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Conjugated Polymers in an Arene Sandwich

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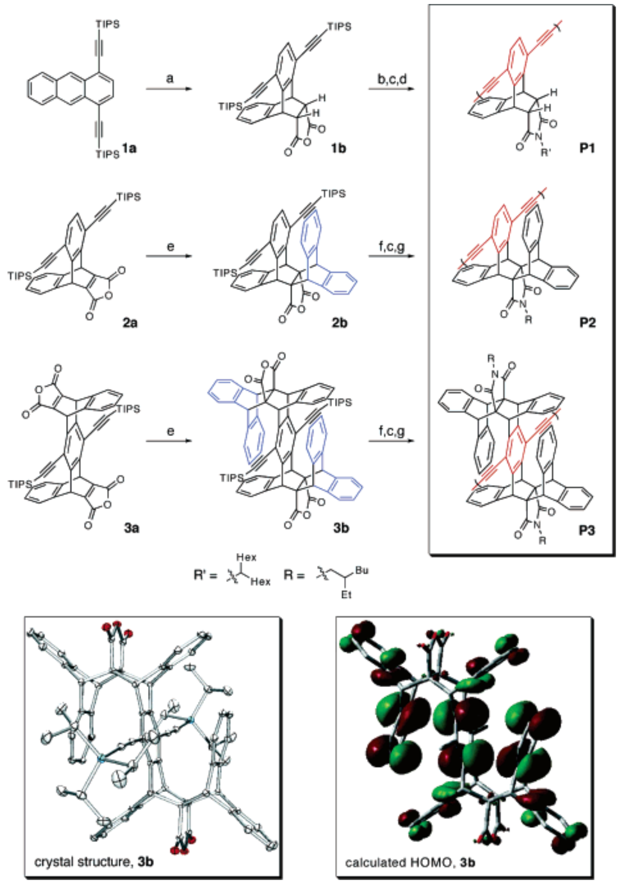
Since the discovery of conducting polyacetylene, π-conjugated polymers have demonstrated utility in applications such as sensors,[1] light-emitting diodes,[2] and photovoltaics.[3] One crucial advantage organic semiconductors have over their inorganic counterparts is that chemists can tailor the physical and electronic properties using the expansive toolbox of organic synthesis. Consequently, there are numerous examples where *direct* modification of the conjugated polymer backbone (e.g., with electron-donating groups) alters the electronic properties (e.g., ionization potential and band gap). In this communication, we report an alternative approach wherein an *indirect* interaction (through-space rather than through-bond) is incorporated into poly(*p*-arylene butadiynylene)s, and the resulting effects on the properties of the polymers are examined.

Our molecular design was inspired by the observation that through-space $\pi-\pi$ interactions in stacked arenes can lead to substantially lower oxidation potentials compared to those of linear analogues.[4] We postulated that similar through-space $\pi-\pi$ interactions could modulate a conjugated polymer's ionization potential. Polymers incorporating paracyclophane have been reported,[5,6] but the conduction pathway relies on the through-space interaction and thus can be considered segmented conjugated polymers.[7,8] Additionally, the arenes in paracyclophane can be severely distorted due to strain, thus minimizing the through-space interaction. In contrast, orthocyclophanes exhibit undistorted, nearly parallel arenes, and both Mataka et al.[9] and Grimme et al.[10] have reported reversible one- and two-electron oxidations of benzene in rigid orthocyclophane frameworks. Therefore, we designed polymers **P1**−**P3**, incorporating zero, one, and two co-facial $\pi-\pi$ interactions, respectively, based on a rigid orthocyclophane linkage that simultaneously included a continuous conduction pathway.

The synthetic routes to **P1**−**P3** are highlighted in Scheme 1. Precursors **2b** and **3b** are prepared through remarkably selective and high-yielding Diels−Alder cycloadditions with anthracene.[11] Their structures were confirmed via single-crystal X-ray crystallography. Surprisingly, **2b** and **3b** are the *only* isolated products even though other isomers are possible. The selectivities can be rationalized by considering the attractive interactions[12] present in the transition structures; for example, the synthesis of **2b** suggests that there is a favorable interaction between the bisalkyne-substituted arene and the incoming anthracene. Additionally, stabilizing edge-to-face arene−arene interactions are only available in the transition structure leading to isomer **3b**. Notably, the resonances of the cofacial arene protons in both **2b** and **3b** are shifted upfield in the ^{1}H NMR spectra,[13] and the closest arene−arene distances are 3.01 Å (cf. the interplanar distance in graphite is 3.4 Å).[14]

It was instructive to first examine precursors **1b**−**3b** for evidence of through-space delocalization. In the UV−vis spectra, we observe a bathochromic shift in the absorption maxima from **1b** (λ_{max} = 284 nm) to **2b** (λ_{max} = 304 nm) to **3b** (λ_{max} = 312 nm), providing strong evidence for through-space $\pi-\pi$ interactions that narrow the HOMO−LUMO gap. Next, we performed B3LYP/6-31G(d) geometry optimizations using the atomic coordinates of the crystal structures as starting points followed by single-point energy calculations to determine the molecular orbitals.[15,16] Scheme 1 depicts the HOMO for **3b**, which extends across all three co-facial arenes and supports the concept of through-space delocalization. Finally, cyclic voltammetry measurements confirm that through-space interactions are present as **2b** and **3b** undergo nearly identical reversible oxidations to give a radical cation and dication.[17] As anticipated, **1b** is not oxidized under these conditions.

Scheme 1 [a]



[a] Reagents and conditions: (a) maleic anhydride (10 equiv), xylenes, reflux (50% anti); (b) 7-tridecylamine (1.2 equiv), imidazole (1.5 equiv), toluene, reflux (58%); (c) TBAF (2.5 equiv), THF, rt (86% **1b**; 81% **2b**; 92% **3b**); (d) Pd(Ph$_3$P)$_4$ (0.03 equiv), CuI (0.3 equiv), 1,4-benzoquinone (1.25 equiv), iPr$_2$NH, toluene, 40 °C (10%); (e) anthracene (20 equiv), *o*-xylene, 180 °C (66% **2b**; 76% **3b**); (f) 2-ethyl-1-hexylamine, imidazole, reflux (89% **2b**; 86% **3b**); (g) Pd(Ph$_3$P)$_4$ (0.03 equiv), CuI (0.3 equiv), 1,4-benzoquinone (1.25 equiv), iPr$_2$NH, toluene, 60 °C (71% **2b**; 42% **3b**).

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Table 1. Polymer Molecular Weight and Photophysical Data

			solution (CHCl$_3$)				film	
	M_n (kDa)	DP	abs λ_{max} (nm)	Em λ_{max} (nm)	τ_F (ns)	$\Phi_F{}^a$	abs λ_{max} (nm)	Em λ_{max} (nm)
P1	64^b	127	412	425	0.24	0.59	417	533
P2	58	95	425	435	0.27	0.67	421	439
P3	17	16	415	428	0.25	0.37	429	450

[a] Fluorescence quantum yields were determined using quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 0.53$) as the fluorescence standard. [b] Molecular weight of the soluble fraction.

Satisfied with the evidence supporting through-space $\pi-\pi$ interactions in **1b**−**3b**, we prepared polymers **P1**−**P3**. The anhydrides were converted to *N*-alkyl imides via condensation with branched, long-chain amines to increase solubility. TBAF deprotection provided the acetylenes, and a subsequent Pd/Cu(I)/benzoquinone oxidative polymerization provided high-molecular weight poly(*p*-arylene butadiynylene)s.[18]

Table 1 summarizes the characterization data for **P1**−**P3**. As expected, all three polymers are highly emissive in solution with subnanosecond lifetimes. Surprisingly, the trend observed in the absorption maxima of precursors **1b**−**3b** was not duplicated in CHCl$_3$ *solutions* of **P1**−**P3**. In contrast, the *thin films* of **P1**−**P3** displayed the expected trend due to a significant red-shift in the maximum absorption (14 nm) for **P3** films. Given that the thin film emission spectrum of **P3** retains its vibrational fine structure, we suspect that these spectral changes result from conformational effects that are magnified in the shorter polymer.[19] Polymer **P1** showed a broad, red-shifted emission (108 nm) in thin films, indicating substantial interchain aggregation; this result is not surprising, given the relatively unhindered polymer backbone.

Ultimately, we wanted to compare each polymer's oxidation potential, but initial efforts using cyclic voltammetry were unsuccessful, possibly because of poor polymer−electrode interactions, the polymer's nonpolar structure, or irreversible polymer degradation. We then turned to ultraviolet photoelectron spectroscopy (UPS) on thin polymer films to quantify the ionization potentials.[20] Unfortunately, thin films of our control polymer, **P1**, proved unsuitable due to the substantial aggregation and interchain interactions. Thin films of **P2** and **P3** gave ionization potentials of 5.8 (± 0.2) eV and 6.0 (± 0.2) eV, respectively. These ionization potentials are identical within the error of the experiment and parallel the electrochemistry results on precursors **2b** and **3b**. Consistent with our experimental results, single-point energy calculations on **2b**−**2b** and **3b**−**3b** dimers[15] showed substantially smaller molecular orbital coefficients on the cofacial arenes compared to the monomers, suggesting that as the conjugation length increases, the perturbation caused by the cofacial arene is diminished.

In summary, we reported the highly selective and efficient syntheses of a series of continuously conjugated poly(*p*-arylene butadiynylene)s containing zero, one, and two cofacial arenes. Although compelling evidence for through-space interactions in precursors **1b**−**3b** was observed, the results for polymers **P1**−**P3** were less conclusive. We continue to explore the potential of these unique systems; preliminary studies suggest the more hindered polymer (**P3**) is more stable to photobleaching than the less hindered polymers, **P1** and **P2** (see Supporting Information). Therefore, our current efforts are focused on incorporating these frameworks into other π-conjugated polymers. The results of these studies will be reported in due course.

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Supporting Information Available: Experimental details, spectroscopic data, electrochemical data; X-ray crystallographic data in CIF format; complete ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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