

Electron-transporting and photopolymerisable liquid crystals

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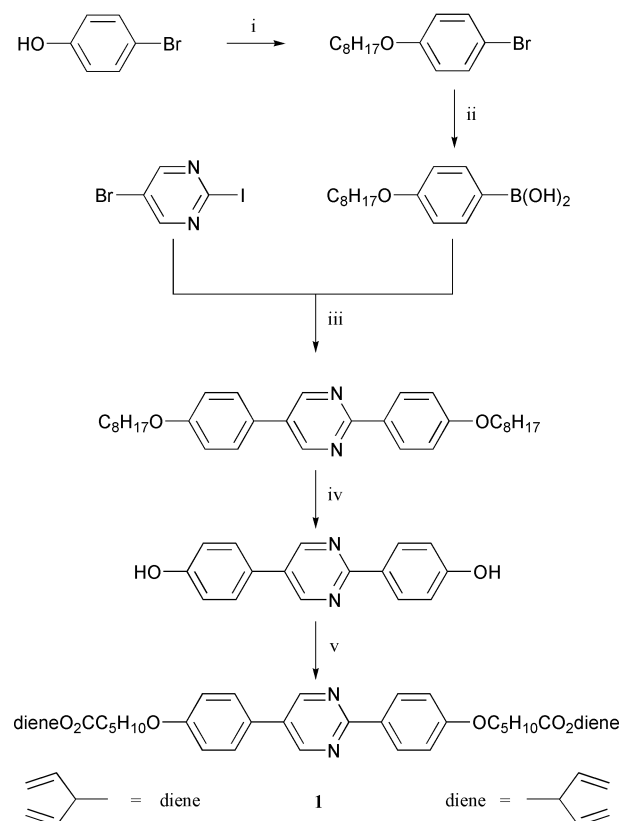
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The synthesis of a novel, photopolymerisable liquid crystal (reactive mesogen) with a high mobility of electrons in the smectic C phase at room temperature is reported for the first time as a potential charge transport layer for OLEDs.

Organic materials with large polyaromatic cores^{1–3} exhibit large charge mobility in the columnar liquid crystalline (LC) state with charge carrier mobilities ($10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} > \mu > 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) intermediate between those observed for organic single crystals ($\mu \approx 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and those of amorphous conjugated polymers^{4,5} used in Organic Light-Emitting Diodes (OLEDs).⁴ Holes represent the majority charge carrier, rather than electrons, in most discotic liquid crystals due to their very limited electron affinity and low ionisation potential, although some electron deficient discotics have been reported.⁶ The processing of materials in columnar mesophases is problematic. There are also stability problems in regard to the fabrication of multilayer OLEDs where the hole transport layer supports the other layers. The charge carriers, even of photocurrent, in the nematic phase, were found to be primarily ions.^{7,8} However, the charge-carrier mobility in ordered lamellar smectic phases of low-molar-mass organic compounds with a rod-like molecular structure is surprisingly high ($10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} > \mu > 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), being comparable with that of LCs in columnar mesophases, much higher than that of the charge-transport materials currently used in commercial OLEDs and undoubtedly electronic in nature.^{9,10} However, the smectic LCs investigated so far are crystals at room temperature with high melting points. Therefore, they are clearly not suitable for use in OLEDs, since the presence of crystal grain boundaries results in charge trapping and, potentially, dielectric breakdown.

We now report the synthesis of a new class of photopolymerisable liquid crystals (reactive mesogens) designed to enable the study of charge transport through smectic phases at room temperature for the first time. They were also intended for use, after photochemical crosslinking, as stable electron transport layers in efficient multilayer OLEDs. The most favourable configuration of an OLED is a combination of at least three discrete layers for hole transport, electron transport and light emission. However, efficient electron transporting materials are rare due to the low electron affinity of most aromatic, *i.e.*, electron rich, organic compounds.⁵ The reaction pathway to the new electron transporting materials is short enough to be of commercial relevance involving just six steps altogether carried out in high overall yield, see Scheme 1. The alkylation of 4-bromophenol with octyl bromide in a Williamson ether synthesis yields 1-bromo-4-octyloxybenzene, which is converted under standard conditions to the corresponding boronic acid. This is then reacted with 5-bromo-2-iodopyrimidine in a Suzuki aryl–aryl cross-coupling reaction to yield 2,5-bis(4-octyloxyphenyl)pyrimidine. An octyloxy chain is used in order to render this diether sufficiently soluble in appropriate organic solvents so that the next step can be carried out. Dealkylation using boron tribromide yields the corresponding bis-phenol, which is alkylated with the product of commercially available ω -bromoalkanoic acids and penta-1,4-dien-3-ol, hexa-1,5-dien-3-ol and hepta-1,6-dien-4-ol to produce a variety of symmetrical bis-dienes with different

spacer lengths. The penta-1,4-dien-3-yl derivative **1**† shown in Scheme 1 melts just above room temperature (Cr-SmC = 25 °C) to form an enantiotropic smectic C phase with a high clearing point (SmC-I = 124 °C). The optical appearance between crossed polarisers of the mesophase exhibited by compound **1** contains the broken focal conic fan texture and the Schlieren texture (with four-point brushes and no two-point brushes) typical of a smectic C phase. The liquid crystal transition temperatures and enthalpies of transition were determined by a combination of optical microscopy and differential scanning calorimetry. The low melting point of compound **1** is attributable to the steric branching effect of the two terminal diene end-groups and the presence of the flexible aliphatic spacers between them and the molecular core. These aliphatic spacers also serve to dilute the van der Waals forces between the rigid aromatic cores. The advantageously low melting point enables the charge mobility in a smectic phase, in this case a smectic C phase, of a low-molar-mass calamitic liquid crystal to be determined at room temperature for the first time. Radiation from an argon ion laser at 300 nm with a total fluence of 2.5 J cm^{-2} was used, without a photoinitiator, to



Scheme 1 Reagents and conditions: i, $\text{C}_8\text{H}_{17}\text{Br}$, $\text{CH}_3\text{COC}_2\text{H}_5$, K_2CO_3 ; ii, a, BuLi , THF, b, $\text{B}(\text{OCH}_3)_3$, c HCl_{aq} ; iii, Na_2CO_3 , H_2O , $\text{Pd}(\text{Ph}_3)_4$, $\text{CH}_3\text{OC}_2\text{H}_4\text{OCH}_3$; iv, a, BBr_3 , CH_2Cl_2 , b, HCl_{aq} ; v, $\text{BrC}_5\text{H}_{10}\text{CO}_2\text{diene}$, $\text{CH}_3\text{COC}_2\text{H}_5$, K_2CO_3 ; diene = penta-1,4-dien-3-yl.

photopolymerise and crosslink the diene end-groups of compound **1** at 30 °C on a quartz substrate. The actual mechanism of radical formation is currently under investigation and an autocatalytic mechanism is suspected. The crosslinking of reactive mesogens results in the formation of an insoluble liquid crystalline polymer network as a thin solid film.^{11–16} We have previously demonstrated the efficacy of this approach using dienes as the polymerisable end-group for the fabrication of bilayer OLEDs without an electron transport layer.¹³ We have also shown recently that the polymerisation of reactive mesogens with the penta-1,4-dien-3-yl end-group in particular results in the formation of stable electroluminescent polymer networks with superior properties to those of the non-polymerised diene monomers.^{13,14} For example, it leads to an increase by up to a factor of two in the magnitude of the hole mobility of a fluorene based liquid crystal.¹⁵ This may be due to favourable conformational changes of the aromatic cores due to the formation of a rigid bicyclo[3.3.0]octane polymer backbone.¹⁶ The provision of an efficient photopolymerisable reactive mesogen with a high electron charge transport would be of use for multilayer OLEDs of all kinds, especially since it is suspected that the presence of reactive residues from initiators reduces the life-time of OLEDs.

The charge mobility through a thin ($\approx 2 \mu\text{m}$) layer of the reactive mesogen **1** was determined by photocurrent time-of-flight measurements with excitation from a pulsed nitrogen laser. The values for the electron mobility are plotted against temperature in Fig. 1. The magnitude of the mobility increases with temperature, indicating a hopping mechanism between molecules. The sudden order of magnitude decrease in the electron mobility at the transition from the smectic C phase to the isotropic liquid suggests that the order present in the smectic phase is indeed responsible for the high charge mobility values. The value for the electron mobility at 25 °C is reasonably high ($\mu_e = 1.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for an organic material. This is

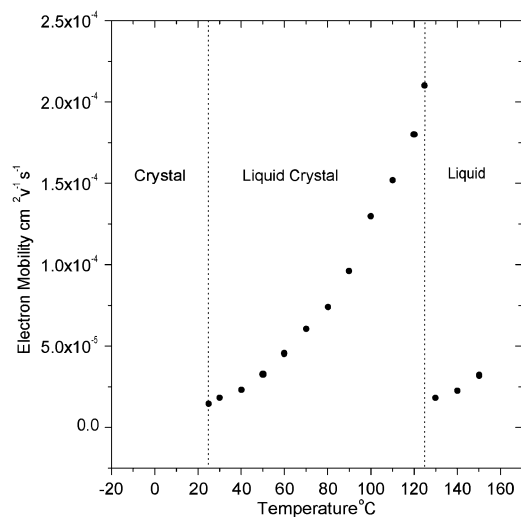


Fig. 1 Electron mobility vs. temperature for compound **1**.

probably due, at least in part, to the presence of the electronegative nitrogen atoms in the pyrimidine ring of compound **1**. The value for the hole mobility is comparable ($\mu_h = 1.8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 25 °C) to that found for electrons. The mobility of a crosslinked sample was not measured because photopolymerisation could not be achieved throughout a sample of length 2 μm , as a result of the small absorption length at 300 nm. However, by analogy with previous results, photopolymerisation is expected to enhance the transport properties. Optical microscopy also shows that crosslinking of a much thinner film of compound **1** maintains the order of the smectic phase below 25 °C.

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Notes and references

† All the compounds were thoroughly characterised with the help of spectral and analytical data. Selected data for **1**: $\nu_{\text{max}}/\text{cm}^{-1}$ 2948, 2874, 1740, 1611, 1521, 1437, 1255, 1168, 831; $\delta_{\text{H}}(400 \text{ MHz, CDCl}_3)$ 8.92 (s, 2H), 8.41–8.38 (d, 2H), 7.54–7.51 (d, 2H), 7.03–6.98 (dd, 4H), 5.88–5.81 (m, 4H), 5.33–5.22 (m, 8H), 4.06–4.00 (dt, 4H), 2.42–2.38 (t, 4H), 1.88–1.50 (m, 12H); APCI-MS (m/z) 623; Calculated: C 73.05, H 7.10, N 4.48; Found: C 72.84, H 7.29, N 4.22%.

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