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Regio-regular poly(thienylene vinylene)s (rr-PTVs) through acyclic diene metathesis (ADMET) polymerization and the impact of alkyl side-chains on polymer molecular weight and solubility

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ABSTRACT

Poly(thienylene vinylene) (PTV) is one of the prototypical conjugated polymers (CPs) that has received relatively little attention. The insertion of one small double bond between every pair of adjacent thiophene units in PTV structures potentially allow direct functionalization of the thienyl rings, which can fine-tune polymer electronic properties without significantly impact main-chain planarity. However, synthetic methods leading to such tailor-designed PTVs are scarce. In this paper, we report a new synthetic strategy that produces a series of regio-regular (rr) PTVs bearing bromine atoms and different alkyl side-chains on every thiophene unit. The methodology starts with synthesis of well-defined dimeric monomers that lead to rr-PTVs upon ADMET polymerization. The monomers and polymers are fully characterized by NMR and absorption spectroscopy. We found that linear and slightly branched alkyl chains led to precipitation during the polymerization process and thus low apparent molecular weight due to limited polymer solubility, while long-branched and bulky silyl-alkyl ether chains led to PTVs with greater solubility and higher molecular weights.

1. Introduction

Since the discovery of metallic conductivity in doped polyacetylene that led to the 2000 Nobel Prize in chemistry [1–4], conjugated polymers (CPs) have evolved into an enormous research field and been considered to revolutionize the next-generation optoelectronic devices [5]. One of the key components in CP research is the synthetic capability towards tailor-designed chemical structures and thorough understanding on the structure-property relationship. For instance, the state-of-the-art CPs possessing low bandgaps are constructed by connecting electron-rich and electron-poor aromatic moieties in alternating fashion along the polymer backbone, resulting in the so-called push-pull motif, and have found wide spread applications in modern flexible optoelectronics including organic electrochromics, organic field-effect transistors, and organic solar cells [6–11].

Poly(thienylene vinylene) (PTV) polymers, as close analogs of the widely studied polythiophenes (PTs), are a class of prototypical CPs but have received relatively little attention [12]. By insertion of a relatively small double bond, when compared with rigid aromatic rings, between every two thiophene units along the polymer backbone, PTVs possess reduced bandgaps than that of PTs due to the enhanced main-chain coplanarity [13–16]. This enhanced main-chain coplanarity of PTVs also leads to high crystallinity, charge mobility, and environmental stability that are all desired properties for optoelectronic device [17,18]. Furthermore, the recent discovery of activated singlet fission processes in PTVs are especially attractive for overcoming the Shockley–Queisser limit [19,20] in single junction solar cells [21–23]. However, the extremely fast non-radiative exciton decays in typical alkylated PTVs, on the order of ps, render these polymers non-emissive and unsuitable for electronic devices including organic light emitting diodes and organic solar cells [24–26]. It has been theoretically shown that attachment of electron-withdrawing and conjugated side-chains directly to the thienyl rings of PTVs can potentially re-order the excited states, resulting in prolonged excited state lifetimes and enhanced emission properties [27]. However, the traditional synthetic methods, including Gilch-type reactions [28–30], McMurry coupling and Wittig-type reactions [31–33], and cross-coupling reactions [34–37] have not been able to produce PTVs beyond the rudimentary structures that bear only alkyl or

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alkoxy side-chains. We have recently developed a facile methodology based on acyclic diene metathesis (ADMET) [38–45] and post-polymerization modification (PPM) techniques for the preparation of a series of PTVs bearing cross-conjugated aromatic groups on every main-chain thienyl rings [46,47]. Some of these cross-conjugated PTVs show re-emerged fluorescence and improved solar cell performance, but their regio-random (ra) nature have been considered limiting factors on the polymer crystallinity and corresponding device performance.

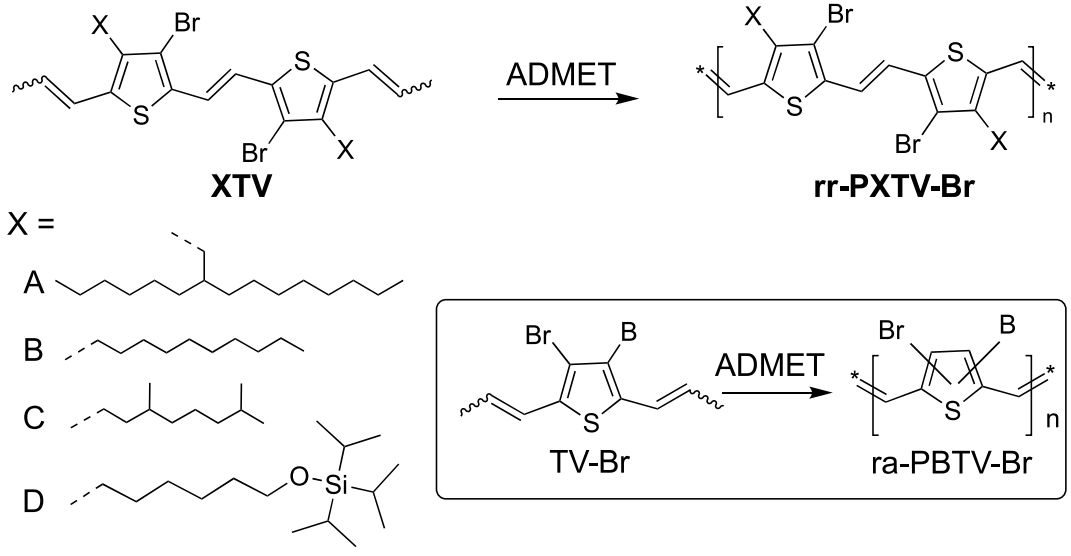
Herein, we report an improved synthetic procedure based on ADMET polymerization of well-defined thienylene vinylene dimers, which leads to regio-regular poly(thienylene vinylene)s (rr-PTVs). We found that linear alkyl chains, which were sufficient for synthesizing high molecular weight ra-PTVs in our previous studies, led to precipitation of rr-PTVs at early reaction stages. Thus, alkyl side-chains with different lengths and branching characteristics were installed on the monomers, and their polymerization behaviors and resulting polymers were studied and compared.

2. Results and discussion

Synthesis of the polymers involved in the current study is summarized in Scheme 1 and detailed synthetic procedures and characterization data are provided in the Experimental Section and Schemes S1 and S2 of the Supporting Information (SI). Four different alkyl side-chains are employed during the synthesis, namely 2-hexyldecyl (A), n-decyl (B), 3,7-dimethyloctyl (C), and 6-triisopropylsilylhexyl (D) groups. Two different synthetic approaches leading up to the dimeric monomers (6) were adopted. Compounds 4A, 4B, and 4C (synthetic procedures in Schemes S1 and SI), all possessing 1-propenyl substituents with mixed *trans* and *cis* configurations (represented by wavy lines in structures) at the 5-thienyl positions, were subjected to alkene metathesis reactions using Grubbs 2nd generation catalyst. By removing the 2-butene byproducts under high vacuum, compounds 5A, 5B, and 5C were obtained in 80–90% isolated yields, respectively. The Br atoms at the 2, 2′ positions were exchanged with Grignard reagents and quenched with anhydrous dimethylformamide (DMF), leading to the bis-aldehyde functionalized dimers 6A, 6B, and 6C. Synthetic yields of these reactions were however unsatisfactorily at ca. 50% after isolation. Simple de-bromination at the 2 and 2′ positions was found to contribute to the formation of major byproducts, indicating insufficient nucleophilicity toward DMF from the di-carboanion intermediates of compounds 5's. Thus, an alternative route was taken in which 5D (Schemes S1 and SI) was converted into 6D in 75% isolated yield. Compounds 6's were converted to the final dimers XTV (X = A, B, C, or D) by installing 1-propenyl groups at the 5 and 5′ positions using Wittig type reactions in ca. 80% isolated yields. The XTV monomers were characterized by ^{1}H and ^{13}C NMR spectroscopy (Figures S21-S28, SI) and their ^{1}H NMR spectra are overlaid in Fig. S1 (SI). All four XTV monomers are mixtures of three stereo-isomers caused by the *cis* and *trans* configurations of the terminal propenyl groups. Based on previous assignments, ATV contains exclusively *trans* propenyl groups, while the other monomers are *cis* dominant but all with significant amount of *trans* double bonds.

These XTV monomers were then subjected to ADMET polymerization. Briefly, the reactions were conducted in 1,2,4-trichlorobenzene at 90 °C under dynamic vacuum of ca. 300 mTorr. Under such conditions, solvents were refluxing in order to efficiently remove the 2-butene byproducts and to drive polymerization processes. Grubbs 2nd generation catalysts were added in aliquots, each of 1 mol% relative to the monomers, every 24 h for a total of 5 days in all cases. The reaction mixtures were then precipitated into a large excess of methanol, and the collected solids from filtrations were purified by Soxhlet extractions with methanol, acetone, hexanes, and finally chloroform. The chloroform solutions were concentrated and precipitated into large excesses of methanol, and the final products were obtained by filtrations followed by drying under high vacuum for 24 h. For comparison and as reported previously [46], a monomer TV-Br (Scheme 1), bearing 3-bromo, 4-n-decyl side-chains and two propenyl groups at the 2,5-positions, was polymerized under identical conditions, giving rise to the regio-random polymer ra-PBTV-Br as shown in Scheme 1. The polymerization process can be monitored qualitatively by the color changes of the reaction mixtures that gradually turn from initially yellow to red, purple, and eventually persistent dark blue, indicating the formation of polymer chains longer than the corresponding conjugation lengths of PTVs. Of the five PTV polymerizations, reaction mixtures of ra-PBTV-Br, rr-PATV-Br, and rr-PDTV-Br proceeded within the first 3 days to persistent dark blue color; while the reaction mixtures of rr-PBTV-Br and rr-PCTV-Br could only reach the color of purple red accompanied by precipitation of insoluble materials. After Soxhlet purification, ra-PBTV-Br, rr-PATV-Br, and rr-PDTV-Br were recovered with over 80% isolated yields and remain soluble in organic solvents including chlorobenzene, tetrahydrofuran, and chloroform. On the other hand, for rr-PBTV-Br and rr-PCTV-Br, significant amount of insoluble materials were left in the Soxhlet thimbles, which could not be dissolved in any solvents even under refluxing conditions. The chloroform soluble fractions were isolated in only ca. 30% yields.

The molecular weights of PTV polymers were estimated by gel



Scheme 1. Structures and synthesis of regio-regular and regio-random PTVs.

permeation chromatography (GPC) against polystyrene standards using chloroform as the eluent. The GPC traces are shown in Fig. S2 (SI) and the results are summarized in Table 1. Consistent with the experimental observations discussed above, rr-PATV-Br and rr-PDTV-Br exhibit relatively high molecular weights with M_n of 10.3 and 12.1 kDa, respectively corresponding to ca. 26 and 28 thienyl units along polymer main-chains. In comparison, the ra-PBTV-Br has an M_n of ca. 14.0 kDa and 42 main-chain thienyl units [46]. On the other hand, the chloroform soluble fractions of rr-PBTV-Br and rr-PCTV-Br show very low M_n values of 1.1 and 1.2 kDa, respectively, corresponding to only oligomers. The insoluble fractions of these two polymers possibly possess higher molecular weights but, judged from the colors of reaction mixtures that could be reached before precipitation happened, they are likely only longer oligomers. These observations, especially the stark contrast between rr-PBTV-Br and ra-PBTV-Br, can be explained by the reduced solubility, and potentially higher crystallinity, of regio-regular PTVs than their regio-random analogs with similar alkyl side-chains and molecular weights.

In order to confirm the regio-regularity of rr-PXTV-Br polymers, they were characterized by ^{1}H and ^{13}C NMR spectroscopy (Figures S29-S35, SI) except for the ^{13}C NMR spectrum of rr-PBTV-Br due to extremely low solubility; and overlays of ^{1}H NMR spectra of the discussed polymers are shown in Fig. 1. Signals from the monomers, those from the propenyl groups in particular, have largely disappeared for ra-PBTV-Br, rr-PATV-Br, and rr-PDTV-Br, but can still be observed for rr-PBTV-Br and rr-PCTV-Br, consistent with the low molecular weights for the later. Due to the oligomeric nature and weak signals caused by low solubility for rr-PBTV-Br and rr-PCTV-Br, we will focus our discussions on NMR spectra of the other three polymers. All three polymers display similar and broad NMR signal patterns, except for rr-PDTV-Br having a signal at ca. 3.7 ppm corresponding to the side-chain -C$\boldsymbol{H}_2$OSi^{i}Pr$_3$ groups. The major difference observed in Fig. 1 is the main-chain double bond signals among the polymers (as inserts in Fig. 1). ra-PBTV-Br display a broad signal between 7.2 and 6.5 ppm, while for rr-PATV-Br and rr-PDTV-Br two distinct signals are observed at ca. 7.0 and 6.8 ppm, respectively. We ascribe such differences to the polymer regio-regularity. As seen in the structure of ra-PBTV-Br (Fig. 1), the main-chain double bond protons have mixed chemical environment caused by the irregular placement of Br and alkyl side-groups on the main-chain thienyl units. On the other hand, for both rr-PATV-Br and rr-PDTV-Br, two chemically distinct double bonds are present along polymer main-chains, *i.e.*, H$_b$'s between two Br substituents and H$_c$'s between two alkyl substituents, leading to the well-resolved ^{1}H NMR signals for these polymers. Based on double bond signals for the XTV monomers (Figs. S1 and SI), for which the central double bond signals appear around 7 ppm, we assign the peaks at ca. 7.0 ppm to H$_b$ and those at ca. 6.8 ppm to H$_c$ for both rr-PATV-Br and rr-PDTV-Br. Furthermore, the ^{13}C NMR spectra of both rr-PATV-Br and rr-PDTV-Br (Figure S30 and S35, SI) displayed a total of six relatively sharp signals in the aromatic region, corresponding to four signals from the thienyl rings and the other two from double bonds C$_b$ and C$_c$, respectively. The NMR observations confirm the regio-regularity for both rr-PATV-Br and rr-PDTV-Br, and suggesting that metathesis of the central double bonds in XTV monomers is insignificant during the polymerization processes. To further corroborate this point, we attempted ADMET reactions on mixtures of equal amount of monomers 5B and 5D under identical conditions as in the polymerization. We did not observe any reactions between these two monomers, suggesting that the central double bonds are indeed unreactive under the ADMET conditions for current studies.

Table 1
Summary of the physical and electronic properties of rr-PXTV-Br's.

Polymer Name	M_n[a] (kDa)	$Đ$[b]	DP[c]	BG_{opt}[d] (eV)
rr-PATV-Br	10.3	1.5	26	1.73
rr-PBTV-Br	2.0	1.1	6	1.90
rr-PCTV-Br	3.8	1.2	12	1.81
rr-PDTV-Br	12.1	1.7	28	1.72

[a] Number-average molecular weight.
[b] Polydispersity index.
[c] Degree of polymerization as the average number of thienyl rings along polymer main-chains calculated from M_n values.
[d] Optical bandgaps calculated from absorption onsets of the polymers in chlorobenzene solutions.

Electronic properties of the rr-PXTV-Br polymers were investigated by UV–vis absorption spectroscopy in dilute chlorobenzene solutions (10^{-5} M repeat units), and the absorption profiles are shown in Fig. 2. The absorption maxima (λ_{max}) are 592 nm, 560 nm, 580 nm, and 622 nm respectively for rr-PATV-Br, rr-PBTV-Br, rr-PCTV-Br, and rr-PDTV-Br, and the optical bandgaps are estimated from absorption edges to be 1.73 eV, 1.90 eV, 1.81 eV, and 1.72 eV (Table 1), respectively. These observations are consistent with the GPC results, in that increasing polymer DP values correspondingly leads to red-shifts in λ_{max} and decreases in optical bandgaps. The bandgaps at ca. 1.73 eV and 1.72 eV for both rr-PATV-Br and rr-PDTV-Br are similar to that observed for ra-PBTV-Br at ca. 1.71 eV, confirming the high molecular weight nature of these polymers with main-chains longer than the persistence length of PTVs. It is noticeable that the line shapes of absorption profiles are structured to various extents. Both rr-PATV-Br and rr-PCTV-Br display similar profiles while rr-PBTV-Br and rr-PDTV-Br show similar and more structured absorption lines. This indicates aggregation of polymer chains even in dilute solutions, which is relatively less pronounced in PTVs bearing branched side-chains and more significant in those having linear side-chains.

To further probe such aggregation effects, we performed variable temperature ^{1}H NMR measurements on rr-PDTV-Br and the results are summarized in Fig. 3. As the temperature is increased gradually from 290 K to 340 K, there seems to be negligible changes in the ^{1}H NMR spectra in terms of peak resolutions and line shapes. Since we needed relatively higher concentrations for NMR studies than those in absorption studies, we suspect that the aggregation states of PTVs at such high concentrations are less sensitive to temperature changes.

To further probe the solid-state morphologies of these PTVs, we have performed powder X-ray diffraction (XRD) measurements and the results are summarized in Fig. 4. All four polymers display largely amorphous nature with only broad signals from the glass substrates, except for a few relatively sharp signals from rr-PBTV-Br and rr-PCTV-Br that are likely due to better packing of short oligomers. Amorphous nature of these PTVs is also demonstrated from absorption profiles in the solid state. As shown in Fig. S3 (SI), the absorption profiles of rr-PDTV-Br in both dilute solution and as thin film are very similar, except that the latter is slightly broader. The lack of significant red-shift and appearance of more structured profiles in thin films suggest similar polymer packing structures in both solutions and solid state. In our previous studies, we have clearly observed a (100) peak at ca. 5.25° (2θ) for ra-PBTV-Br [46], the lack of clear XRD signals in the new regio-regular polymers are thus ascribed to the low molecular weights for rr-PBTV-Br and rr-PCTV-Br, long and branched side-chains for rr-PATV-Br, and bulky silylether groups for rr-PDTV-Br, respectively. We attempted to remove the TIPS groups in rr-PDTV-Br using tetrabutylammonium fluoride and KF/18-crown-6 in various solvents, but only observed loss of blue colors of the reaction mixtures to red or yellow, accompanied by precipitation of the polymer. We are currently looking for ways to analyze the intractable materials resulting from these reactions in order to better understand mechanisms behind such unusual observations.

3. Conclusion

In summary, we have developed a new synthetic method for the preparation of regio-regular PTVs from symmetric dimers by ADMET polymerization. The polymerization progresses are heavily influenced by the alkyl side-chains and only long-branched and bulky side-chains led to high molecular weight polymers. Regio-regularity of these PTVs

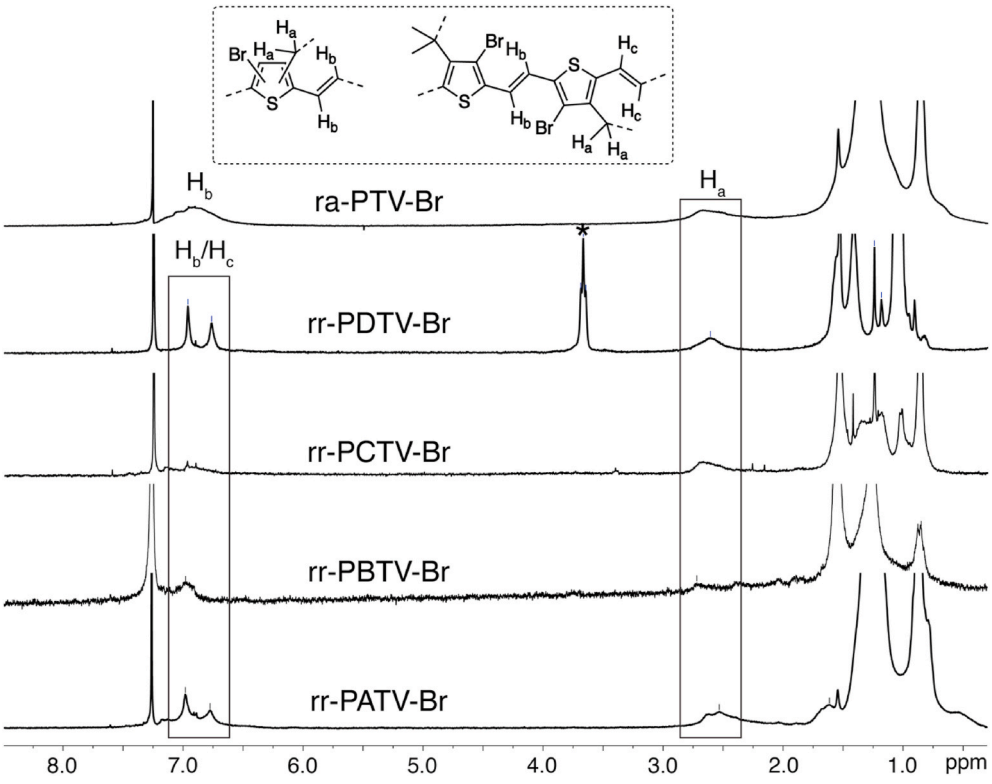


Fig. 1. ^{1}H NMR spectra of rr-PXTV-Br and ra-PTV-Br polymers in $CDCl_3$. (*) signal of -C***H***$_2$OSi^{i}Pr$_3$ groups in rr-PDTV-Br.

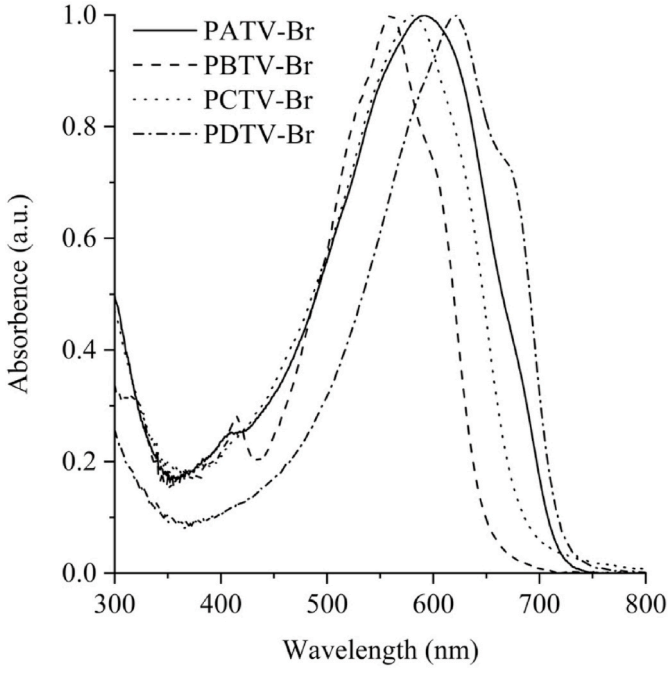


Fig. 2. UV–vis absorption profiles of rr-PXTV-Br's in chlorobenzene solutions (10^{-5} M repeat units).

is confirmed by NMR spectroscopy and aggregation behaviors are observed in dilute solutions. Although XRD experiments did not reveal solid-state ordering of these polymers, the polymerization behaviors and absorption profiles suggest higher aggregation tendencies of the regio-regular PTVs over their regio-random analogs. We are currently investigating the possibility of producing regio-regular PTVs bearing solubilizing side-chains without significantly disrupting packing of polymer main-chains in the solid state, thus leading to better crystallinity.

4. Experimental Section

4.1. Materials and general methods

All chemical reagents and solvents were used as received from Sigma-Aldrich or Alfa Aesar unless otherwise noted. THF was freshly distilled from Na/benzophenone. 300.13 MHz ^{1}H and 75.48 MHz ^{13}C NMR spectra were recorded on a Bruker Avance III Solution 300 spectrometer. All solution ^{1}H and ^{13}C NMR spectra were referenced internally to residual solvent signals. Ultraviolet–visible (UV–vis) absorption spectra were obtained on a Shimadzu UV-2401 PC spectrometer over a wavelength range of 290–900 nm. X-ray diffraction (XRD) data were obtained by using a Rigaku SmartLab diffractometer in Bragg–Brentano mode using Cu Kα radiation and a D/tex 1-dimensional detector. A nickel filter was used to remove the Cu Kβ radiation component. Data were collected over a 2θ range of 3°–40° using a 0.02° step size at a scan rate of 6.2°/min. Size exclusion chromatography (SEC) analyses were performed in chloroform with 0.5% (v/v) triethylamine (1 mL/min) using a Waters Breeze system equipped with a 2707 autosampler, a 1515 isocratic HPLC pump and a 2414 refractive index detector. Two styragel columns (Polymer Laboratories; 5 μm Mix-C), which were kept in a column heater at 35 °C, were used for separation. 6-Bromohexyloxy)triisopropylsilane [48], 2,5-dibromo-3-(2-hexyldecyl)thiophene [49], 2,5-dibromo-3-decylthiophene [44], and 2,5-dibromo-3-(3,7-dimethyloctyl)thiophene [50] were synthesized according to literature procedures.

4.2. Synthetic details (compound labelling in Scheme S1)

Triisopropyl(6-(thiophen-3-yl)hexyloxy)silane (1D). To a suspension of magnesium turnings (5.93 g, 0.24 mol) in THF (300 mL) was added dropwise (6-bromohexyloxy)triisopropylsilane (41.14 g, 0.122 mol)

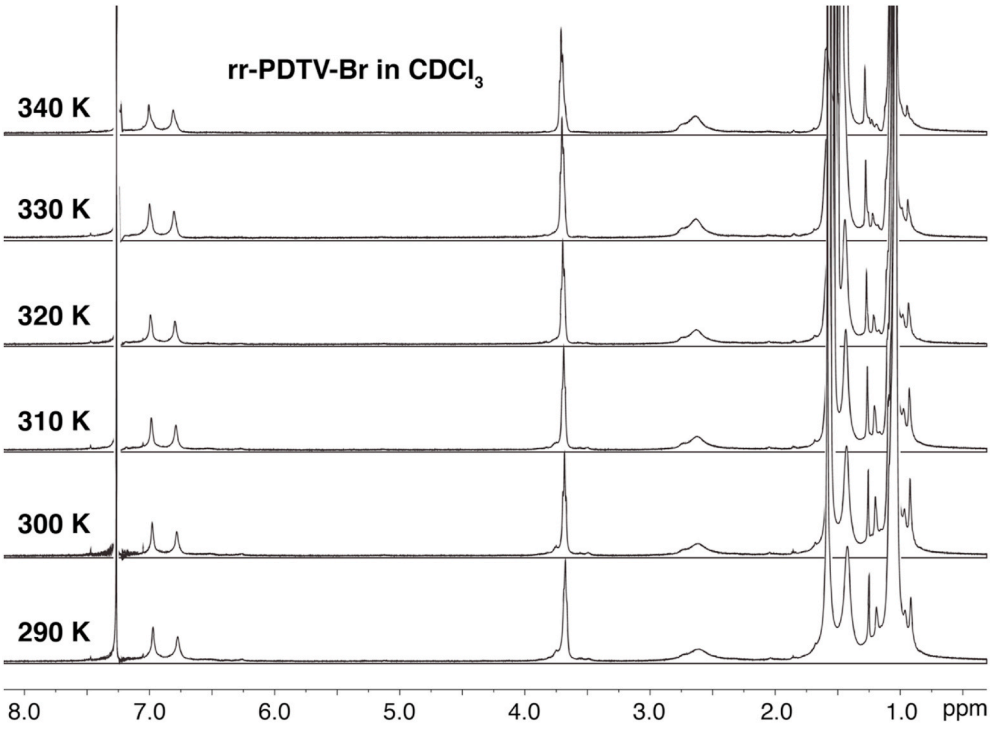


Fig. 3. ^{1}H NMR spectra of rr-PDTV-Br in $CDCl_3$ at variable temperatures.

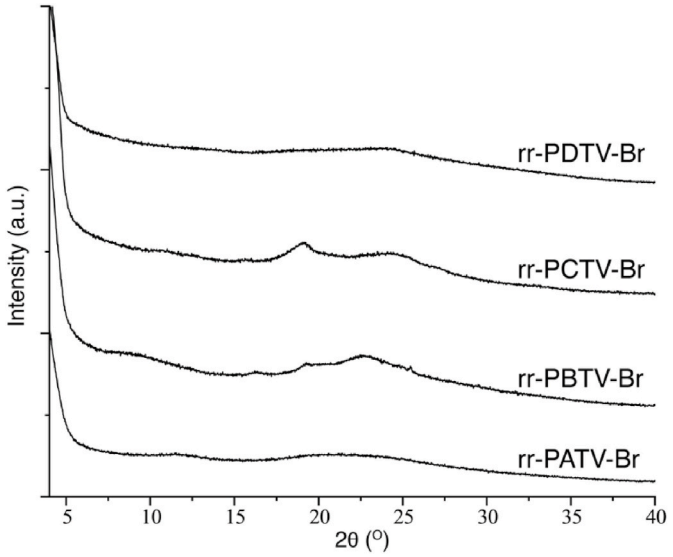


Fig. 4. XRD profiles of rr-PXTV-Br polymer powders.

under nitrogen atmosphere and the mixture was stirred for 2 h. The mixture was then transferred by cannula to a suspension of 3-bromothiophene (18.07 g, 111 mmol) and [1,3-bis(diphenylphosphino)propane]-dichloronickel(II) ($Ni(dppp)Cl_2$) (0.33 g, 0.61 mmol) in THF (200 mL) at 0 °C. The reaction mixture was gradually warmed up to r.t. and stirred overnight before quenched with water. A saturated solution of NH_4Cl (100 mL) was then added to the mixture and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with saturated NaCl and dried over anhydrous Na_2SO_4. After solvent removal under reduced pressure, the residue was purified by vacuum distillation to give the title compound as a colorless liquid (28.1 g, 82.5 mmol, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.95–1.19 (m, 21H), 1.30–1.45 (m, 4H), 1.47–1.70 (m, 4H), 2.63 (t, 2H), 3.67 (t, 2H), 6.92 (m, 2H), 7.23 (m, 1H).

(6-(2,5-Dibromothiophen-3-yl)hexyloxy)triisopropylsilane (2D). To a solution of compound 1D (14.0 g, 41.1 mmol) in 250 mL DMF was added dropwise *N*-bromosuccinimide (NBS) (14.78 g, 83.0 mmol) in 50 mL DMF at 0 °C. The mixture was warmed to r.t., stirred overnight, and then quenched with a saturated aqueous solution of $NaHSO_3$. After standard aqueous workup and solvent removal under reduced pressure, low molecular weight impurities were removed by vacuum distillation and the remaining pot was purified by a short column of silica gel using hexanes as eluent to give 2D as a light-yellow oil (17.20 g, 34.5 mmol, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.95–1.17 (m, 21H), 1.29–1.45 (m, 4H), 1.46–1.66 (m, 4H), 2.51 (t, 2H), 3.67 (t, 2H), 6.77 (s,1H).

General procedure for preparation compounds 3 A, B, C, or D: To a solution of 2,5-dibromo-3-alkylthiophene (1 eq.) in THF (c = 0.05 mM with respect to (w.r.t) 2,5-dibromo-3-alkylthiophene) was added dropwise lithium diisopropylamide (LDA) (2.0 M, 1.1 eq.) at −78 °C. After stirring for 15 min, the temperature was gradually raised to 0 °C, and then to r.t. After stirring for 30 min, the temperature was reduced again to 0 °C, DMF (1.2 eq.) was added dropwise to the mixture. After then the mixture was warmed to r.t. and stirred for 1 h. The reaction mixture was poured into water, washed with 1 M HCl, and extracted with chloroform. The collected organic fractions were dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum.

3,5-Dibromo-4-(2-hexyldecyl)thiophene-2-carbaldehyde (3A). The use of 2,5-dibromo-3-(2-hexyldecyl)thiophene (10 g, 21.4 mmol), LDA (2.0 M, 11.8 mL, 23.6 mmol), and DMF (26.0 mmol, 1.90 g, 2.0 mL) produced the crude 3A, which was purified by silica gel column chromatography using hexanes: DCM (80:20) as eluent to give the pure product as a colorless oil (9.19 g, 18.59 mmol, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.81–0.98 (m, 6H), 1.14–1.1.48 (m, 24H), 1.73–1.87 (m, 1H), 2.61 (d, 2H), 9.89 (s, 1H).

3,5-Dibromo-4-decylthiophene-2-carbaldehyde (3B). The use of 2,5-dibromo-3-decylthiophene (10 g, 26.2 mmol), LDA (2.0 M, 14.4 mL, 28.8 mmol), and DMF (31.4 mmol, 2.29 g, 2.4 mL) produced the crude 3B, which was purified by silica gel column chromatography using hexanes: DCM (80:20) as eluent to give the pure product as a colorless

oil (8.4 g, 20.5 mmol, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.76–0.98 (t, 3H),1.15–1.45 (m, 14H), 1.47–1.60 (m, 2H), 2.61–2.73 (t, 2H), 9.88 (s, 1H).

3,5-Dibromo-4-(3,7-dimethyloctyl)thiophene-2-carbaldehyde (3C). The use of 2,5-dibromo-3-(3,7-dimethyloctyl)thiophene (10 g, 26.2 mmol), LDA (2.0 M, 14.4 mL, 28.8 mmol), and DMF (31.4 mmol, 2.3 g, 2.4 mL) produced the crude 3C, which was purified by silica gel column chromatography using hexane: DCM (80:20) as eluent to give the pure product as a colorless oil (9.2 g, 22.4 mmol, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.87 (d, 6H), 0.98 (d, 3H), 1.1–1.68 (m, 10H), 2.56–2.79 (m, 2H), 9.88 (s, 1H).

3,5-Dibromo-4-(6-(triisopropylsilyloxy)hexyl)thiophene-2-carbaldehyde (3D): The use of 2D (27.00 g, 54.2 mmol), LDA (2.0 M, 29.8 mL, 59.6 mmol), and DMF (65.0 mmol, 4.8 mL) produced the crude 3D, which was purified by silica gel column chromatography using hexanes: diethyl ether (93:7) as eluent to give the pure product as colorless oil (25.0 g, 47.5 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.95–1.22 (m, 21H), 1.32–1.49 (m, 4H), 1.50–1.74 (m, 4H), 2.69 (t, 2H), 3.68 (t, 2H), 9.88 (s,1H).

General procedure for preparation compounds (4A, B, C, or D): In a flame-dried 2-neck round bottom flask equipped with a condenser under nitrogen, ethyltriphenylphosphonium bromide (1.2 eq) was stirred in THF (c = 0.05 mM w.r.t starting material (SM) at 0 °C. Potassium t-butoxide (1.2 eq.) dissolved in a small volume of THF was added portion-wise to the reaction mixture. After 2 h of stirring at 0 °C, compound 3X (1 eq.) in a small amount of THF was added portion-wise to the mixture. The reaction mixture was warmed to r.t. and refluxed for 2 h. The solvent was removed under reduced pressure to give the crude product as a mixture of cis and trans isomers.

2,4-Dibromo-3-(2-hexyldecyl)-5-(prop-1-enyl)thiophene (4A): The use of 3A (5.00 g, 10.1 mmol), ethyltriphenylphosphonium bromide (4.51 g, 12.1 mmol), and potassium t-butoxide (1.36 g, 12.1 mmol) produced the crude 4A, which was purified by silica gel column chromatography using hexanes as eluent to give the pure product as a light yellow oil (4.15 g, 8.2 mmol, 81%): ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.81–0.96 (m, 6H), 1.13–1.41 (m, 24H), 1.72–2.00 (m, 4H), 2.45–2.60 (m, 2H), 5.75–6.12 (m, 1H), 6.50–6.64 (m, 1H).

2,4-Dibromo-3-decyl-5-(prop-1-enyl)thiophene (4B). The use of 3B (4.2 g, 10.2 mmol), ethyltriphenylphosphonium bromide (4.56 g, 12.3 mmol), and potassium tertiary butoxide (1.38 g, 12.3 mmol) produced the crude 4B, which was purified by silica gel column chromatography using hexanes as eluent to give the named product as light yellow oil (3.70 g, 8.8 mmol, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.82–0.94 (m, 3H), 1.17–1.43 (m, 14H),1.44–1.60 (m, 2H), 1.82–1.98 (m, 3H), 2.52–2.69 (m, 2H), 5.73–6.13 (m, 1H), 6.48–6.65 (m, 1H).

2,4-Dibromo-3-(3,7-dimethyloctyl)-5-(prop-1-enyl)thiophene (4C). The use of 3C (6.35 g, 15.5 mmol), ethyltriphenylphosphonium bromide (6.90 g, 18.6 mmol), and potassium t-butoxide (2.09 g, 18.6 mmol) produced the crude 4C, which was purified by silica gel column chromatography using hexanes as eluent to give the named product as light-yellow oil (5.50 g, 13.0 mmol, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.87 (d, 6H), 0.92–1.02 (m, 3H), 1.07–1.65 (m, 10H), 1.82–1.97 (m, 3H), 2.46–2.72 (m, 2H), 5.76–6.12 (m, 1H), 6.49–6.62 (m, 1H).

(6-(2,4-Dibromo-5-(prop-1-enyl)thiophen-3-yl)hexyloxy)triisopropylsilane (4D). The use of 3D (25 g, 47.5 mmol), ethyltriphenylphosphonium bromide (21.16 g, 57.0 mmol), and potassium t-butoxide (6.39 g, 57.0 mmol) produced the crude 4D, which was purified by silica gel column chromatography using hexanes as eluent to give the named product as light-yellow oil (20.90 g, 38.8 mmol, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.95–1.18 (m, 21H), 1.31–1.46 (m, 4H), 1.47–1.64 (m, 4H), 1.8–1.98 (m, 3H), 2.52–2.70 (m, 2H), 3.67 (t, 2H), 5.76–6.12 (m, 1H), 6.48–6.63 (m, 1H).

General procedure for preparation compounds (5A, B, C or 6D): In a flame dried 2-neck flask connected to condenser, plugged with rubric septum, and under inert conditions. Compound (4A, B, C or 5D) (1 eq.), copper iodide (0.1 eq.), and Grubbs catalyst second generation (1 mol%) were mixed in 1, 2, 4-trichlorobenzene (c = 1 mmol/1 mL w.r.t SM.) and transferred to reaction flask. The system was kept under vacuum and the condenser temperature decreased to 10 °C using a circulating chilling system. The temperature of the reaction mixture was raised to 50 °C and stirred for 24 h. The mixture cooled down to room temperature and another portion of Grubbs catalyst second generation (0.5 mol% dissolved in 0.5 mL of solvent) was added under inert conditions. The reaction mixture temperature was gradually raised over 4 h to 90 °C under vacuum, while the condenser temperature was maintained at 5 °C. The mixture was stirred under these conditions for 24 h. After cooling to r.t. the slurry was transferred into stirring methanol (c = 3 mmol/50 mL w.r.t SM.) to precipitate the crude product.

1,2-Bis(3,5-dibromo-4-(2-hexyldecyl)thiophen-2-yl)ethene (5A). The use of 4A (2.00 g, 3.95 mmol), CuI (75 mg, 0.40 mmol), Grubbs second generation (34 mg, 0.04 mmol) for the 1st 24 h, and the Grubbs second generation (17 mg, 0.02 mmol) for the 2nd 24 h, produced the crude 5A, which was filtered, dried under vacuum, and purified by silica gel column chromatography using hexanes as eluent to give the pure product as yellow solid (1.70 g, 1.78 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.77–1.00 (m, 12H), 1.11–1.51 (m, 48H), 1.71–1.86 (m, 2H), 2.49–2.61 (m, 4H), 6.99 (s, 2H).

1,2-Bis(3,5-dibromo-4-decylthiophen-2-yl)ethene (5B). The use of 4B (2.50 g, 5.92 mmol), CuI (112 mg, 0.59 mmol), Grubbs second generation (50 mg, 0.06 mmol) for the first 24 h, and the Grubbs second generation (25 mg, 0.030 mmol) for the second 24 h produced the crude 5B, which was filtered, dried under vacuum, and purified by silica gel column chromatography using hexanes as eluent to give the named product as yellow solid (1.9 g, 2.41 mmol, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.81–0.95 (m, 6H), 1.11–1.43 (m, 28H), 1.44–1.62 (m, 4H), 2.54–2.67 (m, 4H), 6.98 (s, 2H).

1,2-Bis(3,5-dibromo-4-(3,7-dimethyloctyl)thiophen-2-yl)ethene (5C). The use of 4C (5.0 g, 11.84 mmol), CuI (225 mg, 1.18 mmol), Grubbs second generation (100 mg, 0.118 mmol) for the first 24 h, and the Grubbs second generation (50 mg, 0.059 mmol) for the second 24 h produced the crude 5C, which was filtered, dried under vacuum, and purified by silica gel column chromatography using hexanes as eluent to give the named product as yellow solid (3.90 g, 4.95 mmol, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.82–0.92 (d, 12H), 0.93–1.02 (d, 6H), 1.07–1.63 (m, 20H), 2.50–2.70 (m, 4H), 6.97 (s, 2H).

4-Bromo-5-(2-(3-bromo-5-formyl-4-(6-(triisopropylsilyloxy)hexyl) thiophen-2-yl)vinyl)-3-(6-(triisopropylsilyloxy)hexyl)thiophene-2-carbaldehyde (6D). The use of 5D (3.46 g, 7.10 mmol), CuI (135 mg, 0.71 mmol), Grubbs second generation (60 mg, 0.071 mmol) for the first 24 h, and the Grubbs second generation (30 mg, 0.035 mmol)for the second 24 h produced the crude 6D, which was filtered, dried under vacuum, and purified by silica gel column chromatography using hexanes: DCM 50:50 as eluent to give the pure product as yellow solid (2.44 g, 2.65 mmol, 75%) ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.95–1.17 (m, 42H), 1.34–1.49 (m, 8H), 1.50–1.73 (m, 8H), 2.91 (t, 4H), 3.68 (t, 4H), 7.41 (s, 2H), 10.01 (s, 2H). ^{13}CNMR (75.48 MHz, $CDCl_3$): δ (ppm) = 12.01, 18.03, 25.56, 28.31, 29.13, 30.61, 32.78, 63.23, 117.35, 124.56, 135.82, 144.12, 151.63, 181.32.

General procedure for preparation compounds (6A, B, or C): In a Schlenk flask under an inert atmosphere of nitrogen, compound (5A, B or C) (1 eq.) was dissolved in dry THF (c = 0.05 mM w.r.t SM). The resulting solution was cooled to 0 °C and isopropyl magnesium chloride (2 M, 2.2 eq.) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h, quenched with anhydrous DMF (3 eq.), slowly warmed up to r.t., and stirred overnight. A saturated solution of NH_4Cl was added to the mixture, and the product was extracted with chloroform. All collected organic fractions were washed with saturated NaCl, then dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum to give the crude product.

4-Bromo-5-(2-(3-bromo-5-formyl-4-(2-hexyldecyl)thiophen-2-yl) vinyl)-3-(2-hexyldecyl)thiophene-2-carbaldehyde (6A). The use of 5A

(1.7 g, 1.78 mmol), isopropyl magnesium chloride (2 M, 2.0 mL, 4.92 mmol), lithium chloride (151 mg, 3.55 mmol), and DMF (0.39 g, 0.41 mL,5.34 mmol) give the crude product 6A, which was purified by silica gel column chromatography using hexanes: DCM (70:30) as eluent to give the pure product as a yellow solid (0.68 g, 0.80 mmol, 45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.77–1.01 (m, 12H), 1.12–1.51 (m, 48H), 1.66–1.86 (m, 2H), 2.79 (d, 4H), 7.43 (s, 2H), 9.98 (s, 2H).

4-Bromo-5-(2-(3-bromo-5-formyl-4-decylthiophen-2-yl)vinyl)-3-decylthiophene-2-carbaldehyde (6B). The use of 5B (2.0 g, 2.54 mmol), isopropyl magnesium chloride (2 M, 2.80 mL, 5.59 mmol), lithium chloride (215 mg, 5.08 mmol), and DMF (0.56 g, 0.59 mL,7.62 mmol) give the crude product 6B, which was purified by silica gel column chromatography using hexanes: DCM (70:30) as eluent to give the pure product as yellow solid (1.01 g, 1.47 mmol, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.81–0.93 (m, 6H), 1.16–1.47 (m, 28H), 1.56–1.71 (m, 4H), 2.93–3.03 (m, 4H), 7.42 (s, 2H), 10.01 (s, 2H).

4-Bromo-5-(2-(3-bromo-5-formyl-4-(3,7-dimethyloctyl)thiophen-2-yl)vinyl)-3-(3,7-dimethyloctyl)thiophene-2-carbaldehyde (6C): The use of 5C (2.0 g, 2.54 mmol), isopropyl magnesium chloride (2 M, 2.80 mL, 5.58 mmol), lithium chloride (215 mg, 5.07 mmol), and DMF (0.56 g, 0.59 mL,7.62 mmol) give the crude product 6C, which was purified by silica gel column chromatography using hexanes: DCM (70:30) as eluent to give the pure product as yellow solid (0.80 g, 1.17 mmol, 46%) ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.80–0.94 (d, 12H), 0.94–1.06 (d, 6H), 1.08–1.69 (m, 20H), 2.86–3.07 (m, 4H), 7.41 (s, 2H), 10.01 (s, 2H).

General procedure for preparation of compounds XTV (X: A, B, C, or D): In a flame-dried 2-neck round bottom flask connected to a condenser and under an atmosphere of nitrogen, ethyltriphenylphosphonium bromide (2.4 eq) was stirred with THF (c = 0.05 mmoL/ml w.r.t SM) at 0 °C. After then, potassium tert-butoxide (2.4 eq.) dissolved in a small volume of THF was added portion wise to the reaction mixture. After 2 h of stirring at 0 °C, compound 6x (1 eq.) in a small amount of THF was added dropwise and the reaction mixture was allowed to warm to r.t., then, stirred overnight. The solvent was removed under reduced pressure to give the crude product as a mixture of cis and trans isomers.

3-Bromo-2-(2-(3-bromo-4-(2-hexyldecyl)-5-(prop-1-enyl)thiophen-2-yl)vinyl)-4-(2-hexyldecyl)-5-(prop-1-enyl)thiophene (ATV). The use of 6A (0.485 g, 0.567 mmol), ethyltriphenylphosphonium bromide (0.505 g, 1.361 mmol), and potassium tertiary butoxide (0.153 g, 1.361 mmol) produced the crude ATV, which was purified by silica gel column chromatography using hexanes as eluent to give the pure product as yellow solid (0.393 g, 0.447 mmol, 79%) ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.78–0.94 (m, 12H), 1.11–1.42 (m, 48H), 1.58–1.75 (m, 2H), 1.83–2.06 (m, 6H), 2.53 (d, 4H), 5.65–6.16 (m, 2H), 6.39–6.59 (m, 2H), 6.98–7.15 (m, 2H).). ^{13}CNMR (75.48 MHz, $CDCl_3$): δ (ppm) = 14.14, 18.66, 22.70, 26.53, 29.53, 29.37, 29.62, 29.69, 30.00, 31.92, 32.94, 33.24, 33.29, 38.10, 115.46, 121.32, 123.06, 126.93, 133.14, 135.79, 137.23.

3-Bromo-2-(2-(3-bromo-4-decyl-5-(prop-1-enyl)thiophen-2-yl) vinyl)-4-decyl-5-(prop-1-enyl)thiophene (BTV). The use of 6B (0.450 g, 0.655 mmol), ethyltriphenylphosphonium bromide (0.584 g, 1.573 mmol), and potassium tertiary butoxide (0.177 g, 1.573 mmol) produced the crude BTV, which was purified by silica gel column chromatography using hexanes as eluent to give the pure product as yellow solid (0.377 g, 0.530 mmol, 81%) ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.77–0.98 (m, 6H), 1.14–1.42 (m, 28H), 1.42–1.62 (m, 4H), 1.86–2.09 (m, 6H), 2.54–2.69 (m, 4H), 5.70–6.16 (m, 2H), 6.45–6.58 (m, 2H), 7.04–7.19 (m, 2H).). ^{13}CNMR (75.48 MHz, $CDCl_3$): δ (ppm) = 14.12, 15.37, 18.64, 22.69, 28.11, 28.53, 29.35, 29.42, 29.47, 29.61, 29.73, 29.88, 31.91, 114.96, 115.18, 120.93, 121.00, 121.14, 121.22, 122.64, 126.76, 127.06, 132.78, 133.28, 134.92, 134.96, 135.11, 138.07, 140.07.

3-Bromo-2-(2-(3-bromo-4-(3,7-dimethyloctyl)-5-(prop-1-enyl)thiophen-2-yl)vinyl)-4-(3,7-dimethyloctyl)-5-(prop-1-enyl)thiophene (CTV). The use of 6C (0.750 g, 1.092 mmol), ethyltriphenylphosphonium bromide (0.973 g, 2.620 mmol), and potassium tertiary butoxide (0.294 g, 2.620 mmol) produced the crude CTV, which was purified by silica gel column chromatography using hexanes as eluent to give the named product as yellow solid (0.598 g, 0.841 mmol, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.82–0.91 (d, 12H), 0.92–1.01 (m, 6H), 1.08–1.61 (m, 20H), 1.87–2.07 (m, 6H), 2.49–2.74 (m, 4H), 5.72–6.17 (m, 2H), 6.44–6.57 (m, 2H), 7.04–7.17 (m, 2H). ^{13}CNMR (75.48 MHz, $CDCl_3$): δ (ppm) = 15.39, 18.67, 19.63, 22.65, 22.72, 24.70, 25.79, 26.20, 28.01, 32.85, 32.91, 36.70, 36.87, 39.31, 114.88, 115.10, 121.00, 121.21, 122.53, 126.84, 127.13, 132.57, 133.33, 134.90, 135.01, 138.32, 140.31.

3-Bromo-2-(2-(3-bromo-5-(prop-1-enyl)-4-(6-(triisopropylsilyloxy) hexyl)thiophen-2-yl)vinyl)-5-(prop-1-enyl)-4-(6-(triisopropylsilyloxy) hexyl)thiophene (DTV). The use of 6D (0.571 g, 0.621 mmol), ethyltriphenylphosphonium bromide (0.553 g, 1.490 mmol), and potassium tertiary butoxide (0.167 g, 1.49 mmol) produced the crude DTV-Br, which was purified by silica gel column chromatography using hexanes as eluent to give the named product as yellow solid (0.495 g, 0.525 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.91–1.21 (m, 42H), 1.30–1.65 (m, 16H), 1.84–2.09 (m, 6H), 2.54–2.70 (m, 4H), 3.61–3.74 (m, 4H), 5.72–6.15 (m, 2H), 6.45–6.58 (m, 2H), 7.04–7.18 (m, 2H). ^{13}CNMR (75.48 MHz, $CDCl_3$): δ (ppm) = 12.03, 15.37, 18.05, 18.63, 25.65, 28.07, 28.46, 29.20, 29.23, 29.74, 29.91, 32.93, 63.39, 114.95, 115.17, 120.94, 121.01, 121.12, 121.16, 121.22, 122.63, 126.77, 127.07, 132.79, 132.83, 133.27, 133.31, 134.95, 134.99, 135.13, 135.16, 137.97, 139.97.

General procedure for preparation of polymers (rr-PXTV-Br): In a flame dried two-neck flask connected to a condenser, and under inert condition were added XDTV (1eq.), copper iodide (0.1 eq), and Grubbs second-generation catalyst (0.5 mol % w.r.t SM) in a 1,2,4-trichlorobenzene solvent (c = 0.25 M w.r.t SM). After applying a vacuum, the temperature of the condenser was reduced to 7 °C using a circulating chiller, and the reaction mixture temperature was raised to 50 °C, then it was left under stirring for 24 h. After cooling down, and under inert condition, (0.5 mol % w.r.t SM) of Grubbs second-generation catalyst in a small amount of solvent was added to the reaction mixture which was stirred at the same previously mentioned conditions for another 24 h. After cooling down to room temperature and under inert conditions (0.5 mol % w.r.t SM) of Grubbs second-generation catalyst in a small amount of solvent was added to the mixture. After applying a vacuum, the temperature was raised to 90 °C over a period of 8 h and the reaction mixture was stirred for 24 h. The last step was repeated two more times, as the whole process lasted for five days. Finally, the reaction mixture was discharged into methanol to precipitate the polymeric product.

rr-PATV-Br. The use of ATV (250 mg, 0.284 mmol), copper iodide (5 mg, 0.028 mmol), and five additions of Grubbs second-generation each addition (~1 mg, 0.0014 mmol) for five days produced the crude rr-PATV-Br. After further filtration and drying under vacuum, the product was purified by Soxhlet extraction using methanol, acetone, and chloroform to give a black solid polymeric material (188 mg, 0.228 mmol, 80%). SEC ($CHCl_3$, 1 mL/min): M_n = 10.3 kDa, M_w = 15.5 kDa, $Đ$ = 1.5. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.60–0.97 (m, 12H), 0.99–1.79 (m, 50H), 2.25–2.86 (m, 4H), 6.59–7.18 (m, 4H).). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ (ppm) = 14.13, 22.74, 26.68, 29.46, 29.74, 30.12, 31.97, 33.32, 38.68, 116.55, 119.70, 121.10, 134.70, 135.87, 140.15.

rr-PBTV-Br. The use of BTV (320 mg, 0.450 mmol), copper iodide (~9 mg, 0.045 mmol), and five additions of Grubbs second-generation each addition (2 mg, 0.0023 mmol) for five days produced the crude rr-PBTV-Br. After further filtration and drying under vacuum, the product was purified by Soxhlet extraction using methanol, acetone, and chloroform to give a black solid polymeric material (90 mg, 0.137 mmol, 30%). SEC ($CHCl_3$, 1 mL/min): M_n = 2.0 kDa, M_w = 2.2 kDa, $Đ$ = 1.1. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.75–0.97 (m, 6H), 1.13–1.75 (m, 32H), 2.51–2.83 (m, 4H), 6.93–7.23 (m, 4H).

rr-PCTV-Br. The use of CTV (650 mg, 0.914 mmol), copper iodide (17 mg, 0.091 mmol), and five additions of Grubbs second-generation

each addition (4 mg, 0.0046 mmol) for five days produced the crude rr-PCTV-Br. After further filtration and drying under vacuum, the product was purified by Soxhlet extraction using methanol, acetone, and chloroform to give a black solid polymeric material (170 mg, 0.260 mmol, 28%). SEC ($CHCl_3$, 1 mL/min): $M_n = 3.8$ kDa, $M_w = 4.6$ kDa, $Đ = 1.2$. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.52–1.85 (m, 38H), 2.20–2.89 (m, 4H), 6.48–7.17 (m, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ (ppm) = 19.68, 22.70, 24.75, 26.07, 28.02, 29.71, 32.82, 36.88, 39.32, 115.94, 119.48, 121.26, 134.37, 134.83, 141.34.

rr-PDTV-Br. The use of CTV (250 mg, 0.265 mmol), copper iodide (5 mg, 0.027 mmol), and five additions of Grubbs second-generation each addition (1 mg, 0.0013 mmol) for five days produced the crude rr-PDTV-Br. After further filtration and drying under vacuum, the product was purified by Soxhlet extraction using methanol, acetone, and chloroform to give a black solid polymeric material (198 mg, 0.223 mmol, 84%). SEC ($CHCl_3$, 1 mL/min): $M_n = 12.1$ kDa, $M_w = 20.6$ kDa, $Đ = 1.7$. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.93–1.10 (m, 42H), 1.21–1.74 (m, 16H), 2.19–3.01 (s, 4H), 3.53–3.83 (t, 4H), 6.58–7.14 (m, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ (ppm) = 12.04, 18.07, 25.78, 29.24, 29.71, 30.16, 32.98, 63.41, 116.02, 119.45, 121.12, 134.93, 135.24, 140.85.

CRediT authorship contribution statement

Yousef M. Katba-Bader: Data curation, Writing – original draft. **Lingyao Meng:** Data curation. **Chao Guan:** Data curation. **Yang Qin:** Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2021.124150.

References

[1] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)x, J. Chem. Soc. Chem. Commun. (1977) 578–580.
[2] A.J. Heeger, Semiconducting and metallic polymers: the fourth generation of polymeric materials (Nobel lecture), Angew. Chem. Int. Ed. 40 (2001) 2591–2611.
[3] A.G. MacDiarmid, "Synthetic metals": a novel role for organic polymers (Nobel lecture), Angew. Chem. Int. Ed. 40 (2001) 2581–2590.
[4] H. Shirakawa, The discovery of polyacetylene film: the dawning of an era of conducting polymers (Nobel lecture), Angew. Chem. Int. Ed. 40 (2001) 2574–2580.
[5] T.A. Skotheim, J.R. Reynolds, Handbook of Conducting Polymers, third ed., 2 Volume Set, CRC Press, Boca Raton, 2007.
[6] B.C. Thompson, J.M.J. Fréchet, Polymer-fullerene composite solar cells, Angew. Chem. Int. Ed. 47 (2008) 58–77.
[7] L. Dou, Y. Liu, Z. Hong, G. Li, Y. Yang, Low-bandgap near-IR conjugated polymers/molecules for organic electronics, Chem. Rev. 115 (2015) 12633–12665.
[8] A.A. Argun, P.-H. Aubert, B.C. Thompson, I. Schwendeman, C.L. Gaupp, J. Hwang, N.J. Pinto, D.B. Tanner, A.G. MacDiarmid, J.R. Reynolds, Multicolored electrochromism in polymers: structures and devices, Chem. Mater. 16 (2004) 4401–4412.
[9] R.J. Mortimer, A.L. Dyer, J.R. Reynolds, Electrochromic organic and polymeric materials for display applications, Displays 27 (2006) 2–18.
[10] H. Dong, C. Wang, W. Hu, High performance organic semiconductors for field-effect transistors, Chem. Commun. 46 (2010) 5211–5222.
[11] W. Wu, Y. Liu, D. Zhu, π-Conjugated molecules with fused rings for organic field-effect transistors: design, synthesis and applications, Chem. Soc. Rev. 39 (2010) 1489–1502.
[12] Z. Zhang, W. He, Y. Qin, Selenium and tellurium containing conjugated polymers, in: T. Baumgartner, F. Jäkle (Eds.), Main Group Strategies towards Functional Hybrid Materials, John Wiley & Sons, Hoboken, NJ, 2018, pp. 451–482.
[13] H. Eckhardt, L.W. Shacklette, K.Y. Jen, R.L. Elsenbaumer, The electronic and electrochemical properties of poly(phenylene vinylenes) and poly(thienylene vinylenes): an experimental and theoretical study, J. Chem. Phys. 91 (1989) 1303–1315.
[14] I. Jestin, P. Frère, P. Blanchard, J. Roncali, Extended thienylenevinylene oligomers as highly efficient molecular wires, Angew. Chem. Int. Ed. 37 (1998) 942–945.
[15] E.H. Elandaloussi, P. Frère, P. Richomme, J. Orduna, J. Garin, J. Roncali, Effect of chain extension on the electrochemical and electronic properties of δ-conjugated soluble thienylenevinylene oligomers, J. Am. Chem. Soc. 119 (1997) 10774–10784.
[16] A.V. Gavrilenko, T.D. Matos, C.E. Bonner, S.-S. Sun, C. Zhang, V.I. Gavrilenko, Optical absorption of poly(thienylene vinylene)-conjugated polymers: experiment and first principle theory, J. Phys. Chem. C 112 (2008) 7908–7912.
[17] H.E.A. Huitema, G.H. Gelinck, J.B.P.H. van der Putten, K.E. Kuijk, C.M. Hart, E. Cantatore, D.M. de Leeuw, Active-matrix displays driven by solution processed polymeric transistors, Adv. Mater. 14 (2002) 1201–1204.
[18] H. Fuchigami, A. Tsumura, H. Koezuka, Polythienylenevinylene thin-film transistor with high carrier mobility, Appl. Phys. Lett. 63 (1993) 1372–1374.
[19] W. Shockley, H.J. Queisser, Detailed balance limit of efficiency of p-n-Junction solar cells, J. Appl. Phys. 32 (1961) 510–519.
[20] M.C. Hanna, A.J. Nozik, Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers, J. Appl. Phys. 100 (2006), 074510.
[21] A.J. Musser, M. Al-Hashimi, M. Maiuri, D. Brida, M. Heeney, G. Cerullo, R. H. Friend, J. Clark, Activated singlet exciton fission in a semiconducting polymer, J. Am. Chem. Soc. 135 (2013) 12747–12754.
[22] E. Lafalce, U. Huynh, E. Olejnik, T.P. Basel, E. Ehrenfreund, Z.V. Vardeny, X. Jiang, Long-lved-correlated triplet-pair state in an imide substituted polythienylene vinylene-based π-conjugated polymer, J. Photon. Energy 8 (2018), 032217.
[23] A.J. Musser, M. Al-Hashimi, M. Heeney, J. Clark, Heavy-Atom Effects on Intramolecular singlet fission in a conjugated polymer, J. Chem. Phys. 151 (2019), 044902.
[24] A.J. Brassett, N.F. Colaneri, D.D.C. Bradley, R.A. Lawrence, R.H. Friend, H. Murata, S. Tokito, T. Tsutsui, S. Saito, Optical excitations in poly(2,5-thienylene vinylene), Phys. Rev. B 41 (1990) 10586–10594.
[25] J.C. Earles, K.C. Gordon, D.L. Officer, P. Wagner, A spectroscopic and computational study of the neutral and radical cation species of conjugated aryl-substituted 2,5-Bis(2-thien-2-ylethenyl)thiophene-Based oligomers, J. Phys. Chem. 111 (2007) 7171–7180.
[26] E. Olejnik, B. Pandit, T. Basel, E. Lafalce, C.-X. Sheng, C. Zhang, X. Jiang, Z. V. Vardeny, Ultrafast optical studies of ordered poly(3-thienylene-vinylene) flms, Phys. Rev. B 85 (2012) 235201.
[27] Y. Jiang, Q. Peng, X. Gao, Z. Shuai, Y. Niu, S.H. Lin, Theoretical design of polythienylenevinylene derivatives for improvements of light-emitting and photovoltaic performances, J. Mater. Chem. 22 (2012) 4491–4501.
[28] K.-Y. Jen, M. Maxfield, L.W. Shacklette, R.L. Elsenbaumer, Highly-Conducting, poly(2,5-thienylene vinylene) prepared via a soluble precursor polymer, J. Chem. Soc. Chem. Commun. (1987) 309–311.
[29] S. Yamada, S. Tokito, T. Tsutsui, S. Saito, New conducting polymer film: poly(2,5-thienylenevinylene) prepared via a soluble presursor polymer, J. Chem. Soc. Chem. Commun. (1987) 1448–1449.
[30] S. Gillissen, A. Henckens, L. Lutsen, D. Vanderzande, J. Gelan, Synthesis of a processible high molecular weight poly(thienylene vinylene), Synth. Met. 135–136 (2003) 255–256.
[31] F. Goldoni, R.A.J. Janssen, E.W. Meijer, Synthesis and characterization of new copolymers of thiophene and vinylene: poly(thienylenevinylene)s and poly (terthienylenevinylene)s with thioether side chains, J. Polym. Sci. Polym. Chem. 37 (1999) 4629–4639.
[32] K. van de Wetering, C. Brochon, C. Ngov, G. Hadziioannou, Design and synthesis of a low band gap conjugated macroinitiator: toward rod-coil donor-acceptor block copolymers, Macromolecules 39 (2006) 4289–4297.
[33] C. Zhang, T. Matos, R. Li, S.-S. Sun, J.E. Lewis, J. Zhang, X. Jiang, Poly(3-dodedyl-2,5-thienylenevinylene)s from the stille coupling and the horner–emmons reaction, Polym. Chem. 1 (2010) 663–669.
[34] R. Toyoshima, K. Akagi, H. Shirakawa, Synthesis and properties of poly (thienylenevinylene) derivatives with hexyl groups, Synth. Met. 84 (1997) 431–432.
[35] R.S. Loewe, R.D. McCullough, Effects of structural regularity on the properties of poly(3-alkylthienylenevinylenes), Chem. Mater. 12 (2000) 3214–3221.
[36] J. Hou, Z. Tan, Y. He, C. Yang, Y. Li, Branched poly(thienylene vinylene)s with absorption spectra covering the whole visible region, Macromolecules 39 (2006) 4657–4662.
[37] M. Al-Hashimi, Y. Han, J. Smith, H.S. Bazzi, S.Y.A. Alqaradawi, S.E. Watkins, T. D. Anthopoulos, M. Heeney, Influence of the heteroatom on the optoelectronic properties and transistor performance of soluble thiophene-, selenophene- and tellurophene–vinylene copolymers, Chem. Sci. 7 (2016) 1093–1099.
[38] B. Tsuie, K.B. Wagener, J.R. Reynolds, Alkyl substituted poly(thienylene vinylene) by acyclic diene metathesis (ADMET) polymerization chemistry, Polym. Prepr. 40 (1999) 790.
[39] Y. Qin, M.A. Hillmyer, Poly(3-hexyl-2,5-thienylene vinylene) by ADMET polymerization of a dipropenyl monomer, Macromolecules 42 (2009) 6429–6432.

[40] P.A. Delgado, D.Y. Liu, Z. Kean, K.B. Wagener, Synthesis of poly(3-dodecyl-2,5-thienylene vinylene) by solid-state metathesis polycondensation, Macromolecules 44 (2011) 9529–9532.
[41] J.C. Speros, B.D. Paulsen, S.P. White, Y. Wu, E.A. Jackson, B.S. Slowinski, C. D. Frisbie, M.A. Hillmyer, An ADMET route to low-band-gap poly(3-hexadecylthienylene vinylene): a systematic study of molecular weight on photovoltaic performance, Macromolecules 45 (2012) 2190–2199.
[42] J.C. Speros, B.D. Paulsen, B.S. Slowinski, C.D. Frisbie, M.A. Hillmyer, Band gap and HOMO level control in poly(thienylene vinylene)s prepared by ADMET polymerization, ACS Macro Lett. 1 (2012) 986–990.
[43] J.C. Speros, H. Martinez, B.D. Paulsen, S.P. White, A.D. Bonifas, P.C. Goff, C. D. Frisbie, M.A. Hillmyer, Effects of olefin content and alkyl chain placement on optoelectronic and morphological properties in poly(thienylene vinylenes), Macromolecules 46 (2013) 5184–5194.
[44] G. Yang, K. Hu, Y. Qin, Cis/Cis-2,5-Dipropenylthiophene monomers for high molecular weight PTVs through ADMET polymerization, J. Polym. Sci. Part A Polym. Chem. 52 (2014) 591–595.
[45] Z. Zhang, Y. Qin, Synthesis and characterization of poly(selenylene vinylene) and poly(selenylene vinylene)-co-Poly(thienylene vinylene) through acyclic diene metathesis (ADMET) polymerization, ACS Macro Lett. 4 (2015) 679–683.
[46] Z. Zhang, Y. Qin, Structurally diverse poly(thienylene vinylene)s (PTVs) with systematically tunable properties through acyclic diene metathesis (ADMET) and postpolymerization modification, Macromolecules 49 (2016) 3318–3327.
[47] Z. Zhang, X. Zong, Z. Sun, Y. Qin, Impact of side-chain extension on physical and electronic properties of cross-conjugated poly(thienylene vinylene)s (PTVs), Polymer 166 (2019) 115–122.
[48] D.J. Baek, R. Bittman, Synthesis of cholesterol analogs having varying length Alkyl side chains including cholesterol-23, 23, 24, 24, 25, 26, 26, 26, 27, 27, 27-d_{11} as probes of cholesterol's functions and properties, Chem. Phys. Lipids 175–176 (2013) 99–104.
[49] J. Hou, T.L. Chen, S. Zhang, L. Huo, S. Sista, Y. Yang, An easy and effective method to modulate molecular energy level of poly(3-alkylthiophene) for high-voc polymer solar cells, Macromolecules 42 (2009) 9217–9219.
[50] H. Hayashi, T. Iseki, S. Nimori, H. Goto, Vapour-induced liquid crystallinity and self-recovery mechanochromism of helical block copolymer, Sci. Rep. 7 (2017) 3948.