Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 7358–7365

Self-assembly of carbazole-containing gelators: alignment of the chromophore in fibrous aggregates

Kazuhiro Yabuuchi,[a,†] Yusuke Tochigi,[a] Norihiro Mizoshita,[a] Kenji Hanabusa[b] and Takashi Kato[a,*]

[a]*Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[b]*Graduate School of Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan*

Received 4 January 2007; revised 8 March 2007; accepted 16 March 2007
Available online 23 March 2007

Abstract—Carbazole-containing gelators derived from L-isoleucine have been developed. They form elongated self-assembled fibers in common organic solvents and in liquid crystals, leading to the efficient gelation of these solvents. Spectroscopic studies indicate that the carbazolyl moieties are one-dimensionally stacked in the fibers. The stacking of the carbazolyl moieties is reversible by the association and dissociation of the hydrogen bonding. Moreover, anisotropically aligned fibers have been obtained in a homogeneously oriented smectic state of liquid crystals. This template behavior would serve as a versatile approach to the functionalization of self-assembled fibers.

1. Introduction

Supramolecular self-assembly is a promising tool for the fabrication of functional molecular materials.[1] Physical gels based on fibrous self-assembly of low molecular weight gelators are one of the representative examples.[2–23] Physical gels can be functionalized by the introduction of electro-[5–11] and photo-active[12,13] functional moieties to the gelators. Functional solvents such as liquid crystals,[14–20] electrolytes,[21] and ionic liquids[22] have also been used. For the liquid crystalline gels, faster switching of the nematic liquid crystals by the application of electric fields was observed. Gelators containing cationic moieties were used as templates for inorganic synthesis.[23] Recently, one-dimensional (1D) stacking of π-conjugated molecules has attracted attention, because electronic and ionic 1D conducting paths on the nanometer-scale can be obtained.[24,25] Use of fibrous self-assemblies of gelators is one promising approach for the development of functional molecular materials. Gelators incorporating electroactive moieties such as oligothiophene,[5] porphyrin,[6] tetrathiafulvalene (TTF),[7,8] diacetylene,[9] and carbazole[10] have been developed. We have recently prepared unidirectionally aligned fibers of TTF-based gelators in oriented liquid crystals, and measured the electrical conductivity of doped fibers.[8]

Our intention is to induce 1D alignment of carbazolyl moieties by fibrous assembly of gelators. Carbazolyl moieties are known to exhibit photophysical properties such as photoconductivity as seen in poly(*N*-vinylcarbazole)s.[26] Self-assembled fibers bearing functional moieties might act as photoconductive molecular wires by 1D stacking of carbazolyl moieties in the fibers. Moreover, the stacking and dissociation of carbazolyl moieties because of non-covalent self-assembly are expected, which has not been discussed in detail for a previously reported carbazole-based gelator.[10] Here we report on the preparation and self-assembling behavior of new carbazole-based gelators. Stacking behavior of the carbazolyl moieties on fibrous self-assembly has been studied by spectroscopic measurements. Moreover, unidirectionally aligned fibers have been obtained in an oriented smectic liquid crystal.

2. Results and discussion

2.1. Molecular design

Carbazole-containing compounds **1a** and **1b** shown in Figure 1 were prepared by the coupling reaction of the corresponding carbazole-containing amines and *N*-benzyloxycarbonyl-L-isoleucine as shown in Scheme 1. The carbazolyl moiety is attached to an isoleucine-based scaffold via dodecamethylene and hexamethylene chains, respectively. The isoleucine scaffold often exhibits excellent ability to form hydrogen-bonded fibrous aggregates in a wide range of solvents, which leads to gelation of the

Keywords: Organogel; Carbazole; Liquid crystal; Self-assembled fiber.
* Corresponding author. Tel.: +81 3 5841 7440; fax: +81 3 5841 8661; e-mail: kato@chiral.t.u-tokyo.ac.jp
† Present address: Department of Materials Science and Environmental Engineering, Faculty of Science and Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda, Yamaguchi 756-0884, Japan.

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.03.121

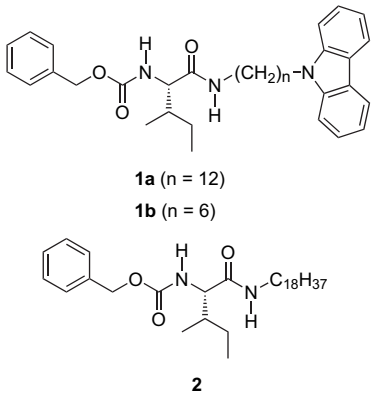


Figure 1. Molecular structures of gelators **1a**, **1b**, and **2**.

Table 1. Gelation properties of isoleucine derivatives for common organic solvents[a]

Solvent	1a	1b	2
Hexane	P	I	P
Ethyl acetate	G	P	G
Ethanol	P	P	G
Methanol	P	P	G
Acetone	G	P	G
Chloroform	S	P	S
Tetrachloromethane	G	G	G
Benzene	G	G	G
Toluene	G	S	G
DMF	S	S	S

[a] Gelation tests were conducted at 40 g L^{-1}. The following abbreviations are used: P, precipitate; I, insoluble; S, solution; G, gel.

solvents.[4,21c] For example, compound **2** is an efficient gelator for common organic solvents and liquid crystals.[16a,19a,20,21c] Therefore, 1D fibrous self-assembly of **1a** and **1b** was expected because of the presence of the isoleucine scaffold.

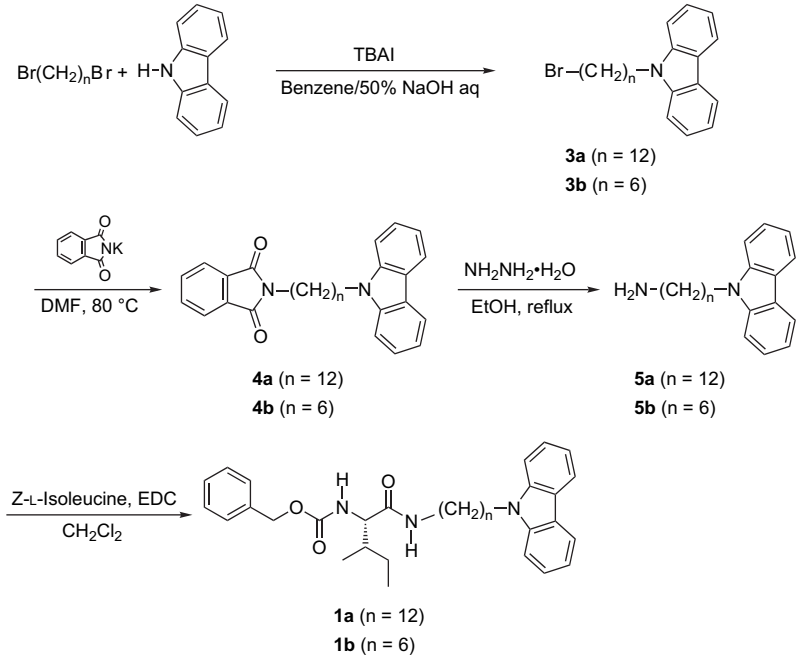
2.2. Gelation of common organic solvents

The gelation properties of these isoleucine-based compounds for common organic solvents at a concentration of 40 g L^{-1} are shown in Table 1. The gelation ability of **1a** slightly decreases compared to that of **2**. Compound **1b** can gelate only tetrachloromethane and benzene of the solvent examined. These results suggest that the interaction of the bulky group does not greatly affect the gelation ability as long as a longer alkyl spacer is used.

Microscopic observation of xerogels reveals that compounds **1a** and **1b** form elongated fibrous aggregates in organic solvents. The SEM image of self-assembled fibers of **1a** is shown in Figure 2. Both compounds form random networks of elongated fibers, which have diameters of several tens of nanometers. The introduction of carbazolyl moieties does not cause changes in the morphologies of the fibers.

2.3. Gelation of liquid crystals

The gelation properties of **1a** and **1b** for liquid crystals **6** and **7** shown in Figure 3 are given in Table 2. Our aim here is to align the gelator in the smectic phases of **6** and **7**. In our previous study, the alignment of gelators was observed in nematic and smectic liquid crystals.[8,18,19] Liquid crystal compound **6** shows a nematic phase between 38 and 32 °C and a smectic A phase below 32 °C, while nematic (79–65 °C) and smectic A (below 65 °C) phases are also observed for **7** at higher temperature ranges. Gelation tests were conducted at a concentration of 3 wt % of the gelators. As shown in Table 2, only **1a** can gelate **6** and **7**, while compound **1b** does not gelate these liquid crystals. Sol–gel transition temperatures ($T_{sol-gel}$) were determined for the LC gels. Figure 4 shows a phase diagram of the mixtures of liquid crystal **6** and gelator **1a**. Compound **1a** exhibits



Scheme 1. Syntheses of **1a** and **1b**.

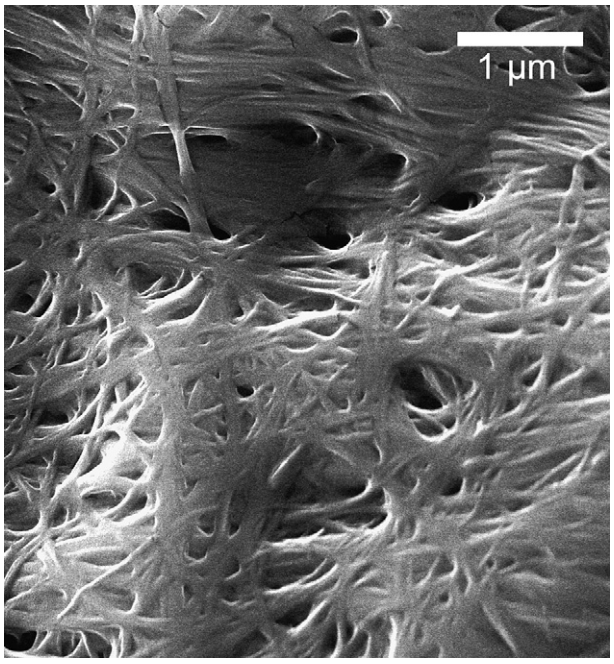


Figure 2. SEM images of self-assembled fibers of **1a** formed in ethyl acetate.

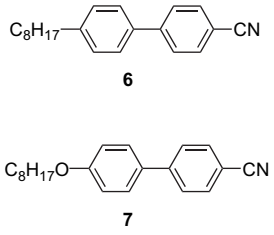


Figure 3. Molecular structures of smectic liquid crystals **6** and **7**.

Table 2. Gelation properties of isoleucine derivatives for liquid crystals[a]

Solvent	1a	1b	2
6	G	P	G
7	G	P	G

[a] Gelation tests were conducted at 3 wt %. The following abbreviations are used: P, precipitate; G, gel.

sol–gel transition temperatures lower than those of **2**.[16a] For example, the $T_{sol-gel}$ of the mixture containing 3 wt% of **1a** is 15 °C. The isotropic–nematic and nematic–smectic A transition temperatures of **6** decrease as the concentration of **1a** increases. In our previous studies,[14–16] the phase transition temperatures of liquid crystals were not changed greatly by the addition of gelators. The present result indicates that the dissolved carbazole-containing molecules disturb the order of the LC molecules.

2.4. Anisotropic fiber growth in liquid crystals

For the mixtures of gelators and liquid crystals, fibrous self-assembly occurs in the anisotropic environment on cooling, if sol–gel transition temperatures are lower than isotropic–anisotropic (LC) transition temperatures.[1e,16b,18,19] We

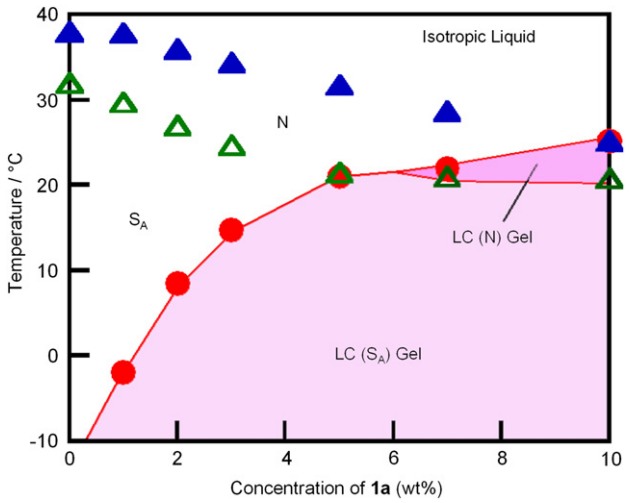


Figure 4. Phase diagram of the mixtures of **6/1a**. N: nematic, S_A: smectic A.

reported that anisotropically aligned fibers of **2** and other gelators were obtained in homogeneously oriented LC states.[18,19] We have found that carbazole-containing gelator **1a** also forms oriented fibers in the temperature range of the smectic A phases of **6** and **7**.

The SEM and optical micrograph of the aligned fibers of **1a** grown in the mixture forming an oriented smectic A state of **7** on the rubbed polyimide surface are shown in Figure 5. The SEM sample was prepared from a xerogel after extracting **7** by immersing the thin film containing aligned **1a** fibers and **7** in hexane. The inset shows an optical micrograph of the SEM sample. The growth direction of fibers is parallel to the direction of the LC molecules. In contrast, in our previous study,[19a] compound **2** formed aligned fibers grown perpendicular to the direction of LC molecules in oriented smectic states. The content of **1a** in the mixture with **7** shown in Figure 5 is 10 wt%, which is much larger than that used in our previous study on **2**. The larger amount of **1a** in the S_A phase might induce less ordered layer structures, which results in the disturbance of the development of fibers along the layer direction.

The anisotropic structures of the gelators have been examined by polarized infrared spectroscopy. Figure 6 shows the polar plot for the peak areas of the C≡N stretching of **7** at 2225 cm^{-1} and C=O stretching of **1a** at 1688 cm^{-1}, which indicates that these two stretching bands are parallel to each other. Therefore, hydrogen-bonded 1D chains of **1a** align along the growing direction of fibers. This spectroscopic result is consistent with the microscopic observations.

2.5. Self-assembled structures of carbazole-containing gelators

The temperature-variable spectroscopic studies of the gels reveal the self-assembling behavior of the gelators on sol–gel transitions. The infrared measurements of the mixture of **6** and **1a** show that the fibrous self-assembly is driven by hydrogen bonding, similar to compound **2**. The peaks at 1726 (C=O stretching of urethane), 1676 (amide I), and 1517 cm^{-1} (amide II) in the sol state shift to 1687, 1644, and 1542 cm^{-1} in the gel state, respectively. As for the

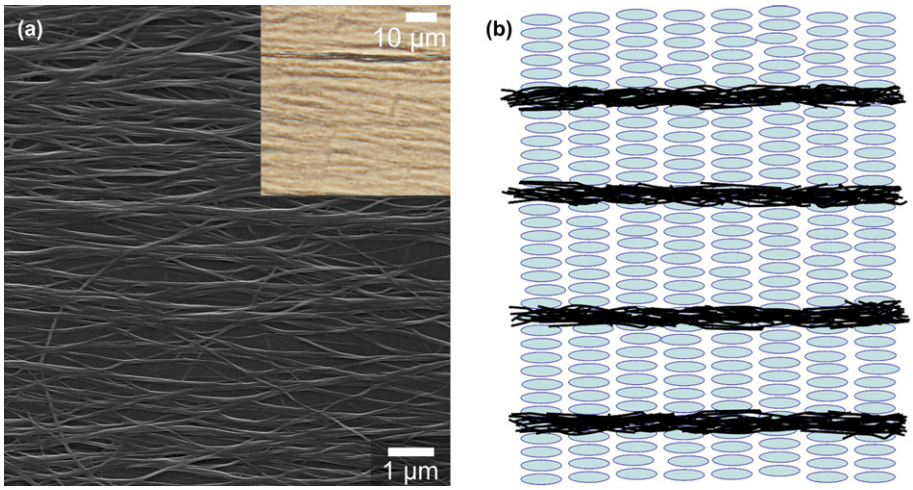


Figure 5. SEM image (a) and schematic illustration (b) of anisotropically aligned fibers of **1a** grown in **7** (**1a**: 10 wt%) on a rubbed polyimide surface. Inset: optical micrograph of aligned fibers after the extraction of **7**.

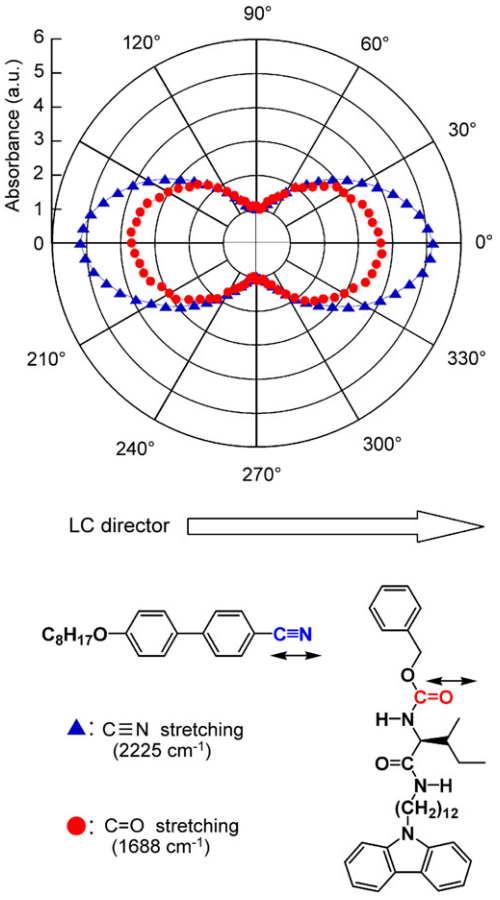


Figure 6. Polar plot of IR bands for the mixture of **7**/**1a** (**1a**: 10 wt%).

UV–vis absorption spectra of thin films of the mixture of **6** and **1a**, the peak attributable to S_1–S_0 transition of a carbazolyl moiety shifts from 347 nm in the sol state to 350 nm in the gel state. Figure 7 shows the fluorescence spectra of **1a** in ethyl acetate. In a sol state, structured emission bands around 353 and 369 nm are observed, which are assigned to the monomer and partially overlapped excimer emission bands of carbazoles, respectively. In the gel state, the monomer emission band at 353 nm disappears, and new emission

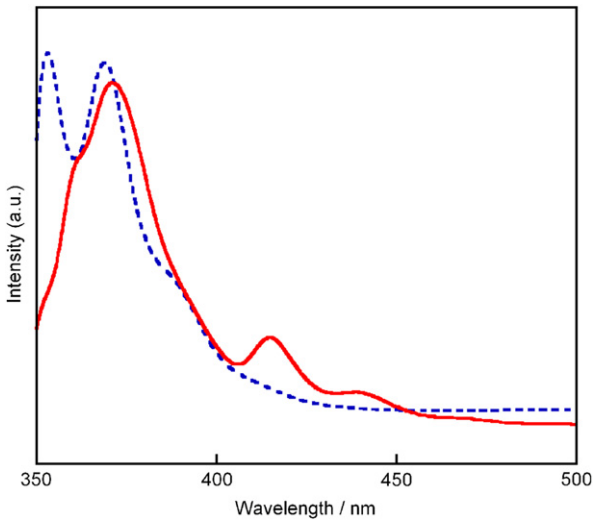


Figure 7. Comparison of fluorescent spectra of **1a** in ethyl acetate; a gel state (line) and a sol state (dotted line).

bands appear around 415 and 440 nm. These lower energy emission bands are attributable to the formation of sandwich-type excimers.[27,28] These spectral changes suggest that stacking of carbazolyl moieties occurs on sol–gel transitions, leading to 1D accumulation of carbazolyl moieties in self-assembled fibers.

Based on the present results, the phase-segregated structures consisting of aligned fibers of carbazole-containing gelators and homogeneously oriented smectic A states are schematically illustrated in Figure 8. The gelator molecules are one-dimensionally assembled through hydrogen bonding involving amide and urethane groups in liquid crystals, resulting in the formation of oriented fibers. In these fibers, carbazolyl moieties are stacked on one another, which will lead to the formation of photoconducting paths.

3. Conclusion

Carbazole-containing gelators with an isoleucine scaffold form elongated self-assembled fibers and act as efficient

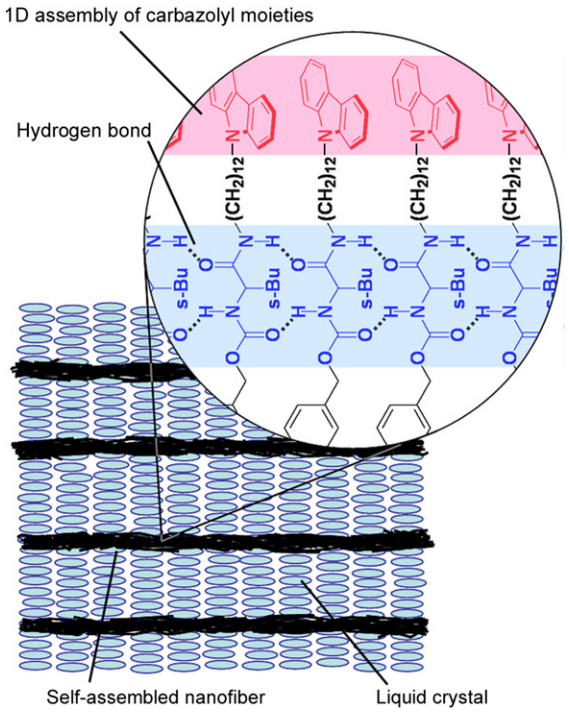


Figure 8. Schematic illustration of phase-segregated structures based on **7** and **1a**.

gelators for common organic solvents and liquid crystals. The carbazolyl moieties are stacked in the one-dimensionally aligned fibers. Aligned fibers have been obtained in the homogeneously oriented smectic liquid crystals. These results may lead to the development of new functional self-assembled 1D fibers, with the direction of their orientation being controlled on the substrates.

4. Experimental

4.1. General method

Unless otherwise noted, chemical reagents and solvents were used without further purification. As for *N*,*N*-dimethylformamide (DMF) and dichloromethane, commercially available anhydrous solvents were used for reaction. All reactions were carried out under an argon atmosphere. As for precursors of gelators, carbazolylbromoalkanes were synthesized according to the procedure reported by Bu et al.[29] Synthetic procedures of isoleucine derivatives are shown in Scheme 1. ^{1}H NMR and ^{13}C NMR spectra were determined with a Jeol JNM-400EX and a JNM-270EX. Infrared spectra were recorded on a Jasco FTIR-660Plus spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400II CHNS/O elemental analyzer. UV–vis spectra were recorded on an Agilent 8453 spectrometer equipped with a Mettler FP-82HT hot stage. Fluorescent spectra were recorded on a Jasco FP-777W equipped with an ECT-271 temperature controller.

4.1.1. 1-Bromo-12-carbazol-9-yldodecane (3a). To a mixture of tetrabutylammonium iodide (TBAI, 0.310 g, 0.8 mmol) and aqueous 50% sodium hydroxide (50 mL), 1,12-dibromododecane (3.51 g, 63 mmol) and a solution of carbazole (3.51 g, 21 mmol) in benzene (50 mL) were added. The reaction mixture was stirred for 3 days at room temperature, and then poured into water. The solution was extracted by dichloromethane. The organic layer was washed with water and brine, and dried on anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography, first with hexane and then with hexane/dichloromethane (8:1) as eluent to afford **3a** (7.03 g, 81%) as a white solid (found: C, 69.35; H, 7.99; N, 3.19. Calcd for $C_{24}H_{32}BrN$: C, 69.56; H, 7.78; N, 3.38%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13–8.10 (m, 2H, Ar*H*), 7.50–7.40 (m, 4H, Ar*H*), 7.25–7.21 (m, 2H, Ar*H*), 4.31 (t, J=6.7 Hz, 2H, NCH_2), 3.41 (t, J=6.5 Hz, 2H, BrCH_2), 1.87–1.81 (m, 4H, NCH$_2$CH_2), 1.40–1.23 (m, 16H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 140.41, 125.54, 122.79, 120.32, 118.67, 108.63, 43.07, 34.07, 32.81, 29.44, 29.40, 29.36, 28.97, 28.72, 28.16, 27.23; IR (KBr): ν 3048, 2920, 2852, 1598, 1484, 749, 723, 645 cm^{-1}.

4.1.2. 1-Bromo-6-carbazol-9-ylhexane (3b). This compound was synthesized as described above for **3a**, starting from 1,6-dibromohexane (11.0 g, 45 mmol) and carbazole (2.51 g, 15 mmol) to afford **3b** (3.87 g, 78%) as a white solid (found: C, 65.49; H, 6.33; N, 4.08. Calcd for $C_{18}H_{20}BrN$: C, 65.46; H, 6.10; N, 4.24%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13–8.10 (m, 2H, Ar*H*), 7.49–7.39 (m, 4H, Ar*H*), 7.25–7.22 (m, 2H, Ar*H*), 4.32 (t, J=4.8 Hz, 2H, NCH_2), 3.37 (t, J=4.4 Hz, 2H, BrCH_2), 1.92–1.88 (m, 2H, NCH$_2$CH_2), 1.83–1.78 (m, 2H, BrCH$_2$CH_2), 1.53–1.40 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 140.36, 125.59, 122.80, 120.36, 118.76, 108.57, 42.84, 33.71, 32.54, 28.81, 27.91, 26.45; IR (KBr): ν 3044, 2926, 2855, 1593, 1484, 755, 726, 638 cm^{-1}.

4.1.3. *N*-(12-Carbazol-9-yldodecyl)phthalimide (4a). A mixture of **3a** (4.14 g, 10 mmol) and potassium phthalimide (2.78 g, 15 mmol) in DMF (70 mL) was stirred for 9 h at 80 °C, and then poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with water and brine followed by drying on anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane/ethyl acetate (7:1) as eluent to afford **4a** (4.79 g, 100%) as a white solid (found: C, 80.06; H, 7.82; N, 5.62. Calcd for $C_{32}H_{36}N_2O_2$: C, 79.96; H, 7.55; N, 5.83%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, J=7.2 Hz, 2H, Ar*H*), 7.84–7.83 (m, 2H, Ar*H*), 7.71–7.69 (m, 2H, Ar*H*), 7.48–7.42 (m, 4H, Ar*H*), 7.24–7.20 (m, 2H, Ar*H*), 4.31 (t, J=7.4 Hz, 2H, NCH_2), 3.67 (t, J=7.4 Hz, 2H, NCH_2), 1.88–1.84 (m, 2H, NCH$_2$CH_2), 1.66–1.64 (m, 2H, NCH$_2$CH_2), 1.30–1.22 (m, 16H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 168.45, 140.41, 133.80, 132.18, 125.52, 123.11, 122.79, 120.29, 118.65, 108.63, 43.07, 38.06, 29.45, 29.36, 29.11, 28.93, 28.57, 27.28, 26.83; IR (KBr): ν 3046, 2926, 2848, 1772, 1718, 1598, 1484, 750, 721 cm^{-1}.

4.1.4. *N*-(6-Carbazol-9-ylhexyl)phthalimide (4b). This compound was synthesized as described above for **4a**, starting from **3b** (3.17 g, 9.6 mmol) and potassium phthalimide (2.13 g, 11.5 mmol) to afford **4b** (3.81 g, 100%) as a yellowish liquid (found: C, 78.70; H, 6.32; N, 6.90. Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07%); ^{1}H NMR

($CDCl_3$, 400 MHz): δ 8.09 (d, J=8.0 Hz, 2H, Ar*H*), 7.84–7.81 (m, 2H, Ar*H*), 7.72–7.69 (m, 2H, Ar*H*), 7.47–7.38 (m, 4H, Ar*H*), 7.23–7.19 (m, 2H, Ar*H*), 4.31 (t, J=7.0 Hz, 2H, NCH_2), 3.66 (t, J=7.4 Hz, 2H, NCH_2), 1.91–1.84 (m, 2H, NCH_2CH_2), 1.68–1.61 (m, 2H, NCH_2CH_2), 1.43–1.37 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 168.39, 140.36, 133.84, 132.13, 125.57, 123.15, 122.80, 120.31, 118.71, 108.57, 42.90, 37.83, 28.83, 28.45, 26.87, 26.62; IR (KBr): ν 3050, 2935, 2857, 1771, 1711, 1596, 1484, 751, 720 cm^{-1}.

4.1.5. 12-Carbazol-9-yldodecylamine (5a). To a solution of **4a** (1.01 g, 2.1 mmol) in ethanol (50 mL), hydrazine monohydrate (0.15 mL) was added. The reaction mixture was stirred for 2 h under reflux followed by the removal of the solvent under reduced pressure. The residue was dissolved in chloroform and 10% aqueous NaOH. The solution was extracted with chloroform. The organic layer was dried on anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure to afford **5a** (0.709 g, 96%) as a yellowish solid (found: C, 82.40; H, 9.98; N, 7.92. Calcd for $C_{24}H_{34}N_2$: C, 82.23; H, 9.78; N, 7.99%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, J=8.0 Hz, 2H, Ar*H*), 7.48–7.38 (m, 4H, Ar*H*), 7.24–7.19 (m, 2H, Ar*H*), 4.28 (t, J=7.2 Hz, 1H, NCH_2), 2.70–2.61 (m, 2H, NH_2CH_2), 1.90–1.83 (m, 2H, NCH_2CH_2), 1.44–1.23 (m, 18H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 140.43, 125.54, 122.80, 120.32, 118.67, 108.63, 43.09, 42.10, 33.44, 29.53, 29.47, 29.44, 28.97, 27.32, 26.85; IR (KBr): ν 3337, 3049, 2923, 2851, 1628, 1597, 1484, 749, 721 cm^{-1}.

4.1.6. 6-Carbazol-9-ylhexylamine (5b). This compound was synthesized as described above for **5a**, starting from **4b** (3.77 g, 9.5 mmol) to afford **5b** (2.00 g, 79%) as a yellowish liquid (found: C, 80.92; H, 8.37; N, 10.28. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, J=7.2 Hz, 2H, Ar*H*), 7.49–7.39 (m, 4H, Ar*H*), 7.25–7.21 (m, 2H, Ar*H*), 4.31 (d, J=7.4 Hz, 2H, NCH_2), 2.66–2.62 (m, 2H, NH_2CH_2), 1.92–1.85 (m, 2H, NCH_2CH_2), 1.44–1.37 (m, 6H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 140.43, 125.59, 122.84, 120.36, 118.74, 108.62, 43.00, 41.90, 33.19, 28.97, 27.15, 26.67; IR (KBr): ν 3431, 3048, 2926, 2856, 1627, 1595, 1484, 750, 725 cm^{-1}.

4.1.7. *N*-Benzyloxycarbonyl-L-isoleucine 12-carbazol-9-yldodecylamide (1a). To a solution of **5a** (1.40 g, 4.0 mmol) and *N*-benzyloxycarbonyl-L-isoleucine (1.06 g, 4.0 mmol) in dichloromethane (40 mL), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.92 g, 4.8 mmol) was added. The reaction mixture was stirred for 3 h. Then the solution was extracted by chloroform. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine followed by drying on anhydrous $MgSO_4$. After filtration, the solution was removed under reduced pressure. The residue was purified by column chromatography with hexane/ethyl acetate (3:1) as eluent to afford **1a** (1.56 g, 65%) as a white solid (found: C, 76.07; H, 8.37; N, 7.41. Calcd for $C_{38}H_{51}N_3O_3$: C, 76.34; H, 8.60; N, 7.03%); mp 106 °C (from hexane/ethyl acetate); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, J=7.6 Hz, 2H, Ar*H*), 7.48–7.21 (m, 11H, Ar*H*), 5.76 (m, 1H, N*H*), 5.30 (m, 1H, N*H*), 5.10 (s, 2H, PhCH_2O), 4.30 (t, J=7.2 Hz, 2H, NCH_2), 3.92 (t, J=6.8 Hz, 1H, NHC*H*CO), 3.21 (m, 2H, NHCH_2), 1.89–1.85 (m, 4H, NCH_2CH_2, $NHCH_2CH_2$), 1.47–1.23 (m, 21H, CH_2), 0.93–0.88 (m, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.93, 156.31, 140.39, 136.18, 128.52, 128.18, 128.00, 125.52, 122.76, 120.30, 118.64, 108.61, 67.00, 59.90, 43.05, 39.50, 37.29, 29.45, 29.39, 29.17, 28.95, 27.29, 26.83, 24.76, 15.51, 11.34; IR (KBr): ν 3295, 3053, 2958, 2924, 2852, 1689, 1646, 1598, 1537, 1485, 784, 721, 696 cm^{-1}.

4.1.8. *N*-Benzyloxycarbonyl-L-isoleucine 6-carbazol-9-ylhexylamide (1b). This compound was synthesized as described above for **1a**, starting from **5b** (1.12 g, 4.2 mmol) and *N*-benzyloxycarbonyl-L-isoleucine (1.06 g, 4.0 mmol). The crude product was purified by column chromatography first with hexane/ethyl acetate/chloroform (2:1:1) and then with chloroform as eluent to afford **1b** (0.91 g, 44%) as a white solid (found: C, 74.88; H, 8.04; N, 8.48. Calcd for $C_{32}H_{39}N_3O_3$: C, 74.82; H, 7.65; N, 8.18%); mp 172 °C (from ethyl acetate/chloroform); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (d, J=7.6 Hz, 1H, Ar*H*), 8.11 (d, J=6.8 Hz, 1H, Ar*H*), 7.50–7.21 (m, 11H, Ar*H*), 5.77–5.76 (m, 1H, N*H*), 5.29–5.27 (m, 1H, N*H*), 5.09 (s, 2H, PhCH_2O), 4.30 (t, J=7.6 Hz, 2H, NCH_2), 3.93–3.88 (m, 1H, NHC*H*), 3.26–3.16 (m, 2H, NHCH_2), 1.87 (m, 3H, NCH_2CH_2, NHCHC*H*), 1.45–1.39 (m, 8H, CH_2), 0.93–0.88 (m, 6H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 170.85, 155.88, 139.89, 137.04, 128.20, 127.62, 127.50, 125.56, 121.95, 120.17, 118.53, 109.09, 65.22, 59.16, 42.07, 38.23, 36.24, 28.74, 28.35, 26.09, 25.99, 24.34, 15.29, 10.81; IR (KBr): ν 3298, 3054, 2955, 2935, 2856, 1689, 1642, 1598, 1541, 1486, 750, 723, 697 cm^{-1}.

4.2. Gelation test

Gelation properties for common organic solvents were tested at 40 g L^{-1}. In a typical gelation experiment, an organic solvent (0.5 mL) was added to a weighed sample (20 mg) in a test tube. The tube was sealed and heated until a clear solution was obtained. The resultant solution was allowed to cool to room temperature. Then gelation was checked visually. When the tube could be inverted without any flow, it was considered as 'gel'. When the mixture remained solution at room temperature, it was further cooled in a refrigerator to check whether gelation occurred at lower temperature. When the gel formed at lower temperature was stable even at room temperature, it was also considered as gel. As for the gelation of liquid crystals, gelators and liquid crystals were mixed in a sealed test tube in various ratios. If needed, chloroform was added to obtain a homogeneous solution. The mixtures were heated to isotropic states, and then cooled to appropriate temperatures after the removal of chloroform.

4.3. Characterization of anisotropic gels

The phase transition behavior of the samples was determined by DSC measurements and microscopic observation. DSC measurements were performed with a Mettler DSC 30. Heating and cooling rates were 5 °C min^{-1} in all cases. The transition temperatures of the gels were taken at the maximum of transition peaks. A polarizing optical microscope, an Olympus BH2 equipped with a Mettler FP82HT hot stage was used for visual observation.

4.4. Anisotropic fiber growth in aligned LC states

For anisotropic fiber growth, a parallel rubbed cell made of glass slides covered with rubbed polyimide layers on its surface was used. The rubbing directions of two glass slides were parallel to homogeneously align LC molecules. Microscopic observation of self-assembled fibers was performed on the samples as described above.

4.5. Scanning electron microscopic (SEM) observation

For the SEM observation of self-assembled fibers of gelators formed in organic solvents, a gelator was dissolved in solvents at a minimum gel concentration. A droplet of the solution was placed on a glass slide (5 mm×5 mm) and frozen by immersion in liquid nitrogen. Then the solvent was removed in vacuo. The glass was attached to the SEM sample stage. As for self-assembled fibers of gelators formed in liquid crystals, a mixture of liquid crystal and gelator in isotropic states was placed between glass slides. This glass cell was cooled to room temperature to form self-assembled fibers of gelators. SEM samples were prepared by immersing the glass cell in hexane for 12 h to extract the liquid crystal followed by drying at room temperature. All the samples were shaded with platinum and used for SEM observation. SEM observation was performed with a Hitachi S-900S. The accelerating voltage was 10 kV.

4.6. Polarized infrared spectroscopy

Polarized Infrared spectra were taken with a Jasco MFT-2000 spectrometer equipped with polarizers and a Mettler FP82 hot stage. Samples were prepared in a parallel rubbed cell using KBr plates instead of glass slides.

Acknowledgements

Partial financial support of Grants-in-Aid for Creative Scientific Research of 'Invention of Conjugated Electronic Structures and Novel Functions' (No. 16GS0209) (T.K.) from the Japan Society for the Promotion of Science (JSPS) and for The 21st Century COE Program of 'The Frontiers of Fundamental Chemistry Focusing on Molecular Dynamism' (T.K.) from the Ministry of Education, Culture, Sports, Science and Technology is gratefully acknowledged. Two of the authors (K.Y. and N.M.) are thankful for financial support by the Research Fellowships of JSPS for Young Scientists. We thank Dr. Tatsuya Nishimura and Mr. Yuki Hirai for their helpful discussion and technical assistance. We are also grateful to JSR Corporation for supplying the polyimide material.

References and notes

1. (a) Lehn, J.-M. *Science* **2002**, *295*, 2400–2403; (b) Ciferri, A. *Supramolecular Polymers*, 2nd ed.; Marcel Dekker: New York, NY, 2005; (c) Reinhoudt, D. N.; Crego-Calama, M. *Science* **2002**, *295*, 2403–2407; (d) Kato, T. *Science* **2002**, *295*, 2414–2418; (e) Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 38–68; (f) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546; (g) Ikkala, O.; ten Brinke, G. *Chem. Commun.* **2004**, 2131–2137.
2. (a) Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237–1247; (b) van Esch, J. H.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263–2266; (c) Shinkai, S.; Murata, K. *J. Mater. Chem.* **1998**, *8*, 485–495; (d) *Molecular Gels*; Weiss, R. G., Terech, P., Eds.; Kluwer Academic: Amsterdam, 2005; (e) Liu, X. Y. *Top. Curr. Chem.* **2005**, *256*, 1–37; (f) Žinic, M.; Vögtle, F.; Fages, F. *Top. Curr. Chem.* **2005**, *256*, 39–76; (g) Fages, F.; Vögtle, F.; Žinic, M. *Top. Curr. Chem.* **2005**, *256*, 77–131; (h) Araki, K.; Yoshikawa, I. *Top. Curr. Chem.* **2005**, *256*, 133–165; (i) Brizard, A.; Oda, R.; Huc, I. *Top. Curr. Chem.* **2005**, *256*, 167–218; (j) Kato, T.; Mizoshita, N.; Moriyama, M.; Kitamura, T. *Top. Curr. Chem.* **2005**, *256*, 219–236; (k) Hirst, A. R.; Smith, D. K. *Top. Curr. Chem.* **2005**, *256*, 237–273; (l) Estroff, L. A.; Hamilton, A. D. *Chem. Rev.* **2004**, *104*, 1201–1218; (m) Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev.* **2005**, *34*, 821–836.
3. (a) Hanabusa, K.; Yamada, M.; Kimura, M.; Shirai, H. *Angew. Chem., Int. Ed.* **1996**, *35*, 1949–1951; (b) Hafkamp, R. J. H.; Feiters, M. C.; Nolte, R. J. M. *J. Org. Chem.* **1999**, *64*, 412–426; (c) Yoza, K.; Amanokura, N.; Ono, Y.; Akao, T.; Shinmori, H.; Takeuchi, M.; Shinkai, S.; Reinhoudt, D. N. *Chem.—Eur. J.* **1999**, *5*, 2722–2729; (d) van Esch, J.; Schoonbeek, F.; de Loos, M.; Kooijman, H.; Spek, A. L.; Kellogg, R. M.; Feringa, B. L. *Chem.—Eur. J.* **1999**, *5*, 937–950; (e) Brotin, T.; Utermöhlen, R.; Fages, F.; Bouas-Laurent, H.; Desvergne, J.-P. *J. Chem. Soc., Chem. Commun.* **1991**, 416–418; (f) Estroff, L. A.; Hamilton, A. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 3447–3450; (g) Yabuuchi, K.; Marfo-Owusu, E.; Kato, T. *Org. Biomol. Chem.* **2003**, *1*, 3464–3469; (h) Dykes, G. M.; Smith, D. K. *Tetrahedron* **2003**, *59*, 3999–4009; (i) Trivedi, D. R.; Ballabh, A.; Dastidar, P.; Ganguly, B. *Chem.—Eur. J.* **2004**, *10*, 5311–5322.
4. (a) Inoue, D.; Suzuki, M.; Shirai, H.; Hanabusa, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 721–726; (b) Suzuki, M.; Sato, T.; Kurose, A.; Shirai, H.; Hanabusa, K. *Tetrahedron Lett.* **2005**, *46*, 2741–2745; (c) Makarević, J.; Jokić, M.; Perić, B.; Tomišić, V.; Kojić-Prodić, B.; Žinić, M. *Chem.—Eur. J.* **2001**, *7*, 3328–3341.
5. (a) Schoonbeek, F. S.; van Esch, J.; Wegewijs, B.; Rep, D. B. A.; Klapwijk, T. M.; Kellogg, R. M.; Feringa, B. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1393–1397; (b) Liu, P.; Shirota, Y.; Osada, Y. *Polym. Adv. Technol.* **2000**, *11*, 512–517.
6. (a) Ishi-i, T.; Jung, J. H.; Shinkai, S. *J. Mater. Chem.* **2000**, *10*, 2238–2240; (b) Kimura, M.; Kitamura, T.; Muto, T.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *Chem. Lett.* **2000**, 1088–1089.
7. (a) Jørgensen, M.; Bechgaard, K. *J. Org. Chem.* **1994**, *59*, 5877–5882; (b) Kitahara, T.; Shirakawa, M.; Kawano, S.; Beginn, U.; Fujita, N.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 14980–14981.
8. Kitamura, T.; Nakaso, S.; Mizoshita, N.; Tochigi, Y.; Shimomura, T.; Moriyama, M.; Ito, K.; Kato, T. *J. Am. Chem. Soc.* **2005**, *127*, 14769–14775.
9. (a) Tamaoki, N.; Shimada, S.; Okada, Y.; Belaissaoui, A.; Kruz, G.; Yase, K.; Matsuda, H. *Langmuir* **2000**, *16*, 7545–7547; (b) Masuda, M.; Hanada, T.; Okada, Y.; Yase, K.; Shimizu, T. *Macromolecules* **2000**, *33*, 9233–9238.
10. Su, L.; Bao, C.; Lu, R.; Chen, Y.; Xu, T.; Song, D.; Tan, C.; Shi, T.; Zhao, Y. *Org. Biomol. Chem.* **2006**, *4*, 2591–2594.

11. (a) Li, X.-Q.; Stepanenko, V.; Chen, Z.; Prins, P.; Siebbelesb, L. D. A.; Würthner, F. *Chem. Commun.* **2006**, 3871–3873; (b) George, S. J.; Ajayaghosh, A.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 3422–3425.
12. Kamikawa, Y.; Kato, T. *Langmuir* **2007**, *23*, 274–278.
13. (a) Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664–6676; (b) de Loos, M.; van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 613–616; (c) Moriyama, M.; Mizoshita, N.; Yokota, T.; Kishimoto, K.; Kato, T. *Adv. Mater.* **2003**, *15*, 1335–1338; (d) Moriyama, M.; Mizoshita, N.; Kato, T. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 962–964; (e) Moriyama, M.; Mizoshita, N.; Kato, T. *Polym. J.* **2004**, *36*, 661–664; (f) Mamiya, J.; Kanie, K.; Hiyama, T.; Ikeda, T.; Kato, T. *Chem. Commun.* **2002**, 1870–1871; (g) Sugiyasu, K.; Fujita, N.; Takeuchi, M.; Yamada, S.; Shinkai, S. *Org. Biomol. Chem.* **2003**, *1*, 895–899; (h) Zhao, Y.; Tong, X. *Adv. Mater.* **2003**, *15*, 1431–1435; (i) Deindörfer, P.; Eremin, A.; Stannarius, R.; Davisa, R.; Zentel, R. *Soft Matter* **2006**, *2*, 693–698.
14. Kato, T.; Kutsuna, T.; Hanabusa, K.; Ukon, M. *Adv. Mater.* **1998**, *10*, 606–608.
15. Yabuuchi, K.; Rowan, A. E.; Nolte, R. J. M.; Kato, T. *Chem. Mater.* **2000**, *12*, 440–443.
16. (a) Mizoshita, N.; Hanabusa, K.; Kato, T. *Adv. Mater.* **1999**, *11*, 392–394; (b) Mizoshita, N.; Hanabusa, K.; Kato, T. *Adv. Funct. Mater.* **2003**, *13*, 313–317.
17. Mizoshita, N.; Suzuki, Y.; Hanabusa, K.; Kato, T. *Adv. Mater.* **2005**, *17*, 692–696.
18. Mizoshita, N.; Kato, T. *Adv. Funct. Mater.* **2006**, *16*, 2218–2224.
19. (a) Mizoshita, N.; Kutsuna, T.; Hanabusa, K.; Kato, T. *Chem. Commun.* **1999**, 781–782; (b) Kato, T.; Kutsuna, T.; Yabuuchi, K.; Mizoshita, N. *Langmuir* **2002**, *18*, 7086–7088.
20. Mizoshita, N.; Monobe, H.; Inoue, M.; Ukon, M.; Watanabe, T.; Shimizu, Y.; Hanabusa, K.; Kato, T. *Chem. Commun.* **2002**, 428–429.
21. (a) Kubo, W.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S. *Chem. Commun.* **2002**, 374–375; (b) Placin, F.; Desvergne, J.-P.; Lassègues, J.-C. *Chem. Mater.* **2001**, *13*, 117–121; (c) Hanabusa, K.; Hiratsuka, K.; Kimura, M.; Shirai, H. *Chem. Mater.* **1999**, *11*, 649–655.
22. (a) Hanabusa, K.; Fukui, H.; Suzuki, M.; Shirai, H. *Langmuir* **2005**, *21*, 10383–10390; (b) Ikeda, A.; Sonoda, K.; Ayabe, M.; Tamaru, S.; Nakashima, T.; Kimizuka, N.; Shinkai, S. *Chem. Lett.* **2001**, 1154–1155.
23. (a) van Bommel, K. J. C.; Friggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980–999; (b) Kobayashi, S.; Hanabusa, K.; Hamasaki, N.; Kimura, M.; Shirai, H.; Shinkai, S. *Chem. Mater.* **2000**, *12*, 1523–1525; (c) Yang, Y.; Fukui, H.; Suzuki, M.; Shirai, H.; Hanabusa, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 2069–2074.
24. (a) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141–143; (b) Hulvat, J. F.; Stupp, S. I. *Angew. Chem., Int. Ed.* **2003**, *42*, 778–781; (c) Bushey, M. L.; Nguyen, T.-Q.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 8264–8269; (d) Li, L.; Beniash, E.; Zubarev, E. R.; Xiang, W.; Rabatic, B. M.; Zhang, G.; Stupp, S. I. *Nature Mater.* **2003**, *2*, 689–694.
25. (a) Beginn, U.; Zipp, G.; Möller, M. *Adv. Mater.* **2000**, *12*, 510–513; (b) Yoshio, M.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2004**, *126*, 994–995.
26. (a) Hogel, H. *J. Phys. Chem.* **1965**, *69*, 755–766; (b) Pai, D. M. *J. Chem. Phys.* **1970**, *52*, 2285–2291.
27. Dutta, A. K. *Langmuir* **1996**, *12*, 5909–5914.
28. (a) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697–4709; (b) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2082–2088.
29. Li, X.; Mintz, E. A.; Bu, X. R.; Zehnder, O.; Bosshard, C.; Günter, P. *Tetrahedron* **2000**, *56*, 5785–5791.