Helical Structures

DOI: 10.1002/ange.200503258

Cholesterol-Aided Supramolecular Control over Chromophore Packing: Twisted and Coiled Helices with Distinct Optical, Chiroptical, and Morphological Features**

Ayyappanpillai Ajayaghosh, Chakkooth Vijayakumar, Reji Varghese, and Subi Jacob George*

Dedicated to Professor S. Chandrasekaran on the occasion of his 60th birthday

The controlled ordering and orientation of chromophores at the supramolecular level on the nano- to micrometer scale is important owing to their potential applications in optoelectronic devices.[1] Although long-range supramolecular ordering of chromophoric assemblies has been extensively studied,[2,3] the control of such hierarchical assemblies to give

[*] Dr. A. Ajayaghosh, C. Vijayakumar, R. Varghese, S. J. George
Photosciences and Photonics Unit
Chemical Sciences and Technology Division
Regional Research Laboratory, CSIR
Trivandrum 695019 (India)
Fax: (+91) 471-490-186
E-mail: aajayaghosh@rediffmail.com

[**] This work was supported by the Department of Science and Technology (DST), the Government of India (New Delhi) and the Council of Scientific and Industrial Research (CSIR, Task Force Program CMM 10). C.V., R.V., and S.J.G. are grateful to the CSIR, Government of India, for research fellowships. This work is contribution No. RRLT-PPU-213.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

functionally and morphologically different nanoscopic architectures through a preferred packing of the individual chromophores remains elusive. This is particularly true with linear π-conjugated systems, which play crucial roles in organic electronic devices, as the charge-transport properties of conjugated molecules are strongly influenced by the long-range ordering of the chromophores.[4–6] In this context, we have been interested in the self-assembly-induced modulation of optical and morphological properties in oligo(*p*-phenylenevinylene) (OPV) derivatives.[7] However, a precise control over the packing of chromophores into a desired morphology in such a system is still a matter of great importance.

Herein, we show that substitution patterns of cholesterol-appended OPVs allow unprecedented control over the alignment of chromophores and result in distinct optical, chiroptical, and morphological properties. There have been several reports on cholesterol-appended chromophoric systems that self-assemble to form supramolecular architectures and gels.[8,9] Nevertheless, this is the first report on the use of cholesterol moieties as the driving force for biasing the organization of chromophores through different packing modes, leading to control over nanoscopic properties of the resultant hierarchical self-assembly.

The mono- and disubstituted cholesterol-appended OPVs **1** and **2**, respectively, were prepared by treatment of the corresponding bis(hydroxymethyl)-OPVs[7a] with cholesteryl chloroformate and characterized by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry.[10] Solutions of the mono- and disubstituted OPVs in chloroform (3×10^{-4} M) showed identical absorption and emission spectra[10] with an absorption maximum at $\lambda = 408$ nm (π–π* transition) and emission maxima at $\lambda = 466$ and 494 nm. The quantum yields of fluorescence (Φ_f) for solutions of **1b** and **2b** in chloroform were measured as $\Phi_f = 0.76$ and 0.82, respectively, using quinine sulfate as standard, and $\Phi_f = 0.32$ and 0.55, respectively, for solutions of **1b** and **2b** in decane at 20 °C using Rhodamine 6G as standard. Similarly, the absorption and emission spectra of solutions of **1b** and **2b** in decane at elevated temperatures showed identical features to those in chloroform. However, the UV/Vis spectrum of **1b** in decane at 20 °C exhibited a broad absorption ($\lambda_{max} = 402$ nm) with a red-shifted shoulder around 470 nm (Figure 1a). This is a general feature of OPV derivatives in nonpolar hydrocarbon solvents.[6a,7a,d] On the contrary, **2b** showed a structured absorption with a blue-shifted maximum ($\Delta\lambda_{max} = 10$ nm) and two new bands at $\lambda = 414$ and 444 nm (Figure 1b). Noticeably, the new band of **2b** at 444 nm is blue-shifted by nearly 26 nm relative to the shoulder band of **1b**. Similar blue-shifted spectra, which are ascribed to the formation of H aggregates, were reported by others for some OPV derivatives.[11]

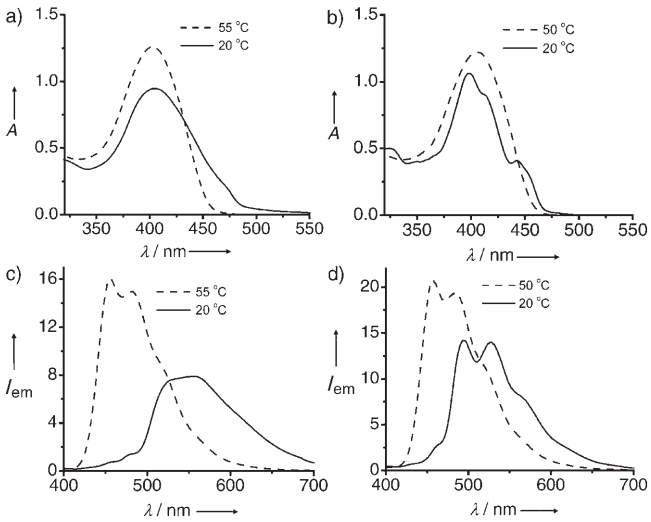
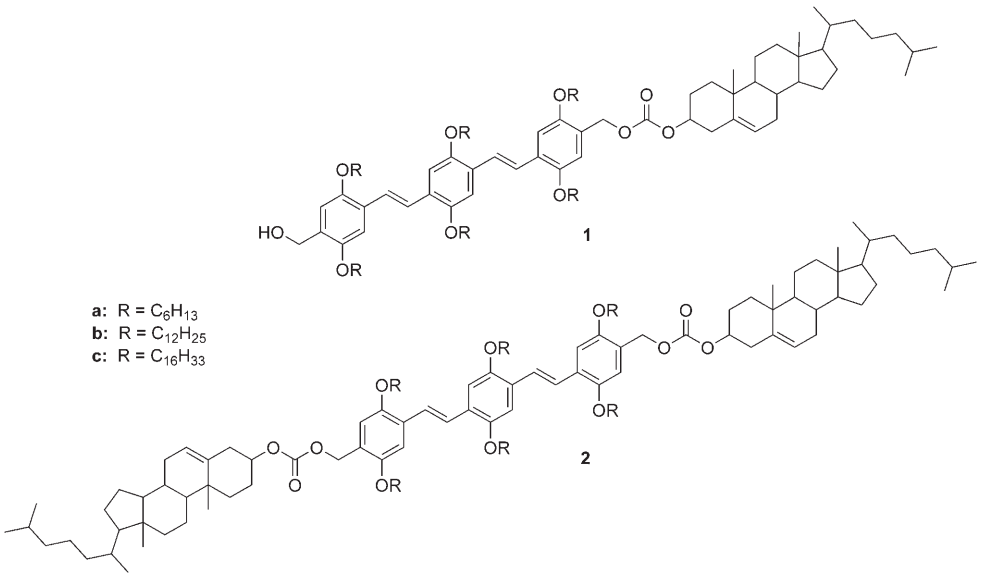


Figure 1. Absorption spectra of a) **1b** and b) **2b**, and emission spectra of c) **1b** and d) **2b** in decane ($c = 3\times10^{-4}$ M, $l = 1$ mm, $\lambda_{ex} = 370$ nm).

The emission spectra of **1b** and **2b** in decane at 50 °C showed identical features with two maxima ($\lambda_{max} = 456$ and 484 nm for **1b**; $\lambda_{max} = 457$ and 485 nm for **2b**). However, in decane at 20 °C, **1b** showed a broad structureless emission between 500–700 nm with a maximum around 560 nm (Figure 1c), whereas **2b** displayed a structured emission with two emission maxima at 494 and 528 nm (Figure 1d). The variation of the absorption and emission spectra with solvents and temperature reveals that in decane at ambient temperatures these molecules form aggregates whose electronic properties are different from each other. Although these observations can be rationalized by invoking H-type[9e,11] and J-type[6a] aggregation in analogy to previous reports,



we find difficulties with such assignments for two reasons: The red and blue shifts of the aggregates of **1b** and **2b** with respect to the corresponding monomers are not very predominant. Furthermore, the emission spectrum of **2b** is more intense than that of **1b**. By normal practice, if the blue-shifted absorption spectrum of **2b** is assigned to the presence of H aggregates, it should be less intense relative to the spectrum of the J aggregates of **1b**. Therefore, we prefer to address these aggregates as "pseudo-H" and "pseudo-J" with twisted and tilted chromophore stacks for **2b** and **1b**, respectively. In such cases, the difference in the excited state dipole moment orientation of the two aggregates results in distinct optical and chiroptical features.

Solutions of **1b** and **2b** in chloroform were circular-dichroism-inactive (Figure 2). However, the CD spectrum of

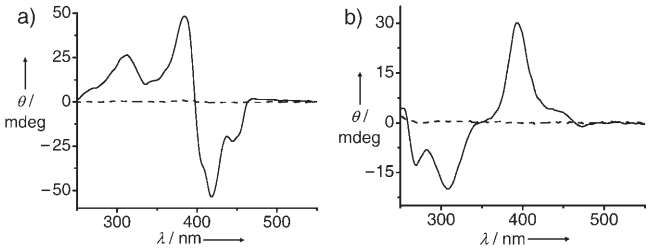


Figure 2. CD spectra of a) **2b** and b) **1b** in chloroform (-----) or decane (——). $c = 3\times10^{-4}$ M, $l = 1$ mm.

2b in decane (3×10^{-4} M) showed an exciton-coupled bisignate signal with negative ($\lambda_{max} = 418$ nm) and positive ($\lambda_{max} = 385$ nm) Cotton effects, which change sign exactly through the π–π* absorption maximum at 398 nm (Figure 2a). This behavior is characteristic of a left-handed helical bias of the supramolecular chirality.[12] In the case of **1b**, the CD spectrum in decane showed a strange behavior with first a positive ($\lambda_{max} = 393$ nm) followed by two negative ($\lambda_{max} = 308$ and 269 nm) Cotton effects. The non-bisignate exciton couplet with opposite signals indicates the possibility of different chiral dispositions. Furthermore, the measure of chirality, g, for **1b** is low ($g_{393nm} = 5.2\times10^{-4}$) relative to that for **2b** ($g_{385nm} = 9.3\times10^{-4}$) which indicates a weak exciton coupling in the former. These differences in the CD spectra reiterate the differences between the aggregates of **1b** and **2b** and agree with the absorption and emission properties.

A striking consequence of the different arrangements of chromophores for **1b** and **2b** is the disparity in the gelation behavior between the two.[10] Although both compounds induce the gelation of a variety of hydrocarbon solvents, gels with **2b** were relatively weaker than those with **1b**. The critical gelator concentration (CGC) of **2b** in decane is 7.0 mM whereas that of **1b** is only 3.4 mM, which is nearly twofold less and points to more efficient gelation of the latter. Plots of the concentration of gelator against the melting temperature of the gel showed enhanced stability for the gel of **1b** (Figure 3a). The gel with **1b** showed a weak yellow emission whereas the gel from **2b** displayed a relatively strong green emission (Figure 3a). Furthermore, the weak yellow emission of the former reveals better electronic conjugation with

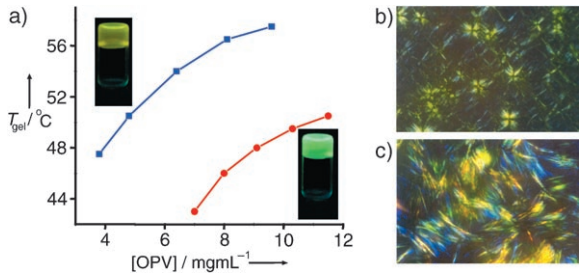


Figure 3. a) Plots of T_{gel} versus the concentration of **1b** (blue) and **2b** (red) in decane. Insets: Photographs of the corresponding gels under illumination; b, c) OPM pictures (400× magnification) of the decane gels of **1b** (3.5×10^{-3} M; b) and **2b** (7.2×10^{-3} M; c).

strong π interaction between the chromophores relative to those of the latter. The optical polarizing microscopy (OPM) textures of **2b** showed streaklike textures[13a] with strong birefringence. On the other hand, **1b** showed four-arm brush textures similar to cholesterol gelators[13b] and chiral OPV

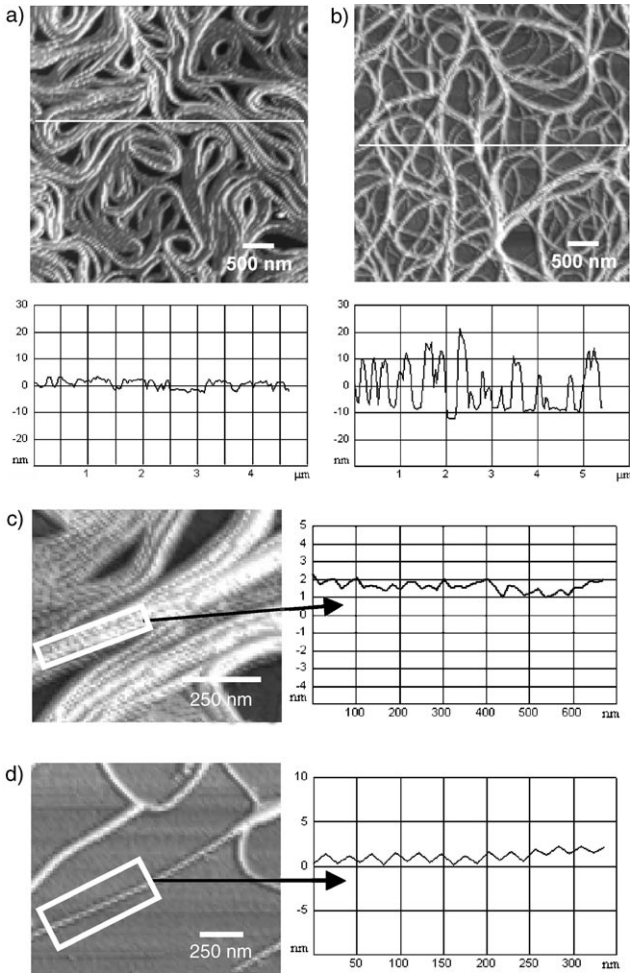


Figure 4. AFM images of a) **1b** and b) **2b** with the corresponding height profiles shown. c) Zoomed region of assembly **1b** and d) isolated fibers of **2b** with the corresponding section analyses. Samples were prepared from solutions in decane ($c = 1\times10^{-5}$ M) and transferred to freshly cleaved mica sheet by drop-casting. See Supporting Information for detailed section analyses.

gelators.[7c] This observation reveals the differences in the supramolecular anisotropy leading to different mesoscopic structures. It is clear that hydrogen bonds in **1b** make significant contributions to the observed differences in the gelation and mesoscopic properties, whereas the orientation of the chromophore plays a crucial role in the optical and chiroptical properties.

The atomic force microscopy (AFM) textures of **1b** and **2b** obtained from solutions in decane showed significant differences, although both assemblies adopt right-handed (*P*) helical structures. The helicity of **1b** is in agreement with the CD spectrum, whereas that of **2b** disagrees with the bisignate CD signal. Such a contradiction of the observed CD and morphological features have previously been reported.[5c,14] In many cases, the initially formed 1D aggregates with a left-handed twist may wind in the opposite direction during the higher-order assembly to result in an ultimate right-handed twist, as can be seen to some extent in some of the large fibers of **2b**. AFM analysis reveals ribbonlike structures of **1b** that are flat and aligned sideways to form coiled superstructures. The width of the individual ribbons varies from 30 to 70 nm, with an average height of 4–8 nm. The height of 8 nm corresponds to two individual tapes lying one over the other. Interestingly, **2b** showed a morphology comprised of entangled helical fibers of different sizes. The width of the smallest fiber is 40 nm, with a height of 4 nm and is several micrometers in length. The height profiles of wide areas of the samples showed a uniform height for **1b**, whereas a height variation of 4–50 nm was observed for **2b**.[10] Furthermore, section analysis along the axis (Figure 4c and d) revealed that assemblies of **1b** have an irregular helical pitch of 40–80 nm whereas those of **2b** are almost uniform with zigzag patterns and have a pitch length of 46 nm. Irregular movements of the AFM tip through the long axis of the assembly with variable pitch length and uniform height profile are characteristic of a flexible and flattened coiled tapelike morphology of **1b**. In contrast, the uniform zigzag patterns along the axis and variable height profiles of **2b** are characteristic of twisted helical fibrillar assemblies of different size that are intertwined.

On the basis of the differences in the optical, chiroptical, gelation, and morphological properties, it is clear that the packing of the chromophores in the assemblies of **1** and **2** are remarkably different. The features of the absorption, emission, and CD spectra strongly support a well-organized twisted helical arrangement of the chromophores in the dicholesterol-substituted molecules **2** whereas a tilted extended packing of the hydrogen-bonded chromophores is favored for the monocholesterol derivatives **1** (Figure 5). The extended supramolecular assembly of the twisted packing (pseudo-H aggregates) leads to twisted helical assemblies, whereas the tilted packing (pseudo-J aggregates) may result in a coiled helical assembly as shown in Figure 5.

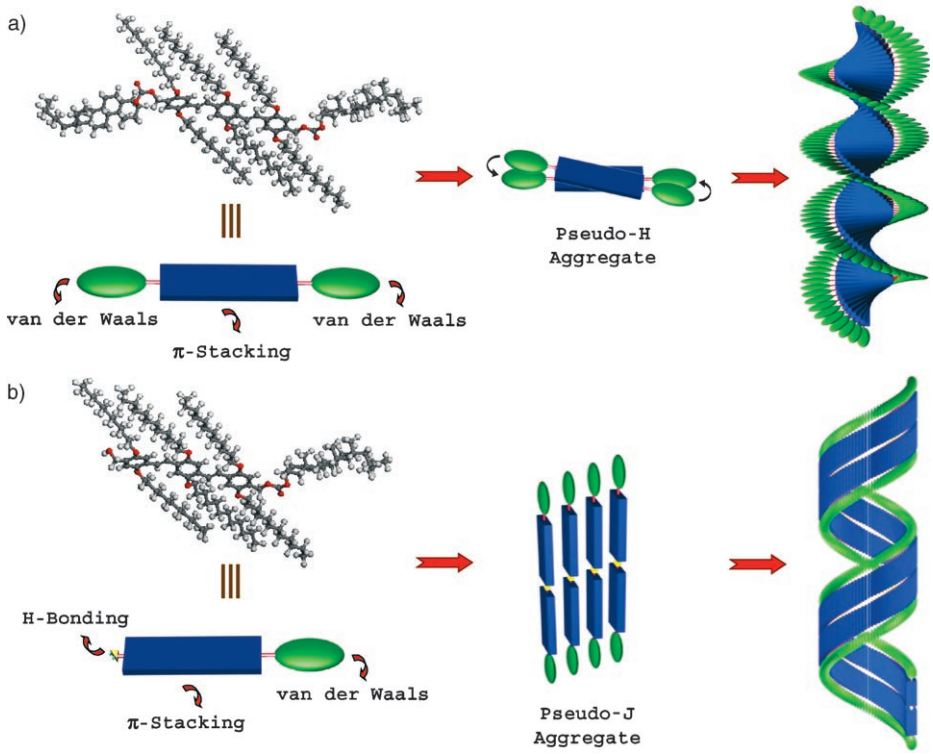


Figure 5. Probable mode of self-assembly of a) **2b** and b) **1b** in decane.

In conclusion, we have shown that symmetrical and unsymmetrical functionalization of OPVs with cholesterol moieties allows a controlled supramolecular organization which results in helical nanoscopic architectures that display remarkable differences in optical, chiroptical, and morphological properties, as illustrated by the two classes of molecules **1** and **2**. The approach described here can be used as a general strategy to control the chromophore ordering which may be useful to the design of nanoscopic functional assemblies for optoelectronic applications.

Received: September 14, 2005
Revised: October 14, 2005
Published online: December 2, 2005

Keywords: cholesterol · gels · helical structures · self-assembly · supramolecular chemistry

[1] a) J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, **1995**; b) S. I. Stupp, V. Le Bonheur, K. Walker, L. S. Li, K. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384–389; c) A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65–71; *Angew. Chem. Int. Ed.* **1998**, *37*, 63–68; d) J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, N. A. J. M. Sommerdijk, *Chem. Rev.* **2001**, *101*, 4039–4070.

[2] For selected chromophore assemblies, see: a) H. Engelkamp, S. Middelbeek, R. J. M. Nolte, *Science* **1999**, *284*, 785–788; b) F. Würthner, C. Thalacker, A. Sautter, W. Schärtl, W. Ibach, O.

Hollricher, *Chem. Eur. J.* **2000**, *6*, 3871 – 3886; c) T. Yamaguchi, N. Ishii, K. Tashiro, T. Aida, *J. Am. Chem. Soc.* **2003**, *125*, 13934 – 13935; d) F. Würthner, S. Yao, U. Beginn, *Angew. Chem.* **2003**, *115*, 3368 – 3371; *Angew. Chem. Int. Ed.* **2003**, *42*, 3247 – 3250; e) M. Kimura, T. Kuroda, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, *Langmuir* **2003**, *19*, 4825 – 4830; f) A. Ajayaghosh, S. J. George, A. P. H. J. Schenning, *Top. Curr. Chem.* **2005**, *258*, 83 – 118.

[3] a) A. C. Grimsdale, K. Müllen, *Angew. Chem.* **2005**, *117*, 5732 – 5772; *Angew. Chem. Int. Ed.* **2005**, *44*, 5592 – 5629; b) P. Leclère, A. Calderone, D. Marsitzky, V. Francke, Y. Geerts, K. Müllen, J. L. Brédas, R. Lazzaroni, *Adv. Mater.* **2000**, *12*, 1042 – 1046; c) D. Wasserfallen, I. Fischbach, N. Chebotareva, M. Kastler, W. Pisula, F. Jäckel, M. D. Watson, I. Schnell, J. P. Rabe, H. W. Spiess, K. Müllen, *Adv. Funct. Mater.* **2005**, *15*, 1585 – 1594.

[4] For reviews on π-conjugated systems, see: a) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491 – 1546; b) A. P. H. J. Schenning, E. W. Meijer, *Chem. Commun.* **2005**, 3245 – 3258.

[5] a) F. S. Schoonbeek, J. H. van Esch, B. Wegewijs, D. B. A. Rep, M. P. de Haas, T. M. Klapwijk, R. M. Kellogg, B. L. Feringa, *Angew. Chem.* **1999**, *111*, 1486 – 1490; *Angew. Chem. Int. Ed.* **1999**, *38*, 1393 – 1397; b) B. W. Messmore, J. F. Hulvat, E. D. Sone, S. I. Stupp, *J. Am. Chem. Soc.* **2004**, *126*, 14452 – 14458; c) J. Bae, J.-H. Choi, Y.-S. Yoo, N.-K. Oh, B.-S. Kim, M. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 9668 – 9669.

[6] a) A. P. H. J. Schenning, P. Jonkheijm, E. Peeters, E. W. Meijer, *J. Am. Chem. Soc.* **2001**, *123*, 409 – 416; b) P. Jonkheijm, A. Miura, M. Zdanowska, F. J. M. Hoeben, S. De Feyter, A. P. H. J. Schenning, F. C. De Schryver, E. W. Meijer, *Angew. Chem.* **2004**, *116*, 76 – 80; *Angew. Chem. Int. Ed.* **2004**, *43*, 74 – 78.

[7] a) A. Ajayaghosh, S. J. George, *J. Am. Chem. Soc.* **2001**, *123*, 5148 – 5149; b) A. Ajayaghosh, S. J. George, V. K. Praveen, *Angew. Chem.* **2003**, *115*, 346 – 349; *Angew. Chem. Int. Ed.* **2003**, *42*, 332 – 335; c) S. J. George, A. Ajayaghosh, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, *Angew. Chem.* **2004**, *116*, 3504 – 3507; *Angew. Chem. Int. Ed.* **2004**, *43*, 3422 – 3425; d) S. J. George, A. Ajayaghosh, *Chem. Eur. J.* **2005**, *11*, 3217 – 3227.

[8] a) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133 – 3159; b) J. H. van Esch, B. L. Feringa, *Angew. Chem.* **2000**, *112*, 2351 – 2354; *Angew. Chem. Int. Ed.* **2000**, *39*, 2263 – 2266; c) K. J. C. van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem.* **2003**, *115*, 1010 – 1030; *Angew. Chem. Int. Ed.* **2003**, *42*, 980 – 999.

[9] a) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 6664 – 6676; b) R. Wang, C. Geiger, L. Chen, B. Swanson, D. G. Whitten, *J. Am. Chem. Soc.* **2000**, *122*, 2399 – 2400; c) K. Sugiyasu, N. Fujita, S. Shinkai, *Angew. Chem.* **2004**, *116*, 1249 – 1253; *Angew. Chem. Int. Ed.* **2004**, *43*, 1229 – 1233; d) P. Xue, R. Lu, D. Li, M. Jin, C. Tan, C. Bao, Z. Wang, Y. Zao, *Langmuir* **2004**, *20*, 11234 – 11239; e) S.-i. Kawano, N. Fujita, S. Shinkai, *Chem. Eur. J.* **2005**, *11*, 4735 – 4742.

[10] See Supporting Information.

[11] a) P. A. van Hal, M. M. Weink, J. M. Kroon, R. A. J. Janssen, *J. Mater. Chem.* **2003**, *13*, 1054 – 1057; b) T. Mori, T. Watanabe, K. Minagawa, M. Tanaka, *J. Polym. Sci. Part A* **2005**, *43*, 1569 – 1578.

[12] N. Berova, K. Nakanishi in *Circular Dichroism: Principles and Applications* (Eds.: N. Berova, K. Nakanishi, R. W. Woody), *4th ed.*, Wiley-VCH, Weinheim, **2000**, p. 337.

[13] a) L. Lu, R. G. Weiss, *Chem. Commun.* **1996**, 2029 – 2030; b) X. Huang, P. Terech, S. R. Raghavan, R. G. Weiss, *J. Am. Chem. Soc.* **2005**, *127*, 4336 – 4344.

[14] A. Lohr, M. Lysetska, F. Würthner, *Angew. Chem.* **2005**, *117*, 5199 – 5202; *Angew. Chem. Int. Ed.* **2005**, *44*, 5071 – 5074.

