NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Self-assembly of Azobenzene-based Two-component Gels

Yuan Zhang,[a] Pengchong Xue,*[b] Boqi Yao,[b] Jiabao Sun,[b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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 system. In gel, molecules self-assembled into one-dimensional nanofibers. Circular dichroism spectral results indicated that the chirality of phenylalanine was passed to azobenzene moiety, which formed a right-handed helical stacking in the gel phase. UV-vis experiments and NMR spectra revealed that azobenzene derivative and lauroyl phenylalanine constructed a complex at 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.

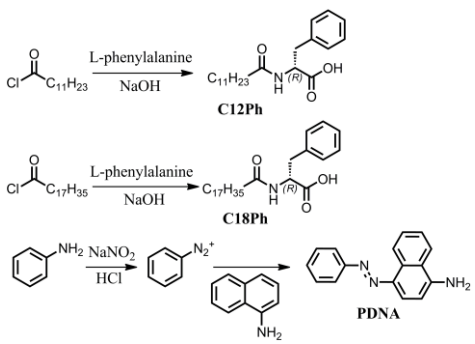
Introduction

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 to the molecular structure through a covalent bond. So far, one-component gels are 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] 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 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 to 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



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

New Journal of Chemistry Accepted Manuscript

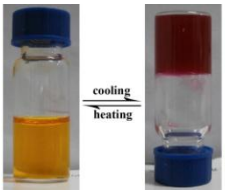


Fig. 1 Mixtures of **PDNA** and **C12Ph** at a ratio of 1:1 in cyclohexane.

Three compounds were easily synthesized by classical methods (Scheme1) and characterized by NMR, IR, MS and elemental analysis. The detail produces see experimental section. First, the mixture of **PDNA** and **C12Ph** at 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 **C12Ph** (1:1) can also form a red gel in these solvents. Therefore, **PDNA** can help **C12ph** to gel solvent.

The light microscopy image (Fig. 2a) of 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 further used 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 one-dimensional fiber. The gel stability was studied by rheological study. 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. G ´and the loss modulu (G ´) remained nearly constant up to 3 % and G ´was greater than G ´´ of gel (Fig. S4). This result suggests that the cyclohexane is stable because of the presence of 3D fibrous network.

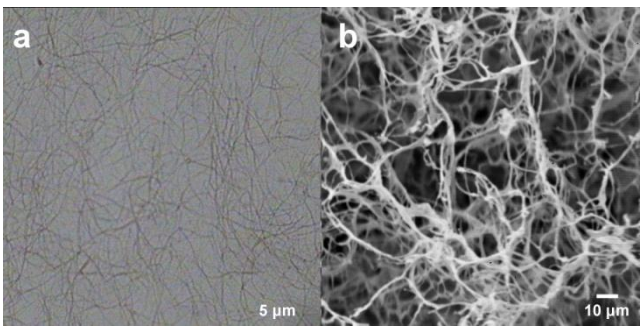


Fig. 2 (a) Optical microscope and (b) SEM images of cyclohexane gel formed by **C12Ph** and **PNDA** (1:1).

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 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 in J-aggregate.[13] Thus, the exciton coupling exists between **PDNA**.

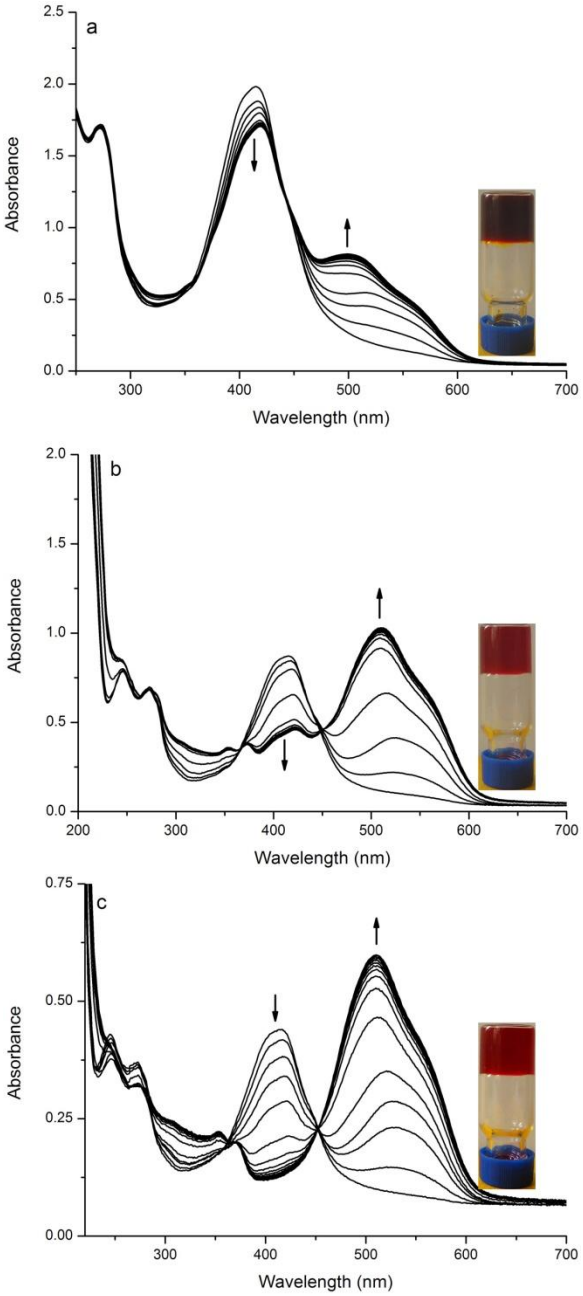


Fig. 3 UV-vis spectral change of **C12Ph** and **PDNA** with different molar ratios of 1:1 (a), 3:1 (b), and 4:1 (c) during gelation (from 80 to 10 ℃, interval of temperature is 5 ℃) in cyclohexane. Concentration for three samples is 1.8 mg/mL. The optical path is 0.2 mm.

The 415 nm absorption peak did not disappear and was stronger than that at 500 nm, thus indicating that many **PDNA** molecules exist as monomeric state in the gel of the mixture (1:1). Such s 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 wet gel. This result affirms that a large amount of **PDNA** did not aggregate in the gel mixture (1:1). The ^{1}H NMR

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry [year]

spectrum of red solid obtained in wet gel suggests that the molar ratio of **C12Ph** and **PDNA** is 4:1 in red solid (Fig. S5). 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 spectroscopy (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). 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 in 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 at 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 ratio were similar. For example, the gels (3:1 and 4:1) were comprised of thin and long fibers (Fig. S7). This result suggests that microstructures of gels are independent on the components of gels. This case is different from that reported by Smith, in which morphologies of gels 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 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. At high concentrations, the absorption band of monomeric state cannot be found. When concentration decreases, the absorbance around 400 nm gradually increases, and the absorption band at 500 nm becomes weaker. When the concentration reaches 0.003 mg/mL, 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. When the molar ratio of **C12Ph** and **PDNA** increased to 3:1, CGC decreased to 0.8 mg/mL. The complex of 4:1 had a smallest CGC (0.74 mg/mL). The excess **PDNA** molecules existing in the solution for 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 complex of 4:1 decreased to 4 mg/mL. 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.

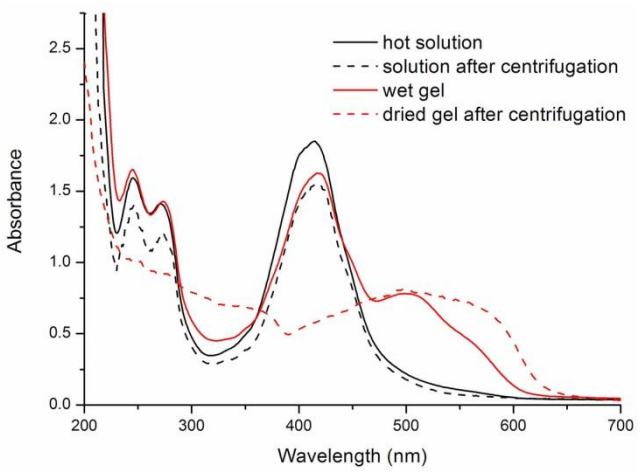


Fig. 4 UV-vis spectra of the mixture of **PDNA** and **C12Ph** at a 1:1 ratio in hot solution and gel, and the solution and dried gel after centrifugation.

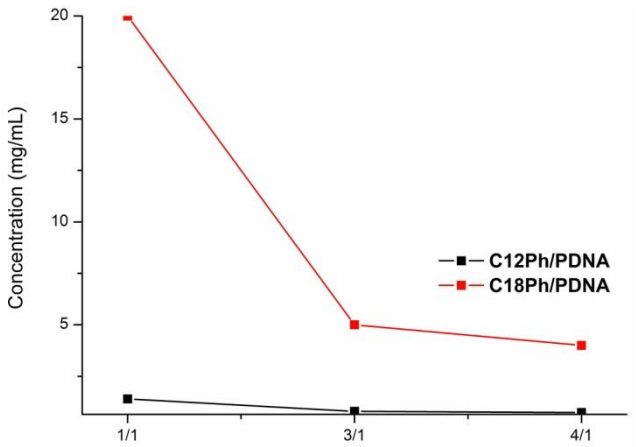


Fig. 5 Critical gelation concentration of the mixtures with different molar ratios.

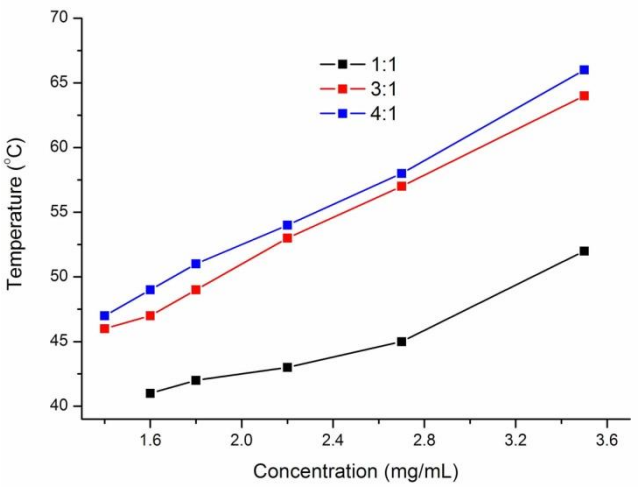


Fig. 6 T_{gel}s of cyclohexane gels of **C12Ph**/**PDNA** vs concentration.

New Journal of Chemistry Accepted Manuscript

The CGCs of gels are found to depend on their components. Thus, gel components can also determine the T_{gel}s. Fig. 6 shows the relation between T_{gel}s and concentration. The T_{gel}s of all gels develop as gelator concentration increases. For instance, the gel of **C12Ph** and **PDNA** (1:1) at a concentration of 1.6 mg/mL transformed into a sol at 41 ℃. When the concentration increased to 3.5 mg/mL, T_{gel} reached 52 ℃. 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 concentration, high temperature (66 ℃) was required for gel-sol transformation. This temperature was higher than that (52 ℃) 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 (positive cotton effect) were found in the 475 nm to 650 nm region (λ_{max} = 524, λ_{min} = 480, $\lambda_{\theta=0}$ = 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 gel.[21] Such a chiral packing of **PDNA** in gel is obviously caused by the chirality of **C12Ph**. As the temperature increased to 40 ℃, CD intensity decreased, indicating that some **PDNA** molecules broke away from the aggregate. When the temperature increased to 60 ℃, at which point the red gel changed into yellow sol, no detectable CD was observed. This finding further reflects that the CD signals in the visible region in gel can indeed be attributed to molecular aggregate of **PDNA**.[22]

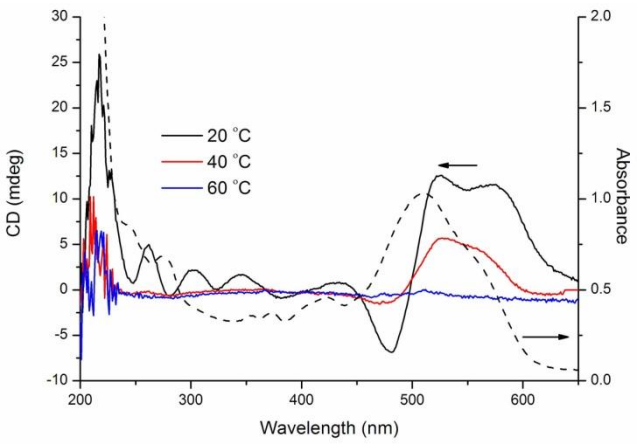


Fig. 7 Circular dichroism and UV-vis absorption spectra of the gel (4:1) in cyclohexane at 1.0 mg/mL concentration.

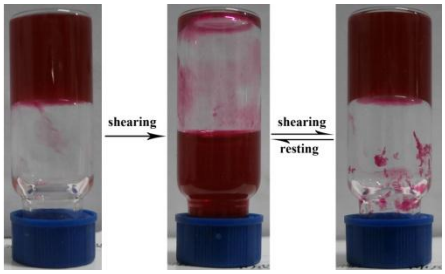


Fig. 8 Photos of the complex (4:1) in cyclohexane

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 transforms 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, 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 to azobenzene moiety, which formed a right-handed helical stacking in the gel phase. The spectral results suggested that the molar ratio of 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 property after being destroyed by strong shaking or stirring. These gels are considered as useful materials for further applications.

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. SEM images were carried out on a Japan Hitachi model X-650 Scan electron microscope. The samples for SEM observation were prepared by a freeze drying method. The optical microscope (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 carried out on the Bruker Avance III 500MHz NMR spectrometer. Circular dichroism (CD) spectra of gels were recorded by using a quartz cuvette of 1 mm path length using a Biologic PMS 450 spectropolarimeter. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR MALDI-TOF (Compact) mass

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry [year]

spectrometers. Rheological measurement was carried out on gels using a TA Instruments AR 2000 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 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.

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

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

Synthetic procedures and characterizations

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

(E)-4-(phenyldiazenyl)naphthalen-1-amine (PDNA)

Aniline (3.39g) was added into the mixture of concentrated HCl (7mL) and water (10 mL). After the solid was dissolved the aqueous solution of $NaNO_2$ (2.5 g) was dropped into above solution at 0-5 ℃. After 2 h, the reaction mixture was neutralized to pH = 6 by potassium acetate. At 0-5 ℃ the above mixture was slowly dropped into the solution consisting of 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 production was obtained by filter and purified by a silica gel column using CH_2Cl_2 as eluent (R_f = 0.63). Yield = 91 %. mp = 127-128 ℃. FT-IR: 3454, 3374, 3324, 3216, 3052, 3055, 1634, 1617, 1571, 1517, 1465, 749 and 682 cm^{-1}. Element 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 at 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 slowing and simultaneously dropped into above solution. The mixture was stirred overnight and acidized to pH = 1 by concentrated HCl. The white solid was obtained by filter and purified by recrystallization in petroleum ether. Yield: 83 %. mp = 97-98 ℃ FT-IR: 3313, 3030, 3068, 2950, 2923, 2854, 2479, 1945, 1891, 1701, 1670, 1604, 1246, 1118, 697 and 538 cm^{-1}: Element 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, $CDCl_3$) δ8.79 (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 ℃ FT-IR: 3317, 3032, 3068, 2950, 2923, 2854, 2478, 1702, 1671, 1604, 1246, 1117, 697 and 538 cm^{-1}: Element 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, and 21374041), the Youth Science Foundation of Jilin Province (20130522134JH), the Open Project of the State Key Laboratory of Supramolecular Structure and Materials (SKLSSM201407), the Open Project of State Laboratory of Theoretical and Computational Chemistry (K2013-02), and the Fundamental Research Funds for the Central Universities.

Notes and references

[a] *Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, 19# XinJieKouWai St., HaiDian District, Beijing, (P. R. China)*
[b] *State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, 2699# Qianjin Street, Changchun, (P.R. China), E-mail: xuepengchong@jlu.edu.cn*

† Electronic Supplementary Information (ESI) available: [^{1}H NMR spectra, eheomerty data, IR spectra and SEM image of complexes, and absorption spectra of complexes (3:1) at different concentrations]. See DOI: 10.1039/b000000x/

1 a) T. Aida, E. W. Meijer and S. I. Stupp, *Science*, 2012, **335**, 813–817; b) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma and E. W. Meijer, *Chem. Rev.*, 2009, **109**, 5687–5754; c) F. J. M. Hoeben, P. Jonkheijm, E.W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491–1546; d) M. Wang, A. R. Mohebbi and Y. Sun, F. Wudl, *Angew. Chem. Int. Ed.*, 2012, **51**, 6920–6924; e) B. K. An, J. Gierschner and S. Y. Park, *Acc. Chem. Res.*, 2012, **45**, 544–554; f) A. Ajayaghosh and V. K. Praveen, *Acc. Chem. Res.*, 2007, **40**, 644–656; g) H. Jintoku, T. Sagawa, M. Takafuji and H. Ihara, *Chem. Eur. J.*, 2011, **17**, 11628–11636.

2 a) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133–3159; b) N. Yan, Z. Xu, K. K. Diehn, S. R. Raghavan, Y. Fang and R. G. Weiss, *J. Am. Chem. Soc.*, 2013, **135**, 8989−8999; c) S. S. Babu, S. Prasanthkumar and A. Ajayaghosh, *Angew. Chem. Int. Ed.*, 2012, **51**, 1766–1776; c) Z. Zhao, J. W. Y. Lam and B. Z. Tang, *Soft Matter*, 2013, **9**, 4564–4579; d) S. K. Samanta and S. Bhattacharya, *Chem. Commun.*, 2013, **49**, 1425–1427; e) S. S. Babu, K. K. Kartha and A. Ajayaghosh, *J. Phys. Chem. Lett.*, 2010, **1**, 3413–3424; f) Y. He, Z. Bian, C. Kang, R. Jin and L. Gao, *New J. Chem.*, 2009, **33**, 2073–2080.

3 a) I. D. Tevis, W. Tsai, L. C. Palmer, T. Aytun and S. I. Stupp, *ACS Nano*, 2012, **6**, 2023–2024; b) Z. Yu, D. Qin, Y. Zhang, H. Sun, Y. Luo, Q. Meng and D. Li, *Energy Environ. Sci.*, 2011, **4**, 1298–1305; c) S. Park, I. Y. Song, J. Lim, Y. S. Kwon, J. Choi, S. Song, J. Lee and T. Park, *Energy Environ. Sci.*, 2013, **6**, 1559–1564.

4 a) J. P. Hong, M. C. Um, S. R. Nam, J. I. Hong and S. Lee, *Chem. Commun.*, 2009, 310-312; b) W. W. Tsai, I. D. Tevis, A. S. Tayi, H.

New Journal of Chemistry Accepted Manuscript

Cui and S. I. Stupp, *J. Phys. Chem. B*, 2010, **114**, 14778–14786; c) D. A. Stone, A. S. Tayi, J. E. Goldberger, L. C. Palmera and S. I. Stupp, *Chem. Commun.*, 2011, **47**, 5702–5704; d) S. Diring, F. Camerel, B. Donnio, T. Dintzer, S. Toffanin, R. Capelli, M. Muccini and R. Ziessel, *J. Am. Chem. Soc.*, 2009, **131**, 18177–18185; e) R. Marty, R. Nigon, D. Leite and H. Frauenrath, *J. Am. Chem. Soc.*, 2014, **136**, 3919−3927.

5 a) X. Liu, X. Zhang, R. Lu, P. Xue, D. Xu and H. Zhou, *J. Mater. Chem.*, 2011, **21**, 8756–8765; b) H. Peng, L. Ding, T. Liu, X. Chen, L. Li, S. Yin and Y. Fang, *Chem.–Asian J.*, 2012, **7**, 1576–1782; c) P. Xue, R. Lu, J. Jia, M. Takafuji and H. Ihara, *Chem. Eur. J.*, 2012, **18**, 3549–3558; d) Q. Xia, Y. Mao, J. Wu, T. Shu and T. Yi, *J. Mater. Chem. C*, 2014, **2**, 1854-1861.

6 a) J. W. Chung, S. Yoon, S. Lim, B. An and S. Y. Park, *Angew. Chem., Int. Ed.*, 2009, **48**, 7030–7034; b) X. Cai, Y. Wu, L. Wang, N. Yan, J. Liu, X. Fang and Y. Fang, *Soft Matter*, 2013, **9**, 5807–5814; c) P. Fatás, J. Bachl, S. Oehm, A. I. Jiménez, C. Cativiela and D. D. Díaz, *Chem. Eur. J.*, 2013, **19**, 8861–8874; d) Y. Hisamatsu, S. Banerjee, M. B. Avinash, T. Govindaraju and C. Schmuck, *Angew. Chem. Int. Ed.*, 2013, **52**, 12550–12554; e) C. Huang, L. Chen, J. Huang and L. Xu, *RSC Adv.*, 2014, **4**, 19538–19549; f) B. Bai, J. Ma, J. Wei , J. Song, H. Wang and M. Li, *Org. Biomol. Chem.*, 2014, **12**, 3478–3483; g) S. Sarkar, S. Dutta, S. Chakrabarti, P. Bairi and T. Pal, *ACS Appl. Mater. Interfaces*, 2014, **6**, 6308−6316; h) Y. Tian, L. Zhang, P. Duan, F. Liu, B. Zhang, C. Liu and M. Liu, *New J. Chem.*, 2010, **34**, 2847–2852.

7 a) Y. Liu, T. Wang, and M. Liu, *Chem. Eur. J.*, 2012, **18**, 14650–14659; b) L. E. Buerklea and S. J. Rowan, *Chem. Soc. Rev.*, 2012, **41**, 6089–6102; c) A. R. Hirst and D. K. Smith, *Chem.–Eur. J.*, 2005, **11**, 5496–5508; d) M. Suzuki, H. Saito, H. Shirai and K. Hanabusa, *New J. Chem.*, 2007, **31**, 1654–1660; e) R. Amemiya, M. Mizutani, and M. Yamaguchi, *Angew. Chem. Int. Ed.*, 2010, **49**, 1995 –1999; f) N. Wu, J. Zhang, X. Xu and H. Yang, *Chem. Commun.*, 2014, DOI: 10.1039/C4CC04039B.

8 a) A. R. Hirst, J. F. Miravet, B. Escuder, L. Noirez, V. Castelletto, I. W. Hamley and D. K. Smith, *Chem.–Eur. J.*, 2009, **15**, 372–379; b) A. R. Hirst, D. K. Smith, M. C. Feiters and H. P. M. Geurts, *Langmuir*, 2004, **20**, 7070–7077; c) D. Cornwell, B.O. Okesola and D. K. Smith, *Soft Matter*, 2013, **9**, 8730–8736; d) W. Edwards and D. K. Smith, *J. Am. Chem. Soc.*, 2013, **135**, 5911–5920; e) A. R. Hirst, D. K. Smith and J. P. Harrington, *Chem. Eur. J.*, 2005, **11**, 6552– 6559.

9 a) A. Dawn, T. Shiraki, H. Ichikawa, A. Takada, Y. Takahashi, Y. Tsuchiya, L. T. N. Lien and S. Shinkai, *J. Am. Chem. Soc.*, 2012, **134**, 2161–2171; b) M. Shirakawa, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, 2003, **125**, 9902–9903.

10 a) X. Yu, X. Cao, L. Chen, H. Lan, B. Liu and T. Yi, *Soft Matter*, 2012, **8**, 3329-3334; b) X, Yu, L. Chen, M. Zhang and T. Yi, *Chem. Soc. Rev.*, 2014, **43**, 5346-5371; c) C. Vijayakumar, V. K. Praveen and A. Ajayaghosh, *Adv. Mater.*, 2009, **21**, 2059-2063; d) C. Vijayakumar, V. K. Praveen, K. K. Kartha and A. Ajayaghosh, *Phys. Chem. Chem. Phys.*, 2011, **13**, 4942–4949; e) R. Abbel, R. van der Weegen, W. Pisula, M. Surin, P. Leclère, R. Lazzaroni, E. W. Meijer and A. P. H. J. Schenning, *Chem. Eur. J.*, 2009, **15**, 9737–9746.

11 a) X. Yang, R. Lu, P. Xue, B. Li, D. Xu, T. Xu and Y. Zhao, *Langmuir*, 2008, **24**, 13730-13735; b) P. Xue, Q. Xu, P. Gong, C. Qian, A. Ren, Y. Zhang and R. Lu, *Chem. Commun.*, 2013, **49**, 5838–5840; c) P. Xue, R. Lu, P. Zhang, J. Jia, Q. Xu, T. Zhang, M. Takafuji, and H. Ihara, *Langmuir*, 2013, **29**, 417−425; d) O. Simalou, X. Zhao, R. Lu, P. Xue, X. Yang and X. Zhang, *Langmuir*, 2009, **25**, 11255–11260; e) P. Xue, Q. Xu, P. Gong, C. Qian, Z. Zhang, J. Jia, X. Zhao, R. Lu, A. Ren and T. Zhang, *RSC Adv.*, 2013, **3**, 26403–26411; f) P. Xue, R. Lu, L. Zhao, D. Xu, X. Zhang, K. Li, Z. Song, X. Yang, M. Takafuji and H. Ihara, *Langmuir*, 2010, **26**, 6669–6675;

12 a) S. S. Babu, V. K. Praveen and A. Ajayaghosh, *Chem. Rev.*, 2014, **114**, 1973−2129; b) A. Hemamalinia and T. M. Das, *New J. Chem.*, 2013, **37**, 2419-2425; c) X. Yang, G. Zhang, D. Zhang and D. Zhu, *Langmuir*, 2010, **26**, 11720–11725; d) C. Mondal, M. Ganguly, J. Pal, R. Sahoo, A. K. Sinha and T. Pal, *Chem. Commun.*, 2013, **49**, 9428–9430.

13 a) P. Xue, R. Lu, G. Chen, Y. Zhang, H.Nomoto, M. Takafuji and H. Ihara, *Chem. Eur. J.*, 2007, **13**, 8231–8239; b) P. Xue, R. Lu, X. Yang, L. Zhao, D. Xu, Y. Liu, H. Zhang, H. Nomoto, M. Takafuji and H. Ihara, *Chem. Eur. J.*, 2009, **15**, 9824–9835; c) S. Yoon, J. H. Kim, J. W. Chung and S. Y. Park, *J. Mater. Chem.*, 2011, **21**, 18971–18973; d) B. An, D. Lee, J. Lee, Y. Park, H. Song and S. Y. Park, *J. Am. Chem. Soc.*, 2004, **126**, 10232–10233; e) X. Li, X. Zhang, S. Ghosh and F. Würthner, *Chem. Eur. J.*, 2008, **14**, 8074–8078.

14 a) C. Bao, R. Lu, M. Jin, P. Xue, C. Tan, G. Liu, and Y. Zhao, *Org. Biomol. Chem.*, 2005, **3**, 2508-2512; b) O. Simalou, P. Xue and R. Lu, *Tetrahedron Lett.*, 2010, **51**, 3685–3690.

15 a) C. Tan, Y. Zhu, R. Lu, P. Xue, C. Bao, X. Liu, Z. Fei and Y. Zhao, *Mater. Chem. Phys.*, 2005, **91**, 44–47; b) V. Doan, R. Köppe and P. H. Kasai, *J. Am. Chem. Soc.*, 1997, **119,** 9810-9815.

16 Y. Q. Tian, X. H. Xu, Y. Y. Zhao, X. Y. Tang and T. J. Li, *Liq. Cryst.*, 1997, **22**, 87–96.

17 a) X. Zhu, Y. Li, P. Duan and M. Liu, *Chem.–Eur. J.*, 2010, **16**, 8034–8040; b) P. Xue, R. Lu, J. Jia, M. Takafuji and H. Ihara, *Chem. Eur. J.*, 2012, **18**, 3549; c) J. Puigmart-Luis, V. Laukhin, Á. P. del Pino, J. Vidal-Gancedo, C. Rovira, E. Laukhina and D. B. Amabilino, *Angew. Chem. Int. Ed.*, 2007, **46**, 238 –241; d) F. Aparicio, B. Nieto-Ortega, F. Nájera, F. J. Ramírez, J. T. L. Navarrete, J. Casado and L. Sánchez, *Angew. Chem. Int. Ed.*, 2014, **53**, 1373 –1377; e) T. K. S. Mukherjee and P. K. Das, *New J. Chem.*, 2014, **38**, 1158–1167; f) M. Suzuki, T. Nigawara, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Org. Biomol. Chem.*, 2003, 1, 4124–4131.

18 a) B. G. Bag, G. C. Maity and S. K. Dinda, *Org. Lett.*, 2006, **8**, 5457-5460; b) U. Maitra, P. V. Kumar, N. Chandra, L. J. D'Souza, M. D. Prasanna and A. R. Raju, *Chem. Commun.*, **1999**, 595–596; c) J. Hu, J. Wu, Q. Wang and Y. Ju, Beilstein, *J Org Chem.*, 2013, **9**, 2877–2885; d) A. Friggeri, O. Gronwald, K. J. C. van Bommel, S. Shinkai and D, N. Reinhoud, *J. Am. Chem. Soc.*, 2002, **124**, 10754-10758

19 a) W. Edwards and D. K. Smith, *J. Am. Chem. Soc.*, 2014, **136**, 1116-1124; b) M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311−312; c) P. N. Borer, B. Dengler, I. J. Tinoco and O. C. Uhlenbeck, *J. Mol. Biol.*, 1974, **86**, 843 –853.

20 a) C. Thalacker and F. Würthner, *Adv. Funct. Mater.*, 2002, **12**, 209 – 218; b) A. Ajayaghosh, C. Vijayakumar, R. Varghese and S. J. George, *Angew. Chem. Int. Ed.*, 2006, **45**, 456 –460; c) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komri, F. Ohseto, K. Ueda and S. Shinkai, *J. Am. Chem. Soc.*, 1994, **116**, 6664-6676; d) V. V. Borovkov and Y. Inoue, *Top Curr. Chem.*, 2006, **265**, 89-146; e) T. Arimura, S. Edamitsu, S. Shinkai, O. Manabe, T. Muramatsu and M. Tashiro, *Chem. Lett.*, 1987, 2269–2272.

21 a) P. Xue, Y. Zhang, J. Jia, D. Xu, X. Zhang, X. Liu, H. Zhou, P. Zhang, R. Lu, M. Takafuji and H. Ihara, *Soft Matter*, 2011, **7**, 8296–8304; b) H. Jintoku, M. Takafuji, R. Oda and H. Ihara, *Chem. Commun.*, 2012, **48**, 4881-4883; c) S. Allenmark, *Chirality*, 2003, **15**, 409–422; e) T. Ishi-i, J. H. Jung and S. Shinkai, *J. Mater. Chem.*, 2000, **10**, 2238-2240; d) G. Qing, X. Shan, W. Chen, Z. Lv, P. Xiong and T. Sun, *Angew. Chem. Int. Ed.*, 2014, **53**, 2124 –2129.

22 a) P. Mukhopadhyay, N. Fujita, A. Takada, T. Kishida, M. Shirakawa and S. Shinkai, *Angew. Chem. Int. Ed.*, 2010, **49**, 6338 –6342; b) X. Yu, X. Cao, L. Chen, H. Lan, B. Liu and T. Yi, *Soft Matter*, 2012, **8**, 3329-3334; c) M. Lescanne, P. Grondin, A. d'Aléo, F. Fages, J. L. Pozzo, O. M. Monval, P. Reinheimer and A. Colin, *Langmuir*, 2004, **20**, 3032-3041.

23 a) V. Percec, M. Peterca, M. E. Yurchenko, J. G. Rudick and P. A. Heiney, *Chem. Eur. J.*, 2008, **14**, 909–918; b) J. Brinksma, B. L. Feringa, R. M. Kellogg, R. Vreeker and J. van Esch, *Langmuir*, 2000, **16**, 9249–9255; c) Y. Feng, Z. Liu, H. Chen, Z. Yan, Y. He, C. Liu and Q. Fan, *Chem. Eur. J.*, 2014, **20**, 7069–7082.

24 a) S. Y. Mhaskar, R. B. N. Prasad and G. Lakshminarayana, *J. Am. Oil Chem. Soc.*, 1990, **67**, 1015-1019; b) A. Pal, Y. K. Ghosh and S. Bhattacharya, Tetrahedron, 2007, 63, 7334–7348.

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry [year]