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SYNTHESIS AND MESOMORPHISM OF THE BIPEDAL LIQUID CRYSTALS WITH A TETRATHIAFULVALENE/DITHIOLE AND TWO CHOLESTEROL MOIETIES

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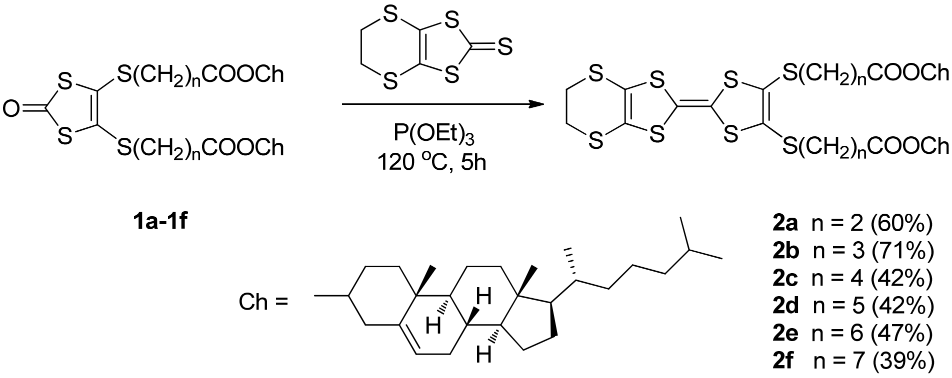
Abstract – The bipedal 1,3-dithiole-2-thiones and the appropriate EDT-TTFs bearing two cholesteryl linked with two ω-thioalkanoyloxy spacers of varying length were synthesized. All of bipedals showed mesogenic phases in a wide temperature region, no crystallization but vitrifying to form glassy mesogens during cooling from the isotropic melt.

Liquid crystals (LCs),[1] possessing nanometre-scale molecular architectures and unique chemical and physical properties, have attracted considerable attention of late on account of their applications in optical memory,[2] display devices,[3] holographic data storage devices,[4] and so on. Tetrathiafulvalene (TTF) derivatives have played a pivotal role in the development of organic materials for optoelectronic application due to their excellent electron-donating properties.[5] The transport properties of TTF-based organic materials are clearly dependent on the molecular architecture in the solid state and so a wide variety of substituents have been introduced at the periphery of the TTF core in order to achieve a suitable solid-state organization.[6] Concerning tetrathiafulvalene derivatives, the most relevant results have been reached via two well-established techniques, namely, electrocrystallization and deposition of Langmuir-Blodgett films. In this respect, another effective approach is based on the preparation of mesogenic compounds. In particular, glassy liquid crystals (GLCs) hold a fast and good orientation, which can be readily processed into macroscopically ordered solid films.[7] Although a considerable number of TTF derivatives have so far been synthesized, there are only a few reports describing TTF derivatives with mesomorphic properties[8] and consequently, it is not yet possible to establish structure-property relationships for this family of compounds. Very recently, we reported that the polypedals derived from TTF and cholesterol exhibited smectic and /or hexagonal columnar phases, which depended on the length of spacers.[9] In order to create new TTF-based mesomorphic states, a series of cholesteryl with various alkyl chain lengths was introduced onto one side of the EDT-TTF core, which has exhibited a good conductive property. Here, we report the synthesis and mesomorphic properties of the dithiole and/or EDT-TTF based unsymmetrical bipedals **1a-1f** and **2a**-**2f** bearing two cholesteryl linked with two ω-thioalkanoyloxy spacers, together with the electron donating property of TTF central core. The structures and synthetic route of the bipedals were shown in Scheme 1. The starting 1,3-dithiole-2-ones (**1a**-**1f**) bearing two cholesteryl linked with two ω-thioalkanoyloxy spacers of varying length were easily transformed to the appropriate EDT-TTF based bipedals (**2a**-**2f**) by cross-coupling reaction with 4,5-ethylenedithio-1,3-dithiole-2-thione (EDDT) in net triethyl phosphate at 120 °C in reasonable yields (48–56%).



Scheme 1. Synthesis route of bipedal liquid crystals

The phase sequences and phase structures of bipedals **1a-1f** and **2a**-**2f** were in vestigated by polarized-light optical microscopy (POM), differential scanning calorimetry (DSC), and small-angle X-ray scatterings (SAXS). All of the synthesized bipedals exhibit mesophases in a wide temperature range including room temperature and no crystallization but vitrifying to form glassy smectic mesogen during cooling from the isotropic melt. In the case of dithiole-based bipetals, **1a**-**1c** exhibited only one mesophase in a wide temperature region in heating as well as in cooling cycle (Table 1). For example, **1c** (*n*=4) exhibited a liquid crystalline phase at a melting state (20.4 °C), which was transformed to an isotropic phase at 93.3 °C. On slow cooling of **1c** from the isotropic liquid to liquid crystalline phase at 89.8 °C, a fan-shaped texture was observed by POM experiment, which was transformed to glassy state at ca. 18.0 °C during cooling (Figure 1a and Figure 2a). The SAXS of **1c** measured at cooling to 60 °C displayed three sharp reflections with *d* spacings of 4.90, 2.40, and 1.60 nm, which were in the ratio of 3:2:1 and agreed well with (100), (200), and (300) reflections of a lamellar packing structure (Figure 1b). Considering that the layer thickness (4.90 nm) obtained from the X-ray diffraction pattern is much larger than the estimated molecular length (2.93 nm by CPK model) and the S…S interaction between dithiole, bimolecule arrangement in lamellar structure is expected, in which dithiole segments interdigitated to fill the space (Figure 3a). In contrast, **1d-1f** with the longer spacer (*n*=5-7) showed two phase transitions after

Table 1. Phase transition temperature and enthalpy changes of **1a**–**1f** and **2a-2f** determined by DSC in the second cooling scan[a] and their cyclic voltammetry vs SCE in CH_2Cl_2 (10^{-3} M).

Compund	Transition temperature (°C) and enthalpy changes (J·g^{-1}), Heating cycle /Cooling cycle	$E^1_{1/2}$/V	$E^2_{1/2}$/V
1a	g 29.7 S_A 117.2 (3.8) I / I 114.4 (4.6) S_A -- g		
1b	g 25.5 S_A 120.5 (2.9) I / I 115.5 (1.5) S_A -- g		
1c	g 20.4 S_A 93.3 (1.0) I / I 89.8 (1.47) S_A -- g		
1d	g 12.0 Col 76.0 (1.2) Ch 86.6 (1.0) I / I 84.3 (0.8) Ch 72.9 (1.2) Col 9.7 -- g		
1e	g 5.7 Col 65.9 (0.6) Ch 81.2 (0.3) I / I 79.9 (0.3) Ch 63.9 (0.6) Col 6.1 -- g		
1f	g 5.6 Col 71.4 (0.6) Ch 88.9 (0.8) I / I 87.3 (4.9) Ch 69.2 (0.7) Col 3.2 -- g		
DMTEDT-TTF[c]	--	0.479	0.718[b]
2a	g 66.3 S_A 97.3 (3.0) I / I 94.1 (2.0) S_A -- g	0.543	0.933
2b	g 55.8 S_A 84.2 (1.1) I / I 81.2 (1.1) S_A -- g	0.534	0.924
2c	g 48.4 S_A 84.6 (3.0) I / I 81.2 (3.2) S_A -- g	0.520	0.905
2d	g 40.0 S_A 58.0 (1.2) I / I 55.7 (1.3) S_A -- g	0.513	0.904
2e	g 37.8 S_A 76.1 (2.8) I / I 71.3 (2.6) S_A -- g	0.508	0.894
2f	g 32.0 S_A 72.6 (2.7) I / I 70.2 (2.6) S_A -- g	0.493	0.884

[a] g=glass state, S_A=smectic A, Col=columnar, I=isotropic; [b] ref 10;
[c] DMTEDT-TTF=Bis(methylthio)ethylenedithiotetrathiafulvalene.

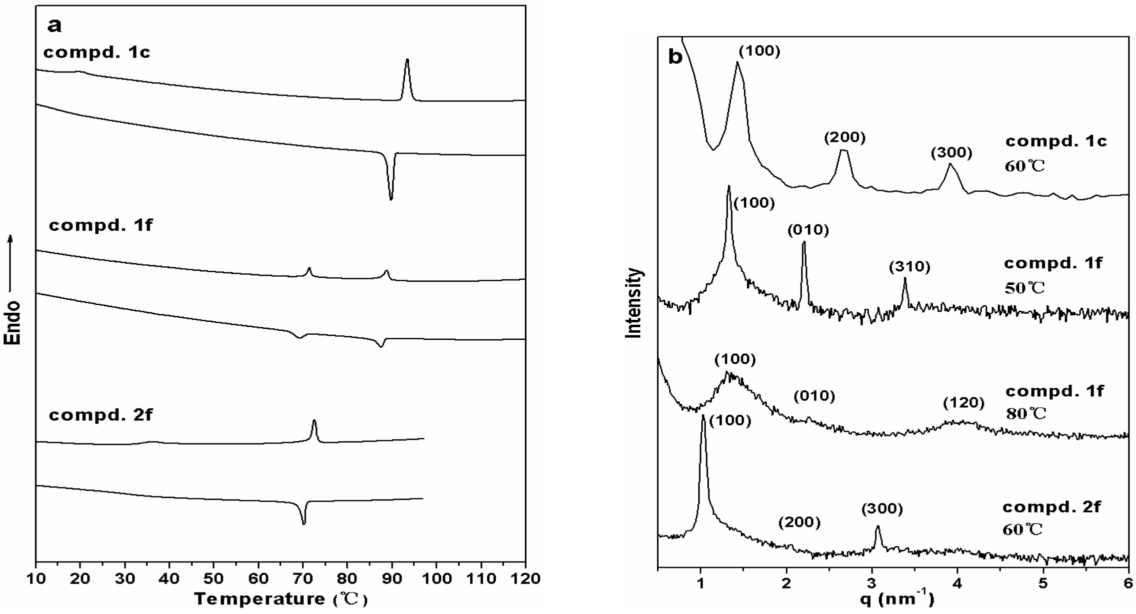


Figure 1. (a) DSC traces (10 °C /min) recorded during the second heating and cooling scans of **1c**, **1f** and **2f**; (b) X-ray diffraction patterns of **1c**, **1f** and **2f** plotted against q = 4π sinθ/λ.

melting of the rod block, while they display a lack of layered smectic phase. For example, **1f** with the longest spacer (n=7) displays two mesophases at 5.6 °C and 71.4 °C, followed by transformation to an isotropic phase at 88.9 °C (Figure 1a). Upon cooling from the isotropic liquid, a pseudo focal-conic texture was observed by POM experiment (Figure 2c). On further cooling to 69 °C, the pseudo

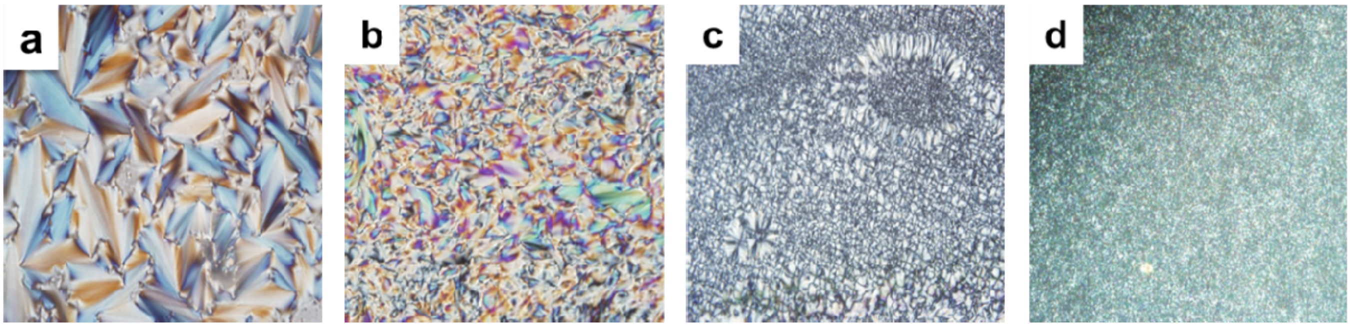


Figure 2. Optical polarized micrographs (40×) of the texture exhibited by (a) the S_{mA} phase of **1c** at 60 °C; (b) the Col_{oq} phase of **1f** at 50 °C; (c) the Col_{hd} phase of **1f** at 60 °C; (d) the S_{mA} phase of **2f**.

focal-conic texture was gradually transformed to a fan-like texture and the systems induce vitrification rather than crystallization during cooling (Table 1 and Figure 2c). The DSC curves together with optical textures preliminarily considered to be the oblique hexagonal columnar phase and disordered hexagonal columnar phase, respectively. To identify the detailed phase structure, SAXS studies were performed. The X-ray diffraction pattern of **1f** measured at cooling to 50°C displays three sharp reflections corresponding to spacing of 4.74, 2.85, and 1.85 nm in the small-angle region which could be indexed as (100), (010), and (310) planes of a 2-D oblique hexagonal columnar structure (Col_{ho}) with lattice parameters *a* =5.57 nm, *b* = 3.35 nm, and γ = 58.3° (Figure 1b). Wide-angle X-ray scattering (WAXS) data of molecule **1f** shows only a broad halo centered at approximately 0.50 nm. On the basis of the lattice constant, estimated molecular length (3.28 nm by CPK model) and the experimental values of the unit cell parameters (*a*, *b*, *c*, and γ) and the density (ρ),[11] the average numbers of molecule per cross-sectional slice of the column is calculated to be about 4, and the schematic representation of the oblipue columnar structure of **1f** can be illustrated as shown in Figure 3b. The X-ray diffractogram of **1f** taken at 80 °C shows two similar 100 and 010 peaks, but the intensity of the peaks was obviously lower and the peaks were diffused. The weaker diffraction and wider full width at half maximum (FWHM) measured at 80 °C are indicative of poorer long-range ordering of molecular stacking than that measured at 50 °C. Moreover, a very diffused peak emerged in 120 plane at the cost of disappearance of the peak of 310 plane, supporting the presence of a disordered hexagonal columnar phase with lattice parameters *a* =5.24 nm, *b* = 3.26 nm, and γ = 58.3° (Figure 3c). Considering the similarity of the phase sequences and optical textures with those of **1f**, **1d** and **1e** could also be expected to be the same phase structures. Unlike the TTF-based bipedals,[9] the EDT-TTF- based bipetals **2a**-**2f** exhibited only one mesophase (Table 1). In contrast the incorporation of the ethylenedithio unit (EDT) in **TTF** suppresses the columnar mesophase exhibited by its TTF-based analogue probably due to the increased rigid volume fraction.[9] For example, compound **2f** exhibits a birefringent liquid crystalline phase at a melting state (32 °C), followed by transformation to an isotropic phase at 72.6 °C (Figure 1a). On slow cooling of the isotropic liquid to 70.2 °C, a sanded texture was observed by POM experiment (Figure 2d), which also vitrifyied to from glassy mesogens with an above-ambient glass transition temperature (T_g) during cooling process upon further cooling. The SAXS of **2f** measured at cooling to 60 °C displayed three sharp reflections corresponding to spacing of 6.13, 3.10, and 2.02 nm, which were in the ratio of 3:2:1, and agreed well with (100), (200), and (300) reflections of lamellar packing structure (Figure 1b). The obtained molecular length of **2f** was 6.13 nm, which was close to the two molecular length (3.73 nm by CPK model), indicative of a bimolecule layer structure in which EDT-TTF segments interdigitated to fill the space (cf. Figure 3a). Considering the similarity of the optical textures with those of **2f**, **2a**-**2e** could also be indexed to lamellar arrangement.

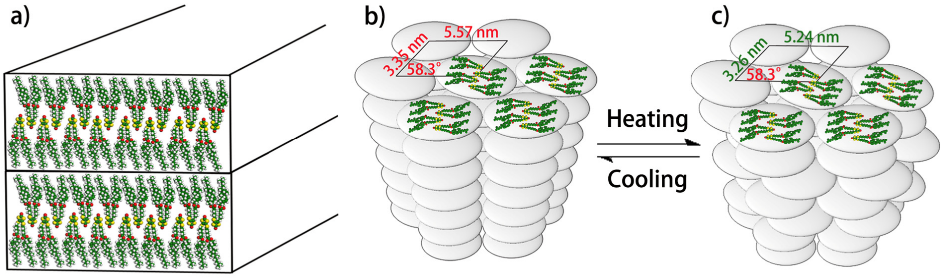


Figure 3. Schematic representation for (a) the smectic phase of **1c**, (b) the oblique columnar phase of **1f**, and (c) the disordered oblique columnar phase of **1f**.

To evaluate electron donating property of EDT-TTF based bipedal **2a**-**2f**, the cyclic voltammetry (CV) measurements were performed in a dry CH_2Cl_2 solution with a scan rate of 100 mV s^{-1} at room temperature. The bipedal **2a**-**2f** show two reversible oxidation peaks at ~0.49 and ~0.95 V, corresponding to the formation of radical cations and dications of TTF core, respectively, indicating two sequential reversible one-electron transfer steps (Figure 4a and Table 1). The oxidation potentials of **2a**-**2f** are higher than those of DMTEDT-TTF[10] probably due to the existence of electron withdrawing ester linkages in the distance. Therefore, as the methylene spacer lengthened (from n=2 to n=7), the halfwave potential was anodic shifted in a regular manner.

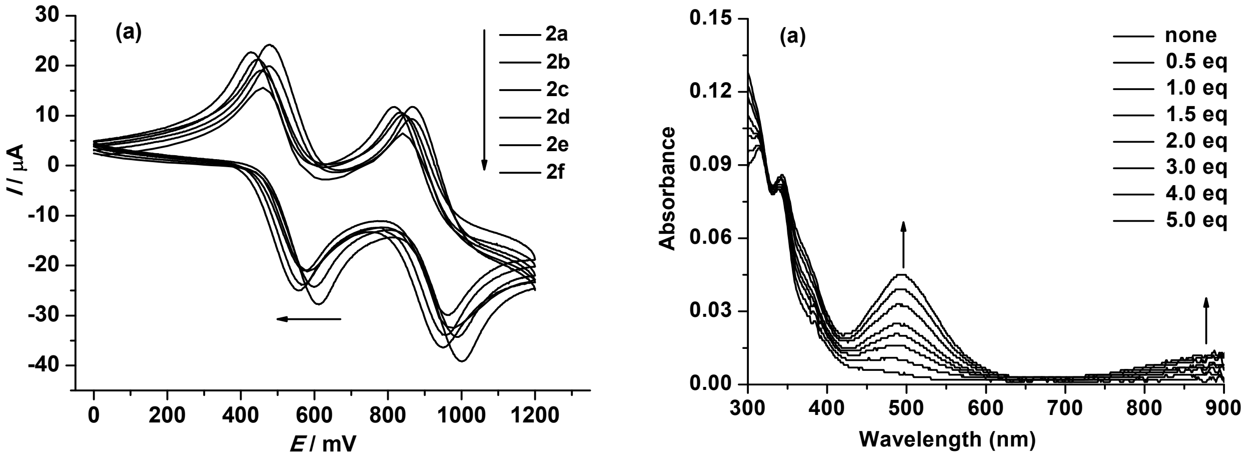


Figure 4. (a) CVs of **2a-2f** (5×10^{-4} M) in CH_2Cl_2 at 0.1 V s^{-1}; (b) UV-vis absorption spectral changes of **2f** (10^{-5} M) in CH_2Cl_2 upon stepwise addition of I_2.

To investigate the potential of these structures to act as a conducting architecture, chemical oxidation of **2f** in a CH_2Cl_2 solution was conducted with stepwise addition of I_2. Upon stepwise addition of I_2 (0.5→5.0 equiv) to a CH_2Cl_2 solution of **2f**, two new CT absorption bands appeared at 488 and >800 nm (Figure 4b). The absorptions at 488 nm was assigned to an intramolecular electron transfer of radical cation, $\mathbf{2f}^{+\bullet}$, while the absorption band at >800 nm was due to a charge transfer arised from **2f** to I_2.[12] All these are in agreement with the results obtained from the CV experiments.

In summary, two series of bipedal liquid crystals based on dithiole and/or EDT-TTF bearing two cholesteryl side chains linked with two ω-thioalkanoyloxy spacers was synthesized. The bipedal **1a**-**1c** and **2a**-**2f** exhibit smectic A phase while the dithiole-based **1d**-**1f** with the longer spacer (n=5-7) exhibit the oblique columnar phase in a wide temperature range including room temperature and no crystallization but vitrifying to form glassy mesogen during cooling from the isotropic melt. These liquid crystals, in combination with the glassy mesogen and excellent electron-donating properties of TTF, may provide new opportunities in the development of soft materials.

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$ with a Bruker AV-300 Spectrometer and chemical shifts were referenced relative to tetramethylsilane (δ_H/δ_C=0). Mass spectra was performed on a Shimadzu Axima CFR^{TM} *Plus* using a 1,8,9-anthracenetriol (DITH) matrix. IR spectra were recorded on a Shimadzu FT-IR Prestige-21 instrument (KBr pressed disc method). UV-vis spectra were recorded on a Hitachi U-3010 spectrophotometer in CH_2Cl_2. Cyclic voltammetric studies were carried out on a Potentiostat/ Galvanostat 273A instrument in CH_2Cl_2 and 0.1 M Bu_4PF_6 as the supporting electrolyte. Counter and Working electrodes were made of Pt and Glass-Carbon, respectively, and the reference electrode was SCE. A Perkin-Elmer Pyris Diamond differential scanning calorimeter was used to determine the thermal transitions, the heating and cooling rates were controlled to 10 °C/min. An Olympus BX51-P optical polarized microscope (40×) was used to observe the thermal transitions and to analyze the anisotropic texture. X-Ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory (Korea) and Philips PW 1700 X-ray diffractometer. Starting compounds **1a-1f** were synthesized according to the previous literature method.[9]

Typical synthetic procedure for 2

1 (0.5 mmol) and 4,5-ethylenedithio-1,3-dithiole-2-thione (1 mmol) was added to $P(OEt)_3$ (5 mL) and the suspension was heated to 120 °C, causing dissolution within 1 min, leaving a yellow reaction mixture. The mixture was stirred for 5 h at 120 °C, cooled to room temperature. Addition of MeOH gave a yellow solid, which was filtered, washed with MeOH, and dried in vacuo. The products were purified by column chromatography (silica gel, CH_2Cl_2: Pet. ether =1:1; v/v) to give a yellow solid. The solid was recrystallized from THF/CH_3COCH_3 to give **2**.

2a. Yellow solid (Yield: 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.68-2.11 (m, 82H, aliphatic and cholesteric protons are overlapped), 2.33 (d, J = 7.4 Hz, 4H), 2.66 (t, J = 7.2 Hz, 4H), 3.05 (t, J = 7.4 Hz, 4H), 3.74 (s, 4H), 4.62-4.65 (m, 2H), 5.38 (brs, 2H); MS (EI): m/z (%) 1239 (M^+, 100); FT-IR (KBr, cm^{-1}): 2943 (C-H), 1730 (C=O), 1179 (C-O); Anal. Calcd for $C_{68}H_{102}O_4S_8$: C, 65.86; H, 8.29. Found: C, 66.01; H, 8.30.

2b. Yellow solid (Yield: 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.68-2.11 (m, 86H, aliphatic and cholesteric protons are overlapped), 2.32 (d, J = 7.5 Hz, 4H), 2.45 (t, J = 7.2 Hz, 4H), 2.88 (t, J = 7.4 Hz, 4H), 3.29 (s, 4H), 4.61 (m, 2H), 5.38 (brs, 2H); MS (EI): m/z (%) 1267 (M^+, 100); FT-IR (KBr, cm^{-1}): 2945 (C-H), 1734 (C=O), 1175 (C-O); Anal. Calcd for $C_{70}H_{106}O_4S_8$: C, 66.30; H, 8.43. Found: C, 66.47; H, 8.31.

2c. Yellow solid (Yield: 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.69-2.31 (m, 98H, aliphatic and cholesteric protons are overlapped), 2.83 (t, J = 7.0 Hz, 4H), 3.29 (m, 4H), 4.62 (m, 2H), 5.38 (brs, 2H); MS (EI): m/z (%) = 1295 (M^+, 100); FT-IR (KBr, cm^{-1}): 2942 (C-H), 1732 (C=O), 1171 (C-O). Anal. Calcd for $C_{72}H_{110}O_4S_6$: C, 66.72; H, 8.55. Found: C, 66.51; H, 8.59.

2d. Yellow solid (Yield: 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.68-2.10 (m, 94H, aliphatic and cholesteric protons are overlapped), 2.25-2.38 (m, δH), 2.89 (t, J = 7.2Hz, 4H), 3.30 (s, 4H), 4.61 (m, 2H), 5.38 (brs, 2H); MS (EI): m/z (%) = 1323 (M^+, 100). FT-IR (KBr, cm^{-1}): 2932 (C-H), 1734 (C=O), 1169 (C-O). Anal. Calcd for $C_{74}H_{114}O_4S_8$: C, 67.12; H, 8.68. Found: C, 66.99; H, 8.73.

2e. Yellow solid (Yield: 47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.67-2.32 (m, 106H, aliphatic and cholesteric protons are overlapped), 2.79 (t, J = 7.0 Hz, 4H), 3.29 (s, 4H), 4.59-4.62 (m, 2H), 5.37 (brs, 2H); MS (EI): m/z (%) = 1351 (M^+, 100). FT-IR (KBr, cm^{-1}): 2934 (C-H), 1732 (C=O), 1171 (C-O). Anal. Calcd for $C_{76}H_{118}O_4S_6$: C, 67.50; H, 8.80. Found: C, 67.71; H, 8.43.

2f. Yellow solid (Yield: 39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.68-2.12 (m, 102H, aliphatic and cholesteric protons are overlapped), 2.28-2.40 (m, 8H), 2.81 (t, J = 7.2 Hz, 4H), 3.29 (s, 4H), 4.62 (brs, 2H), 5.37 (brs, 2H); MS (EI): m/z (%) = 1380 (M^++H, 100). FT-IR (KBr, cm^{-1}): 2932 (C-H), 1732 (C=O), 1171 (C-O). Anal. Calcd for $C_{78}H_{122}O_4S_6$: C, 67.87; H, 8.91. Found: C, 67.81; H, 9.13.

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REFERENCES

1. T. Kato, *Science*, 2002, **295**, 2414.

2. (a) K. Ichimura, *Chem. Rev.*, 2000, **100**, 1847; (b) C. E. Olson, M. J. R. Previte, and J. T. Fourkas, *Nat. Mater.*, 2002, **1**, 225; (c) M. Moriyama, N. Mizoshita, T. Yokota, K. Kishimoto, and T. Kato, *Adv. Mater.*, 2003, **15**, 1335.
3. D. Pauluth and K. Tarumi, *J. Mater. Chem.*, 2004, **14**, 1219.
4. (a) T. Yamamoto, M. Hasegawa, A. Kanazawa, T. Shiono, and T. Ikeda, *J. Mater. Chem.*, 2000, **10**, 337; (b) G. Jiang, T. Michinobu, W. Yuan, M. Feng, Y. Wen, S. Du, H. Gao, L. Jiang, Y. Song, F. Diederich, and D. Zhu, *Adv. Mater.*, 2005, **17**, 2170; (c) A. S. Matharu, S. Jeeva, and P. S. Ramanujam, *Chem. Soc. Rev.*, 2007, **36**, 1868.
5. (a) M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355; (b) M. R. Bryce, *J. Mater. Chem.*, 1995, **5**, 1481.
6. R. Andreu, J. Barberá, J. Garín, J. Orduna, J. L. Serrano, T. Sierra, P. Leriche, M. Sallé, A. Riou, M. Jubault, and A. J. Gorgues, *Mater. Chem.*, 1998, **8**, 881.
7. H. P. Chen, D. Katsis, J. C. Mastrangelo, S. H. Chen, and S. D. Jacobs, *Adv. Mater.*, 2000, **12**, 1283.
8. (a) M. Katsuhara, I. Aoyagi, H. Nakajima, T. Mori, T. Kambayashi, M. Ofuji, Y. Takanishi, K. Ishikawa, H. Takezoe, and H. Hosono, *Synth. Met.*, 2005, **149**, 219; (b) X. Gao, W. Wu, Y. Liu, S. Jiao, W. Qiu, G. Yu, L. Wang, and D. Zhu, *J. Mater. Chem.*, 2007, **17**, 736; (c) R. A. Bissell, N. Boden, R. J. Bushby, C. W. G. Fishwick, E. Holland, B. Movaghar, R. J. Bushby, and G. Ungar, *Chem. Commun.*, 1998, 113; (d) A. González, J. I. Segura, and N. Martín, *Tetrahedron Lett.*, 2000, **41**, 3083; (e) R. Andreu, J. Garín, J. Orduna, J. Barberá, J. L. Serrano, T. Sierra, M. Sallé, and A. Gorgues, *Tetrahedron,* 1998, **54**, 3895; (f) L. Wang, K.-U. Jeong, and M.-H. Lee, *J. Mater. Chem.*, 2008, **18**, 2657; (g) I. C. Pintre, J. L. Serrano, M. Blanca, C. L. Folcia, J. Etxebarria, F. Goc, D. B. Amabilino, J. Puigmartí-Luis, and E. Gomar-Nadald, *Chem. Commun.*, 2008, 2523; (h) J. Martínez-Perdiguero, I. Alonso, J. Ortega, C. L. Folcia, J. Etxebarria, I. Pintre, M. B. Ros, and D. B. Amabilino, *Phys. Rev. E*, 2008, **77**, 0202701; (i) I. Alonso, J. Martínez-Perdiguero, C. L. Folcia, J. Etxebarria, J. Ortega, I. C. Pintre, and M. B. Ros, *Physical Review E*, 2008, **78**, 041701.
9. (a) N. J. Zheng, H. Wang, R. B. Hou, and B. Z. Yin, *Heterocycles*, 2011, **83**, 2329; (b) R. B. Hou, Z. G. Huang, K. L. Zhong, L.-Y. Jin, and B. Z. Yin, *Tetrahedron,* 2011, **67**, 1238.
10. H. Tatemitsu, E. Nishikawa, Y. Sakata, and S. Misumi, *J. Chem. Soc., Chem. Commun.,* 1985, 106.
11. K. Borisch, S. Diele, P. Göring, H. Kresse, and C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 529.
12. H. Spanggaard, J. Prehn, M. B. Nielsen, E. Levillain, M. Allain, and J. Becher, *J. Am. Chem. Soc.*, 2000, **122**, 9486.