Liquid Crystals, Vol. 34, No. 1, January 2007, 19–24

Preparation of a discotic 2,4,7,9-tetraaryl-*6H*-dibenzo[*c,e*][1,2]thiazine and generation of a persistent Radical [1]

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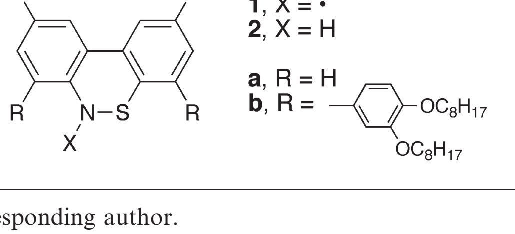
(*Received 15 June 2006; accepted 27 July 2006*)

6H-Dibenzo[d,e][1,2]thiazine substituted with four 3,4-dioctyloxyphenyl groups forms a room temperature discotic phase with a clearing temperature of 104°C. Oxidation of the thiazine **2b** with either metal oxides (PbO_2 or AgO) or SO_2Cl_2 gave a moderately stable radical **1b** (a_N=0.95 mT, g=2.0045). Full conversion of **2b** to **1b** was observed with AgO in a toluene/MeCN mixture or with SO_2Cl_2. The radical **1b** was isolated in the neat form with the latter oxidant. It shows sensitivity to molecular oxygen, which hampered its purification and subsequent thermal and magnetic studies.

1. Introduction

Columnar organization of aromatic discotic materials [2] gives rise to $\pi-\pi$ interactions between their aromatic cores. One manifestation of these interactions is anisotropic electric conduction along the stacks [3]. We have been interested in exploiting this intermolecular electronic communication to engineer spin–spin interactions of open-shell molecules [4] and to study their magnetic properties in discotic phases. In this context, we designed a new class of conventional discotic materials containing an electrically neutral spin delocalized in the π system of the central heteroaromatic core [5, 6].

Several years ago, we demonstrated that dibenzo[*c*,*e*][1,2]thiazinyl (**1a**) and also cinnolino[5,4,3][*c*,-*d*,*e*][1,2]benzothiazinyl can be generated in solution, and have moderate stability sufficient for use as structural elements in paramagnetic discotic liquid crystals [7]. Our investigations of the closely related series of benzo[*c*]-cinnolines [8] and carbazoles [9] indicated that substitution of **1a** with four 3,4-dioctyloxyphenyl groups should induce discotic behaviour in **1b**. This potentially discotic radical could be available from the corresponding thiazine **2b**, and its preparation and characterization constitutes the first step toward discotic radical **1b**.



Here we report progress towards paramagnetic discotic liquid crystals. We describe the preparation and liquid crystalline properties of 2,4,7,9-tetrakis(3,4-dioctyloxyphenyl)-6*H*-dibenzo[*c*,*e*][1,2]thiazine (**2b**). We also report preliminary results on the generation and characterization of radical **1b**.

2. Results and discussion

2.1. *Synthesis*

Thiadiazine **2b** was obtained from tetraarylbiphenyl **3** in three steps (scheme 1) by analogy to the preparation of the parent **2a**. Thus, reduction of the nitro group in **3** and preparation of amine **4** was accomplished using powdered Zn in propionic acid in the absence of air. We found that the highly lipophilic **3** had insufficient solubility in acetic acid to conduct the reduction. Also in the presence of atmospheric oxygen the yield of amine **4** was significantly lower, about 30%. This is presumably due to oxidative degradation of amine **4** by the superoxide anion formed in the presence of Zn, as was observed before for another substrate [10].

The closure of the N–S bridge was accomplished by the treatment of amino sulphide **4** with NCS (scheme 1). The resulting sulphilimine **5** was thermolysed in anhydrous benzene to form thiazine **2b**. The use of toluene instead of benzene for thermolysis increased the yield and rate of the product formation. The resulting thiazine **2b** was purified by column chromatography. Attempts at crystallization from hexane, pentane or alcohol were unsuccessful and resulted in microdroplet suspensions or gel.

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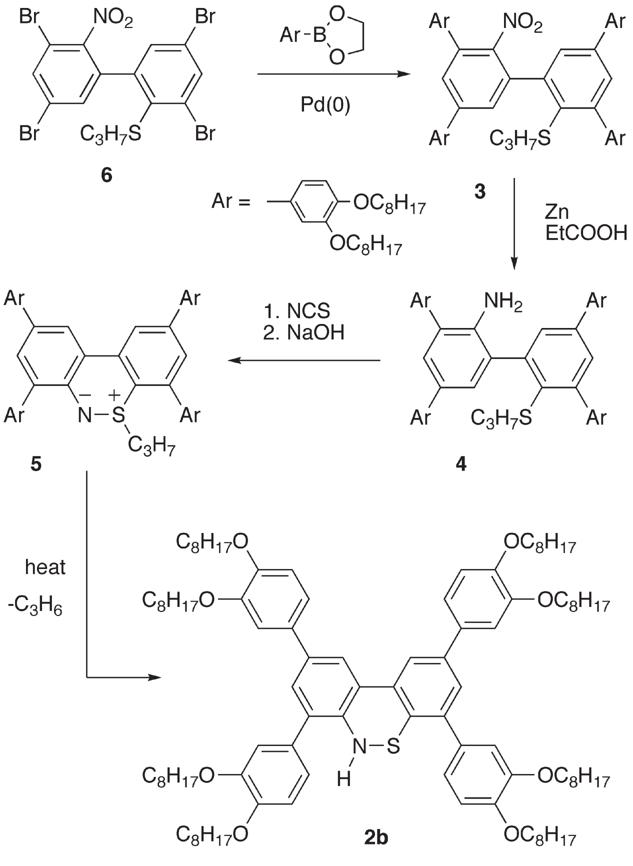
Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290601076445



Scheme 1

The biphenyl **3** was prepared by Suzuki coupling of 3,3′,5,5′-tetrabromo-2-nitro-2′-propylthiobiphenyl (**6**) [11] and 3,4-dioctyloxyphenylboronic acid ethylene glycol ester [8]. The use of DME as a solvent instead of toluene gave higher yields of **3**. The progress of the reaction and the composition of the reaction mixture were monitored by HPLC. The reaction was driven to completion by extending the reaction time and adding more of the boronic ester and the catalyst, when necessary. Almost complete conversion to the product was necessary for the efficient separation of pure **3** from the reaction mixture.

2.2. *Liquid crystalline properties*

Thiazine **2b** is a yellow–green waxy solid at room temperature. A DSC analysis showed only one broad transition to an isotropic phase at 104°C with an enthalpy of $16\,\mathrm{kJ\,mol^{-1}}$ upon heating (figure 1). The second heating reproduced the original heating curve of the virgin sample within 1°C. There was no evidence of crystallization even when the virgin sample was cooled to −50°C, or when it was stored at 0°C for over a year. It is likely, however, that the discotic phase forms an ordered glass at low temperatures, but such a process was not detected on the DSC trace.

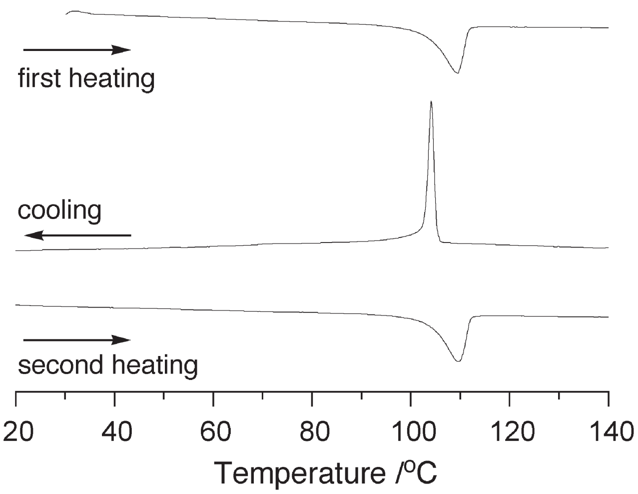


Figure 1. A DSC trace of **2b**; heating and cooling rates are $5°\mathrm{C\,min^{-1}}$.

Optical investigations confirmed that **2b** exhibits liquid crystalline behaviour at ambient temperature. The mesophase obtained on cooling thiazine **2b** from the isotropic liquid displayed a fan-shaped texture, which is characteristic for columnar mesophases [12, 13] (figure 2). It also exhibited domains typical for homeotropically oriented regions of the uniaxial phase.

2.3. *Generation and characterization of radical 1b*

Radical **1b** was generated from thiazine **2b** using 10 equivalents of rigorously dried PbO_2 in benzene, or AgO in a toluene/MeCN mixture, in the presence of K_2CO_3. In both cases a strong EPR signal was detected.

The room temperature benzene solution spectrum of radical **1b** consists of a triplet centred at about 3490 G, which arises from the coupling to the nitrogen atom, $a_N = 0.95\,\mathrm{mT}$ (figure 3). The couplings to hydrogen atoms are unresolved, giving rise to a broad triplet. Results for the parent radical **1a** [7] (figure 4) indicate that the largest hfcc of about 0.1 mT are expected for H atoms in positions 8 and 10 of the dibenzothiazine ring. In addition, at least six smaller hfcc $<0.03\,\mathrm{mT}$ for hydrogens in positions 1 and 3 and *ortho* positions of the substituents in the high spin density positions 7 and 9.

The measured *g* value for radical **1b** is 2.0045 which is smaller than measured for the parent radical **1a** (2.0052) [7]. This is consistent with a significant spin delocalization onto the substituents, especially those in positions 7 and 9 of the dibenzothiazine ring.

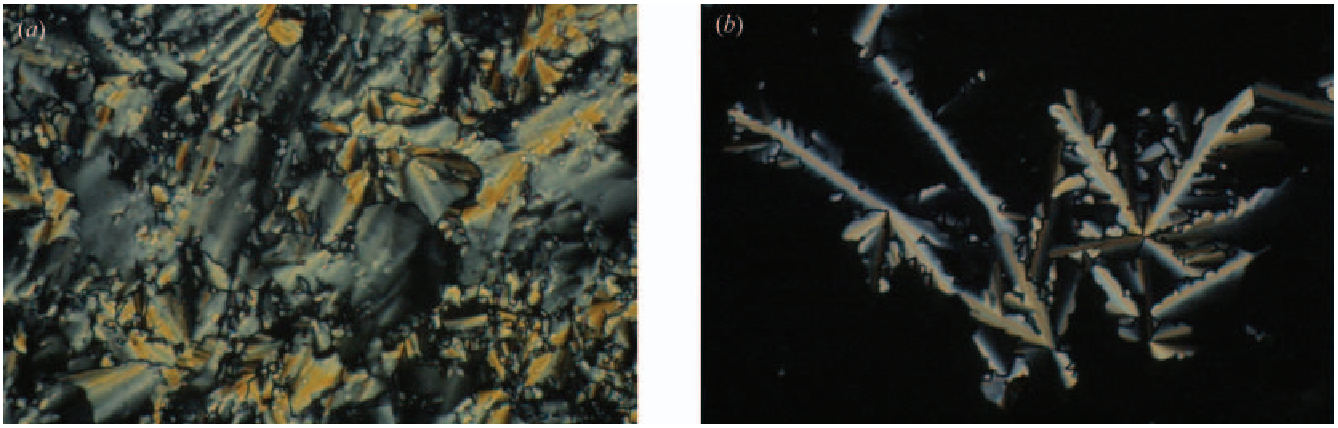


Figure 2. Optical textures of **2b** taken for different regions of the sample at (*a*) 55°C, (*b*) 44°C. Magnification 300 ×; both textures were obtained on cooling.

Careful analysis of the oxidation reactions demonstrated that with PbO_2 the thiazine was oxidized to the radical in <10% yield (by comparison with a TEMPO-ol reference). In contrast, the more potent oxidant AgO in a polar solvent completely converted the starting thiazine **2b** to the radical in less than 15 min. This is consistent with our previous observations of the high effectiveness of AgO in the generation of the parent thiadiazinyls [14]. The rate for full conversion of **2b** to **1b** was significantly lower than that reported for the parent thiadiazinyls (~1.5 min) [14]. This is presumably due to the difficult access of the base to the reaction centre in **2b** in the presence of the large lypophylic 3,4-dioctyloxyphenyl substituents.

The dark green radical **1b** is moderately sensitive to oxygen and decomposes in solutions in the presence of oxygen to a colourless product, presumably the corresponding *S*-oxide [14]. This visual difference in colours of the thiazine (yellow) and the decomposition product(s) (white) was used for establishing the optimum reaction time with AgO (*vide infra*). The colorimetric results were verified by TLC analysis, which took advantage of the significantly higher polarity of radical decomposition products relative to the starting thiazine **2b**. These experiments also indicated that toluene might be interfering with the generation and stability of radical **1b**.

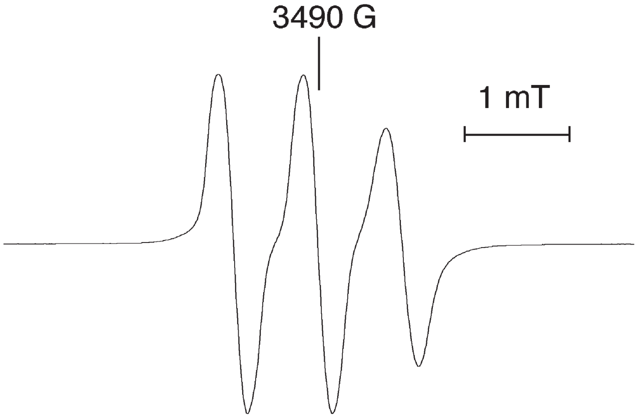


Figure 3. ESR spectrum for **1b** recorded in benzene at ambient temperature. The radical was generated with AgO/K_2CO_3.

The fast and complete conversion of the starting thiazine **2b** achieved with the AgO oxidant opened possibilities for isolation of the radical in the neat form. Unfortunately, radical **1b** formed a gel in a toluene/MeCN mixture at low temperatures, and chromatographic purification with a Florisil column [14] was not possible at either −78 or −40°C. Chromatography of **1b** at ambient temperature or near 0°C resulted in bleaching of the green colour and decomposition of the radical.

To overcome the problem with gel formation, radical **1b** was efficiently generated in pure toluene by oxidation of **2b** with SO_2Cl_2 [14]. The resulting dark green solution of the

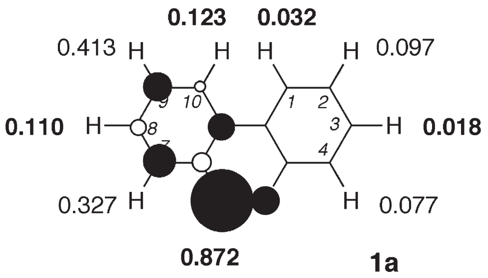


Figure 4. Experimental hyperfine coupling constants (mT) and DFT-derived spin distribution map for **1a**. Values in bold face are relevant to radical **1b**. Circles represent relative total positive (full circles) and negative (open circles) spin densities greater than 0.05; data taken from [7]. Italicized numbers show the ring numbering system.

radical was successfully passed through a short Florisil column at -78°C. Evaporation of the solvent under reduced pressure gave **1b** as a dark green waxy solid. Unfortunately, without rigorous exclusion of oxygen it decomposed within several minutes at room temperature. The apparent lower stability of **1b** towards oxygen relative to the parent **1a** [7] or benzothiadiazinyls [14] is most likely related to diffusion of oxygen through the fluid sample of **1b**, while the parent radicals are crystalline solids.

3. Conclusions and summary

The synthetic availability of discotic thiazine **2b** opened possibilities for the study of the potentially discotic radical **1b**. Microscopic and DSC studies of **2b** demonstrated mesogenic behaviour at ambient temperature, which strongly suggests that the corresponding radical **1b** also forms liquid crystalline phases. The preliminary experiments demonstrated that radical **1b** can be efficiently generated from **2b** and can presumably be purified in a strictly anaerobic atmosphere. The lack of a crystalline form of **1b** significantly complicates the purification and accelerates decomposition in air.

4. Experimental

4.1. *Materials and characterization*

^{1}H NMR spectra were obtained at 400 MHz in CD_2Cl_2 and referenced to the solvent (δ $CHDCl_2$ 5.32 ppm). IR spectra were recorded for neat samples (liquid or microcrystalline) on NaCl plates. Thermal analysis was obtained using a TA Instruments 2920 DSC. Transition temperatures (onset) and enthalpies were obtained using small samples (1–2 mg) and a heating rate of $5^\circ\mathrm{C\,min}^{-1}$ under a flow of nitrogen.

X-band ESR spectra were obtained on a Bruker 2300 EPR instrument in distilled benzene. Solutions were degassed by three freeze/pump/thaw cycles. Samples were referenced using strong pitch with $g=2.0028$. AgO was prepared according to a literature procedure [15]; AgO, PbO_2, and K_2CO_3 were dried under vacuum at 75°C for 24 h. Both solvents for the radical generation were anhydrous: toluene was stored over Na, and acetonitrile was distilled from CaH_2.

4.2. *Generation and isolation of radical 1b*

Method A. Thiazine **2b** (15.3 mg, 0.01 mmol) was dissolved in dry toluene (1 ml) followed by the addition of dry MeCN (1 ml). The solution was vigorously stirred over dried AgO (12.4 mg, 0.1 mmol) and K_2CO_3 (13.8 mg, 0.1 mmol) at ambient temperature under Ar for 11 min. The resulting dark green solution of the radical was diluted with toluene and cooled to -78°C. The solution thickened and it could not be filtered through a Florisil column. Solvents were removed under reduced pressure, leaving a dark green soft solid of the crude radical.

Method B. To a stirred solution of the thiazine **2b** (15.3 mg, 0.01 mmol), a solution of SO_2Cl_2 (0.005 mmol) in dry toluene (0.5 ml) and a solution of Me_2EtN (0.01 mmol) in toluene (0.5 ml) were added alternately and dropwise at -78°C. The resulting dark green solution of radical **1b** was passed through a short Florisil column at -78°C, with toluene as an eluant. The solvent was removed under reduced pressure, giving a dark green waxy solid, which decomposed within several minutes to an off-white product.

4.3. *Determination of the optimum oxidation time for 2b with the AgO/K_2CO_3 method*

Thiazine **2b** (8 mg, 0.005 mmol) was dissolved in dry toluene (0.5 ml) and dry acetonitrile (0.5 ml). A 10-fold excess of freshly prepared and dried AgO (6.5 mg, 0.05 mmol) and K_2CO_3 (7 mg) were added. The reaction mixture was vigorously stirred under Ar. Every 40–60 seconds a sample of ~0.1 ml was taken from the reaction mixture, passed through a microfilter to remove the oxidant, and placed in a test tube. The series of samples was allowed contact with air for several hours before visual inspection. The first colourless sample indicated full consumption of thiazine **2b** and determined the optimum reaction time. The colorimetric results were verified by TLC analysis using CH_2Cl_2/hexane (2/1) mixture as an eluant.

4.4. *2,4,7,9-Tetrakis(3,4-dioctyloxyphenyl)-6H-dibenzo[c,e] [1,2]thiazine (2b)*

A solution of NCS (0.070 g, 0.522 mmol) in dry CH_2Cl_2 (2 ml) was added dropwise to a stirred solution of amine **4** (0.782 g, 0.50 mmol) in dry CH_2Cl_2 (3 ml) at -78°C under Ar. The solution was gradually warmed to room temperature and stirred under Ar overnight. A 5% solution of KOH was added, the mixture stirred for 30 min, and the organic layer separated, washed with water and dried (Na_2SO_4). The solvent was evaporated and the product purified on a silica gel plug using CH_2Cl_2 to elute faster moving fractions, followed by CH_2Cl_2/EtOAc (20/1) to give 0.56 g of sulphilimine **5** as a yellow oil. The resulting crude **5** was thermolysed in dry toluene at 110°C overnight. The solvent was evaporated and the resulting thiazine **2b** purified on a silica gel plug using hexanes/CH_2Cl_2 mixture (2/1 followed by 1/1). The solvent was evaporated leaving 0.183 g (34% yield) of a greenish waxy solid. ^{1}H NMR δ 0.86–0.91 (m, 24H), 1.28–1.35 (m, 64H), 1.44–1.51 (m, 16H), 1.78–1.85 (m, 16H), 3.76 (s, 1H), 3.98–4.06 (m, 16H), 6.85–6.90 (m, 2H), 6.94–7.01 (m, 5H), 7.04 (d, J=1.9 Hz, 1H), 7.20–7.24 (m, 4H), 7.51 (d, J=2.0 Hz, 1H), 7.59 (d, J=1.8 Hz, 1H), 7.94 (d, J=2.0 Hz, 1H), 7.98 (d, J=1.8 Hz, 1H). FAB: *m/z* 1528 (M^+), 1416 ($M^+-C_8H_{17}$). Anal: calcd for $C_{100}H_{153}NO_8S$, C 78.54, H 10.08, N 0.92; found, C 78.74, H 10.03, N 0.96%.

4.5. *2-Nitro-3,3′,5,5′-tetrakis(3,4-dioctyloxyphenyl)-2′-propylthiobiphenyl (3)*

To a stirred solution of 2-nitro-2′-propylthio-3,3′,5,5′-tetrabromobiphenyl [11] (**6**, 0.59 g, 1.0 mmol) and $Pd(Ph_3P)_4$ (0.23 g, 0.2 mmol) in toluene (50 ml), 2M aqueous Na_2CO_3 (4 ml) and a solution of 3,4-dioctyloxyphenylboronic acid ethylene glycol ester [8] (1.78 g, 4.4 mmol) in ethanol (20 ml) were added. The reaction mixture was stirred at 85–90°C under an inert atmosphere for 2 days. An additional portion of $Pd(Ph_3P)_4$ (0.06 g, 0.05 mmol), toluene (10 ml), 2M aqueous Na_2CO_3 (1 ml), and the boronic acid ester (0.40 g, 1.0 mmol) in ethanol (5 ml) were added. The reaction mixture was stirred under the same conditions for an additional 1 day. The progress of the reaction was monitored by HPLC (normal phase column, gradient of CH_2Cl_2 in hexanes) until the absence of the starting material and partially arylated intermediates. The reaction mixture was cooled and extracted with the Et_2O. The organic solution was washed with water twice and dried (Na_2SO_4). The solvent was evaporated to yield 4.03 g of a dark oil, which was passed through a silica gel plug using hexanes/CH_2Cl_2 (2/1) as eluant. The product was purified on a silica gel column using eluant of increasing polarity from pure hexane to a hexanes/CH_2Cl_2 mixture (1/1) to give 0.91 g (57% yield) of **3** as a dark yellow oil. ^{1}H NMR δ 0.65 (t, J=7.3 Hz, 3H), 0.85–0.90 (m, 24H), 1.19 (t, J=7.0 Hz, 2H), 1.29–1.34 (m, 64H), 1.45–1.48 (m, 16H), 1.76–1.82 (m, 16H), 2.19–2.24 (m, 2H), 3.99–4.05 (m, 16H), 6.92–6.99 (m, 6H), 7.08 (dd, J_1=8.2 Hz, J_2=2.0 Hz, 1H), 7.13–7.19 (m, 4H), 7.23 (dd, J_1=8.2 Hz, J_2=2.1 Hz, 1H), 7.46 (d, J=2.2 Hz, 1H), 7.56 (d, J=2.2 Hz, 1H), 7.65 (s, 2H). IR: 1512, 1468, 1377, 1261, 1253, 1142 cm^{-1}. FAB: *m/z* 1557 (M^+-NO_2). Anal: calcd for $C_{103}H_{159}NO_{10}S$, C 77.15, H 9.99, N 0.87; found, C 77.22, H 10.10, N 0.89%.

4.6. *2-Amino-3,3′5,5′-tetrakis(3,4-dioctyloxyphenyl)-2′-propylthiobiphenyl (4)*

Biphenyl **3** (1.25 g, 0.78 mmol) was dissolved in propionic acid (15 ml), Zn dust (1.80 g) was added, and the suspension was stirred at 60°C for 15 h under Ar. The progress of the reaction was monitored by TLC. If necessary, additional amounts of Zn dust were added and the stirring continued. The reaction mixture was cooled, poured into water, and the product extracted with toluene. The organic solution was neutralized with solution of Na_2CO_3 to remove the residual propionic acid, and dried (Na_2SO_4). The solvent was removed to yield 1.144 g of a dark oil. The crude product was separated on a silica gel column using eluant of increasing polarity from pure hexanes to a hexanes/CH_2Cl_2 mixture (2/1) to give 0.782 g (64% yield) of **4** as a pale yellow oil. ^{1}H NMR δ 0.65 (t, J=7.3 Hz, 3H), 0.85–0.92 (m, 24H), 1.18–1.35 (m, 70H), 1.42–1.49 (m, 16H), 1.76–1.85 (m, 16H), 2.19 (t, J=7.3 Hz, 2H), 3.9 (bs, 2H), 3.97–4.06 (m, 16H), 6.90–7.00 (m, 4H), 7.05–7.23 (m, 8H), 7.34 (d, J=2.2 Hz, 1H), 7.37 (d, J=2.2 Hz, 1H), 7.55 (d, J=2.2 Hz, 1H), 7.56 (d, J=2.2 Hz, 1H). IR: 1511, 1463, 1247, 1140 cm^{-1}. FAB: *m/z* 1573 (M^+). Anal: calcd for $C_{103}H_{161}NO_8S$, C 78.62, H 10.31, N 0.89; found, C 79.00, H 10.34, N 0.81%.

Acknowledgements

This project was supported by NSF grants (CHE-9528029 and CHE-0096827).

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