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# Phase transition, optical and photoconductive properties of bay-substituted benzoporphyrin derivatives<sup>†</sup>

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Two benzoporphyrin derivatives substituted with long side chains at the bay positions have been synthesized through a facile route. They were confirmed to show two separate columnar phases upon cooling, *i.e.*, a hexagonal columnar phase and a rectangular columnar phase. In particular, the temperature dependence of the electronic spectra revealed that the Q-band split into two peaks, indicating the existence of typical herringbone-type dimers. Moreover, their photoconductive properties were studied by steady-state and transient photocurrent measurements. It was found that both benzoporphyrins exhibited very fast hole mobility over  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in both columnar phases and a high charge carrier generation efficiency up to 2%, demonstrating that they are potential p-type organic semiconductors for photovoltaic devices.

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### Introduction

Novel, self-organized semiconducting organic materials are constantly emerging with a view to improving their crucial performance metrics, like mobility and to regulate their physical properties, including the energy gap and energy levels.<sup>1</sup> Especially, disc-like condensed aromatic  $\pi$ -conjugated systems, such as triphenylenes,<sup>2</sup> benzocoronenes,<sup>3</sup> and phthalocyanines,<sup>4</sup> can self-organize into columnar phases when bearing long alkyl chains, in which large  $\pi$ - $\pi$  overlaps are formed between neighboring molecules, so that charges are likely to transport along the column axis in a quasi one dimensional pathway.<sup>1a</sup> In principle, electronic systems fabricated using such materials have been expected to find use in the applications of organic field effect transistors (OFET),<sup>5</sup> organic light emitting diodes (OLED)<sup>6</sup> and organic solar cells.<sup>7</sup> However, due to a rather subtle intermolecular interplay between the conjugated cores, such as attractive and repulsive forces, which inevitably causes molecular motions (translational and rotational) in the columns,8 most of discotic liquid crystal (DLC) materials present a relatively low mobility, from  $10^{-4}$  to  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>9-11</sup>

Surprisingly, liquid crystalline phthalocyanines substituted by long side chains (octyl:  $C_8PcH_2$  or hexyl:  $C_6PcH_2$ ) at the bay positions (non-peripheral) as shown in Fig. 1 (compound 1), were found to have a high optical absorption in the visible region and to be very easily controllable for molecular orientation, thus leading to an extraordinarily high photoconductivity with ambipolar mobility over  $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for both the hole and electron in their columnar phases.<sup>12</sup> Additionally, the mobility was almost independent of the temperature and field.<sup>12</sup> Furthermore, a mobility up to  $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the hole was achieved in a polycrystalline state of C<sub>6</sub>PcH<sub>2</sub>,<sup>4b</sup> which has been successfully applied to bulk hetero-junction solar cells with the fullerene derivative 1-(3-methoxy-carbonyl)-propyl-1-1-phenyl-(6,6)C61 (PCBM), generating a power conversion efficiency of 3.1% and an external quantum efficiency (EQE) higher than 70% at the Q-band region.<sup>7b</sup>

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To the best of our knowledge on liquid crystalline organic semiconductors, a high charge transport mobility strongly depends on the long-range ordered structures with less molecular displacement and motion. However, bay-substituted phthalocyanines exceptionally showed such a high mobility in a relatively low-ordered columnar phase, *i.e.* a disordered



Fig. 1 Molecular structures of discotic liquid crystalline benzoporphyrin derivatives.

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hexagonal columnar phase  $(Col_{hd})$ .<sup>12</sup> It is unclear why baysubstituted phthalocyanines show a higher mobility than other discotic liquid crystals. Explicitly, this question has never been addressed in the available literature reports.

We have been focusing on the generality of this molecular design to other systems to help solve this mystery. In fact, analogous to phthalocyanines, benzoporphyrin derivatives are also considered to possess excellent optical and electrical properties, and can be substituted at the bay positions. However, because of the difficulty in chemical synthesis, to introduce flexible chains into the bay positions of benzoporphyrins is reported in limited, early literature.<sup>13</sup> As a consequence, researchers compromised with the study of the parent benzoporphyrin derivative, tetrabenzoporphyrin, which was reported to have a HOMO level of 5.1 eV and a relatively narrow bandgap, of about 2 eV and shows a relatively high intrinsic positive charge concentration.<sup>14,15</sup> Moreover, the high optical absorption in the visible region qualifies it for photovoltaic applications.<sup>15</sup>

Until recently, the discotic liquid crystalline benzoporphyrin derivatives, 1,4,8,11,15,18,22,25-hexyltetrabenzoporphyrin (TBP: compound 2) and 1,4,8,11,15,18,22,25-hexyl tetrabenzomonoazaporphyrin (TBMAP: compound 3), substituted by long side chains at the bay positions, were synthesized starting from thiophene, as shown in Scheme 1.<sup>16</sup> However, their phase transition, optical and electronic properties are still unclear, which possibly resulted from the very low yields over the whole synthetic route.

In this paper, we designed a versatile route for the synthesis of benzoporphyrin derivatives, as shown in Scheme 1. In this new route, the commercial starting material, 2,3-dicyanohydroquinone 7, was firstly triflated, to prepare 8 in a yield of 90%. Then, through a Suzuki coupling, the precursor 9 was synthesized from compound 8 in a high efficiency and under mild conditions. Finally, a cyclization reaction was carried out, as reported in ref. 16, to prepare TBP 2 and TBMAP 3, with a slight modification, by using a 1 : 4 ratio of MeMgBr to the precursor 9. The crude products were carefully isolated and extensively purified by column chromatography, followed by repetitive recrystallization from a mixed solvent of THF and methanol, in order to further the characterization of the thermal and physical properties. Compared with the previous route, ours showed quite a high efficiency, mild conditions and functional group tolerance.

## **Results and discussion**

#### Phase transition

The phase transitions of 2 and 3have been characterized, in which two mesophases were observed for both TBP and TBMAP. On heating, their clear points appeared at 178 °C and 177 °C, respectively. Then, as the temperature decreased from the isotropic phase, a phase transition from the first mesophase to the second one took place at 162 °C and 161 °C, respectively and entered into crystal states at the same temperature of 149 °C. These results are consistent with a previous report.<sup>16</sup>

The polarized optical micrograph (POM) textures of TBP and TBMAP are shown in Fig. 2. It can be seen that both compounds exhibit quite characteristic textures in their separate mesophases. At 175 °C, upon cooling, fan-like textures appeared (Fig. 2(a) and (c)), which are typical for the hexagonal columnar phase,<sup>3b</sup> while, the black region can be considered as the existence of homeotropic columns.<sup>9</sup> At 155 °C, their textures turned to be a broken fan type (Fig. 2(b) and (d)), which are commonly observed in the rectangular columnar phase.<sup>12</sup>

As can be seen in Fig. 3, the XRD patterns exhibited quite characteristic peaks for both TBP and TBMAP, self-organizing into hexagonal and rectangular columnar phases, which agrees with the results of the POM textures. As the temperature decreased, the hexagonal columnar phase quickly transformed to a rectangular one, which can be observed in some DLC materials, and the latter shows a higher order than the former.<sup>12</sup>

In addition, we can see that XRD patterns of TBP and TBMAP in the rectangular columnar phase did not show the rather clear



Scheme 1 Synthetic routes for benzoporphyrin derivatives. (i):  $BrC_6H_{13}$ , *n*-BuLi, THF; (ii): *m*-CPBA,  $CH_2CI_2$ ; (iii):  $CHCI_3$ , 150 °C, in a sealed tube; (iv): tri-fluoromethanesulfonic anhydride, pyridine, dry  $CH_2CI_2$ ; (v):  $C_6H_{13}B(OH)_2$ ,  $Pd(dppf)CI_2$ , AgO,  $K_2CO_3$ , THF, 80 °C; (vi): (a) BrMgMe, THF, reflux, 30 min; (b) quinoline, 200 °C, 12 h; (c) AcOH, reflux.





judging from the absence of a  $\pi$ -stacking reflection within the column at the wide angle region. Interestingly, the intracolumnar distances for both TBP and TBMAP are arranged to be 20 to 22 Å, which seemed significantly small compared with those of peri-substituted compounds.<sup>18</sup> Even though both TBP and TBMAP exhibited disordered hexagonal columnar phases, their mean intracolumnar distances, around 3.5 Å, probably can be estimated from the alkyl chains reflection (3.8 Å), indicative of a relatively stronger  $\pi$ - $\pi$  electronic interaction than usual.<sup>4b,18</sup> In the rectangular columnar phase, the molecules are tilted to

Fig. 2 Polarized optical micrographs of TBP (a: 175 °C; b: 155 °C) and TBMAP (c: 175 °C; d: 155 °C).

splitting peaks (200) and (110) (results by the splitting of the (100) reflection of the hexagonal columnar phase lattice, Fig. 3(b) and (d)) as usual,<sup>8b</sup> which has been reported for some phthalocyanines with a very unique molecular alignment.<sup>17</sup> These uncommon results actually led to the difficulty in distinguishing the two separate columnar phases. So, the authors of ref. 16 defined the second phase as the other hexagonal columnar phase.

The XRD data are summarized in Table 1. Both TBP and TBMAP showed disordered hexagonal columnar phases,

	$T(^{\circ}C)$	<i>d</i> -spacing (Å)	Miller index ( <i>hlk</i> )	Phase (lattice parameter)
ТВР	175	17.5	(100)	Col <sub>hd</sub>
		10.8	(110)	a=21.6 Å
		9.3	(200)	
		3.8	Alkyl	
	155	18.3	(200)	Col <sub>r</sub>
		17.5	(110)	a = 36.6  Å
		3.9	Alkyl	$b=19.9~{ m \AA}$
TBMAP	175	17.9	(100)	Col <sub>hd</sub>
		10.8	(110)	a=21.6 Å
		9.2	(200)	
		3.9	Alkyl	
	155	18.8	(200)	$\operatorname{Col}_{r}$
		17.4	(110)	a = 37.6 Å
		3.8	Alkyl	b=19.6 Å



Fig. 3 XRD patterns of TBP (a: 175 °C; b: 155 °C) and TBMAP (c: 175 °C; d: 155 °C).

form a herringbone configuration.<sup>17</sup> This type of arrangement is very common in the field of organic crystallography, which is the lowest free energy possible arrangement for rigid molecules, leading to the closest stacks.<sup>19</sup>

#### Temperature-dependent electronic spectra

The temperature-dependent electronic spectra of thin films of the representative derivative TBP are recorded in Fig. 4. According to Kasha' report,<sup>20</sup> they theoretically illustrated that an interaction between two neighbouring molecules in dimers affects their electronic spectra. Additionally, only the oblique dimers show the split related band. As can be seen from Fig. 4, TBP gave split Q bands at the isotropic phase, hexagonal columnar phase and rectangular columnar phase. The split Q bands in these phases correspond to oblique (roof-top-shaped) dimers, even in the liquid state. In the amorphous state, the intensity of the Q band decreased, but was also split (Fig. S2†).

Taking account for both results of the X-ray diffraction and electronic spectra, it could be understood that the absence of  $\pi$ stacking reflection (intracolumnar order) at wide angle region originated from molecular oblique configuration. In this case, although it is not the most favorable packing for transport, in view of the large angle between the planes of adjacent molecules along the herringbone diagonal (which tends to reduce the strength of intermolecular interactions), this oblique conformation with a tilt angle to the columnar axis is the most convenient to relax the repulsion of rigid cores and suppress molecular translational motion which makes long range columns possible.<sup>21</sup> Actually, a herringbone configuration in a hexagonal columnar phase was also found in other DLCs, such as hexabenzocoronene<sup>8c</sup> and phthalocyanine<sup>8b,17b</sup> due to the strong steric hindrance of the swallow-tailed chains at the peripheral positions. Here, although linear alkyl chains are used, they are located at the crowded bay areas and, more or less, arranged out of cores' plane, according to the available single crystal data,<sup>12c</sup> thus exhibiting a strong steric repulsion, as the swallow-tailed ones.

#### Steady state photocurrent measurement

A steady-state photocurrent measurement of TBP was carried out by using two types of devices: an Al/TBP (9.1 µm)/Al and Al/ TBP (50 nm)/ITO (Fig. S3-S5<sup>†</sup>). The measured photocurrent spectra of the TBP thin films are shown in Fig. 5, where the photocurrent spectra were normalized to the number of absorbed photons. We can see that TBP showed a relative low photocurrent in the long wavelength region, compared with that in the short wavelength region, mainly because the photons in the long wavelength region have a low excitation energy, of less than 2 eV (bandgap of TBP).14 Interestingly, compared with the electronic spectra in Fig. 4 and S2,† the photocurrent spectra show minima at the maximal absorption, but maxima at the minimal absorption when a large positive bias was applied to the thick sample. On the other hand, current response of the thin film almost resembles the shape of the whole absorption spectrum. The striking relationship between the photocurrent and absorption spectra can be classified as antibatic for the former and symbatic for the latter.<sup>22</sup>

Similar results have been reported by other researchers on tetrabenzoporphyrin derivatives.<sup>23</sup> This effect is usually called



Fig. 5 Normalized photocurrent spectra of TBP. The photocurrents were measured at 20 V and 175 °C for the thick film and 5 V at room temperature for the thin film. The voltage was applied on the same side of Al as the incident light.



Fig. 4 Temperature-dependent electronic spectra of the visible region of the film of the representative derivative TBP and an illustration of the exciton energy diagrams for the dimers.

photocurrent rectification, which was interpreted as resulting from the interaction between the bulk photoconductivity and the injection current.<sup>23b</sup> For thick cells, the weakly absorbed light will penetrate into the sample deeply, leading to a relatively small resistance and a relatively large current at these wavelengths, while its resistivity and current at strongly absorbed wavelengths are still practically at its dark level. However, for the thin cell, the strongly absorbed light will penetrate a substantial portion of the sample, while only a fraction of the weakly absorbed light will be absorbed by the cell. At this point, the spectral characteristics of the bulk and injected currents should be similar.

#### Transient photocurrent measurement

In order to investigate the charge carrier transport and photocarrier generation properties in benzoporphyrins in detail, a transient photocurrent measurement was performed by a conventional time-of-flight (TOF) experiment (Fig. S6†), using a nitrogen gas laser ( $\lambda = 337$  nm, pulse duration time = 600 ps, power per pulse =  $13.6 \mu$ J) for the photo-excitation. Liquid crystal cells with Al and ITO electrodes for the TOF experiments were prepared, and TBP and TBMAP were capillary-filled into the cells at their isotropic temperatures. The resulting transient photocurrents were recorded by a digital oscilloscope and were analysed in linear and double logarithmic plots. The carrier mobility  $\mu$  was obtained through the equation of  $\mu = d^2/V\tau_{\rm T}$ , where d is the sample thickness, V is the applied voltage, and  $\tau_{\rm T}$  is the transit time of the photo-generated carriers traversing the sample layer. The  $\tau_{T}$  is determined from an inflection point in a double logarithmic plot of the transient photocurrent as a function of time.

Fig. 6(a) and (b) show a well-defined, non-dispersive hole transient photocurrent of both materials in the  $\text{Col}_{hd}$  phase at 175 °C. Each photocurrent exhibits a slow rise of the photocurrent, which is probably due to thermally activated detrapping of the photo-generated charges at the electrode interface,<sup>24</sup> so that a peak instead of a shoulder was shown, followed by a slow decay of the current. The mobility exceeded 0.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in the Col phases, which is high enough to be attributed to the hole conduction.<sup>15,24</sup> This value is comparable to those of bay-substituted phthalocyanine derivatives<sup>12</sup> and about one order of magnitude higher than that of a polycrystalline non-mesomorphic tetrabenzoporphyrin determined by the field effect transistor (FET) technique<sup>14b,25</sup> and two orders of magnitude higher than that using the space charge limited current (SCLC) technique.<sup>26</sup>

The positive carrier mobility for both TBP and TBMAP, as shown in Fig. 7(a), is almost the same and increases in a stepwise manner from  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in the isotropic phase, to  $10^{-1}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in both the disordered hexagonal and rectangular columnar phases, when the phase transition takes place. Judging from such a high mobility over  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, the conductivity was surely confirmed to be electronic but not ionic,<sup>2b</sup> which indicated a high purity in both compounds.<sup>27</sup> However, after the samples entered into crystalline states, due to many grain boundaries, the signals of their photocurrent became quite dispersive, so that the charge transport mobility could not be obtained.



**Fig. 6** Typical transient photocurrents for positive carriers of TBP (a) (9.1  $\mu$ m) and TBMAP (b) (13.4  $\mu$ m) as a function of time under various applied voltages. The insets show double logarithmic plots of photocurrents.

This high mobility indicates that bay-substituted benzoporphyrin derivatives are surely beneficial for the enhancement of charge transport in columnar phases. It implies that molecular motions in the packed columns probably can be suppressed through introducing side chains into the bay positions, which allows the special herringbone configuration to construct in the disordered hexagonal columnar phase and rectangular columnar phase. Coincidentally, bay-substituted phthalocyanines having a high mobility also showed the split Q band in their electronic spectra,28 but those peripheral substituted phthalocyanines with low mobility did not show the split Q band even though they exhibited a highly ordered hexagonal columnar phase.9,29 Furthermore, the relationship between the high mobility and herringbone configuration has been explored in single crystals, like pentacene,30 and a calamitic liquid crystalline smectic E phase.31

The hole mobility hardly depends on the temperature in both mesophases, irrespective of the compound, which was often reported in other discotic<sup>6</sup> and smectic liquid crystals.<sup>32</sup> These features have been well explained by a narrow distribution of density, ranging from 40 to 60 meV comparable to kT, where *T* is the temperature for the TOF experiments.<sup>33</sup> Also, the hole mobility of TBP and TBMAP as a function of the electric field is illustrated in Fig. 7b. It is very clear that the hole mobility in the two samples does not have a dependence on the electric field, which is also quite a common behaviour in the electronic conduction of liquid crystals, which is attributed to a small intermolecular distance of around 3.5 Å in the liquid crystalline



Fig. 7 Mobility of TBP and TBMAP as a function of temperature at a fixed electric field (a) and as a function of electric field at 175 °C in the Col<sub>hd</sub> phase (b).



**Fig. 8** Photo-generation efficiency of carriers for TBP and TBMAP as a function of temperature at a fixed electric field.

phases (as mentioned above) and a small dipole moment of the molecules.<sup>34,35</sup>

#### Photo-generation efficiency

Based on the fact that a transient photocurrent shows a fast decay after the transit time, indicating a small density of deep trapping states for carriers, we estimated the photo-generation efficiency of the charges from the collected charges, calculated by integrating a transient photocurrent at a given condition as a function of time and the absorbed photons in the cell. The related experimental conditions have been reported in our earlier work.<sup>34</sup> Here, all of the present experiments described in this article meet the requirements. Thus, the yield of the photocarrier generation can be calculated by the following equation:

$$Q_{\rm e} = \frac{h\nu \int_0^t I_{\rm TOF}(t) dt}{eI_0 T_{\rm tr}} = \frac{h\nu Q_{\rm c}}{eI_0 T_{\rm tr}}$$
(1)

where  $I_{\text{TOF}}(t)$  is the transient photocurrent based on the hole transport;  $Q_c$  is the collected charges;  $I_0$  is the laser energy per pulse, which was always limited to less than one-tenth of the geometrical capacitance of the sample C-V;  $T_{\text{tr}}$  is the

transmittance of the electrode,  $\nu$  is the frequency of the laser light used, e is the unit charge, h is Planck's constant, and T is the end time of the measurement at which the photocurrent becomes zero.

Fig. 8 shows the photogeneration efficiency of charges for TBP and TBMAP as a function of temperature. It should be noted that the photogeneration efficiency for TBP did not depend on the temperature when a semi-transparent Al electrode was employed, while the efficiency for TBMAP exhibited an abrupt decrease in the isotropic phase, when an ITO electrode was employed. This can be explained by the different mechanisms for photo-carrier generation. The photo-carriers are generated in the bulk, because of fewer interactions of excitons with Al electrodes;36 in another case, the charges are photo-injected from the ITO electrode, depending on the concentration of excitons diffused to the ITO electrode. The fact that the photo-generation efficiency of 2% in the TBMAP cell with the ITO electrode is one order of magnitude higher that the 0.2% in the TBP cell with Al electrodes supports the idea discussed in our previous report.24a

#### Conclusion

In conclusion, a facile synthetic route was proposed to prepare high-purity bay-substituted benzoporphyrin derivatives of TBP and TBMAP, having alkyl groups at the bay positions for the characterization of the phase transition, optical and photoconductive properties. The results from the characterization by POM and XRD confirmed that both compounds showed disorder hexagonal and rectangular columnar phases. The temperaturedependent electronic spectra illustrated that these bay-substituted DLCs exhibited a split Q band, which has been theoretically explained as resulting from a herringbone configuration.

Also, we investigated the charge carrier transport and photoconductive behaviours in two discotic liquid crystalline benzoporphyrin derivatives. Interestingly, through the time of flight technique, these materials exhibited a very high hole mobility, over 0.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in Col<sub>hd</sub> and Col<sub>r</sub>, which originated from the herringbone configuration within the long range

columns. Moreover, a very high photo-generation efficiency, up to 2%, in the columnar phase has been achieved.

According to the present results, TBP is very promising as a p-type organic semiconductor for photovoltaic applications. Furthermore, TBMAP is a good derivative, whereby its availability and potential may also be worthy of attention. We are now focusing on how we can develop more efficient synthetic methods, as well as the application in high performance photovoltaic devices.

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# Notes and references

- 1 (a) S. Sergey, W. Pisula and Y. H. Geerts, *Chem. Soc. Rev.*, 2007, 36, 1902; (b) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer and H. Duan, *Nature*, 2002, 419, 384.
- 2 (a) S. Kumar, *Liq. Cryst.*, 2005, 32, 1089; (b) D. Adam,
  P. Schuhmacher, J. Simmerer, L. Haussling,
  K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and
  D. Haarer, *Nature*, 1994, 371, 141.
- 3 (a) J. Wu, M. D. Watson, L. Zhang, Z. Wang and K. Müllen, J. Am. Chem. Soc., 2004, 126, 177; (b) P. Herwig, C. W. Kayser, K. Müllen and H. W. Spiess, Adv. Mater., 1996, 8, 510.
- 4 (a) M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1987, 1086; (b) Y. Shimizu, Y. Miyakea, H. Yoshid, H. Monobe, M. J. Cook, A. Fujii and M. Ozaki, *Mol. Cryst. Liq. Cryst.*, 2011, 549, 127.
- 5 Y. Kikuzawa, T. Mori and H. Takeuchi, *Org. Lett.*, 2007, 9, 4817.
- 6 M. Ghedini, D. Pucci, A. Crispini, A. Bellusci, M. L. Deda, I. Aiello and T. Pugliese, *Inorg. Chem. Commun.*, 2007, **10**, 243.
- 7 (a) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen,
  E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001,
  293, 1119; (b) T. Hori, Y. Miyake, N. Yamasaki, H. Yoshida,
  A. Fujii, Y. Shimizu and M. Ozaki, *Appl. Phys. Express*, 2010,
  3, 101602.
- 8 (a) V. Lemaur, D. A. Silva Filho, V. Coropceanu, M. Lehmann,
  Y. Geerts, J. Piris and J. Cornil, J. Am. Chem. Soc., 2004, 126, 3271; (b) E. Fontes, P. A. Heiney, M. Ohba, J. N. Haseltine and
  A. B. Smith, Phys. Rev. A: At., Mol., Opt. Phys., 1988, 37, 1329;
  (c) W. Pisula, M. Kastler, D. Wasserfallen, M. Mondeshki,
  J. Piris, I. Schnell and K. Mullen, Chem. Mater., 2006, 18, 3634–3640.
- 9 H. Fujikake, T. Murashige, M. Sugibayashi and K. Ohta, *Appl. Phys. Lett.*, 2004, **85**, 3474.
- 10 C. Deibel, D. Janssen, P. Heremans, V. De Cupere, Y. Geerts, M. L. Benkhedir and G. J. Adriaenssens, *Org. Electron.*, 2006, 7, 495.

- 11 H. Iino, J. I. Hanna and D. Haarer, *Phys. Rev. B.*, 2005, 72, 193203.
- 12 (a) H. Iino, J. I. Hanna, R. J. Bushby, B. Movaghar, B. J. Whitaker and M. J. Cook, Appl. Phys. Lett., 2005, 87, 132102; (b) Y. Miyake, Y. Shiraiwa, K. Okada, H. Monobe, T. Hori, N. Yamasaki, H. Yoshida, M. J. Cook, A. Fujii, M. Ozaki and Y. Shimizu, Appl. Phys. Express, 2011, 4, 021604; (c) I. Chambrier, M. J. Cook, M. Helliwell and A. K. Powell, J. Chem. Soc., Chem. Commun., 1992, 444.
- 13 Y. Matsuzawa, K. Ichimura and K. Kudo, *Inorg. Chim. Acta*, 1998, **277**, 151.
- 14 (a) S. Aramaki, Y. Sakai and N. Ono, *Appl. Phys. Lett.*, 2004,
  84, 2085; (b) P. B. Shea, J. Kanicki and N. Ono, *J. Appl. Phys.*, 2005, 98, 014503.
- 15 M. Guide, X. Dang and T. Nguyen, *Adv. Mater.*, 2011, 23, 2313.
- 16 A. N. Cammidge, I. Chambrier, M. J. Cook, D. L. Hughes, M. Rahman and L. Sosa-Vargas, *Chem.-Eur. J.*, 2011, 17, 3136.
- 17 (a) G. Schweicher, G. Gbabode, F. Quist, O. Debever, N. Dumont, S. Sergeyev and Y. H. Geerts, *Chem. Mater.*, 2009, 21, 5867; (b) P. Weber, D. Guillon and A. Skoulios, *Liq. Cryst.*, 1991, 9, 369.
- 18 M. K. Engel, P. Bassoul, L. Bosio, H. Lehmanns, M. Hanacks and J. Simon, *Liq. Cryst.*, 1993, 15, 709.
- 19 Y. Kitaigorodske, *Molecular Crystals and Molecules*, Academic Press, 1973.
- 20 M. Kasha, H. R. Rawls and M. A. El-Bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371.
- 21 P. Weber, D. Guillon and A. Skoulios, *Liq. Cryst.*, 1991, 9, 369.
- 22 (a) K. J. Donovan, K. Scott, S. Spagnoli and J. Berrehar, *Chem. Phys.*, 1999, 250, 61; (b) M. G. Harrison, J. Gruner and G. C. W. Spencer, *Phys. Rev. B: Condens. Matter*, 1997, 55, 7831.
- 23 (a) H. Gerischer, M. Liibke and B. J. Bressel, J. Electrochem. Soc., 1983, 130, 2112; (b) B. A. Gregg, M. A. Fox and A. J. Bard, J. Phys. Chem., 1990, 94, 1586; (c) Y. Shimizu, A. Ishikawa, S. Kusabayashi, M. Miya and A. Nagata, J. Chem. Soc., Chem. Commun., 1993, 656.
- 24 (a) H. Zhang and J. Hanna, *J. Phys. Chem. B*, 1999, **103**, 7429;
  (b) D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher and K. Siemensmeier, *Phys. Rev. Lett.*, 1993, **70**, 457.
- 25 (a) S. Aramaki, Y. Sakai and N. Ono, *Appl. Phys. Lett.*, 2004, **84**, 2085.
- 26 M. Guide, X. Dang and T. Nguyen, *Adv. Mater.*, 2011, 23, 2313.
- 27 (a) H. Ahn, A. Ohno and J. Hanna, *Jpn. J. Appl. Phys.*, 2005, 44, 3764; (b) M. Funahashi, F. Zhang, N. Tamaoki and J. Hanna, *ChemPhysChem*, 2008, 9, 1465.
- 28 N. B. Chaure, C. Pal, S. Barard, T. Kreouzis, A. K. Ray, A. N. Cammidge, I. Chambrier, M. J. Cook, C. E. Murthy and M. G. Cain, *J. Mater. Chem.*, 2012, 22, 19179.
- 29 F. Nekelson, H. Monobe, M. Shiroc and Y. Shimizu, *J. Mater. Chem.*, 2007, **17**, 2607.
- 30 D. H. Kim, D. Y. Lee, H. S. Lee, W. H. Lee, Y. H. Kim, J. I. Han and K. Cho, *Adv. Mater.*, 2007, **19**, 678.

- 31 (a) H. Iino and J. I. Hanna, *Adv. Mater.*, 2011, 23, 1748; (b)
  M. A. Stokes, R. Kortan, S. R. Amy, H. E. Katz, Y. J. Chabal,
  C. Kloc and T. Siegrist, *J. Mater. Chem.*, 2007, 17, 3427.
- 32 (a) M. Funahashi and J. Hanna, Appl. Phys. Lett., 2000, 76, 2574; (b) M. Funahashi and J. Hanna, Appl. Phys. Lett., 1997, 71, 602.
- 33 A. Ohno, J. Hanna and D. Dunlap, *Jpn. J. Appl. Phys.*, 2008, 47, 1079.
- 34 M. K. Engel, P. Bassoul, L. Bosio, H. Lehmanns, M. Hanacks and J. Simon, *Liq. Cryst.*, 1993, **15**, 709.
- 35 (a) M. Funahashi and J. Hanna, Appl. Phys. Lett., 1998, 73, 3733; (b) T. Kreouzis, K. J. Donovan, N. Boden, R. J. Bushby, O. R. Lozman and Q. Liu, J. Chem. Phys., 2001, 114, 1797; (c) K. Zhao, C. Chen, H. Monobe, P. Hu, B. Wang and Y. Shimizu, Chem. Commun., 2011, 47, 6290.
- 36 H. Zhang and J. Hanna, J. Appl. Phys., 2000, 88, 270.