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An Efficient, Modular Synthetic Route to Oligomers Based on Zirconocene Coupling: Properties for Phenylene – Thiophene-1-Oxide and Phenylene – Thiophene-1,1-Dioxide Chains**

Min Chul Suh, Biwang Jiang, and T. Don Tilley*

The increasing interest in π-conjugated polymers has resulted in a very large research effort, focused on the development of new conducting materials for electronic devices.[1] Associated with this effort has been the synthesis and study of conjugated oligomers with well-defined structures and properties.[2] Oligomeric species allow detailed investigations of the fundamental properties of conjugated chains, and provide insight into the behavior of the analogous polymers. In addition, the discrete properties of the oligomers make them attractive materials in their own right, since they may exhibit properties that are not associated with the related polymers.

We have developed a new route to conjugated polymers based on the zirconocene coupling of diynes.[3, 4] This approach provides synthetic intermediate polymers containing zirconacyclopentadiene units, which are readily converted into a variety of new structures. These chemical transformations provide a modular approach to control the electronic and optical properties of the polymer, through substitution at a particular site in the conjugated chain by various structural units (for example dienylene, phenylene, thiophene, selenophene, germole, and phosphole). Related strategies which complement this approach involve the zirconocene coupling of functionalized diynes, to provide new monomers for polymerization[3f, 4] and the incorporation of zirconacyclopentadiene units by the coupling of diyne segments in a preexisting polymer.[3b,c,g]

A recent discovery in our laboratories[4] allows the efficient incorporation of thiophene-1-oxide (T_O) and thiophene-1,1-dioxide (T_{O2}) rings into the backbone of a conjugated polymer by the reaction of zirconacyclopentadiene derivatives with SO_2. Thus, we have been able to prepare the first polymers containing T_O groups and develop general routes to alternating arylene – T_O and arylene – T_{O2} copolymers.[3g] Interestingly, these polymers have more narrow band gaps, and have higher electron affinities than the corresponding thiophene-based polymers. In related work based on a different synthetic strategy, Barbarella et al. have shown that T_{O2} groups may be incorporated into oligomers which exhibit decreased electronic band gaps and higher electron affinities than the

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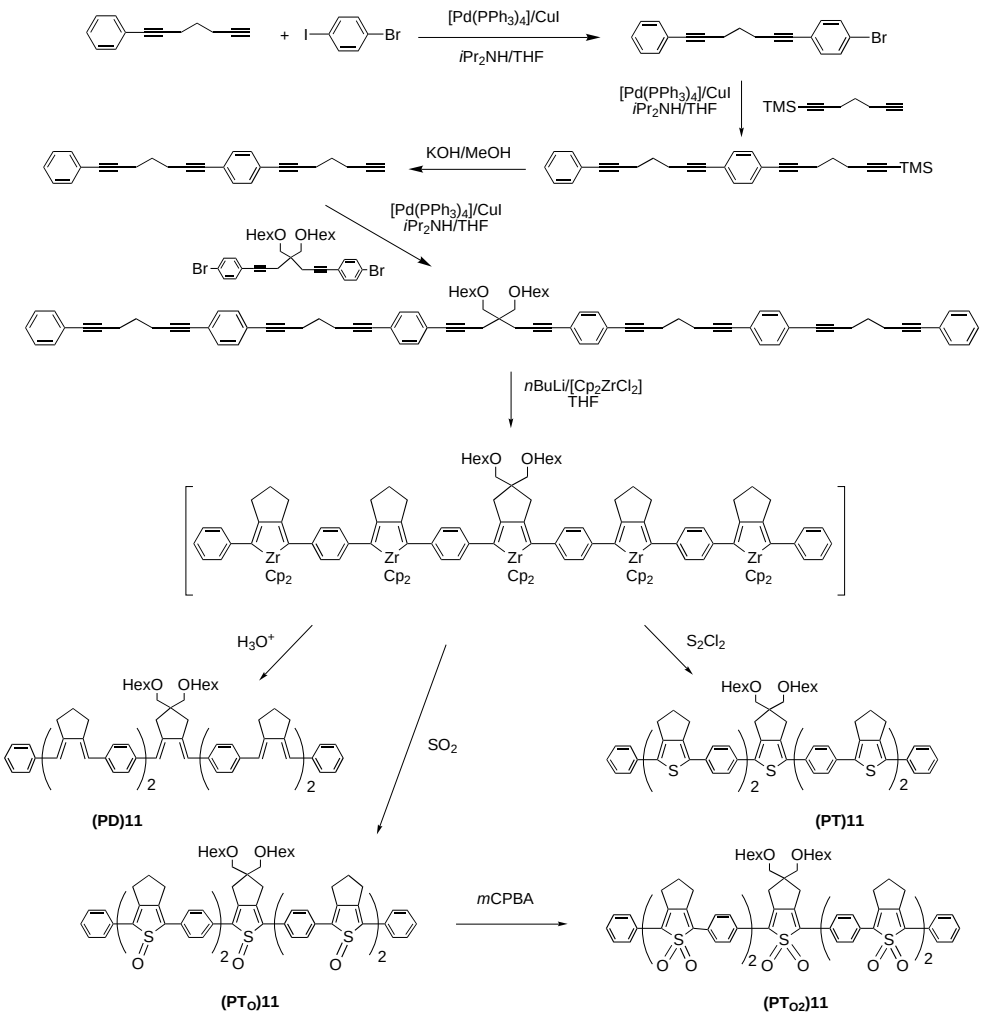
analogous thiophene oligomers.[5] Thus, T_O- and T_{O2}-based polymers have emerged as good candidates for electron-transporting materials in polymer-based devices.

To further investigate the fundamental electronic properties of T_O- and T_{O2}-based conjugated systems we have prepared a series of well-defined oligomers which allows systematic comparison of T_O, T_{O2}, thiophene (T), and dienylene (D) groups. Our synthetic route to these oligomers takes advantage of versatile and efficient methods based on zirconocene couplings. Traditional synthetic approaches to oligomers principally rely on series of coupling steps to produce a particular structure. Such step by step procedures are tedious and provide only one type of oligomer.[2] The method described here makes use of a high-yielding coupling reaction (the palladium coupling of alkynes and aryl halides) to produce oligomers which, by zirconocene coupling methods, may be converted into a family of new conjugated structures with fundamentally different properties.



Scheme 1. Modular synthesis of various oligomers by zirconocene coupling methods.

The general strategies for conversions of linked diyne units to diene, thiophene, thiophene-1-oxide, and thiophene-1,1-dioxide groups by zirconocene coupling have been described.[4] A high-yielding route to the required precursor diyne oligomers (of arbitrary length) is described in Scheme 1. This procedure relies on the availability of unsymmetrical diynes, such as 1-phenyl-1,6-heptadiyne and 1-trimethylsilyl-1,6-heptadiyne, which are obtained in high yields by a literature method.[6] By repeated sequences of coupling reactions of alkyne and aryl halides (with the high-yielding Hagihara procedure) and deprotection chain lengths may be built up rapidly. The precursor diyne oligomers were converted into the corresponding zirconacyclopentadiene derivatives by the Negishi method,[7] and these compounds were then converted in situ into four different types of oligomers (Scheme 1). The zirconocene coupling and subsequent transformations are very efficient as indicated by the high yields for the latter conversions (92–99%). This procedure provided oligomers with phenylene–dienylene, phenylene–thiophene, phenylene–thiophene-1-oxide, and phenylene–thiophene-1,1-dioxide, structures (Table 1; (PD)*n*, (PT)*n*, (PT_O)*n*, and (PT_{O2})*n*, respectively, where P = phenylene and *n* indicates the total number of rings and/or diene units).

Figure 1 provides views of the molecular structure of (PT)5.[8] This oligomer crystallized (with 0.5 equivalents of chloroform solvent) as pairs of loosely associated molecules related by inversion. The inner phenylene and thiophene rings are coplanar (with angles between the least-squares planes of $< 6.5^\circ$), while the terminal phenyl rings are rotated by 31.4 and 27.6° with respect to the central phenylene ring. The association of the oligomers is such that a symmetry related pair of carbon atoms in the central phenylene group (C19) are separated by 3.24 Å.

To investigate the electronic properties of each type of oligomer structure, and to determine the conjugation lengths for the corresponding polymers, we examined the UV/Vis spectra for each oligomer. The (PT_O)*n* oligomers exhibit a distinct bathochromic shift which is associated with elongation of the oligomer chain (Figure 2a). The λ_{max} values for these oligomers asymptotically approach the observed value for poly(phenylene–thiophene-1-oxide) (PPT_O, 497 nm). The corresponding optical band gaps, determined from the band edges, are plotted as a function of oligomer length (Figure 2b). This smooth convergence curve indicates that the oligomers and polymers obtained by zirconocene coupling are

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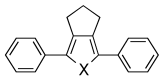
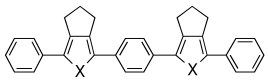
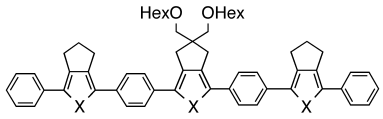
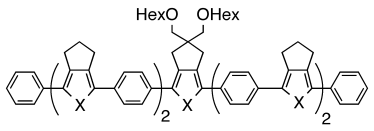
Table 1. Optical properties of oligomers.

Oligomer structure	Oligomers	λ_{max} [nm]	ε [10^5 cm^{-1}M^{-1}]	$E_{g,opt}$ [eV][a]
	X = 2H, (PD)3	338	0.33	3.23
	X = S, (PT)3	330	0.32	3.31
	X = SO, (PT_O)3	392	0.14	2.71
	X = SO_2, (PT_{O2})3	378	0.20	2.86
	X = 2H, (PD)5	392	0.66 (0.39)[b]	2.75
	X = S, (PT)5	384	0.66 (0.39)	2.86
	X = SO, (PT_O)5	440	0.39 (0.23)	2.44
	X = SO_2, (PT_{O2})5	430	0.27 (0.16)	2.51
	X = 2H, (PD)7	412	0.81 (0.35)	2.55
	X = S, (PT)7	408	1.10 (0.47)	2.66
	X = SO, (PT_O)7	462	0.44 (0.19)	2.29
	X = SO_2, (PT_{O2})7	452	0.56 (0.24)	2.35
	X = 2H, (PD)11	436	1.20 (0.33)	2.40
	X = S, (PT)11	430	1.25 (0.34)	2.49
	X = SO, (PT_O)11	484	0.56 (0.15)	2.11
	X = SO_2, (PT_{O2})11	476	1.01 (0.28)	2.24

[a] Optical band gap from absorption edge. [b] Molar absorption values in parantheses are based on the fundamental repeating unit of the oligomer.

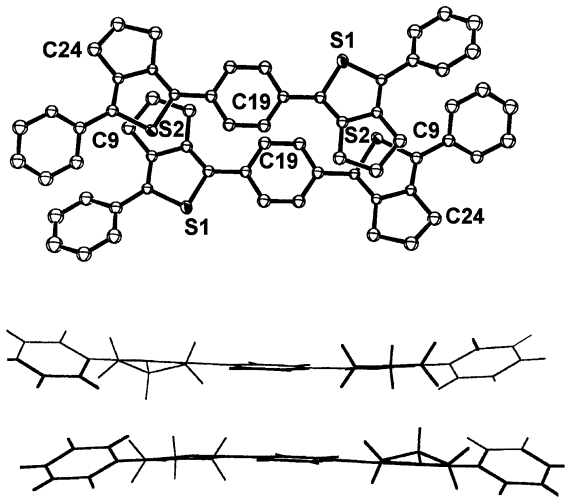


Figure 1. Views of the molecular structure of (PT)5.

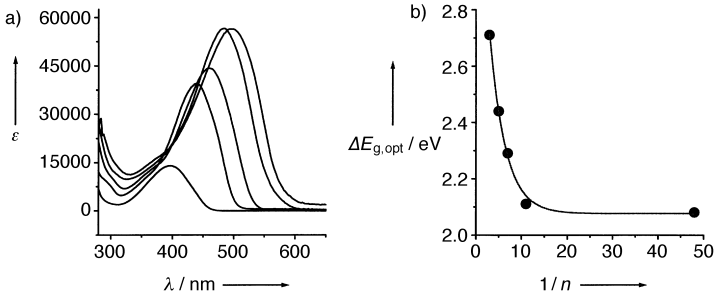


Figure 2. a) UV/Vis spectra and b) optical band gap convergence curve, for the (PT_O)*n* series.

well defined and largely defect free, and allows the conjugation length in PPT_O to be estimated at 15 rings (7–8 monomer units). Note that similar convergence curves were observed for the (PD)*n*, (PT)*n*, and (PT_{O2})*n* systems, from which conjugation lengths of 15–20 rings may be estimated (see Supporting Information). This estimate is consistent with results for polythiophenes which exhibit conjugation lengths of approximately 12 rings,[9] whereas polyphenylenes have been estimated to have a conjugation length of only 4–5 rings.[10]

A comparison of the convergence curves for all the oligomeric systems described above reveals that the phenylene–thiophene-1-oxide structure has the lowest energy optical band gap: PPT_O (2.08 eV) < PPT_{O2} (2.18 eV) < PPD (2.35 eV) < PPT (2.44 eV).[11] This trend in band gap energy reflects the generally greater conjugation along the chain for diene (compared to aromatic) structures, and also reflects the more planar diene units present in thiophene-1-oxide and thiophene-1,1-dioxide (compared to the acyclic diene).[12] Barbarella and co-workers have previously shown that incorporation of thiophene-1,1-dioxides into thiophene oligomers results in a reduction of the band-gap energy, and their data indicates that this narrowing of the band gap principally occurs by a stabilization of the LUMO level.[5a]

Cyclic voltammetry data for the oligomers and polymers give the same ordering of the band gaps, with values that are slightly greater: PPT_O (2.12 eV) < PPT_{O2} (2.31 eV) < PPD (2.50 eV) < PPT (2.69 eV). These data also allow estimates for the HOMO and LUMO energy levels (Figure 3).[13] The calculated energy levels reveal that the more narrow band gaps for the thiophene-1-oxide and thiophene-1,1-dioxide systems result mainly from a stabilization of the LUMO levels, as has been observed for thiophene–thiophene-1,1-dioxide oligomers.[5] However, this LUMO stabilization is similar for PPT_O and PPT_{O2}, and the narrower band gap for the thiophene-1-oxide chains results because the more electronegative sulfonyl group stabilizes both the HOMO and LUMO, whereas the sulfoxide does not stabilize the HOMO significantly relative to the thiophene polymer. An alternative explanation for the difference in band gaps for (PT_O)*n* and (PT_{O2})*n* oligomers is based on differences in dihedral angles between moieties in the chains. This is suggested by the structural data for 2,5-diphenylthiophene and its sulfoxide and its sulfone derivatives. In these

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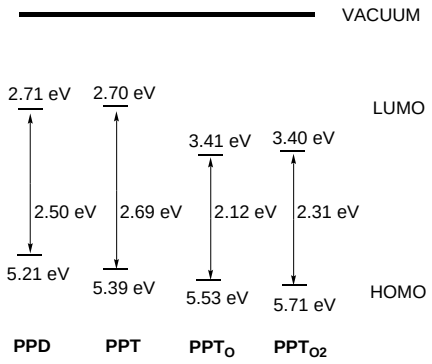

Figure 3. Estimated HOMO and LUMO energy levels of **PPD**, **PPT**, **PPT_O**, and **PPT_{O2}**.

structures, the dihedral angles between the central ring and those of the phenyl groups vary from an average of 8.5° for the thiophene to 12.5° for the sulfoxide and 7.4(2) and 39.1(2)° for the sulfone.[14] Thus, conjugation in the thiophene-1-oxide derivative may be more effective because it is more planar than the corresponding sulfone; this planarity may result from a lower barrier to rotation about the ring–ring bonds.[15]

The fluorescence properties of the oligomers and polymers were investigated for dilute samples dissolved in chloroform. The chains containing T_O and T_{O2} units exhibit very low luminescence efficiencies, and for the polymers the ordering of the quantum efficiencies is: PPT (0.12) > PPT_O (0.016) > PPD (0.012) > PPT_{O2} (0.003).[3h] The Stokes shifts associated with these emissions range from 50 to 80 nm. For the highly luminescent (PT)*n* oligomers, the Stokes shift is approximately 50 nm and the quantum efficiency decreases with molecular weight from the very high value for (PT)5 ($\Phi = 0.77$) to a value of 0.36 for (PT)11 (for (PT)7, $\Phi = 0.50$).[16]

In conclusion, we have described a versatile new approach to the synthesis of a series of conjugated oligomers, based on the zirconocene coupling of diynes. This has allowed us to prepare the first arylene–T_O and arylene–T_{O2} co-oligomers, and investigate fundamental electronic properties for conjugated chains involving thiophene-1-oxide and thiophene-1,1-dioxide. Of particular note are the narrow band gaps and high electron affinities associated with such monomers, and that the presence of the less electron-withdrawing sulfoxide group results in the lowest band gap.

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[8] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139792. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[11] Band gaps for the idealized, linear polymer chains of infinite length were estimated from linear plots of the optical band gaps for the oligomers versus 1/*n* (where *n* is the number of rings or diene units in the oligomer). The values obtained were: PPT_O (1.92 eV) < PPT_{O2} (1.99 eV) < PPD (2.07 eV) < PPT (2.18 eV).

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