DOI: 10.1002/chem.200501058

Helical Stacking Tuned by Alkoxy Side Chains in π-Conjugated Triphenylbenzene Discotic Derivatives

Chunyan Bao,[a] Ran Lu,*[a] Ming Jin,[b] Pengchong Xue,[a] Changhui Tan,[a]
Tinghua Xu,[a] Guofa Liu,[a] and Yingying Zhao[a]

Abstract: We report on the synthesis and self-assembly of a new series of discotic molecules containing triphenylbenzene as the core and alkoxy side chain with varying length. It was found that compounds **3a**–**c**, **4b** and **5b** could form stable gels in several apolar solvents. Transmission electron microscopy (TEM) images revealed that their morphologies were very different for the different alkoxy-substituted organogels. In toluene or hexane, **3b** and **3c** resulted in both left- and right-handed helical fibers, whereas **3a** resulted in straight rigid fibers; **4b** and **5b** resulted in most straight fibers with a few twisted fibers. The results from FT-IR and UV/Vis absorption spectroscopy indicated that the hydrogen bonding and π–π interactions were the main driving forces for the formation of the self-assembled gels. Further detailed analysis of their aggregation modes were conducted by UV-visible absorption spectra and X-ray diffraction (XRD) measurements. Based on these findings, the influence of these peripheral alkoxy substituents on the gel formation and the aggregation mode were discussed. The special enhanced fluorescent emissions, which resulted from aggregation, were also found in the gel phase.

Keywords: discotic molecules · fluorescence · gels · helical structures · self-assembly

Introduction

Helical architectures are very common in nature and have always found the wide interest of scientists. Examples are the DNA double helix, the collagen triple helix, and the α-helical motifs in proteins. Inspired by the unique functions of helical superstructures performed by biological systems, a variety of aesthetically appealing helical supramolecular assemblies have been designed with the help of noncovalent forces, such as hydrogen bonding, π–π interactions, and van der Waals interactions.[1,2] Recently, the supramolecular architectures found in organogels attracted broad attention for the preparation of helical fibers or ribbons, in which the chiral groups (such as chiral alkyl chains,[3] amino acids,[4] glucose,[5] and cholesterol[6]) in the molecules can influence the formation of the helices. However, few reports have described the formation of an artificial helix from achiral molecules.[2b,7,8] In these cases, racemic products could be obtained when no optical active species were used. The phenomenon that helical structures can be built by achiral molecules is known as spontaneous symmetry breaking,[9–11] which was explained by packing restrictions between different parts of the molecules or by the interplay of surface and volume effects. In this context, a series of organogels consisted of π-conjugated core were designed to obtain the helices by adjusting the peripheral alkoxy substituents, as the resulting structures could find potential photonics applications due to their unique optical properties.[12]

A new series of C_3-symmetrical discotic molecules, in which alkoxy chains as the side chains connected to the triphenylbenzene cores through amide groups (as seen in Scheme 1), were synthesized and their self-assembling properties and optical properties were studied. Most of the compounds, such as **3a**–**c**, **4b**, and **5b**, could form stable gels in several apolar solvents; the morphologies and the packing structures of the organogels were significantly influenced by

---

[a] C. Bao, Prof. R. Lu, P. Xue, C. Tan, T. Xu, G. Liu, Y. Zhao
Key Laboratory of Supramolecular Structure and Materials
College of Chemistry, Jilin University, 2519 Jiefang Road
Changchun 130023 (P.R. China)
Fax: (+86) 431-892-3907
E-mail: luran@mail.jlu.edu.cn

[b] Dr. M. Jin
Present address:
Kanagawa Academy of Science and Technology (KSP)
KSP East-412
3-2-1 Sakado, Takatsu-ku, Kawasaki-shi
Kanagawa 213 (Japan)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: CPK models for the molecules, possible packing for the gels, and FT-IR data.

the length and the number of the substituted alkoxy chains. Notably, both left- and right-handed helical fibers with different helical pitches could be generated by tuning the alkoxy chain due to the steric hindrance of the self-assembled molecules cooperating with the packing of the alkoxy chains instead of any chiral groups. In particular, the formation of aggregates for the discotic molecules in gel phase exhibited unusually enhanced fluorescent emission, which was novel and totally different from those of conventional discotic supramolecular materials.

Results

Synthesis: The synthetic routes for the triamides **3a–c**, **4a–c** and **5a–c** were shown in Scheme 1. They were prepared through acylation of 1,3,5-tris(4-aminophenyl) benzene with the according alkoxybenzoyl chloride. All compounds were characterized with FT-IR spectroscopy, ^{1}H NMR and MALDI-TOF spectrometry.

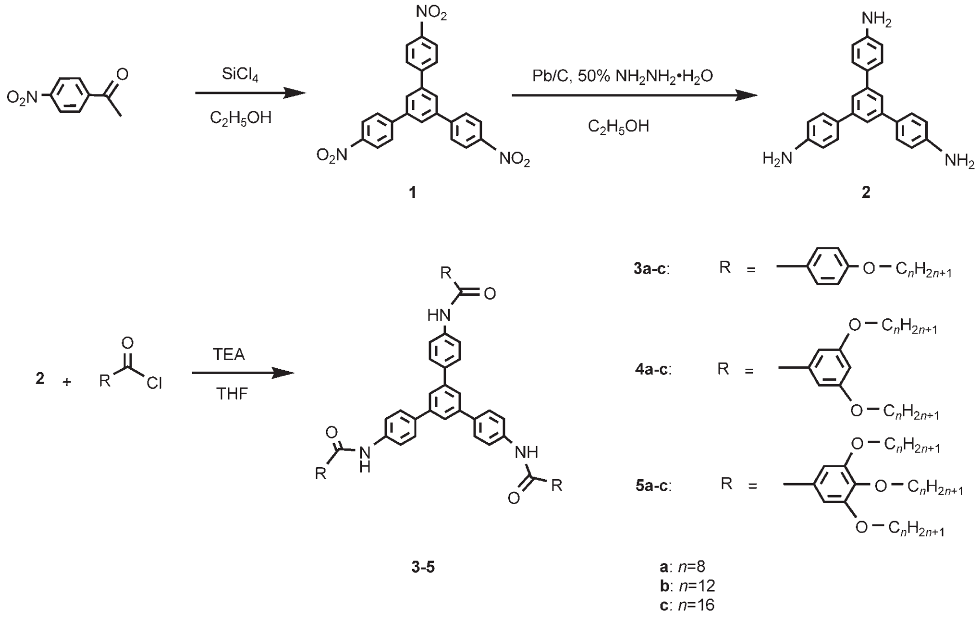
Gelation: The gelation properties of the discotic compounds were investigated in various solvents. As summarized in Table 1, the molecules with three alkoxy chains (compound **3a–c**) could form stable fibrous gel in benzene, toluene, xylene, and mesitylene even at 0.1 wt%. As for compounds **4a–c** and **5a–c**, the increase in size of the alkoxy side chains induced a good solubility in most solvents; only **4b** and **5b** could form gels in apolar solvent at the lowest concentration of 1 wt%. The formation of self-assembled gels was thermoreversible in the organic medium, for example, the gelators were insoluble at room temperature, and then turned into a clear solution by heating to reflux, upon cooling to room temperature, the immobile gels appeared. It was also found that compounds **3a–c** formed gels in fifteen minutes after cooling the hot transparent solution to the room temperature, while **4b** and **5b** formed gels in 24 h. This could be attributed to the lower tendency to crystallize in **4b** and **5b**; also the steric effects hindered and slowed the stacking process of the discotic molecules.

Table 1. Gelation properties of discotic compounds in organic solvents.

Gelator	**3a**	**3b**	**3c**	**4b**	**5b**
benzene	OG	OG	OG	TG	S
toluene	OG	OG	OG	TG	S
xylene	OG	OG	OG	TG	S
mesitylene	TG	TG	TG	TG	S
cyclohexane	IS	IS	IS	S	S
hexane	IS	IS	IS	S	TG
chloroform	PG	PG	PG	S	S

OG: opaque gel, TG: transparent gel, S: soluble, IS: insoluble, PG: partly gel. The low critical gelation concentrations (cgc) of gelators **3a–c** were 0.1 wt% and of **4b**, **5b** were 1 wt%.

Self-assembled behaviours: The structures of the organogels in toluene or hexane have been investigated by TEM (Figure 1). The gels exhibited well-defined fibers with different morphologies. For example, gel **3a** gave fibers with the diameter of 100–150 nm with high axial ratios, while gel **3b** generated both right- and left-handed superhelical fibers with diameter of about 80–120 nm. It seemed that most of the superhelical fibers in gel **3b** were composed of several thinner twisted fibers with the diameter of 30–50 nm, which intertwined into helix with non-uniform helical pitch. And also some single twisted fibers could be observed with the diameter of 30–50 nm in the gel **3b**. In gel **3c**, the fibers formed were similar to those of **3b**, but the helical pitch was longer and even some straight fibers were observed, which



Scheme 1. Synthesis of discotic molecules **3a–c**, **4a–c** and **5a–c**.

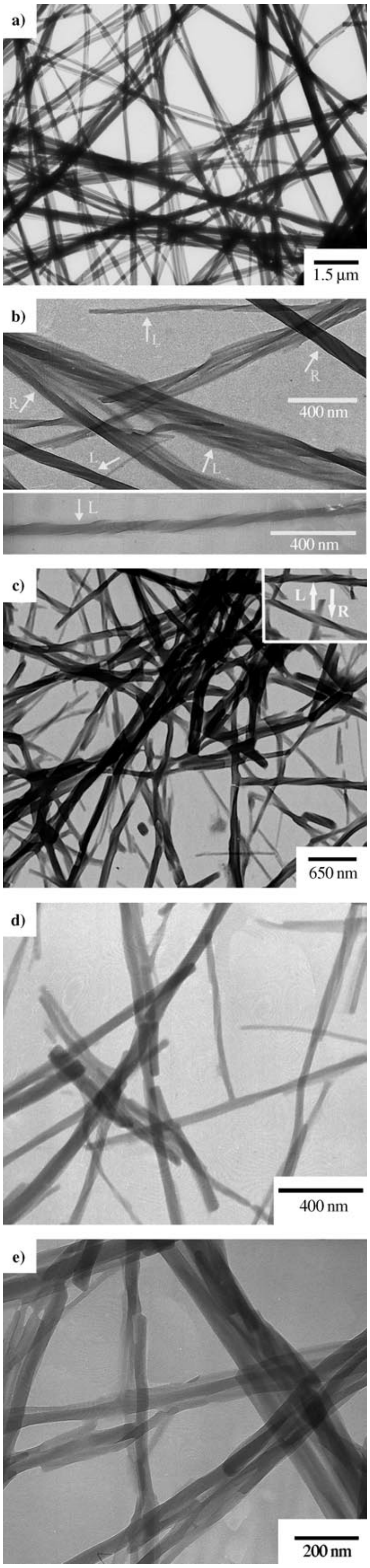


Figure 1. TEM images for gels a) **3a**, b) **3b**, c) **3c**, d) **4b** obtained from toluene, and e) **5b** obtained from hexane. The inset c) shows the amplified left- and right-handed helical fibers, respectively.

may be due to the looser packing of **3c** which consisted of longer carbon chains. The TEM images of **4b** and **5b** showed much thinner and less helical fibers with the diameter of 30–80 nm, which was similar to the single fibers in **3b** and **3c**, but the helical pitch increased and even formed straight fibers. The results outlined above suggested that the volume of peripheral alkoxy groups could tune the morphologies of gels. In these samples, right- and left-handed helices were present in equal quantities, thus resulting in overall racemic mixtures. It could be confirmed by the absence of any CD signal (not shown). In order to reveal the reason why the achiral molecules can stack into helical fibers in organogel phase, FT-IR spectra, UV-visible spectra and XRD measurement were recorded for the gels.

In order to ascertain how the discotic molecules aggregated into the gels, both FT-IR and UV/Vis investigations were performed. In THF, the compounds were soluble at all concentrations, for example, the FT-IR spectra of compound **3b** in THF showed an H-free N–H stretch band at 3560 cm^{-1} and an amide I band at 1675 cm^{-1}, respectively. While in the gel phase, **3b** showed an N–H stretch band at 3292 cm^{-1} and an amide I band at 1646 cm^{-1}, which was contributed to the characteristic of H-bonded amides (as shown in Figure 2).

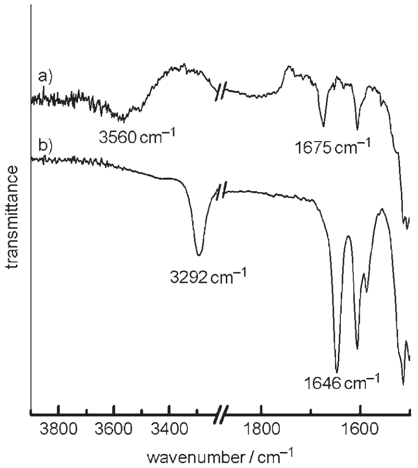


Figure 2. FT-IR spectra of a) a THF solution of compound **3b** and b) a xerogel of compound **3b** from toluene.

These results confirmed that hydrogen bonds between the amide groups contribute to the self-assembly process.[13] The UV/Vis absorption spectra for the gels were measured and compared with the corresponding dilute solution 1×10^{-6} M, in which the molecules may be considered in monomer state. For example (as seen in Figure 3), for the **3b**, the peak assignable to the triphenylbenzene absorption gave a much broadened and red-shifted band in gel phase than the one in the monomer state. It suggested that the π–π interaction also played a key role on the formation of the gels.[14]

To reveal the packing conformations of the molecules in gel phase, XRD were measured. The XRD patterns (as seen in Figure 4) of the xerogels **3a** and **3b** revealed a hexagonal

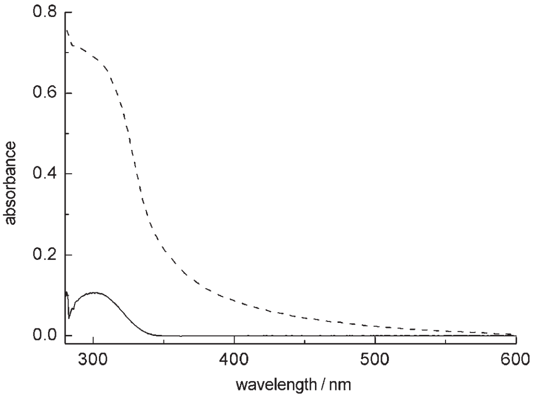


Figure 3. UV-visible absorption of gel **3b** in toluene at 1.0 wt% (-----) and monomer state **3b** in dilute toluene solution at 10^{-6} M (——).

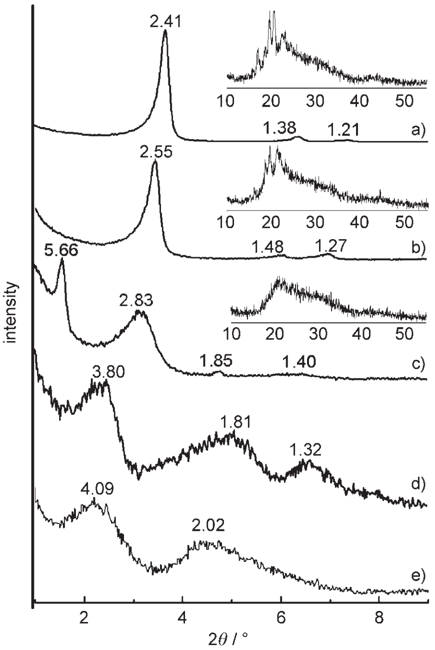


Figure 4. Small-angle X-ray diffraction diagrams of the xerogels: a) **3a**, b) **3b**, c) **3c**, d) **4b**, and e) **5b**. The insets show the respective wide-angle X-ray diffraction.

columnar structure with the column diameters of 2.78 and 2.94 nm in the low angle region with a reciprocal spacing ratio of $1:1/\sqrt{3}:1/\sqrt{4}$, respectively; the peaks of **3a** in the small-angle region were narrower than that of **3b**, which suggested more ordered and closed packing in xerogel **3a**. In addition, the diffractions of the wide-angle region for xerogels **3a** and **3b** gave a series of sharp peaks, which supported the view that long alkoxy chains presumably packed into some ordered arrangement due to hydrocarbon crystallization by van der Waals interaction.[15] When the length and the number of the alkoxy chains increased, the self-assembled structures changed into lamellar ones for xerogels **3c**, **4b** and **5b** with the interlayer distance of 5.66, 3.80 and 4.09 nm, respectively, with a reciprocal spacing ratio of $1:{}^{1}\!/_{2}:{}^{1}\!/_{3}$. This was indeed a very interesting phenomenon since it was not expected that the discotic molecules arranged into a lamellar instead of a columnar architecture.[16,17] For xerogels **3c**, only one broad peak in wide-angle region was observed and it was indicated that the packing of the alkoxy chains were slight disordered. The wide peaks in the small-angle region and the absence of peaks in the wide-angle region for xerogels **4b** and **5b** (not shown) suggested the disordered and loose stacking of the alkoxy chains in **4b** and **5b**.[18] Given the packing structural differences between the gels, one can presume that the van der Waals interaction among alkoxy chains should have a significant effect on their packing modes.

Moreover, the vibration frequencies for CH_2 antisymmetric $\nu_{as}(CH_2)$ and symmetric $\nu_s(CH_2)$ stretching as well as the CH_2 scissoring deformation $\delta(CH_2)$ band frequency of the xerogels would somewhat reflect the packing conformation of alkyl chains.[5a,19] For the xerogels, both of the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ band frequencies appeared at relatively low wavenumber regions (2920–2923 and 2850–2852 cm^{-1}, respectively), which suggested that the alkyl chains adopted the all-*trans* conformation. The $\delta(CH_2)$ band frequency can give the information on the packing of oligomethylene chain. As seen in Figure 5, gels **3a**, **3b** displayed a peak at 1467 cm^{-1} with full width at half-maximum of 5.1, 7.5 cm^{-1}, respectively, which can be ascribed to a triclinic chain packing for **3a** and slight distorted hexagonal packing for **3b**; gels **3c**, **4b** and **5b** showed increased full width at half-maximum (>9 cm^{-1}) which suggested the disordered packing.[20] These results agreed well with those from XRD observation.

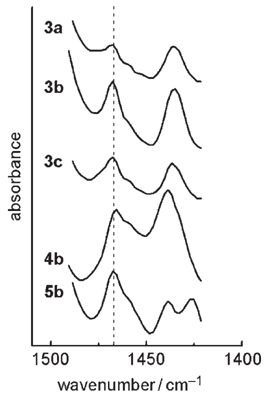


Figure 5. FT-IR spectra of the $\delta(CH_2)$ band region (1450–1480 cm^{-1}) for the assembled xerogels.

Combining the above results from the FT-IR spectra and XRD data as well as the molecular conformation, the reason for the generation of helical fibers from achiral molecules could be deduced. It was known that the core of the triphenylbenzene was not planar and the dihedral angle between the benzene ring was about 35° in the monomeric state derived from the CPK model, which might induce the same rotational direction of benzene rings due to the steric hindrance. It had been proposed that coplanarisation of chromophores could be induced by aggregation.[21] In the process for the formation of the gels, the hydrogen bonding and π–π interactions arranged the molecules to aggregate into fibrous structure, the coplanarisation of the cores might be induced to a certain extant. But the cores in the aggregates could not, however, assume a perfect coplanar conformation due to the steric hindrance and hydrogen-bonding interactions between the amide groups, and the phenyl rings might still rotate to some degree to cope with the formation of the hydrogen bonding, such rotation would preclude the co-facial alignment of the cores (see Chart S2 in the Supporting Information). Therefore the cores would be aggregated in a propeller-like conformation, which might provide an induction for the formation of helices. One could think that such perfect propeller-like conformation would only induce straight linear packing. Therefore, there must be some defect in the molecular packing, such as slightly disordered packing of the alkoxy chains, which induced the formation of twist propeller-like conformations and gave macroscopic helical structures. From the XRD and FT-IR results, the side chains in xerogels **3a** were packed tightly and highly ordered, and this tight propeller-like structure stacking could only cause the straight fibers as shown in Figure 1s. As for xerogel **3b**, the IR spectroscopic analysis suggested that the arrangement of side chains were slightly distorted and the packing of the molecules was not as tight xerogel **3a**, which might reflect some defect in the molecular packing and both right- and left-handed fibers were generated. When the volume of the side chains was increased, the amount of helical fibers decreased and the helical pitches increased as in gel **3c**, **4b** and **5b**. From FT-IR and XRD observation, it was known that the packing of the molecules were changed from hexagonal to lamellar and the packing of the alkoxy chains in gels **3c**, **4b** and **5b** were disordered, in which the van der Waals interactions between the peripheral alkoxy chains might play a more important role on the arrangement of the discotic molecules than the helical inducement of the core, which caused the less helical configuration of fibers. All of above results indicate that the helical fibers were formed based on the steric hindrance in the cores cooperating with the packing of the alkoxy chains.

Fluorescent emission spectra: Fluorescence spectroscopy provides important information on the molecular organization of fluorophores,[22] such as triphenylbenzene moieties in present system. Figure 6 shows emission spectra of the solutions of **3b**, **4b**, and **5b** at concentrations of 1×10^{-6} M and 1×10^{-4} M, in which the compounds may be considered in the monomer state and aggregated state, respectively. Compounds **3a**, **3b** and **3c** showed similar fluorescent emission behaviors, so that we used **3b** as an example. When excited at 300 nm, **3b** resulted in an emission peak at 340 nm under the $\lambda_{ex}=295$ nm in 10^{-6} M toluene solution and displayed purple under an UV lamp at $\lambda_{ex}=365$ nm. When the concentration was increased to 10^{-4} M, the fluorescence maximum shifted to longer wavelength with an obviously broadened peak and displayed blue color under 365 nm UV light (as shown in Figure 6a, and inset). The noteworthy difference for **4b** is that an unusual new peak at around 525 nm was observed at the concentration 10^{-4} M under the $\lambda_{ex}=300$ nm, which was attributed to the excimer emission.[22] The luminescent property of compound **5b** was similar to that of **3b** ($\lambda_{ex}=310$ nm), except that a weak peak at about 450 nm appeared at the concentration of 10^{-6} M, which suggested that aggregates of **5b** formed even in the quite dilute hexane solution. All luminescent emission bands of the aggregates red-shifted to high wavelength, which could be due to the co-facial stacking of the cores, in which a better conjugation between the cores could be obtained, thus lead to red-shift its emission bands.[23]

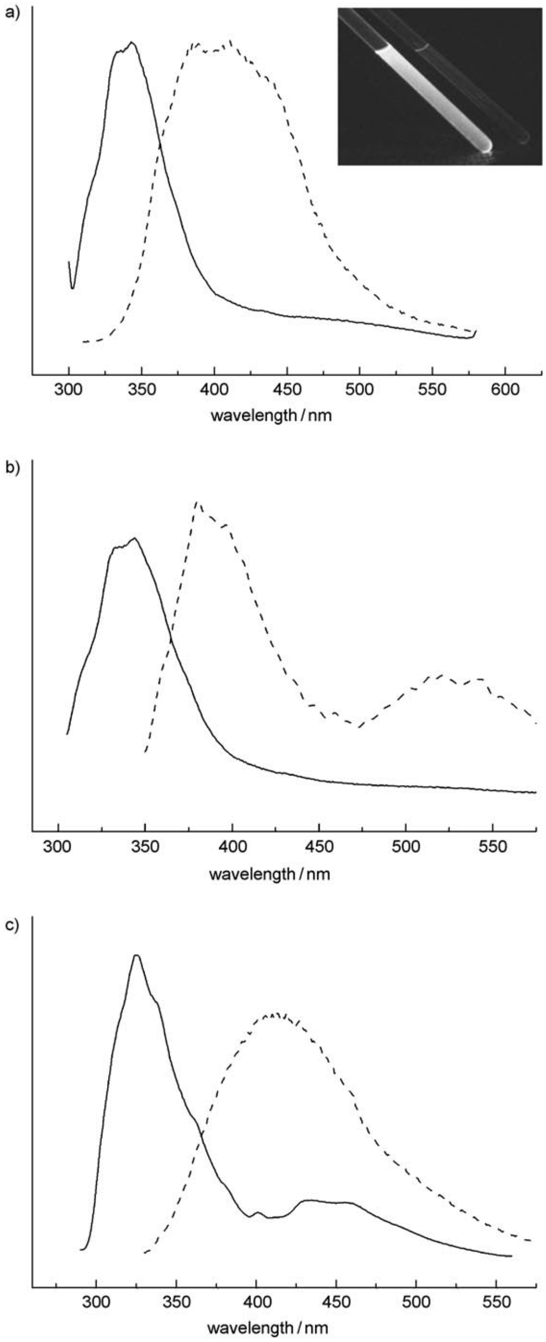


Figure 6. Fluorescence emission spectra of discotic compounds of a) **3b**, b) **4b**, and c) **5b**. The solid lines represent the emission spectra at concentration of 10^{-6} M and the dash lines represented those at the 10^{-4} M in the homogeneous solution for compound **3a** and **3b** in toluene and **3c** in hexane, respectively. The inset in a) shows the photograph illuminated by 365 nm light at 10^{-6} M (right) and 10^{-4} M (left).

Another remarkable phenomenon was that the fluorescence enhancement of all the gels obtained here could be unambiguously observed. As shown in Figure 7, for example, when excited at 350 nm, organogel **5b** exhibited strong emission band, while the solution of **5b** in THF didn't under the same concentration. This novel and significant property can be explained with the context of the aggregation-induced enhanced fluorescent emission phenomenon, which has been reported previously.[23] In the gel state, more planar conformation of the cores was formed due to the intermolecular forces, which enhanced the fluorescent emission, while in THF, **5b** was in the monomeric state confirmed by FT-IR measurement and the molecules were considered to be high twisted due to the steric interactions in triphenylbenzene, which generally suppressed the radiative decay channel and decreased the fluorescence emission. As known, the aggregation quenching has been the thorniest problem in the development of organic light-emitting diodes with high efficiency, the aggregation-induced emission enhancement herein will stimulate new molecular engineering endeavors in the design of the luminescent organic compounds and polymers with highly emissive aggregation states.

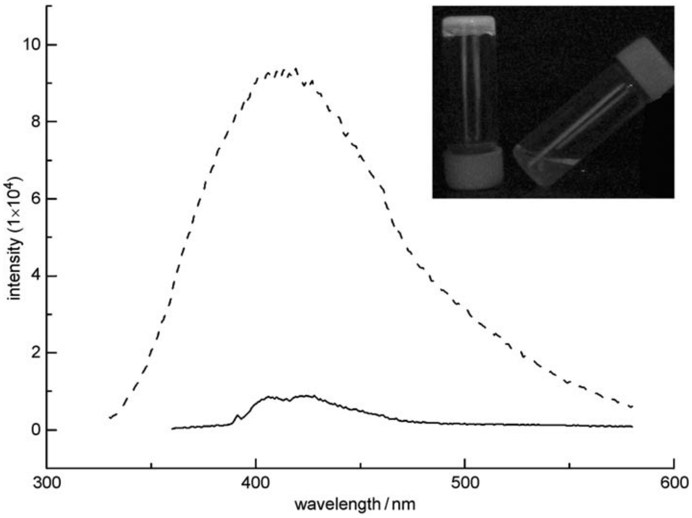


Figure 7. Fluorescence emission spectra of compound **5b** in THF solution (——) and in the hexane gel state (-----) at the same concentration 1.0 wt%. The inset shows the photographs of in hexane (left) and in THF (right) illuminated by 365 nm light.

Conclusion

In this paper, we have designed a new series of achiral discotic organogelators consisting of triphenylbenzene as core to prepare well-defined helical fibers by tuning the peripheral substituted alkoxy chains. The FT-IR and UV/Vis absorption revealed that hydrogen bonding and π–π interactions were the main driving forces for the formation of the self-assembly. The XRD diagrams suggested that the self-assembled structure of the gels changed from hexagonal columnar phases to lamellar ones when the volume of the alkoxy chain of molecules increased. The formation of the helical fibers was due to the helical inducement of the core cooperating with the packing and arrangement of the alkoxy chains. The novel fluorescence emission enhancement of the organogels was discovered, which was induced by the aggregation of the molecules.

Experimental Section

General methods: Dry ethanol was obtained by distillation from Na, and dry tetrahydrofuran (THF) by distillation from Na/K/benzophenone. The alkoxybenzoyl chlorides were prepared according to a general procedure and were used without any further distillation. Other chemicals were used as received.

Characterization: ^{1}H NMR spectra were determined with Varian-300 EX and JEOL JNM-500EX. Mass spectral data were obtained by MALDI-TOF mass spectrometry using α-cyano-4-hydroxycinnamic acid as the matrix on a spectrometer. UV-visible absorption spectra were recorded with a Shimadzu UV-2201 UV-visible spectrophotometer. FT-IR spectra for the samples of xerogels and in THF solutions (10^{-2} M) were measured at 20 °C (room temperature) on a Nicolet Impact 410 FT-IR spectrometer. X-ray diffraction (XRD) patterns were obtained on a Japan Rigaku D/max-γA. XRD equipped with graphite monochromatized $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.5418$ Å), employing a scanning rate of $0.02°\,\mathrm{s}^{-1}$ in the 2θ range from 0.7 to 10° and $0.05°\,\mathrm{s}^{-1}$ in the 2θ range from 10 to 50°. The sample was prepared by casting the gels on glass slide and dried at room temperature. Transmission electron microscopy (TEM) was taken with a Hitachi mode H600 A-2 apparatus. Samples for TEM measurement were prepared by wiping small amount of gel onto a 200-mesh copper grid followed by natural evaporating the solvent. Fluorescence spectra were measured on a Japan Hitachi 850 fluorescence spectrophotometer at room temperature.

1,3,5-Tris(4-aminophenyl)benzene (2): $SiCl_4$ (20 mL, 0.18 mol) was added dropwise to a solution of *p*-nitroacetophenone (10 g, 0.06 mol) in absolute ethanol (60 mL) 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 (100 mL) was added and stirred for 10 min. The obtained yellow precipitate was filtered and dried, and added ethanol (100 mL) directly with Pd/C (0.8 g), which was heated to reflux. Then $NH_2NH_2{\cdot}H_2O$ (80 %, 20 mL) was added dropwise to the hot solution. After refluxing for 10 h, the precipitate was taken off by filtration and the solution was cooled to room temperature, and the white precipitate was collected. The solid was recrystallized in ethanol and dried at vacuum and finally obtained white solid (5.6 g, 80 %). M.p. > 200 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.59$ (s, 3H; ArH), 7.50 (m, 6H; ArH), 6.78 (m, 6H; ArH), 3.73 (s, 6H; NH_2); FT-IR: $\tilde{\nu} = 3420$, 3344, 1618, 1592, 1515 cm^{-1}.

1,3,5-Tris(4-octyloxybenzoylamino)phenylbenzene (3a): A dry THF solution (10 mL) containing 4-octyloxybenzoyl chloride (0.612 g, 2.3 mmol) was added dropwise to another dry THF (15 mL) solution consisting of 1,3,5-tris(4-aminophenyl)benzene (**2**) (0.2 g, 0.57 mmol) and triethylamine (0.42 mL, 3.0 mmol) at 0 °C. After stirring at room temperature for 12 h, the solution was poured into water (200 mL), and the precipitate was filtered and recrystallized in $CHCl_3$/THF 4:1 twice, followed by drying in a vacuum oven (0.36 g, 60 %). M.p. > 200 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.86$ (m, 9H; ArH), 7.74 (m, 12H; ArH), 6.98 (d, 6H; ArH), 4.02 (t, 6H; OCH_2), 1.84(m, 6H; CH_2), 1.56–1.43 (m, 30H; CH_2), 0.88 (t, 9H; CH_3); FT-IR: $\tilde{\nu} = 3435$, 3301, 2925, 2854, 1646, 1606, 1513 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 1048.4, found: 1049.2.

1,3,5-Tris(4-dodecyloxybenzoylamino)phenylbenzene (3b): Compound **3b** was synthesized according to a similar method as that of **3a**; yield: 0.45 g, 65 %. M.p. > 200 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.85$ (m, 9H; ArH), 7.73 (m, 12H; ArH), 6.97 (d, 6H; ArH), 4.02 (t, 6H; OCH_2), 1.85 (m, 6H; CH_2), 1.54–1.27 (m, 54H; CH_2), 0.87 (t, 9H; CH_3); FT-IR:

$\tilde{\nu}$ = 3431, 3297, 2922, 2852, 1647, 1606, 1514 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 1216.7, found: 1216.2.

1,3,5-Tris(4-cetyloxybenzoylamino)phenylbenzene (3c): Compound **3c** was synthesized according to a similar method as that of **3a**; yield: 0.51 g, 65%. M.p. > 200 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.86 (m, 9H; ArH), 7.72 (m, 12H; ArH), 6.97 (d, 6H; ArH), 3.99(t, 6H; OCH$_2$), 1.82 (m, 6H; CH$_2$), 1.52–1.26 (m, 78H; CH$_2$), 0.88 (t, 9H; CH$_3$); FT-IR: $\tilde{\nu}$ = 3439, 3293, 2921, 2851, 1646, 1606, 1514 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 1385.4, found: 1385.6.

1,3,5-Tris(3,5-dioctyloxybenzoylamino)phenylbenzene (4a): 3,5-Dioctyloxylbenzoylchloride (0.913 g, 2.3 mmol) was dissolved in dry THF (10 mL), and the solution was added dropwise to the dry THF (15 mL) solution consisting of 1,3,5-tris(4-aminophenyl)benzene (**2**) (0.2 g, 0.57 mmol) and triethylamine (0.42 mL, 3.0 mmol) at 0 °C. After stirring at room temperature for 12 h, the solution was poured into water (200 mL), and the product was extracted with CHCl$_3$. After evaporating the solvent, the product was recrystallized with CHCl$_3$/C$_2$H$_5$OH at volume ratio of 1:3, and dried in a vacuum (0.41 g, 50%). M.p. > 200 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.94 (s, 3H; ArH), 7.74 (m, 12H; ArH), 6.98 (s, 6H; ArH), 6.61 (s, 3H; ArH), 3.98 (t, 12H; OCH$_2$), 1.79 (m, 12H; CH$_2$), 1.60–1.29 (m, 60H; CH$_2$), 0.9 (t, 18H; CH$_3$); FT-IR: $\tilde{\nu}$ = 3285, 2926, 2855, 1649, 1594, 1512 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 1433.0, found: 1433.7.

1,3,5-Tris(3,5-didodecyloxybenzoylamino)phenylbenzene (4b): Compound **4b** was synthesized according to a similar method as that of compound **4a**; yield: 0.65 g, 65%. M.p. 160 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.85 (s, 3H; ArH), 7.77 (m, 12H; ArH), 6.99 (s, 6H; ArH), 6.62 (s, 3H; ArH), 4.00 (t, 12H; OCH$_2$), 1.88 (m, 12H; CH$_2$), 1.59–1.26 (m, 108H; CH$_2$), 0.88 (t, 18H; CH$_3$); FT-IR: $\tilde{\nu}$ = 3275, 2922, 2851, 1647, 1592, 1518 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 1601.5, found 1601.2.

1,3,5-Tris(3,5-dicetyloxybenzoylamino)phenylbenzene (4c): Compound **4c** was synthesized according to a similar method as that of compound **4a**; yield: 0.60 g, 60%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.83 (s, 3H; ArH), 7.75 (m, 12H; ArH), 6.89 (s, 6H; ArH), 6.62 (s, 3H; ArH), 3.98 (t, 12H; OCH$_2$), 1.86 (m, 12H; CH$_2$), 1.59–1.26 (m, 156H; CH$_2$), 0.89 (t, 18H; CH$_3$); FT-IR: $\tilde{\nu}$ = 3274, 2923, 2851, 1646, 1592, 1518 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 1769.7, found 1769.0.

1,3,5-Tris(3,4,5-trioctyloxybenzoylamino)phenylbenzene (5a): A dry THF solution (10 mL) containing 3,4,5-trioctyloxylbenzoyl chloride (1.2 g, 2.3 mmol) was added dropwise to another dry THF solution (15 mL) consisting of 1,3,5-tris(4-aminophenyl)benzene (**2**) (0.2 g, 0.57 mmol) and triethylamine (0.42 mL, 3.0 mmol) at 0 °C. After stirring at room temperature for 12 h, the solution was poured into water (200 mL), and the precipitate was filtered and recrystallized in CHCl$_3$/C$_2$H$_5$OH at volume ratio 1:4 twice and dried in a vacuum (0.52 g, 50%). M.p. > 200 °C; ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.92 (s, 3H; ArH), 7.72 (m, 12H; ArH), 7.08 (s, 6H;ArH), 4.03 (m, 18H; OCH$_2$), 1.82 (m, 18H; CH$_2$), 1.59–1.29 (m, 90H; CH$_2$), 0.87 (m, 27H; CH$_3$); FT-IR: $\tilde{\nu}$ = 3268, 2924, 2854, 1644, 1584, 1531, 1511 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 1817.6, found: 1817.5.

1,3,5-Tris(3,4,5-tridodecyloxybenzoylamino)phenylbenzene (5b): Compound **5b** was synthesized according to a similar method as that of compound **5a**; yield: 0.86 g, 65%, liquid crystal phase: 60–140 °C; ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.91 (s, 3H; ArH), 7.72 (m, 12H; ArH), 7.08 (s, 6H; ArH), 4.04 (m, 18H; OCH$_2$),1.83(m, 18H; CH$_2$), 1.59–1.29 (m, 162H, CH$_2$), 0.88 (m, 27H, CH$_3$); FT-IR: $\tilde{\nu}$ = 3298, 2923, 2852, 1648, 1585, 1513 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 2322.6, found: 2322.5.

1,3,5-Tris(3,4,5-tricetyloxybenzoylamino)phenylbenzene (5c): Compound **5c** was synthesized according to a similar method as that of compound **5a**; yield: 1.13 g, 70%. M.p. 158 °C; ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.81(s, 3H; ArH), 7.75 (m, 12H; ArH), 7.08 (s, 6H; ArH), 4.04 (m, 18H; OCH$_2$), 1.82 (m, 18H; CH$_2$), 1.50–1.25 (m, 234H; CH$_2$), 0.87 (m, 27H; CH$_3$); FT-IR: $\tilde{\nu}$ = 3265, 2920, 2850, 1645, 1584, 1522 cm^{-1}; MALDI-TOF MS: *m*/*z*: calcd for: 2827.6, found:2827.5.

Acknowledgements

The work was financially supported by the National Natural Science Foundation of China (NNSFC, No. 20574027).

---

[1] a) J. C. Nelson, J. G. Saven, J. S. Moore, P. G. Wolyness, *Science* **1998**, *280*, 1427–1430; b) A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65–71; *Angew. Chem. Int. Ed.* **1998**, *37*, 63–68; c) R. Oda, M. Schmutz, S. J. Candau, F. C. MacKintosh, *Nature* **1999**, *399*, 566–568.

[2] a) E. R. Zubrarev, M. U. Pralle, E. D. Sone, S. I. Stupp, *J. Am. Chem. Soc.* **2001**, *123*, 4105–4106; b) E. D. Sone, E. R. Zubrarev, S. I. Stupp, *Angew. Chem.* **2002**, *114*, 1781–1785; *Angew. Chem. Int. Ed.* **2002**, *41*, 1705–1709; c) H. Fenniri, B.-L. Deng, A. E. Ribbe, *J. Am. Chem. Soc.* **2002**, *124*, 11064–11072; d) T. Giorgi, S. Lena, P. Mariani, M. A. Cremonini, S. Masiero, S. Pieraccini, J. P. Rabe, P. Samori, G. P. Spada, G. Gottarelli, *J. Am. Chem. Soc.* **2003**, *125*, 14741–14749; e) R. Iwaura, K. Yoshida, M. Masuda, M. O. Kameyama, M. Yoshida, T. Shimizu, *Angew. Chem.* **2003**, *115*, 1039–1042; *Angew. Chem. Int. Ed.* **2003**, *42*, 1009–1012.

[3] a) L. Brunsveld, H. Zhang, M. Glasbeek, J. A. J. A. Vekemans, E. W. Meijer, *J. Am. Chem. Soc.* **2000**, *122*, 6175–6182; b) J. J. Van Gorp, J. A. J. A. Vekemans, E. W. Meijer, *J. Am. Chem. Soc.* **2002**, *124*, 14759–14769; c) H. Engelkamp, S. Middelbeek, R. J. M. Nolte, *Science* **1999**, *284*, 785–788; d) S. J. George, A. Ajayaghosh, P. Jonkheijin, A. P. H. J. Schenning, E. W. Meijer, *Angew. Chem.* **2004**, *116*, 3504–3507; *Angew. Chem. Int. Ed.* **2004**, *43*, 3422–3425.

[4] a) T. Sagawa, S. Fukugawa, T. Yamada, H. Ihara, *Langmuir* **2002**, *18*, 7223–7228; b) L. A. Estroff, A. D. Hamilton, *Angew. Chem.* **2000**, *112*, 3589–3592; *Angew. Chem. Int. Ed.* **2000**, *39*, 3447–3450.

[5] a) I. Nakazawa, M. Masuda, Y. Okada, T. Hanada, K. Yase, M. Asai, T. Shimizu, *Langmuir* **1999**, *15*, 4757–4764; b) G. John, M. Masuda, Y. Okada, K. Yase, T. Shimizu, *Adv. Mater.* **2001**, *13*, 715–718; c) G. John, J. H. Jung, H. Minamikawa, K. Yoshida, T. Shimizu, *Chem. Eur. J.* **2002**, *8*, 5494–5500; d) S. Tamaru, S. Uchino, M. Takeuchi, M. Ikeda, T. Hatano, S. Shinkai, *Tetrahedron Lett.* **2002**, *43*, 3751–3755.

[6] a) P. C. Xue, R. Lu, D. M. Li, M. Jin, C. H. Tan, C. Y. Bao, Z. M. Wang, Y. Y. Zhao, *Langmuir* **2004**, *20*, 1123411239; b) E. Snip, K. Koumoto, S. Shinkai, *Tetrahedron* **2002**, *58*, 8863–8873; c) J. H. Jung, S. Shinkai, T. Shimizu, *Chem. Mater.* **2003**, *15*, 2141–2145; d) P. C. Xue, R. Lu, D. M. Li, M. Jin, C. Y. Bao, Y. Y. Zhao, Z. M. Wang, *Chem. Mater.* **2004**, *16*, 3702–3707; e) S. Kawano, N. Fujita, S. Shinkai, *J. Am. Chem. Soc.* **2004**, *126*, 8592–8593.

[7] a) W. Yang, X. Chai, L. Chi, X. Liu, Y. Cao, R. Lu, Y. Jiang, X. Tang, H. Fuchs, T. Li, *Chem. Eur. J.* **1999**, *5*, 1144–1149; b) U. Siemeling, I. Scheppelmann, B. Neumann, A. Stammel, H.-G. Stammler, J. Frelek, *Chem. Commun.* **2003**, 2236–2237; c) D. Ogata, T. Shikata, K. Hanabusa, *J. Phys. Chem. B* **2004**, *108*, 15503–15510; d) T. Shikata, D. Ogata, K. Hanabusa, *J. Phys. Chem. B* **2004**, *108*, 508–514.

[8] K. Köhler, G. Föester, A. Hauster, D B. obner, U. F. Heiser, F. Ziethe, W. Richter, F. Steiniger, M. Drechsler, H. Stettin, A. Blume, *J. Am. Chem. Soc.* **2004**, *126*, 16804–16813.

[9] A. Jákli, G. G. Nair, C. K. Lee, R. Sun, L. C. Chien, *Phys. Rev. E* **2001**, *63*, 061710/1-5.

[10] R. Viswanathan, J. A. Zasadzinski, D. K. Schwartz, *Nature* **1994**, *368*, 440–443.

[11] D. K. Kondepudi, R. J. Kaufman, N. Singh, *Science* **1990**, *250*, 975–979.

[12] X. Cao, W. Zhang, J. Wang, X. Zhou, H. Lu, J. Pei, *J. Am. Chem. Soc.* **2003**, *125*, 12430–12431.

[13] a) G. Socrates, In *Infrared Characteristic Group Frequencies*, Wiley, Chichester, **1994**, 2nd ed., pp. 104–107; b) S. J. Lee, C. R. Park, J. Y. Chang, *Langmuir* **2004**, *20*, 9513–9519; c) F. Camerel, C. F. J. Faul, *Chem. Commun.* **2003**, 1958–1959.

[14] T. Kunitake, *Angew. Chem.* **1992**, *104*, 692–710; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 709–726, and references therein.

[15] a) J. H. Jung, G. John, K. Yoshida, T. Shimizu, *J. Am. Chem. Soc.* **2002**, *124*, 10674–10675; b) J. H. Jung, S. Shinkai, T. Shimizu, *Chem. Eur. J.* **2002**, *8*, 2684–2690.

[16] M. Shitakawa, S. Kawano, N. Fujita, K. Sada, S. Shinkai, *J. Org. Chem.* **2003**, *68*, 5037–5044.

[17] J. Kadam, C. F. J. Faul, U. Scherf, *Chem. Mater.* **2004**, *16*, 3867–3871.

[18] M. Masuda, T. Hanada, Y. Okada, K. Yase, T. Shimizu, *Macromolecules* **2000**, *33*, 9233–9238.

[19] a) M. Masuda, V. Vill, T. Shimizu, *J. Am. Chem. Soc.* **2000**, *122*, 12327–12333; b) T. Shimizu, M. Masuda, *J. Am. Chem. Soc.* **1997**, *119*, 2812–2818.

[20] N. Garti, K. Sato, *Crystallization and Polymorphism of Fats and Fatty Acids,* Marcel Dekker, **1988**.

[21] M. Levitus, K. Schmieder, H. Ricks, K. D. Shimizu, U. H. F. Bunz, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2001**, *123*, 4259–4265.

[22] a) N. J. Turro, *Molecular photochemistry*, University Science Books, **1991**; b) J. B. Brikd, *Photophysics of Aromatic Molecules*, Wiley-Interscience, **1970**; c) S. Y. Ryu, S. Kim, J. Seo, Y. W. Kim, O. H. Kwon, D. J. Jang, S. Y. Park, *Chem. Commun.* **2004**, 70–71.

[23] a) B.-K. An, S.-K. Kwon, S.-D. Jung, S. Y. Park, *J. Am. Chem. Soc.* **2002**, *124*, 14410–14415; b) B.-K. An, D.-S. Lee, J.-S. Lee, Y.-S. Park, H.-S. Song, S. Y. Park, *J. Am. Chem. Soc.* **2004**, *126*, 10232–10233; c) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* **2001**, 1740–1741.

Received: August 29, 2005