ORGANIC LETTERS

2007
Vol. 9, No. 16
3041−3044

Methano[10]annulene Revisited: Extended Delocalization through Conjugated Polymers Bearing Larger Hückel Aromatics

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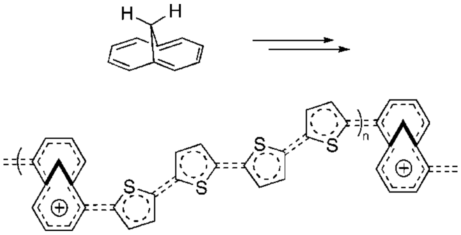
Received May 7, 2007

ABSTRACT



A comparative study of conjugated polymers derived from the two 10 π electron circuits of *naphthalene* and *methano[10]annulene* is presented. The annulene π topology allows for a greater degree of intrapolymer charge delocalization, a key structural parameter for enhancing the performance of organic semiconductors. Molecular design and synthesis based upon unusual aromatic cores will enable facile transport properties that would not ordinarily be realized under the 6 π electron aromatic paradigm.

Functionalizable aromatic molecules make up a cornerstone of the burgeoning field of organic electronics.[1] Subunits of a conducting polymer require electronic structures that can distort to stabilize charge carriers. These distortions typically involve localized *aromatic* and delocalized *quinoidal* resonance structures, which describe to differing degrees the electronics of the polymer in the insulating and the conductive states.[2,3] Since the quinoidal form requires disruption of aromaticity among several repeat units of a polyaromatic system, polarizable aromatics with lower resonance stabilization energies (thiophene, pyrrole) have proven useful as components of electronic materials.[4] More complex aromatics have also received substantial experimental[5−8] and theoretical[9,10] treatment; however, experimental comparative studies with benzenoid counterparts are lacking.

A planar [10]annulene should be the closest *neutral* homologue of benzene,[11,12] but conformational preferences of the cyclic oligoene prevent true aromatic delocalization. Vogel installed a methano bridge to force the [10]annulene into a near planar conformation thereby imparting aromatic physical properties.[13] Although this fascinating molecule has

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10.1021/ol071062y CCC: $37.00

been the subject of intense study, its use to realize advanced materials has been rare,[14−16] and we are aware of no reports in the context of semiconducting polymers. Larger $[4n+2]$-annulenes are attractive building blocks for electronic materials since their aromatic properties are attenuated to some degree by a strong polyene character. Aromatics offer stability and facile synthetic elaboration while polyenes serve as effective conduits for charge carriers (e.g., polyacetylene). To understand and apply unusual aromatic circuits that take advantage of both criteria, we report a comparative study of conjugated polymers bearing two different yet well-established 10 π electron circuits: 1,6-methano[10]annulene and naphthalene. As illustrated in Figure 1, we find that the annulene core dramatically facilitates delocalization of charge carriers relative to the classical aromatic thereby offering more direct encouragement for new charge transporting organic materials beyond the 6 π electron structural paradigm.

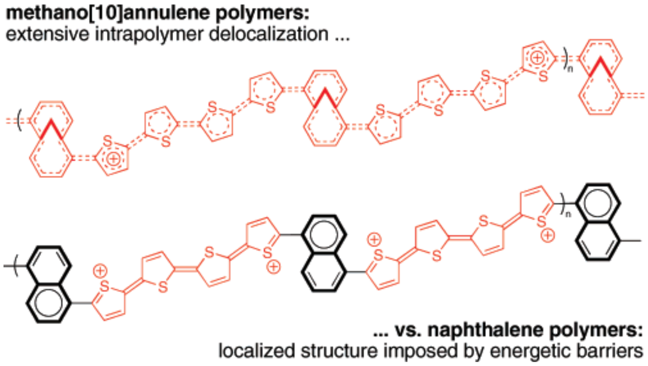

Figure 1. Exaggerated resonance structures associated with oxidized/doped methano[10]annulene (top) and naphthalene (bottom) polymers.

This study intentionally employed the nonlinear 2,7 pathway of **1** and the 1,5 pathway of **2** (Scheme 1).[17,18] Stille cross-coupling provided electropolymerizable monomers **3** and **4** where bithiophene moieties flank the central 10 π cloud. Sonogashira copolymerizations with a solubilizing dialkyne[19] led to fluorescent poly(arylene-ethynylene, PAE)s **5** and **6** for studies in solution, while phenylacetylene coupling provided known molecules **7** and **8**.[20,16] All materials seemed robust under ambient lab conditions. Any delocalization through these kinked linkages would engage the entire aromatic system vis-à-vis the *para*-like 2,5 pathway through **1** or the 1,4 pathway through **2** that might lead to the possibility of localized aromatic sextets similar to the situation for quinoidal benzo[*c*]thiophene.[21] This critical design component allowed us to assess the extent to which the parent core served as a simple end-capping unit rather than a willing participant in the delocalization of introduced charge.

UV−vis measurements revealed a substantial red-shift of the lowest energy absorption in the bithiophene-flanked annulene **3** (λ_{max} 420 nm) relative to **4** (λ_{max} 350 nm). The value for **3** compares well to other common aromatic motifs flanked by bithiophene moieties such as 1,4-phenyl (391 nm, CH_2Cl_2),[22] 2,7-fluorenyl (399 nm, $CHCl_3$),[23] and 2,5-thienyl (431 nm, CH_2Cl_2).[24] The 70 nm shift between **3** and **4** arises from conformational *and* electronic effects since the slightly nonplanar annulene moiety within **3** may facilitate greater π orbital overlap with the pendant thiophenes due to relieved steric clashing with the *pseudo-peri* hydrogens present in **3**. Free rotation about the ethynes of **7** and **8** would eliminate such a conformational bias, and the λ_{max} of the annulene **7** was red-shifted 40 nm relative to that of the naphthalene **8** (Figure 2b). As opposed to a purely conformational effect, the extension of the effective conjugation length through conjugated molecules built upon the kinked pathway of **1** stems from electronic differences imparted by the *monocyclic* π circuit of the annulene core.

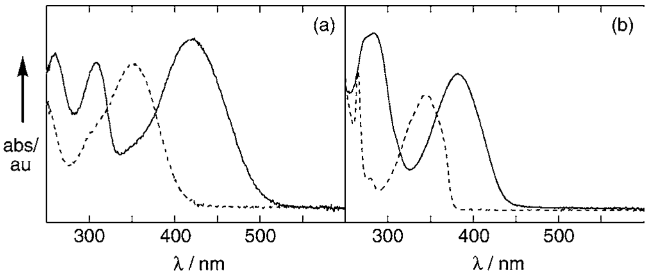

Figure 2. UV−vis absorbance of (a) **3** (solid) and **4** (dashed) and (b) **7** (solid) and **8** (dashed). All spectra were obtained at room temperature in $CHCl_3$. For comparison, the absorption onsets for the parent hydrocarbons fall at 295 (naphthalene) and 330 nm (1,6-methano[10]annulene).

The initial electropolymerization scans of **3** and **4** occurred with potentials of peak anodic current (E_{pa}) at 0.85 and 1.05 V, respectively. The oxidation of **3** appeared more electrochemically reversible highlighting the greater stability enjoyed by radical cations of **3** due to the extended delocalization. While this may potentially limit the molecular weight of poly(**3**),[25] it further illustrates the greater ability of the annulene to delocalize charge through the presumably weaker

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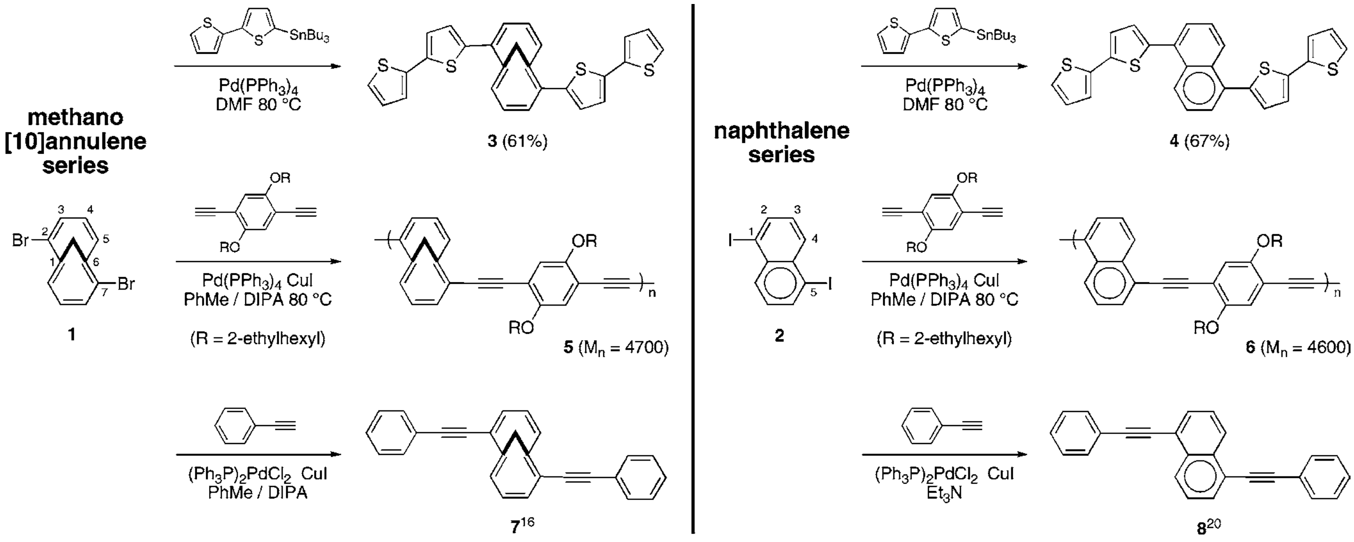
Scheme 1. Synthesis of Electronic Materials Derived from Methano[10]annulene and Naphthalene



aromatic core.[26] Films of poly(**3**) had fairly reversible electroactivity more typical of thiophene-based conducting polymers with an E_{pa} centered at 0.76 V accompanied by decomposition of the medium at higher applied potentials (Figure 3a). In contrast, poly(**4**) displayed two strongly irreversible redox processes at 1.00 and 1.36 V that suggest very slow electrochemical kinetics as expected for an electrode modifying layer of limited electrical conductivity. The two well-defined redox waves for poly(**4**) also hint at a more localized electronic structure. This is consistent with the premise that the annulene moiety facilitates intrapolymer charge delocalization relative to naphthalene as further substantiated below.

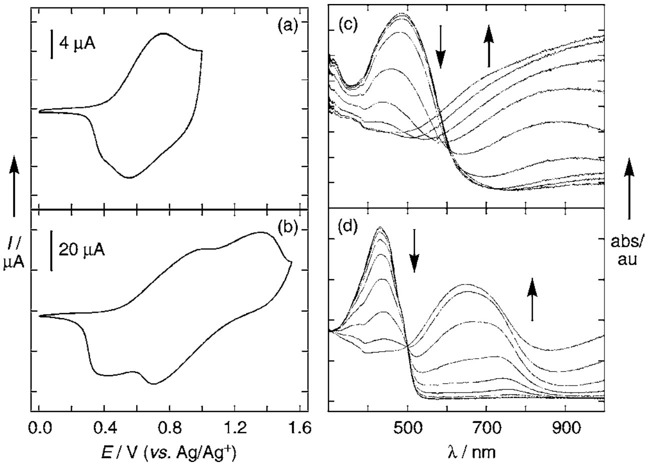


Figure 3. Cyclic voltammetry of (a) poly(**3**) and (b) poly(**4**) thin films at a 2 mm^2 Pt button electrode in 0.1 M n-Bu$_4$PF$_6$ (CH$_2$Cl$_2$), $\nu = 100$ mV/s; spectroelectrochemical profiles for films of (c) poly(**3**) and (d) poly(**4**) grown on ITO-coated electrodes and held at ca. 100 mV steps between 0.2 and 1.0 V (c) or 0.4−1.2 V (d).

To reveal the nature of the polymer charge carriers and how they evolve during oxidation, we examined their spectroelectrochemistry after electropolymerization on indium-doped tin oxide (ITO).[27] In the undoped state, poly(**3**) presented a λ_{max} of 480 nm (Figure 3c) while poly(**4**) had a blue-shifted λ_{max} of 430 nm (Figure 3d). In comparison, high-quality films of neutral electrochemically grown polythiophene have a peak absorption at ca. 500 nm (CH$_3$CN).[28] The lowest energy λ_{max} associated with the neutral polymer decreased as the films were held at progressively more positive potentials, accompanied by lower energy optical signatures characteristic of charge carriers. The transitions for oxidized poly(**3**) were centered around 875 nm at moderate doping levels, and their broad profiles suggest a greater contribution from the superposition of absorption bands that would result from the presence of multiple absorbing species of varying conjugation length. This would be expected if the charge carriers were able to delocalize easily over subunits of the polyaromatic conjugation pathway shorter in length than the true effective conjugation length given the conformational demands imposed in the solid state.

In contrast, poly(**4**) displayed fairly well-defined transitions, with a narrower polaronic peak absorption at 650 nm. In a most remarkable effect, poly(**4**) displayed a clear isosbestic point at 500 nm between the neutral and polaronic transitions, further illustrating a localized electronic structure of limited effective conjugation length. Compared to the much more diffuse nature of poly(**3**), the defined profile for poly(**4**) is reminiscent of a *segmented* electronic polymer.

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This follows from the limited extent of intrapolymer mobility available to charge carriers formed within poly(**4**) upon oxidation as regulated by the energetic barrier of the naphthalene core. It seems more reasonable to consider doped states of poly(**4**) as a polymeric series of cationic quaterthiophenes isolated by naphthalene spacers (Figure 1, bottom) rather than a classic (bi)polaron delocalized over multiple aromatic units.

Since the methano bridges throughout poly(**3**) should impact interpolymer π-stacking in thin solid films confined to the electrode surface, we also examined the optical properties of polymers **5** and **6** in solution. Polymer **5** absorbed at 450 nm with a very broad emission at 510 nm (Figure 4a) while polymer **6** absorbed at 390 nm (with a higher energy shoulder) and emitted with more fine structure at 435 nm (Figure 4b). Similar blue shifts have been observed in related 1,5-naphthalene ethynylenes as the naphthyl content was increased.[29] In the present case we can attribute the smaller optical band gap of **5** to the presence of a longer effective conjugation length. Differing degrees of transannular interactions resulting from excited-state reorganization within **5** in order to better accommodate exciton delocalization could also be operative.[30] Although poor solubility limited the current analysis to lower molecular weight material, both samples are of comparable length, and more soluble polymers will allow us to explore their rich photophysics and to quantify key radiative processes.

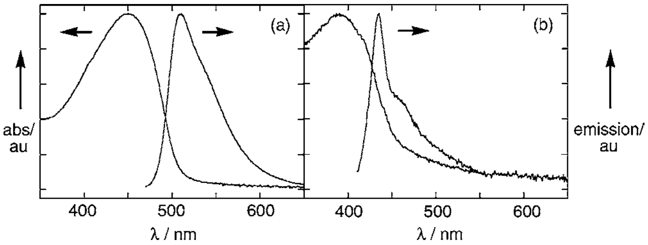

Figure 4. Normalized absorption and emission spectra for (a) **5** and (b) **6** taken at room temperature in $CHCl_3$ (excitation wavelengths of 450 and 390 nm, respectively).

In conclusion, the monocyclic 10 π electron aromatic circuit of the annulene core promotes a longer effective conjugation pathway for charge carriers—both excitons and "holes"—compared to the relatively more localized circuit of naphthalene. Oligoenes are established conduits for effective energy migration, and the electronic impacts of nondegenerate ground states of polyaromatics are well-known. We now provide a detailed experimental consideration where both of these issues are potentially operative in the same system. Using a well-established annulene scaffold, we affirmed an emerging design strategy utilizing larger aromatic topologies to realize higher performance organic electronic materials. Despite the fact that the studies at hand purposefully employed a disjointed conjugation pathway, the bulk electrochemical and optical properties of the annulene polymers compared well to those observed for polyaromatics derived from typical 6 π-electron monomers without sacrificing environmental stability. Efficient conjugation pathways through less commonly employed aromatic topologies stand to provide equally exciting new electronic materials, and chemical synthesis of complex structures will be a critical component of these ongoing efforts. The general approach described herein as enabled by unusual and synthetically elaborate aromatic motifs remains a subject of continued research in our laboratories.

Acknowledgment. Johns Hopkins University, Princeton Applied Research (New Young Investigator Award to J.D.T.), the donors of the Petroleum Research Fund (administered by the American Chemical Society, PRF-45738-G7), and the National Science Foundation (CAREER, DMR-0644727) provided generous and continued support. We thank Ms. Amanda Fond and Dr. Jovan Giaimo (Meyer Lab) for help with fluorimetry, and the Cornell Center for Materials Research for GPC.

Supporting Information Available: Experimental procedures, characterization data, fluorescence spectra, and monomer electropolymerization profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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