Band Gap and HOMO Level Control in Poly(thienylene vinylene)s Prepared by ADMET Polymerization

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S *Supporting Information*

ABSTRACT: Three dipropenyl monomers were prepared for ruthenium-catalyzed acyclic diene metathesis (ADMET) polymerization. Homopolymerization afforded three poly-(thienylene vinylene)s (PTVs) with distinct optoelectronic properties. Binary combinations of the monomers over a range of compositions gave three series of copolymer samples with tunable HOMO levels and band gaps. The utility of this method was further demonstrated by the preparation of a stoichiometric terpolymer. Polymers were characterized by ^{1}H NMR spectroscopy, size-exclusion chromatography, ultra-violet−visible spectroscopy, and cyclic voltammetry. This copolymerization approach effectively demonstrates the ability of ADMET polymerization to prepare conjugated copolymers with tuned optoelectronic properties that span a broad composition window.
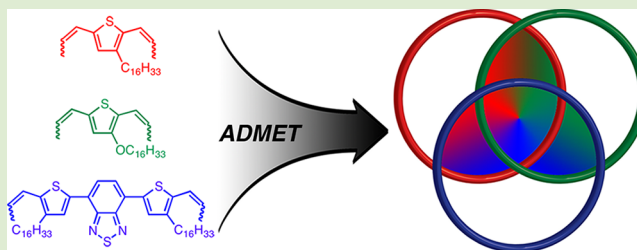
The ability to tune the properties of conjugated polymers (CPs) through chemical modification has allowed for their integration in sensors,[1] organic light-emitting diodes,[2] field-effect transistors,[3] and organic photovoltaics (OPVs).[4] OPVs are of particular interest because cost-effective solution processing techniques can be used for their preparation. State-of-the-art OPV power conversion efficiencies now lie in the 7−9% range[5−8] as a result of both device optimization and the development of low band gap CPs typically having a perfectly alternating sequence of donor and acceptor (D-A) monomeric units.[9] Low band gap CPs are desirable because they often afford efficient and broad absorption of the solar spectrum. Systematic tuning of the band gap in a homologous set of CP materials can be ideally used to optimize OPV performance. However, such tunability can be synthetically difficult to achieve in conventional D-A polymers. Here we describe an approach to tunable energy levels based on copolymerization of structurally and electronically distinct monomers.

Few researchers have explored statistical copolymerization methods for the preparation of CPs. Unlike the alternating D-A approach,[10] a primary advantage of this strategy is the ability to probe nonstoichiometric monomer combinations instead of the 1:1 composition imposed by an alternating architecture. Some of the earliest examples of random CPs were aimed at tuning photoluminescence properties and were prepared by Yamamoto coupling of various dibromo monomers.[11,12] However, a broad composition range was not studied. More recent examples of random CPs make use of palladium-catalyzed Suzuki and Stille coupling strategies.[13,14] These routes require lengthy syntheses of, for example, one diboronic ester/ditin

monomer and two dibromo monomers. Additionally, given the alternating nature of these polymerizations, only half of the composition window is accessible. Recently, Thompson and co-workers built on the utility of this approach by demonstrating "semi-random" CPs using 2-bromo-5-trimethyltin-3-hexylthio-phene, 2,5-bis(trimethyltin)-thiophene, and 4,7-dibromo-2,1,3-benzothiadiazole or dibromo-bisthiophene-diketopyrrolopyr-role monomers and Stille coupling conditions.[15,16] They demonstrated that a small percentage of acceptor moiety in the copolymer backbone had a significant impact on the optoelectronic properties. More recently, this group expanded their Stille coupling approach to "semi-random" CPs by demonstrating control of open-circuit voltage[17] and optimiza-tion of OPV efficiency.[18] Inspired by this approach, we sought a methodology that would tolerate a wide variety of function-alities, only require two monomers, and avoid the use of tin-containing monomers.

Acyclic diene metathesis (ADMET) polymerization is a step-growth polymerization that typically links α,ω-dienes to generate linear polymers with unsaturated repeat units.[19] ADMET polymerization has been used to prepare polymers for diverse applications.[20] In the CP arena, poly(acetylenes),[21] poly(phenylene vinylenes),[22] poly(fluorene vinylenes),[23] poly-(carbazole vinylenes),[24] and poly(thienylene vinylenes)[25,26] (PTVs) have all been prepared by ADMET polymerization.

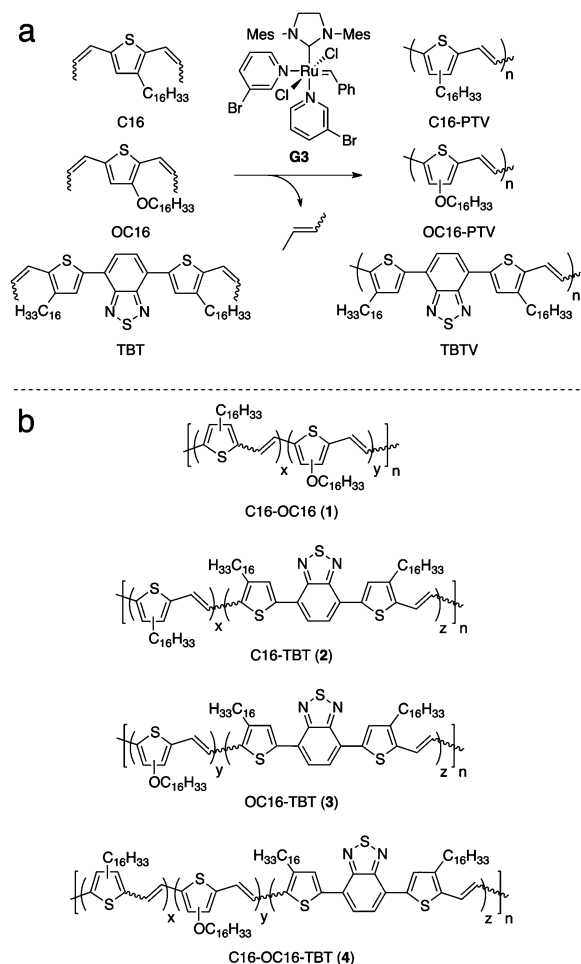This polymerization technique has also been used to prepare statistical nonconjugated copolymers.[27,28]

We synthesized three monomers all sharing the same reactive propenyl functionality (Scheme 1a). The respective low band

Scheme 1. Homopolymer Synthesis by ADMET (a) and Copolymer Structures (b)

gap homopolymers and a broad range of copolymers were synthesized by ADMET polymerization. All polymers were prepared using a highly active 3-bromopyridine functionalized ruthenium metathesis catalyst (G3).[29] For consistency, the same hexadecyl solubilizing side chain was installed in all three monomers. Monomers were also designed to be electron-rich (OC16) or electron-poor (TBT) as compared to the "neutral" variant (C16).

The C16 monomer was prepared following a previous literature report[26] in 68% overall yield with a Z/E ratio of 83:17. The synthesis of OC16 began by treating 3-bromothiophene with the sodium alkoxide of 1-hexadecanol in the presence of copper iodide. Lithiation of the 3-hexadecyloxythiophene product with n-butyllithium followed by treatment with N,N'-dimethylformamide (DMF) and acidic workup afforded the dialdehyde. A salt-free Wittig reaction provided OC16 in 52% overall yield with a Z/E ratio of 65:35. Synthesis of the TBT monomer began with the Stille coupling of 4,7-dibromo-2,1,3-benzothiadiazole and 2-tributylstannyl-4-hexadecylthiophene catalyzed by bis(triphenylphosphine) palladium(II) chloride. The product was treated with DMF

and phosphorus oxychloride under Vilsmeier–Haack conditions to afford the dialdehyde.[30] The conversion of dialdehyde to TBT under salt-free Wittig conditions gave an overall yield of 16% and a Z/E ratio of 62:38 (see Supporting Information for synthetic details).

Homo- and copolymerization of C16, OC16, and TBT monomers was conducted under reduced pressure (20–50 mtorr) in anhydrous 1,2,4-trichlorobenzene with G3 (1 mol %). Polymerizations were allowed to proceed for 16–48 h before precipitation in a nonsolvent (methanol or acetone) and purification by Soxhlet extraction with the same nonsolvent. Relative number-average molecular weights were determined by size-exclusion chromatography (SEC) in chloroform versus polystyrene standards. ^{1}H NMR spectroscopy was employed to characterize all polymers (Figures S11–S17) and to determine the average monomer composition in the copolymer structures. However, the NMR data was not useful with respect to sequence distribution determination. Optical behavior was analyzed in dilute chloroform solutions (10^{-5} M in monomer repeat units) by ultraviolet–visible spectroscopy (UV–vis; see Figure S19 in Supporting Information). Absorption maxima (λ_{max}) for C16-PTV, OC16-PTV, and TBTV homopolymers were 582, 634, and 662 nm, respectively. As observed previously, C16-PTV displayed a second λ_{max} (623 nm) suggesting aggregation-induced vibronic fine structure.[26] TBTV also showed a second peak at 422 nm likely due to the $\pi-\pi^*$ transition; we attribute the peak at 662 nm to intramolecular charge transfer.[31] Thin film UV–vis spectra demonstrated predictable red shifts in absorption maxima as compared to solution spectra (Figure 1). Values of the optical band gaps (E_g^{opt}) were determined from the onset of absorption in the polymer thin film ($E_g^{opt} = 1240/\lambda_{onset}$). C16-PTV was found to have an E_g^{opt} of 1.66 eV, while both OC16-PTV and TBTV gave a value of 1.49 eV. All spectroscopic and chromatographic data are summarized in Table 1.

The C16/OC16 ratios in isolated copolymers (**1a–i**) were quantified using ^{1}H NMR spectroscopy (Figure S14) and were within a few percent of the feed ratios in all cases (Table 1). Additionally, λ_{onset} of C16-OC16 thin films shifted to longer wavelengths (lower E_g^{opt}) as more OC16 was incorporated into the copolymer (Figure 1a). Although the molar mass range in this polymer series was large (3–34 kg/mol), this likely had minimal impact on E_g^{opt}, which in PTVs has been shown to saturate around ten repeat units.[32] Therefore, we posit that the observed differences in E_g^{opt} are largely the result of copolymer composition. Figure S20 demonstrates the agreement between the predicted and actual E_g^{opt} based on the sum of the mole fraction weighted values of the homopolymer bandgaps.

The second copolymer series employed the C16 and TBT monomers (**2a–e**), and again the feed ratios closely matched the average copolymer compositions as determined by ^{1}H NMR spectroscopy (Figure S15). All isolated polymers were of roughly the same apparent molar mass (M_n ca. 6 kg/mol) and molar-mass dispersity allowing for direct comparison of optical behavior. Copolymers in this series could be monitored qualitatively by color change (Figure S21). Unlike series **1**, which showed a progressive shift in E_g^{opt}, the E_g^{opt} of this series saturated upon addition of 20% TBT monomer. As suggested by Thompson and co-workers,[15,16,18] applying this "trace acceptor" concept to other CP systems may allow for significantly altered absorptive properties with minimal changes to the overall polymer composition.
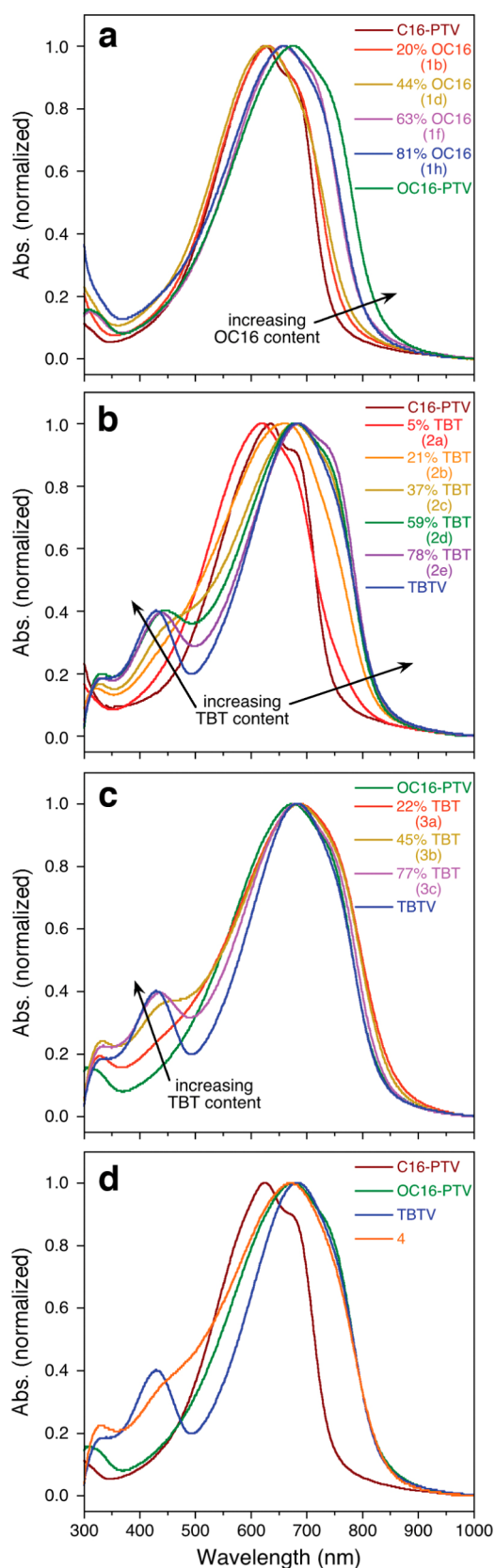
Figure 1. UV−vis spectra of (a) C16-OC16 (**1**), (b) C16-TBT (**2**), (c) OC16-TBT (**3**), and (d) C16-OC16-TBT (**4**) as thin films on glass substrates. Corresponding homopolymers are shown in each series to highlight trends.

The OC16 and TBT monomers were used in preparation of the third copolymer series (**3a−c**), and average copolymer composition calculated using ^{1}H NMR spectroscopy was very close to the feed ratios (Figure S16). The $\pi-\pi^*$ transition from TBT proved a useful means of confirming the increase in TBT content (Figures 1c and S19c). Interestingly, the E_g^{opt} of all three copolymers was slightly lower than that of the parent homopolymers. This is possibly the result of intramolecular charge transfer; the same phenomenon attributed to reduced band gap in D-A materials.[33]

To demonstrate the synthetic versatility of this copolymerization approach a terpolymer (**4**) was prepared by combining equimolar amounts of the three monomers. The terpolymer composition from ^{1}H NMR spectroscopy (Figure S17) was close to the feed ratio. In addition, **4** exhibited a much broader absorption than the respective homopolymers in solution (Figure S19d) and as a thin film (Figure 1d) by UV−vis spectroscopy.

The homo- and copolymers were characterized by cyclic voltammetry (CV) to quantify the impact of copolymerization on the position of the highest occupied molecular orbital (HOMO). The room temperature ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([P14]-[TFSA]) was employed as the electrolyte system as its broad window of electrochemical stability provided high sweep-to-sweep stability and sample-to-sample reproducibility.[34] The HOMO level of each polymer was calculated from the onset of electrochemical oxidation (Figures S22 and S23). The measured reference potentials for each sample were internally calibrated using the standard redox couple cobaltocenium hexafluorophosphate (CcPF$_6$) known to undergo a reversible reduction at −1350 mV versus the ferrocene redox couple in ionic liquids.[35,36] Taking the ferrocene oxidation potential to lie 5.1 eV below vacuum level,[37] the HOMO levels were calculated as $E_{HOMO} = -(E_{(onset,ox\ vs\ Cc+/o)} + 3.75)$ eV. The HOMO level positions of C16-PTV, OC16-PTV, and TBTV were −5.12, −4.81, and −5.23 eV, respectively. For reference, regioregular poly(3-hexylthiophene) measured in the same electrolyte system gave a HOMO level position of −5.06 eV.

Copolymers of C16-TBT demonstrated saturation behavior in both HOMO level and E_g^{opt} (Figure 2a). Upon incorporation of 22% C16 into the TBTV polymer chain the HOMO level position was immediately pinned to that of the C16-PTV homopolymer ($\approx$ −5.1 eV). On the other hand, the E_g^{opt} saturated at the TBTV homopolymer value of ~1.5 eV at 21% TBT monomer incorporation. This behavior is consistent with the generally accepted concept that the acceptor monomer (TBT) sets the LUMO level, and the donor monomer (C16) sets the HOMO level[9] even at low levels of incorporation.[15]

Interestingly, the C16-OC16 and OC16-TBT copolymers did not follow the saturation behavior observed for C16-TBT. Instead, the HOMO level increased (310 meV range) and the E_g^{opt} decreased (170 meV range) monotonically with increasing OC16 content in the C16-OC16 copolymers (Figure 2b). Likewise, the HOMO levels of OC16-TBT copolymers could be tuned over a 420 meV range (Figure 2c). However, despite the increase in HOMO level in the OC16-TBT copolymers, the E_g^{opt} varied little as the respective homopolymers had identical band gaps.

Finally, the HOMO level position of the terpolymer (**4**; 36% C16, 34% OC16, and 30% TBT) was determined by CV (−5.09 eV, Figure S23) and was consistent with that of the copolymers containing approximately 36% OC16. The E_g^{opt}

Table 1. NMR, SEC, and UV−Vis Data for Homo- and Copolymers

sample ID[a]	observed ratio[b]	$M_n{}^c$ (kg/mol)	$Đ_M{}^c$	$\lambda_{max,soln}{}^d$ (nm)	$\lambda_{max,film}{}^e$ (nm)	$E_g{}^{optf}$ (eV)
C16-PTV		33	2.2	582 (623)	625 (677)	1.66
OC16-PTV		4	1.6	634	676	1.49
TBTV		7	1.9	662 (422)	683 (429)	1.49
C16-OC16	C16/OC16					
1a (90:10)	89:11	34	2.8	591 (626)	632 (682)	1.64
1b (80:20)	80:20	14	1.9	593 (629)	630	1.62
1c (70:30)	68:32	9	1.7	595	630	1.59
1d (60:40)	56:44	7	3.3	587	627	1.58
1e (50:50)	47:53	8	1.5	602	639	1.56
1f (40:60)	37:63	7	2.2	621	656	1.55
1g (30:70)	27:73	3	1.4	601	644	1.55
1h (20:80)	19:81	8	1.5	619	659	1.53
1i (10:90)	8:92	5	1.3	600	635	1.53
C16-TBT	C16/TBT					
2a (95:5)	95:5	10	1.7	580 (611)	620	1.59
2b (80:20)	79:21	6	1.2	622	660	1.50
2c (60:40)	63:37	6	1.4	641 (435)	678 (460)	1.49
2d (40:60)	41:59	5	1.4	649 (433)	680 (446)	1.49
2e (20:80)	22:78	6	1.5	662 (430)	686 (439)	1.49
OC16-TBT	OC16/TBT					
3a (75:25)	78:22	3	1.1	638	686	1.46
3b (50:50)	55:45	4	1.2	640 (433)	685 (452)	1.46
3c (25:75)	23:77	4	1.2	645 (423)	681 (437)	1.48
C16-OC16-TBT	C16/OC16:TBT					
4 (1:1:1)	0.36:0.34:0.30	4	1.2	624 (434)	670 (440)	1.49

[a]Values in parentheses are monomer feed ratios. [b]Determined by integration of appropriate resonances in ¹H NMR spectra. [c]Determined by SEC in CHCl₃ vs polystyrene standards. [d]About 10^{-5} M in repeat unit in CHCl₃; values in parentheses are secondary peaks/shoulders. [e]Polymer film spin coated from CHCl₃ onto glass substrates; values in parentheses are secondary peaks/shoulders. [f]Determined from onset absorption of thin film ($E_g{}^{opt} = 1240$ (nm eV)/λ_{onset} (nm)).
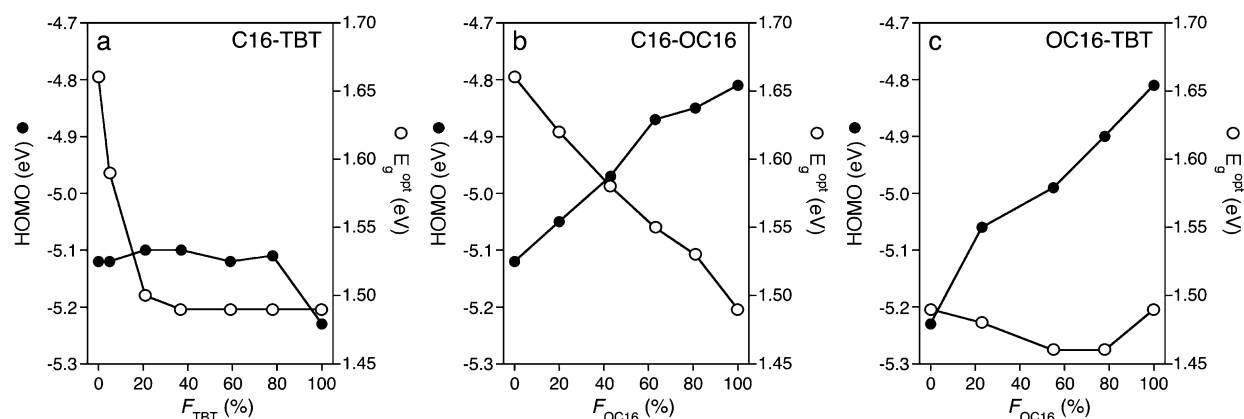

Figure 2. HOMO level position from CV (filled circles) and $E_g{}^{opt}$ from UV−vis (open circles) vs copolymer composition (F) of (a) C16-TBT, (b) C16-OC16, and (c) OC16-TBT thin films.

(1.49 eV) was consistent with that of the copolymers containing approximately 30% TBT according to the relationships shown in Figure 2.

The nonlinear behavior observed in C16-TBT copolymers is consistent with related phenomena in other D−A polymers. However, this explanation does not adequately describe the monotonic behavior observed for the HOMO levels in the C16-OC16 and OC16-TBT copolymers. This is perhaps due to the relatively large differences between HOMO levels of the corresponding homopolymers. As illustrated by Figure 3, we have shown that ADMET polymerization is an ideal means of generating CPs with precisely controlled optoelectronic

properties and allows for systematic combination and optimization of various CP properties (e.g., HOMO/LUMO levels, band gap, photoluminescence, absorption strength, charge transport, etc.) with minimal synthetic effort. The application of this approach to CP systems with broader optoelectronic properties and integration of those polymers into OPV devices is currently underway.
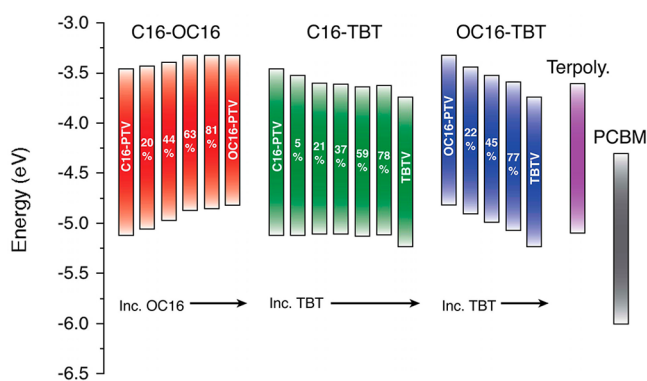
Figure 3. Band diagram of C16-OC16 (red), C16-TBT (green), and OC16-TBT (blue) series. The terpolymer (purple) and PCBM (gray) are shown for completeness. LUMO levels were estimated from HOMO levels and E_g^{opt} (LUMO = HOMO + E_g^{opt}).

ASSOCIATED CONTENT

S Supporting Information

Synthesis of monomers and polymers, NMR spectra, UV–vis spectra, and cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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