

Columnar liquid crystalline π -conjugated oligothiophenes†

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Polycatenar oligothiophenes possessing three alkoxy chains at each terminal self-organise into columnar liquid crystalline phases, and one-dimensional columnar stacks can be oriented uniaxially by mechanical shearing in the mesophases.

Liquid crystalline π -conjugated materials have recently attracted much attention because they have applications as electronic materials that easily form macroscopically ordered nanostructures.^{1–3} Among them, columnar liquid crystals, *e.g.*, triphenylene, hexabenzocoronene and perylene diimide derivatives, have been prepared for one-dimensional transportation of charge carriers, and give rise to high mobilities along the columns.² In order to attain electronic and anisotropic conduction properties, precise control of the mesoscopic order is of great importance for such materials.^{4,5}

π -Conjugated oligothiophenes are promising organic semiconductors in the application of field-effect transistors (FETs).⁶ Recent research efforts have been devoted to the exploitation of oligothiophene derivatives that could construct well-ordered molecular assemblies having unique electrical and optical properties.⁷ Several smectic and nematic liquid crystalline oligothiophenes have been reported so far,^{8–10} and some have also been applied in FETs.¹⁰ Herein we present the first example of thermotropic columnar liquid crystals based on π -conjugated oligothiophene (Fig. 1). Our molecular design features three alkoxy chains tethered to each terminal of the central aromatic core,^{11,12} which facilitates one-dimensional molecular stacks in the liquid crystalline phase.

New polycatenar quinquethiophenes (**1a–c**) and sexithiophenes (**2a–c**) were synthesised by using palladium-catalysed coupling reactions, and obtained as orange and reddish purple solids,

respectively (see ESI†). They were soluble in common organic solvents such as chloroform, dichloromethane, THF and toluene.

The mesomorphic properties of **1a–c** and **2a–c** were examined by differential scanning calorimetry (DSC) and polarised optical microscopy. As summarised in Table 1, compounds **1a,b** and **2b,c** exhibit enantiotropic columnar (Col) phases, whereas **1c** and **2a** show monotropic Col phases only on cooling from the isotropic melt. As a typical example, **1a** bearing six dodecyloxy substituents forms a Col phase at 79 °C ($\Delta H = 27 \text{ kJ mol}^{-1}$) that becomes an isotropic state at 101 °C ($\Delta H = 1.7 \text{ kJ mol}^{-1}$).† A fan texture characteristic of columnar phases is observed under crossed polarisers, as shown in Fig. 2. In contrast, analogous terthiophene- and quaterthiophene-based compounds having six terminal alkoxy chains did not show any liquid crystalline properties.† Therefore, it should be pointed out that appropriate choice of the core length leads to the polycatenar oligothiophenes that are capable of forming Col phases. The phase behaviour of these new compounds is markedly different from that of previously reported liquid crystalline oligothiophenes,^{8–10} in which nematic and/or smectic

Table 1 Liquid crystalline behaviour of **1a–c** and **2a–c**

Compound	Phase transition behaviour ^a	Lattice parameter ^c (Å)
1a	Cr 79 Col _h 101 Iso	45.6
1b	Cr 62 Cr' 80 Col _h 100 Iso	47.8
1c	Cr 69 Cr' 109 (Col 90) ^b Iso	— ^d
2a	Cr 118 Cr' 131 (Col _h 109) ^b Iso	49.5
2b	Cr 91 M 109 Col _h 116 Iso	51.4
2c	Cr 85 Cr' 102 Col _h 117 Iso	55.3

^a Transition temperatures (°C) determined by DSC (second heating; 5 °C min^{−1}). Cr: crystalline; M: mesophase; Col_h: hexagonal columnar; Iso: isotropic. ^b Observed only on cooling. ^c Col_h phase at 90 °C for **1a,b** and 105 °C for **2a–c**. ^d Impossible to obtain the XRD pattern of the mesophase, but the optical texture is consistent with a Col phase.

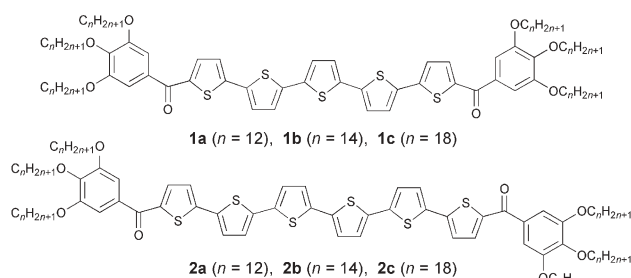


Fig. 1 Structures of columnar liquid crystalline oligothiophenes.

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterisation for **1a–c** and **2a–c** and DSC, XRD and polarised IR data. See DOI: 10.1039/b606144c

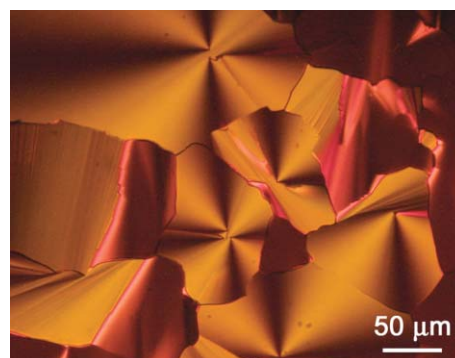


Fig. 2 Polarised optical photomicrograph of **1a** in the Col_h phase at 90 °C.

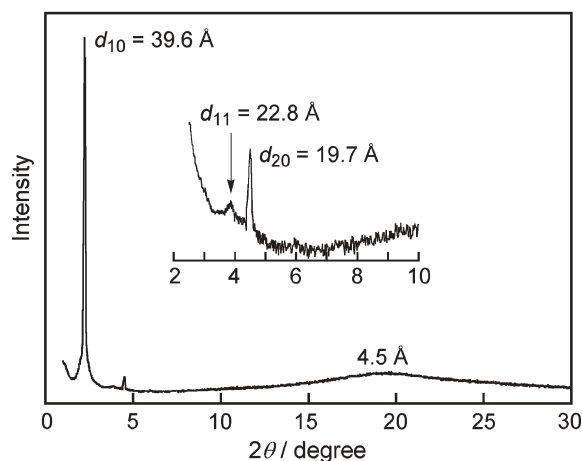


Fig. 3 X-ray diffraction pattern of **1a** at 90 °C.

phases are exclusively observed on account of their calamitic molecular structures.

To confirm the columnar structures of the mesophases, X-ray diffraction (XRD) measurements were performed for the oligothiophenes. A representative XRD pattern of **1a** is shown in Fig. 3. In the small-angle region, an intense peak at 39.6 Å and two weak peaks at 22.8 and 19.7 Å with a reciprocal *d*-spacing ratio of 1 : $\sqrt{3}$: 2 are observed. These peaks correspond to the (10), (11) and (20) reflections, respectively, indicative of a two-dimensional hexagonal arrangement of the columns with the intercolumnar distance of 45.6 Å. It should be noted that the intercolumnar distance of **1a** is much smaller than the fully extended molecular length (*ca.* 57 Å calculated by AM1). This discrepancy may indicate that the oligothiophene molecules are tilted with respect to the cross section of each column.^{3c} The intercolumnar distance increases with the elongation of the alkoxy chain length or of the oligothiophene core length (Table 1).†

Taking these results into account, it is reasonable to assume that the rigid-rod oligothiophene moieties self-assemble into a one-dimensional domain and the outer part of the columns is filled with the molten alkoxy segments, similar to the previously reported polycatenar mesogens^{11,12} and rod-coil block molecules.¹³ For these oligothiophenes, it can be estimated that approximately 2.3–3.4 molecules are included inside a stratum of each column on average.‡ The intermolecular co-facial π – π interaction between the oligothiophene moieties as well as nano-segregation of the aromatic centre from the surrounding alkoxy moieties will facilitate the organisation of these molecules into such a columnar assembly in the mesophase.^{1b,14}

Uniaxial orientation of the columnar structures is readily attainable after the polydomain of the Col_h phase of **1a** is mechanically sheared within the sandwiched glass plates.⁵ Polarised optical microscopy reveals that the columnar material tends to align parallel to the shearing direction. As can be seen in Fig. 4, the birefringence of the oriented sample of **1a** alternately changes from light to dark upon a 45° rotation under the crossed Nicols condition.^{2e,5} In addition, polarised infrared spectra of the oriented **1a** in the Col_h phase exhibited dichroism for the aromatic C=C stretching band of the oligothiophene core at 1435 cm^{−1}.† This observation can support the assumption that the π – π stacking direction of the oligothiophenes is parallel to the shear direction.

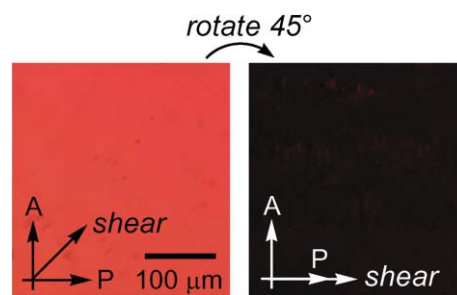


Fig. 4 Polarised optical photomicrographs of the uniaxially oriented **1a** in the Col_h phase at 90 °C by means of mechanical shearing. Rotating the sample by 45° produces periodic bright (left) and dark (right) images under the crossed Nicols condition. Arrows indicate the directions of the mechanical shear force and polariser (P) and analyser (A) axes.

The macroscopically uniform alignment of columns might lead to anisotropic charge carrier transport along the molecular stacking.⁴

We next studied spectroscopic properties of the polycatenar oligothiophenes in the solution and condensed states (Fig. 5). The UV–vis absorption spectrum of **1a** in chloroform displays the π – π^* absorption maximum at 462 nm,§ which is shifted by about 40 nm with respect to α,ω -dialkyl-quinquethiophenes.¹⁵ This implies that the carbonyl groups in **1a** are effectively conjugated with the central oligothiophene core. In the liquid crystalline and solid states, the absorption peak is blue-shifted (*ca.* 10 nm) compared with that in the solution, besides a new broad band arises around 540 nm. The photoluminescence (PL) spectrum of **1a** in the Col_h phase exhibits a broad and red-shifted emission peak at 585 nm, while the solution displays a structured emission with maxima at 544 and 575 nm (Fig. 5b). These spectral changes can be ascribed to the formation of π -stacked aggregates with *H*-type parallel stacking mode;¹⁶ these optical features support the aforementioned self-organised π -stacked structure observed in the Col_h phase.

In summary, we have demonstrated for the first time that oligothiophenes exhibit columnar liquid crystalline phases. We incorporated six flexible chains into the oligothiophenes to form polycatenar mesogens. The intermolecular π – π interaction of oligothiophene moieties and the nano-segregation are attributed predominantly to the formation of such one-dimensional supra-molecular assemblies. Uniaxial orientation of columnar structures has been achieved in the mesophase. These columnar liquid crystalline π -conjugated oligothiophenes are expected to be

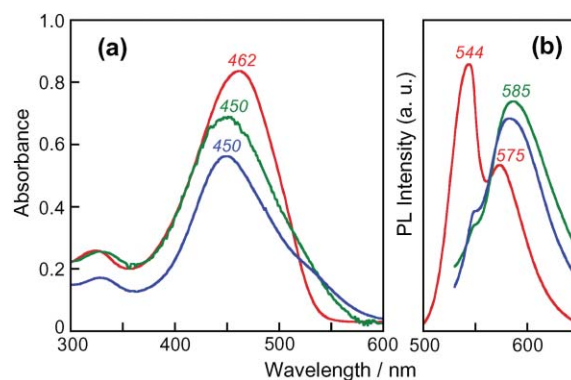


Fig. 5 (a) UV–vis absorption and (b) PL spectra of **1a** in chloroform solution (red), Col_h phase at 90 °C (green) and solid thin film (blue).

attractive candidates for charge-transporting materials in organic optoelectronic devices.

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Notes and references

† The average number of molecules in a column stratum (μ) was estimated according to the following equation: $\mu = (\sqrt{3} N_A a^2 h \rho) / 2M$, where N_A is Avogadro's number, a is the lattice parameter (cf. Table 1), h is the layer thickness (estimated as ca. 3.6–4.8 Å based on the X-ray crystal structures of oligothiophene derivatives),^{6a,15} ρ is the density (assumed to be 1 g cm⁻³) and M is the molecular weight of the compound.

§ Compound **2a** in chloroform showed the UV–vis and PL peaks at 470 and 548 nm, respectively.

- For recent reviews, see: (a) R. J. Bushby and O. R. Lozman, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 569; (b) T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 38; (c) F. J. M. Hoeben, P. Jonkhøj, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491; (d) S. Kumar, *Chem. Soc. Rev.*, 2006, **35**, 83; (e) M. O'Neill and S. M. Kelly, *Adv. Mater.*, 2003, **15**, 1135; (f) A. C. Grimsdale and K. Müllen, *Angew. Chem., Int. Ed.*, 2005, **44**, 5592.
- (a) D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, *Nature*, 1994, **371**, 141; (b) A. M. van de Craats, J. M. Warman, K. Müllen, Y. Geerts and J. D. Brand, *Adv. Mater.*, 1998, **10**, 36; (c) Z. An, J. Yu, S. C. Jones, S. Barlow, S. Yoo, B. Domercq, P. Prins, L. D. A. Siebbeles, B. Kippelen and S. R. Marder, *Adv. Mater.*, 2005, **17**, 2580; (d) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyonovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson and H. Duan, *Nature*, 2002, **419**, 384; (e) S. Xiao, M. Myers, Q. Miao, S. Sanaur, K. Pang, M. L. Steigerwald and C. Nuckolls, *Angew. Chem., Int. Ed.*, 2005, **44**, 7390.
- (a) P. Hindmarsh, M. J. Watson, M. Hird and J. W. Goodby, *J. Mater. Chem.*, 1995, **5**, 2111; (b) P. H. J. Kouwer and G. H. Mehl, *Angew. Chem., Int. Ed.*, 2003, **42**, 6015; (c) B. Donnio, B. Heinrich, H. Allouchi, J. Kain, S. Diele, D. Guillon and D. W. Bruce, *J. Am. Chem. Soc.*, 2004, **126**, 15258; (d) M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato and E. Nakamura, *Nature*, 2002, **419**, 702; (e) B. Dardel, D. Guillon, B. Heinrich and R. Deschenaux, *J. Mater. Chem.*, 2001, **11**, 2814; (f) C. F. van Nostrum and R. J. M. Nolte, *Chem. Commun.*, 1996, 2385; (g) M. C. Artal, K. J. Toyne, J. W. Goodby, J. Barberá and D. J. Photinos, *J. Mater. Chem.*, 2001, **11**, 2801; (h) J. Wu, J. Li, U. Kolb and K. Müllen, *Chem. Commun.*, 2006, 48; (i) I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee and M. F. Toney, *Nat. Mater.*, 2006, **5**, 328.
- (a) I. O. Shklyarevskiy, P. Jonkhøj, N. Stutzmann, D. Wasserberg, H. J. Wondergem, P. C. M. Christianen, A. P. H. J. Schenning, D. M. de Leeuw, Ž. Tomović, J. Wu, K. Müllen and J. C. Maan, *J. Am. Chem. Soc.*, 2005, **127**, 16233; (b) A. M. van de Craats, N. Stutzmann, O. Bunk, M. M. Nielsen, M. Watson, K. Müllen, H. D. Chanzhy, H. Shirringhaus and R. H. Friend, *Adv. Mater.*, 2003, **15**, 495.
- (a) M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994; (b) M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2006, **128**, 5570.
- (a) P. Bäuerle, in *Electronic Materials: The Oligomer Approach*, eds. K. Müllen and G. Wegner, Wiley-VCH, Weinheim, 1998, ch. 2; (b) *Handbook of Oligo- and Polythiophenes*, ed. D. Fichou, Wiley-VCH, Weinheim, 1999; (c) H. Akimichi, K. Waragai, S. Hotta, H. Kano and H. Sakaki, *Appl. Phys. Lett.*, 1991, **58**, 1500; (d) F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries and P. Alnot, *J. Am. Chem. Soc.*, 1993, **115**, 8716; (e) H. E. Katz, J. G. Laquindanum and A. J. Lovinger, *Chem. Mater.*, 1998, **10**, 633; (f) F. Garnier, R. Hajlaoui, A. El Kassmi, G. Horowitz, L. Laigre, W. Porzio, M. Armanini and F. Provasoli, *Chem. Mater.*, 1998, **10**, 3334; (g) A. Facchetti, Y. Deng, A. Wang, Y. Koide, H. Shirringhaus, T. J. Marks and R. H. Friend, *Angew. Chem., Int. Ed.*, 2000, **39**, 4547; (h) T. Otsubo, Y. Aso and K. Takimiya, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 1789; (i) J. A. Letizia, A. Facchetti, C. L. Stern, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 13476.
- For selected oligothiophene assemblies, see: (a) A. P. H. J. Schenning, A. F. M. Kilbinger, F. Biscarini, M. Cavallini, H. J. Cooper, P. J. Derrick, W. J. Feast, R. Lazzaroni, P. Leclère, L. A. McDonnell, E. W. Meijer and S. C. J. Meskers, *J. Am. Chem. Soc.*, 2002, **124**, 1269; (b) F. S. Schoonbeek, J. H. van Esch, B. Wegewijs, D. B. A. Rep, M. P. de Haas, T. M. Klapwijk, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1393; (c) B. W. Messmore, J. F. Hulvat, E. D. Sone and S. I. Stupp, *J. Am. Chem. Soc.*, 2004, **126**, 14452; (d) S. Kawano, N. Fujita and S. Shinkai, *Chem.–Eur. J.*, 2005, **11**, 4735; (e) E. Mena-Osteritz, A. Meyer, B. M. W. Langeveld-Voss, R. A. J. Janssen, E. W. Meijer and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2000, **39**, 2680; (f) J. Krömer, I. Rios-Carreras, G. Fuhrmann, C. Muschel, M. Wunderlin, T. Debaerdemaeker, E. Mena-Osteritz and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2000, **39**, 3481; (g) J. J. Apperloo, R. A. J. Janssen, P. R. L. Malenfant and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2001, **123**, 6916.
- (a) R. Azumi, G. Götz and P. Bäuerle, *Synth. Met.*, 1999, **101**, 544; (b) H. Zhang, S. Shiino, A. Shishido, A. Kanazawa, O. Tsutsumi, T. Shiono and T. Ikeda, *Adv. Mater.*, 2000, **12**, 1336; (c) T. Yamada, R. Azumi, H. Tachibana, H. Sakai, M. Abe, P. Bäuerle and M. Matsumoto, *Chem. Lett.*, 2001, **30**, 1022; (d) P. Liu, H. Nakano and Y. Shirota, *Liq. Cryst.*, 2001, **28**, 581; (e) S. Ponomarenko and S. Kirchmeyer, *J. Mater. Chem.*, 2003, **13**, 197; (f) P. Liu, Y. Zhang, G. Feng, J. Hu, X. Zhou, Q. Zhao, Y. Xu, Z. Tong and W. Deng, *Tetrahedron*, 2004, **60**, 5259; (g) H.-F. Hsu, S.-J. Chien, H.-H. Chen, C.-H. Chen, L.-Y. Huang, C.-H. Kuo, K.-J. Chen, C. W. Ong and K.-T. Wong, *Liq. Cryst.*, 2005, **32**, 683; (h) J. Leroy, J. Levin, S. Sergeev and Y. Geerts, *Chem. Lett.*, 2006, **35**, 166.
- (a) M. Funahashi and J. Hanna, *Adv. Mater.*, 2005, **17**, 594; (b) M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, 2000, **76**, 2574.
- (a) A. J. J. M. van Breemen, P. T. Herwig, C. H. T. Chlon, J. Sweelssen, H. F. M. Schoo, S. Setayesh, W. M. Hardeman, C. A. Martin, D. M. de Leeuw, J. J. P. Valetton, C. W. M. Bastiaansen, D. J. Broer, A. R. Popa-Merticaru and S. C. J. Meskers, *J. Am. Chem. Soc.*, 2006, **128**, 2336; (b) I. McCulloch, W. Zhang, M. Heeney, C. Bailey, M. Giles, D. Graham, M. Shkunov, D. Sparrowe and S. Tierney, *J. Mater. Chem.*, 2003, **13**, 2436; (c) B.-H. Huisman, J. J. P. Valetton, W. Nijssen, J. Lub and W. ten Hoeve, *Adv. Mater.*, 2003, **15**, 2002.
- (a) B. P. Hoag and D. L. Gin, *Adv. Mater.*, 1998, **10**, 1546; (b) B. P. Hoag and D. L. Gin, *Liq. Cryst.*, 2004, **31**, 185.
- (a) H.-T. Nguyen, C. Destradre and J. Malthête, *Adv. Mater.*, 1997, **9**, 375; (b) D. Fazio, C. Mongin, B. Donnio, Y. Galerne, D. Guillon and D. W. Bruce, *J. Mater. Chem.*, 2001, **11**, 2852.
- M. Lee, B.-K. Cho and W.-C. Zin, *Chem. Rev.*, 2001, **101**, 3869.
- T. Kato, *Science*, 2002, **295**, 2414.
- A. Facchetti, M.-H. Yoon, C. L. Stern, G. R. Hutchison, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2004, **126**, 13480.
- (a) Y. Kanemitsu, N. Shimizu, K. Suzuki, Y. Shiraishi and M. Kuroda, *Phys. Rev. B*, 1996, **54**, 2198; (b) A. Yassar, G. Horowitz, P. Valat, V. Wintgens, M. Hmyene, F. Deloffre, P. Srivastava, P. Lang and F. Garnier, *J. Phys. Chem.*, 1995, **99**, 9155.