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Side-chain shuffling: regioselective synthesis of mixed tail discotic mesogens

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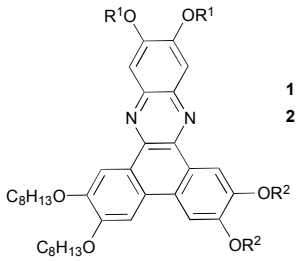
A procedure for the regioselective synthesis of discotic mesogens bearing multiple side chains of different lengths is reported. A series of isomeric dibenzoquinoxaline mesogens obtained by this route showed phase behaviour that was highly sensitive to chain location.

Over the past two decades, columnar liquid crystals have emerged as promising organic semiconductors for a variety of applications, including photovoltaics, OLEDs and field effect transistors.[1] A key challenge in the design of these materials is the need to tune their phase ranges to meet the processing and operational requirements of the target application while preserving the desired molecular electronic properties. In this context, varying the flexible chains that surround the aromatic core is particularly attractive because changes in chain length, branching and pendant functional groups all strongly impact phase behaviour.[2]

An alternative to changing the identity of the side chains is to alter how these groups are disposed around the central core. For example, we have shown that swapping the positions of the hexyloxy and decyloxy chains from **1** to **2** leads to a decrease in the clearing and melting temperatures by 18°C and 33°C, respectively.[3] However, relatively few studies have explored the effects of this kind of side chain shuffling,[4–12] likely due to the challenges associated with regioselectively preparing discotic mesogens bearing several different chains.



1 $R^1 = C_6H_{13}$, $R^2 = C_{10}H_{21}$
2 $R^1 = C_{10}H_{21}$, $R^2 = C_6H_{13}$

Figure 1. Discotic mesogens **1** and **2**.

We report herein a modular synthetic strategy that permits us to systematically alter the substitution pattern on a discotic mesogen. Our target compounds were the three dibenzoquinoxaline derivatives **BQ(6.10.6.10)**, **BQ(6.10.10.6)** and **BQ(10.6.6.10)**; these mesogens each have two hexyloxy and two decyloxy chains and represent three of the four possible permutations for this set of chains. We selected these compounds both to highlight our synthetic approach, and to provide the opportunity to study the effects of chain pattern across a series of isomers. The fourth regioisomer, **BQ(6.6.10.10)**, was previously prepared in our lab by a route that was restricted to derivatives with identical alkyl chains on the same ring,[13] a limitation not shared by the current approach.

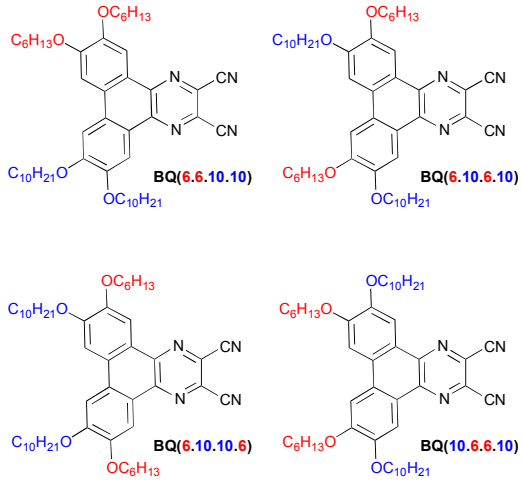


Figure 2. Target molecules discussed in this work.

As a representative example, the synthesis of **BQ(6.10.6.10)** is shown in Schemes 1 and 2. As a low symmetry derivative with two distinct groups on each ring, this target would be difficult to synthesize using other procedures. The key intermediate in this route was the diphenylacetylene, **7**. We have previously shown that electron rich tolanes can be converted in three steps to dibenzoquinoxalines such as **BQ(6.6.10.10)**;[13] as such, preparation of **7** should provide access to our target mesogen.

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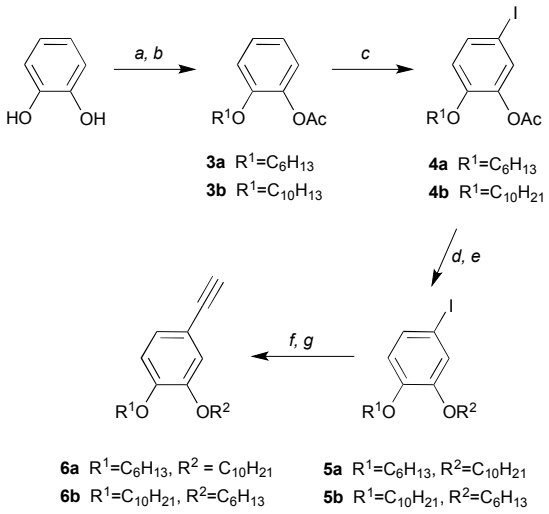
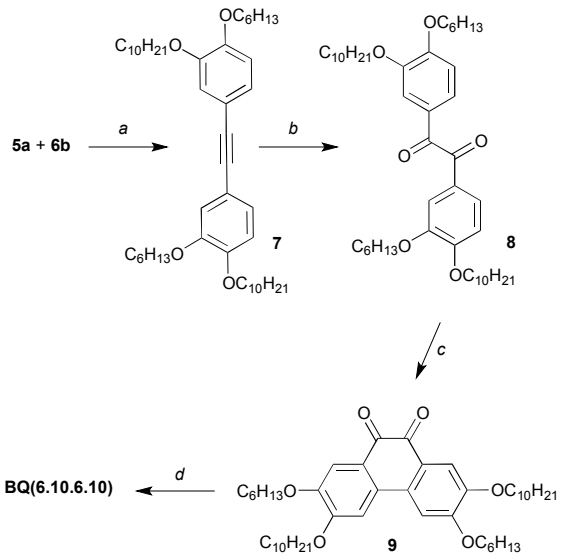


3a $R^1=C_6H_{13}$ **4a** $R^1=C_6H_{13}$
3b $R^1=C_{10}H_{13}$ **4b** $R^1=C_{10}H_{21}$

6a $R^1=C_6H_{13}$, $R^2=C_{10}H_{21}$ **5a** $R^1=C_6H_{13}$, $R^2=C_{10}H_{21}$
6b $R^1=C_{10}H_{21}$, $R^2=C_6H_{13}$ **5b** $R^1=C_{10}H_{21}$, $R^2=C_6H_{13}$

Scheme 1. *Reagents and conditions a*. $C_nH_{2n+1}Br$, K_2CO_3, NBu_4Br, butanone, reflux, 24 h; *b*. acetic anhydride, pyridine, reflux 6h; *c.* ICl, CH_2Cl_2, 0°C; *d.* LiOH•H_2O, MeOH, H_2O, THF, RT, 4h; *e*. $C_mH_{2m+1}Br$, K_2CO_3, NBu_4Br, butanone, reflux, 24 h; *f.* TMS-acetylene, CuI, $PdCl_2(PPh_3)_2$, $(i\text{-Pr})_2NH$, THF, 60°C, 24 h; *g.* K_2CO_3, MeOH, THF, RT 3h.



Scheme 2. *Reagents and conditions* a. CuI, $Pd(PPh_3)_4$, $(i\text{-Pr})_2NH$, THF, reflux, 12 h; *b*. I_2, DMSO, reflux, 12 h; *c.* VOF_3, BF_3•Et_2O, CH_2Cl_2, 2 h; *d.* 1,2-diaminomaleonitrile, AcOH, reflux, 24 h.

Monoalkylation of catechol with the appropriate 1-bromoalkane followed by acetylation of the free phenolic group afforded the 2-alkoxyphenylacetates **3a** and **3b**, respectively. These intermediates were iodinated to yield the 2-alkoxy-5-iodophenylacetates **4a** and **4b** using the conditions reported by Boden and coworkers.[14] Although this regioselectivity was expected *a priori*, it was experimentally confirmed by the observation of an NOE cross peak between the methylene protons of the ether (3.9 ppm) and the proton at the 3-position of the ring, which indicated that substitution took place at the 5- rather than the 4-position. Hydrolytic removal of the acetyl group and subsequent alkylation of the resulting phenol afforded the derivatives **5a** and **5b**. Pd-catalyzed coupling of these halides with TMS-acetylene, followed by deprotection afforded the terminal alkynes **6a** and **6b**.

Cross coupling of the iodide **5a** and the alkyne **6b** under standard Sonogashira-Hagihara conditions afforded the tolane **7** in 77% yield. Oxidation of this diphenylacetylene with stoichiometric I_2/DMSO gave the benzil **8**, which was readily cyclized to the phenanthrene quinone **9**. Condensation of this quinone with diaminomaleonitrile yielded the target mesogen **BQ(6.10.6.10)**.

Because of the modularity of this approach, the intermediates **5a/b** and **6a/b** also provided access to **BQ(6.10.10.6)** and **BQ(10.6.610)**. Coupling **5a** and **6a** yielded a diphenylacetylene intermediate that was then converted to **BQ(6.10.10.6)** using the same tolane-to-dibenzoquinoxaline reaction sequence shown in Scheme 2. **BQ(10.6.6.10)** was likewise obtained via the Pd cross-coupled product of **5b** and **6b** (see ESI).

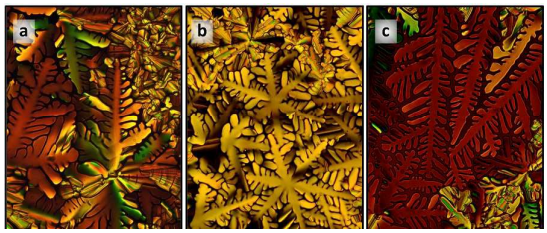


Figure 3. POM images of **BQ(10.6.6.10)** (a), **BQ(10.6.10.6)** (b), and **BQ(6.10.10.6)** (c). Samples (a) and (c) were imaged through 530 nm wave plate to improve viewing contrast of homeotropic domains.

Analyses of the phase behaviour of the three benzoquinoxalines were carried out using polarized optical microscopy (POM), differential scanning calorimetry (DSC) and variable temperature x-ray diffraction (XRD), the results of which are summarized in Table 1. Each compound forms a single liquid crystal phase over a broad temperature range. Dendritic textures characteristic of columnar phases were observed for all compounds by POM (Figure 3) when samples were cooled slowly from their isotropic phases. The observation of domains with approximately 6-fold symmetry (Fig. 3b) suggests that these phases are columnar hexagonal (Col_h) phases. XRD experiments confirmed this assignment for all compounds, with the observation of low angle peaks that indexed to the (100) and (110) peaks of Col_h phases. In every case, two additional broad peaks were observed at wider angles, corresponding to distances of approximately 4.3 Å and 3.5 Å; these were attributed to the alkyl chain halo and π-stacking peaks, respectively.

Whereas **BQ(6.10.10.6)** and **BQ(10.6.6.10)** have nearly identical melting points (~80°C), their less symmetrical isomers **BQ(6.10.6.10)** and **BQ(6.6.10.10)** melt into their columnar phases at markedly lower temperatures (47°C and 37°C, respectively). This is consistent with our earlier observation that reducing the molecular symmetry tends to depress the crystal-to-columnar transition temperature within a series of isomers.[3]

Phase		T_t/°C (ΔH/J g^{-1})[a]		Phase[b]
BQ(10.6.6.10)	Cr	80.0 (56.2) ⇌ 15.6 (-3.4)	Col_h *a* = 21.8 Å[c]	251.4 (5.3) → 245.2 (-3.1) I
BQ(6.10.10.6)	Cr	77.8 (56.8) ⇌ 14.9 (-3.5)	Col_h *a* = 21.9 Å	251.1 (5.0) ⇌ 247.4 (-6.1) I
BQ(6.10.6.10)	Cr	47.0 (30.0) ⇌ 15.1 (-5.1)	Col_h *a* = 21.5 Å	250.0 (5.1) ⇌ 248.3 (-6.1) I
BQ(6.6.10.10)[d]	Cr	37.8 (56.0) →	Col_h *a* = 22.1 Å	215.6 (1.2) ⇌ I

a) transition temperatures/enthalpies determined by DSC (scan rate = 10°C/min.); b) Cr = crystal, Col_h = columnar hexagonal, I = isotropic; c) lattice spacings determined by XRD at 125°C ; d) data for **BQ(6.6.10.10)** from ref. 13

Table 1. Phase properties of dibenzoquinoxaline derivatives.

The same generalization does not apply to the clearing temperatures. The three mesogens prepared for the current study have nearly identical Col_h-isotropic transition temperatures (~250°C), despite the lower symmetry of **BQ(6.10.6.10)**. In contrast, **BQ(6.6.10.10)** clears at 216°C. Because **BQ(6.10.6.10)** and **BQ(6.6.10.10)** belong to the same point group, the large disparity in their clearing temperatures cannot be attributed to symmetry effects. The anomalously low clearing temperature of **BQ(6.6.10.10)** may result from it being less disc-shaped than its isomers due to the disposition its side chains. Investigations aimed at separating the effects of shape and symmetry on phase behaviour are underway in our laboratory, using the synthetic approach outlined above.

In conclusion, we have prepared a series of isomeric dibenzoquinoxalines using a new regiospecific synthetic strategy. Although the current work has focused on a series of isomers containing just two pairs of side chains, it is worth noting that mesogens with any combination of alkoxy groups can be regioselectively prepared in this manner. Moreover, quinones such as **9** and tolanes such as **7** are potential precursors to a range of mesogens, including triphenylenes,[15–17] dibenzoquinoxalines,[13,18,19] dibenzophenazines,[3,20–27,27–29] phthalocyanines[18,30] and metallomesogens.[31,32] As such, this synthesis provides a general regioselective route to a wide range of discotic mesogens.

Acknowledgements

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Notes and references

1 W. Pisula and K. Müllen, in *Handbook of Liquid Crystals*, Wiley-VCH, Germany, 2nd edn., 2014, vol. 8, pp. 627–673.
2 S. Kumar in Handbook of Liquid Crystals, Wiley-VCH Verlag GmbH & Co. KGaA, 2014, vol. 4, pp. 467–520.
3 E. Voisin, E. Johan Foster, M. Rakotomalala and V. E. Williams, *Chem. Mater.*, 2009, **21**, 3251–3261.
4 M. T. Allen, S. Diele, K. D. M. Harris, T. Hegmann, B. M. Kariuki, D. Lose, J. A. Preece and C. Tschierske, *J. Mater. Chem.*, 2001, **11**, 302–311.
5 S. Setia, A. Soni, M. Gupta, S. Sidiq and S. K. Pal, *Liq. Cryst.*, 2013, **40**, 1364–1372.
6 N. Boden, R. Bushby, A. Cammidge and G. Headdock, *Synth.-Stuttg.*, 1995, 31–32.
7 R. Borner and R. Jackson, *J. Chem. Soc.-Chem. Commun.*, 1994, 845–846.
8 S. J. Cross, J. W. Goodby, A. W. Hall, M. Hird, S. M. Kelly, K. J. Toyne and C. Wu, *Liq. Cryst.*, 1998, **25**, 1–11.
9 Z. Ke-Qing, H. Ping, W. Bi-Qin, Y. Wen-Hao, C. Hong-Mei, W. Xin-Ling and Y. Shimizu, *Chin. J. Chem.*, 2007, **25**, 375–381.
10 P. Ruan, B. Xiao, H.-L. Ni, P. Hu, B.-Q. Wang, K.-Q. Zhao, Q.-D. Zeng and C. Wang, *L*, 2014, **41**, 1152–1161.
11 P. J. Stackhouse and M. Hird, *Liq. Cryst.*, 2008, **35**, 597–607.
12 J. Szydlowska, P. Krzyczkowska, P. Gniewek, D. Pociecha and A. Krowczynski, *Liq. Cryst.*, 2015, Ahead of Print.
13 E. J. Foster, J. Babuin, N. Nguyen and V. E. Williams, *Chem. Commun.*, 2004, 2052–2053.
14 N. Boden, R. Bushby and A. Cammidge, *J. Am. Chem. Soc.*, 1995, **117**, 924–927.
15 C. Feng, X.-L. Tian, J. Zhou, S.-K. Xiang, W.-H. Yu, B.-Q. Wang, P. Hu, C. Redshaw and K.-Q. Zhao, *Org. Biomol. Chem.*, 2014, **12**, 6977–6981.
16 G. Wenz, *Makromol. Chem.-Rapid Commun.*, 1985, **6**, 577–584.
17 B. Mohr, V. Enkelmann and G. Wegner, *J. Org. Chem.*, 1994, **59**, 635–638.
18 B. Mohr, G. Wegner and K. Ohta, *J. Chem. Soc.-Chem. Commun.*, 1995, 995–996.
19 J. Babuin, J. Foster and V. E. Williams, *Tetrahedron Lett.*, 2003, **44**, 7003–7005.
20 C. W. Ong, J.-Y. Hwang, M.-C. Tzeng, S.-C. Liao, H.-F. Hsu and T.-H. Chang, *J. Mater. Chem.*, 2007, **17**, 1785–1790.
21 C. W. Ong, C.-Y. Hwang, S.-C. Liao, C.-H. Pan and T.-H. Chang, *J. Mater. Chem.*, 2009, **19**, 5149–5154.
22 M.-C. Tzeng, S.-C. Liao, T.-H. Chang, S.-C. Yang, M.-W. Weng, H.-C. Yang, M. Y. Chiang, Z. Kai, J. Wu and C. W. Ong, *J. Mater. Chem.*, 2011, **21**, 1704-12.
23 C. W. Ong, Y.-C. Chan, M.-C. Yeh, H.-Y. Lin and H.-F. Hsu, *RSC Adv.*, 2013, **3**, 8657–8659.
24 K. J. A. Bozek, K. I. Ho, T. Saint-Martin, P. Argyropoulos and V. E. Williams, *Materials*, 2015, **8**, 270–284.
25 K. J. A. Bozek and V. E. Williams, *Soft Matter*, 2014, **10**, 5749–5754.
26 E. J. Foster, R. B. Jones, C. Lavigueur and V. E. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 8569–8574.
27 E. J. Foster, C. Lavigueur, Y. C. Ke and V. E. Williams, *J. Mater. Chem.*, 2005, **15**, 4062–4068.
28 C. Lavigueur, E. J. Foster and V. E. Williams, *J. Am. Chem. Soc.*, 2008, **130**, 11791–11800.
29 C. W. Ong, C. Q. Yan, M.-C. Yeh and M.-C. Tzeng, *Mol. Cryst. Liq. Cryst.*, 2015, **610**, 249–254.
30 M. Ichihara, M. Miida, B. Mohr and K. Ohta, *J. Porphyrins Phthalocyanines*, 2006, **10**, 1145–1155.
31 K. Ohta, M. Ikejima, M. Moriya, H. Hasebe and I. Yamamoto, *J. Mater. Chem.*, 1998, **8**, 1971–1977.

32 K. Ohta, R. Higashi, M. Ikejima, I. Yamamoto and N. Kobayashi, *J. Mater. Chem.*, 1998, **8**, 1979–1991.