ORGANIC
LETTERS

2008
Vol. 10, No. 22
5139−5142

A Facile Synthesis of Elusive Alkoxy-Substituted Hexa-*peri*-hexabenzocoronene

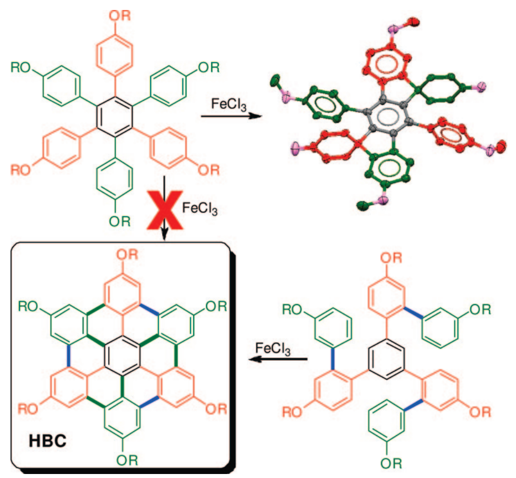
Shriya H. Wadumethrige and Rajendra Rathore*

Department of Chemistry, Marquette University,
P.O. Box 1881, Milwaukee, Wisconsin 53201

rajendra.rathore@marquette.edu

Received September 1, 2008

ABSTRACT



Oxidative cyclodehydrogenation of hexakis(4-alkoxyphenyl)benzene produces a quantitative yield of an indenofluorene derivative rather than the expected alkoxy-substituted hexa-*peri*-hexabenzocoronene (HBC). The structure of the unexpected indenofluorene was established by X-ray crystallography. The mechanistic considerations for the formation of the indenofluorene derivative led us to devise an alternative synthesis of elusive alkoxy-substituted HBC—a potentially important, disk-shaped structure for the preparation of liquid crystalline materials for practical applications in the emerging areas of molecular electronics and nanotechnology.

The study of polycyclic aromatic hydrocarbons (PAH), such as triphenylenes (TP) and hexa-*peri*-hexabenzocoronenes (HBC), has attracted considerable attention[1] since these materials hold promise for applications in the emerging areas of molecular electronics and nanotechnology.[2]

It is noteworthy that hexaalkoxytriphenylenes (**1**) have been extensively explored as building blocks for the preparation of liquid crystalline materials, owing to their disk-shaped structure which allows efficient columnar packing.[3] Columnar discotic liquid crystals have received considerable attention as functional materials for applications such as

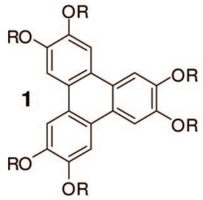
---

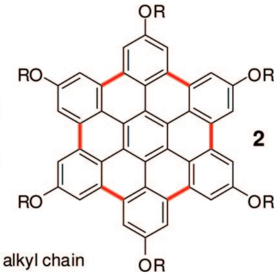
(1) (a) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747–1785. (b) Watson, M. D.; Fechtenkotter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300. (c) Chebny, V. J.; Gwengo, C.; Gardinier, J. R.; Rathore, R. *Tetrahedron Lett.* **2008**, *49*, 4869–4872.

(2) (a) *Introduction to Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Oxford University Press: New York, 1995. (b) Maiya, B. G.; Ramasarma, T. *Curr. Sci.* **2001**, *80*, 1523–1530. (c) Gross, M.; Muller, D. C.; Nothofer, H.-G.; Scherf, U.; Neher, D.; Brauchle, C.; Meerholz, K. *Nature* **2003**, *405*, 661–665. (d) *Organic Electronics*; Klauk, H., Ed.; Wiley-VCH: Weinheim, 2006.

(3) (a) Mori, H. *Proc. SPIE−Int. Soc. Opt. Eng.* **2006**, 6135 (Liquid Crystal Materials, Devices, and Applications XI), 613503/1613503/8. (b) Tschierske, C. *J. Mater. Chem.* **2001**, *11*, 2647–2671. (c) Goodby, J. W.; Saez, I. M.; Cowling, S. J.; Gortz, V.; Draper, M.; Hall, A. W.; Sia, S.; Cosquer, G.; Lee, S.-E.; Raynes, E. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 2754–2787.

10.1021/ol8020429 CCC: $40.75

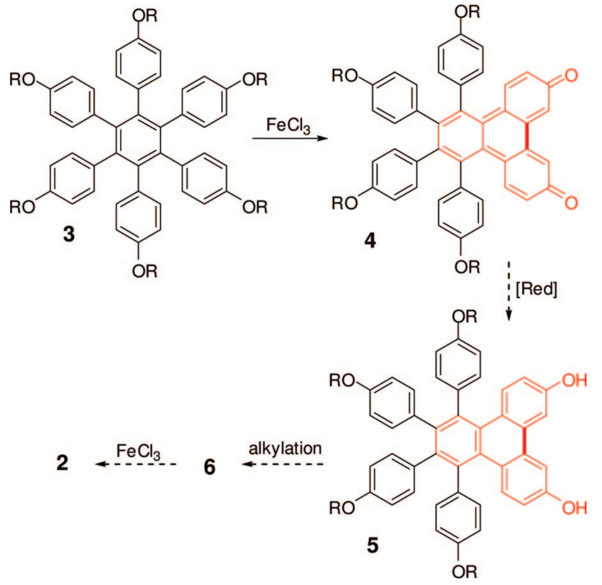




R = long alkyl chain

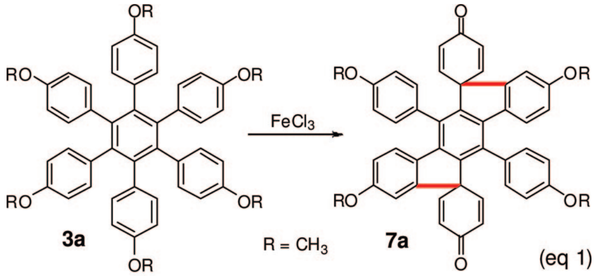
photovoltaic solar cells, light emitting diodes, and field effect transistors.[4] It can be envisioned that a corresponding HBC analogue (**2**), possessing a disk of relatively large size, may prove to be superior for the preparation of liquid crystalline materials.[3,4] Unfortunately, the synthesis of the parent hexaalkoxy HBC (**2**) has thus far eluded chemists.[5] Müllen and co-workers have reported[6] that attempted preparation of **2** from hexakis(4-alkoxyphenyl)benzene via oxidative cyclodehydrogenation led to a quantitative yield of a phenanthroquinone **4**, i.e., Scheme 1.

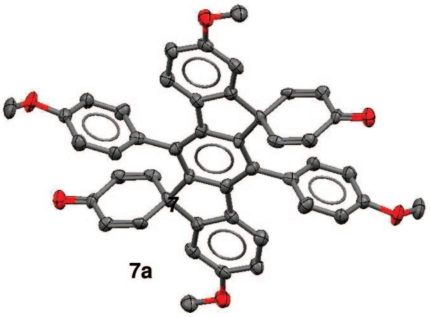
Scheme 1. Postulated Synthesis of Hexaalkoxy-HBC **2**



It was conjectured that a reduction of quinone **4** to the corresponding hydroquinone **5** followed by *O*-alkylations and oxidative cyclization may allow the preparation of the long-sought hexaalkoxy-HBC **2** (Scheme 1). However, we now describe that the oxidative cyclization of **3** unfortunately does not produce quinone **4** but rather an unexpected indeno[1,2-*b*]fluorene derivative (**7**), whose structure is confirmed by X-ray crystallography. Mechanistic consideration for the formation of indenofluorene **7** via oxidative cyclodehydrogenation of **3** now leads us to an alternative route to access the elusive **2**. The details of these preliminary findings are described herein.

Thus, addition of a solution of $FeCl_3$ in nitromethane to a solution of **3** in dichloromethane at ∼0 °C produces a green solution which was stirred for 1 h while a slow stream of argon was bubbled through the solution to remove gaseous hydrochloric acid, which was formed in the reaction. The standard workup[7] afforded a pale yellow solid in quantitative yield. The $^1H/^{13}C$ NMR analysis of the above solid suggested that it is a single compound that has lost two alkyl groups and two "H" atoms. As such, the preliminary spectral analysis was in accord with the phenanthroquinone-like structure **4**; however, further experimentation[8] and X-ray crystallography showed that it is indenofluorene **7** (i.e., eq 1). Note that the thermal ellipsoids for the ORTEP representation of **7** ($R = CH_3$), in eq 1, are shown in 50% probability, and hydrogens are omitted for the sake of clarity.





Moreover, both **3a** (R = methyl) and **3b** (R = *n*-hexyl) formed the corresponding indenofluorenes (**7a** and **7b**) upon oxidative cyclodehydrogenation as judged by the similarity of their $^1H/^{13}C$ NMR spectra (Figure S1) and by mass spectrometry (see the Supporting Information for the details).

---

(4) (a) Nelson, J. *Science* **2001**, *293*, 1059–1060. (b) Hassheider, T.; Benning, S. A.; Lauhof, M. W.; Kitzerow, H. S.; Bock, H.; Watson, M. D.; Müllen, K. *Mol. Cryst. Liq. Cryst.* **2004**, *413*, 461–472. (c) Oukachmih, M.; Destruel, P.; Seguy, I.; Ablart, G.; Jolinat, P.; Archambeau, S.; Mabiala, M.; Fouet, S.; Bock, H. *Sol. Energy Mater. Sol. Cells* **2005**, *85*, 535–543. (d) Bayer, A.; Zimmermann, S.; Wendorff, J. H. *Mol. Cryst. Liq. Cryst.* **2003**, *396*, 1–22. (e) Katsuhara, M.; Aoyagi, I.; Nakajima, H.; Mori, T.; Kambayashi, T.; Ofuji, M.; Takanishi, Y.; Ishikawa, K.; Takezoe, H.; Hosono, H. *Synth. Met.* **2005**, *149*, 219–223.

(5) See: Zang, Q.; Prins, P.; Jones, S. C.; Barlow, S.; Kondo, T.; An, Z.; Siebbeles, L. D.; Marder, S. R. *Org. Lett.* **2005**, *7*, 5019–5022.

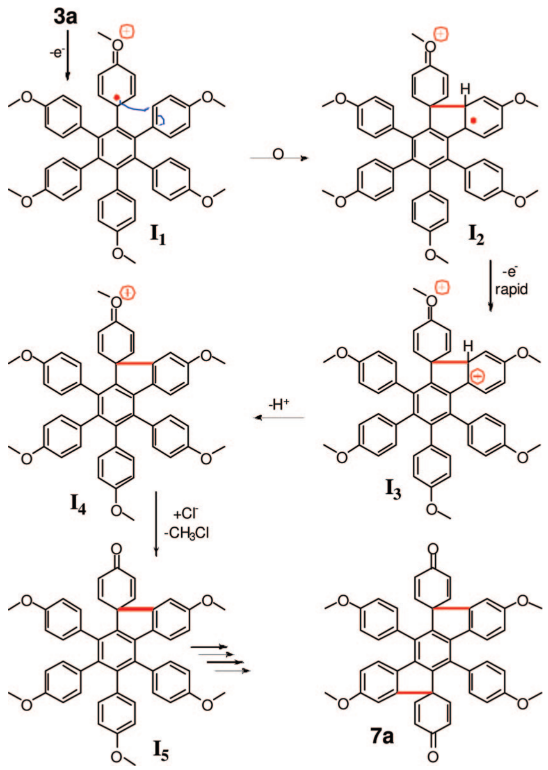
(6) (a) Weiss, K.; Beernink, G.; Dötz, F.; Birkner, A.; Müllen, K.; Wöll, C. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3748–3752. (b) Dou, X.; Yang, X.; Bodell, G. J.; Wagner, M.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2007**, *9*, 2485–2488. (c) Feng, X.; Pisula, W.; Takase, M.; Dou, X.; Enkelmann, V.; Wagner, M.; Ding, N.; Müllen, K. *Chem. Mater.* **2008**, *20*, 2872–2874.

(7) Rathore, R.; Burns, C. L. *J. Org. Chem.* **2003**, *68*, 4071–4074.

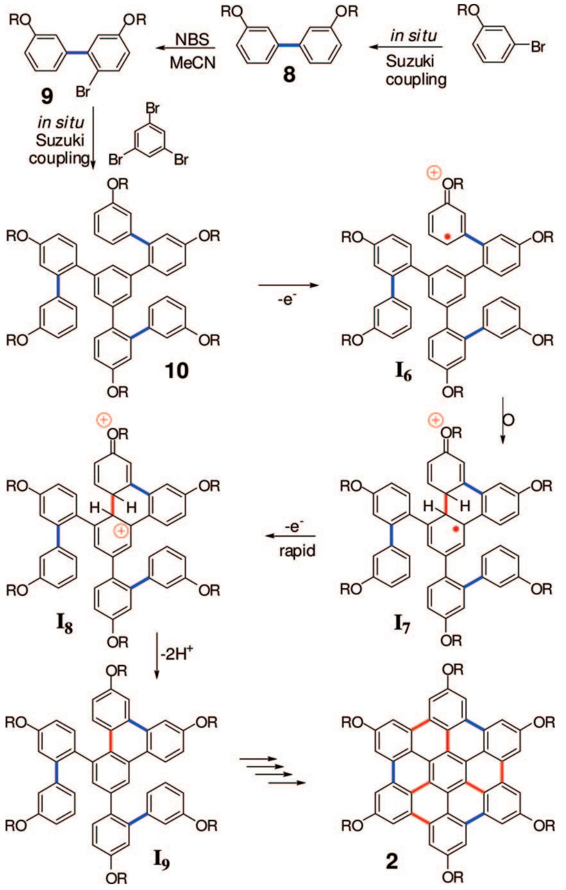
(8) A hydrogenation of **7b** (**4**) in ethyl acetate using Pd/C as a catalyst did not afford the corresponding hydroquinone **5** but a reduced indenofluorene derivative containing cyclohexanone moieties; see the Supporting Information.

The transformation in eq 1 can be carried out using a variety of 1-e$^-$ oxidants such as NO$^+$SbCl$_6^-$,[9] PhI(OCOCF$_3$)$_2$,[10] DDQ−TFA,[11a] and FeCl$_3$ as well as electrochemical oxidation.

Scheme 2. Postulated Mechanism for the Formation of **7**



Scheme 3. Synthesis of Hexaalkoxy HBC **2**



The oxidative transformation in eq 1 can be reconciled according to an ECECC mechanism (Scheme 2)[11,12] based on the spectroscopic and structural data. Thus, one-electron oxidation of **3** generates its radical cation where a single charge is stabilized via quinoidal distortion in such a way that the radical character is largest at the *p*-carbon of the anisyl group (see **I$_1$**).[13] The radical cation **I$_1$** undergoes an intramolecular C−C bond formation to yield a distonic radical cation (**I$_2$**).[14] It is the distonic nature of this rearranged radical cation which facilitates the removal of a second electron at a much lower potential[15] and leads to the formation of a dication (**I$_3$**).[14b] The loss of a proton and an alkyl group produces the fluorene derivative (**I$_5$**), which in turn undergoes a similar sequence of ECECC events to produce indenofluorene **7**. Note that indenofluorene **7** does not suffer further oxidative transformations owing to the fact that it undergoes oxidation (E_{ox} = 1.18 V vs SCE) at a relatively low potential to its cation radical which is stable under the reaction conditions. (See Figures S2 and S3 in the Supporting Information for a cyclic voltammogram and the cation radical spectrum of **7**, respectively.)

From the mechanistic considerations in Scheme 2, it was clear that an alternative C−C bond-forming sequence was desired to access HBC **2**. It was conjectured that if some of the C−C bonds were preformed in a new precursor of HBC **2**, it should be feasible to produce **2** rather than indenofluorene **7**.[16]

Accordingly, we chose 1,3,5-tris(5,5′-di-*n*-hexyloxy-2-biphenyl)benzene (**10**) as a precursor to HBC **2**, which was obtained by a one-pot Suzuki coupling[17] of 3 equiv of

---

(9) Rathore, R.; Abdelwahed, S. H.; Guzei, I. A. *J. Am. Chem. Soc.* **2004**, *126*, 13582–13583.

(10) Takada, T.; Arisawa, M.; Gyoten, M.; Hamada, R.; Tohma, H.; Kita, Y. *J. Org. Chem.* **1998**, *63*, 7698–7706.

(11) For a discussion of the arenium ion versus cation-radical mechanisms in various organic transfromations, see: (a) Rathore, R.; Kochi, J. K. *Acta Chem. Scand.* **1998**, *52*, 114–130. (b) Rathore, R.; Zhu, C.-J.; Lindeman, S. V.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1837–1840. (c) Rathore, R.; Wygand, U.; Kochi, J. K. *J. Org. Chem.* **1996**, *61*, 5426–5436.

(12) The ECEC mechanism is also applicable to other (oxidative) biaryl syntheses; see: (a) Ronlan, A.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1973**, *95*, 7132–7138. (b) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 7479–7490. The electron-tranfer or cation-radical mechanisms proposed in Schemes 2 and 3 may alternatively be considered to be occurring via carbocation intermediates. For example, an intramolecular attack of the protonated anisyl moiety on the adjecent anisyl group will result into a dearomatized intermediate which can then undergo oxidative aromatization. Although we strongly favor a cation-radical mechanism for the Scholl reactions (such as in Scheme 3), the carbocation pathways can not be easily ruled out. Compare: (c) King, B. T.; Kroulık, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279–2288.

(13) Compare: Chebny, V. J.; Shukla, R.; Rathore, R. *J. Phys. Chem. B* **2006**, *110*, 13003–13006, and references cited therein.

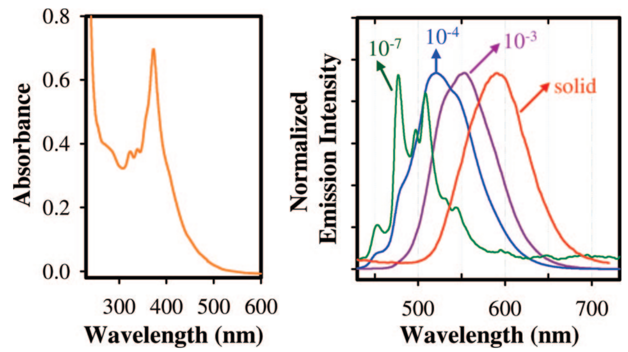


Figure 1. (Left) UV−vis absorption spectrum of 1.75×10^{-5} M **2** in CH_2Cl_2 at 22 °C. (Right) Concentration-dependent emission spectra of **2** in CH_2Cl_2 at 22 °C and in the solid state.

boronic acid, derived from 5,5′-dihexyloxy-2-bromobiphenyl (**9**) with 1 equiv of 1,3,5-tribromobenzene in the presence of Pd(0) catalyst. The desired brombiphenyl **9**, in turn, was obtained by a one-pot Suzuki coupling of 3-bromohexyloxybenzene followed by a bromination using NBS in acetonitrile in excellent yield (see Scheme 3). Indeed, when **10** (R = *n*-hexyl) was subjected to an oxidative cyclodehydrogenation using $FeCl_3$ in a mixture of dichloromethane−nitromethane (3:1), it yielded a readily soluble hexahexyloxy-HBC **2** as a yellow-orange solid in nearly quantitative yield (see Scheme 3).

The molecular structure of HBC **2** was established by the simplicity of its $^1H/^{13}C$ NMR spectra[18] and was further confirmed by MALDI mass spectrometry (see Figure S4, Supporting Information). Note that a calculated isotope distribution for mass ion of HBC **2** matches the prediction quite well (see Figure S4 in the Supporting Information).

As detailed in Scheme 3, the mechanism for conversion of **10** to HBC **2** simply followed a standard ECEC mechanism applicable to other (oxidative) biaryl syntheses.[12,14] Thus, a coupling of an anisyl-type cation radical ($\mathbf{I_6}$) with the central benzene ring produces a distonic cation radical ($\mathbf{I_7}$) which undergoes a ready loss of an electron ($\mathbf{I_8}$) followed by two proton ($\mathbf{I_9}$) to form a biaryl-type bond. Multiple repetitions of the ECEC sequence finally produce HBC **2** (Scheme 3).

With the hexaalkoxy HBC **2** at hand, we examined its optical characteristics in dichloromethane at 22 °C as follows. The absorption and emission spectra of **2** in dichloromethane (Figure 1) showed highly structured absorption (λ_{max} = 380 nm, log ϵ_{380} = 4.61) and emission (λ_{max} = 478 and 509 nm) bands. The optical spectra of **2** were characteristically similar to those observed with the alkyl-substituted HBC derivatives.[1c] Excited state emission of **2** was also found to be highly concentration dependent and is in accord with the observations made with the alkyl-substituted HBC derivatives.[1c] For example, at higher concentrations (10^{-6} to $\sim 10^{-4}$ M), a lower energy emission band centered near 554 nm, tentatively assigned as excimer-based,[1c] grow in intensity at the expense of the higher energy (478 nm) band, with an apparent bathochromic shift. A further bathochromic shift of ~30 nm was observed upon increasing the concentration of **2** by a factor of 10 (i.e., 10^{-4} to $\sim 10^{-3}$ M). In the solid state, the emission of **2** occurs as a broadband at λ_{max} = 591 nm. The observation of concentration dependent emission of **2** is tentatively attributed to the formation of molecular aggregates such as dimers, trimers, tetramers, and higher-order aggregates.[1c]

The preliminary X-ray diffraction pattern of **2** was found to be characteristically similar to those observed for the other HBC derivatives[19] (see Figure S6 in the Supporting Information) which are known to display liquid crystalline behavior.[20]

In summary, we have demonstrated that the oxidative cyclodehydrogenation of hexakis(4-alkoxyphenyl)benzenes (**3**) produces indenofluorenes **7** in quantitative yields rather than HBC **2**, as confirmed by X-ray crystallography. This finding led us to design an alternative (simple) synthesis of HBC **2** from an easily synthesized 1,3,5-tris(dialkoxybiphenyl)benzene **10**. The structure of hexaalkoxy HBC **2** was confirmed by NMR spectroscopy and MALDI mass spectrometry. Moreover, the absorption and emission characteristics of **2** were found to be similar to those observed with the other HBC derivatives. The ready availability of hexaalkoxy HBC **2** should spur theoretical and experimental interest in the exploration of its materials' properties.

Acknowledgment. We thank the National Science Foundation (CAREER Award) for financial support and Sergey V. Lindeman (Marquette University) for X-ray crystallography.

Supporting Information Available: Preparation and spectral data for various compounds in Schemes 1−3, $^1H/^{13}C$ NMR spectra, cyclic voltammogram of **7b** and electronic spectrum of its cation radical, and the X-ray structural data for **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL8020429

---

(14) (a) The distonic radical cations have ample literature precedent in the syntheses of a variety of biaryls; see: Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55–190, and references cited therein. (b) For the feasibility of the dicationic interemediates $\mathbf{I_3}$ and $\mathbf{I_8}$ in Schemes 2and 3, see: Rathore, R.; Magueres, P. L.; Lindeman, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 809–812.

(15) Cyclohexadienyl-type radicals are known to undergo oxidation at ~0 V (vs SCE); see: Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629–7633.

(16) Compare: Feng, X.; Wu, J.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2006**, *8*, 1145–1148.

(17) Anderson, N. G.; Maddaford, S. P.; Keay, B. A. *J. Org. Chem.* **1996**, *61*, 9556–9559.

(18) Owing to the large size of HBC **2**, the signals in its ^1H and ^{13}C NMR spectra were broad at 22 °C but, however, were sharpened at higher temperatures (90 °C); see Figure S5 in the Supporting Information.

(19) Fechtenkötter, A.; Saalwächter, K.; Harbison, M. A.; Müllen, K.; Spiess, H. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3039–3041.

(20) A detailed evaluation of the liquid crystalline properties of **2** and its derivatives with varying chain lengths will be undertaken, and the results will be reported in due course.