

Cite this: *Chem. Commun.*, 2011, **47**, 6290–6292

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## COMMUNICATION

## Three-chain truxene discotic liquid crystal showing high charged carrier mobility†

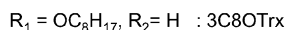
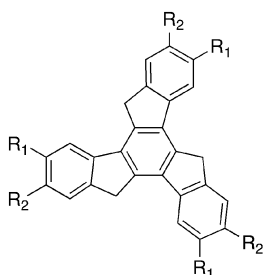
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Received 17th January 2011, Accepted 28th March 2011

DOI: 10.1039/c1cc10299k

A new truxene discotic liquid crystal possessing only three octyloxy chains (3C8OTRX) was studied on the mesomorphic and semiconducting properties to reveal that it exhibits a high drift mobility of positive carriers in the order of  $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in the hexagonal ordered columnar ( $\text{Col}_h$ ) mesophase.

Organic electronics have been so extensively studied in this decade and nowadays the research goes to a new field called “printed electronics” toward novel optoelectronic devices such as thin film transistors<sup>1</sup> and thin film solar cells,<sup>2</sup> which are fabricated under low energy consumption processes by use of printing technology on flexible polymer substrates.



On the other hand, liquid crystals (LCs) have characteristic properties derived from the self-assembling nature of dynamic molecular systems such as a spontaneous alignment behaviour to form a large mono-domain film.<sup>3</sup> Furthermore, recent studies on LC-based semiconductors have revealed that a variety of compounds could exhibit fast mobility of charged carriers ( $\sim 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) in mesophases, comparable to that of a-Si.<sup>4</sup> Also LCs are typical molecular materials performing a variety of self-assembling behaviours as well as high solubility into common organic solvents, coming from their characteristic chemical structure of aromatics attached with aliphatic chains.

These are important properties for the use of organic semiconductor inks toward “printed electronics”. Therefore, LC-based organic semiconductors are an interesting and important category of organic semiconductors to attain high performance of devices fabricated by solution processing.<sup>5</sup>

Especially in the case of discotic liquid crystals (DLCs), molecules self-organise to molecularly stacked columnar mesophases and these molecular orders could be active as a 1-dimensional path for charge transport by an electronic hopping process. Therefore, the density of aromatic parts within a columnar structure should be higher, considering that the more efficient charge hopping requires a higher transfer integral based on the semi-classical Marcus theory of electron transfer.<sup>6</sup> Thus, a shorter number of peripheral chains and/or chain length would be one possible strategy of molecular design for novel LC semiconductors, in which one has to avoid the missing of liquid crystallinity.<sup>7</sup> From this point of view, such a strategy would concern raising the aromatic/aliphatic ratio for the exclusive volume of molecule that directly relates to the concentration of aromatic core in the entire molecular structure.

Here in this work, a truxene mesogen (3C8OTRX) having only three peripheral chains and exhibiting a columnar mesophase was studied to find a fast drift mobility of charged carriers in the order of  $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

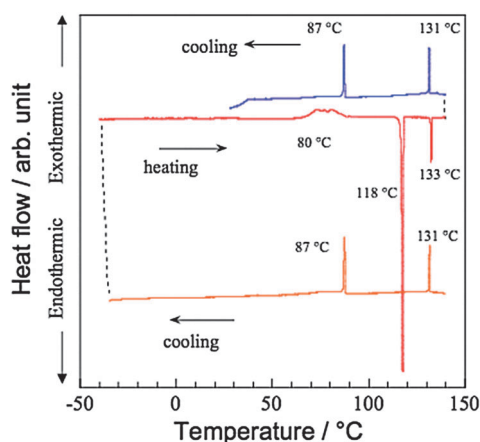
The synthesis of 3C8OTRX was carried out according to the synthetic scheme described in the ESI. The product was purified by column chromatography followed by recrystallisation from EtOAc-EtOH solution.<sup>8</sup>

Fig. 1 shows DSC curves of 3C8OTRX. One can see two endothermic peaks on heating at 118 °C and 133 °C and two exothermic peaks on the cooling runs are seen to indicate this compound exhibits an enantiotropic mesophase. The optical texture observation by a polarised microscope revealed that the phase transitions at 118 °C and 133 °C are the melting and clearing points, respectively. On cooling, a metastable mesophase comes up at 87 °C and this is relaxed at 70–90 °C on heating to the thermodynamically most stable crystal. The XRD pattern at 120 °C for a non-aligned sample (Fig. 2) shows diffraction peaks at 17.9 Å, 10.2 Å and 8.68 Å in the small angle region, of which the reciprocal spacing ratio is  $1:1/\sqrt{3}:1/2$ , which can be assigned to the (100), (110) and (200) reflections for  $\text{Col}_h$  mesophase. The broad peak around

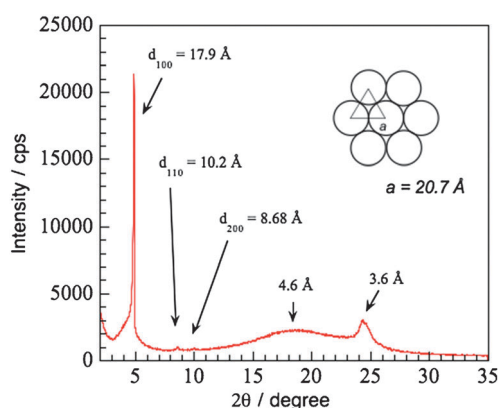
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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1cc10299k



**Fig. 1** DSC curves of 3C8OTRX at  $0.5\text{ }^{\circ}\text{C min}^{-1}$  heating and cooling rates.

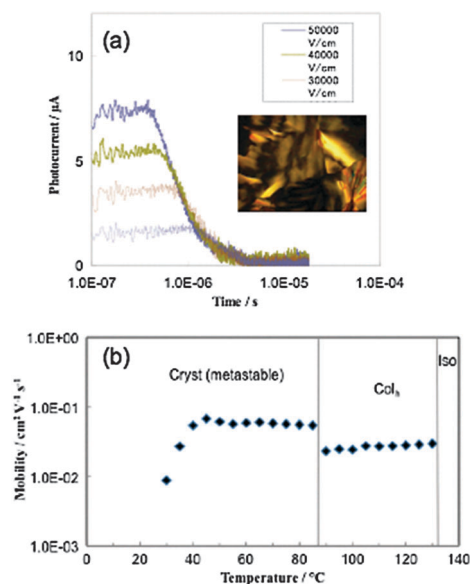


**Fig. 2** An XRD pattern of 3C8OTRX at  $100\text{ }^{\circ}\text{C}$ .

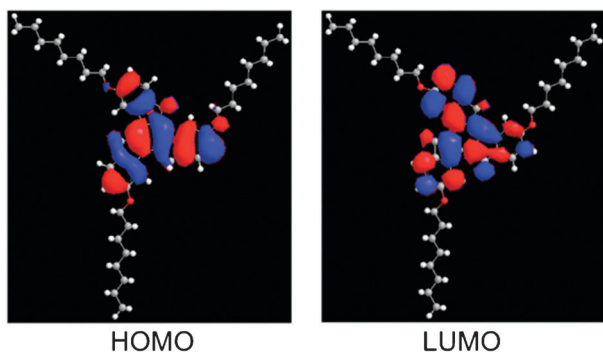
$4.6\text{ }\text{\AA}$  in the wide-angle region represents the averaged distance among the molten aliphatic chains surrounding the truxene core. Another diffraction peak appears at  $3.6\text{ }\text{\AA}$  corresponding to the stacking periodicity within a column, indicating it is an ordered columnar phase. The lattice parameter of the  $\text{Col}_h$  phase was calculated to be  $20.7\text{ }\text{\AA}$  and this value is less than  $2/3$  of the molecular diameter with fully extended chains (*ca.*  $36\text{ }\text{\AA}$ ), indicating deeply interdigitated chains surrounding the truxene core.<sup>9</sup> It was reported that the homologues of hexa-alkoxy-substituted truxene exhibit an ordered  $\text{Col}_h$  mesophase with a higher thermal stability (clearing:  $> 200\text{ }^{\circ}\text{C}$ ).<sup>10</sup> The corresponding homologue to 3C8OTRX exhibits the wider temperature range and a higher thermal stability (melting:  $86\text{ }^{\circ}\text{C}$ , clearing:  $> 300\text{ }^{\circ}\text{C}$ ). Furthermore, the lattice parameter of  $\text{Col}_{ho}$  mesophase was reported to be *ca.*  $25\text{ }\text{\AA}$ , which is rather larger than that of 3C8OTRX, also supporting more deeply interdigitated chains in 3C8OTRX. It would be reasonable to think that 3C8OTRX molecules could stack tightly to form an ordered columnar structure because of the lower number of peripherally attached chains more easily avoid the steric problem for the stacks with molecular rotations around the columnar axis. However, the lower thermal stability of columnar phases indicates that the lower number of chains leads to weaker nano-segregation between the aromatic core and the peripheral aliphatic chains. The homologue with hexyl chains for 3C8OTRX was already reported to exhibit a  $\text{Col}_h$

mesophase characterized only by the optical texture observation and no detailed characterization of mesophase was shown.<sup>11</sup>

On the other hand, the drift mobility of charged carriers was determined by a Time-Of-Flight (TOF) technique under controlled temperature.<sup>12</sup> A typical decay curve was observed for the positive electrode incidence to give  $2 \times 10^{-2}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  for its hole mobility (Fig. 3a). The mobility is almost independent of applied field in the range of  $10$  to  $50\text{ kV cm}^{-1}$ . The negative electrode incidence did not give any clear decay curves. The molecular alignment in the cell for TOF measurements was observed by a polarised microscope to exhibit mostly non-homeotropic alignment as seen in Fig. 3a. The temperature dependence is shown in Fig. 3b. Even in the metastable phase, the decay curves could be detected to determine the hole mobility which reaches  $7 \times 10^{-2}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  at  $70\text{ }^{\circ}\text{C}$  as its maximum, going down to  $4 \times 10^{-2}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  at  $25\text{ }^{\circ}\text{C}$ . It is rare for poly-domain cells of crystalline solid to see such a typical decay curve in TOF measurements,<sup>13</sup> while the clear decay curves could be observed for the poly-domain film of a highly ordered smectic mesophase of calamitics.<sup>14</sup> A Gaussian calculation of 3C8OTrx (RHF/6-31G) indicates the symmetry of the HOMO is favourable for the molecular rotation around the columnar axis, instead of the less symmetrical LUMO as shown in Fig. 4. This might support the fact that the smaller photocurrent was observed in a dispersive way for the negative electrode incidence in the TOF measurements. Considering the lower number of chains for this tri-substituted truxene mesogen than the hexa-substituted one, one may be able to think that the charges could transport even among the columns by the contacts of molecules at the edges of central aromatic moieties for realising electronic charge transport not along the columnar axis.<sup>13</sup> Recent studies on truxene analogues with six aliphatic chains for organic electronics have shown that the



**Fig. 3** Results of drift mobility measurements. (a) Transient photocurrent decay curves ( $100\text{ }^{\circ}\text{C}$ ,  $16.6\text{ }\mu\text{m}$ -thick film) with the optical texture of cell viewed under crossed polarisers and (b) temperature dependence of mobility (applied field:  $10\text{ kV cm}^{-1}$ , steady-temperature measurements on cooling process).



**Fig. 4** Schematic views of HOMO and LUMO in 3C8OTrx calculated by Gaussian 03W (RHF/6-31G).

carrier mobilities observed are  $1.03 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for FET<sup>15</sup> and  $\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for liquid crystalline semiconductors.<sup>16</sup>

In summary, a trioctyloxytruxene discoticogen was synthesised as a candidate for liquid crystalline semiconductors. It was found that it exhibits a Col<sub>ho</sub> mesophase, even though only three peripheral chains are attached to a truxene core. Also surprisingly it shows lower thermal stability than the corresponding hexa-substituted homologue, indicating that the weaker nano-sized segregation takes place between the central aromatics and the peripheral aliphatics, while a high carrier mobility of positive charges was found in the Col<sub>ho</sub> and metastable mesophases, which are  $2 \times 10^{-1}$  and  $7\text{--}4 \times \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. This columnar mesomorphism and high drift mobility are so interesting in terms of structure-mesomorphism relationship for liquid crystalline semiconductors and would give an inspiration for a new molecular design concept for LC-based semiconductors, particularly, in terms of the volume ratio of central aromatic and peripheral aliphatic moieties with an appropriate symmetry of HOMO and LUMO of the molecule.

This research was financially supported by the National Natural Science Foundation of China (No.20872104, 50673069) and the NSFC-JSPS Bilateral International Joint Research Project (No. 50811140156).

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- Compound identification data: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.49 (d,  $J$  = 8.4 Hz, 3H), 7.35 (d,  $J$  = 1.8 Hz, 3H), 6.91 (dd,  $J$  = 7.8 Hz, and  $J$  = 2.4 Hz, 3H), 4.08 (t,  $J$  = 6.6 Hz, 6H), 4.02 (s, 6H), 1.91–1.86 (m, 6H), 1.58–1.53 (m, 6H), 1.45–1.36 (m, 24H), 0.92 (t,  $J$  = 6.6 Hz, 9H). HRMS: calcd. for C<sub>51</sub>H<sub>66</sub>O<sub>3</sub>, 726.5012; found ( $M$ )<sup>+</sup>: 726.5013. Elemental Analysis, calcd. for C<sub>51</sub>H<sub>66</sub>O<sub>3</sub> C 84.25, H 9.15; found C 84.68, H 8.98%.
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