Towards crystal engineering of solid-state polymerization in dibromothiophenes[†]

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Three new dibromothiophene monomers for solid-state polymerization have been synthesized and their solid-state structure was studied by X-ray crystallography. The substituents in the thiophene ring are introduced to induce an *anti*-orientation of the monomer to resemble the *s*-trans structure of the polythiophene. The details of the solid-state packing of the new monomers are compared to those of the previously studied 2,5-dibromo(3,4-ethylenedioxythiophene) and related to their reactivity and to the conductivity of the resulting polymers. The same polymers have also been prepared by electrooxidative polymerization on the surface of an electrode.

Introduction

Conjugated polymers have been a focus of attention in organic materials chemistry for the last three decades, due to their conductive properties that are unusual for organic compounds, and numerous applications in electronic and optoelectronic devices, including organic light-emitting diodes (OLEDs), photovoltaic cells (OPVs), field-effect transistors (OFETs), and chemical and bio-sensors.1 Among all intrinsically-conductive polymers, polythiophenes and particularly poly(3,4-ethylenedioxythiophene) (PEDOT) stand as the most industrially important (and commercially successful) materials, owing to their very high conductivity and unsurpassed stability.² One of the major problems for application of conducting polymers is their very low solubility, which hampers processing. The solubility of a neutral (non-doped) polymer can be enhanced by introducing long alkyl-chain substituents, although these also act as insulators, effectively "diluting" the conductive part (conjugated backbone) of the material. For PEDOTs, a clever way to bring the polymer into solution, introduced by the Bayer company,^{2a} was to prepare the polymer in the presence of a polyelectrolyte (polystyrene sulfonic acid, PSS) which, acting as a doping counter-anion, makes the positively charged doped PEDOT soluble/dispersable in water. The resulting suspension, sold as Baytron P, is widely used to produce uniform conductive films which are currently used in OLEDs, OPVs, anti-static coatings, sensors, etc. Despite the tremendous commercial success of Baytron P, a possible phase separation between the conductive PEDOT and insulating PSS chains3 has been limiting the high intrinsic conductivity of PEDOT, and poses problems for long-term device operation.

An intriguing alternative for insoluble conjugated polymers is to process a (soluble) precursor and to produce the conjugated polymer directly in the solid state. Sotzing and co-workers have recently demonstrated solid-state conversion of a soluble thiophene-silane pre-polymer into a highly conducting PEDOT by electrodesilanation reaction;⁴ however, the pre-polymer has to be deposited on a surface of an electrode, which somewhat limits its applicability.

The pioneering work on topochemical solid-state synthesis of conjugated polymers was done by Wegner on poly(diacetylenes),⁵ and MacDiarmid, Heeger and co-workers on poly(sulfur nitride).⁶ In both cases, the spontaneous polymerization does not require any reagent or electrode to occur and is favored by specific arrangement/proximity of atoms in the monomer crystal structure (and dramatically suppressed in disordered (liquid) state). In some cases a single crystal-to-single crystal polymerization has been observed.⁷ The possibility of achieving crystalline order in conjugated polymers is probably the most attractive feature of the solid-state polymerization (SSP).

A few years ago, Wudl and co-workers showed that the concept of spontaneous topochemical SSP can be realized in the polythiophene series, and that highly conductive semi-crystalline PEDOTs can be prepared by simple heating of 2,5-dibromo(3,4ethylenedioxy)thiophene (DBEDOT) and 2,5-diiodo(3,4-ethylenedioxy)thiophene (DIEDOT).⁸ Similar behavior was earlier observed (although not as a topochemical process) by Audebert and Bidan for dibromopyrroles,⁹ and further evidence for SSP in halogenated electron-rich heteroaromatics was found by Skabara *et al.* for 2,5-dibromo(3,4-ethylenedithio)thiophenes (DBADTTs)¹⁰ and 2,5-dibromo(3,4-ethylenediseleno)thiophene,¹¹ and Bendikov *et al.* for 2,5-dibromo(3,4-ethylenedioxy)selenophene (DBE-DOS).¹²



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However, the mechanism of the topochemical SSP in dihalothiophenes is not well understood. It was suggested that close intermolecular halogen…halogen contacts¹³ are important for the SSP which propagates along the π -stack of the monomer.,^{8b} Similar conclusions on the importance of halogen…halogen contacts and π -stacking were drawn by Skabara and coworkers for SSP of DBADTT derivatives.¹⁰ In DBEDOT, the C2…C5 separation between the adjacent thiophene monomers of the same stack (4.09 Å) are the closest possible contacts between the reacting centers. However, the all-*syn* (parallel) orientation of the DBEDOT in the stack is in contrast to the necessary all-*anti* conformation of the PEDOT, which requires a significant rotational displacement of the monomer during the SSP and could limit the structural order in the resulting polymer.

With this in mind, we have synthesized and studied the SSP of functionalized DBEDOT monomers. Bulky substituents in the ethylenedioxy bridge were introduced to disfavor the parallel molecular orientation in the stack, which could promote an antiparallel (all-*anti*) stacking. In the present paper we describe the synthesis of EDOT monomers **3a–c** and their electropolymerization, and solid-state polymerizations of the brominated derivatives **4a–c** to produce disubstituted PEDOT polymers **A–C**. The possible effects of the solid-state packing of **4a–c** on their SSP are analyzed by X-ray crystallography. We also note that, despite a plethora of studies on mono-substituted PEDOT derivatives,¹⁴ the only example of a disubstituted PEDOT reported to date is electropolymerized 3,4-(cyclohexyliden-1,2-dioxy)thiophene.¹⁵

Synthesis

The 3,4-ethylenedioxythiophene (EDOT) derivatives **1a–c** were prepared by Mitsunobu coupling of diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate with the corresponding diols (*meso*-butan-2,3-diol (**a**), *meso*-tetrahydrofuran-3,4-diol (**b**) or *meso*-tetrahydrothiophen-3,4-diol (**c**)) as previously reported for other 1,2-diols (Scheme 1).¹⁶ The mechanism of the Mitsunobu reaction involves a clean S_N2 process that inverts the configuration of chiral secondary alcohols.¹⁷ Accordingly, the structure of the formed ethers (both substituents on the same side of the dioxane ring) is dictated by the *meso*-configuration of the starting alcohols, and no sign of racemization was observed in the NMR spectra. The steric hindrance in the diol generally lowers the yield of the Mitsunobu reaction,^{17,18} but acceptable yields of 33% to 70% were obtained for compounds **1a–c**.

Saponification of the diethyl esters 1a-c followed by copper chromite-catalyzed decarboxylation of the obtained acids and bromination with *N*-bromosuccinimide leads to the brominated derivatives 4a-c with moderate total yields (over these three steps) of 67%, 35% and 72%, respectively.^{8,16} Alternatively, compounds 4a, b have been obtained with yields of 44% and 41%, respectively, in a one-pot brominating decarboxylation reaction by simultaneous action of sodium hydroxide and *N*-bromosuccinimide.¹⁹

One of the initial objectives behind the synthesis of 1c was a possible aromatization to yield the unknown bifunctional thiophene monomer dithieno-[3,4-b;3',4'-e]-1,4-dioxine. However, attempts at dehydrogenation of 4c using molecular bromine or NBS, or strong π -acceptors (2,3-dichloro-4,5dicyano-*p*-benzoquinone (DDQ)) have failed. The only isolated products were sulfoxide 5c (in NBS and bromine reactions) or sulfone derivative 6c (in DDQ reaction) (Scheme 2). The latter can also be prepared by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA) in 36% yield. Such behavior of 4c is perhaps not surprising; all reported oxidative aromatization reactions forming thiophene derivatives started from partially unsaturated



c

Scheme 1 Synthesis of new EDOT monomers for solid-state polymerization.



Scheme 2 Oxidation of the tetrahydrothiophene derivative 1c.

cycles (an sp² carbon on C3 and/or C4 atoms). Attempts to aromatize the sulfoxide **5c** under various previously published conditions²⁰ have also proved unsuccessful; the aryloxy substituent in the β -position to sulfoxide group acts as an excellent leaving group, thus resulting in β -elimination of the intermediate α -carbanion, which leads to a vinylsulfoxide and opens the dioxane ring (followed by decomposition reactions).

Electropolymerization

The oxidative electropolymerization of **3a-c** was performed under potentiodynamic conditions. The oxidation of the monomers 3a,b was observed at Eonset ~1.0 V vs. Ag/AgCl and repeating cycling of the potential between -0.5 and 1.25 V leads to a progressive growth of the polymer with concomitant increase of the anodic peak and formation of a characteristic black film on the electrode (Fig. 1). Cyclic voltammetry (CV) of thus-modified electrodes in fresh electrolyte solution reveals characteristic reversible p-doping/dedoping process with an oxidation onset at about -0.7 V vs. Ag/AgCl, similar to the doping characteristics of PEDOT obtained under identical conditions, thus indicating a negligible electronic effect of the substituents in the ethylenedioxy bridge (Fig. 2). Somewhat surprisingly, no polymerization was observed for 3c in these conditions, which is probably due to its low solubility in propylene carbonate. However, normal polymer growth was observed in dichloromethane, at somewhat higher potentials.

Fig. 1 Electropolymerization of 3a-c in 0.2 M Bu₄NPF₆ solution, scan rate 40 mV/s. Solvent is propylene carbonate for 3a,b and dichloromethane for 3c.

All three polymers A–C are very stable and repeating doping/ dedoping electrochemical cycling in ambient atmosphere (*i.e.*, no protection from oxygen or moisture) results in less than 3% loss of electrochemical activity after 15 cycles (Fig. 2).

X-ray crystallographic analysis of the monomers

Single crystals of the three dibromo derivatives 4a-c were grown from ethanol solutions and studied by X-ray analysis in order to understand structural features of SSP. The molecular structures of 4a-c do not reveal any abnormalities which might be responsible for SSP. The C–Br bond lengths (1.87 Å) are typical for bromoaromatics. In the ethylenedioxy bridges, one of the alkyl substituents (CH₃ for 4a and CH₂ for 4b, 4c) is axial and another one is equatorial, which renders the molecule chiral. In solution, however, a fast interconversion between the axial and equatorial positions takes places, as the NMR pattern is completely symmetric.

In the solid state a 1:1 (achiral) mixture of two enantiomers is formed. All three compounds pack in a relatively complex fashion (*Pbca*) with a large orthorhombic unit cell which contains eight molecules. Earlier we have suggested that short halogen…halogen intermolecular contacts might be responsible for solid-state polymerization in DBEDOT and DCEDOT, as no solid-state polymerization was observed for 2,5-dichloro-3,4ethylenedioxythiophene that lacked such contacts.⁸ Short Br… Br contacts were also reported for the DBEDTT molecule, which undergoes similar SSP.¹⁰ However, the current study indicates



Fig. 2 CVs of polymers A-C (prepared as shown in Fig. 1). Electrolyte is 0.2 M Bu₄NPF₆ in propylene carbonate (**A**, **B**) or dichloromethane (**C**); scan rate 40 mV/s.

that such contacts are not critical for the SSP. While slightly shortened Br...Br contacts (3.57-3.64 Å) were observed for **4a**, the shortest Br...Br contacts for compounds **4b** and **4c** (3.91 Å) and 4.04 Å, respectively) are much larger than the double van der Waals radius of bromine (3.7 Å), and the SSP was indeed observed for all three monomers.

Compound 4a forms antiparallel dimers, with an interplanar distance of 5.26 Å. Such a large distance is dictated by the interaction of the axial CH3 substituent in one molecule with the thiophene ring of another, and no π -stacking similar to that observed in DBEDOT is formed. The closest Br...Br contacts are 3.57 Å and 3.64 Å and are found between molecules of neighboring dimers. The shortest intermolecular C2...C5 distance of 4.22 Å is found between two thiophenes with a dihedral angle of 46°. These C2…C5 intermolecular contacts form chains running along crystallographic direction a and provide the most realistic pathway for the polymerization (Fig. 3). The Br...Br contacts occur between these chains, providing a sensible route for the elimination of bromine, which then can occupy the interchain spacing as a dopant. It should be, however, noted, that the C2... C5 distance is larger than what is typically required in solid-state topological reactions for C-C bond formation (<4 Å),²¹ and larger than the corresponding distance in DBEDOT (4.09 $Å^{8b}$). Furthermore, the C2…C2 distance between each third molecule in the chain (8.73 Å) is $\sim 11\%$ longer than the corresponding distance in polythiophene (7.85 Å²²); this would lead to a significant crystal deformation during the SSP.

The packing of compound **4b** also shows antiparallel dimers, but, in contrast to **4a**, the alkyl substituents (tetrahydrofuran moiety) point outside the dimer, which allows for $\pi \cdots \pi$ interactions between the thiophene moieties (interplanar distance 3.50 Å) (Fig. 4a). The shortest C2…C5 contacts (3.56 Å) occur within the dimer. Unfortunately, however, such interactions cannot translate into a continuous π -stacking, which otherwise would have provided an ideal pathway for SSP. The second shortest C2…C5 contacts, observed between the thiophene units with a dihedral angle of 58° (4.58 Å), is even larger than a corresponding distance in **4a**. These contacts form chains similar to those observed for **4a**, but running along the crystallographic direction *b*. In this case, the C2…C2 distance between each third molecule in the chain (12.14 Å) is 55% longer than the corresponding distance in polythiophene chain (7.85 Å²²), which is too large for a SSP along this direction. Thus, while the initial C–C bond formation most likely occurs within the dimer, the following polymerization direction is not clear. Considering the observed by-side reaction of the bromine with tetrahydrofuran (see below), a disordered polymerization can be expected in this case.

The packing of compound **4c** doesn't show any obvious pathway for SSP. The antiparallel molecules of **4c** do not form dimers, but are separated by tetrahydrothiophene units of other molecules (Fig. 4b). The sulfur atoms of these tetrahydrothiophene units interact with the thiophene rings of adjacent molecules with (thiophene)...S distance of 3.40 Å. The shortest observed C2...C5 distance is 5.15 Å and such an arrangement can be expected to be the least favorable for the SSP.

Solid-state polymerization

Prolonged storage of the brominated derivatives **4a–c** transforms the initially white monomer into the black material which shows all features of a doped PEDOT (characteristic absorbance, conductivity), in line with the previous observations.⁸ This spontaneous solid-state polymerization is most rapid for **4a**, for which the color change is already observed after less than a day at room temperature (or after about one week when stored at 5 °C). SSP can be greatly accelerated by heating and the polymer samples for analysis were obtained by incubating monomers **4a– c** at 60 °C, 90 °C and 100 °C (that is, just below the melting points), respectively, for 72 h. The polymerization is accompanied by appearance of a brown bromine vapor and results in black powders of polymers **A**, **B** and **C**, which were completely insoluble in organic solvents.

The polymer A was dedoped by treatment with hydrazine hydrate and characterized by solid-state ¹³C NMR (Fig. 5). The absence of a signal at $\delta = 85.2$ ppm, characteristic for the C–Br bond, and the new signal at $\delta = 109.0$ ppm typical of C–C bonds formed between thiophene rings indicate the formation of a conjugated polymer. The mass loss during dedoping



Fig. 3 The unit cell (left) and suggested polymerization direction (right) in 4a. The oval highlights the antiparallel dimers; pink dashed lines show short Br \cdots Br contacts; green dashed lines show the shortest C2 \cdots C5 contacts; the numbers indicate corresponding distances in Å.



Fig. 4 Crystal packing of monomers 4b (a) and 4c (b). The dimer is highlighted with an oval; white and green dashed lines show the shortest C2 \cdots C5 contacts; yellow dashed line shows thiophene \cdots S intermolecular contacts for 4c; the numbers indicate corresponding distances in Å.



Fig. 5 CP-MAS ¹³C NMR spectrum of SSP A.

corresponds to 0.6 of Br_3^- doping ions per thiophene unit (*i.e.*, *ca*. one charge per two thiophene units). This is an extremely high doping level, higher than that of the unsubstituted SSP-PEDOT.^{8b} The low residual Br in the dedoped polymer (<2%) is associated with terminal C–Br bonds and suggests that the molecular weight of **A** is at least 4 kDa. No GPC analysis could be performed due to insolubility of the polymer.

For the polymers **B** and **C**, solid-state NMR (see ESI^{\dagger}) indicates a partial reaction of the eliminating bromine with the tetrahydrofuran and tetrahydrothiophene side groups, respectively. However, this side-group reactivity does not seem to interfere with the polymerization reaction *per se*.

Isothermal DSC measurements were performed in order to semi-quantitatively estimate the kinetics of the SSP. Unfortunately, the very different reactivity and the melting points (which



Fig. 6 SSP of 4c followed by isothermal DSC.

set the highest temperature for SSP experiments) of monomers 4a-c does not allow one to study their SSP at the same temperature. Fig. 6 shows temperature dependence of the polymerization 4c. As previously observed for DBEDOT,^{8b} the exothermic polymerization reaction occurs after a significant inductive period which likely corresponds to accumulation of the molecular bromine (acting as a catalyst). The maximum reaction rates (corresponding to the DSC peaks maxima) are observed at 40 min, 120 min and at \geq 400 at 110 °C, 100 °C and 90 °C, respectively (Fig. 6). Integration of the exothermic peak indicates an SSP enthalpy of only -2.6 kcal/mol (at 110 °C) which is significantly lower than that observed for DBEDOT (-14 kcal/ mol^{8b}). While the reason for this difference is not entirely clear, it is likely associated with post-polymerization attack of bromine (Br₃⁻) on the EDOT side-group (see above) and also perhaps the extensive structural rearrangements required to transform the solid monomer into the very differently packed polymer (see X-ray crystallography). Such low reaction enthalpy prevents accurate kinetic studies by DSC. Nevertheless, the general trend of the reactivity $4a > 4b \sim 4c$ is clear from the DSC and visual observation of the polymerization at room temperature.

Conductivity

The conductivity of polymers prepared by SSP has been measured with a two-probe method²³ in compressed pellets. Facile oxidation of the stainless steel probes significantly obstructs the measurements of halogen-doped polymer (Br₃dopant in this case); however, this problem can be eliminated by adding a thin buffer layer of single-walled carbon nanotubes (HipCO type) between the compressed pellet and the probe. The highest conductivity was found for the polymer A (4.2 S/cm), followed by lower values for polymer B (0.35 S/cm) and C (0.13 S/cm). This order corresponds to the reactivity of the corresponding monomers (4a-c) and is line with X-ray crystallographic findings of unfavorable molecular arrangements of 4b and 4c (see above). We note that parent SSP-PEDOT measured under identical conditions shows even higher conductivity of 11.8 S/cm (although for materials with conductivity greater than ~ 5 S/cm the two-probe method can be grossly inaccurate due to relatively large contact resistance).

Conclusions

We have synthesized three new thiophene monomers which undergo spontaneous solid-state polymerization upon heating. The effect of substituents in the ethylenedioxythiophene ring on the packing of the monomer and on the subsequent polymerization was studied with X-ray crystallography. While the original goal of inducing an *anti*-orientation of the adjacent molecules in the crystal was achieved, the increased intermolecular spacing disfavors the topochemical polymerization reaction. As a result, the conductivity of the prepared polymers, while still high (0.13–4.2 S/cm), is lower than that of the parent PEDOT prepared by solid-state polymerization (11.8 S/cm in the same measurement). The intermolecular Hal…Hal contacts, which were suggested earlier to be important, do not appear to be critical for the solid-state polymerization.

Experimental section

meso-Tetrahydrothiophen-3,4-diol (c) was prepared according to Benazza *et al.* from the *meso*-erithritol with 56% overall yield.²⁴ Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate was prepared according to Overberger and Lal from diethyl thiodiglycolate and diethyl oxalate with 80% yield.²⁵

Synthesis

EDOT-R-COOEt (1a–c). To a solution of diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (2.00 g, 7.68 mmol), diols (*meso*-butan-2,3-diol **a**, *meso*-tetrahydrofuran-3,4-diol **b** or *meso*tetrahydrothiophen-3,4-diol **c**) (7.68 mmol) and tributylphosphine (4.74 mL, 19.2 mmol) in THF (15 mL) was added diisopropyl azodicarboxylate (3.78 mL, 19.2 mmol) over 20 min. The reaction mixture was heated at reflux for 48 h. Then, it was cooled down to room temperature and the solvent was evaporated to afford an orange oil which was purified by column chromatography on silica gel and recrystallized from ethanol to give products **1a-c** as white powders. **1a** (0.8 g, 33%). mp 110–111 °C (lit.: 105 °C for a mixture of isomers^{16b}). ¹H NMR (300 MHz, CDCl₃, ppm): 4.47 (m, 2H), 4.35 (q, 4H, ${}^{3}J = 6.9$ Hz), 1.39 (d, ${}^{3}J$ = 6.0 Hz, 6H), 1.37 (t, 6H, ${}^{3}J = 6.9$ Hz). ${}^{13}C$ NMR (125 MHz, CDCl₃), 160.8, 144.8, 111.1, 73.3, 61.1, 14.4, 14.0. MS (EI) m/z =314.2 (100%) [M⁺]. **1b** (1.76 g, 70%). mp 121–122 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: 4.83 (m, 2H), 4.34 (q, 4H, ${}^{3}J = 6.9 \text{ Hz}), 4.20$ (m, 2H), 4.00 (m, 2H), 1.36 (t, 6H, ${}^{3}J = 6.9$ Hz). ${}^{13}C$ NMR (125 MHz, CDCl₃, ppm): 160.8, 142.9, 112.3, 74.0, 69.7, 61.5, 14.4. MS (ESI) m/z = 351.0 (100%) [M + Na]. HRMS (EI) Calcd. for C₁₄H₁₆O₇S 328.06167; Found 328.06077. 1c (1.32 g, 50 %). mp 178 °C. ¹H NMR (300 MHz, CDCl₃): 4.83 (m, 2H), 4.34 (q, 4H, ${}^{3}J = 7.0$ Hz), 3.20 (m, 2H), 3.09 (m, 2H), 1.36 (t, 6H, ${}^{3}J = 7.0$ Hz). ¹³C NMR (125 MHz, CDCl₃): 160.8, 143.2, 112.4, 76.9, 70.2, 61.6, 14.5. MS (EI) m/z = 344.2 (100 %) [M⁺]. HRMS (EI) Calcd. for C₁₄H₁₆O₆S₂ 344.03883; Found 344.03802.

EDOT-R-COOH (2a–c). To a solution of potassium hydroxide (1.4 g, 25 mmol) in water (50 mL) was added EDOTdiacid diethyl ester derivatives **1a–c** (2.50 mmol). The reaction mixture was stirred at reflux until complete dissolution (2 h). After cooling down to room temperature, the solution was acidified with HCl (1 M), the formed precipitated was filtered and dried under vacuum to give the products as white powders. **2a** (0.60 g, 93 %). mp > 300 °C (dec.). ¹H NMR (300 MHz, DMSO-d₆, ppm): 4.47 (m, 2H), 1.21 (d, ³J = 5.7 Hz, 6H). MS (EI) *m*/*z* = 257.9 (52 %) [M⁺]. **2b** (0.67 g, 99 %). mp > 300° ¹H NMR (300 MHz, DMSO-d₆, ppm): 6.53 (s, 2H), 4.97 (m, 2H), 4.06 (m, 2H), 3.74 (m, 2H). MS (EI) *m*/*z* = 271.2 (48 %) [M⁺]. **2c** (0.68 g, 95 %). mp > 300° ¹H NMR (300 MHz, DMSO-d₆, ppm): 4.94 (m, 2H), 3.18 (m, 2H), 2.86 (m, 2H). MS (EI) *m*/*z* = 287.0 (57 %) [M⁺].

EDOT-R-H (3a-c). To a solution of the diacid derivatives 2a-c (2.00 mmol) in freshly distilled guinoline (5 mL) was added $Cr_2Cu_2O_5$ (62 mg, 0.20 mmol). The reaction mixture was heated at 180 °C for 2 h. After cooling down to room temperature, 100 mL of HCl (1 M) were added and the product was extracted with 3×50 mL of ethyl acetate. The organic phase was washed with water and dried over MgSO₄. After evaporation, the residue was purified by column chromatography to give the product as oils (3a-b) or a white powder (3c). 3a (0.27 g, 80 %). ¹H NMR (300 MHz, CDCl₃, ppm): 6.30 (s, 2H), 4.25 (m, 2H), 1.27 (d, ${}^{3}J = 6.6$ Hz, 6H). ¹³C NMR (125.8 MHz, CDCl₃): 141.4, 99.5, 72.9, 14.6. MS (EI) m/z = 170.1 (100 %) [M⁺]. **3b** (m = 0.28 g, 77 \%). ¹H NMR (300 MHz, CDCl₃, ppm): 6.39 (s, 2H), 4.66 (m, 2H), 4.13 (m, 2H), 3.95 (m, 2H). ¹³C NMR (125.8 MHz, CDCl₃, ppm): 140.0, 100.3, 73.9, 69.8. MS (EI) m/z = 183.9 (100 %) [M⁺]. HRMS (EI) Calcd. for C₈H₈O₃S 184.01942; Found 184.01904. **3c** (m = 0.32 g, 80 %). mp 50 °C. ¹H NMR (300 MHz, CDCl₃, ppm): 6.37 (s, 2H), 4.66 (m, 2H), 3.10 (m, 2H), 3.02 (m, 2H). ¹³C NMR (125.8 MHz, CDCl₃, ppm): 139.8, 100.5, 76,7, 30.5. MS (EI) $m/z = 200.0 (100 \%) [M^+]$. HRMS (EI) Calcd. for C₈H₈O₂S₂ 199.99657; Found 199.99628.

EDOT-R-Br (4a–c). (i) To a solution of the thiophene derivatives **3a–c** (1.00 mmol) in CHCl₃ (4 mL) and AcOH (2 mL) under argon at 0 °C was added *N*-bromosuccinimide (360 mg, 2.02 mmol). The reaction mixture was stirred at 0 °C overnight.

Then, 50 mL of water were added and the product was extracted with 3×50 mL of CHCl₃. The organic phase was washed with NaHCO₃ (5%), water and dried over MgSO₄. After evaporation, the residue was purified by column chromatography and crystallised from EtOH to give products 4a-c as white powders. 4a (0.13 g, 41%). mp 65 °C. ¹H NMR (300 MHz, CDCl₃): 4.31 (m, 2H), 1.32 (d, ${}^{3}J = 6.6$ Hz, 6H). ${}^{13}C$ NMR (125.8 MHz, CDCl₃): 139.5, 85.2, 73.7, 14.5, MS (APCI) m/z = 328.88 (100%) [M⁺]. HRMS (EI) Calcd. for C₈H₈O₂SBr₂ 325.86117; found 325.86057. 4b (0.15 g, 44%). mp 97 °C. ¹H NMR (300 MHz, CDCl₃): 4.72 (m, 2H), 4.16 (m, 2H), 3.96 (m, 2H). ¹³C NMR (125.8 MHz, CDCl₃): 138.0, 86.2, 74.4, 69.6. MS (APCI) m/z = 342.92 [M⁺]. HRMS (EI) Calcd. for C₈H₆O₃SBr₂ 339.84044; Found 339.83923. 4c (0.33 g, 91%). mp >100 °C (dec.). ¹H NMR (300 MHz, CDCl₃, ppm): 4.72 (m, 2H), 3.15 (m, 2H), 3.04 (m, 2H). ¹³C [¹H] NMR (125.8 MHz, CDCl₃, ppm): 138.0, 86.3, 77.2, 30.3. MS (EI) m/z = 357.9 (71%) [M⁺]. HRMS (EI) Calcd. for C₈H₆O₂S₂Br₂ 355.81760; Found 355.81684.

(ii) To a suspension of the diester derivatives 1a-b (1.0 mmol) in ethanol (20 mL) was added sodium hydroxide (0.168 g, 7 mmol). The reaction mixture was refluxed for 2 h. After cooling down to room temperature, water (20 mL) and *N*-bromosuccinimide (0.80 g, 4.5 mmol) were added. The reaction mixture was then stirred overnight and the product was extracted with 3×50 mL of chloroform. The organic phase was then washed with $3 \times$ 100 mL aqueous NaOH (1 M) and dried over MgSO₄. The product was purified by column chromatography and crystallised from ethanol to give products **4a–b** as white powders. **4a** (0.30 g, 91%). **4b** (0.14 g, 41%).

EDOT-tthO-COOEt (5c). To a solution of **1c** (32 mg, 0.093 mmol) in acetonitrile (2 mL) at -20 °C under argon was added *N*-bromosuccinimide (40 mg, 0.23 mmol). The reaction mixture was stirred for 1 h. Then water (20 mL) was added and the product was extracted by dichloromethane (3 × 30 mL). The organic phase was then dried over MgSO₄ and the solvent has been evaporated to give product **5c** as a white powder (17 mg, 51%). ¹H NMR (300 MHz, CDCl₃, ppm): 5.34 (m, 1H), 4.85 (m, 1H), 4.32 (q, ${}^{3}J = 7.2$ Hz, 2H), 4.31 (q, ${}^{3}J = 7.2$ Hz, 2H), 3.77 (dd, ${}^{2}J = 14.7$ Hz, ${}^{3}J = 5.1$ Hz, 1H), 3.50 (dd, ${}^{2}J = 14.7$ Hz, ${}^{3}J = 6.0$ Hz, 1H), 3.23 (m, 2H), 1.35 (m, 6H). MS (EI) *m*/*z* = 359.7 (27%) [M⁺].

EDOT-tthO₂-COOEt (6c). To a solution of **1c** (50 mg, 0.145 mmol) in CHCl₃ (5 mL) under argon at RT was added *m*-CPBA (36 mg, 0.16 mmol). The reaction mixture was stirred for 3 h and then, 20 mL of an aqueous solution of NaHCO₃ (5%) was added and the product was extracted with dichloromethane (3 × 20 mL). The organic phase was dried over MgSO₄ and the solvent was evaporated to give product **6c** as a white powder (20 mg, 37%). ¹H NMR (300 MHz, CDCl₃, ppm): 5.35 (m, 2H), 4.34 (q, ³J = 7.2 Hz, 4H), 3.51 (dd, ²J = 14.7 Hz, ³J = 5.4 Hz, 2H), 3.25 (dd, ²J = 14.7 Hz, ³J = 5.4 Hz, 2H). MS (EI) *m*/*z* = 365.5 (100%) [M⁺].

Solid-state polymerization

In a closed 5 mL vial, the brominated compounds 4a-c (300 mg) were incubated at 60 °C, 90 °C and 100 °C, respectively, for 72 h.

The color of the material changed from white to black with the appearance of bromine vapor in the vial. Then the polymer was vacuum-dried overnight to afford the bromine-doped polymers A–C. For dedoping, the polymers was stirred in $\sim 1\%$ solution of hydrazine in ethanol overnight at room temperature, filtered and rinsed with ethanol under Ar.

Polymer A: 100 mg of **4a** produced 95 mg of the heavily bromine-doped polymer. Prolonged (3 days) drying of the asprepared material in vacuum (0.1 mbar) resulted in partial loss of the dopant. Anal. Calcd. for $C_8H_8O_2SBr$: C, 38.7; H, 3.22; S, 12.9; Found: C, 37.44; H, 3.64; S, 13.21%. 31.7 mg of as-prepared doped SSP-A were dedoped with hydrazine to give 16.8 mg of neutral **A**. Anal. calcd. for $C_8H_8O_2S$: C, 57.12; H, 4.79; O, 19.02; S, 19.06; Br, 0%; Found: C, 56.77, H, 4.60; O, 18.77; S, 18.39; Br < 2%

Electrochemistry

Electrochemical experiments were carried out with CH Instruments 760C electrochemical station in a three-electrode cell equipped with a platinum disk (\emptyset 1.6 mm) as working electrode, platinum wire as a counter electrode and Ag/AgCl reference electrode. Electropolymerizations were performed at room temperature in dry DCM or propylene carbonate solutions (5 mM of monomer), deoxygenated by argon bubbling, with 0.2 M Bu₄NPF₆ as supporting electrolyte. Ferrocene (Fc) was used as an internal standard and showed $E_{ox}^0 = +0.49$ V (*vs.* Ag/AgCl in DCM), +0.46 V (*vs.* Ag/AgCl in propylene carbonate) under our conditions.

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