An alignable fluorene thienothiophene copolymer with deep-blue electroluminescent emission at 410 nm†

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An alignable, liquid-crystalline fluorene fused-ring thienothiophene copolymer has been synthesized with electroluminescence peaking at 410 nm for deep blue, polarised emission in polymer light-emitting diodes, light-emitting transistors and photonic structures.

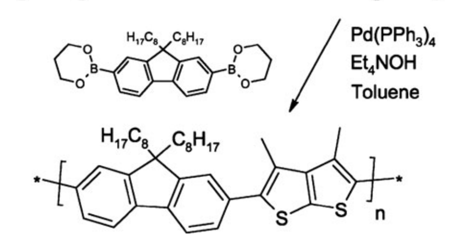
Poly(9,9-dioctylfluorene) (F8) and its copolymers have proved to be highly suitable for use in polymer light-emitting diodes (LEDs), including blue-emitting devices.[1–3] Due to their liquid-crystalline properties, a high degree of chain alignment is possible, resulting in polarised emission.[4–6] Combined with their high photoluminescent efficiencies, this makes them very suitable for optical amplification and photonic gain structures.[6–8]

Poly(3-hexylthiophene) has, instead, proved to be highly suitable for use in polymer field-effect transistors (FETs) due to its ability to form highly-ordered and -orientated crystallites at the semiconductor–insulator interface.[9,10] Properties of these two polymers have been combined in poly(9,9-dioctylfluorene-co-bithiophene) (F8T2).[1,4,11–13] F8T2 can be used in both polymer LEDs and FETs, allowing the fabrication of chain-aligned optical films and mobility-enhanced transistors.[4,11,12]

Recently, thiophene co-polymers containing thienothiophene have demonstrated very high mobilities in FETs.[14,15] Polymers containing the *syn* (thieno[2,3-*b*]thiophene) or *ant* (thieno[3,2-*b*]thiophene) isomers have achieved values of 0.15 and 0.8 cm^2 V^{-1} s^{-1}, respectively.[14,15] An interesting feature of these isomers is that the *syn* derivative contains a central double bond that is cross-conjugated, whereas the *ant* isomer does not. The inclusion of the cross-conjugated *syn* isomer into the polymer backbone was shown to significantly limit the delocalization of the polymer backbone in comparison to the fully conjugated *ant* isomer, resulting in an increase in ionization potential of approximately 0.2 eV.[14–16] A fluorene copolymer containing the *ant* thieno[3,2-*b*]thiophene derivative has been synthesized. This has a blue-green emission peaking at 478 nm and liquid crystalline properties.[13] We were interested to see whether inclusion of the cross-conjugated *syn* isomer would result in a blue-emitting polymer. Here, we report the synthesis and properties of a fluorene thienothiophene copolymer with this *syn* arrangement.

The synthesis of poly(9,9-dioctylfluorene-co-3,4-dimethylthieno[2,3-*b*]thiophene) (F8TT) is shown in Scheme 1. 3,4-Dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylic acid was readily prepared by the reaction of carbon disulfide with pentane-2,4-dione in the presence of base and ethyl bromoacetate, followed by hydrolysis of the resulting ester.[17] Subsequent bromodecarboxylation with two equivalents of *N*-bromosuccinimide afforded 2,5-dibromo-3,4-dimethylthieno[2,3-*b*]thiophene in good yield. Polymerisation was performed under Suzuki cross-coupling conditions with 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester as the co-monomer. The use of tetraethylammonium hydroxide as both a base and phase transfer catalyst afforded polymers with the highest degree of polymerisation.[18] The crude polymer was purified by a combination of Soxhlet extraction and precipitation to afford a pale yellow powder. The weight average molecular weight (M_w), measured using GPC against polystyrene standards, was 90 000 g mol^{-1} with a polydispersity of 2.6.

Fig. 1 shows the photoluminescent (PL) emission from spin-coated films of F8TT. The 0–0 emission peak is at 417 nm, with vibrational sidebands at about 435 and 470 nm. This is



Scheme 1 Synthetic route to poly(9,9-dioctylfluorene-co-3,4-dimethylthieno[2,3-*b*]thiophene).

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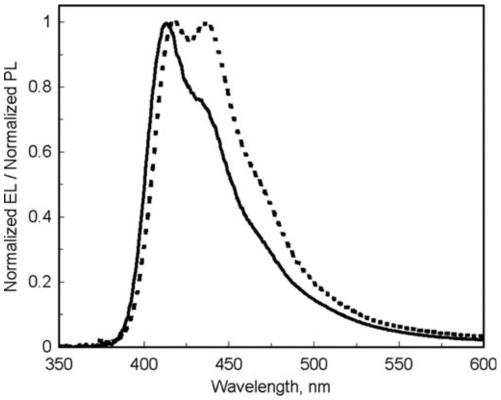

Fig. 1 Photoluminescent (PL, dashed line) and electroluminescent (EL, solid line) emission spectra of F8TT.

significantly blue-shifted compared to the fluorene thienothiophene copolymer with the *ant* linkage, which has a 0–0 emission peak at 478 nm.[13] This is due to the cross-conjugated central double bond of the *syn* isomer limiting delocalization over the conjugated system. Indeed, the energy gap of F8TT is very similar to the F8 fluorene homopolymer, which has an almost identical deep-blue emission, with the 0–0 transition at 414 nm.[1,5,6,13]

To investigate the effect of the reduced electron delocalization further, thin films of F8TT were cooled from 300 to 20K in a cryostat. Upon cooling, the vibrational sidebands in the PL spectrum became better resolved. The intensity of the 0–0 peak became stronger compared to the 0–1 transition, indicating less change in the position of the conjugated system between the excited and ground states at lower temperatures. However, there is no change in the π to π^* transition energy upon cooling. The delocalisation of the conjugated system is therefore not affected by any changes in backbone planarity upon cooling. Furthermore, this observation suggests that changes in the interchain distance due to thermal contraction have little effect on the exciton energy.

To test the electro-optical properties of F8TT, we fabricated polymer LEDs consisting of an indium tin oxide anode on a glass substrate coated with PEDOT:PSS, a spin-coated layer of F8TT, followed by a thermally-evaporated Ba cathode with an Al capping layer.

Fig. 1 shows the EL emission from F8TT LEDs, which peaks at 410 nm in the deep-blue region. Compared to the bulk PL emission, the EL spectrum is slightly blue-shifted and the 0–0 transition intensity is increased relative to that of the 0–1. This is due to the presence of a microcavity structure that is formed by the highly reflective metal cathode. Depending on the distance between the recombination zone and the cathode, the outcoupling of shorter wavelengths is favoured compared to longer wavelengths.[19] The CIE (Commission International de L'Eclairage) 1931 colour coordinates of the EL emission are 0.163 and 0.086. This is close to the saturated blue emission needed for a full colour display (PAL blue: 0.15 and 0.06).

The current density–voltage–luminosity characteristics of F8TT LEDs were recorded for polymer film thicknesses between 30 and 160 nm. The thinnest devices reached a current density of 10^3 mA cm^{-2} at a bias of about 8 V. The onset of visible emission occurred at a bias of about 4 V, fairly typical for blue-emitting polymers. The variation of the luminance with drive bias was also found to be very similar to that of F8 LEDs up to 8 V.

Differential scanning calorimetry (DSC) upon heating showed an exothermic peak at 140 °C and an endothermic peak at 280 °C. The first peak can be associated with crystallization, which must occur once the glass transition temperature is exceeded. The second peak can be associated with the melting of these crystals. Optical hot-stage microscopy at 290 °C indicated that F8TT was in a nematic liquid crystal (LC) phase. Therefore, melting into the true isotropic phase must occur at a higher temperature. Upon cooling to 180 °C, the F8TT showed a high birefringence and a different texture, indicative of a smectic LC phase. F8TT therefore contains crystalline, smectic, nematic and isotropic phases.

DSC of the *ant* variant of F8TT shows an exothermic peak at 161 °C and an endothermic peak at 243 °C.[13] One might expect that the variation in chemical structure effects both the backbone flexibility and its ability to pack in the more ordered phases, which will influence the entropy and enthalpy changes at the transitions, and therefore the transition temperatures. However, the variation between the *ant* and *syn* variants of F8TT are relatively minor compared to the difference with the much more flexible F8 homopolymer, where these transitions lie at 93 and 173 °C, respectively.[20]

F8TT films were spin-coated onto a rubbed polyimide LC alignment layer. This gave an initial dichroic ratio of 1.2, as measured by the optical absorption parallel and perpendicular to the rubbed alignment direction. Upon heating, this ratio remains constant until 120 °C, when the anisotropy in the absorption begins to increase. This temperature corresponds to the start of the first exothermic DSC peak. As the F8TT film is heated to 200 °C, the anisotropy continuously increases, providing strong supporting evidence that a smectic LC phase occurs at these temperatures.

The F8TT films were heated to 290° and then cooled slowly at 1 °C min^{-1} to room temperature. The absorption and PL spectra perpendicular and parallel to the alignment layer

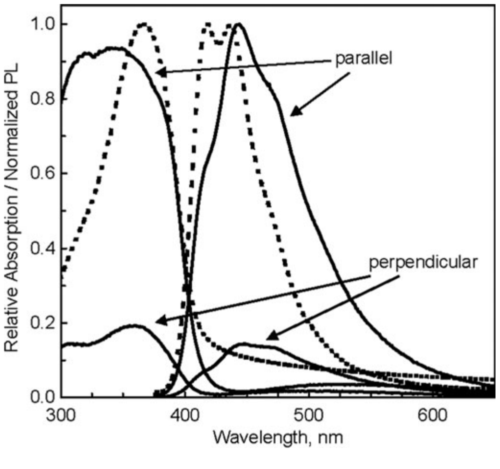

Fig. 2 Absorption and PL spectra of aligned (solid lines) and non-aligned (dashed lines) films of F8TT.

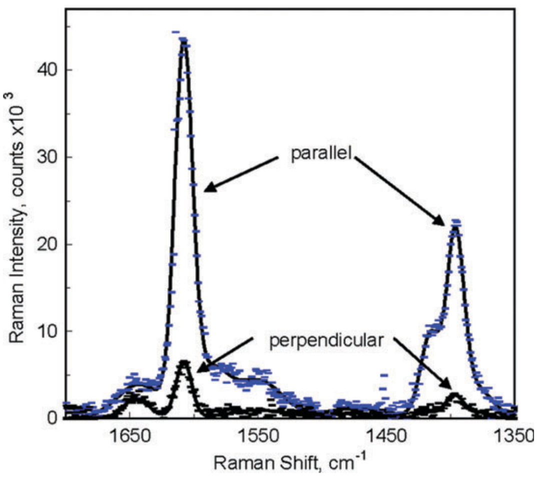

Fig. 3 Raman depolarisation spectra of F8TT for both incident and detected light being, respectively, parallel- and perpendicular-polarized to the alignment direction of the F8TT film.

rubbing direction are shown in Fig. 2. The achieved dichroic ratio reached values of about 6. This should be compared to the value for aligned F8T2 films of about 8.[4] Also shown in Fig. 2 are the absorption and PL spectra of a non-aligned film. Compared to the PL spectra of the non-aligned film, there is a redistribution of intensity between the vibrational sidebands. This indicates that the overlap between the excited and ground states has decreased, indicating a change in chain conformation. Such a change would normally be associated with a decrease in the delocalisation of the conjugated system, and a blue-shift in the absorption and PL spectra. However, the spectra of the aligned films are slightly red-shifted. The aligned films will be more crystalline and will have better interchain packing. This will increase the gas-to-crystal shift (the solvation effect) and thus decrease the energy of the exciton. This appears to overcompensate for any decrease in conjugation length due to changes in conformation.

To investigate this further, Raman depolarisation measurements were conducted on the aligned films. Using this technique, one can measure to what extent the polymer chains are aligned on the substrate, *i.e.* the average orientation of the polymer backbone. By measuring the intensity of specific Raman bands with laser excitation polarized perpendicular and parallel to the rubbing direction, the Raman measurement also allowed estimation of the tilt, β, between the transition dipole moment and the polymer backbone.[12] The results for F8TT are shown in Fig. 3. The vibrational peak at 1396 cm^{-1} is attributed to a stretching mode of the thienothiophene group, whereas the peak at 1608 cm^{-1} can be identified as the in-plane stretching mode of the fluorene unit.[12,21] The latter mode, which is known to be highly axial, features an intensity ratio for perpendicular and parallel excitation of 8.7. By combining this result with the dichroic absorption ratio, it is possible to estimate the tilt $\beta \approx 16^\circ$. This compares to the value for F8 of 21°, indicating that F8TT-based devices can, in principle, reach higher degrees of deep-blue polarized emission than F8-based LEDs or photonic structures.[12]

In summary, we have synthesized a new fluorene thienothiophene copolymer. The *syn* arrangement of the thienothiophene units disrupt conjugation, leading to deep-blue photoluminescent and electroluminescent emission. It also has liquid crystal properties and can be prepared in highly-aligned films. The fluorene thienothiophene backbone should also lead to a high mobility. This polymer should therefore be suitable for use in light-emitting diodes, light-emitting transistors and photonic structures that require deep-blue polarised emission and anisotropic charge transport. This backbone structure should also be the basis of a new range of blue-emitting polymers.

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