Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 47 (2006) 8209–8213

A new liquid crystalline derivative of dibenzotetraaza[14]annulene: synthesis, characterization and the preliminary evaluation of mesomorphic properties

Jarosław Grolik,[a] Lesław Sieroń[b] and Julita Eilmes[a,*]

[a]*Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland*
[b]*Institute of General and Ecological Chemistry, Technical University of Łódź, Żeromskiego 116, 90-924 Łódź, Poland*

Received 2 August 2006; revised 11 September 2006; accepted 22 September 2006

Abstract—A new dibenzotetraaza[14]annulene ligand has been synthesized that contains two 2-hydroxybenzoyl and four 3,7-dimethyloctyloxy peripheral substituents. Its mesomorphic textures were observed by means of a polarizing optical microscopy.

It has been well established for over 28 years from Chandrasekhar's early work[1] that many compounds composed of disc-shaped molecules exhibit liquid crystalline properties. The conventional mesogenic molecule has a rigid core, usually flat and aromatic, and is equipped with several (4–8) flexible aliphatic side chains that surround the core. A remarkable number of known liquid crystalline materials are based on macrocyclic systems such as porphyrins, phthalocyanines, azacrowns and macrocyclic Schiff bases.[2] Among them, transition metal complexes of substituted dibenzotetraaza[14]annulenes[3] have been found to exhibit liquid crystalline properties. Hunziker[4] and Veber and coworkers[5] have studied their mesomorphic behaviour as a function of the structure, length and number of peripheral groups. An optical storage effect was later demonstrated in one of these mesomorphic nickel complexes.[6]

We have recently elaborated synthetic routes to various peripherally functionalized dibenzotetraaza[14]annulenes.[7] Herein, we describe a new liquid crystal based on a metal-free dibenzotetraaza[14]annulene macrocycle bearing two *meso* 2-hydroxybenzoyl substituents and four 3,7-dimethyloctyloxy groups attached to *o*-phenylene moieties (compound **7** in Scheme 1).

The properties-directed design of **7** was based on the known crystal structure[8] of *meso*-bis(2-hydroxybenzoyl)dibenzotetraaza[14]annulene precursor **1**.[9] As shown in Figures 1 and 2, **1** is nearly flat and is rich in π delocalized areas, and therefore seemed to be well suited to play the role of a disc-shaped building block. In addition, aromatic $\pi\cdots\pi$ stacking interactions, involving planar central moieties and *meso* phenyl rings of neighbouring molecules, are clearly evidenced by the crystal structure (Fig. 3). Recent detailed studies on mesomorphic materials[10] have established that in the most often encountered *columnar* mesophases, the disc-like molecules self-assemble into columns by stacking one upon another and self-organize into various arrangements that differ in the degree of order and in the two-dimensional symmetry of the column packing. Accordingly, the *columnar* mesophases can be further sub-classified into those referred to as *hexagonal, rectangular* and *oblique*. Within discotic liquid crystals, there are also less common and less ordered *nematic* mesophases.

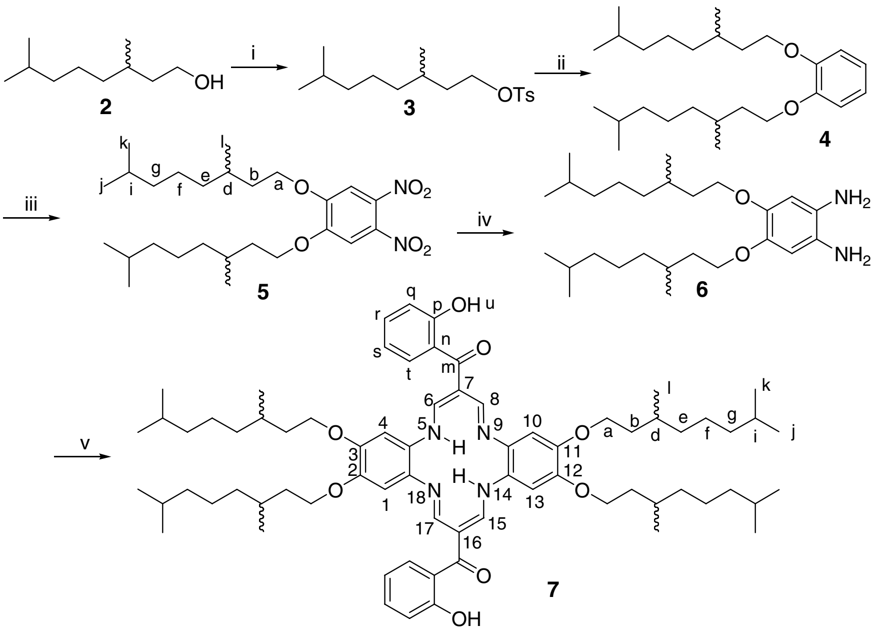
In designing mesogens it is of importance, that self-assembly and self-organisation, crucial for inducing mesomorphic behaviour to discotic materials, are mostly influenced by the structure and number of flexible pendant chains that surround the discotic units. Therefore, in order to generate such supramolecular processes in our product, we introduced four additional peripheral substituents to the macrocyclic core of the precursor **1**, by incorporating them onto the benzenoid rings. We chose 3,7-dimethyloctyloxy groups, since, as

---

Keywords: Dibenzotetraaza[14]annulene; Liquid crystal; Discotic; Textures; Polarizing optical microscopy; $\pi\cdots\pi$ Stacking.

* Corresponding author. Tel.: +48 12 6632294; fax: +48 12 6340515; e-mail: jeilmes@chemia.uj.edu.pl

doi:10.1016/j.tetlet.2006.09.134



Scheme 1. Reagents and conditions: (i) py, TosCl, rt, (84%); (ii) catechol, K_2CO_3/DMF, 80 °C, (56%); (iii) CH_2Cl_2/HNO_3, H_2SO_4, rt, (81%); (iv) 10% Pd/C, $NaBH_4$, MeOH, Ar and (v) 3-formylchromone, MeOH, reflux, (41%).

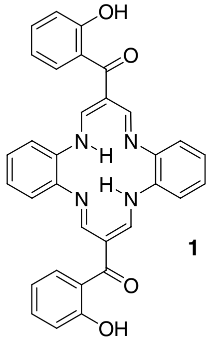


Figure 1. 7,16-Bis(2-hydroxybenzoyl)-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine **1**.[9]

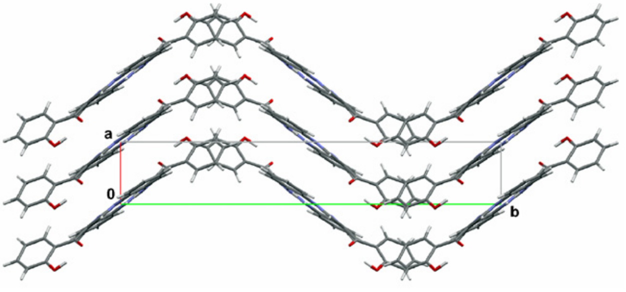


Figure 3. Packing diagram viewed down the *c* axis, showing $\pi\cdots\pi$ stacking interactions between adjacent molecules.

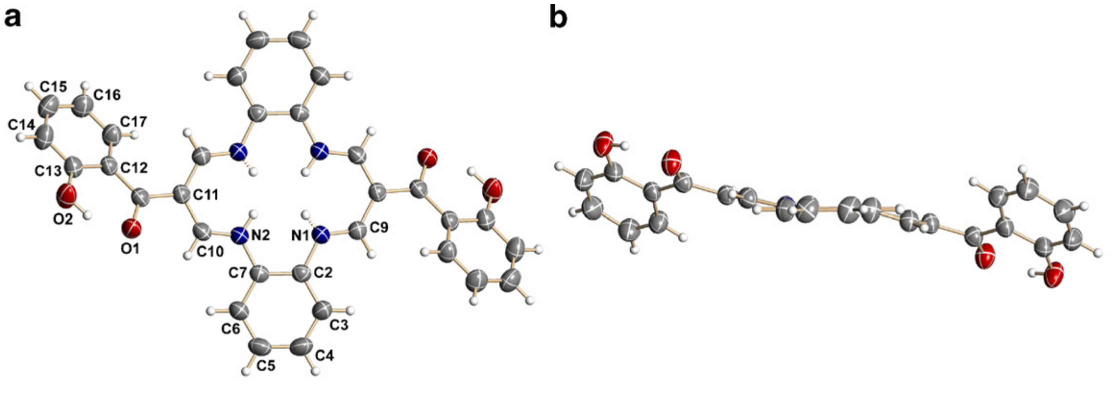


Figure 2. X-ray crystal structure of compound **1**: (a) top-view; (b) side-view. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

previously reported, this kind of flexible aliphatic chain appeared capable of inducing mesomorphic properties.[11]

To the best of our knowledge, **7** is the first mesomorphic metal-free dibenzotetraaza[14]annulene synthesized in a reasonable yield (41%). Previously, Veber and Forget reported liquid crystalline properties[5c] of a hexasubstituted dibenzotetraaza[14]annulene ligand prepared in 5% yield via an unpractical synthetic procedure.[5b] It seems therefore, that the easy and relatively efficient synthesis described here can be of practical significance. First of all, the procedure can be easily extended to other derivatives of the *meso* bis(hydroxybenzoyl) macrocycle, which may also be potential liquid crystals. Moreover, subsequent metallation of these ligands could give rise to a variety of corresponding metallomesogens.

The synthesis of dibenzotetraaza[14]annulene **7** is shown in Scheme 1. The preparation is based on a general method described elsewhere,[9] involving the condensation of *o*-phenylenediamine with 3-formylchromone to give *meso*-bis(2-hydroxybenzoyl)dibenzotetraaza[14]-annulene **1** (Fig. 1). Here, in the last step of the synthesis, 4,5-bis(3,7-dimethyloctyloxy)-*o*-phenylenediamine **6** is used in place of *o*-phenylenediamine in order to incorporate four additional substituents. Diamine **6** was prepared in four steps starting from 3,7-dimethyl-1-octanol **2**, which was initially transformed to the corresponding tosylate **3**[12] then used for alkylation of catechol to give **4**.[13] Dinitro derivative **5** was synthesized in 81% yield by a procedure analogous to that described earlier.[5a] The nitro groups of **5** were successfully reduced by means of $NaBH_4$/methanol in the presence of 10% Pd/C. Since diamine **6** appeared very reactive and easily oxidizable, the reaction mixture containing **6** was carefully filtered under argon in order to remove the catalyst, solid by-product and undissolved reducing agent, and immediately subjected to the reaction with 3-formylchromone. The product **7** was obtained in a reasonable yield of 41%, after recrystallization from acetone–methanol (4:1).

The new products **5** and **7** were fully characterized by elemental analysis, ESI-MS, ^1H and ^{13}C NMR spectra. The HETCOR spectrum of **7** used in the assignment of ^{13}C NMR signals is shown in the Supplementary data.

Our preliminary studies performed with the use of a polarizing optical microscope revealed the birefringence of **7** evidenced by the appearance of textures typical for liquid crystals. A sample of **7** was placed between a slide and a coverslip and slowly heated until it melted at $T_{iso} =$ 192 °C, then it was very slowly cooled to the room temperature. A variety of textures were observed on heating, below the clearing point. Two representative textures are shown in Figure 4a and b, others are collected in the Supplementary data. For each texture, the sample was annealed for 15 min before a photograph was taken. On cooling from the isotropic liquid, a new texture appeared just below the clearing point and remained stable at room temperature. This texture, shown in Figure 5, seems to be very similar to that recognized theoretically as characteristic of discotic hexagonal columnar phases[14] and observed experimentally for mesogens reported recently.[15] The thermal behaviour of **7** was also examined by differential scanning calorimetry (DSC). DSC traces recorded at different scan rates and corresponding to various temperature ranges are shown in the Supplementary data. Since more advanced methods are required to unambiguously elucidate the exact nature of the mesophases, a detailed study has been undertaken including X-ray diffraction measurements (XRD), which is currently in progress. The results will be reported elsewhere.

The X-ray crystal structure of **1** was reported by Rihs et al.[8] The present structure has been redetermined from new intensity data, with appreciably improved precision. The difference in the Fourier map analysis exhibited two peaks located in the expected positions of H amine atoms which indicated the presence of two tautomeric states of a tetraaza[14]annulene ring.[16] The found H atoms were disordered with a ratio of 0.39:0.61.

In the solid state, the central 14-membered ring of the macrocycle has an almost planar conformation and lies across the centre of inversion. The dihedral angle between the C(2–7)/N1/N2 central flat plane and C(11–17)/O2 benzoyl group is 43.24(3)°, and between the C(2–7)/N1/N2 and N1/C9/C8^i/N2^i planes it is 12.64(8)° (symmetry: $^i = -x, -y, -z$).

The carbonyl O1 atom is involved in a strong intramolecular hydrogen bond [O_2–$H_2O = 0.94(2)$, $H_2O \cdots O1 = 1.67(2)$, $O1 \cdots O2 = 2.5297(16)$ Å, $\angle O_2$–$H_2O \cdots O1 = 150(2)°$], and deviates from the plane of the benzoyl group, with a dihedral angle O1–C11–C12–C13 of 12.6(2)°.

The distance of the most outlying atom (O2) of the benzoyl group from the centre of the molecule is about 2 Å. The shortest intermolecular distance between adjacent macrocyclic rings is about 3.25 Å, indicating $\pi \cdots \pi$

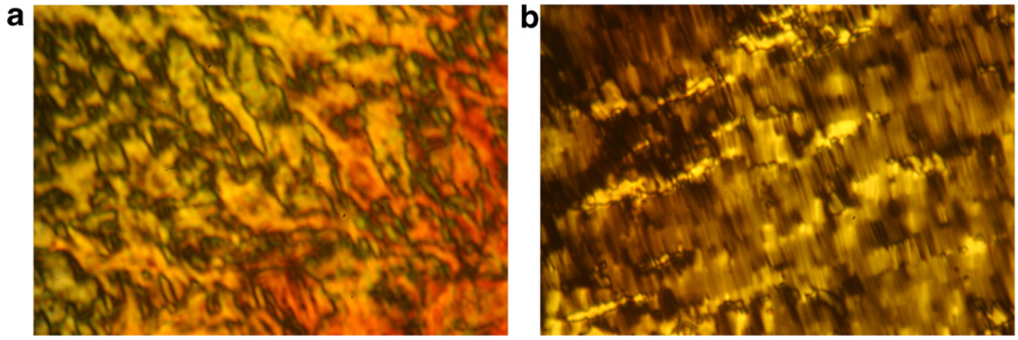


Figure 4. Textures of **7** viewed on heating, under crossed polarizers: (a) at 94 °C and (b) at 177 °C.

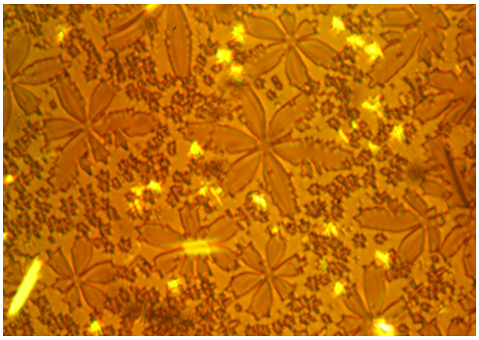


Figure 5. Texture of **7** observed on cooling, at 160 °C, under partially crossed polarizers.

stacking interactions. The molecules are linked by C5–H5 $\cdots$ O1^{ii} hydrogen bonds [C5–H5 = 0.97(2), H5 $\cdots$ O1^{ii} = 2.57(2), C5 $\cdots$ O1^{ii} = 3.398(2) Å, $\angle$C5-H5 $\cdots$ O1^{ii} = 144.4(13)°] (symmetry: $^{ii} = -x, -y, 1 - z$).

3,7-Dimethyl-1-octanol **2** and 3-formylchromone were purchased from Sigma–Aldrich and were used as received. Products **3** and **4** were prepared according to the procedures reported elsewhere.[12,13] Compound **1** was synthesized using the previously reported procedure.[9] Crystals suitable for X-ray measurements were grown from ethyl acetate.

1,2-Dinitro-4,5-bis(3,7-dimethyloctyloxy)benzene **5**: A solution of **4** (3.5 g, 9.1 mmol) in dichloromethane (50 ml) was added dropwise to vigorously stirred concentrated HNO_3 (20 ml) over a period of 30 min. Concentrated sulfuric acid (10 ml) was then added in portions and stirring was continued for 1.5 h at room temperature. The reaction mixture was next poured onto crushed ice and the resultant suspension was extracted with dichloromethane (2 × 50 ml). The organic layer was washed thoroughly with saturated aqueous sodium carbonate, then with water, and finally dried over anhydrous $MgSO_4$. The solvent was evaporated to give a crude product which was crystallized from ethanol. Pale-yellow crystals, yield 3.5 g (81%), mp 81–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.87 (d, $J = 6.6$ Hz, 12H, $H_{j,k}$), 0.96 (d, $J = 6.3$ Hz, 6H, H-1), 1.1–2.0 (m, 20H, $H_{b,d,e,f,g,i}$), 4.13 (t, 4H, $J = 5.9$ Hz, H_a), 7.31 (s, 2H, H-3); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 19.6 (C-1), 22.5, 22.6 ($C_{j,k}$), 24.6, 27.9, 29.8, 35.5, 37.1, 39.1 ($C_{b,d,e,f,g,i}$), 68.6 (C_a), 107.7 (C-3,6), 136.4 (C-1,2), 151.7 (C-4,5); IR (KBr) ν_{max} (cm^{-1}): 3072, 2958, 2926, 2870, 2845, 1538, 1221, 1048, 875; ESI-MS (m/z) 481.4 $(M+H)^+$; Anal. Calcd. for $C_{26}H_{44}N_2O_6$: C, 64.97; H, 9.23; N, 5.83. Found: C, 65.05; H, 9.12; N, 5.86.

2,3,11,12-Tetra(3,7-dimethyloctyloxy)-7,16-bis(2-hydroxybenzoyl)-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine **7**: To a reaction mixture containing **5** (1 g, 2.1 mmol) and 10% Pd/C (0.2 g) in methanol (75 ml), powdered $NaBH_4$ (1.59 g, 42 mmol) was added slowly in small portions, so as to maintain gentle boiling of the mixture until the supernatant solution became colourless (about 30 min). The catalyst, solid by-products and excess of undissolved $NaBH_4$ were removed by filtration through a pad of Celite under argon. 3-Formylchromone (0.36 g, 2.1 mmol) was immediately added to the filtrate and the mixture was allowed to reflux under argon for 2 h. The crude product which precipitated after cooling was filtered off and recrystallized from acetone–methanol (4:1). Brown crystals, yield 0.49 g (41%), mp 192 °C. ^{1}H NMR (300 MHz; $CDCl_3$, δ ppm): 0.87 (d, $J = 6.6$ Hz, 24H, $H_{j,k}$), 0.93 (d, $J = 6.3$ Hz, 12H, H-1), 1.17 (m, 8H, H_g), 1.18 (m, 4H, H_e), 1.33 (m, 8H, H_f), 1.33 (m, 4H, H_e), 1.54 (m, 4H, H_i), 1.60 (m, 4H, H_b), 1.66 (m, 4H, H_d), 1.84 (m, 4H, H_b), 3.96 (t, $J = 6.75$ Hz, 8H, H_a), 6.64 (s, 4H, H-1,4,10,13), 6.88 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H, H_s), 7.06 (d, $J = 7.8$ Hz, 2H, H_q), 7.45 (dd, $J = 7.8$ Hz, $J = 7.8$ Hz, 2H, H_r), 7.55 (d, $J = 7.8$ Hz, 2H, H_t), 8.34 (d, $J = 6$ Hz, 4H, H-6,8,15,17), 11.37 (s, 2H, H_u), 14.97 (t, $J = 6.6$ Hz, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 19.6 (C_i), 22.6, 22.69 ($C_{j,k}$), 24.7 (C_f), 27.98 (C_i), 29.9 (C_d), 36.2 (C_b), 37.3 (C_e), 39.2 (C_g), 68.0 (C_a), 100.6 (C-1,4,10,13), 108.9 (C_h), 118.1 (C_s), 118.4 (C_q), 120.2 (C-7,16), 130.1 (C-5a,9a,14a,18a), 131.1 (C_t), 134.6 (C_r), 148.6 (C-2,3,11,12), 150.7 (C-6,8,15,17), 161.5 (C_p), 195.9 (C_m); IR (KBr) ν_{max} (cm^{-1}): 2954, 2927, 2869, 1565, 1216, 1009, 815; ESI-MS (m/z) 1154.2 $(M+H)^+$; Anal. Calcd. for $C_{72}H_{104}N_4O_8$: C, 74.96; H, 9.09; N, 4.86. Found: C, 74.04; H, 9.03; N, 4.93.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 616527. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].

Supplementary data

The photographs of the mesomorphic textures observed on heating, the HETCOR spectrum and DSC curves of **7** are given in the Supplementary data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.09.134.

References and notes

1. Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana* **1977**, *9*, 471–480.
2. Dalcanale, E. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, New York, 1996; Vol. 10, pp 583–635.
3. Mountford, P. *Chem. Soc. Rev.* **1998**, *27*, 105–115, and references therein.
4. Hunziker, M. *Eur. Pat.* 162804 (**1984**) (*Chem. Abstr.* **1987**, *106*, 41716p).
5. (a) Forget, S.; Veber, M.; Strzelecka, H. *Mol. Cryst. Liq. Cryst.* **1995**, *258*, 263–275; (b) Forget, S.; Veber, M. *New J. Chem.* **1997**, *21*, 409–411; (c) Forget, S.; Veber, M. *Mol. Cryst. Liq. Cryst.* **1997**, *300*, 229–243; (d) Forget, S.; Veber, M. *Mol. Cryst. Liq. Cryst.* **1997**, *308*, 27–42.
6. Forget, S.; Kitzerow, H. S. *Liq. Cryst.* **1997**, *23*, 919–922.

7. (a) Pawlica, D.; Radic-Stojkovic, M.; Sieroń, L.; Piantanida, I.; Eilmes, J. *Tetrahedron* **2006**, *62*, 9156–9165; (b) Eilmes, J.; Ptaszek, M.; Dobrzycki, Ł.; Woźniak, K. *Polyhedron* **2003**, *22*, 3299–3305; (c) Eilmes, J.; Ptaszek, M.; Woźniak, K. *Polyhedron* **2002**, *21*, 7–17.
8. Rihs, G.; Sigg, I.; Haas, G.; Winkler, T. *Helv. Chim. Acta* **1985**, *68*, 1933–1935.
9. Sigg, I.; Haas, G.; Winkler, T. *Helv. Chim. Acta* **1982**, *65*, 275–279.
10. For a review see: (a) Donnio, B.; Guillon, D.; Deschenaux, R.; Bruce, D. W. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Pergamon: Amsterdam, 2003; Vol. 7, pp 357–607; (b) Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83–109.
11. Schouten, P. G.; Van der Pol, J. F.; Zwikker, J. W.; Drenth, W.; Picken, S. J. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 291.
12. Mori, K.; Harada, H.; Zagatti, P.; Cork, A.; Hall, D. R. *Liebigs Ann. Chem.* **1991**, 259–267.
13. Mohr, B.; Enkelmann, V.; Wenger, G. *J. Org. Chem.* **1994**, *59*, 635–638.
14. (a) Bouligand, Y. *J. Phys. (Paris)* **1980**, *41*, 1307–1315; (b) Oswald, P. *J. Phys. Fr.* **1988**, *49*, 1083–1089; (c) Oswald, P. *J. Phys. Fr.* **1988**, *49*, 2119–2124; (d) Spong, J. K.; LaComb, L. J.; Dovek, M. M.; Frommer, J. E.; Foster, J. S. *J. Phys. Fr.* **1889**, *50*, 2139–2146; (e) Livolant, F.; Leforestier, A. *Biophys. J.* **2000**, *78*, 2716–2729.
15. (a) Kraft, A.; Reichert, A.; Kleppinger, R. *Chem. Commun.* **2000**, 1015–1016; (b) Bushey, M. L.; Hwang, A.; Stephens, P. W.; Nuckolls, C. *J. Am. Chem. Soc.* **2001**, *123*, 8157–8158; (c) Chien, C.-W.; Liu, K.-T.; Lai, C. K. *J. Mater. Chem.* **2003**, *13*, 1588–1595.
16. Azuma, N.; Tani, H.; Ozawa, T.; Niida, H.; Tajima, K. *J. Chem. Soc., Perkin Trans. 2* **1995**, 343–348.