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Emerging Prospects for Unusual Aromaticity in Organic Electronic Materials: The Case for Methano[10]annulene

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Unusual aromatics outside of the 6π-electron motif offer promise for functional electronic materials, and we frame this claim in the context of 10π-electron aromatics. The evolution of our understanding of 10π-electron aromatics is discussed briefly, from azulene to the [10]annulenes to finally 1,6-methano[10]annulene. A survey of annulene research of both fundamental and applied nature is then presented. Finally, our recent contributions to this area are highlighted with a comparison of annulene-based electronic materials to more classical benzenoid counterparts. The annulene core greatly facilitates the delocalization of mobile charges as determined through voltammetry and spectroelectrochemistry. We show that this important hydrocarbon can indeed be viewed as a viable building block for advanced polymeric semiconducting materials.

Introduction

Synthetic chemistry continues to play a major role to further our understanding of aromaticity. Following the advancement of the aromatic sextet concept for benzene and related molecules, Hückel's generalization of this phenomenon to monocyclic rings bearing $4n+2$ conjugated π-elec-

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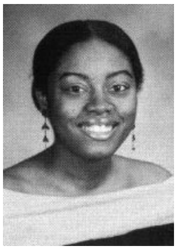

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trons inspired the synthesis and investigation of a wide variety of unsaturated hydrocarbons and heteroatom-containing molecules designed to test the validity of this now quotable "4*n*+2 rule." Historical landmarks include Breslow's synthesis of the 2π-electron cyclopropylium cations,[1] the formation of aromatic cyclooctatetraene dianions (by Katz)[2] and dications (by Olah)[3] from tub-shaped nonaromatic hydrocarbon parents as well as Sondheimer's synthetic contributions that yielded even larger molecules spanning 14 to 30π-electrons (Figure 1).[4,5] These classic molecules also fueled the fires associated with the debates over the nature of aromaticity and its quantification. For the purposes of this article, "aromaticity" will simply refer to the criterion of 4*n*+2π-electrons in a conjugated cyclic circuit, acknowledging that the electronic, magnetic and structural criteria for aromaticity may not be strictly met by all 4*n*+2 aromatics.

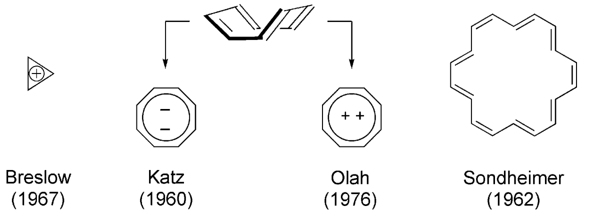


Figure 1. Charged and neutral non-benzenoid aromatics that obey Hückel's rule.

Current research in molecular aromatic systems could not be adequately summarized here, and an authoritative thematic issue of *Chemical Reviews* in 2001 dealt with the multiple facets of modern aromatic research.[6] One exciting area of research where aromatic systems play a key role is in the field of π-conjugated organic electronic materials, where "plastics" serve as active device components able to emit light, conduct electrical current or harness solar energy. The vast majority of aromatic building blocks used to construct new electronic materials arises from the historically dominant 6π-electron motifs of benzene, thiophene or pyrrole, or synthetically fused variants thereof. This is not to imply that they do not offer deep insight into how electronic structure impacts performance (key examples of the latter, from Wudl's polymerized benzo[*c*]thiophenes to Sotzing's processable thienothiophenes, have furthered the development of low-bandgap conducting polymers);[7,8] rather, we wish to draw attention to the prospects that *non-benzenoid* aromatics beyond this 6-π paradigm may bring to the table. As a representative example, this review will highlight materials-oriented work with one particular non-benzenoid system, 1,6-methano[10]annulene. We will first address the research paths that led to the establishment of this important hydrocarbon. We will follow this with elegant examples of new molecules that impart new function primarily in the context of spectroscopically dilute solutions of non-interacting molecules. Finally, we will turn to a relatively unexplored arena for non-benzenoid aromatics, that of semiconductive organic polymers. It is our intention to introduce the techniques employed to study semiconducting organic polymers in the context of our own work while conveying the excitement that waits for materials chemists wishing to apply unusual aromatic systems towards emerging organic electronics applications.

A Rationale for Unusual Aromatics

The concept of aromaticity has intrigued chemists since the discovery of benzene by Faraday in 1825. Debates raged soon thereafter regarding benzene's chemical structure and still rage regarding the definition and quantification of aromaticity. The high-profile scholarship associated with the subtle semantics of aromaticity clearly shows that the physical organic chemistry of aromatic systems remains a thriving area of research. Equally exciting are the prospects for transitioning this science into more applied avenues of technological relevance.

Aromatic structures are key components of organic electronic materials, be they small molecule semiconductors such as pentacene, electrically conductive polymers such as regioregular polythiophenes or electroluminescent polymers such as poly(phenylene vinylene)s (Figure 2). All of these materials can be processed at temperatures much lower than their inorganic counterparts under ambient conditions to construct functional devices. Important scientific milestones that gave birth to organic electronics include the

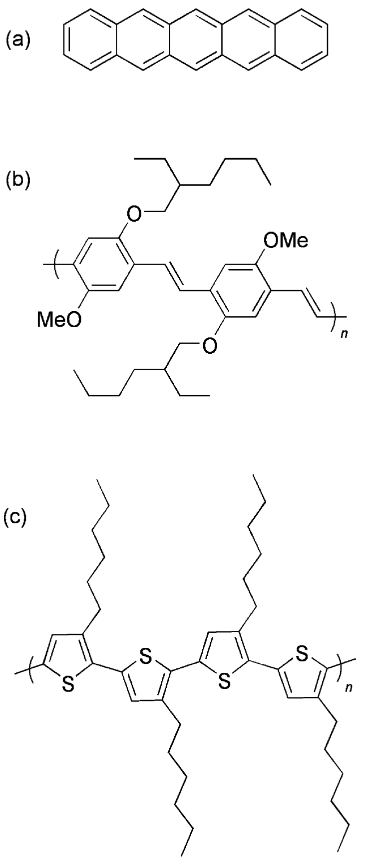


Figure 2. Some of the "gold standards" of organic electronics: (a) pentacene; (b) MEH-PPV, poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]; and (c) P3HT, poly(3-hexylthiophene).

measurement of carrier mobilities through acene single crystals,[9–11] the development of highly conductive organic ion-radical salts and charge transfer compounds,[12–15] and the achievement of near-metallic conductivity in polyacetylene through chemical doping.[16,17] Although important in its own right as a novel material, it is unfortunate that technological applications employing polyacetylene have been limited by poor processability and high reactivity. The development of *polyaromatic*-conjugated polymers based upon benzene, thiophene or pyrrole led to more tractable materials whose properties could be easily tuned through choice of monomer precursor. The synthetic chemistry of simple (hetero)aromatic systems is now quite mature, allowing researchers to incorporate almost at will substituents to tune electronics or enhance solubility. Pd and Ni-catalyzed cross-couplings have played an equally important role to enable the preparation of a large variety of well-defined oligomers and polymers with useful function.[18] New structures with unusual electronic properties stand to add excitement to the next generations of organic electronic materials.

One should initially question the motivation for studying unusual electronic structures as functional components of organic electronic materials. After all, great strides have been and will continue to be made by more readily available 6π aromatic components built from functionalizable benzene, pyrrole or thiophene rings. It is now well accepted that simple polyaromatics such as polyphenylenes have two non-degenerate ground states, the so-called aromatic and quinoidal forms (Scheme 1, top). While both may be considered as conjugated structures, it is important to recognize that the localization of aromaticity in the former leads to less intrapolymer delocalization. In the neutral insulating state, the aromatic form is the dominant contributor to the polymer's actual electronic structure, and this results in a fairly large HOMO–LUMO gap. Upon removal of an electron, two chemical scenarios may be envisioned (Scheme 1, bottom). First, the radical cation can remain localized on one repeat unit thereby preserving aromaticity in the units around this "defect." Second, we can invoke a series of resonance structures that ultimately delocalize this charge over multiple subunits. This leads to a quinoidal electronic structure that progressively evolves upon oxidation or doping in order to better stabilize nascent charge carriers,[19–22] accompanied with a decreased optical bandgap given the substantial polyene character now present in the backbone. These electronic alterations are well reflected in spectroelectrochemical measurements that allow one to interrogate polymer optical properties as a function of applied potential and deduce the dominant electronic structure.[23]

The quinoidal delocalization over multiple repeat units on the one hand is stabilizing, on the other hand, it requires the energetically unfavorable disruption of aromaticity within the component rings. The ability to achieve the planar quinoidal geometry is also hampered by the sterics associated with the hydrogen atoms *ortho* to the aryl–aryl linkages. Nevertheless, the quinoidal forms are the most commonly invoked structures for conducting polymers in their doped states. Related to the extent of quinoidal delocalization is an important parameter, the *effective conjugation length*, which describes the number of repeat units within a particular polymer over which an excited state/charge carrier is spread. Monomers with lower resonance stabilization energies (such as thiophenes, pyrroles and furans depicted in Figure 3)[24] reduce the energetic penalty that must be paid to adopt the quinoidal structure and have played critical roles in the development of modern organic electronics. These common five-membered rings also alleviate much of the steric costs required in order to achieve planarity. Other aromatics that lie on the interface between cyclic oligoenes and truly aromatic systems larger than 6π-electrons may minimize the steric issues while easing the energetic requirements for electronic reorganization. They may offer greater environmental stabilities and processability relative to localized benzenoid (hetero)aromatics or the intractable polyacetylenes.

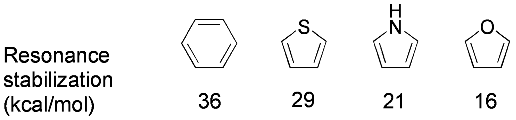
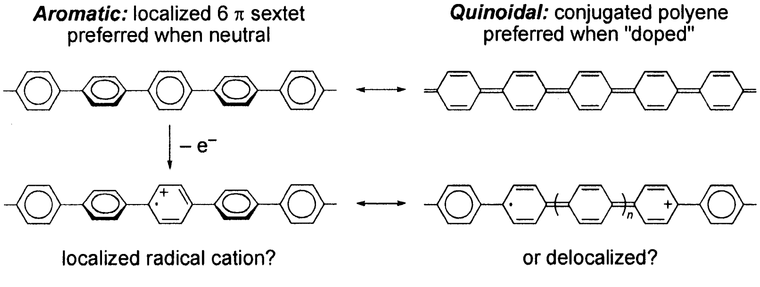


Figure 3. Resonance stabilization energies for common aromatics and heteroaromatics.

The extensive theoretical and experimental studies of molecules built around non-benzenoid aromatic cores have provided a solid foundation upon which our current work is



Scheme 1. Resonance structures associated with the *aromatic* and *quinoidal* bonding geometries, as relevant for both the neutral (insulating) and oxidized/doped (conducting) polymer.

based. Among the most investigated systems are the many different flavors of the *annulenes* as thoroughly documented in the timely reviews of theoretical considerations by Kertesz and experimental examples by Haley.[25,26] Both of these surveys frame the annulenes in the context of individual molecules and as components of more complex systems. Despite the great interest in these and other unusual aromatic systems outside the realm of 6π-electron motifs, it would appear that the difficult syntheses associated with functionalizable ring systems has impacted their evaluation as useful materials. This is not meant to undermine the elegant syntheses and emerging functional applications already established for unusual molecular aromatics ... rather the contrary, we could further claim an additional element of usefulness in the knowledge gained from thorough physical investigation of their topologically complex (and aesthetically pleasing!) molecular architectures.

From an application perspective, it is important to realize that the vast majority of the annulenes were studied in solution or *in silicio*. Although many sensory and light-emission schemes have been realized in solution, the extension of any molecularly engineered properties to the solid state can be a daunting task. However, recent reports with "liquid metamaterials" would suggest that even this assertion is subject to debate.[27] Two of the most common device architectures utilized for organic electronics are simplistically depicted in Figure 4, the diode (left) and the transistor (right). In the first, passing charge through the device ultimately leads to electron-hole recombination in an emissive layer that is accompanied by the emission of light. A careful balancing of the energy levels of the component molecules with the electrode work functions is one of many critical elements required to optimize the efficiency of charge injection across the metal-semiconductor interfaces (the physical reverse of this process leads to a photovoltaic). In the second, a suitable gate bias generates mobile charges that, at a certain threshold concentration, establish a conductive channel connecting the independent source and drain electrodes. This device serves as a "switch" that is on or off depending on the magnitude of the gate bias. In both cases, the active organic layers can be deposited through evaporation, spin-coating or with ink-jet technology, and this sophistication with respect to materials processing has enabled the construction of a diverse and complex array of electronic device architectures. However, exerting control over intermolecular interactions or even over the extent of thin-film crystallinity is not always easily achieved, and these properties dramatically impact overall device performance for both cases.

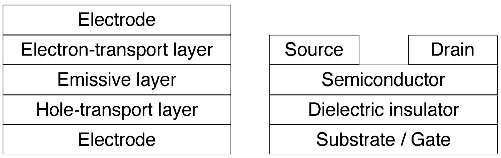
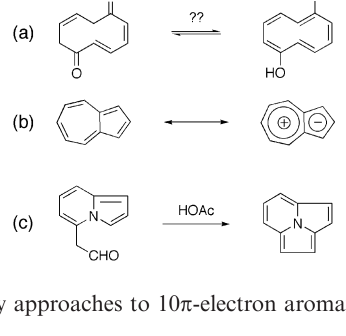


Figure 4. Device architectures commonly encountered in the evaluation and application of organic electronic materials: the diode (left) and the transistor (right).

Although the device physics associated with these examples are well beyond the scope of this review,[28–30] it is safe to say that the full potential of organic electronic materials will not be realized unless their properties can be routinely harnessed in such solid-state devices. The possibilities are endless: flexible and large area displays, light-weight photovoltaics, wearable electronics, biosensors, smart cards, and the list goes on.[31–33] These high-impact applications have brought together a diverse array of disciplines looking to tackle the forefronts of organic electronics. Theory, materials synthesis, device fabrication, application development, and marketing all play important roles in the continued evolution and expansion of the field. From the perspective of an organic chemist, exciting opportunities await for those who seek to explore new materials with unusual electronic structures, be they synthesizing new entities not yet known or be they taking established molecular frameworks and pushing them into new frontiers. This review will focus on the latter.

A Bigger Benzene: [10]Annulene

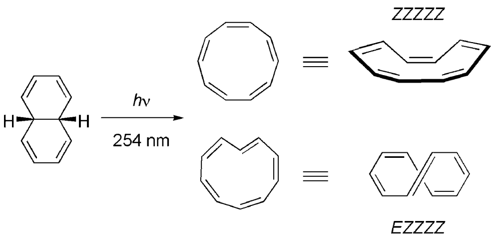
The [10]annulene π-system is the next neutral aromatic structure in the Hückel sense (where $n = 2$), and it struck us as a logical first entry as a surrogate for the "benzene" building block for new organic semiconductors. Although charged monocyclic compounds with 10π-electrons prepared in the 60s meet several aromatic criteria,[2,34,35] and the [10]annulene framework has often been invoked as a transient intermediate in the course of valence isomerizations (for example, in the dihydronaphthalene to bullvalene photoisomerization),[36] extensive efforts primarily in the 60s and 70s failed to isolate a truly aromatic and neutral 10π-electron annulene circuit.[37] Sondheimer sought to rely upon keto-enol equilibrium to force aromaticity within a ring-substituted variant through enol tautomers (Scheme 2, a).[38] The enolization of the cyclic dione necessarily imparts the requisite 10π-electron circuit within the hydrocarbon scaffold, but this enol form could not be trapped or isolated. At a first glance, *azulene* seems to be a close surrogate for [10]annulene where a carbon–carbon bond connects the 1 and 5 positions and allows for a 10π-electron perimeter (Scheme 2, b). The large dipole found experimentally affirms that the ground state can be viewed as a fused aromatic seeking to optimize sextets within each ring, in essence a tropylium-fused cyclopentadienide rather than a



Scheme 2. Early approaches to 10π-electron aromatic perimeters.

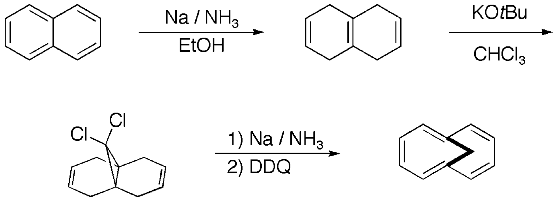
single delocalized current. Boekelheide synthesized the *cyclazines*, polycyclic frameworks with 10π-electrons on the perimeter bearing a bridging nitrogen within (Scheme 2, c).[39] Given that the nitrogen lone pair is not an electronically innocent bystander and this system can no longer be considered monocyclic, the 4*n*+2 rule no longer holds, and this 12π-electron heterocycle has aromatic properties much in the vein of the phenalenyl anions.

The most notable preparative efforts for the parent [10]-annulene hydrocarbon came from the laboratories of van Tamelen and Masamune,[40–42] who used valence isomerizations of *cis*- and *trans*-9,10-dihydronaphthalene to form the 10π-electron systems. This ring size can comfortably accommodate trans double bonds within the unsaturated macrocycle, but conformational dynamics of the ring and steric clashing of internal ring protons prohibited a truly planar aromatic circuit. In van Tamelen's hands, direct hydrogenation of dihydronaphthalene photolysate mixtures led to decent yields of the completely saturated cyclodecane, presuming the fleeting presence of monocyclic 10-π cyclodecapentaene circuits. Masamune isolated two distinct conjugated molecules from the photolysis of *cis*-9,10-dihydronaphthalene (isolated in pure form after chromatography at –80 °C) that on paper give distinct (*ZZZZZ*) and (*EZZZZ*) geometries within a planar monocycle (Scheme 3). They also demonstrated that these molecules were distorted from planarity in order to relieve ring strain associated with the perfectly planar architecture thereby rendering the molecules nonaromatic. Masamune concluded "without reservation that the [10]annulenes by no means belong to the category of aromatic compounds."[41] To this date, the aromatic properties of simple [10]annulenes have yet to be revealed experimentally, although theory has found a possibility for aromaticity.[43]



Scheme 3. Photolysis of *cis*-9,10-dihydronaphthalene as reported by Masamune: isolated [10]annulenes were determined to be nonaromatic.

In 1964, Vogel and Roth achieved an impressive synthetic feat to enforce aromaticity within the [10]annulene ring.[44] They installed a methylene bridge to link the 1 and 6 positions of the carbocycle that forced the π system into a more stable configuration that could indeed foster an aromatic ring current among the entire π system. This was achieved by trading the strain associated with the methano bridge for the severe steric clashing that the internal protons of the (*ZEZZE*) system would experience in a fully planar conformation. The construction was by no means trivial (Scheme 4), but Vogel's procedure was powerful enough to render it suitable for inclusion in *Organic Syntheses*.[45] Naphthalene undergoes a Birch reduction to isotetralin that then undergoes cyclopropanation with dichlorocarbene primarily at the internal olefin. Reductive dehalogenation followed by oxidation with DDQ facilitates ring opening and subsequent aromatization of the annulene ring. This procedure is amenable to the preparation of multi-gram quantities of 1,6-methano[10]annulene, although in our hands the separation of undesired carbene addition products proved incredibly frustrating!



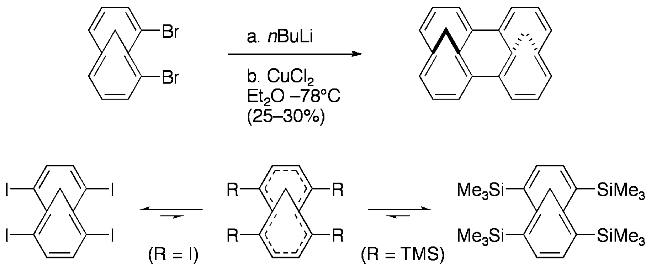
Scheme 4. Vogel's large-scale synthesis of 1,6-methano[10]annulene.

As alluded to in the introduction, classifying any cyclic π-system as "aromatic" is subject to multiple criteria that may or may not be in complete agreement. This is indeed the case for methano[10]annulene. Structurally, it maintains the small bond length alternation often associated with aromatic compounds (varying between 1.37–1.42 Å).[46] Electronically, the lowest energy absorption $\lambda_{\max}$ is red-shifted about 15 nm relative to naphthalene. Magnetically, the methylene protons positioned directly above the π circuit are strongly shielded, resonating upfield (at $\delta = -0.51$ ppm) as to be expected in the presence of a diatropic ring current. These magnetic properties are also found computationally, with strongly negative NICS values calculated within the interior of the annulene.[47,48] So is it aromatic?

Its reactivity suggests olefinic character in that addition-elimination processes are operative when exposed to halogen electrophiles.[49,50] This stands in contrast to the electrophilic substitution commonly invoked in aromatic halogenation chemistry. The resonance stabilization energy is modest when compared to benzene or naphthalene, but substantial nonetheless.[51] Furthermore, it is not formally monocyclic due to the bridging methylene moiety, and the strain imposed by this linkage enforces a π system that is bent 40° out of planarity. So is it aromatic? Regardless of the answer, this unique molecule has properties that suggest both aromaticity and olefinic character, and it is for this reason that we focused some of our initial studies on this fascinating molecule.

Fundamental interest and intellectual curiosity of the methano[10]annulenes led several groups to carefully probe their photophysics and redox chemistry in more depth. Charged [10]annulene frameworks were studied by Gerson et al. through alkali metal chemical reduction and subsequent EPR observation.[52,53] It was found that the coupling constants for the peripheral hydrogens on the annulene ring were quite small and had a pronounced temperature dependence relative to naphthalene radical anions. These results were attributed to the non-planarity of the annulene π system that in effect facilitated spin transfer among the C(2p) system and the peripheral H(1s) orbitals. Creary studied the enhanced stability that radicals and carbocations experience when adjacent to the annulene relative to other aromatic systems.[54,55] Their findings imply that the weaker aromatic stabilization energies associated with larger annulenes can be overcome in order to delocalize cations over larger areas. Dewey et al. studied the photophysics of methano-bridged annulenes in order to learn more about their transannular interactions in the excited state.[56] These insights are particularly important given the prospects for *homoaromaticity* within the annulene core as well as the importance of the underlying σ-framework as a factor for aromatic delocalization.[57] Efforts such as the examples above provide a strong foundation for the development of new π-conjugated materials whose performance depends upon the formation and mobility of *quasi*-particle excitons or radical ion charge carriers. Despite the extensive studies of this annulene and related molecular systems, there is a surprising lack of new constructs built upon these molecules that may be considered as functional materials.

One of the earlier efforts in this regard came from the groups of Vogel and Wudl who sought to incorporate methano[10]annulene into more exotic electronic systems that mimicked perylene for use as aromatic donors for conductive charge-transfer salts (Scheme 5, top).[58] Using copper(II) mediated oxidative coupling, they prepared isomers of what they called *bishomoperylene* that consist of two annulenes dimerized through the *peri*-positions similar to the bonding arrangement found in perylene. The reported low-energy optical transition was indeed reminiscent of perylene but red-shifted approximately 15 nm, quite similar to the trend found when comparing methano[10]annulene and naphthalene. These two authors also have long-standing interests in the effects imposed by other substitutions of the annulene periphery. For example, Vogel synthesized a tetra(trimethylsilyl) derivative and Wudl prepared a tetraiodo derivative, both involving substitution at all four *peri*-positions (Scheme 5, bottom).[59,60] X-ray crystal structures for both of these molecules revealed substantial bond fixation suggestive of localized olefinic electronic structures rather than delocalized ring current. This localization could also be deduced by proton NMR from the diminished shielding evident in the bridging methylene: +1.53 ppm for the tetrasilyl, +0.71 ppm for the tetraiodide compared to –0.51 ppm for the parent aromatic annulene. However, theory (NICS) suggests that these bond-fixed structures still maintain aromatic magnetic properties.[61] These attenuations of aromaticity were attributed to the severe steric biases imparted by the bulky silyl or iodo substituents and may also be interpreted in the context of σ-framework distortivity.



Scheme 5. Sterically demanding modifications of the annulene periphery: direct fusion preserves the aromatic properties (top) while exhaustive *peri*-substitution with bulky groups leads to greater bond localization (bottom).

By taking these lessons into account, it is possible to construct numerous ring- or bridge-substituted variants that still maintain their aromatic properties. These properties may then be exploited as, among other things, electronic conduits or as unusual lipophilic quadrupoles. Gellman used the nonpolar concave face associated with the annulene in the construction of "contrafacial amphiphiles" as an alternative to the linear alkyl chains found in more common surfactants.[62,63] Their design provided a substantial molecular footprint given that the structure of this molecule frustrates a specific assembly scheme that will isolate the nonpolar hydrocarbon faces from an aqueous environment (Figure 5). In the course of this work, they developed a substantial repertoire of chemistry relevant to additional annulene functionalization.[64] The unique amphiphilicity of this system imparted different assembly characteristics and supramolecular architectures relative to surfactants that possess more clearly segregated polar and nonpolar functionalities. For example, the contrafacial amphiphiles aggregated weakly, but they did not form defined supramolecular objects capable of sequestering small molecule hydrophobic dyes as commonly found for other surfactants. They postulated that this unusual topology might prove less disruptive for protein or membrane manipulation relative to surfactants that readily form hydrophobic microenvironments upon assembly.

Small molecules relevant to organic electronics have been constructed through relatively straight-forward cross-coupling chemistry with known halogenated methano[10]annul-

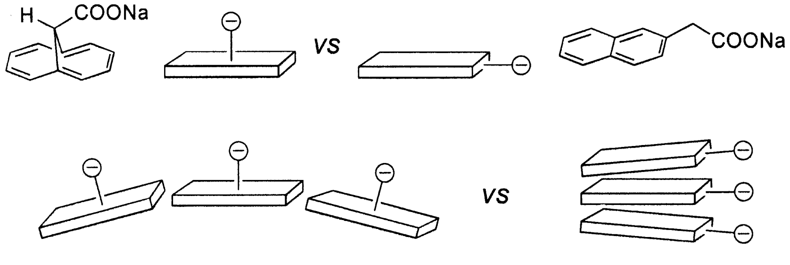


Figure 5. Gellman's contrafacial amphiphiles juxtaposed with a standard aromatic surfactant.

enes (Figure 6). Neidlein constructed ethynylated molecules under Sonogashira conditions with the initial intention apparently of examining the cyclization chemistry of the alkynes in the presence of organometallic reagents and how this would affect the valence isomerization of the annulene core.[65] This work led them to prepare several donor-acceptor molecular systems for study in solution,[66] and their chemistry was extended to the synthesis of diazo molecules that have potential as new dyes or as light-responsive chromophores that can harness *cis*/*trans* isomerization events. Iyoda et al. prepared several ferrocenyl-substituted annulenes through Negishi-type couplings with the hopes of constructing ferromagnetic materials on account of the cofacial interactions and electronic communication present among the organometallic fragments.[67] Starting synthetically from a cycloheptatriene, recent work by Kajioka et al. prepared hole-transporting triarylamines whose amorphous solid-state properties made them suitable electroluminescent OLED materials.[68] To the best of our knowledge, there are no reports describing the incorporation of the methano[10]-annulenes into the backbones of semiconducting organic polymers.

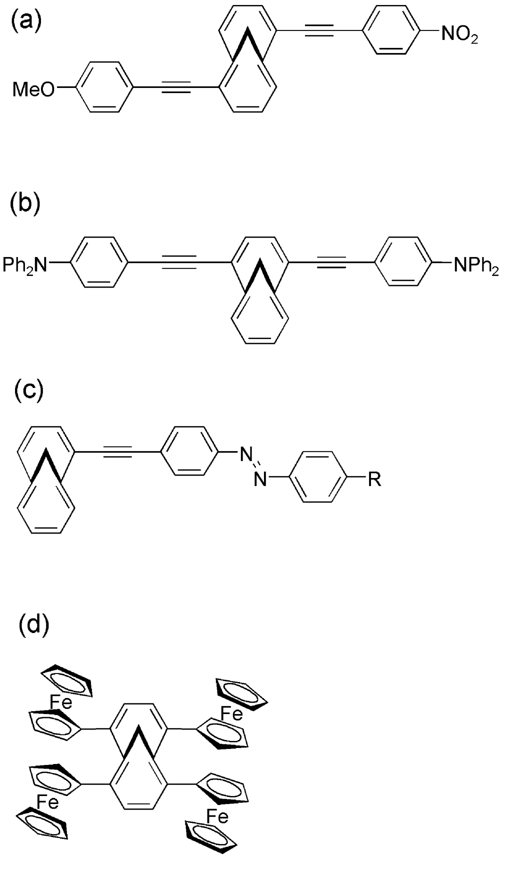


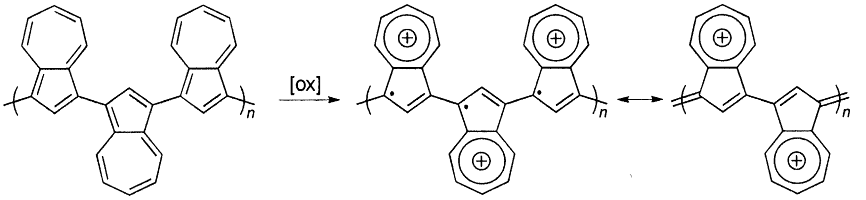
Figure 6. Electronically interesting molecules built upon the methano[10]annulene circuit: (a) a donor-acceptor molecule for nonlinear optics; (b) an amorphous donor-bridge-donor scaffold used for OLEDs; (c) an azo dye, and (d) a redox-active organometallic.

Unusual Aromatics in Semiconducting Polymers

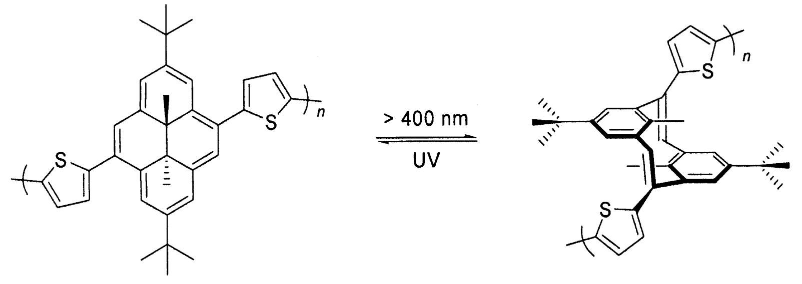
The larger [*n*]annulenes should make ideal components for conjugated polymers given their dual aromatic/cyclic polyene nature. The oligoene nature should impart desirable electronic properties given the low band-gaps associated with polyenes relative to polyaromatics. At the same time, aromatic delocalization should offer additional environmental stability, albeit not to the extent of classical aromatics. Poly(phenylene-vinylene)s (PPVs), one of the workhorse classes of OLED materials, are notorious for their undesired photobleaching upon extended device operation, a feature attributed to the oxidation of the vinyl moiety.[69] We expect that this reactivity may be tempered through incorporation of the olefinic unit into a weakly aromatic circuit such as an annulene while still maintaining a high degree of charge carrier delocalization. Although the dual electronic nature of the [*n*]annulenes might make them attractive components of advanced electronic materials, the difficult syntheses to install chemically reactive handles that will allow for specialized reaction chemistries has hampered many of these efforts: regiospecific halogenation is expected to be difficult for [*n*]annulenes, and rational installation of a halogen or a functional surrogate at an early stage of a long synthesis has its drawbacks. This unfortunately limits the extent to which these systems may be oligomerized or co-polymerized under the Pd-catalyzed reaction conditions that are fairly ubiquitous for the construction of well-defined π-conjugated organic semiconductors.

These issues are exemplified by the *polyazulenes*, prepared initially through electropolymerization in the early 1980s by Tourillon and Garnier.[70] Unlike polythiophenes and other smaller aromatics, the regiochemistry of azulene polymerization under anodic conditions is not particularly straightforward to determine, leading to a material with an ill-defined (if not dearomatized) electronic structure. In actuality, even polythiophene connectivities are not purely through the α-sites.[71–74] Electrophilic substitution occurs readily at the 1,3 positions of azulene, and Lai et al. recently prepared poly(1,3-azulene) through Ni-catalyzed chemical polymerization of 1,3-dibromoazulene to provide a more well-defined structure.[75] Protonic-acid doping was used to inject charge carriers, specifically radical cations and other polycations, and they speculated that the *quasi*-reversibility observed during electrochemical doping might reflect stabilized electronic structures. Nonetheless, iodine-doped samples offered high conductivities in bulk samples. While the polyazulenes are very interesting electronic materials, in the context of our review, we can still envision their π-electrons to form localized interactions that maintain aromaticity within fused fragments rather than serving as completely delocalized 10π-electron circuits (Scheme 6). This again raises comparisons to the benzo[*c*]thiophene monomers addressed earlier.[7]

In 2002, another landmark aromatic structure was employed in the context of an advanced electronic polymer. Marsella and Mitchell reported an annulene-based conducting polymer built from the dimethyldihydropyrene scaffold (DHP), a 14π-electron aromatic ring (Scheme 7).[76] They copolymerized the DHP ring with bithiophene and cast the resulting polymer as a thin film for electrochemical studies. It appears that the primary motivation for this work



Scheme 6. Poly(1,3-azulene) and associated charge carriers.



Scheme 7. A photochromic polymer built from the aromatic 14π-electron *dimethyldihydropyrene* framework.

was to capitalize on the electronic reorganization that occurs in the DHP structure upon photochemical irradiation: an electrocyclic ring opening that yields a metacyclophane. They sought to use this functional property in order to realize *switchable* electrical conductivity achieved with light, in effect, a conductive photochromic polymer. Specifically, the ground-state aromatic DHP-bithiophene polymer should be conductive, but upon a ring-opening electrocyclic process, the disruption of intra-polymer conjugation should attenuate it. This change in chemical structure could also be associated with a change in molecular dimension thereby serving as a potential actuator material for artificial muscles. Indeed, the poly(DHP-bithiophene) was conductive, but the solid-state switching times were too slow to realize the noble goal of attenuated electrical response.

As an initial investigation, we viewed the smaller 10π-electron fragment of methano[10]annulene as an ideal candidate to include into conjugated polymers since the halogenation chemistry of this core is well established.[77] Another important criterion for our studies was to have a suitable benzenoid system in order to gauge what impacts the unusual aromatic core would impart to the bulk electronic properties, and there already exists a related naphthalene core with a comparable substitution topology.[78] In the final section of this review, we highlight our recent work with organic semiconductors built from the methano[10]annulene core and show how it enhances the intrapolymer delocalization relative to materials built from the analogous naphthalene unit. To do so, we present cyclic voltammetry and spectroelectrochemical data for the two 10-π systems as obtained from thin solid polymer films, and we will address future directions.

A Case Study with Methano[10]annulene

Polymers containing aromatic compounds such as the polythiophenes and fused polycyclic oligomers such as pentacene have both shown great promise as organic semiconductors. Polycyclic aromatics have π-conjugated systems and therefore electrons may move within delocalized π-electron clouds. For some polyacenes, their ability to π-stack allows for even greater delocalization. It is possible, however, that greater delocalization could also be gained from the use of monocyclic aromatic compounds such as the annulenes. Annulenes possessing ($4n+2$) π-electrons are expected to be aromatic if planar, with the archetypal example being benzene. Our work here capitalizes on two key synthetic contributions from Vogel's laboratory: synthesis of the 1,6-methano[10]annulene framework where the methano bridge forces the molecule into a more planar form rendering it aromatic, and bromination at the 2,7-positions allowing for later cross-coupling modifications. It is with this in mind that 1,6-methano[10]annulene was chosen for use as an unusual aromatic component of a conductive polymer. In order to investigate the hypothesis that monocyclic aromatic compounds may provide greater delocalization than polycyclic compounds, the properties of the 1,6-methano[10]annulene compounds were compared with

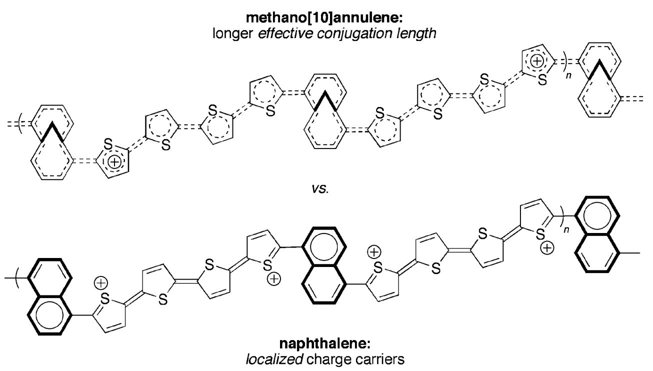
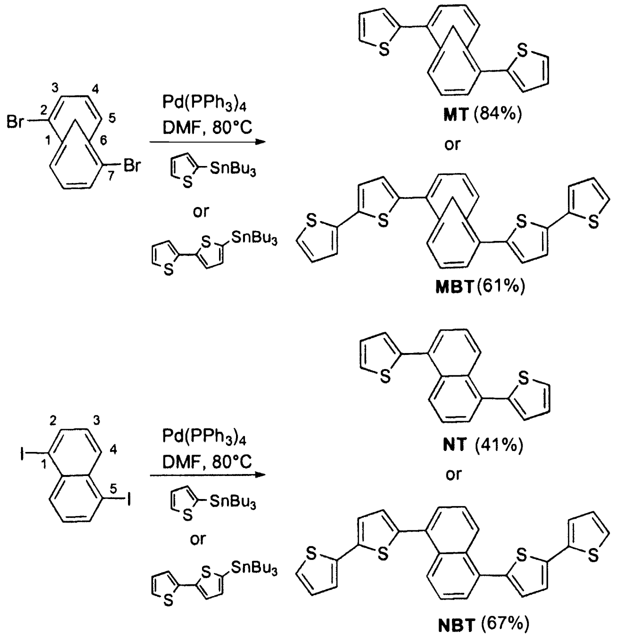


Figure 7. Exaggerated resonance structures expected for charge carriers in the annulene-based polymers (top) and the naphthalene-based polymers (bottom).

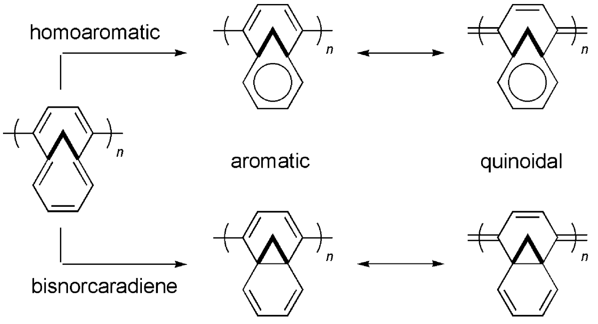
those of its 1,5-naphthyl counterparts because naphthalene is a 10π polycyclic benzenoid analog. In the course of our studies, we found that the annulene component supported greater degrees of delocalization for charge carriers compared to the benzenoid derivative, as illustrated in Figure 7.

Monomer Synthesis: Thiophenyl (**MT** and **NT**[79]) and bithiophenyl (**MBT** and **NBT**) monomers of 1,6-methano[10]-annulene and naphthalene were synthesized via Stille couplings as shown in Scheme 8. The reactions were carried out under nitrogen using dimethylformamide (DMF) as the solvent and tetrakis(triphenylphosphane)palladium(0) as the catalyst. The structure and purity of the monomers synthesized were confirmed by ^{1}H NMR, ^{13}C NMR and mass spectrometry. We previously reported **MBT** and **NBT**, and we now compare those units to the electronic systems with single thiophenes.[80] The data presented in this paper are collected in Table 1 and are discussed below.



Scheme 8. Synthesis of monomers. Representative characterization data for **MT**: m.p. 139–140 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.86 (d, J = 8.8 Hz, 2 H), 7.49 (m, 2 H), 7.43 (d, J = 9.6 Hz, 2 H), 7.37 (m, 2 H) 7.15 (m, 2 H), 7.10 (d, J = 9.2 Hz, 2 H), –0.073 (s, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 143.3, 135.1, 130.2, 128.2, 128.1, 127.7, 126.8, 118.1, 36.1. HRMS (FAB) for $C_{19}H_{14}S_2$ [M$^+$] calcd. 306.0537, found 306.0534.

The choice of the (*Z*)-shaped nonlinear conjugation pathway was a critical design component with respect to probing the efficiency of the annulene to participate in the extended delocalization of charge carrier “defects.” By requiring a kinked conjugation pathway, we expected that the entire aromatic circuit would need to be disrupted in order to delocalize charges. In contrast, conjugation through the more linear 2,5-sites of the annulene might lead to the formation of homoaromatic structures such as shown in Scheme 9. While homoaromaticity has been debated in the context of neutral molecules, it would be interesting to speculate on the nature of the quinoidal structures associated with charge-carrying species present within our annulene-based materials. For fused polycyclic aromatic monomers, competing aromaticity can dictate unusual ground states as exemplified by Wudl’s polybenzo[*c*]thiophene where the ground state maintains a quinoidal bonding arrangement along the polymer backbone given the energetic preference for the fused benzo fragment to maintain an aromatic sextet.[7] For the annulene case, a homoaromatic localization (top) or even a defined bisnorcaradiene valence isomerization (bottom) could be conceived to alter the energetics of quinoidal delocalization associated with the conductive states of more traditional conjugated polymers. We chose the more nonlinear pathway herein in order to alleviate some of these concerns.



Scheme 9. Potential resonance contributors to annulene-based materials conjugated through the “*para*-like” 2,5-position that invoke homoaromaticity (top) and valence isomerization (bottom).

Monomer UV/Vis Spectra: UV/Vis spectra were obtained for all four monomers in chloroform (Figure 8). In both the thiophene and the bithiophene-functionalized systems, the annulene-containing monomer exhibited a longer absorption λ_{max} relative to the naphthyl system, reflecting the smaller HOMO–LUMO gaps associated with more conjugated π systems. The red-shift observed for **MT** vs. **NT** was 60 nm while the difference between **MBT** and **NBT** was slightly greater at 70 nm. This supports the idea that we get greater delocalization throughout the annulene relative to naphthalene: the two groups attached at the 1- and 5-posi-

Table 1. Monomer and polymer oxidation potentials and electronic properties.

Name	Monomer λ_{max} [nm]	Monomer oxidation E_{pa} [V]	Polymer oxidation E_{pa} [V]	Polymer neutral λ_{max} [nm]
NT	315	1.36	0.60, 0.95	342
MT	375	0.97	0.68	440
NBT	345	1.06	1.01, 1.30	426
MBT	415	0.86	0.78	480

tions of naphthalene do not communicate with each other as effectively as do the two groups at the 2- and 7-positions of the annulene.

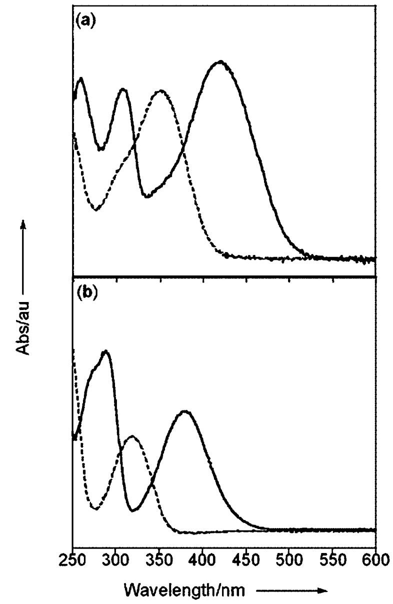


Figure 8. Solution UV/Vis spectra ($CHCl_3$, room temperature) of (a) bithiophenyl monomers **NBT** (dashed) and **MBT** (solid), and (b) thiophenyl monomers **NT** (dashed) and **MT** (solid).

Figure 9 presents the absorption λ_{max} values for bithiophene-flanked molecules **NBT** (a) and **MBT** (d) along with other more common aromatic motifs employed in the construction of π-conjugated materials. Among these are the prototypical 1,4-phenyl (b),[81] 2,7-fluorenyl (c),[82] and 2,5-thienyl (e).[83] Data were selected for inclusion on the basis of the spectroscopic solvent used. Despite the disjointed (*Z*)-shaped conjugation circuit carved through **MBT**, this list shows that the λ_{max} values are quite comparable to the more linear pathways found in the simpler aromatics. Even fluorene, with 12 total π-electrons, falls at a higher energy λ_{max}. Although this data does not necessarily indicate superiority for any of these molecular materials, it does emphasize the point that we can view the aromatic segments of more unusual subunits to have comparable properties to their standard 6π-electron counterparts, regardless of the colinearity of their conjugation pathways.

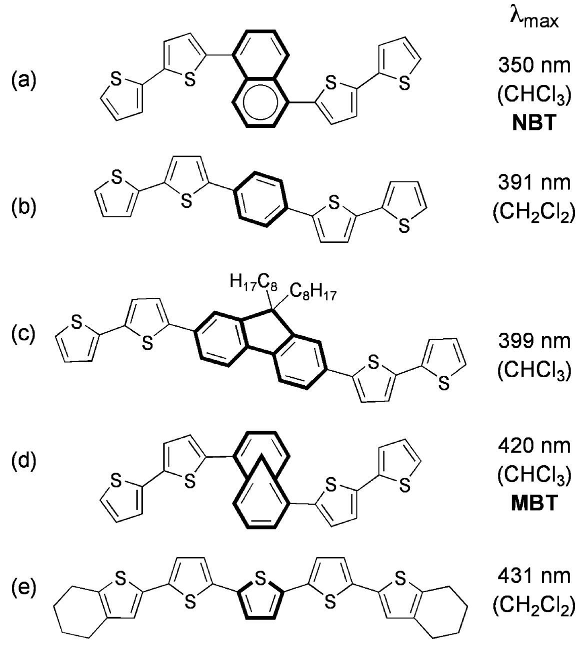


Figure 9. UV/Vis data for the lowest energy transitions associated with several common motifs in organic electronics juxtaposed with new materials from our work.

Monomer Oxidation and Electropolymerization: The monomers were electrochemically polymerized on Pt electrodes using cyclic voltammetry (CV, Figure 10). In the first scan of each, a single oxidation peak for the formation of the monomer radical cation was observed and in subsequent scans a second peak indicative of polymer growth appeared at less positive potential. With each scan the current for each peak increased, a feature representative of polymer growth. It was noted that the monomer oxidation potential was always more positive for the naphthalene compound than for the respective annulene compound. The ease of oxidation (and radical cation formation) in **MT** and **MBT** may be facilitated by the greater intramolecular delocalization afforded by the annulene ring, in line with Creary's observations.[55] The anodic peak potential (E_{pa}) for **MBT** was 0.86 V while that of the naphthyl counterpart **NBT** was 1.06 V. The thiophenyl monomers had E_{pa} values of 0.97 V for **MT** and 1.36 V for **NT**.

The polymer growth profiles obtained from both annnulene monomers showed little increase in the current passed in scans subsequent to the initial monomer oxidation, suggestive of sluggish growth of the polymer on the electrode. This resistance to polymer growth reflects the attenuated reactivity for annulene-based radical cations. Both the reversibility and poor growth could be a testament to the stability provided for the radical cation as mediated by the annulene component, allowing these charged intermediates to persist in solution rather than undergo rapid follow-up chemical oligomerization and polymerization. It should be emphasized that the E_{pa} for **MT** was only 110 mV more positive than that for **MBT**, while that of **NT** was 300 mV more positive than **NBT**. The CVs of **MT** and **MBT** indicated a substantial degree of electrochemical reversibility, more so for **MBT**. We attribute this to the idea that **MT** is already highly conjugated, so increasing the conjugation length by two thiophene rings has a smaller effect relative to that found for the more poorly conjugated naphthalene monomers.

Polymer Oxidation: Once the polymer was obtained its electronics were evaluated with CV by using the polymer-coated Pt electrode as the working electrode (Figure 11). The polymer-coated electrode was rinsed and placed in a monomer-free electrolyte solution in order to record the polymer CV. Interestingly the polymers' oxidation trend did not follow that of the monomers. For example poly(**NT**) and poly(**MT**) had E_{pa} values substantially lower than their respective bithiophene variants [poly(**NBT**) and po-

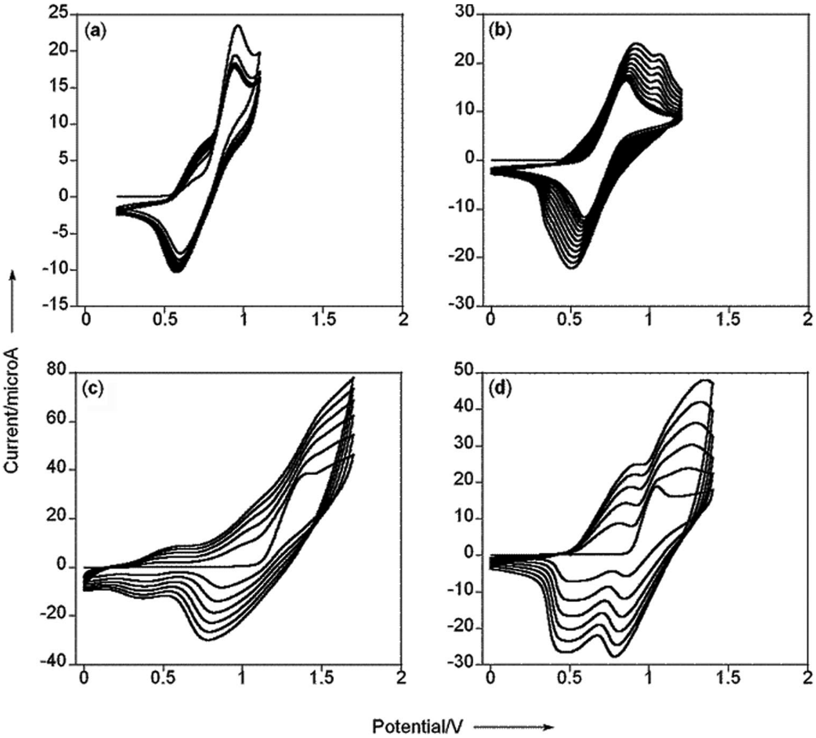


Figure 10. Polymer growth profiles plotted relative to Ag/Ag$^+$ for (a) **MT,** (b) **MBT**, (c) **NT** and (d) **NBT** were obtained in 0.1 M TBAP/CH_2Cl_2 using a 2 mm^2 Pt-button working electrode, coiled Pt wire as the counter electrode, and a silver wire reference electrode submersed in 0.01 M $AgNO_3$ and 0.1 M TBAP in CH_3CN. Scan rate: 100 mV/s.

ly(**MBT**), respectively]: poly(**MT**) and poly(**MBT**) had single peak oxidations with E_{pa} values of 0.68 V and 0.78 V respectively while the naphthalene polymers had 2 peak oxidations at ca. 0.60 V and 0.95 V [for poly(**NT**)] and 1.01 and 1.35 V [for poly(**NBT**)]. Although this could be related to the length of the polymer and the surface packing on the electrode, it is not possible to determine this through simple CV analysis alone. With respect to the annulene polymers, we conjecture that this also reflects the percentage of thiophene rings that comprise the expected polymer repeat unit

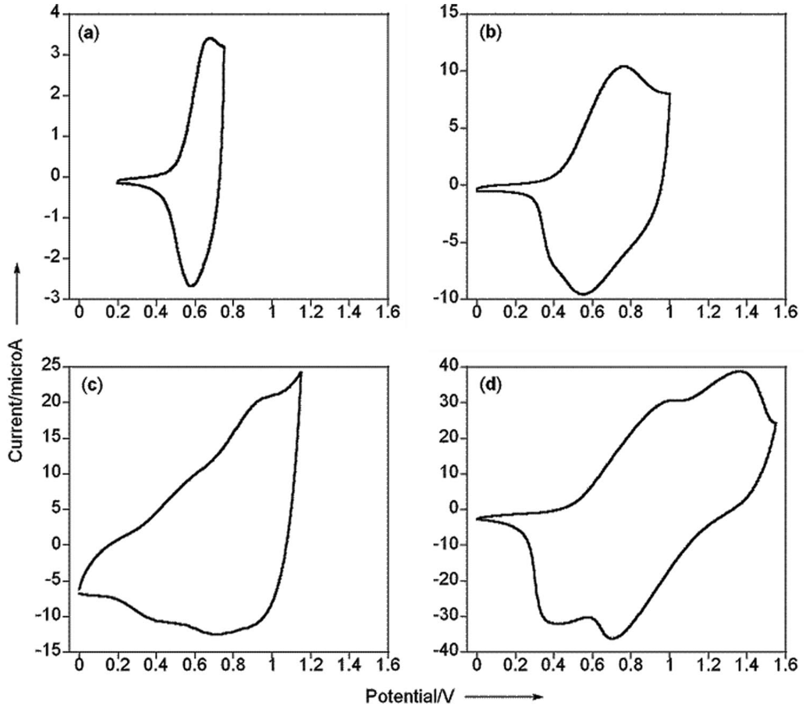


Figure 11. Polymer cyclic voltammograms of (a) poly(**MT**), (b) poly(**MBT**), (c) poly(**NT**), and (d) poly(**NBT**). Conditions as listed in Figure 10.

[two for poly(**MT**) and four for poly(**MBT**)]. It may be deduced that the polymers with greater annulene content exhibited the lower E_{pa} due to the annulene's stronger ability to stabilize the radical cations or dications formed upon oxidation. The diffuse nature of the annulene's 10π-electron system presumably allows for greater delocalization than the smaller thiophene rings and as such aid the formation of the aforementioned charge carriers. In addition, we do not observe any substantial differences in environmental stability between our polymers and standard benzenoid systems: all measurements were made under ambient lab conditions without obvious degradation as evidenced by stable and reproducible electroactivity. We are currently exploring both of these topics in more depth.

Spectroelectrochemistry: To further investigate and compare the properties of the annulene-containing polymers and their naphthyl counterparts, spectroelectrochemical data was obtained (Figure 12). This was done by growing the polymers on indium-doped tin oxide (ITO) electrodes that were then placed in a quartz cuvette filled with an electrolyte solution. In these experiments, the polymer-coated ITO acted as the working electrode that was held at various potentials while UV/Vis spectra were recorded. The potential was varied from that corresponding to the neutral polymer (ca. 0 mV) to just beyond the point at which the polymer film was fully oxidized. Note that a blank using the quartz cuvette containing the electrolyte and an ITO electrode was taken before any of the UV/Vis spectra were recorded. As the polymers were oxidized, new peaks grew in at longer wavelengths. These peaks are indicative of polaron formation in the polymer. It is also possible for a second peak to grow in at even longer wavelength as a result of other charge carriers. While all this is happening, the absorbance corresponding to the neutral polymer should decrease. This reflects the influence of the quinoidal structure on the overall electronic structures of the polymer, in accord with standard conducting polymer electrochromic materials. Electrochemically returning the films to neutrality restored their initial optical properties.

Neutral poly(**MT**) absorbed with a λ_{max} of 440 nm while poly(**MBT**) had a λ_{max} at 480 nm. In contrast, their naphthyl counterparts poly(**NT**) and poly(**NBT**) fell at 342 nm and 426 nm, respectively. As with the monomers, this data suggests that the annulene supports a greater effective conjugation length than through naphthalene, even in the solid-state. Strengthening this point is the fact that the poly(**NT**) and poly(**NBT**) polymers appeared to grow more readily than poly(**MT**) and poly (**MBT**) and as such could have longer length polymers yet they have smaller λ_{max} values. The λ_{max} for poly(**MBT**) was red-shifted 54 nm vs. poly(**NBT**) while poly(**MT**) was red-shifted 98 nm vs. poly(**NT**). In comparing trends within the annulene family, we find a 40 nm redshift moving from poly(**MT**) to poly(**MBT**). In contrast, there is an 84 nm red-shift in progressing from the neutral λ_{max} of poly(**NT**) to poly(**NBT**). We interpret this trend to suggest that the increasing thiophene content from poly(**MT**) to poly(**MBT**) is not as significant with respect to the overall effective conjugation length on account of the ability of the annulene to participate in the extended delocalization (Figure 7, top). This trend is more pronounced in the **NT**-**NBT** series since the dominant chromophore has changed from a naphthalene-capped bithiophene in poly(**NT**) to a naphthalene-capped *quaterthiophene* in poly(**NBT**), as depicted in Figure 7 (bottom).

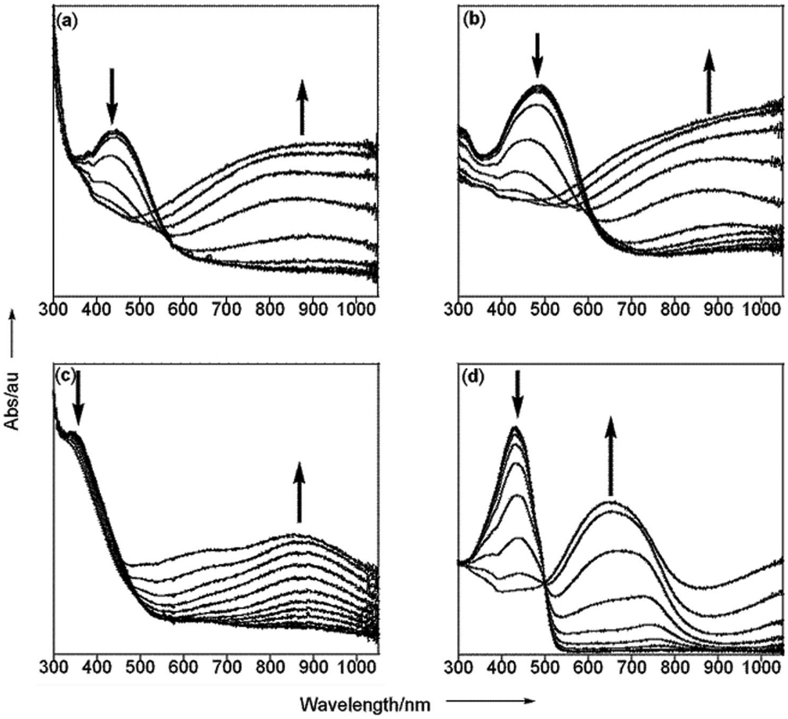


Figure 12. Spectroelectrochemical data obtained on an ITO working electrode for (a) poly(**MT**) between 0–1.1 V, (b) poly(**MBT**) between 0–1.1 V, (c) poly(**NT**) between 0–1.2 V and (d) poly(**NBT**) between 0–1.3 V. Other conditions as listed in Figure 10.

Poly(**NBT**) displayed a clear isosbestic point at ca. 500 nm, a trait often associated with processes such as redox titrations between two defined and spectroscopically observable states. In the present case, this hints that there is one dominant electronic transition for poly(**NBT**) and one associated with a lower energy mid-gap state assigned to the polaronic mobile charge carrier. This was expected since the effective conjugation lengths in the poly(**NBT**) are limited by the energetic barrier imposed by the naphthalene thereby keeping these lengths similar. The annulene polymers poly(**MT**) and poly(**MBT**) had no clear isosbestic points, indicating that the solid-state ensemble is comprised of different absorbing chromophores that have varying electronic transitions due to fact that these materials can support a larger effective conjugation length. The broadness of the peaks observed for poly(**MBT**) also supports this conclusion. Poly(**NT**) did not show any clear isosbestic points, but it had a fairly narrow neutral absorption peak. The data again suggests some amount of uniformity in the effective conjugation lengths of the naphthalene polymers.

Copolymerization Studies: In the expected backbone of the present conjugated polymers, we are limited to defined annulene/thiophene ratios as pre-determined by the monomer precursor, where poly(**MT**) has a 1:2 ratio while poly(**MBT**) has a 1:4 ratio. We were curious to probe the impacts that continued dilution of the annulene core would impart, but the synthesis of longer oligothiophenes appended to the annulene core would be rather prohibitive in terms sparing solubility and ease of polymerization. To circumvent this, we examined *copolymerized* films with spectroelectrochemistry. Solutions of defined ratios of bithiophene and **MT** were electrochemically copolymerized on ITO and the resulting films were studied. Although we cannot rigorously quantify the extent of bithiophene incorporation in each sample ("x" in Figure 13), we did observe a gradual red-shift in the λ_{max} (over ca. 50 nm) as the annulene content decreased from the 1:2 ratio [where $x = 0$; that is, poly(**MT**)] to pure polythiophene (where $x = 1$, generated from bithiophene electropolymerization). While this might have been anticipated based on the monomer λ_{max} comparison presented in Figure 9, it further emphasizes that the annulene component can be considered as a viable building block for new organic electronic materials, both in solution and in the solid state.

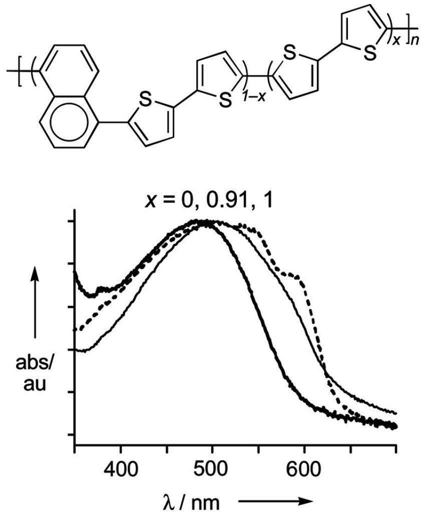


Figure 13. Polymer UV/vis as a function of annulene percentage within a random copolymer: plotted spectra show the absorption profiles at annulene:thiophene copolymer ratios of 1:2 (x = 0, bold trace), 1:22 (x = 0.91, solid) and "pure" polythiophene (x = 1, dashed) as determined after electropolymerization on ITO electrodes. Conditions as in Figure 10.

Outlook

Our recent results indicate that the annulene core is a viable component for solid-state organic electronics materials, as determined through electrochemical studies of radical cation formation and the associated electronic reorganization that accompanies these redox processes. Preliminary data from our new monomers indicates that their electrodeposited polymers exhibit windows of electrical conductivity as commonly found for other electroactive polymers deposited across interdigitated microelectrodes. We are currently exploring the semiconductor characteristics of chemically synthesized polymers in order to prepare devices from more processable and structurally defined polymers. We are also exploring the photophysical properties of fluorescent polymers derived from these annulenes in order to understand how exciton migration may be impacted. We feel confident in expressing that annulenes can be considered as powerful building blocks to realize new organic electronic functionality alongside their more widespread 6π-electron aromatic analogues. These investigations consume a large portion of our current research, and we hope this review may serve as an inspiration for continued interest in this active area of inquiry.

Acknowledgments

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