

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

## Bundled-Stack Discotic Columnar Liquid Crystalline Phase with Inter-Stack Electronic Coupling

Received 00th January 20xx,  
Accepted 00th January 20xx

B. Wang,<sup>a</sup> R. Sun,<sup>a</sup> D. D. Günbaş,<sup>b</sup> H. Zhang,<sup>a</sup> F. C. Grozema,<sup>b</sup> K. Xiao<sup>c</sup> and S. Jin<sup>\*a</sup>

DOI: 10.1039/x0xx00000x

www.rsc.org/

**The first compound capable of forming a bundled-stack discotic columnar liquid crystalline (BSDCLC) phase was designed and synthesized. The unique perylene anhydride inter-stack interaction was found to be the key to the formation of the BSDCLC structure and inter-stack electronic coupling (ISEC).**

In the family of organic semiconductors, discotic columnar liquid crystalline (DCLC) materials with a conjugated mesogen are attractive due to their excellent processability and unique advantages such as self-healing and self-organization.<sup>1-4</sup> In a typical DCLC phase, each column consists of a conducting stack of piled-up aromatic cores surrounded by fluid insulating flexible chains. Such a structure is at the root of many advantages of a DCLC phase. However, having only a single stack in each column translates into the lack of inter-stack/column electronic coupling, which makes charge carrier migration in such a phase vulnerable to the occurrence of defects<sup>5</sup> and hinders the use of DCLC materials in the currently most efficient bulk heterojunction organic photovoltaic cells<sup>6,7</sup>. Here, we demonstrate a novel molecular design to the first bundled-stack DCLC (BSDCLC) phase which features several  $\pi$ -stacks bundled together in each column. Its hierarchical structure permits inter-stack electronic coupling (ISEC) which is potentially useful to circumvent defects in charge or energy transport<sup>8,9</sup> and enable the fabrication of highly efficient photovoltaic cells using DCLC materials.

DCLC phases involving multiple  $\pi$ -stacks per column have been proposed for DCLC chlorophyll derivatives<sup>10</sup> and semifluorinated dendrons with a conjugated charge transport

unit attached to the apex<sup>11-13</sup>. However, there is no evidence of electronic coupling between adjacent stacks since aromatic cores are separated by either alkyl groups or peripheral hydrogen atoms. Furthermore, in the latter case, the strategy only works with relatively small charge transport units,<sup>13</sup> which results in limited charge carrier mobility.<sup>14</sup> Here we show that perylene tetracarboxylic diester monoanhydride (PEA) (Figure 1) molecules self-assemble into a true BSDCLC phase for the first time. Its formation is promoted by dipole-dipole interaction between anhydride groups and the appropriate mesogen/flexible chain interfacial curvature (the collective lateral area of branched alkyl chains is  $\sim 80 \text{ \AA}^2$ , whereas a  $\pi$ -stacked perylene ring is  $\sim 32 \text{ \AA}^2$ )<sup>15,16</sup>. The potential role of the anhydride group in the BSDCLC phase is threefold. First, the attractive intermolecular inter-stack dipole-dipole force could drive the formation of BSDCLC structure. Second, it avoids the conjugated charge transport unit from being fully wrapped with peripheral atoms. Finally, the partial overlap of anhydride groups may lead to inter-stack  $\pi$ -orbital overlap.

**1** was synthesized in two straightforward steps according to a slightly modified literature procedure<sup>17</sup> given in the Electronic Supplementary Information (ESI). The DSC traces are shown in Figure 1b. The isotropization temperature of **1** is 206.7 °C (onset,  $\Delta H = 6.3 \text{ kJ/mol}$ ). The dendritic texture presented in Figure 1d is indicative of the formation of a DCLC phase upon cooling from the isotropic liquid state, which is in agreement with the associated exothermic enthalpy value ( $\Delta H = 4.5 \text{ kJ/mol}$ ) and the small undercooling (onset at 205.5 °C,  $\Delta T = 1.2 \text{ °C}$ ) needed to develop the phase from liquid. The fact that there are no transitions between room temperature (RT) and the isotropization temperature suggests that **1** is a RT DCLC material. This finding is verified by the RT one-dimensional (1D) X-ray diffraction (XRD) pattern shown in Figure 1c. The ordered nature of the phase is testified by the appearance of multiple sharp diffraction peaks at the small-angle region. In contrast, the alkyl chains are in a disordered, liquid-like state as indicated by the absence of sharp diffraction peaks between 1.3 and 1.7  $\text{\AA}^{-1}$ . The peak at 1.742  $\text{\AA}^{-1}$  (d-spacing = 0.3606 nm) can be attributed to  $\pi$ -stacked perylene units. The formation

<sup>a</sup> Center for Engineered Polymeric Materials, Department of Chemistry, College of Staten Island and Graduate Center of the City University of New York, Staten Island, NY 10314 (USA). E-mail: shi.jin@csi.cuny.edu

<sup>b</sup> DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL Delft (Netherlands).

<sup>c</sup> Center for Nanophase Materials Sciences Division, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831 (USA).

Electronic Supplementary Information (ESI) available: [Experimental procedures, synthesis of PEA **1** and PEI **2**, details of characterization and simulation, as well as discussion on the role of long alkyl peripheral chains in the formation of the bundled-stack discotic liquid crystalline phase]. See DOI: 10.1039/b000000x/]. See DOI: 10.1039/x0xx00000x

of  $\pi$ -stacks is also supported by fluorescence spectra of **1** depicted in Figure 1e. The spectrum of **1** in a dilute chloroform solution features three bands peak at 523, 567 and 618 nm, in the order of decreasing intensity. These bands can be assigned to one electronic transition of unassociated **1** molecules coupled with vibrational transitions, similar to what has been suggested for perylene diimides.<sup>18</sup> However, in the RT DCLC phase, the  $\lambda_{\text{max}}$  red-shifted by more than 120 nm to 650 nm, indicating extensively  $\pi$ -stacked perylene units.<sup>19, 20</sup>

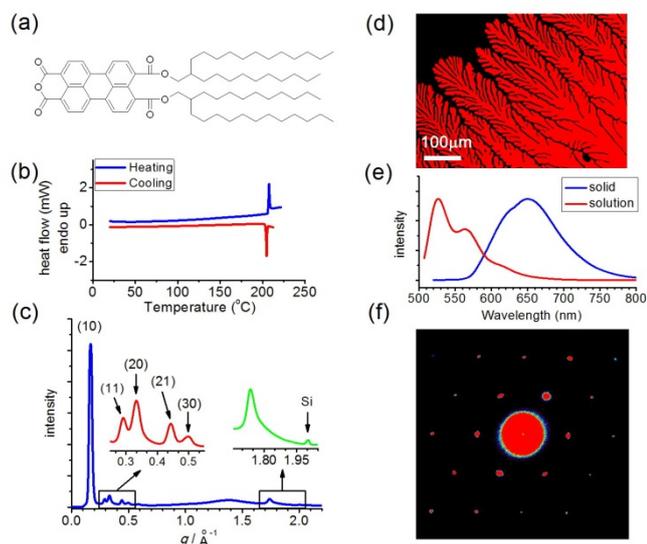


Fig. 1 (a) Structure of **1**. (b) First cooling and second heating DSC traces of **1** at a ramp rate of 10 °C/min. (c) 1D XRD pattern of **1** at RT with small-angle diffractions indexed. Insets show the weak small-angle diffractions (red) and the peak arising from  $\pi$ -stacking order (green). The peak marked "Si" corresponds to the diffraction from crystalline silicon powder that were added as the calibration standard. (d) PLM micrograph of **1** taken at 202.0 °C after slowly cooled from the isotropic liquid state. (e) Fluorescence spectra of **1** in chloroform solution (2.1  $\mu\text{M}$ ) and in RT DCLC form. (f) 2D small-angle diffraction pattern of **1** at RT (the incident X-ray beam was parallel to the column axis).

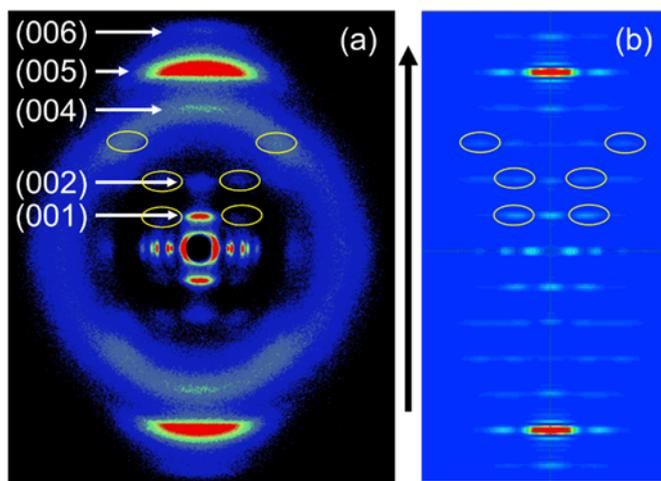


Fig. 2 (a) 2D XRD pattern of a shear-oriented **1** with the incident beam along the thickness direction (the detailed indexing of reflects is included in ESI). (b) Simulated X-ray fiber pattern of **1** in the composite structure shown in Figure 5a. The arrow marks the shear/fiber (for the simulated pattern) direction. Intra-column diffractions in quadrants were circled.

As a proper alignment is essential for high device performance, we have explored the possibility of achieving homoerotically

aligned **1** columns in a thin film sandwiched between two substrates by cooling from the isotropic phase slowly and stepwise (see ESI). Such an alignment is preferred for photovoltaic and light-emitting applications. The molecular orientation in a DCLC phase can be probed by measuring optical<sup>21</sup> and IR<sup>22</sup> dichroism, polarized Raman scattering,<sup>23</sup> neutron scattering<sup>24</sup> and grazing incidence X-ray diffraction,<sup>25</sup> as well as PLM and XRD employed here. Figure 1f shows the small angle XRD pattern of such a film with the incident beam normal to the film plane. The hexagonally related sharp diffraction spots suggest that **1** molecules form columns perpendicular to the substrate. PLM textures (Figure S5) also confirm the homeotropic orientation of **1**.

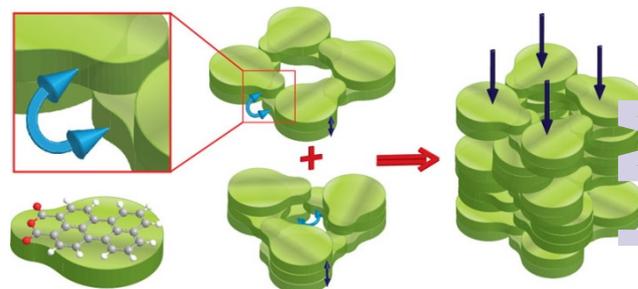


Fig. 3 Schematic of a single column packing showing bundled-stack organization of mesogens, charge and energy transport directions (inter-stack: light blue arrow, intra-stack: dark blue arrow). The inset shows magnified drawing of inter-stack anhydride overlap and ISEC, which will be discussed later.

The in-depth phase structure was unveiled by analysing a 2D XRD pattern collected on a well-aligned DCLC sample of **1** produced by mechanical shearing. As displayed in Figure 2a, the series of diffractions on the equator originate from hexagonally packed ( $a = 4.35$  nm), supramolecular columns well-aligned along the shearing direction. The strongest meridian diffraction ((005)) at  $d = 0.3606$  nm can be assigned to  $\pi$ -stacking order of perylene units. The fact that this diffraction does not split means that on average discotic mesogens are perpendicular to the column axis. Assuming only one perylene  $\pi$ -stack per column, the density calculated from given cell parameters would be  $0.30$  g/cm<sup>3</sup>. However, the measured value is  $1.027 \pm 0.001$  g/cm<sup>3</sup>, necessitating 3.4  $\pi$ -stacks per column. The  $d$ -spacing of (005) reflection relates to a further intracolumnar period of 1.8 nm (five stacked **1** molecules) over which there are 17  $\pi$ -stacked molecules per column. To fit 17 molecules in 5 strata into unit cell, we propose an intracolumnar structure involving two  $\pi$ -stacking modes, as shown in Figure 3. Nine of molecules form 3  $\pi$ -stacks in 3 strata. The remaining 8 molecules organize into 4  $\pi$ -stacks in 2 strata. The  $\pi$ -stack spacing is always 0.3606 nm. Inside each  $\pi$ -stack, the mesogen rotates around its plane normal with respect to the neighboring mesogen and the direction of rotation alternates along the stacking axis. With this proposed packing scheme, (005) diffraction can be accounted for as arising from the electron density contrast between three-stack and four-stack region. This packing scenario is supported by the good agreement between the experimental diffraction pattern and the simulated one (Figure 2b) which was generated from the

energy-minimized proposed structure using Cerius 2 (detailed information and explanation of the molecular modeling are included in ESI).

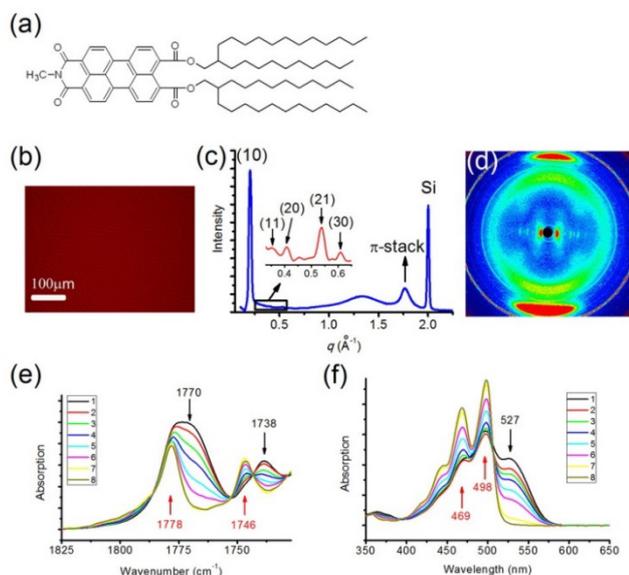


Fig. 4 (a) Structure of **2**. (b) PLM micrograph of **2** taken at 109.9 °C after slowly cooled from the isotropic liquid state, with polarizers slightly uncrossed. (c) 1D XRD pattern of **2** at 99 °C with small-angle diffractions indexed. The peak marked "Si" corresponds to the diffraction from crystalline silicon powder that were added as the calibration standard. (d) 2D XRD pattern of a shear-oriented **2** at 99 °C with the incident beam along the thickness direction (the detailed indexing of reflects is included in ESI). (e) IR absorption spectra of a series hexane solution of **1**. (f) UV-visible absorption spectra of the same hexane solutions of **1**. (For concentrations of hexane solutions 1 to 8, see Table 1 in ESI)

With the hierarchical structure of the BSDCLC phase solved, the next important question we would like to answer is the role of the anhydride group in the formation of the phase. For this purpose, PEI **2** (Figure 4a) was designed and synthesized. Interestingly, **2** exhibits a multi-stack DCLC phase between 84 and 112 °C (Figure 4b, c, d, S15), with a stronger *intra-stack*  $\pi$ -stacking interaction as indicated by the smaller  $\pi$ -stack spacing (0.356 nm). However, the columnar structure of **2** is much *less* stable than that of **1** as evidenced by the drastic decrease (92.6 °C) of clearing point and much easier dissociation of  $\pi$ -stacks in the hexane solution (Figure S8, S11). Therefore, the extra stability of the columnar structure of **1** must be of *inter-stack* origin. Taking the molecular structure difference between **1** and **2** into consideration, the anhydride dipole-dipole interaction is the most probable source of such stabilization force. This is indeed supported by FTIR and UV-visible results on hexane solutions of **1** (Figure 4e, f). As the concentration decreases, the anhydride carbonyl stretching ( $\nu_{C=O}$ ) bands at 1770 and 1738  $\text{cm}^{-1}$  (from aggregated **1** in both hexane solutions and the DCLC phase) decrease in absorptivity while two new bands at 1778 and 1746  $\text{cm}^{-1}$  (from unassociated **1**, Figure 4f, S8) grow at their expense. The noticeably bathochromically shifted anhydride  $\nu_{C=O}$  with respect to those of unassociated **1** suggests that the anhydride groups are engaged in attractive dipole-dipole interaction in the DCLC phase,<sup>26</sup> which is also supported by the molecular modelling.

As depicted in Figure 5, in an energy minimized bundled-stack columnar unit cell, anhydride groups (especially in the four stack region) adopt a dislocated overlap geometry to offer the inter-stack inter-stratum dipole-dipole attractive force. Such feature is absent in the DCLC phase of **2** due to the steric hindrance of the imide methyl group which hinders the carbonyl head-to-head overlap. Note that anhydride-ester carbonyl dipole-dipole interaction is highly unlikely in the DCLC phase of **1** as they are in quite different locations in a supramolecular column. Moreover, hexane solution IR spectra (Figure S14) suggest that the anhydride group of **1** interacts very weakly with aromatic systems. Therefore, a conclusion can be drawn that the columnar structure of **1** is stabilized by the inter-stack inter-stratum anhydride-anhydride dipole-dipole interaction associated with the dislocated interdigitation of anhydride groups. We view this inter-stack anhydride overlap of great importance since it also enables ISEC (Figure S17) which may greatly increase the chance of the inter-stack charge and energy transport. For this reason, the DCLC phase of **1** is recognized as the first ever BSDCLC structure.

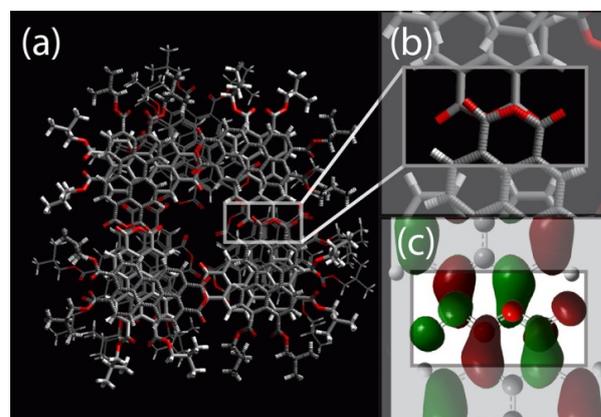


Fig. 5 (a) The energy-minimized unit cell of BSDCLC phase of **1** obtained from simulation, with the four-stack strata on the top. The top stratum molecules are shadowed for the sake of clarity. (b) Magnified anhydride groups in top strata from adjacent stacks showing the dislocated overlap geometry (c) Inter-stack LUMO in-phase overlap and ISEC

The similar dipole interaction has been suggested as a key force driving half-disk anhydride molecules forming a DCLC phase.<sup>27</sup> However, the absence of  $\pi$ -stacks makes efficient charge transport in those materials unlikely. In contrast, the large perylene ring itself in **1** is capable of forming conducting  $\pi$ -stacks, the role of the anhydride group is to provide the extra cohesion force to bundle  $\pi$ -stacks together in each column and offer ISEC. The aspect ratio of perylene anhydride, the rigid core of **1**, is fairly close to 1, if the anhydride part is excluded. This is also important for the formation of the BSDCLC phase, as it allows the anhydride part to engage in interdigitation while the perylene part being  $\pi$ -stacked without leaving a large destabilizing intra-bundle void. We believe that the following molecular features of **1** are essential for the BSDCLC phase formation: 1. A plate-shaped core with the right aspect ratio (somewhat larger than 1); 2. The anhydride group at one end of the core, providing inter-stack bundling force.

and ISEC; 3. Flexible tails attached to the other end of the core with an appropriate core/tail interfacial curvature. It is expected that other plate-shaped discotic molecules with the same structure features can also self-assemble into a BSDCLC phase. It is also worth noting that there is no built-in limitation on the size of the mesogen.

Currently, the presence of ISEC is supported by the structural characterization and simulation. The charge carrier mobility of **1** in its RT BSDCLC phase is  $5.41 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , measured by pulse-radiolysis time resolved microwave conductivity (PR-TRMC) technique, in line with the highest PR-TRMC mobility values reported<sup>28-30</sup> on closely related perylene diimides (PDIs) in their conventional DCLC phase. However, this value is modest in comparison to recently reported high mobility ( $> 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , by time-of-flight method) DCLC PDIs.<sup>31, 32</sup> To gain a clearer understanding of the role of ISEC in charge and energy transport, a thorough and systematic study on more BSDCLC systems is being conducted.

We reason that the large  $\pi$ -stack spacing and intrinsic defects arise from the competing needs of strongly interacting cores and space-demanding tails (See detailed discussion in ESI). However, such conflict is not intrinsic to the BSDCLC structure. Single-stacking-mode BSDCLC phase with tight  $\pi$ -stacks is expected to be generated by tuning the side chains.

In summary, we have shown that PEA **1** molecules aggregate into a BSDCLC structure promoted by the inter-stack anhydride dipole-dipole interaction. Due to the ISEC resulted from inter-stack  $\pi$  overlap, generating a BSDCLC phase may be a versatile strategy to improve charge/energy transport. Furthermore, it may enable the fabrication of highly efficient bulk heterojunction photovoltaic cells using DCLC materials by exploiting the large intra-column inter-stack interfacial areas, if donor and acceptor stacks can be bundled in the same column. NSF is gratefully acknowledged for funding the acquisition of the SAXS/WAXS system through Award CHE-0723028. This research was supported by PSC-CUNY grant and the Joint Solar Programme (JSP) of the Foundation for Scientific Research on Matter (FOM), which is part of the Netherlands Organization for Scientific Research (NWO). The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC Grant agreement nr. 240299. Part of the research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

## Notes and references

- 1 L. Chen, K. S. Mali, S. R. Puniredd, M. Baumgarten, K. Parvez, W. Pisula, S. De Feyter and K. Müllen, *J. Am. Chem. Soc.*, 2013, **135**, 13531-13537.
- 2 Z. S. An, J. S. 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**, 2580-2583.
- 3 K. Takashi, M. Norihiro and K. Kenji, *Angew. Chem. Int. Ed.*, 2006, **45**, 38-68.
- 4 F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491-1546.
- 5 S. Sergeev, W. Pisula and Y. H. Geerts, *Chem. Soc. Rev.*, 2007, **36**, 1902-1929.
- 6 L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001, **293**, 1119-1122.
- 7 O. Thiebaut, H. Bock and E. Grelet, *J. Am. Chem. Soc.*, 2010, **132**, 6886-6887.
- 8 Z. Wang, M. D. Watson, J. Wu and K. Müllen, *Chem. Commun.*, 2004, 336-337.
- 9 W. Pisula, X. Feng and K. Müllen, *Adv. Mater.*, 2010, **22**, 3634-3649.
- 10 S. Sengupta, S. Uemura, S. Patwardhan, V. Huber, F. C. Grozema, L. D. A. Siebbeles, U. Baumeister and F. Würthner, *Chem. Eur. J.*, 2011, **17**, 5300-5310, S5300/S5301-S5300/S5315.
- 11 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**, 384-387.
- 12 V. Percec, M. Glodde, M. Peterca, A. Rapp, I. Schnell, H. W. Spiess, T. K. Bera, Y. Miura, V. S. K. Balagurusamy, E. Aqad and P. A. Heiney, *Chem. Eur. J.*, 2006, **12**, 6298-6314.
- 13 V. Percec, E. Aqad, M. Peterca, M. R. Imam, M. Glodde, T. Bera, Y. Miura, V. S. K. Balagurusamy, P. C. Ewbank, F. Würthner and P. A. Heiney, *Chem. Eur. J.*, 2007, **13**, 3330-3345.
- 14 A. M. van de Craats and J. M. Warman, *Adv. Mater.*, 2001, **13**, 130-133.
- 15 C. W. Struijk, A. B. Sieval, J. E. J. Dakhorst, M. van Dijk, P. Kimkes, R. B. M. Koehorst, H. Donker, T. J. Schaafsma, S. J. Picken, A. M. van de Craats, J. M. Warman, H. Zuilhof and L. J. R. Sudhölter, *J. Am. Chem. Soc.*, 2000, **122**, 11057-11066.
- 16 C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485-1508.
- 17 C. Xue, R. Sun, R. Annab, D. Abadi and S. Jin, *Tetrahedron Lett.*, 2009, **50**, 853-856.
- 18 M. Sadrai, L. Hadel, R. R. Sauers, S. Husain, K. Krogh-Jespersen, J. D. Westbrook and G. R. Bird, *J. Phys. Chem.*, 1992, **96**, 7988-7996.
- 19 P. Yan, A. Chowdhury, M. W. Holman and D. M. Adams, *J. Phys. Chem. B*, 2005, **109**, 724-730.
- 20 Y. J. Xu, S. W. Leng, C. M. Xue, R. K. Sun, J. Pan, J. Ford and S. Jin, *Angew. Chem. Int. Ed.*, 2007, **46**, 3896-3899.
- 21 E. Charlet and E. Grelet, *Phys. Rev. E*, 2008, **78**, 041707.
- 22 T. S. Perova, A. Kocot and J. K. Vij, *Supramol. Sci.*, 1997, **4**, 529-534.
- 23 Z. Burhanudin and P. Etchegoin, *Chem. Phys. Lett.*, 2001, **336**, 7-12.
- 24 C. V. Cerclier, M. Ndao, R. Busselez, R. Lefort, E. Grelet, P. Huber, A. V. Kityk, L. Noirez, A. Schonhals and D. Morineau, *Phys. Chem. C*, 2012, **116**, 18990-18998.
- 25 E. Grelet, S. Dardel, H. Bock, M. Goldmann, E. Lacaze and F. Nallet, *Eur. Phys. J. E*, 2010, **31**, 343-349.
- 26 E. Galbiati, M. D. Zoppo, G. Tieghi and G. Zerbi, *Polymer*, 1993, **34**, 1806-1810.
- 27 K. Kishikawa, S. Furusawa, T. Yamaki, S. Kohmoto, M. Yamamoto and K. Yamaguchi, *J. Am. Chem. Soc.*, 2002, **124**, 1597-1605.
- 28 Z. Chen, V. Stepanenko, V. Dehm, P. Prins, Laurens D. A. Siebbeles, J. Seibt, P. Marquetand, V. Engel and F. Würthner, *Chem. Eur. J.*, 2007, **13**, 436-449.
- 29 V. Dehm, Z. J. Chen, U. Baumeister, P. Prins, L. D. A. Siebbeles and F. Würthner, *Org. Lett.*, 2007, **9**, 1085-1088.
- 30 F. May, V. Marcon, M. R. Hansen, F. Grozema and D. Andrienko, *J. Mater. Chem.*, 2011, **21**, 9538-9545.
- 31 M. Funahashi and A. Sonoda, *J. Mater. Chem.*, 2012, **22**, 25190-25197.
- 32 M. Funahashi and A. Sonoda, *Phys. Chem. Chem. Phys.*, 2011, **16**, 7754-7763.