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Self-Assembly and Regioselective Photodimerization of Anthracene Having a Dendritic Substituent

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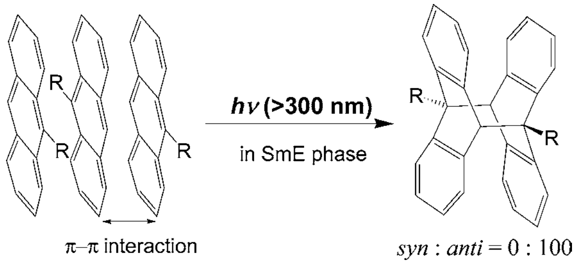
ABSTRACT



Thermotropic liquid crystallinity can be induced for an anthracene having a dendritic substituent. The photodimerization reaction of an anthracene moiety in the smectic phase proceeded quantitatively and regioselectively.

A new kind of well-defined regularly branched macromolecules of nanoscopic size called dendrimers have widely attracted scientific attention in past two decades.[1] In particular, there is an increasing focus on developing applications for photoresponsive dendrimers.[2] Recently, we have described dechalcogenation reaction of dendrimer dichalcogenides upon irradiation,[3] photoreactivity of dendron sulfenyl iodide,[4] a new photoreactive anthracenyl dendron that undergoes reversible photocyclization,[5] and fullerodendrimer as a photosensitzer for the generation of singlet oxygen.[6] Meanwhile, photochemical and photophysical processes conducted in thermotropic liquid crystals have been of considerable interest because of a variety of features in supramolecular chemistry and materials.[7] Self-assembly of dendritic macromolecules has been widely explored for the design of well-defined mesoscopic materials and also in relation to self-organization events in natural systems.[8]

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(1) (a) *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds., John Wiley & Sons: Chichester, 2001. (b) *Dendrimers, Topics in Current Chemistry*; Vögtle, F., Ed.; Springer: Berlin, 1998; Vol. 197. (c) *Dendrimers II, Topics in Current Chemistry*; Vögtle, F., Ed.; Springer: Berlin, 2000; Vol. 210. (d) *Dendrimers III, Topics in Current Chemistry*; Vögtle, F., Ed.; Springer: Berlin, 2001; Vol. 212. (e) *Dendrimers IV, Topics in Current Chemistry*; Vögtle, F., Schalley, C. A., Eds.; Springer: Berlin, 2001; Vol. 217.

(2) (a) Archut, A.; Azzellini, G. C.; Balzani, V.; De Cola, L.; Vögtle, F. *J. Am. Chem. Soc.* **1998**, *120*, 12187 and references therein. (b) Tominaga, M.; Konishi, K.; Aida, T. *Chem. Lett.* **2000**, 374. (c) Junge, C. M.; McGrath, D. V. *J. Am. Chem. Soc.* **1999**, *121*, 4912. (d) Junge, D. M.; McGrath, D. V. *Chem. Commun.* **1997**, 857. (e) Jiang, D.-L.; Aida, T. *Nature* **1997**, *388*, 454. (f) Nagasaki, T.; Tamagaki, S.; Ogino, K. *Chem. Lett.* **1997**, 717. (g) Yokoyama, S.; Nakahama, T.; Otomo, A.; Mashiko, S. *Chem. Lett.* **1997**, 1137. (h) Smet, M.; Liao, L.-X.; Dehaen, W.; McGrath, D. V. *Org. Lett.* **2000**, *2*, 511. (i) Cao, D.; Meier, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 186.

(3) Takaguchi, Y.; Suzuki, S.; Mori, T.; Motoyoshiya, J.; Aoyama, H. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1857.

(4) Takaguchi, Y.; Suzuki, S.; Ohta, K.; Motoyoshiya, J.; Aoyama, H. *Phosphorus, Sulfur Silicon* **2001**, *176*, 61.

(5) Takaguchi, Y.; Tajima, T.; Ohta, K.; Motoyoshiya, J.; Aoyama, H. *Chem. Lett.* **2000**, 1388.

(6) Takaguchi, Y.; Tajima, T.; Ohta, K.; Motoyoshiya, J.; Aoyama, H.; Wakahara, T.; Akasaka, T.; Fujitsuka, M.; Ito, O. *Angew. Chem., Int. Ed.* **2002**, *41*, 817.

(7) Weiss, R. G. Photochemical Process in Liquid Crystals. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed., Wiley-VCH: Chichester, 1991; Chapter 14.

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However, much less is known about the photoreactivity of dendromesogens. This paper describes the liquid crystalline properties and photoreactivity of poly(amidoamine) dendron **1** having an anthryl group at the focal point. To our knowledge, this is the first example of an intermolecular photoreaction process of a dendrimer that shows liquid crystalline arrangements.

Poly(amidoamine) dendron **1**, which has an anthryl group at the focal point, was synthesized by the use of a divergent approach as reported before.[5] The structure of **1** was confirmed by ^{1}H and ^{13}C NMR spectroscopies, elemental analysis, and MALDI-TOF mass spectrometry.[9] In addition, the phase behavior of **1** was established with the aid of polarizing optical microscopy and differential scanning calorimetry (DSC). A thin sample of dendron **1**, sandwiched between untreated glass plates, was examined between crossed polarizers at 100x magnification. Dendron **1** forms a smectic mesophase (rt−29 °C) and clears at 50 °C (Figure 1). The DSC profile of dendron **1** shows a clear endothermic peak at 28 °C ($\Delta H = 16.5$ kJ/mol), which is assignable to the melting temperature of the self-organized structure (T_m), as a possible consequence of the breakdown of the weak $\pi-\pi$ interaction. It is notable that dendrimer **1** is the first example of a liquid crystal based on 9-substituted anthracene.

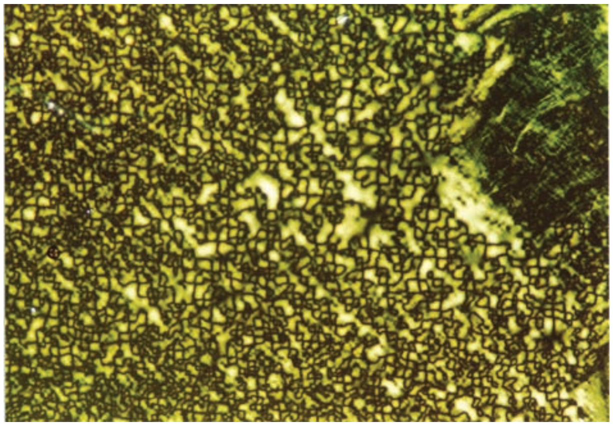
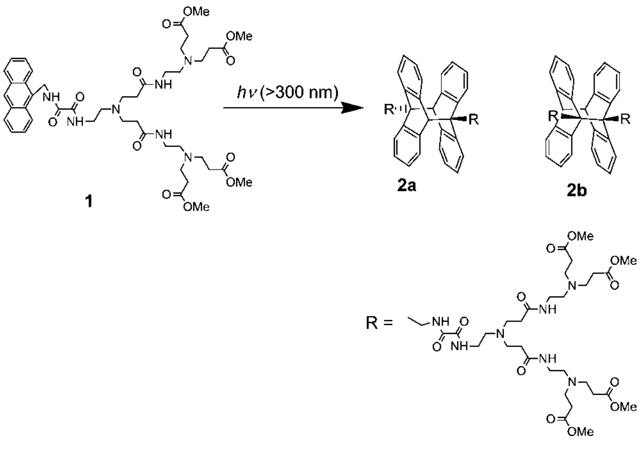


Figure 1. Polarized optical micrograph (x100) of dendron **1**.

The packing arrangement of dendron **1** in its liquid-crystalline phase was investigated by analyzing the distributions of photodimers. Photodimerization reactions of anthracene derivatives emanate from the singlet state of the anthracenyl group.[10] Especially in viscous media, the short lifetime of the singlet states ($\tau \approx 5-15$ ns)[11] precludes significant motion between the moment of excitation and intermolecular cycloaddition. Weiss et al. reported that the anthracene derivative in the cholesteric liquid-crystalline phase underwent the photodimerization reaction with low regioselectivity because of random parallel and antiparallel packing.[12] To clarify the regioselectivity of photodimerization of **1** in the mesophase, the liquid crystalline dendron was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 3 h to give photodimer **2** in quantitative yield (Scheme 1).

Scheme 1. Photodimerization of Dendron 1



Interestingly, only anti photodimer **2a** was obtained in the reaction within the liquid crystalline state, while a mixture of syn and anti dimers (syn/anti = 30/70), dendrimers **2a** and **2b**, respectively, were formed upon irradiation of a

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(8) (a) Percec, V.; Cho, W.-D.; Möller, M.; Prokhorova, S. A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2000**, *122*, 4249. (b) Yeardley, D. J. P.; Ungar, G.; Percec, V.; Holerca, M. N.; Johanson, G. *J. Am. Chem. Soc.* **2000**, *122*, 1684. (c) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 9526. (d) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161. (e) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusumy, V. S. K. *Science* **1977**, *278*, 449. (f) Kanie, K.; Nishii, M.; Yasuda, T.; Taki, T.; Ujiie, S.; Kato, T. *J. Mater. Chem.* **2001**, *11*, 2875. (g) Kanie, K.; Yasuda, T.; Nishii, M.; Ujiie, S.; Kato, T. *Chem. Lett.* **2001**, 480. (h) Kanie, K.; Yasuda, T.; Ujiie, S.; Kato, T. *Chem. Commun.* **2000**, 1899. (i) Enomoto, M.; Kishimura, A.; Aida, T. *J. Am. Chem. Soc.* **2001**, *123*, 5608. (j) Barberá, J.; Marcos, M.; Serrano, J. L. *Chem. Eur. J.* **1999**, *5*, 1834. (k) Barberá, J.; Garcés, A. C. *Adv. Mater.* **2001**, *13*, 175. (l) Dardel, B.; Guillon, D.; Hinrich, B.; Deschenaux, R. *J. Mater. Chem.* **2001**, *11*, 2814. (m) Goodby, J. W.; Bruce, D. W.; Hird, M.; Imrie, C.; Neal, M. *J. Mater. Chem.* **2001**, *11*, 2631. (n) Ikeda, A.; Numata, M.; Shinkai, S. *Chem. Lett.* **1999**, 929. (o) Ponomarenko, S. A.; Boiko, N. I.; Shibaev, V. P.; Richardson, R. M.; Whitehouse, I. J.; Rebrov, E. A.; Muzafarov, A. M. *Macromolecules* **2000**, *33*, 5549. (p) Baars, M. W. P. L.; van Boxtel, M. C. W.; Bastiaansen, C. W. M.; Broer, D. J.; Söntyens, S. H. M.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 715. (q) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539. (r) Suárez, M.; Lehn, J.-M.; Zimmerman, S. C.; Skoalios, A.; Heinrich, B. *J. Am. Chem. Soc.* **1998**, *120*, 9526. (s) Stocker, W.; Karakaya, B.; Schüramann, B. L.; Rabe, J. P.; Schlüter, A. D. *J. Am. Chem. Soc.* **1998**, *120*, 7691.

(9) Selected data for dendron **1**: ^{1}H NMR ($CDCl_3$) δ 2.31−2.46 (m, 12H), 2.51−2.61 (m, 6H), 2.67−2.76 (m, 8H), 2.77−2.88 (m, 4H), 3.29−3.43 (m, 6H), 3.62 (s, 12H), 5.40 (d, $J = 5.6$ Hz, 2H), 6.87−7.00 (m, 2H), 7.46 (t, $J = 8.0$ Hz, 2H), 7.54 (t, $J = 5.6$ Hz, 2H), 7.80 (t, $J = 5.6$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 2H), 8.07 (t, $J = 5.6$ Hz, 1H), 8.24 (d, $J = 8.0$ Hz, 2H), 8.42 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 32.4, 33.0, 35.9, 36.90, 36.92, 49.0, 49.7, 51.5, 52.0, 52.7, 123.5, 125.1, 126.6, 127.1, 128.3, 129.1, 130.2, 131.3, 159.3, 159.6, 171.8, 172.9; MALDI-TOF MS for $C_{45}H_{67}N_7O_{12}$ *m/z* calcd 895.02 [MH^+], found 894.34. Anal. Calcd for $C_{45}H_{67}N_7O_{12}$: C, 60.46; H, 7.10; N, 10.97. Found: C, 60.33; H, 7.25; N, 10.93.

(10) Costa, S. M.; Melo, E. C. C. *J. Chem. Soc., Faraday Trans.* **1980**, *76*, 1.

(11) (a) Hirayama, S.; Lampert, R.; Phillips, D. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 371. (b) Ferguson, J.; Mau, A. W. H. *Mol. Phys.* **1974**, *27*, 377. (c) Marcondes, M. E. R.; Toscano, V. G.; Weiss, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 4485.

(12) Lin, Y.-C.; Weiss, R. G. *Liquid Crystals* **1989**, *4*, 367.

solution of “normal” solvents.[13] The structures of syn and anti photodimers **2a** and **2b** were confirmed by the ^{1}H and ^{13}C NMR spectroscopies, elemental analysis, and MALDI-TOF mass spectrometry.[14] The ratio of syn/anti dimers should reflect, at least indirectly, the ground-state distribution of the orientation of dendron **1**. This result indicated that the arrangement of anthracene within the liquid crystalline phase of **1** is suitable for regioselective photodimerization.

Hence, the structural determination in the liquid crystalline phase by XRD was carried out in order to obtain more information about the molecular arrangements present in the mesophase. X-ray diffraction measurements showed that **1** exhibited a smectic E phase (SmE phase at 25 °C: $d_{001} = 30.2$, $d_{002} = 15.4$, $d_{003} = 10.3$, $d_{200} = 8.7$, $d_{004} = 7.8$, $d_{110} = 7.0$, $d_{005} = 6.2$, $d_{310} = 4.5$ Å) with cell parameters $a = 17.3$ Å, $b = 8.67$ Å, and $c = 30.9$ Å. Interestingly, a one-dimensionally unique arrangement could be supposed from adequate consideration of the molecular model shown in Figure 2.[15] Neighboring molecules are aligned in an anti-parallel orientation.[16] This result indicated that the dendron **1** self-assembles via $\pi-\pi$ stacking of the anthracene moiety and van der Waals interactions of dendron units to form SmE phase.

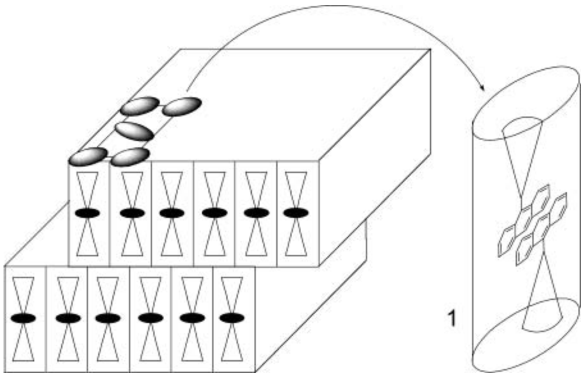

Figure 2. Schematic illustration of the molecular arrangement of dendron **1** in the liquid-crystalline phase.

The results described herein show the first example of the regioselective photodimerization of anthryl dendron in the SmE liquid-crystalline phase. Supramolecular aggregation of the photoreactive dendrimer is potentially important for applications of information storage and photomechanical devices. Further work is in progress to explore the applications and advantages of the photoreactive dendrimer that shows the mesophase.

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Supporting Information Available: DSC chart of dendron **1** upon heating. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Ratio of syn/anti photodimers was determined by HPLC experiment and ^{1}H NMR.

(14) Selected data for **2a**: ^{1}H NMR (CDCl$_3$) δ 2.31−2.37 (m, 8H), 2.41−2.48 (m, 16H), 2.53−2.61 (m, 8H), 2.74−2.84 (m, 24H), 3.26−3.40 (m, 16H), 3.67 (s, 32H), 3.88 (s, 2H), 4.53 (d, $J = 4.0$ Hz, 4H), 6.79−6.88 (m, 16H), 6.89−6.93 (m, 6H), 7.95 (t, $J = 4.0$ Hz, 2H); MALDI-TOF-MS for $C_{90}H_{126}N_{14}O_{24}$ m/z calcd 1789.04 [MH$^+$], found 1788.41. For **2b**: ^{1}H NMR (CDCl$_3$) δ 2.31−2.39 (m, 8H), 2.42−2.49 (m, 16H), 2.54−2.61 (m, 8H), 2.74−2.84 (m, 24H), 3.28−3.39 (m, 16H), 3.65 (s, 32H), 4.50 (s, 2H), 4.70 (d, $J = 4.0$ Hz, 4H), 6.77−6.95 (m, 16H), 7.26 (brs, 6H), 7.84 (t, $J = 4.0$ Hz, 2H); MALDI-TOF MS for $C_{90}H_{126}N_{14}O_{24}$ m/z calcd 1789.04 [MH$^+$], found 1788.53.

(15) On the assumption that the density of the liquid crystal is 1.28 ($\rho = 1.28$), the number of molecules in dendrimer **1** per unit cell is estimated to be 4 ($Z = 4$). Since the number of molecules per unit cell of the SmE phase is 2 ($Z = 2$), dimer formation can be predicted as shown in Figure 2.

(16) UV/Vis spectrum of **1** in the SmE phase exhibited broad absorption ($\lambda_{max} = 392$ nm), although **1** in solution showed the absorption band ($\lambda_{max} = 366$ nm) with vibronic peaks in the 320−400 nm region. Fluorescence spectrum of **1** in the SmE phase also showed a broad and red-shifted peak (EM $\lambda_{max} = 441$ nm) compared with that in homogeneous solution. This result indicated interactions of the anthracene moiety in the ground state.