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Clockwise helical stacking of triphenylbenzene-based organogelator induced by peripheral chirality

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Abstract—We report on the synthesis and self-assembly of a new discotic organogelator based on π-conjugated triphenylbenzene with three peripheral chiral substituents. It is found that the introduction of chiral groups to the C_3-symmetric molecule led to a hexagonal columnar chiral stacking of the molecules in a clockwise direction in the organogel fibers. And the fluorescent emission of the gel decreased significantly compared to the monomer state at the same concentration, as a result of the aggregation of the nonplanar triphenylbenzene core in the gel phase.

1. Introduction

Helical architectures are very common in nature, such as the DNA double helix,[1] the collagen triple helix,[2] and the α-helical motifs in proteins,[3] and they have received considerable interests of scientists. Recently, the control of helicity in the supramolecular chemistry is an attractive goal because of its possible applications in material science, chemical sensing, enantioselective catalysis and so on.[4–9] The remarkable control of helicity in supramolecular self-assemblies usually depends on cooperative hydrogen bonding[10,11] and π–π stacking.[12–14] In particular, the preparation of helical fibers or ribbons in low molecular weight organogel systems has attracted broad attention, with the introduction of chiral groups, such as chiral alkyl chains,[15–17] amino acids,[18,19] glucose,[20–22] and cholesterol,[23–25] into the organogel molecules playing an important role in the formation of helical microstructures.

To increase insight into helical stacking phenomena in organogels, the exact nature and relative importance of the secondary interactions were studied. For this purpose, discotic molecules were selected as highly suitable building blocks for the formation of the helical structures because of their predisposition for stacking. Over the past few years, several examples have been presented to show perfect helical stacking in gel systems due to the introduction of chirality in the discotics.[15,16,26,27] However, reports on the chiral self-assembly of discotic molecules based on a π-conjugated core are limited. Such system could find potential photonics applications due to their unique optical properties. In our previous work,[28] it was found that triphenylbenzene-based organogelators with achiral side chains can self-assemble into right-handed and left-handed helical fibers simultaneously with equal probability. These fibers showed unusual aggregation-induced emission enhancement. The formation of helical fibers was due to the helical inducement of the core cooperating with the packing and arrangement of the alkoxy chains. The morphologies of the obtained helixes can be adjusted by the peripherally substituted alkoxy chains.

In this paper, we intended to bring chiral groups into the periphery of this triphenylbenzene-based system to prepare a fibrous organogel with a single direction of helical stacking. Therefore, a C_3-symmetrical discotic molecule **5** with chiral side chains ((*R*)-(−)-1-cyclohexyl-ethylamine) connected to the triphenylbenzene core through amide groups (as shown in Scheme 1) was synthesized, and its self-assembly and optical properties were studied. Compound **5** could form stable fibrous organogels in aromatic solvents and CCl_4, and the introduction of the chiral groups into the periphery of the molecules induced the hexagonal columnar stacking of the molecules in a clockwise direction. It was also found that the emission could be adjusted by the sol–gel transition, which may find some useful applications in sensors and other photoelectric devices.

Keywords: Organogel; Self-assembly; Helical stacking; Triphenylbenzene; Fluorescence.
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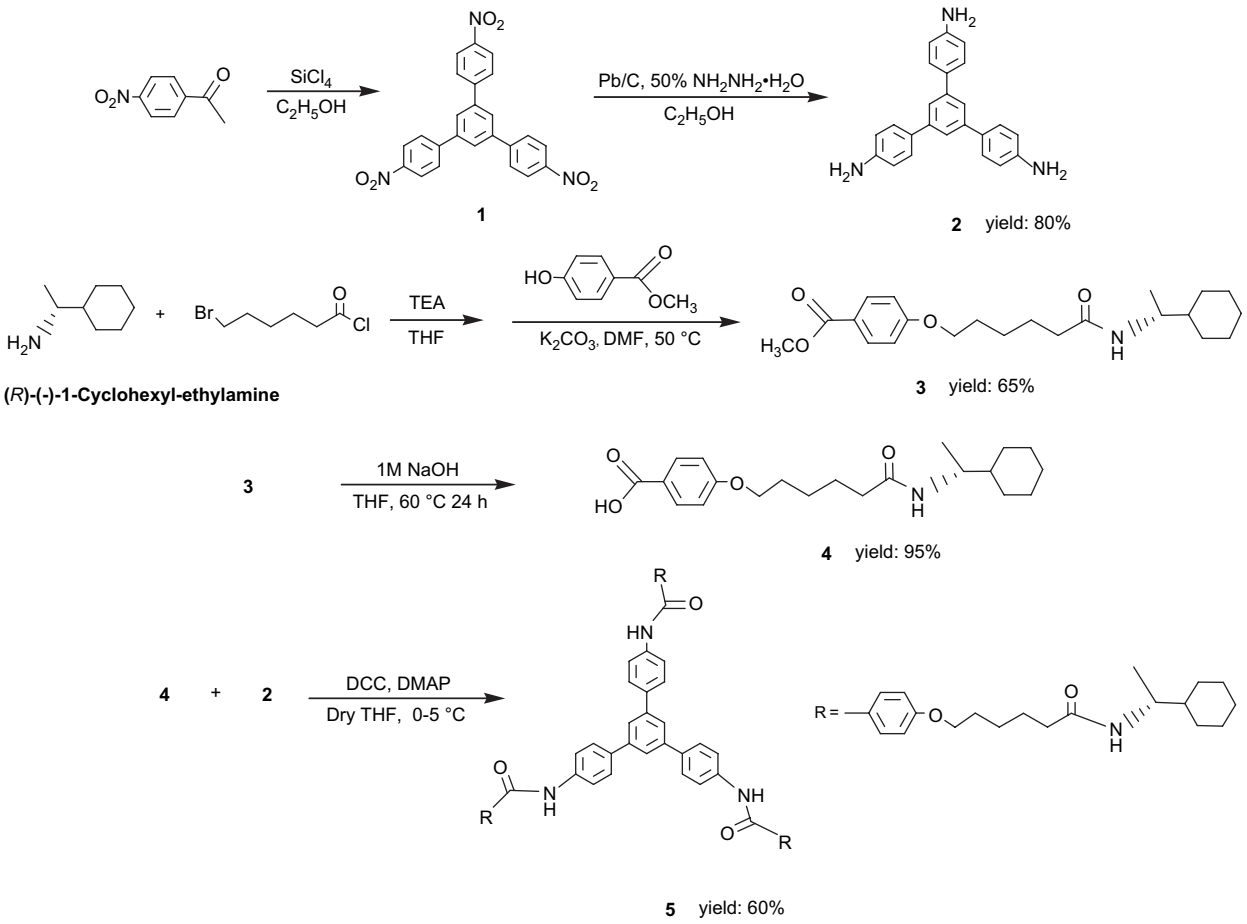


Scheme 1. The synthetic route for compound **5**.

2. Results and discussion

2.1. Synthesis

The synthetic route for the triphenylbenzene derivative **5** is shown in Scheme 1. It was prepared through acylation of 1,3,5-tris(4-aminophenyl)benzene with the corresponding chiral benzoyl chloride. Compounds **3** and **4** were synthesized according to the methods described in Refs. 29 and 30. All the compounds were characterized with Fourier transform infrared (FTIR) spectroscopy, ^{1}H NMR, C, H, and N elemental analyses and matrix assisted laser desorption ionization/time-of-flight mass spectrometry (MALDI-TOFMS).

2.2. Gelation ability of compound 5

The gelation properties of the discotic compound **5** were investigated in various solvents. As summarized in Table 1, compound **5** could form stable fibrous gel in benzene, toluene, xylene, and CCl_4 at a concentration of 1.0 wt %. The obtained gels are thermoreversible in the organic solvents, for example, the gelator is insoluble at room temperature, turns into clear solutions by heating to reflux, and upon cooling to room temperature, the immobile gel appears. This process can be repeated many times. The microstructures of the gels were observed by SEM and TEM. Figure 1a shows the SEM image of the gel obtained from toluene, which exhibits well-defined fibers with diameter of ca. 100 nm. The fibers have a tendency to be parallel to each other and form fibrous bundles, and then three-dimensional networks. For the gel in CCl_4, the SEM investigation did not image clear morphologies, while the TEM image (see Fig. 1b) shows short intertwined fibers with diameter of 30–50 nm, without a network structure. The gel in CCl_4 broke into solution and precipitated after one week, while the gel in toluene remained for several months. These phenomena suggest that the chiral compound **5** could form more stable gel in toluene than in CCl_4, and the solvents play an important role in process of gel formation.

Table 1. Gelation test of compound **5** in different solvents at 1.0 (wt/vol)% (5.0 mg compound **5** in 5.0 mL solvent)

Entry	Solvent	Gelation	Entry	Solvent	Gelation
1	THF	S	5	CCl_4	TG
2	Toluene	TG	6	Ethanol	S
3	Benzene	TG	7	Chloroform	S
4	Xylene	TG	8	Ethanol/water (1:2)	G

G, turbid gel; TG, stable transparent gel; S, soluble.

2.3. Self-assembling properties of compound 5

FTIR and UV–vis absorption spectra were used to elucidate the driving forces of the gelation process for compound **5**. The FTIR spectra (not shown here) for the xerogel from toluene showed that the N–H stretching band appeared at

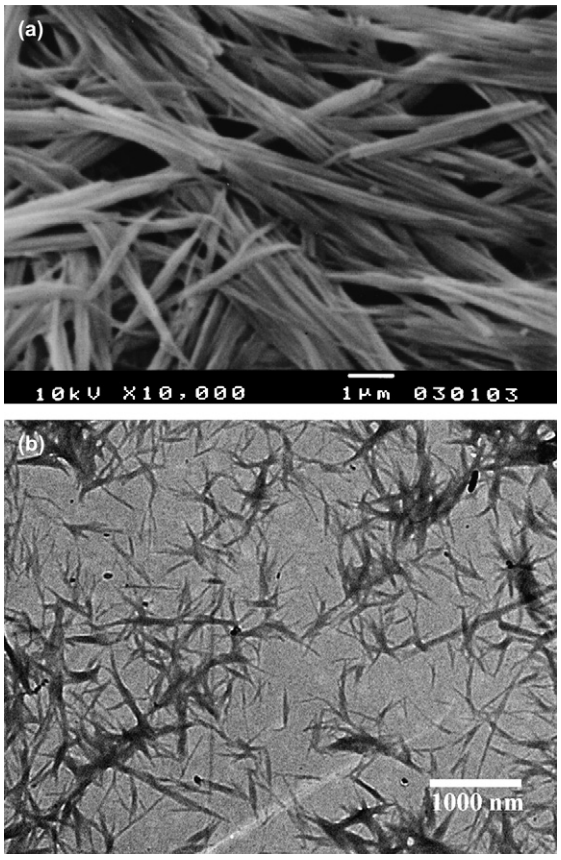


Figure 1. (a) SEM image of gel obtained from toluene and (b) TEM image of gel obtained from CCl_4, the concentration in both is 1.0 wt %.

3321 cm^{-1} and two amide bands were located at 1663 and 1641 cm^{-1}, respectively, with nearly equal intensities. As known, peaks of 3321 and 1641 cm^{-1} can be attributed to the characteristic peaks of intermolecular H-bonded amides,[31,32] which indicates that hydrogen bonding has participated in the formation of the gel. However, the peak located at 1663 cm^{-1} can be ascribed to free amide units, in other words, there are some non-H-bonded amide groups in the gel phase. As shown in Scheme 1, there are six amide groups in compound **5**, three of them are connected directly to the triphenylbenzene core while the others are further away from the benzene rings and are connected to chiral cyclohexyl groups at periphery. Based on the molecular conformation, it is reasonable to deduce that the amide groups close to the triphenylbenzene can more easily form H-bonds due to the π–π stacking of the cores than the peripheral ones, which existed as free amides.

Figure 2 shows the UV–vis spectra of the CCl_4 gel at 1.0 wt % (7.2×10^{-3} M, tested using the 0.1 cm thin quartz cell) and of the ethanol solution of compound **5** at a concentration of 1×10^{-5} M (in monomer state since the ethanol can break hydrogen bonds). The absorption band red-shifts to 281 nm in the gel phase compared with that at 256 nm in the ethanol solution, which indicates that J-aggregates have formed in the molecules in gel phase as a result of the π–π interaction between triphenylbenzene cores. This actually plays a key role in the formation of the gel. Generally, the discotic molecules prefer to form H-aggregates by the stacking of the coplanar cores, so the formation of J-aggregates in

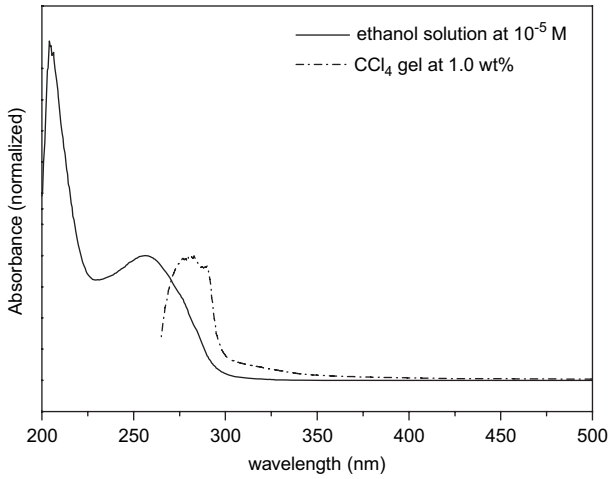


Figure 2. UV–vis absorption spectra (the absorptions around 230–300 nm for the triphenylbenzene were normalized) of compound **5** in CCl_4 gel at 1.0 wt % (the dash line), and in ethanol solution at 10^{-5} M (the solid line).

compound **5** suggests that the triphenylbenzene cores of the molecules have formed coplanar stagger or co-facial stacking. The optimized Chemdraw 3D CPK model of the molecule **5** showed that the triphenylbenzene core was not planar and the dihedral angle between the benzene rings was about 35° in the monomeric state. Therefore, the triphenylbenzene core must form co-facial stacking in the self-assembly of compound **5**. By combining these facts with the results of FTIR spectra, it is concluded that compound **5** in the gel should form helical stacking by the cooperation of π–π interactions and H-bonds, as reported in our previous work.[28]

CD spectroscopy is a very good tool to test the chiral structures of the aggregates,[21,22] so the CD spectra of the gel and of the solution were compared to investigate the effect of a chiral periphery on the stacking of the discotic molecules. As shown in Figure 3, the ethanol solution of compound **5** does not show any CD signal, while the gel in CCl_4 shows a strong positive Cotton effect, and the crossover λ_θ=0 value is very close to the λ_{max} values (280 nm) in the UV–vis absorption spectra, which suggests that CD bands are attributed

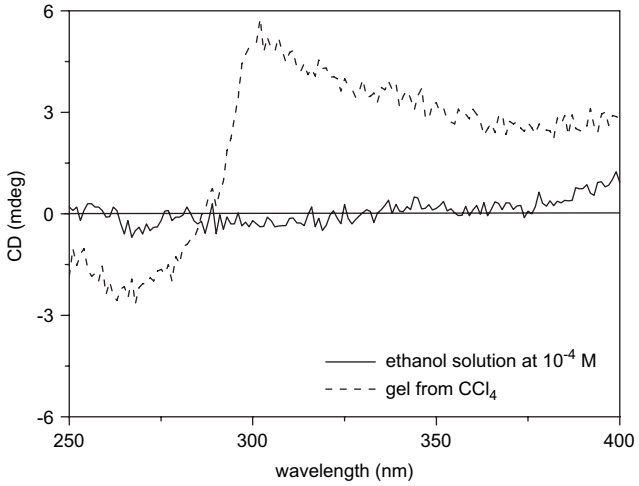


Figure 3. CD spectra for compound **5** in ethanol solution at 10^{-4} M (the solid line) and in gel from CCl_4 (the dash line).

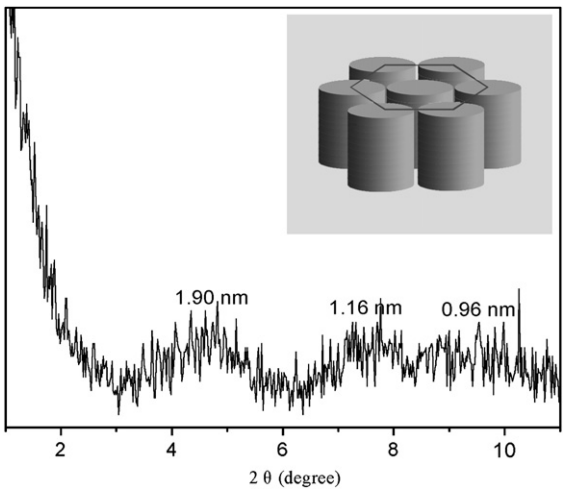
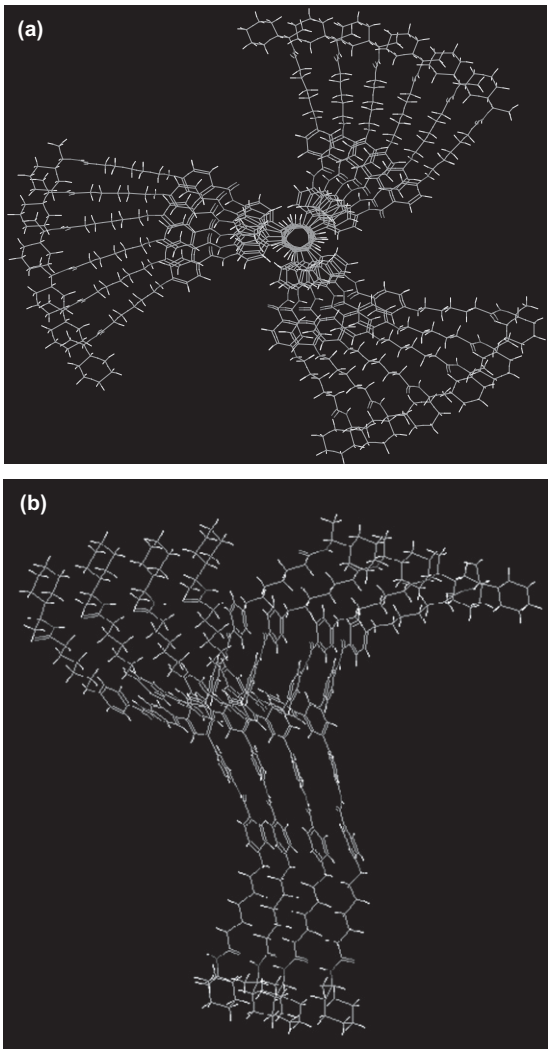


Figure 4. The XRD pattern for xerogel of compound **5** from CCl_4.

to the exciton coupling and the dipole moments are oriented in a clockwise direction in the aggregate of the organogelators. As reported in our previous work,[28] the co-facial stacking of the triphenylbenzene core induced the same rotational direction of benzene rings due to the steric hindrance and the probability for left- and right-handed rotations was equal. Here, the difference of the compound is due to the introduction of the chiral groups ((*R*)-(−)-1-cyclohexyl ethyl) in the side chains of compound. Therefore, the appearance of a positive Cotton effect in the CD spectra for the gel indicates that the introduction of the chiral groups in discotic molecules induces the triphenylbenzene cores to rotate in a clockwise direction to form the chiral stack.

XRD was then used to investigate how the clockwise-stacked molecules further stacked into fibers. Figure 4 shows the small-angle XRD pattern of the self-assembling xerogel of compound **5** from CCl_4. It gives three weak and broad peaks at the d-spacing of 1.90 nm, 1.16 nm, and 0.96 nm, respectively, with the proportion of $1 : 1/\sqrt{3} : 1/\sqrt{4}$, indicating the lattice to be indexed to a hexagonal arrangement of columns. The low intensity and the broad peaks suggest that the columns are not well correlated with each other and the molecular stacking is not very close. This is perhaps the reason why the helical structure could not be observed easily in the SEM and TEM images. Based on the above results, a tentative stacking model can be proposed as the inset of Figure 4 and Scheme 2, the clockwise-stacked molecules further aggregate into hexagonal column, which finally self-assemble into fibers and networks.

Fluorescent spectroscopy can also provide important information about the molecular organization of fluorophores,[33,34] such as the triphenylbenzene cores in the present system. Figure 5 gives the fluorescent emission spectra of **5** in the toluene gel and in a solution of toluene/methanol (v/v=9:1) at the same concentration of 1.0 wt %, in which the molecules are presented as aggregates and monomers, respectively, because the addition of trace amount of methanol could avoid the molecular aggregation. It was found that the emission of the toluene gel is much weaker than that in the solution, when excited at 300 nm. This suggested that the aggregation of the molecules results in the decrease



Scheme 2. The possible stacking model of compound **5** in the gel phase: (a) face-on view and (b) edge-on view.

of the PL intensity. As reported, J-aggregates as well as the coplanarity of the molecules in the aggregates favor an enhancement of the emission.[35,36] In this gel system, the

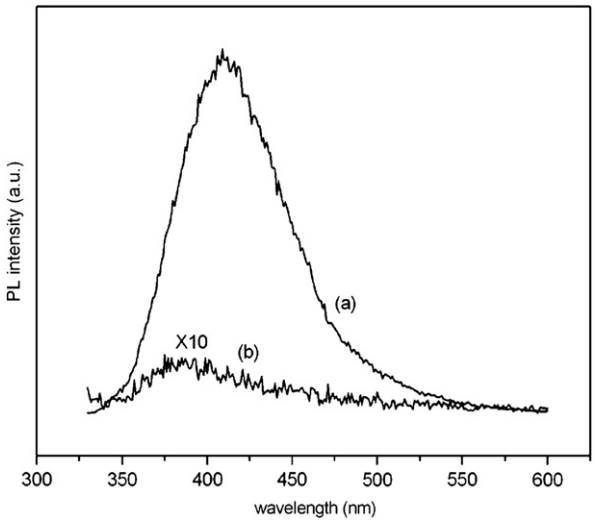


Figure 5. PL spectra of compound **5** in (a) toluene/methanol (9:1) solution and (b) in toluene gel at 1.0 wt % (excited at 300 nm).

molecules aggregated into J-aggregates for compound **5**, but the triphenylbenzene cores of the molecule are not stacked in a coplanar manner but rather twisted into clockwise columns. We argue that the two competitive factors may induce the emission of gel to decrease greatly to 1/50 of that in the solution. This emission change between the solution and gel state may find some potential applications in optical materials.

3. Conclusions

In summary, we synthesized a new discotic organogelator consisting of a π-conjugated triphenylbenzene core and chiral peripheral groups. The FTIR and UV–vis absorption spectra indicated that hydrogen bonds and π–π interactions provided by the amides and π-conjugated triphenylbenzene favored the formation of helical organogel fibers, and the chiral groups in the side chains induced the stacking in a single clockwise direction. At the same time, the aggregation of the molecules resulted in the decrease of the emission in the gel phase. This chirality-induced single direction helix may find some useful applications in designing new supramolecular systems.

4. Experimental section

Dry ethanol was obtained by distillation from Na and dry tetrahydrofuran (THF) by distillation from Na/K/benzophenone. (*R*)-(−)-1-Cyclohexyl-ethylamine (Aldrich, 98%, ee: 95%, $[\alpha]_D^{20}$ −4, neat) was used as received.

4.1. Characterization

^{1}H NMR spectra were determined with Varian-300 EX and JEOL JNM-500 EX. UV–vis absorption spectra were recorded with a Shimadzu UV-2201 UV–vis spectrophotometer. Fourier transform infrared (FTIR) spectra for the samples of xerogels were measured at room temperature on a Nicolet Impact 410 FTIR spectrometer. C, H, and N elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. Optical rotations were measured on a WZZ-1S polarimeter at λ=589 nm. X-ray diffraction (XRD) patterns were obtained on a Japan Rigaku D/max-γA. XRD is equipped with graphite monochromatized Cu Kα radiation (λ=1.5418 Å) and employs a scanning rate of 0.02 °/s in the 2θ range from 0.7° to 10°. The measured sample was prepared by casting the gels on glass slide and dried at room temperature. Transmission electron microscopy (TEM) images were taken with a Hitachi mode H600A-2 apparatus. The samples for TEM measurement were prepared by wiping a small amount of gel onto a 200-mesh copper grid followed by natural evaporation of the solvent. Fluorescence spectra were measured in a Japan Hitachi 850 fluorescence spectrophotometer at room temperature.

4.1.1. 1,3,5-Tris(4-aminophenyl)benzene (2).[28] $SiCl_4$ (20 mL, 0.18 mol) was added dropwise to a dry ethanol solution (60 mL) containing 10 g (0.06 mol) *p*-nitroacetophenone at 0 °C. A yellow precipitate was formed immediately and then the mixture was refluxed for 10 h. After the mixture was cooled to room temperature, saturated NH_4Cl aqueous solution (100 mL) was added and stirred for 10 min. The obtained yellow precipitate was filtered and dried, and directly added in 100 mL ethanol containing Pd/C (10%, 0.8 g). The mixture was heated to reflux, then 80% $NH_2NH_2\cdot H_2O$ (20 mL) was added dropwise to the hot solution. After refluxing for another 10 h, the precipitate was collected by filtration, the solution was cooled to room temperature, and the white precipitate was collected. The solid was recrystallized in ethanol and dried at vacuum, and 5.6 g white solid was obtained. Yield: 80%. Mp>200 °C; FTIR (KBr, cm^{-1}): 3420, 3344, 1618, 1592, 1515. Elemental analysis calculated for $C_{24}H_{21}N_3$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.04; H, 6.01; N, 11.94%; ^{1}H NMR ($CDCl_3$, 300 MHz): 7.59 (s, 3H, ArH), 7.50–7.45 (m, 6H, ArH), 6.78–6.48 (m, 6H, ArH), 3.73 (s, 6H, NH_2).

4.1.2. Methyl-4-(5-(1-cyclohexylethylcarbamoyl)pentyloxy)benzoate (3). A dry THF solution (10 mL) containing 6-bromo-hexanoyl chloride (0.011 mol, 1.68 mL) was slowly added to a dry THF solution (20 mL) with (*R*)-(−)-1-cyclohexyl-ethylamine (0.01 mol, 1.47 mL) and NEt_3 (0.025 mol, 3.4 mL) at 0 °C with stirring, and then the reaction mixture was stirred at room temperature for 12 h. The resulting solution was filtered and the filtrate was evaporated to dryness. The obtained liquid (1-cyclohexyl-ethyl)-amide-6-bromo-hexanoic acid was directly added to DMF (70 mL) solution containing 4-hydroxy-benzoic acid methyl ester (0.005 mol, 0.77 g), tetrabutyl ammonium bromide (0.17 g), and K_2CO_3 (0.05 mol, 6.9 g), which was heated to 50 °C for 96 h. Then the mixture was poured into water (150 mL) and acidified with HCl aq (10%) to pH=2. The obtained white solid was recrystallized from ethyl acetate. Yield: 65%. Mp 124.0–125.0 °C; $[\alpha]_D^{20}$ +17.9 (*c* 1, THF); FTIR (KBr, cm^{-1}): 3294, 2941, 2854, 1724, 1640, 1607, 1550, 1510, 1435. Elemental analysis calculated for $C_{22}H_{33}NO_4$: C, 70.37; H, 8.86; N, 3.73. Found: C, 70.35; H, 8.84; N, 3.75%; ^{1}H NMR ($CDCl_3$, 500 MHz): 7.97 (d, *J*=8.5, 2H, ArH), 6.88 (d, *J*=8.5, 2H, ArH), 4.00 (t, *J*=6.0, 2H, OCH_2), 3.88 (m, 4H, OCH_3, CH), 2.19 (t, *J*=8.5, 2H, $COCH_2$), 1.83 (m, 2H, CH_2), 1.72 (m, 5H, CH_2, CH), 1.65 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.33–1.22 (m, 4H, CH_2), 1.07 (d, *J*=6.5, 3H, CH_3), 0.98 (m, 2H, CH_2).

4.1.3. 4-(5-(1-Cyclohexylethylcarbamoyl)pentyloxy) benzoic acid (4). Compound **3** (0.005 mol, 1.88 g) was dissolved in THF (150 mL), and NaOH aq (1 M, 25 mL) was added. After the reaction mixture was heated at 60 °C for 24 h, the resulting solution was evaporated to dryness. The obtained solid was dissolved in water (300 mL) and the aqueous solution was acidified by concentrated HCl to pH=1. The obtained white precipitate was filtered, washed with water, and then dried. The product was obtained by recrystallization from ethanol. Yield: 95%. Mp>200 °C; $[\alpha]_D^{20}$ +25.0 (*c* 1, THF); FTIR (KBr, cm^{-1}): 3296, 2936, 2853, 1693, 1640, 1607, 1549, 1429. Elemental analysis calculated for $C_{21}H_{31}NO_4$: C, 69.87; H, 8.64; N, 3.87. Found: C, 69.90; H, 8.60; N, 3.90%; ^{1}H NMR ($CDCl_3$, 300 MHz): 8.02 (d, *J*=8.7, 2H, ArH), 6.91 (d, *J*=9.0, 2H, ArH), 4.02 (t, *J*=6.7, 2H, OCH_2), 3.74 (m, 1H, CH), 2.20 (t, *J*=6.5, 2H, $COCH_2$), 1.85 (m, 2H, CH_2), 1.73 (m, 5H, CH_2, CH), 1.62 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 1.30–1.20 (m, 4H, CH_2), 1.06 (d, *J*=6.0, 3H, CH_3), 0.98 (m, 2H, CH_2).

4.1.4. 1,3,5-Tris{4-[5-(1-cyclohexylethylcarbamoyl)pentyloxy]-benzoylamino}phenyl benzene (5). A THF solution (5 mL) of 1,3,5-tri(4-aminophenyl) benzene (**2**) (0.12 g, 0.34 mmol) was added dropwise to a THF solution (15 mL) containing **4** (0.6 g, 1.65 mmol), DCC (dicyclohexyl-carbodiimide) (0.8 g, 3.9 mmol), and DMAP (4-dimethylamino pyridine) (0.05 g) at 0 °C. After stirring overnight at room temperature the solution was filtered and the remaining solution was evaporated until the gel-like solid was formed. The precipitate was filtered and recrystallized in little THF twice, followed by drying in a vacuum oven. Yield: 60%. Mp>200 °C, $[\alpha]_D^{20}$ +53.3 (*c* 1, THF); FTIR (KBr, cm^{-1}): 3321, 2931, 2853, 1665, 1640, 1609, 1527. Elemental analysis calculated for $C_{87}H_{108}N_6O_9$: C, 75.62; H, 7.88; N, 6.08. Found: C, 75.97; H, 7.82; N, 6.02%; ^1H NMR ($CDCl_3$, 500 MHz) (present as aggregates): 7.56 (m, 9H, ArH), 6.89 (m, 12H, ArH), 6.09 (d, J=9.0, 6H, ArH), 3.96 (t, J=6.0, 6H, OCH_2), 3.60 (m, 3H, CH), 2.05 (m, 6H, $COCH_2$), 1.74 (m, 9H, CH_2, CH), 1.67–1.15 (m, 36H, CH_2), 1.12 (d, J=6.5, 9H, CH_3), 1.08–0.84 (m, 6H, CH_2); MALDI-TOF MS: *m*/*z*, calcd for 1,3,5-tris{4-[5-(1-cyclohexylethylcarbamoyl)pentyloxy]-benzoylamino}phenyl benzene: 1381.8; found: 1382.4.

4.2. Gelation test in solvents

Gelator **5** (5 mg) in different solvents (0.5 mL) was heated in sealed test tubes in an oil bath until the solid dissolved. After the solutions were allowed to stand at room temperature for 5 h, the state of the mixture was evaluated by the 'stable to inversion of a test tube' method.[37]

Acknowledgements

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