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Decreasing Aromaticity in π-Conjugated Materials: Efficient Synthesis and Electronic Structure Identification of Cyclopentadiene-Containing Systems

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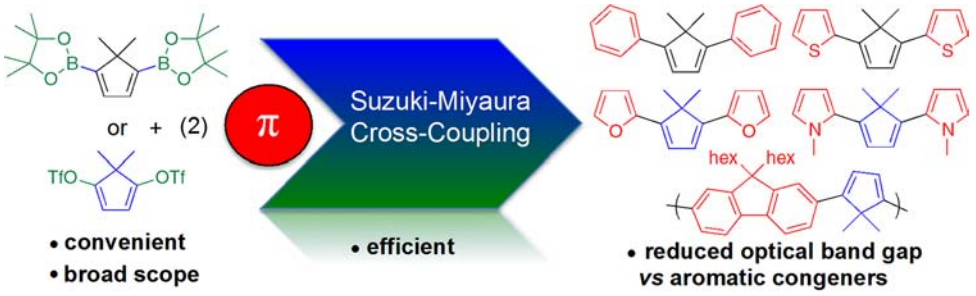
ABSTRACT



An efficient route to cyclopentadiene-containing π-conjugated molecules is reported. A comparative analysis between the aryl/dienyl hybrids and their aromatic congeners shows a propensity of the diene moiety to reduce the optical band gap of a π-conjugated system without compromising a planar structural topology. Moreover, a novel poly(fluorene) derivative bearing alternating cyclopentadiene repeat units was synthesized to demonstrate the applicability of this method in polymer synthesis.

π-Conjugated organic materials are studied extensively for their (opto)electronic properties that are attractive for device applications such as organic field-effect transistors,[1] light-emitting diodes,[2] electrochromic displays,[3] sensors,[4] and photovoltaics.[5] The properties of these materials are a consequence of successive sp^2/sp-hybridized carbon atoms along the polymer backbone that give rise to extended π-conjugated networks. (Macro)molecules of this sort typically comprise aromatic repeat units (e.g., phenylene, (hetero)arylenes, fluorenylenes, carbazolylenes, etc., and fused derivatives thereof) that lend chemical tunability, processability, and atmospheric stability to these systems, despite inherent resonance stabilization energies that can suppress the formation of polyene-like quinoidal structures that are necessary for charge carrier delocalization (Figure 1).[6] Recently, there has been interest in introducing

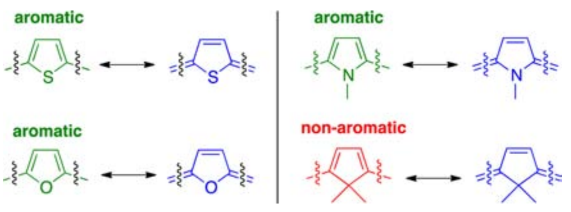


Figure 1. π-Conjugated systems and their mesomeric (quinoid) forms.

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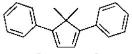
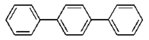
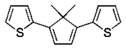
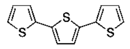
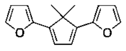
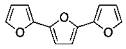
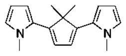
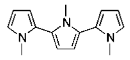
[5] Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868–5923.

10.1021/ol402824m

Table 1. Characterization Data for Aryl/Dienyl Hybrids and Their Aromatic Congeners

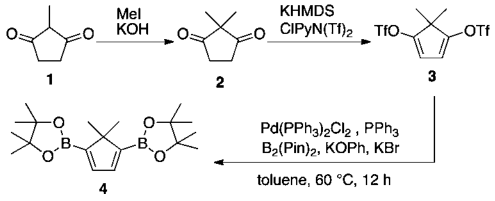
entry	aryl/dienyl hybrid	λ_{max}[a]	λ_{em}[b]	E_{ox}[c]	yield	entry	aromatic congener	λ_{max}[a]	λ_{em}[b]	E_{ox}[c]
1	 Ph-C5-Ph	340	420	1.12	86	5		279	342	1.84
2	 Th-C5-Th	386	457	0.93	98	6		355	429	1.29
3	 Fur-C5-Fur	367[d]	429[d]	0.78[d]	95	7		329[e]	371[e]	0.75[e]
4	 Pyr-C5-Pyr	355	447	0.50	81	8		276[f]	-	0.06[f]

[a] UV/vis absorption maximum, λ_{max} (nm), in dichloromethane (CH_2Cl_2). [b] Emission maximum, λ_{em} (nm), in CH_2Cl_2. [c] Oxidation potential, E_{ox} (V vs SCE), in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate. [d] Data acquired in acetonitrile (CH_3CN). [e] Data obtained from ref 8. [f] Data obtained from ref 9.

subunits into (macro)molecules that reduce a material's aromatic character as a means to extend effective conjugation lengths and improve delocalization,[7] attributes that are essential to advancing band gap engineering and charge transport control technologies. Unfortunately, the pool of nonaromatic π-conjugated precursors[10] is severely limited compared to its aromatic counterpart, an issue that must be addressed if materials that exhibit the desirable attributes of both a polyene and a polyaromatic are to be realized.

Supplanting aromatic units with cyclopentadienyl-based alternatives is an attractive approach to reducing the aromatic character of a π-conjugated system. In this context, the diene moiety is inherently devoid of the reorganization energy that is required to break aromaticity upon doping while its cyclic nature is analogous to many common aromatics (e.g., thienyl, furyl, and *N*-methylpyrrolyl) and, therefore, should not significantly affect the overall structural topology of the system. Literature reports on the synthesis and reactivity of bifunctional cyclopentadienyl-based precursors are rare,[11] and to the best of our knowledge, a (convenient) route to the aryl/dienyl hybrids described herein has not been reported. In this communication, we disclose a convenient route to such systems and examine their spectroscopic properties and structure. In all cases, the hybrids exhibit reduced optical band gaps compared to their aromatic congeners. Given the reaction scope of the reagents used in this work and the optical band gap reducing effect of the diene moiety, the methods described herein could serve as a general synthetic tool toward the preparation of novel π-conjugated materials with attractive (opto)electronic properties.

Scheme 1. Synthesis of **3** and **4**



The syntheses of the diene precursors are outlined in Scheme 1. Dione **2** is prepared by reacting **1** with base and methyl iodide (MeI)[12] and converted to **3** upon treatment with potassium bis(trimethylsilyl)amide (KHMDS) and *N*-(5-chloro-2-pyridyl)bis(trifluoromethanesulfonimide) ($ClPyN(Tf)_2$). Subsequently, **4** was prepared via palladium-catalyzed cross-coupling of bis(pinacolato)diboron ($B_2(Pin)_2$) and **3** using methods reported by Miyaura et al.[13] Single-crystal X-ray diffraction analysis confirmed the targeted structure with boronate ester groups located on the 1 and 4 positions of the planar cyclic scaffold.

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(9) (a) Rohde, N.; Eh, M.; Geißler, U.; Hallensleben, M. L.; Voigt, B.; Voigt, M. *Adv. Mater.* **1995**, *7*, 401–404. (b) Geißler, U.; Hallensleben, M. L.; Rohde, N. *Macromol. Chem. Phys.* **1996**, *197*, 2565–2576. (c) Kauffmann, T.; Lexy, H. *Chem. Ber.* **1981**, *114*, 3674–3683.

(10) For examples, see: (a) Yamamoto, T.; Saito, H.; Osakada, K.; Ando, I.; Kikuchi, M. *Polym. Bull.* **1992**, *29*, 597–603. (b) He, G.; Kang, L.; Delgado, W. T.; Shynkaruk, O.; Ferguson, M. J.; McDonald, R.; Rivard, E. *J. Am. Chem. Soc.* **2013**, *135*, 5360–5363.

(11) For examples, see: (a) Yamaguchi, S.; Tamao, K. *Tetrahedron Lett.* **1996**, *37*, 2983–2986. (b) Yamaguchi, S.; Itami, Y.; Tamao, K. *Organometallics* **1998**, *17*, 4910–4916. (c) Willis, M. C.; Claverie, C. K. *Tetrahedron Lett.* **2001**, *42*, 5105–5107. (d) Willis, M. C.; Powell, L. H. W.; Claverie, C. K.; Watson, S. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1249–1251.

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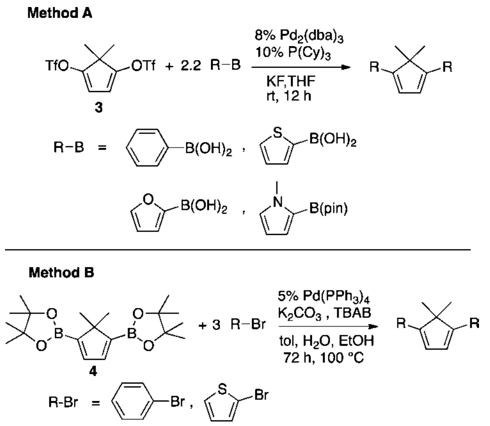
Scheme 2. Synthesis of Aryl/Dienyl Hybrids



In 2001, Willis and Claverie reported on the Suzuki–Miyaura cross-coupling of a 1,4-ditriflate-1,3-cyclopentadiene with excess 4-methoxyphenylboronic acid that afforded only monocoupled product.[11c] In subsequent studies, dicoupled products were isolated in good yield at the expense of using two separate catalytic systems to complete the transformation.[11d] Here, dicoupled π-conjugated products (entries 1–4, Table 1) were prepared in good to excellent yield (ca. 81–98%) by reacting **3** with 2.2 equiv of aryl boronic acid (ester) at ambient temperature using a modification of a procedure (Scheme 2, Method A) reported by Fu et al.[14] Ambient temperature is a critical condition for this reaction as experiments conducted at ca. 60 °C afford mostly starting material after workup, inferring that elevated temperatures give rise to catalyst poisoning. The scope of this reaction was examined further by reversing the functional group identities on the diene and aromatic reagents. Using experimental conditions outlined in Scheme 2, Method A, diboronate ester **4** was treated with 3 equiv of either bromobenzene or 2-bromothiophene; however, only starting material was recovered. Indeed, the yields of Ph–C5–Ph[15] and Th–C5–Th were improved to 81 and 40% respectively, when more insistent conditions (Scheme 2, Method B) were employed, thus prompting a mechanistic investigation into reactivity differences between **3** and **4** that is currently underway.

Characterization of the diene-containing compounds was accomplished using spectroscopic and XRD methods. All ^{1}H NMR spectra possess singlets at ca. 6.94 and 1.26 ppm that are assigned to the olefinic and aliphatic protons of the diene unit, respectively, suggesting that competing Heck reactions[16] are minimized under the aforementioned conditions. A red shift in the absorption maxima λ_{max} of the aryl/dienyl hybrids (entries 1–4, Table 1, Figure 2a) clearly indicates a reduction of the optical band gap when compared to their aromatic congeners (entries 5–8, Table 1), a trend that is supported by the fluorescence emission profiles of Ph–C5–Ph, Th–C5–Th, and Fur–C5–Fur (Figures S12–S14). When compared against their silole-containing congeners, Ph–C5–Ph and Th–C5–Th exhibit both blue-shifted λ_{max} (by ca. 36 and 29 nm, respectively) and λ_{em} (by ca. 43 and 48 nm, respectively).[17]

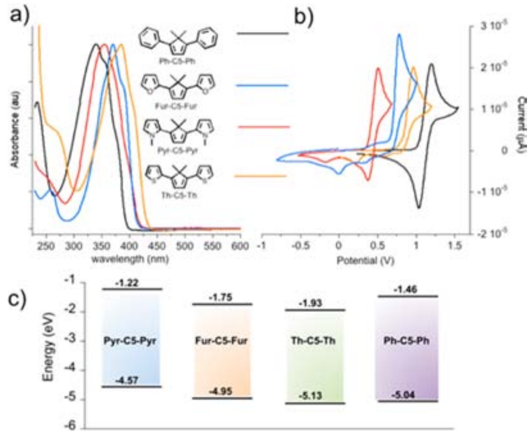


Figure 2. (a) UV/vis absorption spectra and (b) cyclic voltammograms of Ph–C5–Ph (CH$_2$Cl$_2$), Pyr–C5–Pyr (CH$_2$Cl$_2$), Fur–C5–Fur (CH$_3$CN), and Th–C5–Th (CH$_2$Cl$_2$). (c) Energy level diagram showing the calculated HOMO/LUMO levels (B3LYP/6-31+G*).

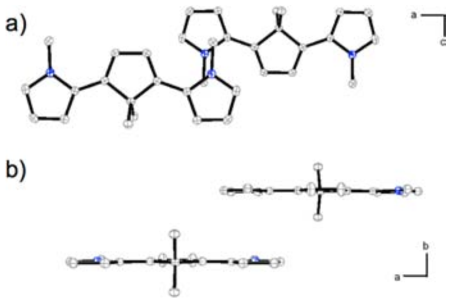


Figure 3. Representations of the X-ray crystal structure of Pyr–C5–Pyr as 50% thermal ellipsoids (except H atoms). (a) View down the *b*-axis of the unit cell. (b) View down the *c*-axis of the unit cell. Key: C = gray, N = purple.

The electronic structures of the hybrids were examined using cyclic voltammetry (CV) and DFT methods. Highlights include oxidation potentials (E_{ox}, Table 1, Figure 2b) that decrease in the order of Ph–C5–Ph, Th–C5–Th, Fur–C5–Fur, and Pyr–C5–Pyr, a trend that is consistent among the aromatic congeners under near identical conditions. Moreover, the calculated (DFT(B3LYP)/6-31+G*) HOMO and LUMO energy levels (Figure 2c) are in

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(14) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020–4028.

(15) Ph–C5–Ph has been prepared by an alternative route. See: Paquette, L. A.; Leichter, L. M. *J. Org. Chem.* **1974**, *39*, 461–467.

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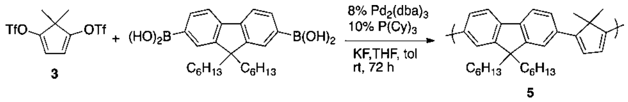
reasonable agreement with experimental values (Supporting Information, Table S1) determined by CV and UV/vis spectroscopy. In terms of shape, all frontier orbital densities were found to be comparable with each other (Figure S16) with some showing conjugation across the entire molecular scaffold.

Topological affects by the diene moiety were examined by XRD. In short, Pyr–C5–Pyr packs into a *Pmmn* space group (Figure 3) with the diene ring inverted with respect to the outer *N*-methylpyrrolyl rings. Perhaps the most intriguing aspect of the structure is the high degree of planarity across the system, a packing motif that is markedly different from *tert*-(1-methylpyrrole), where the central ring is inclined ca. 44.9(2) and 46.6(2)° with respect to the outer rings.[18] Indeed, XRD studies also show Th–C5–Th,[19] Fur–C5–Fur, and Ph–C5–Ph (Supporting Information) to possess small mean dihedral angles (ca. < 25.4(6)°), confirming that the planarity of these systems are not compromised by the diene moiety.

Scheme 3. Synthesis of **5**



As a natural extension of this work, we applied this methodology toward the synthesis of a polymer composed of alternating cyclopentadiene and aromatic repeat units. Toward this end, ditriflate **3** and 9,9-dihexylfluorene-2,7-diboronic acid were used as comonomers to afford polymer **5** (Scheme 3). Consistent with the small-molecule systems described above, the ^{1}H NMR spectrum possesses a single resonance at ca. 6.94 ppm that is assigned to the olefinic protons of the diene repeat units. The number-average molecular weight (M_n) was estimated by GPC analysis to be ca. 21.8 kg/mol with a broad PDI of 2.65, typical of Suzuki–Miyaura polycondensation reactions. Additional evidence of structural composition was acquired from a matrix-assisted laser desorption/ionization time-of-flight mass spectrum (Figure 4a) that illustrates spectral patterns with a repeat unit of ca. m/z 424, a value in line with the assigned repeat unit structure. Differential scanning calorimetry (DSC) revealed a glass transition temperature (T_g) of 286 °C and a crystalline melting temperature (T_m) of 331 °C.

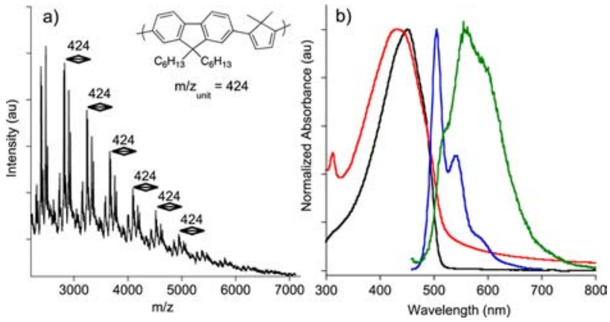


Figure 4. (a) MALDI-TOF mass spectrum of **5**. (b) Solution (black) and solid-state (red) UV/vis absorption spectra of **5**. Solution (blue) and solid-state (green) emission spectra of **5**. All spectra were obtained in dichloromethane at ca. 25 °C.

The solution and solid-state UV/vis absorption and emission spectra of **5** are shown in Figure 4b. Notable features include (1) a solid-state absorption maximum (ca. 432 nm) that is ca. 20 nm blue-shifted with respect to λ_{max} in solution and (2) a solid-state emission maximum (ca. 560 nm) that is ca. 50 nm red-shifted with respect to λ_{em} in solution. To assess the effect of the diene moieties on the optoelectronic properties of a π-conjugated macromolecule, low molecular weight **5** was prepared (M_n = 6.9 kg/mol, PDI = 2.09) and characterized against a poly(fluorene) derivative (PFT) of comparable molecular weight (M_n = 6.0 kg/mol, PDI = 1.30) bearing thienyl repeat units in lieu of diene units.[20] In line with observations described above, the UV/vis absorption and emission spectra of **5** (Supporting Information)[21] exhibit maxima that are indeed red-shifted (λ_{max} = 15 and 35 nm, respectively) compared to the aromatic congener.

In conclusion, we report a convenient route to cyclopentadiene-containing π-conjugated (macro)molecules. Diene precursors bearing either triflate or boronate ester groups were used in the syntheses; however, only the Suzuki–Miyaura reactions employing the former afford products in good to excellent yield. Based on the results reported here, a facile means to reducing aromatic character without compromising coplanarity can be achieved in π-conjugated systems by introducing cyclopentadienes into the (macro)molecular scaffolds. Incorporating cyclopentadiene-containing (macro)molecules into (opto)electronic devices is a topic of future studies.

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Supporting Information Available. Synthetic details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Lynch, D. E.; Geissler, U.; Byriel, K. A. *Synth. Met.* **2001**, *124*, 385–391.

[19] Th–C5–Th has been prepared as an oil. See: Berlin, A.; Zotti, G.; Zecchin, S.; Schiavon, B. *Macromol. Chem. Phys.* **2002**, *203*, 1228–1237.

[20] (a) Davis, A. R.; Peterson, J. J.; Carter, K. R. *ACS Macro Lett.* **2012**, *1*, 469–472. (b) Asawapirom, U.; Güntner, R.; Forster, M.; Farrell, T.; Scherf, U. *Synthesis* **2002**, *9*, 1136–1142.

[21] Samples of low molecular weight **5** exhibit a wavelength absorption band at ca. 550 nm that is not observed in high molecular weight samples. The origin of this peak is currently under investigation.

The authors declare no competing financial interest.