mixtures are associated with the component of two compounds (Fig. 5). For example, 1 mL of cyclohexane requires an equimolar mixture of 20 mg for gelation. The CGC of the complex of 4 : 1 decreased to 4 mg mL^{-1}. The mixture of **C18Ph** and **PDNA** clearly exhibited a higher CGC than those of **C12Ph** and **PDNA** at the same molar ratio. **C18Ph** demonstrates higher solubility than **C12Ph** in cyclohexane, which may explain the difference in CGC.

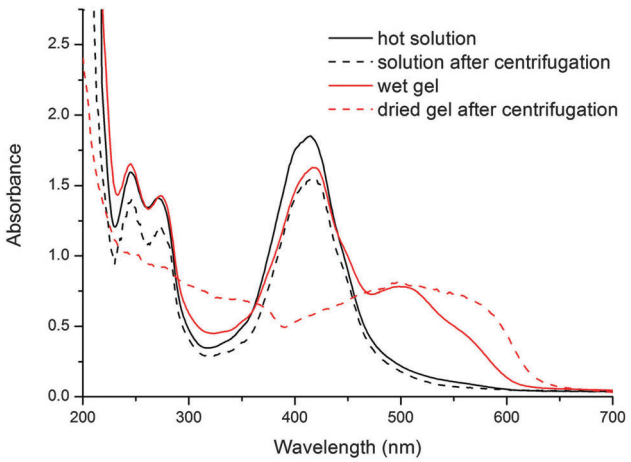


Fig. 4 UV-vis spectra of the mixture of **PDNA** and **C12Ph** in a 1 : 1 ratio in hot solution and gel, and the solution and dried gel after centrifugation.

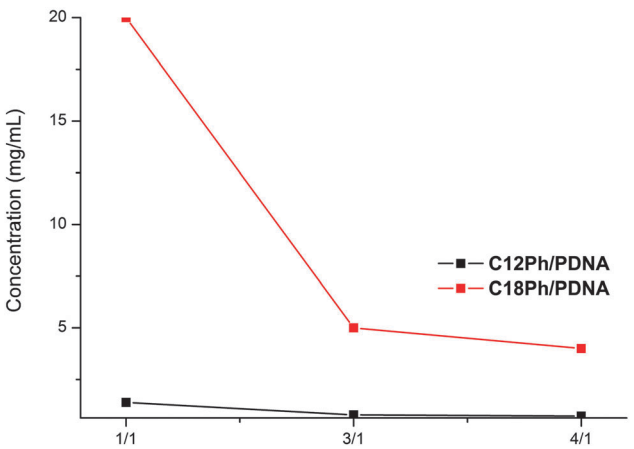


Fig. 5 Critical gelation concentration of the mixtures with different molar ratios.

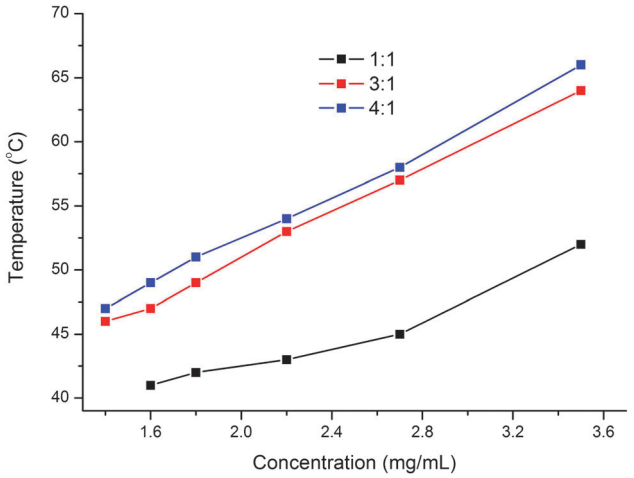


Fig. 6 T_{gel}s of cyclohexane gels of **C12Ph**/**PDNA** *vs.* concentration.

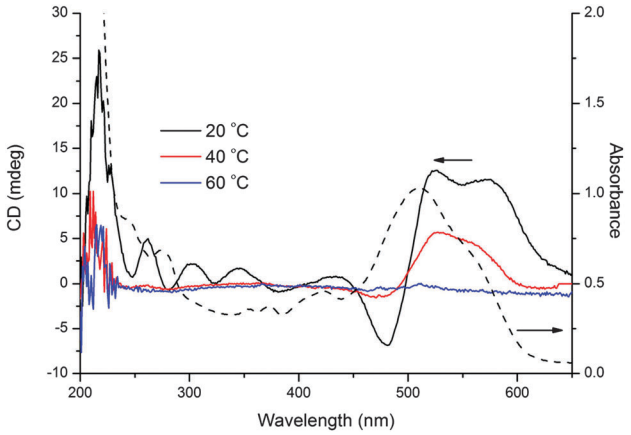


Fig. 7 Circular dichroism and UV-vis absorption spectra of the gel (4 : 1) in cyclohexane at 1.0 mg mL^{-1} concentration.

The CGCs of gels are found to depend on their components. Thus, gel components can also determine T_{gel}s. Fig. 6 shows the relationship between T_{gel}s and concentration. T_{gel}s of all gels increase as gelator concentration increases. For instance, the gel of **C12Ph** and **PDNA** (1 : 1) at a concentration of 1.6 mg mL^{-1} transformed into a sol at 41 °C. When the concentration increased to 3.5 mg mL^{-1}, T_{gel} reached 52 °C. As the amount of **C12Ph** increased, the corresponding T_{gel} also improved. The gels of the complex (4 : 1) exhibited the highest T_{gel}s at the same concentration. At a 3.5 mg mL^{-1} concentration, high temperature (66 °C) was required for gel–sol transformation. This temperature was higher than that (52 °C) of the gel (1 : 1) at the same concentration. This result is similar to that in CGC observation and indicates that the complex (4 : 1) is an optimal two-component gelator relative to other two mixtures.

The thermodynamic parameters (ΔH°, ΔS°) associated with the sol–gel phase transition can be obtained by using the van't Hoff method that plots ln(C) against 1/T. ΔH° and ΔS° were determined to be −44.9 kJ mol^{-1} and −95.6 J mol^{-1} K^{-1}, respectively.[19] The Gibbs free-energy change ΔG was calculated to be −16.4 kJ mol^{-1}, indicating the occurrence of spontaneous gel formation.

Owing to the occurrence of exciton coupling between **PDNA** molecules and molecular chirality of **C12Ph**, CD spectroscopy may be an appropriate method for further studying the assembly process. Strong bisignated-induced CD bands (the positive cotton effect) were found in the 475 nm to 650 nm region (λ_{max} = 524 nm, λ_{min} = 480 nm, $\lambda_{\theta=0}$ = 500 nm, Fig. 7). **PDNA** is not a chiral molecule. Thus, CD signals are induced by the chiral packing of **PDNA**.[20] The positive cotton effect implies a right-handed helical aggregate in the gel.[21] Such a chiral packing of **PDNA** in gel is obviously caused by the chirality of **C12Ph**. As the temperature increased to 40 °C, CD intensity decreased, indicating that some **PDNA** molecules broke away from the aggregate. When the temperature increased to 60 °C, at which point the red gel changed into the yellow sol, no detectable CD was observed. These findings further reflect that the CD signals in the visible region in the gel can indeed be attributed to molecular aggregates of **PDNA**.[22]

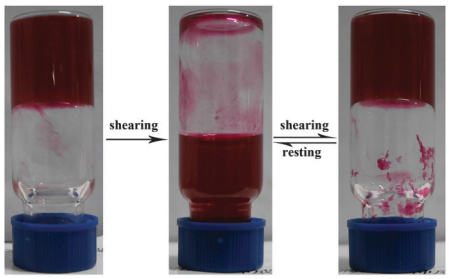


Fig. 8 Photos of the complex (4 : 1) in cyclohexane.

Gels also exhibited thixotropic behavior. When we applied external mechanical stress, such as shaking and stirring, the cyclohexane gel of the complex (4 : 1) lost its viscosity and transformed into a sol (Fig. 8).[23] After resting for almost 1 h at room temperature, the gel could be recovered. The self-healing process after the gel-to-sol transition can be repeated many times. The self-healing time of the destroyed gel is inversely proportional to its concentration. At a concentration of 5 mg mL^{-1}, the sol can change into a gel after 5 min. The two-component gel containing **C18Ph** and **PDNA** also possesses thixotropic activity.

Conclusions

An azobenzene derivative can aid lauroyl or stearoyl phenylalanine to form two-component gels. During gelation, the yellow sols turned into red gels, and molecules self-assembled into one-dimensional nanofibers. Circular dichroism spectral results indicated that the chirality of phenylalanine was passed on to the azobenzene moiety, which formed a right-handed helical stacking in the gel phase. The spectral results suggested that the molar ratio of the azobenzene derivative and lauroyl phenylalanine in gel fibers is 1 : 4. Moreover, the UV-vis spectra, critical gelation concentration, and T_{gel}s were found to be dependent on the ratio of two compounds. Interestingly, the two-component gels exhibited outstanding self-healing properties after being destroyed by vigorous shaking or stirring. These gels are considered as useful materials for further applications.

Experimental section

Instruments

Infrared spectra were recorded 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. SEM images were recorded on a Japan Hitachi model X-650 Scanning electron microscope. The samples for SEM observation were prepared by a freeze-drying method. The optical microscopy (OM) images were obtained on a XP-213 polarizing microscope. The samples for OM observation were prepared by a method of drop-cast film. The samples were then kept overnight in a vacuum oven at room temperature. ^{1}H NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer. Circular dichroism (CD) spectra of gels were recorded by using a quartz cuvette of 1 mm path length and using a Biologic PMS 450 spectropolarimeter. Mass spectra were obtained using Agilent 1100 MS series and AXIMA CFR MALDI-TOF (Compact) mass spectrometers. Rheological measurements were carried out on gels using a TA Instruments AR 2000 and using parallel plates (25 mm diameter).

Gelation test

The solution containing weighed compound in organic solvent was heated in a sealed sample bottle 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.

Gel-to-sol transition temperature (T_{gel})

The gel-to-sol transition temperature (T_{gel}) was determined in an oil bath by slowly raising the temperature of the bath at a rate of 1 °C min^{-1}. The T_{gel} was defined as the temperature (±0.5 °C) at which the gel melted and started to flow.

Synthetic procedures and characterization

C12Ph and **C18Ph** were synthesized by the reported method (Scheme 1).[24]

***(E)*-4-(Phenyldiazenyl)naphthalen-1-amine (PDNA).** Aniline (3.39 g) was added into the mixture of concentrated HCl (7 mL) and water (10 mL). After the solid was dissolved the aqueous solution of $NaNO_2$ (2.5 g) was dropped into the above solution at 0–5 °C. After 2 h, the reaction mixture was neutralized to pH = 6 using potassium acetate. At 0–5 °C the above mixture was added slowly into the solution containing naphthalen-1-amine (5.2 g), water (100 mL), ethanol (12 mL) and dense HCl (3 mL). After 10 h, the solution was neutralized by potassium acetate aqueous solution (pH = 8–9). The crude product was obtained by filtration and purified by a silica gel column using CH_2Cl_2 as the eluent (R_f = 0.63). Yield = 91%. mp = 127–128 °C. FT-IR: 3454, 3374, 3324, 3216, 3052, 3055, 1634, 1617, 1571, 1517, 1465, 749 and 682 cm^{-1}. Elemental analysis (%): calculated for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99; found: C, 77.73; H, 5.33; N, 16.92. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (d, J = 8.5 Hz, 1H), 7.99 (dd, J = 8.4, 1.1 Hz, 2H), 7.93 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.65 (ddd, J = 8.3, 6.8, 1.1 Hz, 1H), 7.56 (ddd, J = 8.3, 6.8, 1.1 Hz, 1H), 7.53 (tt, J = 8.0, 1.6 Hz, 2H), 7.43 (tt, J = 7.3, 1.3 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 4.6 (s, 2H). MALDI-TOF MS: m/z: calcd for $C_{16}H_{13}N_3$: 247.1; found: 248.1 $[M + H]^+$.

***N*-Dodecanoyl (L)-phenylalanine (C12Ph).** The solution containing L-phenylalanine (2.26 g, 13.7 mmol) and NaOH (0.55 g, 13.8 mmol), H_2O (90 mL) and acetone (30 mL) was cooled for 30 min in an ice-water bath. The acetone solution of dodecanoyl chloride (3.0 g, 13.8 mmol) and the aqueous solution of NaOH (0.55 g, 13.8 mmol) were slowly and simultaneously added into the above solution. The mixture was stirred overnight and acidified to pH = 1 using concentrated HCl. The white solid was obtained by filtration and purified by recrystallization in petroleum ether. Yield: 83%. mp = 97–98 °C FT-IR: 3313, 3030, 3068, 2950, 2923, 2854, 2479, 1945, 1891, 1701, 1670, 1604, 1246, 1118, 697 and 538 cm^{-1}: elemental analysis (%): calculated for $C_{21}H_{33}NO_3$: C, 72.58; H, 9.57; N, 4.03; found: C, 72.54; H, 9.54; N, 4.04. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.31–7.15 (m, 5H), 5.92 (d, J = 7.3 Hz, 1H), 4.87 (dd, J = 13.0, 6.3 Hz, 1H), 3.24 (dd, J = 14.1, 5.5 Hz, 1H), 3.13 (dd, J = 14.1, 6.4 Hz, 1H), 2.25–2.03 (m, 2H), 1.56 (d, J = 6.6 Hz, 2H), 1.40–1.08 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H). MALDI-TOF MS: m/z: calcd for $C_{21}H_{33}NO_3$: 347.2; found: 346.2 $[M - H]^+$.

***N*-Octadecanoyl (L)-phenylalanine (C18Ph).** Yield: 80%. mp = 64–65 °C FT-IR: 3317, 3032, 3068, 2950, 2923, 2854, 2478, 1702, 1671, 1604, 1246, 1117, 697 and 538 cm^{-1}: elemental analysis (%): calculated for $C_{27}H_{45}NO_3$: C, 75.13; H, 10.51; N, 3.24; found: C, 75.11; H, 10.54; N, 3.25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (b, 1H) 7.40–7.07 (m, 5H), 6.02 (s, 1H), 4.85 (s, 1H), 3.24 (dd, J = 13.8, 4.6 Hz, 1H), 3.11 (dd, J = 13.5, 5.9 Hz, 1H), 2.15 (s, 2H), 1.53 (s, 2H), 1.30–1.19 (m, 28H), 0.88 (t, J = 6.8 Hz, 3H).. MALDI-TOF MS: m/z: calcd for $C_{27}H_{45}NO_3$: 431.3; found: 431.2 M^+.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21103067), the Youth Science Foundation of Jilin Province (20130522134JH), the Open Project of State Laboratory of Theoretical and Computational Chemistry (K2013-02), and the Fundamental Research Funds for the Central Universities.

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