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FOCUS REVIEW

A new class of nanostructured supramolecular organic semiconductors based on intertwined multi-lamellar co-assemblies in π-conjugated liquid-crystalline side-chain polymers

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The control of both the mesoscopic and nanoscale organizations within thin semiconducting films is a key issue for the improvement of the charge transport properties and the achievement of high charge-carrier mobilities. In this review, we summarized our previous work devoted to the design and synthesis of a new type of side-chain liquid crystal π-conjugated polymeric system associating regioregular poly(3-alkylthiophene) backbones with laterally pending π-conjugated mesogenic groups. Depending on the nature of the mesogenic side groups, this specific polymer design permits the production of lamellocolumnar or lamellolamellar mesophases, resulting in an intertwined co-assembly either of lamellae and columns or of two different types of lamellae. These optimized polymeric architectures based on two chemically different moieties constitute an interesting basis for the design of novel self-organized complex semiconducting materials. By associating with judicious side groups such as n-type entities, we demonstrated that this simple and versatile strategy can produce distinct conductive channels for both types of charge carrier and can lead to a new class of supramolecular ambipolar materials that is easily processable and potentially suitable for electronic and optoelectronic applications.
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INTRODUCTION

Control of the supramolecular self-assemblies and the nanoscale morphologies of π-conjugated macromolecular architectures with long-range order and the establishment of reliable structure-property relationships are major and fundamental issues in the field of organic electronics.[1–3] In particular, better control of both the mesoscopic and nanoscale organizations within thin organic semiconducting films is crucial to improving their charge-carrier mobilities.

Currently, most efforts essentially focus on two different approaches, either based on the elaboration of conjugated block copolymers, (with different block functionalities)[4,5] or alternatively on liquid-crystalline π-conjugated polymers bearing conjugated mesogenic side groups.[6–23] The first class of materials takes advantage of the block copolymer's ability for phase separation into well-ordered morphologies (spherical, cylindrical or lamellar) to form separate conduction pathways for charge carriers, thanks to the antagonistic chemical nature of each block at the origin of the nanosegregation.[24–27] However, the optimal charge transport properties also require the formation of long-range correlated structures with an orientational control of regular pathway alternation. This last objective is difficult to achieve by tuning the block structures and lengths, but can be more easily accomplished with a liquid-crystalline polymeric architecture. Liquid-crystalline materials are indeed outstanding examples of soft self-assemblies that combine order and fluidity within components self-organizing into a wide diversity of long-range ordered, periodic structures.[28–35] In addition, liquid crystal assemblies can form thin films that are intrinsically self-healing because their structural defects are automatically corrected during the process of self-assembly and their morphology can be controlled at the molecular level.

In this context, side-chain liquid-crystalline π-conjugated polymers consisting of π-conjugated backbones bearing side-on semiconducting mesogenic groups can be considered a promising approach to control

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the phase separation into well-ordered morphologies of different functional components with periodicities ranging in the nanometer scale. Up to now, few examples of such macromolecular architectures have been considered for the exploitation of their charge transport properties and, to the best of our knowledge, no charge-carrier mobility has been evidenced.[36–40] In addition, associated with judicious choices of the electro-active components (donor and acceptor), these well-ordered morphologies offer the possibility of forming separate conduction pathways for charge carriers by playing on their antagonistic chemical nature.

In this manuscript, we review previous work devoted to the design and synthesis of a new type of side-chain liquid crystal π-conjugated polymer consisting of intricate polymeric systems associating regioregular poly(3-alkylthiophene) backbones with laterally pending π-conjugated mesogenic groups. Several series of polymeric architectures have been prepared using different polymer backbone structures and various side groups to evaluate the impact of the macromolecular structure on the geometrical packing parameters and molecular ordering. This comprehensive study provides important insight into the relationships between the polymeric architecture, nano- and macroscale organization and charge transport properties in such self-organized multi-lamellar macromolecular systems.

DISCOTIC SIDE-CHAIN LIQUID CRYSTAL POLYMERS

Triphenylene side-chain homopolymers

The first series of side-chain liquid crystal polymers designed in this study consisted of homopolymers based on a regioregular poly(3-alkylthiophene) backbone post-functionalized with side-on discotic triphenylene moieties.[41,42] In this series, we first examined the influence of pertinent structural parameters such as the length of the aliphatic spacer between the polymeric backbone and the discotic side groups on the molecular ordering. Figure 1a displays the chemical structures of the triphenylene side-chain PT_mT homopolymers and the general synthetic procedure used to prepare these materials. The synthetic approach consists of the substitution of precursory regioregular PT_m polythiophenes prepared according to the McCullough methodology[43–45] (Grignard metathesis GRIM) and bearing bromide end-terminated lateral alkyl chains of various lengths. As expected from the GRIM method, the precursory PT_m polymers presented well-defined architectures with narrow polydispersity indices (PDI = 1.2–1.4) and highly controlled molecular weights ($DP_n = 45$). They were then post-functionalized by triphenylene derivative T under standard Williamson ether reaction conditions, leading to nearly quantitative substitution.

The thermal and self-organization behaviors of this series of triphenylene side-chain homopolymers were investigated by several complementary techniques such as polarized-light optical microscopy (POM), differential scanning calorimetry (DSC), temperature-dependent small-angle X-ray scattering (SAXS), atomic force microscopy (AFM), transmission electron microscopy (TEM) in bright field (BF), high-resolution (HR) and electron diffraction (ED) modes, and grazing incidence SAXS (GISAXS).[41,42]

These measurements provided a deep insight into the supramolecular organization and permitted the complete elucidation of the

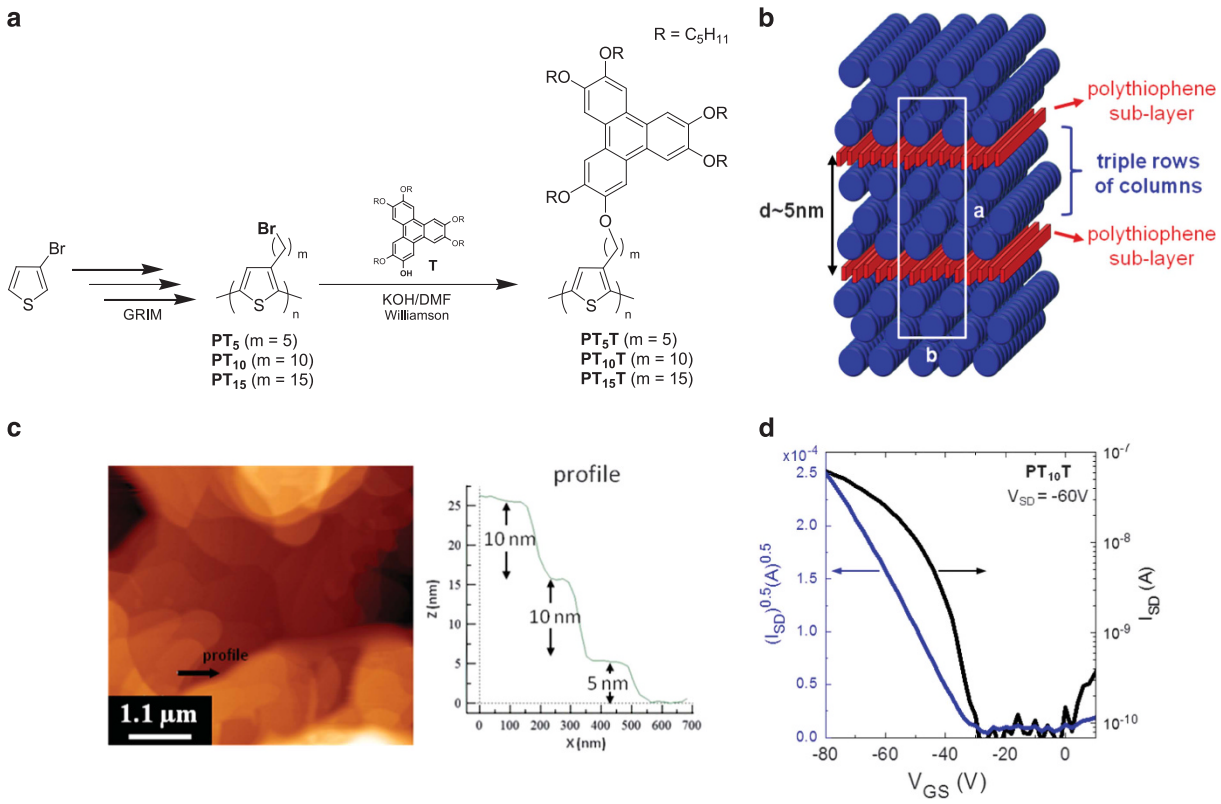

Figure 1 (**a**) General synthetic route for the preparation of triphenylene side-chain PT_mT homopolymers with different lengths of the aliphatic spacer. (**b**) Schematic view of the lamello-columnar structure of $PT_{10}T$ consisting of alternating triple rows of triphenylene columns and polythiophene sub-layers, arranged in a rectangular *p2gg* lattice involving twelve columns and two sub-layers (white frame). (**c**) Topographic AFM image of PT_mT nanostructured thin film on silanized silicon wafer and terrace step profile determined from topography. (**d**) Typical transfer characteristic of a top-contact bottom-gate OFET based on PT_mT polymers ($PT_{10}T$).

bulk polymer structures, showing that most of these polymers self-organize into mesophases possessing intertwined lamellocolumnar morphologies resulting from the co-existence of lath-like backbones arranged face-to-face into layers, columns of stacked triphenylene rings aligned into rows, and molten aliphatic chains forming a continuum around the columns and between the layers and rows. The lamellae naturally emerge from the alternation of layers, continuum and rows, but the effective appearance of a mesophase, the type of structure, and the range are largely determined by the length of the aliphatic spacer connecting the backbones to the rings. Accordingly, with short pentyl spacers, the homopolymers self-organize without any positional long-range order, as the backbones are prevented from forming separate layers and perturbing the regular spacing of the columns. The lamellar long-range order is logically maintained with long pentadecyl spacers but only within a shrunken mesomorphous range due to the irregular arrangement of triphenylene columns between successive backbone layers. With intermediate decyl spacers, the mesophase exists over a broad range and exhibits bidimensional long-range order, since the formation of the backbone layers creates regular parallel rows of columns occupying defined positions in a large-size lattice. A combination of reciprocal and direct space techniques was necessary to demonstrate the crystallographic arrangement schematically represented in Figure 1b, where the polymer backbones and columns are both directed perpendicularly to the lattice plane and form monolayers and triple rows, respectively.[42] The central row originated from both adjacent backbone layers and was shown to adapt the lateral extension of the lamellae to the space requirement of the segments. In relation to the constraint from the spacer, the formation of the central row also implies a modulation of the positions of the columns, which leads to a rectangular p2gg lattice including 2 lamellae of ~5-nm thickness and 12 columns.

Nanostructured thin films with a thickness of a few tenths of a nanometer were fabricated by several techniques such as epitaxial crystallization,[46] spin-coating and drop-casting,[42] and their morphologies were then studied by TEM, GISAXS and AFM. The results demonstrated the possibility of orienting the anisotropic lamellocolumnar structure depending on the method of film preparation and the nature of the substrate. For example, AFM investigations showed a proper nanostructured film with terraces on the silanized surfaces, indicative of lamellae oriented parallel to the substrate (Figure 1c). Consistently, the heights of the terraces determined from topography images were multiples of 5 nm and coincide with the lamellar periodicity in the bulk structure.

Table 1 Field-effect transistor parameters of $PT_{10}T$, P2TT, PTO and PTPe

Polymers	*Change carrier type*	*Mobility ($cm^2\ V^{-1}\ s^{-1}$)*	*Threshold Voltage (V)*	*$I_{ON}/_{OFF}$ Ratio*
$PT_{10}T$	Hole	1.4×10^{-5}	−24	7.3×10^{3}
	Electron	—	—	—
P2TT	Hole	1.6×10^{-3}	−1	5.3×10^{2}
	Electron	—	—	—
PTO	Hole	1.2×10^{-3}	−28	1×10^{4}
	Electron	—	—	—
PTPe	Hole	3.0×10^{-5}	−49	1×10^{2}
	Electron	3.3×10^{-6}	45	5.6×10^{3}

The charge transport properties of the oriented triphenylene side-chain homopolymer thin films were examined in OFETs with a bottom-gate top-contact configuration.[47] The devices used a 300 nm thick SiO_2 gate dielectric layer treated with octadecyltrichlorosilane, and the gold source drain electrodes were vapor-deposited on top of the semiconducting polymer layers through a shadow mask. A typical transfer characteristic of PT_mT is displayed in Figure 1d. These polymers exhibited only p-type conduction, and the mobilities in the saturation regime were found to be $\sim1.4\times10^{-5}$ $cm^2\,V^{-1}\,s^{-1}$ ($PT_{10}T$; see Table 1), which is around two orders of magnitude lower than the value usually found for comparable short poly (3-hexylthiophene).[48] This low value is obviously related to the deleterious effect of the triphenylene insertion on the molecular organization within the polymer layers. As a matter of fact, the bulkiness of the triphenylene moieties and their connection to the polymer backbone through relatively short linkers introduces important geometric constraints limiting the polymer stacking. This leads to a lack of π–π interactions between polythiophene chains, which certainly explains the low conduction performance.

Triphenylene side-chain alternating copolymers

The second series of side-chain liquid crystal polymers consisted of alternating copolymers based on a regioregular alternating copolythiophene backbone post-functionalized with side-on discotic triphenylene moieties.[42] In this series, consisting of alternating copolymers with thiophene/triphenylene ratios varying between 2:1 and 4:1, we were interested in evaluating the influence of the controlled dilution of the discotic side group mesogen, that is to say, the degree of polymer lateral substitution, on the supramolecular organization. Figure 2a displays the chemical structures of the triphenylene side-chain alternating PkTT copolymers together with their general synthetic procedure. The synthetic approach first consisted of preparing the dibromo bi-, ter- or quaterthiophene key kT monomers, which were then polymerized by the GRIM method. That led to the precursory regioregular alternating PkT co-polythiophenes with controlled architectures (PDI = 1.4–1.6 and DP_n = 36–45), possessing one bromide end-terminated lateral decyl chain regularly alternating with one, two or three 3-octylthiophene units, respectively. The final regioregular alternating PkTT co-polythiophenes were obtained by grafting the triphenylene derivative T onto the corresponding polythiophene backbones using an etherification reaction, as previously described.

The thermal and self-organization properties of this series of triphenylene side-chain alternating copolymers PkTT with thiophene/triphenylene ratios varying between 2:1 to 4:1 were investigated using POM, DSC, temperature-dependent SAXS and GISAXS.[42] The results showed first that the alternating copolymer with a ratio of 2:1 (P2TT) presents the same lamellocolumnar structure as the homopolymers. More particularly, the alternation of the triple rows of columns and the backbone sub-layers was maintained with very similar geometrical parameters. The main differences in the SAXS patterns with respect to the homopolymers were the appearance, next to the triphenylene core π-π stacking scattering (h_T) at 3.56 Å, of an additional scattering (h_{PT}) at 3.81 Å, attributed to the stacking of polythiophenes, and in the extension of the visible lamellar order series up to the eighth order (Figure 2b). These results demonstrated a more regular stacking of the backbones, related to an improved segregation in sub-layers, sharper interfaces, and a more cohesive molecular packing (Figure 2c). Concerning the other copolymers, the increase of the ratio to 3:1 and 4:1 led to the complete suppression of the mesomorphic properties. Indeed,

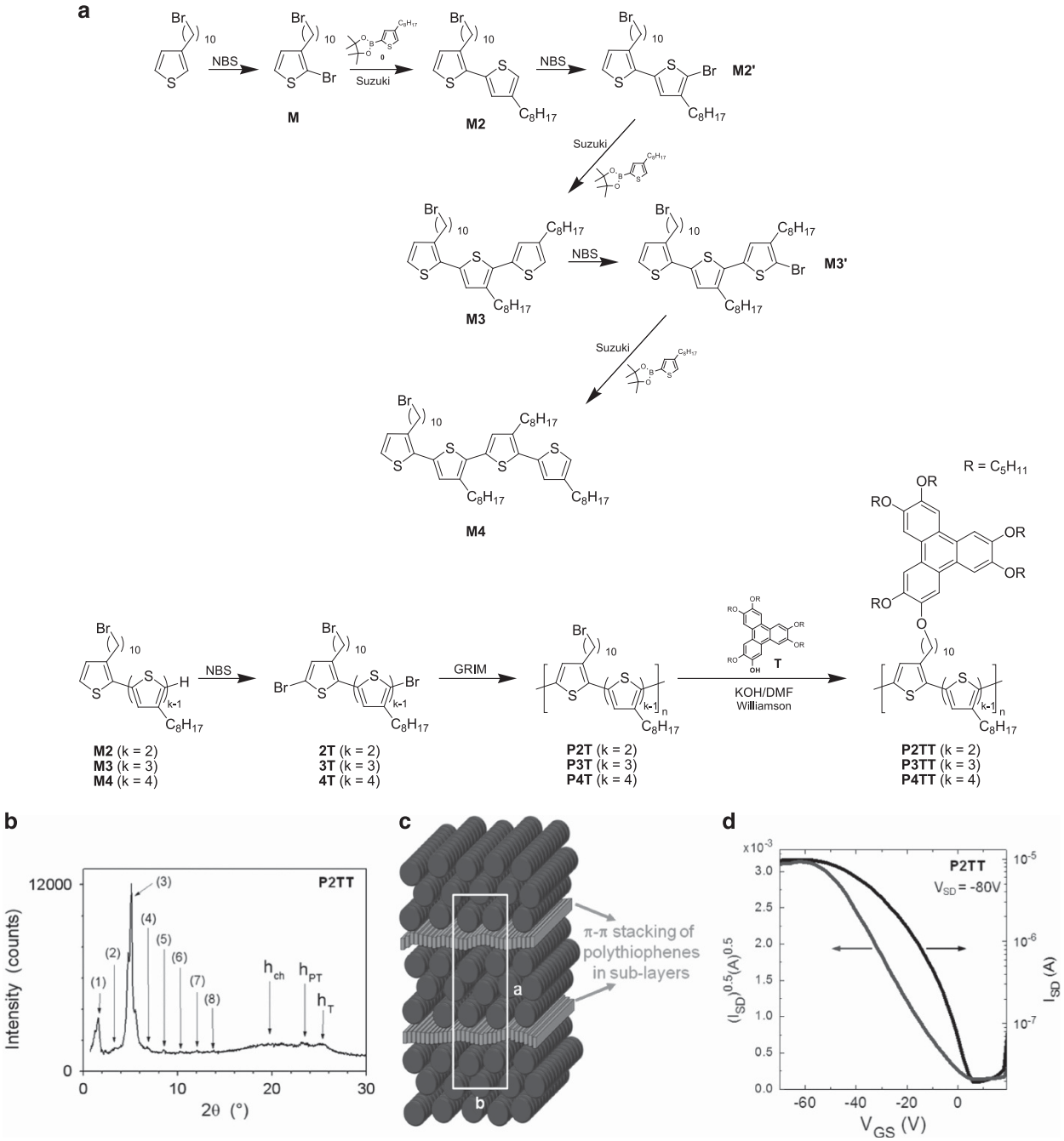

Figure 2 (**a**) General synthetic route for the preparation of triphenylene side-chain alternating copolymers PkTT with different thiophene/triphenylene ratios. (**b**) SAXS pattern of alternating copolymer P2TT at 50 °C upon cooling from the isotropic state.[42] (**c**) Schematic view of the lamellocolumnar structure of copolymer P2TT showing a rectangular *p2gg* lattice similar to that of $PT_{10}T$, but with an improved packing of the backbones due to the intercalation of the thiophene repeat units devoid of pending mesogens. (**d**) Typical transfer characteristic of a top-contact bottom-gate OFET based on P2TT. SAXS, small-angle X-ray scattering. A full color version of this figure is available online at *Polymer Journal* online.

P3TT and P4TT copolymers did not exhibit any lamellocolumnar mesophases and were found to be essentially amorphous at all temperatures, exclusively exhibiting a glass transition close to room temperature.

As described above, a more regular stacking of the polythiophene chains was evidenced in P2TT, which should have a clear influence on the conduction properties. With this in mind, we investigated the charge transport properties of oriented P2TT thin films in OFETs with a bottom-gate top-contact configuration.[47] The devices were prepared following the same procedures as previously described for the triphenylene side-chain PT_mT homopolymers. The transfer characteristic of a representative P2TT transistor is given in Figure 2d. The alternating copolymer exhibited only p-type conduction. The field-effect mobility in the saturation regime is approximately 1.6×10^{-3} cm^2 V^{-1} s^{-1} (Table 1), which is two orders of magnitude higher than that measured in the $PT_{10}T$ homopolymer and is consistent with the values typically reported in the literature for comparable short regioregular P3HT.[48]

This improvement in the charge-carrier mobility can be attributed to the different thiophene/triphenylene ratios between P2TT and $PT_{10}T$. As the lamello-columnar structures of the polymers were nearly identical, the density of the thiophene backbones was consequently doubled in the layers of P2TT. This feature leads to a better packing of the polythiophene chains with improved π-π interactions, resulting in a significant enhancement of the charge-carrier mobility. The interpretation of the above results assumes that the hole transport occurs exclusively within the polythiophene sublayers. This is fully supported by the fact that the two-dimensional charge transport taking place in the polythiophene sublayers is always more efficient than the one-dimensional charge transport taking place in the columnar organization of the triphenylene units, at least as long as the orientation of the columns in the plane of the film cannot be well controlled.

In that regard, liquid-crystalline polymers functionalized with calamitic mesogens,[33,49,50] forming multi-lamellar structures by self-assembly, might be more suitable for high-performance devices since the charges could in this case migrate efficiently in the two directions defined by each sublayer.

CALAMITIC SIDE-CHAIN LIQUID CRYSTAL POLYMERS

The next series of side-chain liquid crystal polymers was based on a regioregular poly(3-alkylthiophene) backbone and a side-on calamitic π-conjugated moiety.[51] For this purpose, we focused on oxadiazole derivatives as calamitic side groups, which are well known to give typical 'rod-like' mesogens exhibiting nematic or smectic mesophases.[52] The main objective of this work was to study the influence of the discotic side group substitution with calamitic ones on the molecular ordering and the supramolecular organization of the polymers. In addition, the 1,3,4-oxadiazole heterocycle containing oxygen and nitrogen atoms, is generally electron-deficient and exhibits n-type conduction.[53,54] In this context, the side-chain polymer based on a polythiophene backbone and side-on calamitic oxadiazole derivatives could present both mesogenic and ambipolar properties.

Figure 3a displays the chemical structures of the calamitic side-chain liquid crystal polymer PTO and its general synthetic procedure. The polymer was prepared according to the procedure previously described for discotic side-chain polymers. More precisely, the regioregular precursory poly(3-alkythiophene) PT_{10} with a narrow polydispersity index (PDI = 1.2) and highly controlled molecular weight ($DP_n = 45$) was post-functionalized by oxadiazole derivatives 'O' bearing a hydroxy function under standard Williamson ether reaction conditions, leading to a nearly quantitative substitution.[41,51]

The thermal and self-organization properties of the calamitic side-chain liquid crystal PTO polymer were investigated by POM, DSC, temperature-dependent SAXS and GISAXS.[51] The results showed that the PTO polymer presents a liquid-crystalline organization with a lamellolamellar structure consisting of the alternation of double sub-layers of oxadiazole moieties and polythiophene sub-layers (Figure 3c). The SAXS patterns of PTO indeed contain several sharp and equidistant Bragg reflections in the small-angle region and two scattering halos in the wide-angle region (Figure 3b). This set of sharp and intense small-angle reflections comes from a lamellolamellar structure, and their sharpness indicates that the lamellae are long-range correlated (with a lamellar periodicity

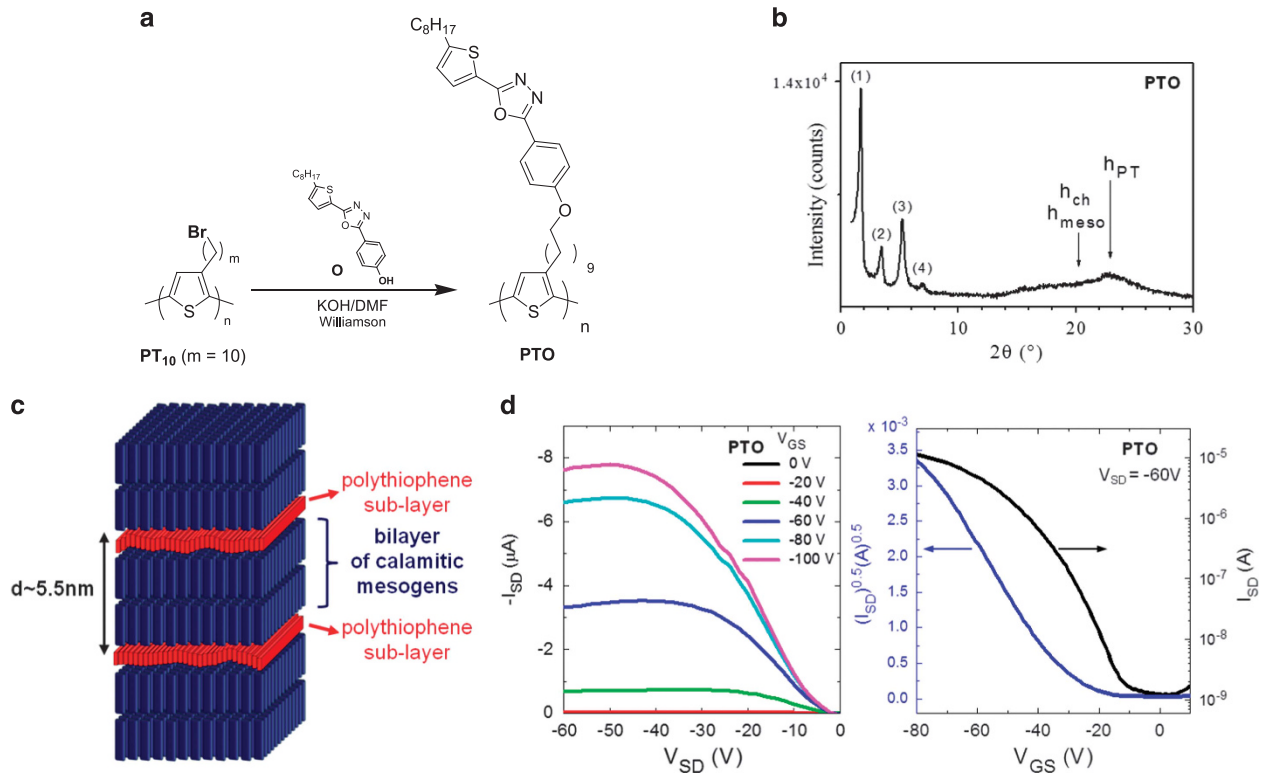

Figure 3 (**a**) Synthetic approach for the preparation of the calamitic side-chain liquid crystal polymer PTO based on oxadiazole derivative side groups. (**b**) SAXS pattern of the calamitic side-chain liquid crystal polymer PTO at 25 °C upon cooling from the isotropic state. (**c**) Schematic view of the lamellolamellar structure consisting of alternating double sub-layers of oxadiazole calamitic derivatives and polythiophene sub-layers. (**d**) Typical output and transfer characteristics of a top-contact bottom-gate OFET based on the polymer PTO. SAXS, small-angle X-ray scattering.

of ~5.5 nm). The broader scattering corresponds to the molten state of the aliphatic chains (h_{ch}) and to the liquid-like lateral arrangement of pendent groups (h_{meso}), which reflects the liquid nature of the mesophase, whereas the second signal (h_{PT}) at 3.81 Å is associated with the stacking of the polythiophene backbones (Figure 3b).

The charge transport properties of the oriented PTO thin films were examined in OFETs with a bottom-gate top-contact configuration. These devices were prepared following the same procedures as those previously described for triphenylene side-chain PT_mT homopolymers. The typical output and transfer characteristics of a PTO transistor are given in Figure 3d. The oxadiazole side-chain polymer PTO exhibited only p-type conduction, and the charge-carrier mobility in the saturation regime was found to be $\sim 1.2 \times 10^{-3}$ cm^2 V^{-1} s^{-1} (Table 1). This value is similar to that measured in the alternating P2TT copolymer and is also consistent with those typically reported in the literature in comparable to short regioregular P3HT.[48] This can be explained by the good packing of the polythiophene chains in PTO films, as evidenced by the presence of the scattering halo (h_{PT}) in the SAXS pattern (Figure 3b).

Considering the bilayer organization of the calamitic oxadiazole moieties that is more favorable for two-dimensional charge transport, on the hand, and the potential electron-transport properties of this derivative, on the other hand, we then carefully checked the n-type conduction of the PTO films in the OFET configuration. Unfortunately, no electron transport could be detected in the devices. This could be due to the large difference between the work functions of the gold source and drain electrodes ($W_f \sim -5.1$ eV) and the lowest unoccupied molecular orbital energy level of the oxadiazole derivative (~ -3.2 eV by cyclic voltammetry[51]), which would strongly hinder electron injection into the n-type organic moieties (Figure 4a). However, we cannot exclude at this stage the possibility that the molecular packing of the oxadiazole moieties in its sub-layers is not favorable enough to enable the observation of electron conduction during the device operation.

DONOR–ACCEPTOR SIDE-CHAIN LIQUID CRYSTAL POLYMERS

Taking into account the promising results described above, we recently designed and synthesized new liquid-crystalline polythiophenes functionalized with more appropriate electron conducting units (acceptor) such as perylene diimide moieties.[55] In addition to their mesomorphic properties,[56–58] perylene diimide derivatives are indeed archetypal electron-deficient units exhibiting electron-transport properties (n-type) with a lowest unoccupied molecular orbital energy level of ~ −4.1 eV (Figure 4a).[56,59] Combined with the donor properties of the polythiophene backbones, the goal of this work was to demonstrate the possibility of elaborating novel multi-lamellar donor–acceptor complex semiconducting polymeric materials producing distinct conductive channels for hole and electron

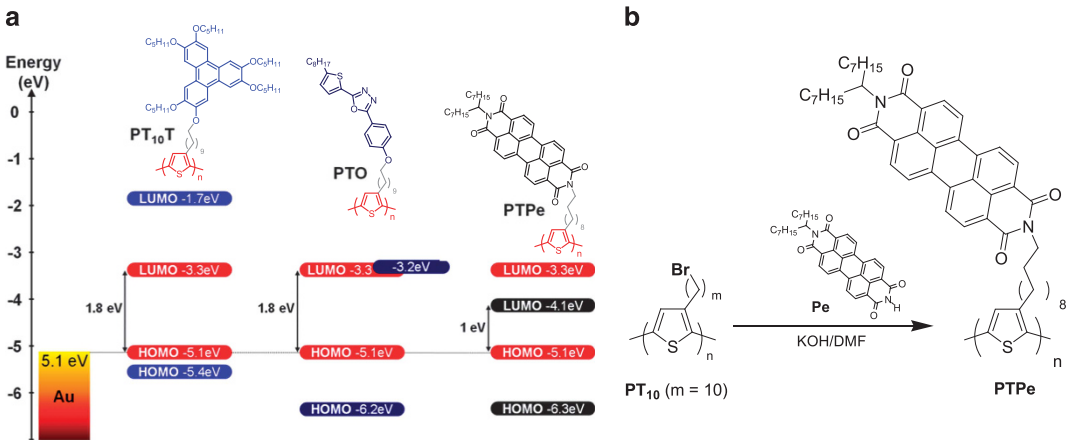

Figure 4 (**a**) Comparison of HOMO/LUMO energy levels of PT10T, PTO and PTPe with gold (Au) work function. (**b**) Synthetic approach for the preparation of the donor–acceptor side-chain liquid crystal PTPe polymer based on perylene derivative side groups. LUMO, lowest unoccupied molecular orbital.

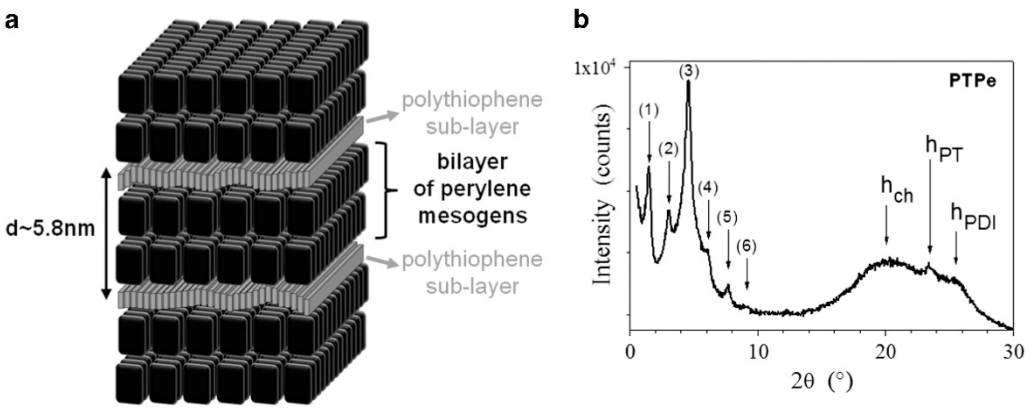

Figure 5 (**a**) Schematic view of the lamellolamellar structure consisting of alternating double sub-layers of perylene moieties and polythiophene sub-layers. (**b**) SAXS pattern of the perylene side-chain liquid crystal PTPe polymer at 25 °C (after annealing at 100 °C). SAXS, small-angle X-ray scattering. A full color version of this figure is available online at *Polymer Journal* online.

transport, leading to a new class of well-balanced ambipolar self-organized macromolecular materials.

Figure 4b displays the chemical structures of the donor–acceptor side-chain liquid crystal PTPe polymer based on side-on perylene derivatives and its general synthetic procedure. The polymer was prepared according to the procedure previously described for the discotic and calamitic side-chain polymers. More precisely, the regioregular precursory PT_{10} poly(3-alkythiophene) with a narrow polydispersity index (PDI = 1.2) and highly controlled molecular weight ($DP_n = 45$) was post-functionalized by the asymmetrically substituted diimide derivative Pe via nucleophilic substitution SN_2 under basic conditions, leading to a high substitution ratio.[41,47]

The thermal and self-organization properties of the donor–acceptor side-chain liquid crystal PTPe polymer were investigated by POM, DSC, temperature-dependent SAXS and GISAXS.[47] The results showed that the PTPe polymer presents a liquid-crystalline organization with a lamellocolumnar structure consisting of alternating double sub-layers of diimide perylene moieties and polythiophene sub-layers (Figure 5a). The SAXS patterns of PTPe indeed contain several sharp and equidistant Bragg reflections in the

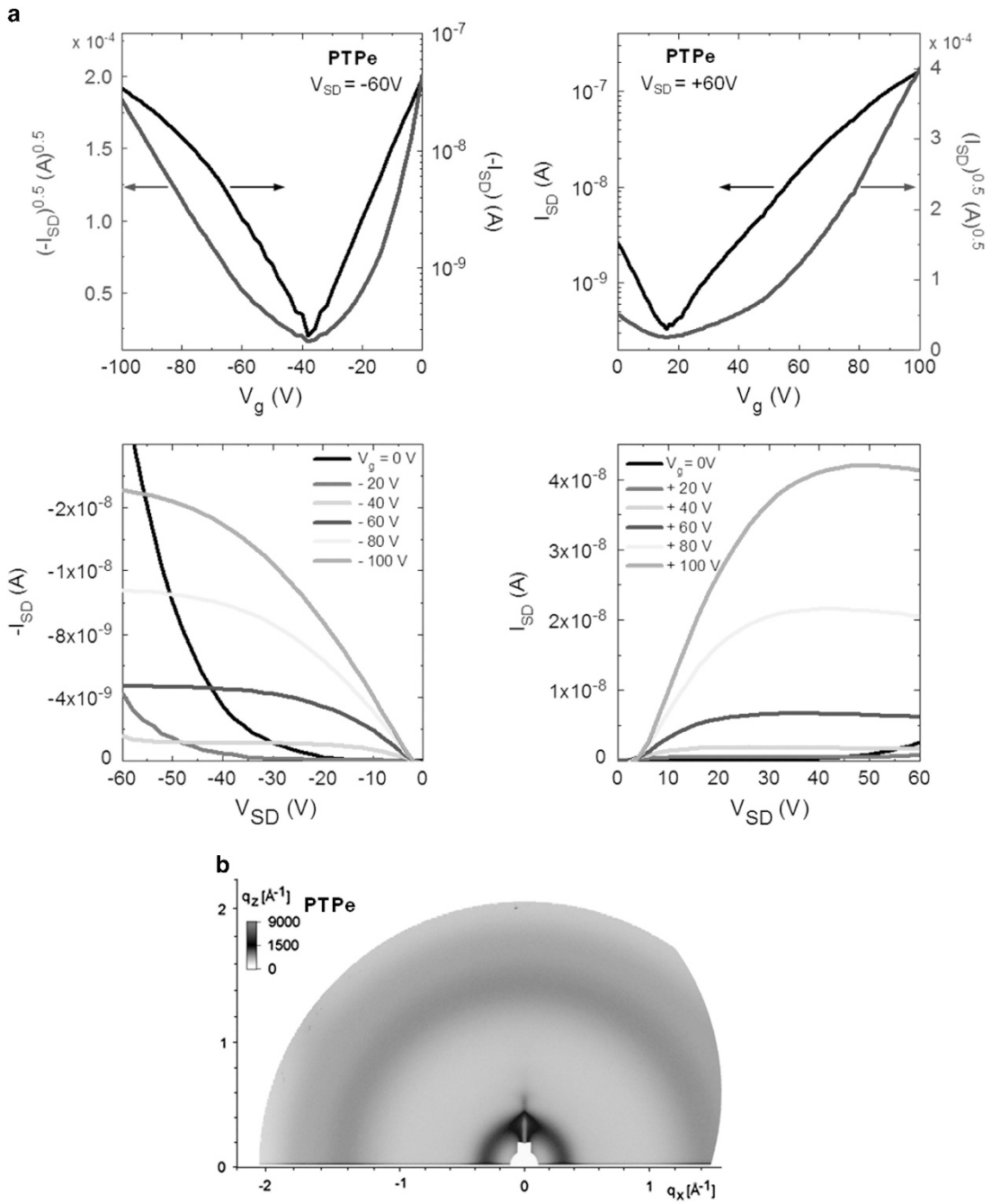

Figure 6 (**a**) Typical output and transfer characteristics of a top-contact bottom-gate OFET based on the donor–acceptor side-chain liquid crystal polymer PTPe based on perylene derivative side groups. (**b**) GISAXS pattern of PTPe transistor thin films spun-cast on silicon wafers. A full color version of this figure is available online at *Polymer Journal* online.

small-angle region and three scattering halos in the wide-angle region (Figure 5b). This set of sharp and intense small-angle reflections comes from the lamellar structure, with a lamellar periodicity of 5.8 nm. This value and the intensity modulation in the small-angle harmonic series, in particular the enhanced third-order reflection, are consistent with the two perylene and one polythiophene electron-rich sub-layer alternation. The three scattering signals in the wide-angle region at 4.5, 3.8, and 3.5 Å correspond to the molten state of the aliphatic chains (h_{ch}), the stacking of the polythiophene backbones (h_{PT}) and the face-to-face stacking of the perylene diimide cores (h_{PDI}), respectively.

This multi-lamellar structure resulting in intertwined layers of donor and acceptor moieties is very promising to provide distinct channels for holes and electrons. In this context, we investigated the charge transport properties of PTPe thin films in the OFET configuration. Bottom-gate top-contact devices were prepared following the same procedures as those previously described for the triphenylene side-chain PT_mT homopolymers. Typical output and transfer characteristics for both the hole and electron channels are provided in Figure 6a. The perylene side-chain PTPe polymer exhibited clear p-type and n-type conductions, and the charge-carrier mobilities in the saturation regime were found to be $\sim 3 \times 10^{-5}$ and 3.3×10^{-6} $cm^2 V^{-1} s^{-1}$, respectively (Table 1). It is worth mentioning that the GISAXS measurements performed in the thin-film transistors evidenced a poor lamellar structure with short correlation distances. More importantly, the samples did not show any preferential orientation of the lamellar system, which is highly detrimental to device performance and can explain the low mobilities (Figure 6b). Despite these low values, the results are nevertheless promising regarding the ambipolar conduction and validate the approach described in this focused review. With further optimization of the design and the chemical engineering of the π-conjugated side-chain polymers, together with improved control of the film morphology, it should be possible to access self-organized ambipolar materials with a high-mobility hole and electron transport.

CONCLUSIONS

In this manuscript, we reviewed previous work devoted to the design and synthesis of a new type of side-chain liquid crystal π-conjugated polymer consisting of intricate polymeric systems associating regioregular poly(3-alkylthiophene) backbones with laterally pending π-conjugated mesogenic groups. Several series of polymeric architectures have been prepared using different polymer backbone structures and various side groups to evaluate the impact of the macromolecular structure on the geometrical packing parameters and molecular ordering. This comprehensive study provides important insight into the relationships between the polymeric architecture, nano- and macroscale organization and charge transport properties in such self-organized multi-lamellar macromolecular systems. In particular, we demonstrated that the appropriate selection of n-type side groups for attachment to the polymer backbone combined with the optimization of the structural properties by chemical engineering led to the formation of two distinct channels for holes and electrons. This contribution validates a route toward new promising classes of high-mobility ambipolar self-organized materials, of paramount importance for future electronic and optoelectronic applications.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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