

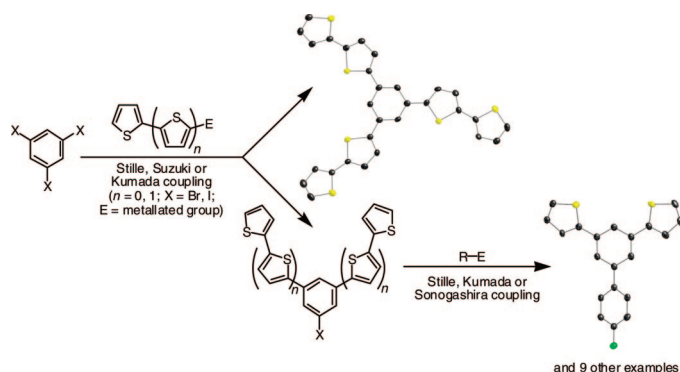
Meta-Substituted Thienyl Benzenes: A Comparative Synthetic, Structural and Computational Study

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A selection of metal-catalyzed C–C bond-forming strategies has been evaluated in the synthesis of a series of meta-substituted thienyl benzenes, $(T_n)_2C_6H_4$ and $(T_n)_3C_6H_3$ ($n = 1, 2$; $T_1 = 2$ -thienyl; $T_2 = 2,2'$ -bithien-5-yl). Kumada coupling reactions catalyzed by $PdCl_2(dppf)$ between the appropriate thienyl Grignard and either 1,3- or 1,3,5-bromo- or iodobenzenes were found to be the most reliable in terms of convenience, selectivity and yield ($dppf = 1,1'$ -bis(diphenylphosphino)ferrocene). These conditions also allowed the optimized syntheses of mixed (thienyl)(halo)benzenes, $(T_n)C_6H_3X_2$ and $(T_n)_2C_6H_3X$ ($X = Br, I$); the latter bromides could be further elaborated in subsequent Stille, Sonogashira, or Kumada reactions to furnish bis(thienyl) compounds bearing electron-donating or -withdrawing groups in the third meta position, $(T_n)_2C_6H_3R$ ($R = Ph, p$ -MeOC₆H₄, p -FC₆H₄; $n = 1, 2$) and $(T_1)_2C_6H_3R'$ ($R' = Me, C\equiv CPh, Fc$; $Fc = ferrocenyl$). The relative effects of R, R' , and n were evaluated by electronic spectroscopy, cyclic voltammetry and calculation. The absorption and emission characteristics and calculated ionization potentials and HOMO–LUMO gaps of these compounds were strongly dependent on n and largely insensitive to R/R' . These measured and calculated properties were also found to be largely invariant with respect to the degree of substitution about the central ring in the meta-substituted benzenes $(T_n)_mX_{3-m}C_6H_3$ ($m = 1–3$; $n = 1, 2$; $X = Br, H$), although in the case of $n = 1$, there was a smooth, albeit small, increase in the emission maximum with increasing thienyl substitution. These findings essentially confirmed earlier theoretical predictions that the thienyl “arms” of meta-substituted phenyl-cored dendrimers were predominantly responsible for absorption and that excitons were localized to the “arms” without any electronic coupling between them, but also introduced the caveat that there was a minimum of two contiguous thiophene rings required for *strict* exciton localization to the arms. The oxidation potentials of the compounds in solution ranged from 0.9 to 1.6 V and were not rationally dependent on the degree of substitution or the nature of R/R' .

Introduction

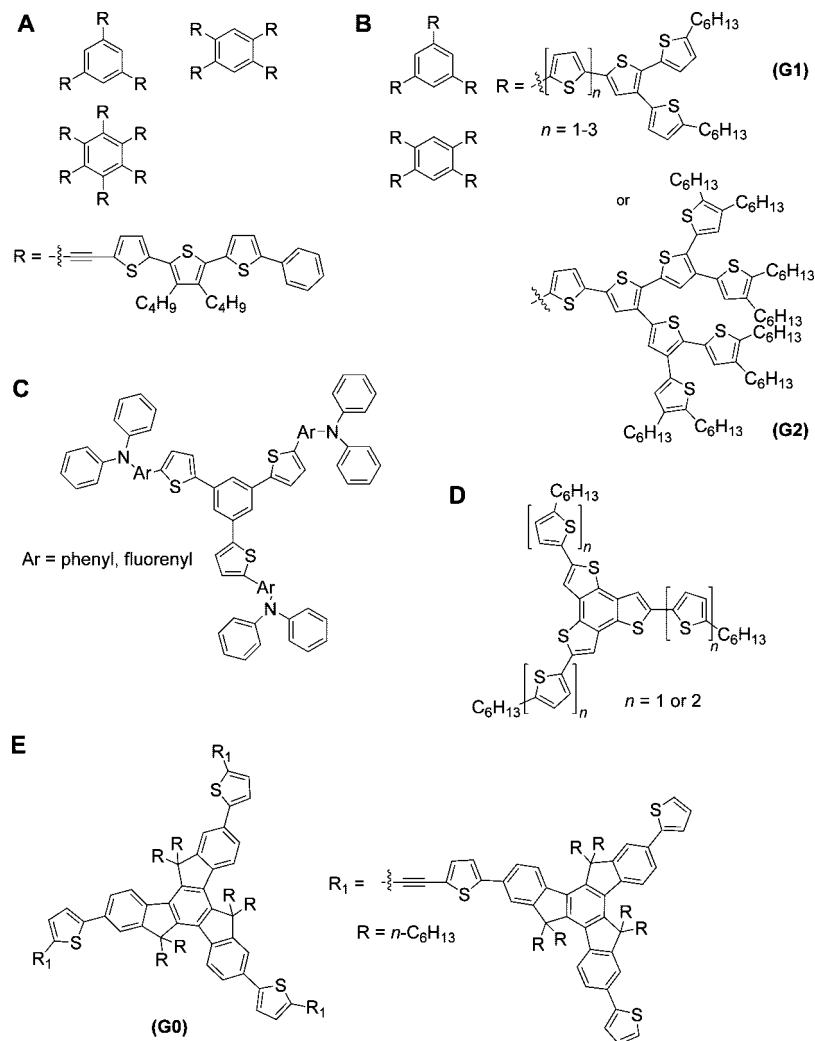
Branched oligothiophenes based on central phenyl (or, occasionally, thienyl^{1–3}) rings (Chart 1) have come to the fore over

the last several years, both as monomers in cross-linked semiconducting polymers^{3–6} and as the components of conjugated dendrimers.^{1,2,7–9} These and closely related materials have potential

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CHART 1. Examples of Branched Oligothiophenes Based On a Central Benzene Ring



application in a wide range of devices, for example, field-effect transistors,¹⁰ organic light-emitting diodes (OLEDs; C),¹¹ photovoltaics (B, D^{12,13}) and other light-harvesting applications (E),¹⁴ that exploit the unique optical and electronic properties of oligothiophenes (UV-visible absorption and fluorescence, semiconductivity, etc.), and the physical advantages conferred by their dendrimeric nature (determinate syntheses, flexibility, processability from solution, etc.). In addition, these several physical character-

istics can be “tuned.” For example, the absorption and emission maxima of A were red-shifted by increasing the degree of substitution around the core,¹⁵ as were those of B by increasing the number of generations in the dendrimer;⁹ and the incorporation of more rigid benz-fused and truxene cores in D¹³ and E,¹⁴ respectively, led to enhanced conjugation and even greater bathochromic shifts.

In these and simpler systems, the meta-disubstituted thienylbenzene motif has played an important role. It has been

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CHART 2. Relevant Thienylbenzenes

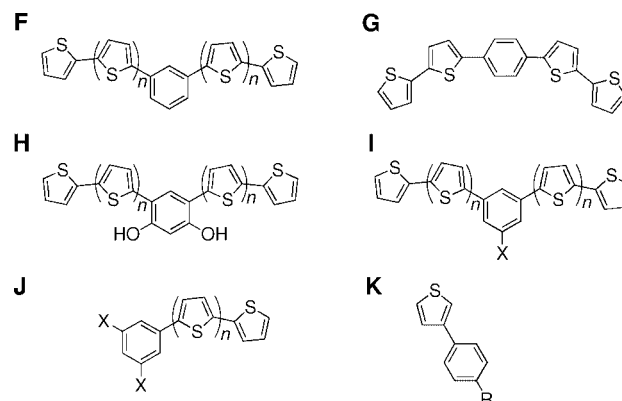
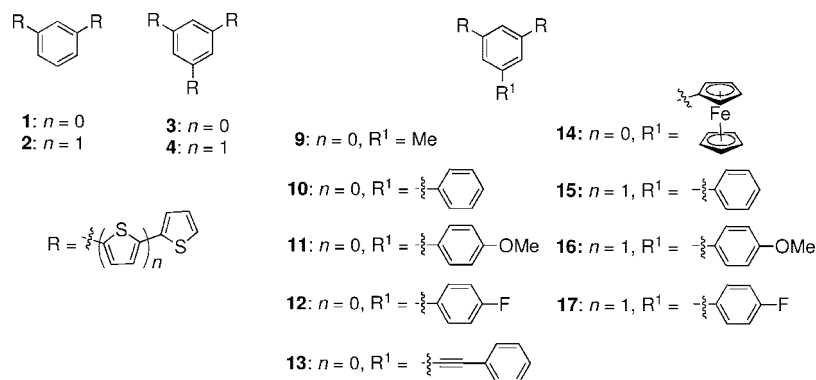


CHART 3. Compounds Made in this Study



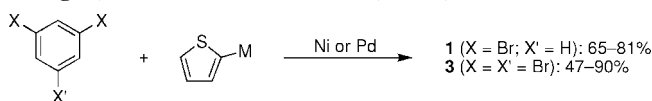
incorporated by way of monomers **F**^{16–18} and **H**¹⁸ (Chart 2) into conjugated polymers, and has also found application in singlet oxygen-generating photosensitizing agents (**F** and **G**, $n = 0$).¹⁹

It is now well established that the physical properties of thiophenes (and of their respective polymers) can be tuned by the introduction of electron-donating or -withdrawing groups to the ring.^{20–23} Studies of a series 3-(*p*-R-phenyl)thiophene “monomers” **K** (Chart 2, $R = -\text{H}, -\text{CMe}_3, -\text{Me}, -\text{OMe}, -\text{COMe}, -\text{CO}_2\text{Et}, -\text{F}, -\text{Cl}, -\text{Br}, -\text{CF}_3, -\text{SO}_2\text{Me}$) by Guerrero et al. have demonstrated that the oxidation potentials of both the monomers and resulting polymers correlated well with the Hammett sigma constants of the substituents.²³ As expected, the addition of an electron-donating substituent ($\sigma_p < 0$) to the *para*-position on the phenyl ring shifted the redox potentials of the thienyl compounds cathodically, whereas addition of electron-withdrawing substituents ($\sigma_p > 0$) shifted them anodically.

It has also been recognized that the incorporation of aryl substituents into poly(thiophenes) is potentially advantageous for two reasons: not only do the aryl rings provide potential anchoring sites for onward elaboration, but also they introduce stereoelectronic effects that alter the physical and conducting properties of the polymer.^{20,24}

Despite the considerable interest in molecules of this type, however, convenient syntheses are not always available, and progress in the field has been limited by practical difficulties. Although overall yields in some cases are respectable given the synthetic challenge, for example, about 15% over 5–7 steps for **B**,⁹ the reality is often daunting, for example, about 3% over 9 ($n = 1$) or 11 ($n = 2$) steps for **D**.¹³ Even apparently simple thienylbenzene compounds are often difficult to access. Reported syntheses are typically plagued by the problems generally associated with Pd-catalyzed coupling of aromatic rings: pre-functionalization of reagents, long reaction times, arduous separations of partially substituted products,⁵ and low isolated yields. The eminently valuable meta-substituted benzenes that bear both thiophene and halogen groups (**I** and **J**, Chart 2), which would allow both electrochemical and chemical elaboration, respectively, are known primarily as unintended byproducts of other reactions.²⁵ Targeted approaches to these compounds would furnish new monomers for electropolymerized conducting materials, but remain undeveloped. Moreover, solid-state X-ray crystallographic data for the product monomers are lacking.²⁶

In this paper, we combine the aspects of meta-substitution, aryl incorporation, and inclusion of both electron-donating and -withdrawing groups, in a synthetic, structural, and computational study of meta-substituted thienylbenzenes. We systematically compare Suzuki, Stille, Kumada, and Negishi coupling approaches to the syntheses of both di- and trisubstituted thienyl

SCHEME 1. Reported Metal-Catalyzed Syntheses of **1** ($M = \text{MgBr}, \text{ZnCl}$) and **3** ($M = \text{SnBu}_3, \text{ZnCl}, \text{B}(\text{OH})_2$)

benzenes (**1–4**, Chart 3). Although a selection of these^{9,27–29} (and other noncatalytic)^{4–6,30–32} methods have been used in the past, we present improved syntheses for these known compounds as well as new rational methods to make the valuable mixed (halo)(thienyl)benzene compounds **I** and **J** in synthetically useful yields (Chart 2, $X = \text{Br}, \text{I}; \text{J}: n = 0$ (**5^{Br}**, **5^I**); $n = 1$ (**6^{Br}**, **6^I**); **I}: $n = 0$ (**7^{Br}**, **7^I**); $n = 1$ (**8^{Br}**, **8^I**)). We demonstrate that the halogen handle in group **I** may be used to give a family of elaborated compounds (**9–17**, Chart 3) whose properties depend in principle on the nature of the R^1 group in the third meta-position. We use density functional theory methods to calculate the gas-phase first ionization potential and HOMO–LUMO gap for all compounds and correlate these data with the nature of the R^1 group, the degree of substitution about the central phenyl ring, and the number of contiguous thienyl rings. In addition, we present the molecular structures of **4** and **12**, including an analysis of their packing in the solid state.**

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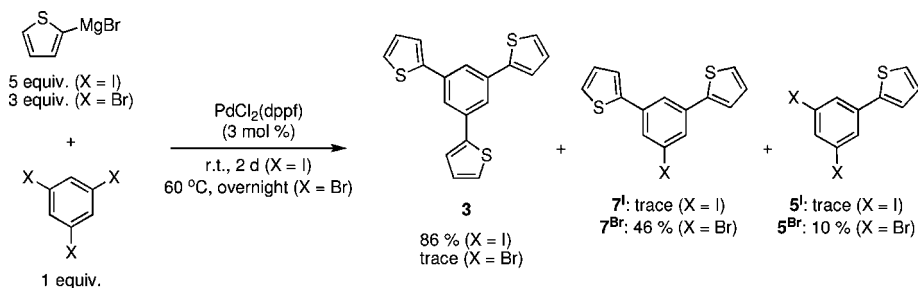
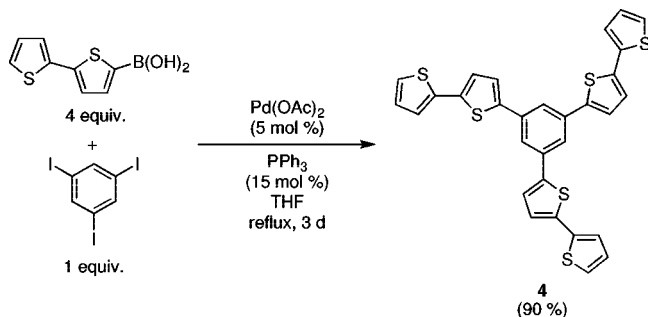
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SCHEME 2. Palladium-Catalyzed Kumada Couplings of Trihalobenzenes and 2-Thienylmagnesium Bromide To Give 3, 5 and 7

SCHEME 3. Palladium-Catalyzed Synthesis of 4 by Suzuki Coupling

Results and Discussion

Syntheses of 1 and 3. The syntheses of 1,3-bis- (**1**)^{27,28} and 1,3,5-tris(2'-thienyl)benzene (**3**)^{9,28,29} have been reported previously; a variety of metal-catalyzed coupling reactions and, in the case of **3**, cyclotrimerization reactions^{4–6,30–32} have been used. In the synthesis of **1**, both nickel-catalyzed Negishi (65%)²⁸ and Kumada (81%)²⁷ couplings have been used (isolated yields in parentheses), while **3** has been made by Pd-catalyzed Stille (47%),⁹ Negishi (60%),²⁸ and Suzuki (90%)²⁹ reactions. In every case but that of the Kumada reaction, the zinc, tin, or boron-containing precursors were relatively straightforward to prepare but required a prelithiation step (e.g., 2-tributylstannylthiophene was generated from 2-lithiothiophene and tributylstannyl chloride). All of these couplings used either 1,3-di- or 1,3,5-tribromobenzene starting materials (Scheme 1).

In our synthetic survey, we found that the most reliable method was instead the Kumada cross-coupling of either 1,3-di- or 1,3,5-triiodobenzene and 2-thienylmagnesium bromide using PdCl₂(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene) as catalyst, which gave **1** or **3** in 80 or 86% yield, respectively. We chose PdCl₂(dppf) as our key catalyst because it was the most discriminating between iodo- and bromobenzenes of all the Pd complexes we surveyed and it, therefore, permitted excellent control over product distribution based on the choice of halide in the starting material. Thus, in contrast to the excellent cross-coupling involving 1,3,5-triiodobenzene, the PdCl₂(dppf)-catalyzed reaction between 2-thienyl Grignard and tribromobenzene gave predominantly 1-bromo-3,5-bis(2'-thienyl)benzene (**7^{Br}**) and only traces of **3** (Scheme 2).

In the synthesis of **3**, we used triiodo- instead of tribromobenzene to encourage complete substitution; this did not introduce significant complications because 1,3,5-triiodobenzene was readily accessible from its commercially available bromo analogue.³³ (At the time of this writing, 1,3,5-triiodobenzene

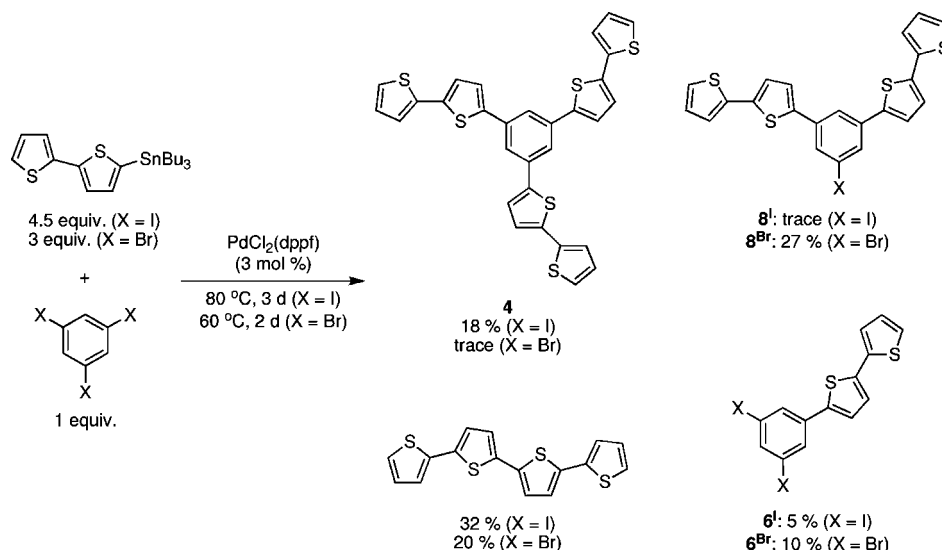
is also commercially available, but significantly more expensive.) The Kumada reactions featured only slight excesses of the thienyl starting material (<2 mol equiv of Grignard reagent per halide) and low catalyst loadings (3 mol %) and were conducted under mild synthetic conditions (rt for 48 h). The Grignard reagent, 2-thienylmagnesium bromide, was easily generated in situ from commercially available 2-bromothiophene.

Although the synthesis of **1** by Negishi cross-coupling was comparable to our Kumada reaction (81 vs 80%, respectively), the necessity for prelithiation in the generation of the 2-thienylzinc chloride starting material in the former case made it less desirable. The Suzuki cross-coupling reaction reported in the patent literature²⁹ gave the highest reported yield of **3** (90%) in the shortest reaction time, but in our hands synthesis of the requisite boronic acid precursor by the reported method was unreliable. We had similar experience with the preparation of 2,2'-dithienyl-5'-boronic acid for attempted Suzuki synthesis of **4** (vide infra). Therefore, the Kumada reaction was once again preferable based on the relative ease of in situ preparation of the Grignard reagent.

Compound **3** has also been made using various cyclotrimerization reactions,^{4–6,30–32} but the overall yields (starting from thiophene) were significantly lower than that of our Kumada reaction (e.g., 86 vs 56% for trimerization of 2-acetylthiophene⁵). In addition, this approach was limited to production of trisubstituted species, while stepwise metal-catalyzed coupling routes gave access compounds of lower symmetry (vide infra).

Our Pd-catalyzed synthesis of **3** gave predominantly the intended product, but also trace quantities of 1,3-diiodo-5-(2'-thienyl)benzene (**5^I**) and 1-iodo-3,5-bis(2'-thienyl)benzene (**7^I**; Scheme 2; X = I). Compounds like **7^I**, which have previously been considered only as unwanted byproduct, and for which dedicated syntheses have not been developed, are potentially very useful in their own rights because they offer both chemical and electrochemical handles for onward manipulation. Therefore, the Kumada reaction was optimized in order to favor the production of the disubstituted product. We reasoned that 1,3,5-tribromobenzene would be a better starting material than 1,3,5-triiodobenzene for the production of mixed (halo)(thienyl)benzenes because the more sluggish reaction of the arylbromide would make controlled partial substitution more feasible. Thus, **7^{Br}** was produced in the highest yield (46%) when a 2:1 ratio of 2-thienylmagnesium bromide and 1,3,5-tribromobenzene was used, and the reaction mixture was heated gently overnight (60 °C) in the presence of PdCl₂(dppf) catalyst. Only traces of **3** and a small quantity of **5^{Br}** (10%) were formed in addition to the intended **7^{Br}** (Scheme 2). We also assayed under identical conditions Pd₂(dba)₃·CHCl₃/4PPh₃, PdCl₂(PPh₃)₂, and Pd(PPh₃)₄ as precatalysts for this transformation; these produced **7^{Br}** in 56, 49, and 54% yields, respectively. However, they also gave

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SCHEME 4. Palladium-Catalyzed Stille Couplings of Trihalobenzenes and 5'-Tributylstannyl-2,2'-bithiophene To Give 4, 6, 8, and Unwanted Tetrathiophene Side-Product


significant quantities of the unwanted trisubstituted product **3** (34, 44, and 16%, respectively). Therefore, the PdCl₂(dppf) precatalyst was deemed better for the selective production of meta-disubstituted thienylbenzenes.

Syntheses of 2 and 4. Due to the tedious synthesis of the required 5'-bromo-2,2'-bithiophene precursor for the Kumada syntheses of 1,3-bis- (**2**) and 1,3,5-tris{5'-(2,2'-bithienyl)}benzene (**4**), we opted instead to take a Stille cross-coupling approach. Reactions between either 1,3-di- or 1,3,5-triodobenzene and 5'-tributylstannyl-2,2'-bithiophene using PdCl₂(dppf) as the catalyst gave **2** and **4** in 83 or 18% yield, respectively; a similar synthesis by Song and Swager using PdCl₂(PPh₃)₂ as catalyst gave **2** in 86% yield. Another reported synthesis of **2** involved the Ni-catalyzed Kumada coupling of 2-thienylmagnesium bromide with 1,3-bis{5'-bromo-5'-(2,2'-bithienyl)}benzene, but this gave only a 9% yield.

As was the case in the synthesis of **1** and **3**, these reactions used slight excesses of the bithienyl starting materials (1.5 mol equiv per halide) and low catalyst loadings (3 mol %). Although the stannyl reagent was straightforward to synthesize by reaction of 2,2'-bithiophene with *n*-BuLi followed by addition of *n*-Bu₃SnCl, purification of the tin-containing product by vacuum distillation required high temperature (~450 °C) and resulted in only moderate yields (76%). Because the isolated yield of **4** was low, we investigated other possible synthetic routes.

Inspired by the reported synthesis of **3** by Obara and Tada,²⁹ we applied the Suzuki cross-coupling reaction to the synthesis of **4**. In this reaction, 2,2'-dithienyl-5-boronic acid was coupled with 1,3,5-triodobenzene in the presence of Pd(OAc)₂ (5 mol %) and PPh₃ to afford **4** in high yield (90%, Scheme 3). The disadvantage to this approach was that the synthesis of the boronic acid starting material proved to be very unreliable; on some occasions, no product was formed. Moreover, there was no reported method of purification of the acid. The crude mixture was therefore used in the Suzuki coupling reaction; this gave a reaction mixture that was difficult to purify using flash chromatography. Although the Stille reaction was very low yielding by contrast, the metallated coupling reagent, 5'-tributylstannyl-2,2'-bithiophene, could be obtained relatively easily.

Although ours is the first metal-catalyzed synthesis of **4**, the compound has also been made using cyclotrimerization reactions,^{5,34} but reported yields were only moderate (56–65%).

As expected, the Stille coupling synthesis of **4** gave a mixture of products from which 1,3-diiodo-5-{5'-(2,2'-bithienyl)}benzene (**6^I**), and 1-iodo-3,5-bis{5'-(2,2'-bithienyl)}benzene (**8^I**) were also isolated in trace quantities (Scheme 4; X = I). A significant side-product was tetrathiophene. We once again altered the synthesis to favor production of either **6** and **8**: When a 2:1 ratio of stannylthiophene:bromobenzene was heated to 60 °C for 48 h in the presence of PdCl₂(dppf) (3 mol %), the desired products were obtained in poor yield (**6^{Br}**, 10% and **8^{Br}**, 27%); under these conditions, **4** was not formed, and the production of tetrathiophene was limited to 20%. The low isolated yields of **4**, **6^{Br}**, and **8^{Br}** in these reactions were in part due to difficulty in separating them from tetrathiophene, which was prone to streaking during purification by column chromatography.

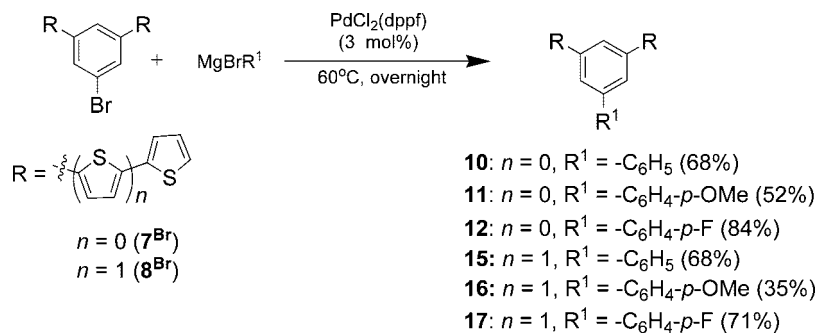
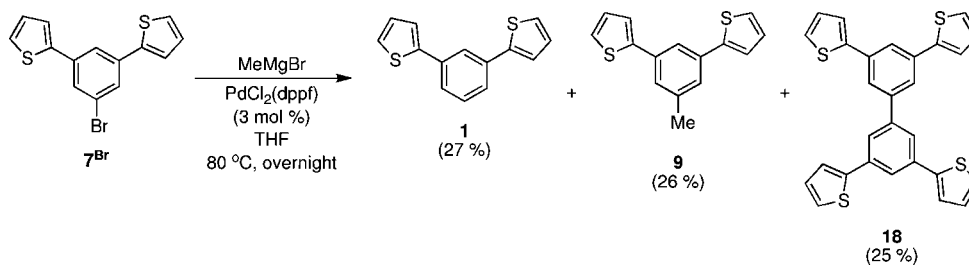
Syntheses of 9–17. To explore the effects of electron-donating and -withdrawing groups on the physical properties of the meta-substituted thienylbenzenes, we made a series of new compounds (Chart 3) with the general formula 1,3-bis(2'-thienyl)-5-R-benzene, where R = Me (**9**), Ph (**10**), *p*-C₆H₄OMe (**11**), *p*-C₆H₄F (**12**), CCPh (**13**), and Fc (**14**; Fc = ferrocenyl). We also made a smaller family of the analogous bithienyl-substituted compounds, 1,3-bis({5'-(2,2'-bithienyl)})-5-R-benzene, where R = Ph (**15**), *p*-C₆H₄OMe (**16**), *p*-C₆H₄F (**17**).

Coupling of **7^{Br}** or **8^{Br}** with the appropriate Grignard reagent in the presence of PdCl₂(dppf) as catalyst gave compounds **10–12** and **15–17** in modest to good yields (35–84%; Scheme 5). Slight excesses of the Grignard reagent (1.5 mol equiv) and low catalyst loading (3 mol %) were used.

The synthesis of **9** by Kumada coupling of MeMgBr and **7^{Br}** in the presence of PdCl₂(dppf) gave three products: the intended compound **9**, **1**, and the homocoupled compound **18** (Scheme 6). Compound **1** presumably resulted from the hydrolysis of the Grignard reagent derived from **7^{Br}**, probably during workup, and could not be separated from unreacted **7^{Br}** by column chromatography. Compound **18**, isolated in 25% yield, was

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SCHEME 5. Kumada Syntheses of Compounds 10–12 and 15–17

SCHEME 6. Palladium-Catalyzed Reaction between Methyl Grignard and **7^{Br}**

thought to be the product of Kumada coupling between compound **7^{Br}** and its corresponding Grignard reagent. An attempt to make **18** in a rational method from 2 equiv of **7^{Br}** and 1 equiv of Mg turnings failed in the absence of added MeMgBr. This implied that formation of a Grignard reagent from **7^{Br}** was not favorable, but that transmetalation from MeMgBr was facile. Other Kumada reactions were uncomplicated.

Compound **13** was made in moderate yield (68%) using a Sonogashira coupling reaction between **7^{Br}** and phenylacetylene. A slightly higher catalyst loading was required in this reaction (5 mol % Pd(PPh₃)₂Cl₂ and 10 mol % CuI) than in the Kumada reactions.

There is much current interest in incorporating redox-stable metallic components into organic conducting polymers for the purpose of generating materials with interesting structural and electrical properties,³⁵ and also for memory applications.³⁶ Therefore, we set about making a thiophenyl monomer that included ferrocene. Compound **14** was successfully made albeit in low yield via the Stille cross-coupling of tributylstannylferrocene and **7^{Br}** using PdCl₂(dppf) as catalyst.

Solid-State Characterization of 4 and 12. ORTEP representations of the molecular structures and packing diagrams of compounds **4** and **12** are given in Figures 1–4. The crystal structure of **3** has been reported previously.³⁷

Compound **4** crystallized in the chiral space group $P2_12_12_1$ (No. 19) and had eight molecules per unit cell; these fell into two crystallographically independent groups of four. One of the two configurations (absent from Figure 1) showed disorder in one of its three terminal thieryl rings. Although the relative orientation of the thieryl rings in each of the bithienyl substituents was head-to-tail, as expected, the molecule did not adopt pseudo- C_3 symmetry in the solid state. Instead, it assumed an asymmetric “scorpion-like” configuration, shown most clearly

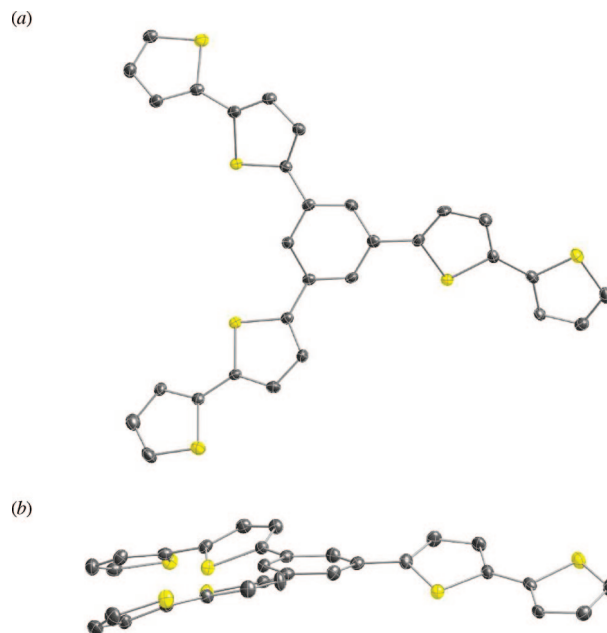


FIGURE 1. ORTEP representation (20% ellipsoids, H-atoms removed for clarity) of the molecular structure of one of the crystallographically independent forms of **4** with the central phenyl ring in the plane of the page (a) and nearly perpendicular to the page (b). Carbon atoms are shown in gray and sulfur in yellow.

in Figure 1a, with one of the substituents serving as the “tail” and the other two as the “claws”. As shown in Figure 1b, **4** was discoidal, but not planar in the solid state, although two of the bithienyl substituents featured essentially coplanar thieryl rings; the dihedral angles between the rings in these substituents were approximately 1.6 and 12.5°, while that between the rings in the remaining substituent was 32.1°. The “inner” thieryl rings made torsion angles with the central phenyl ring of about 24.1, 26.5, and 14.3°. Bond distances and angles were generally unremarkable.

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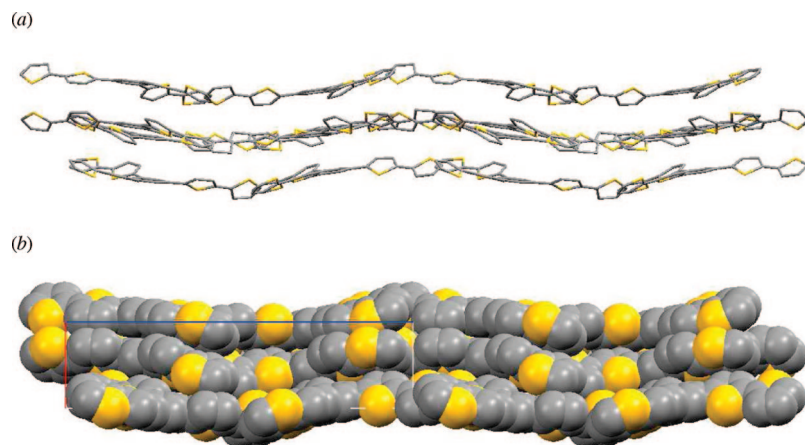


FIGURE 2. Packing view of the solid state structure of **4** viewed along the *b*-axis for two contiguous unit cells in (a) capped-stick and (b) space-filling representations with the thienyl ring disorder and H-atoms removed for clarity. The unit cell is indicated in (b) with the *a*-axis in red and the *c*-axis in blue. Carbon atoms are shown in gray and sulfur in yellow.

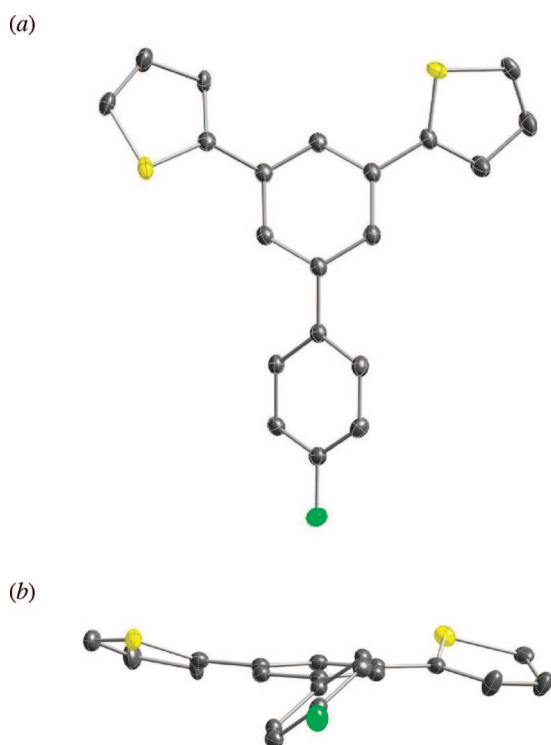


FIGURE 3. ORTEP representation (20% ellipsoids) of the molecular structure of **12** with the central phenyl ring in the plane of the page (a) and nearly perpendicular to the page (b). Disorder in the thienyl rings and H-atoms have been removed for clarity. Carbon atoms are shown in gray, sulfur in yellow, and fluorine in green.

Compound **4** packed (Figure 2) as lamellae of canted discs, with the interlamella distance, as defined by the separation between equivalent phenyl carbon atoms, being 4.84 Å.

In the solid-state structure of **12** (Figure 3), both thienyl rings were disordered; these were modeled as 0.81:0.19 occupancies of positions corresponding to approximate 180° rotations about the thienyl-phenyl bonds. Once again, the compound was not planar: the torsion angles between the thienyl and phenyl rings were approximately 23.7 and 31.4°. The torsion angle between the two phenyl rings was about 38.2°. Figure 4 shows a view of the unit cell along the *b*-axis in (a) stick and (b) spacefilling representations. Like **4**, **12** was packed in layers, with the distance between layers being 5.07 Å.

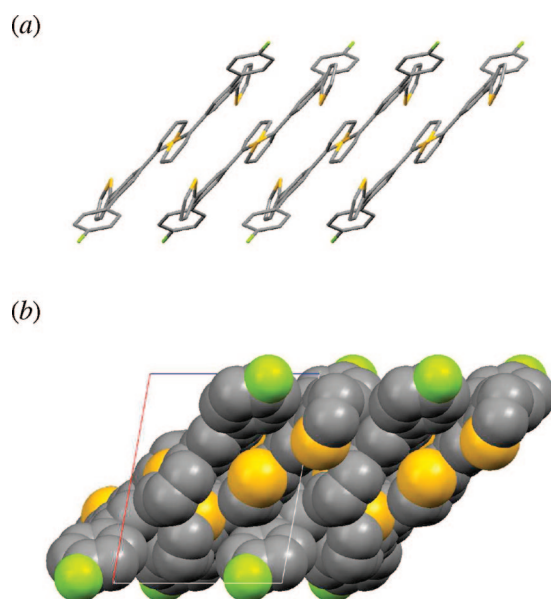


FIGURE 4. Packing view of the solid state structure of **12** viewed along the *b*-axis for two contiguous unit cells in (a) capped-stick and (b) space-filling representations with the thienyl ring disorder and H-atoms removed for clarity. The unit cell is indicated in (b) with the *a*-axis in red, the *c*-axis in blue. Carbon atoms are shown in gray, sulfur in yellow, and fluorine in green.

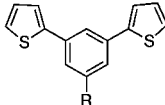
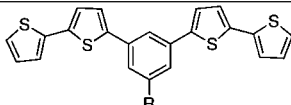
Physical Characterization by Electronic Spectroscopy, Cyclic Voltammetry, and DFT Calculations. Pertinent physical data for compounds **1–4** and **9–17** are collected in Table 1. Gas-phase first ionization potentials (IP), molecular orbitals, and HOMO–LUMO gaps were calculated by density functional theory (DFT) using the B3PW91 functional³⁸ and the 6-31G* basis set as described in the Experimental Methods section. B3PW91 was chosen because it is one of the best standard functionals for calculating ionization potentials.³⁹

To determine the nature of the chromophore in these compounds, we compared their electronic spectra to those of related species containing phenyl and thienyl rings. As was the case for the known compounds, all oligothiophenes

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TABLE 1. Collected Calculated and Measured Properties of Meta Di- and Trisubstituted Thienylbenzenes

General structure	R	Experiment				Theory ^a	
		Absorption (λ_{\max}/nm) [$\log_{10}\epsilon$]	Emission (λ_{\max}/nm) [eV]	Estimated conjugation length	First oxidation potential (V)	First ionization potential (eV)	HOMO- LUMO gap (eV)
	-H (1)	284 [4.38], 4.48	361 [3.44]	3.45	1.55	7.12	4.58
	-C ₆ H ₅ S (3)	292 [4.26], 4.71	370 [3.36]	3.66	1.60	7.05	4.56
	-Me (9)	285 [4.36], 4.69	363 [3.42]	3.47	1.30	7.04	4.58
	-Ph (10)	281 [4.42], 4.46	376 [3.31]	3.39	1.29	7.03	4.57
	-C ₆ H ₄ - <i>p</i> -OMe (11)	284 [4.38], 4.88	375 [3.31]	3.45	1.15	6.87	4.53
	-C ₆ H ₄ - <i>p</i> -F (12)	283 [4.39], 4.50	374 [3.32]	3.44	1.24	7.08	4.57
	-CCPh (13)	288 [4.32], 4.92	379 [3.28]	3.55	1.32	7.00	4.30
		295 (sh) 306 (sh)					
	-Fc (14)	287 [4.33], 4.66	381 [3.26]	3.54	0.00, 1.13	6.77	4.15
		-H (2)	351 [3.54], 4.84	423 [2.94]	5.72	1.12	6.42
-C ₈ H ₅ S ₂ (4)		357 [3.48], 4.78	408 [3.05]	6.00	1.22	6.33	3.70
-Ph (15)		352 [3.53], 4.82	419 [2.97]	5.76	0.90	6.38	3.71
-C ₆ H ₄ - <i>p</i> -OMe (16)		351 [3.54], 4.73	420 [2.96]	5.72	1.22	6.33	3.72
-C ₆ H ₄ - <i>p</i> -F (17)		352 [3.53], 4.77	418 [2.97]	5.76	1.27	6.42	3.71

^a Gas-phase values calculated at the B3PW91/6-31G* level.

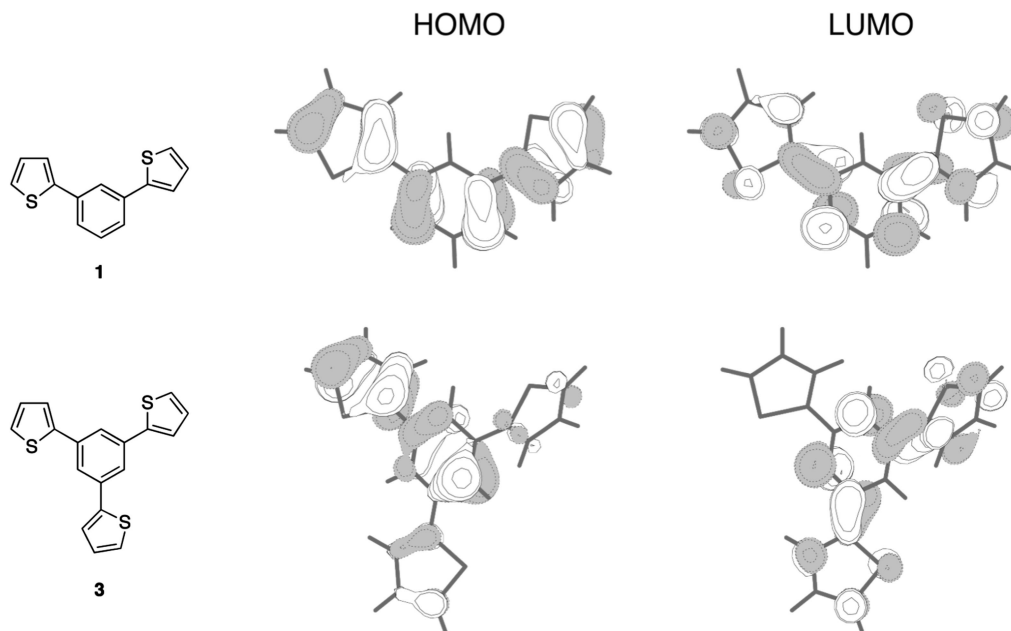


FIGURE 5. Representations of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of **1** and **3**.

reported in this article, except **13**, exhibited broad, featureless absorption bands, which were assigned to π - π^* transitions. The energies of the absorption maxima were inversely proportional to conjugation length, as expected, owing to enhanced spatial distribution of the singlet excited-state in more highly conjugated systems. Thus, absorption maxima fell cleanly into two ranges based on the number of contiguous thienyl rings: those of the “monothienyl” com-

pounds (**1**, **3**, **9**–**14**) ranged from 284–292 nm and were significantly red-shifted with respect to thiophene (**T**, 231 nm),⁴⁰ but fell within the span marked by 2-phenylthiophene (**PT**, 282 nm) and 2,2'-bithiophene (**BT**, 303 nm),⁴⁰ while those of the “bithienyl” compounds (**2**, **4**, **15**–**17**) ranged from 351–357 nm and were instead closest to that of 2,2':5',2''-terthiophene (**TT**, 354 nm).⁴⁰ The same analysis could be applied to the molar extinction coefficients (ϵ) that, with

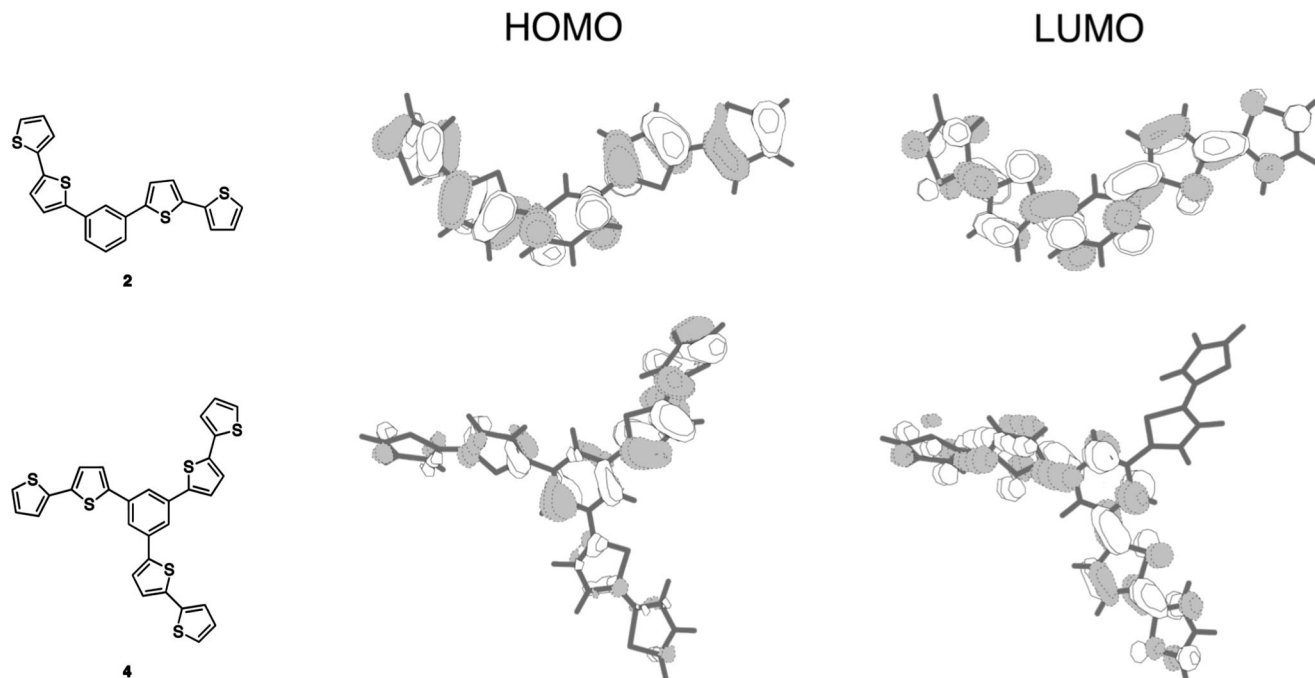


FIGURE 6. Representations of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of **2** and **4**.

the exception of **11** and **13** (vide infra), were significantly larger for the bithienyl ($5.37\text{--}6.92 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) than for the monothieryl compounds ($2.88\text{--}5.13 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

The emission maxima of **1**, **3**, and **9–14** (361–381 nm) approximated that of **BT** (362 nm),⁴⁰ while those of **2**, **4**, and **15–17** (408–423 nm) were similar to those of 5-phenyl-2,2'-bithiophene (**PBT**, 413 nm)²⁷ and **TT** (426 nm).⁴⁰ Unlike the absorption spectra, the rt solution-phase emission spectra of all compounds, and those of related compounds in the literature,²⁷ exhibited structured bands. The difference has been attributed to the transition from a nonrigid, nonplanar ground-state to a more rigid, planar excited state.²⁷ This is readily rationalized by reference to calculated representations of the HOMO and LUMO of compounds **1** and **3**, and **2** and **4**, which are shown in Figures 5 and 6, respectively. Clearly evident from these diagrams is that the HOMO and LUMO have aromatic and quinoid character, respectively. Thus, population of the LUMO by excitation results in the development of partial double bond character, and therefore increased rigidity and planarity, between the thienyl and phenyl rings. A similar analysis of **2** by semiempirical methods has been reported.²⁷

For **1** and **2**, both MOs were distributed over the entire molecule, but there was a nodal plane that perpendicularly bisected the phenyl ring. In **3** and **4**, the HOMO did not encompass one of the three substituents as extensively as it did the other two, and the LUMO was strictly confined to only two of them.

The HOMO and LUMO of analogous mono- (**10–12**) and bithienyl (**15–17**) compounds bearing phenyl, *para*-methoxyphenyl, and *para*-fluorophenyl substituents are shown in Figures 7 and 8, respectively. With the exception of **11**, these compounds shared characteristic orbital features with **1** and **2**, respectively, meaning that both the “arms” as well as the “heads”

and “tails” of these species were electronically distinct and, therefore, that the nature of the third substituent in all cases had little effect on optical properties.

Empirical studies by Sato et al.²⁷ have shown that the approximate conjugation length as represented by the number of contiguous double bonds (m) in a series of *ortho*-, *meta*-, and *para*-bis(bithienyl) benzenes may be estimated from the absorption energy E (in eV) using eq 1

$$E = (7.32/m) + 2.26 \quad (1)$$

Table 1 includes a column giving m for each of the compounds. The electronic data and derived approximate conjugation lengths indicated some electronic coupling between the thienyl and phenyl rings in all of the compounds, but also showed that the coupling did not extend from one thienyl ring to another through the central phenyl ring in this family of compounds. These empirical findings essentially confirmed the detailed ab initio calculations of Köse and co-workers,⁷ which showed that the thienyl “arms” of related dendrimers were predominantly responsible for absorption, and that meta substitution about the phenyl ring localized excitons to the arms without any electronic coupling between them. A qualitatively similar result would be derived simply by drawing charge-separated quinoidal resonance forms for the compounds, which would demonstrate “on the back of the envelope” that naive arrow pushing should not permit delocalization between thienyl rings in different meta positions (Chart 4).

A hypothesis consistent with these data was that the optical spectra should depend primarily on the number of contiguous thienyl rings, and not on the degree of substitution around the central phenyl ring. Given that we had developed methods to make mono-, bi- and trithienyl benzenes selectively, we were able to test this directly. Figure 9 correlates the excitation and emission maxima for monothieryl (**1**, **3**, **5^{Br}**, **7^{Br}**, **PT**), and bithienyl (**2**, **4**, **6^{Br}**, **8^{Br}**, **PBT**) compounds with the degree of meta-substitution about the central phenyl ring.

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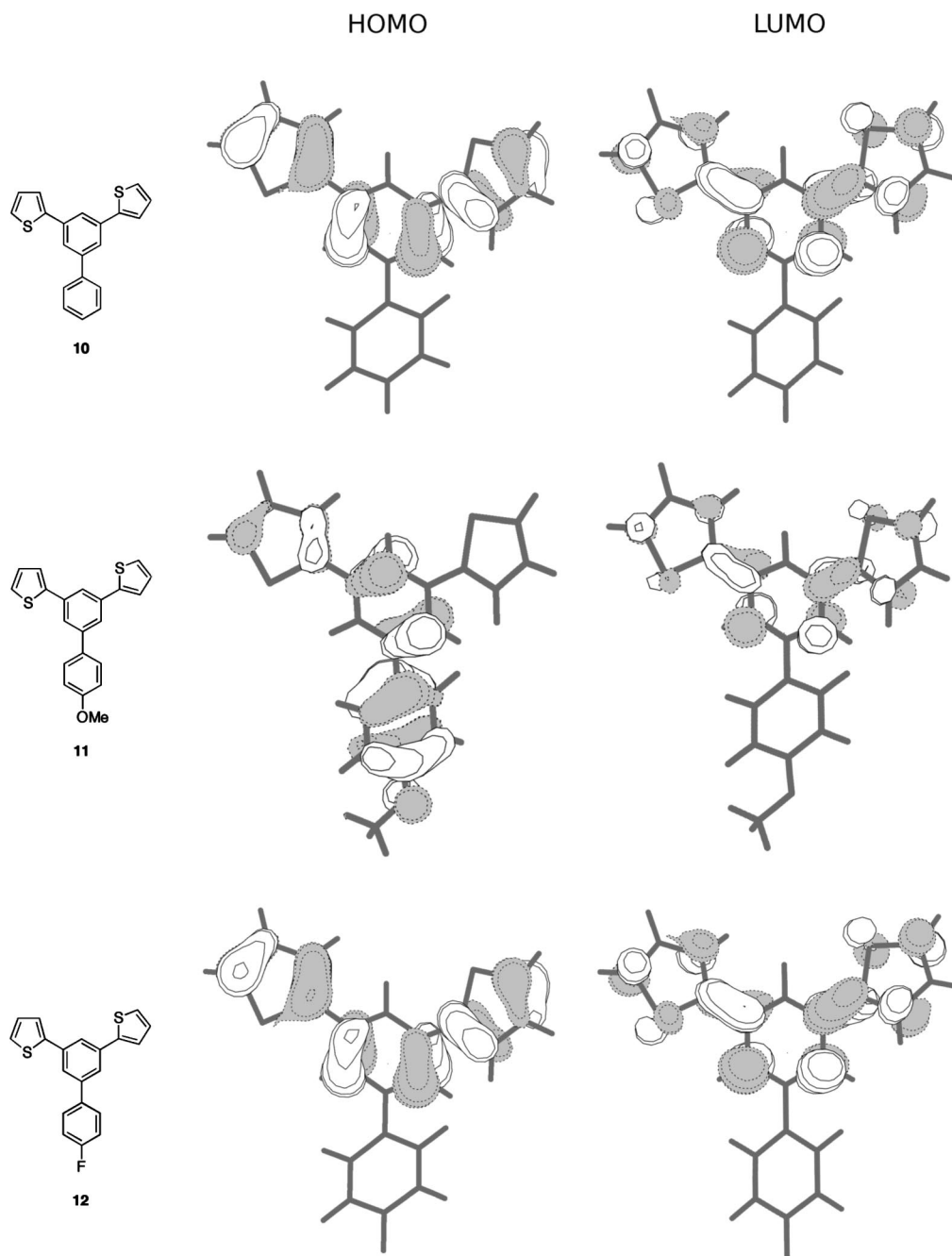


FIGURE 7. Representations of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of **10–12**.

Clearly evident from this representation of the data is that there was only a slight variation in the optical properties with the degree of substitution about the ring. It was also interesting to note that the brominated compounds **5^{Br}**–**8^{Br}** had absorbance (287–354 nm) and emission (354–408 nm) spectra that were very similar to those of their bromine-free analogues, **1–4** (284–357 and 361–423, respectively), which emphasized the insensitivity of the electronic spectroscopy not only to the degree, but also to the nature of the meta substitution in this family of thienyl benzenes.

Only the emission maxima of the monothieryl compounds **1**, **3**, **5^{Br}**, **7^{Br}**, and **PT** demonstrated a smooth, albeit weak, dependence on the degree of substitution. Therefore, it was possible that a minimum of two contiguous thienyl rings was required for absorption by, and strict localization of the exciton on, electronically independent “arms” in meta-

substituted thienyl benzenes. When arms were restricted to only a single thienyl ring, weak electronic coupling between them became apparent.

For all compounds, the calculated gas-phase first ionization potentials (IP) were significantly lower than those of thiophene (8.55 eV calculated; 8.86 eV observed⁴¹) and benzene (8.88 eV calculated; 9.24 eV observed⁴¹), which was expected on the basis of extended conjugation. As for the electronic spectra, the calculated IPs fell cleanly into two ranges based on the number of contiguous thienyl rings: for the monothieryl compounds (**1**, **3**, and **10–12**), they ranged from 6.87–7.12 eV, while for the bithienyl compounds (**2**, **4**, and **15–17**), IP were significantly lower and spanned a

(41) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 88th ed.; CRC Press: Boca Raton, FL, 2008.

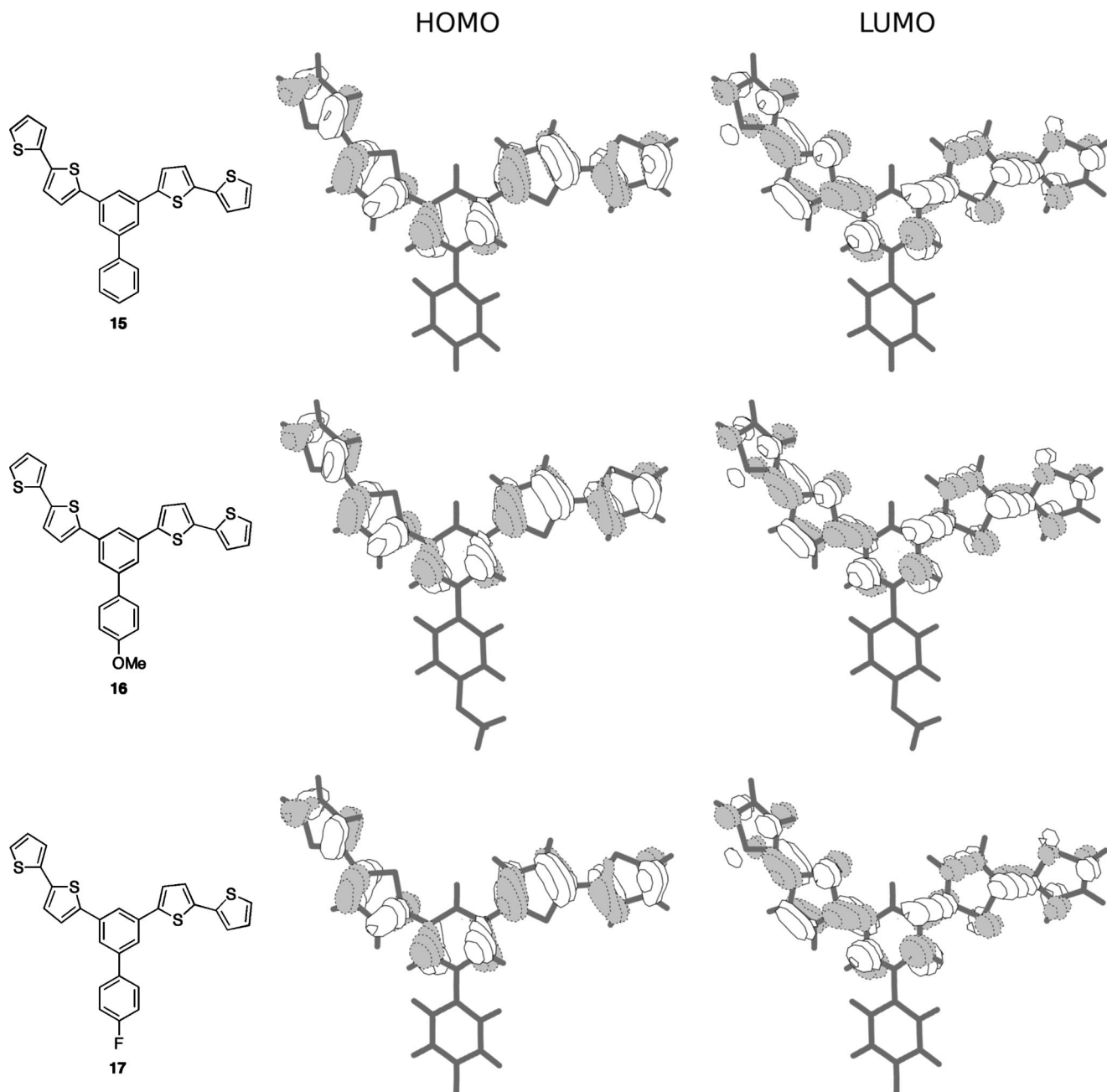
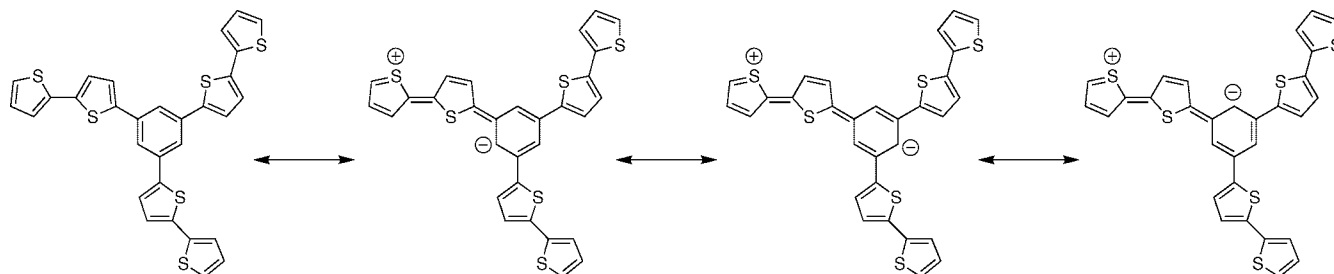


FIGURE 8. Representations of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of 15–17.

CHART 4. Quinoidal Resonance Forms for 4 Showing Localization to Only One of the Bithienyl “Arms”



mere 0.09 eV (6.33–6.42 eV). The HOMO–LUMO gaps for the monothieryl compounds showed only a very slight dependence on the nature of the third meta-substituent and fell in the narrow range 4.53–4.58 eV. The corresponding gaps of the bithienyl compounds were essentially independent

of the substituent (3.70–3.72 eV) but were significantly lower than those of the monothieryl compounds by about 0.8 eV because of extended conjugation in these systems.

A pair of compounds had remarkable properties: (i) Substantial contribution to the HOMO by the OMe group in **11** (Figure

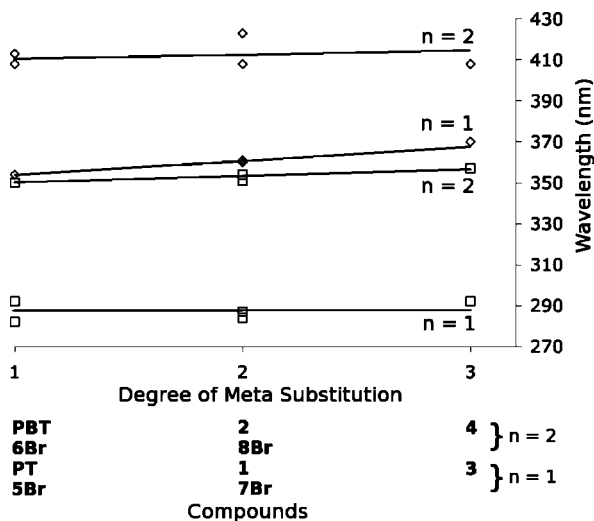


FIGURE 9. Variation of absorption (□) and emission (◇) maxima with degree of meta-substitution about a central phenyl ring for compounds incorporating thienyl groups with one ($n = 1$; **1**, **3**, **5Br**, **7Br**, and **PT**) and two ($n = 2$; **2**, **4**, **6Br**, **8Br**, and **PBT**) contiguous rings. Absorption data for **PBT** and emission data for **PT** were not available. Lines are meant only to guide the eye.

7) had the effect of lowering the IP and HOMO–LUMO gap of this compound and raising its measured molar extinction coefficient with respect to other members of the monothienyl family. (ii) The C≡C “bridge” allowed significant electronic interaction between the head and tail of **13** (Figure 10) and gave it a lower HOMO–LUMO gap, a more complex absorption spectrum, a bathochromically shifted emission, and a much larger molar extinction coefficient than either the biphenyl- (**10–12**) or phenyl-based compounds (**1** and **3**). In **13**, the HOMO essentially encompassed the diphenylacetylene “core” of the molecule, while the HOMO-1 orbital (-5.9 kJ mol^{-1}) had essentially the same character as the HOMO in the other monothienyl compounds.

Table 1 also lists the solution oxidation potentials, approximated by anodic peak potentials, for compounds **1–4** and **9–17** as measured by cyclic voltammetry. Values for the monothienyl species ranged from 1.13–1.60 V, while those of the bithienyl compounds were significantly less positive and spanned a narrower range (0.90–1.27 V); these values were in accord with those of related compounds reported in the literature.^{5,16–18} We have calculated the Gibbs free energies of oxidation for **1–4** and **9–17** in CH_2Cl_2 solution, but found that these values (expressed in eV) were much greater than the measured oxidation potentials, apparently because the oxidized

forms of **1–4** and **9–17** are not free solvated cations (see Table S5 in the SI). There also appeared not to be a rational Hammett-type connection between either the electronic nature of the substituent in the third meta-position or between the degree of meta-substitution and the measured oxidation potential. Instead, the number of contiguous thienyl rings was once again the prime determinant. Further work is required to rationalize the observed oxidation potentials.

Conclusions

Kumada coupling reactions catalyzed by $\text{PdCl}_2(\text{dppf})$ between the appropriate thienyl Grignard and either 1,3- or 1,3,5-bromo- or iodobenzenes are the most reliable of the typical metal-catalyzed approaches for the production of meta-substituted thienylbenzenes. These reactions are generally higher yielding than the catalyzed routes previously reported in the literature, and are more convenient because they circumvent the need for prelithiation. In addition, they are more flexible in that they also permit the controlled generation of mixed (halo)(thienyl)benzenes, which are valuable compounds possessing both electrical and chemical “handles” and which cannot be accessed by cyclotrimerization reactions.

UV–visible absorption and fluorescence data show clearly that the electronic character of these compounds is determined primarily by the number of contiguous thienyl rings, not by the degree of meta-substitution about the central phenyl ring nor by the nature of the third substituent in the case of compounds **9–12** and **15–17**. This finding essentially confirms *ab initio* calculations of ref 7, which show that the thienyl “arms” of phenyl-cored dendrimers are predominantly responsible for absorption and that meta-substitution about the phenyl ring localizes excitons to the arms without any electronic coupling between them. However, a smooth increase in the emission maximum of the “monothienyl” compounds with increasing meta-substitution about the central phenyl ring demonstrates that a minimum of two contiguous rings is necessary for *strict* localization of the excitons to the arms.

Within the field of conducting polymers, meta-substitution is generally avoided because it blocks conjugation. In some cases, it has been introduced into poly(phenylene)s specifically to interrupt conjugation in a rational manner.^{42,43} Our findings for these model systems (or monomers) are in accord with this sentiment. However, we note that their oxidation potentials can be varied (albeit unpredictably, rather than by rational “tuning”) over a large and useful range by introduction of different groups meta to the thienyl substituent. In addition, the steric qualities of the groups may give rise to enhanced physical properties of

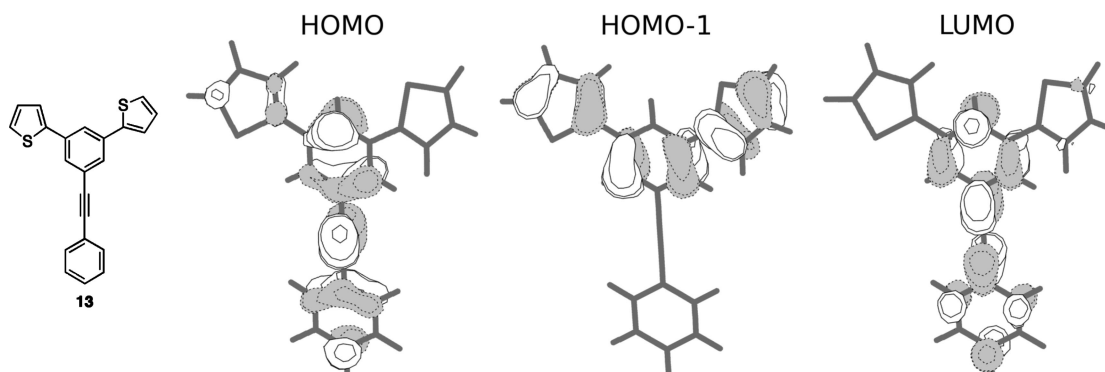


FIGURE 10. The HOMO, HOMO-1, and LUMO of compound **13**.

resultant polymers. Finally, compounds **3** and **4**⁵ lead in principle to highly cross-linked polymers that should have interesting properties. These things in combination make polymers of the compounds reported in this paper worthwhile targets that we are currently pursuing.

Experimental Section

Calculations. All calculations of the first ionization potentials (IP) and HOMO–LUMO gaps were carried out using the Gaussian 03 program.⁴⁴ Each IP was evaluated as the difference between the zero-point-energy (ZPE)-corrected total energies of the molecular cation and the corresponding neutral species. The geometries of the neutral molecules and molecular cations were optimized at the B3PW91/6-31G* level without symmetry constraints. The zero-point energies were also evaluated at the B3PW91/6-31G* level using a scale factor of 0.9573 recommended by Scott and Radom.⁴⁵

Compounds **1–4** and **9–17** had multiple local minima (conformations), but because the IP and HOMO–LUMO gaps were much larger than energy differences between the various conformations, it was not necessary to use the most stable conformations to evaluate an IP. The optimized Cartesian coordinates of the conformations used in this work are given in the Supporting Information. Harmonic vibrational analysis of the conformers showed that none of the 13 neutral species and 13 cations had imaginary frequencies, and therefore, these structures represent true minima on the potential energy surfaces.

The B3PW91/6-31G* ionization potentials of benzene (calculated, 8.88 eV; experimental, 9.24 eV⁴¹) and thiophene (calculated, 8.55 eV; experimental, 8.86 eV⁴¹) were about 0.3 eV lower than the experimental values. This suggests that the calculated IPs of compounds **1–4** and **9–17** may also be underestimated.

1,3-bis(2'-thienyl)benzene (1). In a 500 mL three-neck flask equipped with a bubbler, an orange suspension of 1,3-diiodobenzene (1.50 g, 4.55 mmol) and PdCl₂(dppf) (0.099 g, 0.137 mmol) in THF (15 mL) was added dropwise to an ice cold suspension of 2-thienylmagnesium bromide (0.17 M, 160 mL, 27 mmol) in the same solvent to give a yellow slurry. This mixture was stirred magnetically at r.t. for 2 d before being hydrolyzed on ice with 1 M HCl (200 mL), followed by H₂O (100 mL). The aqueous layer was extracted with Et₂O (3 × 100 mL). The combined organic fractions were washed with saturated NaHCO₃ (50 mL), followed by H₂O (50 mL) before being dried over MgSO₄ and reduced to a dark brown liquid by rotatory evaporation. The desired product, a white microcrystalline solid, was obtained by flash column chromatography using petroleum ether as eluent (*R*_f = 0.4): mp (lit.) 83–85 °C (85–86 °C). Yield: 0.880 g (73%). HRMS C₁₄H₁₀S₂ calcd (found): 242.0224 (242.0223). ¹³C{¹H} NMR: δ 123.7, 123.8, 125.4, 128.3, 129.7, 135.3, 144.2 (one quaternary carbon atom not observed). ¹H NMR data for this compound were the same as those reported in the literature.²⁸

1,3-Bis[5'-(2',2''-bithienyl)]benzene (2). In a 250 mL three-neck flask equipped with a condenser, a yellow solution of 5'-tributylstannyl-2,2'-bithiophene (2.08 g, 4.58 mmol) in toluene (5 mL) was added to an orange suspension containing 1,3-diiodobenzene (0.504 g, 1.53 mmol) and PdCl₂(dppf) (0.100 g, 0.777 mmol) in the same solvent (50 mL). This gave a pale brown suspension, which was brought to reflux for 3 d. The dark brown reaction mixture was then cooled under a slow flow of Ar and hydrolyzed with H₂O (50 mL). The aqueous layer was extracted with Et₂O (3 × 50 mL). The combined organic fractions were washed with an aqueous solution of KF (3 × 50 mL), dried over MgSO₄, and evaporated to dryness to give a yellow solid. The desired product, a yellow powder, was obtained by flash column chromatography using petroleum ether as eluent (*R*_f = 0.2): mp 168–172 °C. Yield: 0.528 g (71%). HRMS C₂₂H₁₄S₄ calcd (found): 405.9978 (405.9968). The NMR spectroscopic data for this compound were the same as those reported in the literature.⁹

1,3,5-Tris(2'-thienyl)benzene (3). This compound and **1** were made similarly. Thus, the reaction of a THF (100 mL) solution of 1,3,5-triiodobenzene (1.34 g, 2.94 mmol) and solid PdCl₂(dppf) (0.064 g, 0.088 mmol) with a suspension of 2-thienylmagnesium bromide (0.117 M, 150 mL, 18 mmol) in the same solvent gave, after workup and purification by flash column chromatography (20:1 hexanes/CHCl₃, *R*_f = 0.3), the desired product as a white crystalline solid: mp (lit.) 160–162 °C (156–158 °C). Yield: 0.820 g (86%). HRMS C₁₈H₁₂S₃ calcd (found): 324.0101 (324.0112). The spectroscopic data for this compound were the same as those reported in the literature.²⁸

1,3,5-Tris[5'-(2',2''-bithienyl)]benzene (4). *By Stille coupling.* This was similar to the synthesis of **2**. Thus, the reaction of 1,3,5-triiodobenzene (0.184 g, 0.402 mmol) and 5'-tributylstannyl-2,2'-bithiophene (1.10 g, 2.42 mmol) in refluxing toluene (40 mL) catalyzed by PdCl₂(dppf) (0.062 g, 0.048 mmol) gave after workup and purification using flash column chromatography (neat hexanes, *R*_f = 0.1) the desired product as a yellow powder. Yield: 0.92 g (18%). *By Suzuki coupling.* In a 250 mL three-neck flask equipped with a condenser, Pd(OAc)₂ (0.014 g, 0.063 mmol), PPh₃ (0.050 g, 0.190 mmol), and an aqueous solution of Na₂CO₃ (1 M, 3.6 mL) were added to a pale yellow solution of 2,2'-bithienyl-5'-boronic acid (0.381 g, 1.81 mmol) and 1,3,5-triiodobenzene (0.207 g, 0.453 mmol) in THF (100 mL). The resulting green solution was brought to reflux for 3 d. The brown solution was removed from heat, cooled under a slow flow of N₂ and quenched on ice with H₂O (100 mL). Dichloromethane (50 mL) was added and the aqueous layer was extracted with the same solvent (3 × 50 mL). The organic layers were combined and dried over MgSO₄ and the solvent was evaporated to give a light brown solid from which the product was isolated by chromatography as above. Yield: 0.234 g (90%). Mp (lit.) 210–214 °C (136 °C). HRMS C₃₀H₁₈S₆ calcd (found): 569.9733 (569.9740). ¹³C{¹H} NMR: δ 122.1, 124.1, 124.8, 124.8, 128.2, 135.7, 137.5, 137.7, 142.2. ¹H NMR spectroscopic data for this compound were the same as those reported in the literature.²⁸ Crystals of this compound suitable for X-ray diffraction analysis were grown at 4 °C from CH₂Cl₂/hexane over a period of 2 weeks.

1,3-Dibromo-5-(2'-thienyl)benzene (5^{Br}). This compound, a white crystalline solid (mp 56–59 °C), was isolated using column chromatography (neat hexanes, *R*_f = 0.6) as a byproduct of the synthesis of **7^{Br}** (below). Yield: 0.38 g (10%). HRMS C₁₀H₆Br₂S calcd (found): 315.8557 (315.8567). ¹H NMR: δ 7.09 (dd, 1H, ³J_{HH} = 3.8, ³J_{HH} = 5.0), 7.31 (pdd, 1H), 7.35 (pdd, 1H), 7.56 (pt, 1H), 7.67 (pd, 2H). ¹³C{¹H} NMR: δ 123.6, 124.9, 126.7, 127.7, 128.5, 132.8, 138.0, 141.2. This compound has been prepared previously by the Suzuki reaction of 2-thienylboronic acid and 1,3,5-tribromobenzene.⁴⁶

1,3-Dibromo-5-[5'-(2',2''-bithienyl)]benzene (6^{Br}). This compound, a pale yellow solid (mp 139–143 °C), was isolated using column chromatography (neat hexanes, *R*_f = 0.4), as a byproduct of the synthesis of **8^{Br}** (below). Yield: 0.038 g (4%). HRMS C₁₀H₆Br₂S₂ calcd (found): 397.8434 (397.8433). ¹³C{¹H} NMR: δ 123.6, 124.4, 124.9, 125.2, 125.6, 127.3, 128.2, 132.8, 137.6 (4 quaternary carbon atoms not observed). ¹H NMR spectroscopic data for this compound were the same as those reported in the patent literature.²⁹

1-Bromo-3,5-bis(2'-thienyl)benzene (7^{Br}). This compound and **1** were made similarly, with the modification that the reaction mixture was heated to 60 °C overnight. Thus, a reaction between 1,3,5-tribromobenzene (3.90 g, 12 mmol), PdCl₂(dppf) (0.09 g, 0.13 mmol), and 2-thienylmagnesium bromide (0.08 M, 330 mL, 26

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mmol) in dry THF (100 mL) gave, following workup and chromatography (neat hexanes, $R_f = 0.2$), of the desired product as a white solid (mp 73–74 °C). Yield 1.85 g (46%). HRMS $C_{14}H_9BrS_2$ calcd (found): 319.9329 (319.9332). 1H NMR: δ 7.11 (dd, 2H, $^3J_{HH} = 3.6$, $^3J_{HH} = 4.8$), 7.35 (m, 4H), 7.66 (pd, 2H), 7.73 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 122.4, 123.6, 124.5, 126.1, 127.8, 128.4, 137.0, 142.5.

1-Bromo-3,5-bis(5'-(2',2''-bithienyl)benzene (8^{Br}). This compound and **2** were made similarly. Thus, reaction of 5'-tributylstannyl-2,2'-bithiophene (3.26 g, 7.17 mmol) and 1,3,5-tribromobenzene (1.12 g, 3.58 mmol) in toluene (75 mL) catalyzed by $PdCl_2(dppf)$ (0.079 g, 0.11 mmol) gave after workup and purification by flash column chromatography (neat hexanes, $R_f = 0.1$) the desired product as a yellow solid (mp 175–179 °C). Yield: 0.302 g (27%). HRMS $C_{22}H_{13}BrS_4$ calcd (found): 483.9083 (483.9082). 1H NMR: δ 7.05 (dd, 2H, $^3J_{HH} = 3.6$, $^3J_{HH} = 5.2$), 7.18 (d, 2H, $^3J_{HH} = 3.8$), 7.24 (m, 4H), 7.29 (d, 2H, $^3J_{HH} = 3.8$), 7.64 (pd, 2H), 7.69 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 101.5, 110.0, 124.3, 124.8, 125.1, 125.2, 127.4, 128.2, 132.4 (3 quaternary carbon atoms not observed).

1-Methyl-3,5-bis(2'-thienyl)benzene (9). A solution of methylmagnesium bromide (3.0 M, 0.62 mL, 1.9 mmol) in Et_2O and solid $PdCl_2(dppf)$ (0.027 g, 0.037 mmol) were added to an ice cold solution of **7^{Br}** in the same solvent (100 mL) to give an orange solution. After heating to 60 °C overnight, standard aqueous workup and purification by flash column chromatography (neat hexanes, $R_f = 0.2$) gave the desired product as a white solid (mp 55–57 °C). Yield: 0.0824 g (52%). HRMS $C_{15}H_{12}S_2$ calcd (found): 256.0380 (256.0376). 1H NMR: δ 2.44 (s, 3H), 7.11 (dd, 2H, $^3J_{HH} = 3.6$, $^3J_{HH} = 5.2$), 7.31 (d, 2H, $^3J_{HH} = 5.2$), 7.37 (m, 4H), 7.67 (s, 1H). $^{13}C\{^1H\}$ NMR: δ 21.7, 121.1, 123.61, 125.2, 126.2, 128.2, 135.2, 139.4, 144.3.

1-Phenyl-3,5-bis(2'-thienyl)benzene (10). This compound and **9** were made similarly. Thus, reaction of a solution of phenylmagnesium bromide in Et_2O (3.0 M, 0.78 mL, 2.3 mmol), $PdCl_2(dppf)$ (0.034 g, 0.047 mmol), and **7^{Br}** (0.500 g, 1.55 mmol) in THF (100 mL) gave the desired product as a white solid (mp 133–135 °C), following workup and purification by flash column chromatography (neat hexanes, $R_f = 0.1$). Yield: 0.334 g (68%). HRMS $C_{20}H_{14}S_2$ calcd (found): 318.0537 (318.0536). 1H NMR: δ 7.13 (dd, 2H, $^3J_{HH} = 3.6$, $^3J_{HH} = 4.8$), 7.34 (dd, 2H, $^3J_{HH} = 4.8$, $^4J_{HH} = 1.0$), 7.43 (m, 3H), 7.50 (t, 2H, $^3J_{HH} = 7.6$), 7.67 (dd, 2H, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.6$), 7.74 (pd, 2H), 7.83 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 122.8, 123.9, 124.36, 125.5, 127.5, 128.0, 128.3, 129.1, 135.8, 140.9, 142.9, 144.1.

1-(4'-Methoxyphenyl)-3,5-bis(2'-thienyl)benzene (11). This compound and **9** were made similarly. Thus, reaction between **7^{Br}** (0.400 g, 1.24 mmol), 4-methoxyphenylmagnesium bromide in THF (0.5 M, 3.72 mL, 1.87 mmol) and solid $PdCl_2(dppf)$ (0.027 g, 0.037 mmol) in THF (100 mL) gave, following workup and purification by flash column chromatography (5:2 hexanes/ CH_2Cl_2 , $R_f = 0.4$), the desired product as a white solid (mp 121–123 °C). Yield: 0.225 g (52%). HRMS $C_{21}H_{16}OS_2$ calcd (found): 348.0643 (348.0644). 1H NMR: δ 3.88 (s, 3H, H), 7.03 (m, 2H), 7.13 (dd, 2H, $^3J_{HH} = 5.2$, $^3J_{HH} = 3.6$), 7.34 (dd, 2H, $^3J_{HH} = 1.2$, $^3J_{HH} = 5.2$), 7.42 (dd, 2H, $^3J_{HH} = 1.2$, $^3J_{HH} = 3.6$), 7.61 (m, 2H), 7.69 (pd, 2H), 7.78 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 55.6, 114.5, 122.2, 123.8, 124.0, 125.4, 128.3, 128.6, 133.3, 135.7, 142.5, 144.2, 159.8.

1-(4'-Fluorophenyl)-3,5-bis(2'-thienyl)benzene (12). This compound and **9** were made similarly. Thus, the reaction of 4-fluorophenylmagnesium bromide in THF (0.5 M, 1.89 mL, 1.87 mmol), $PdCl_2(dppf)$ (0.027 g, 0.037 mmol), and **7^{Br}** (0.400 g, 1.24 mmol) in THF (100 mL) gave, following workup and purification by flash column chromatography (20:1 hexanes/ CH_2Cl_2 , $R_f = 0.2$), the desired product as a white solid (mp 95–98 °C). Yield: 0.350 g (84%). HRMS $C_{20}H_{13}FS_2$ calcd (found): 336.0443 (336.0437). 1H NMR: δ 7.16 (m, 4H), 7.35 (dd, 2H, $^3J_{HH} = 5.2$, $^4J_{HH} = 1.2$), 7.43 (dd, 2H, $^3J_{HH} = 3.6$, $^4J_{HH} = 1.2$), 7.63 (m, 2H), 7.67 (pd, 2H), 7.82 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 116.0 (d, $^1J_{CF} = 85.6$), 122.7, 124.1,

125.6, 128.4, 129.1, 135.9, 136.9, 141.9, 144.0, 161.7, 164.2. Colorless crystals suitable for analysis by X-ray diffraction were grown from a concentrated CH_2Cl_2 solution by slow diffusion of hexanes.

1-(Phenylacetylenyl)-3,5-bis(2'-thienyl)benzene (13). In a 50 mL three-neck flask equipped with a condenser and bubbler, **7^{Br}** (0.253 g, 0.786 mmol) was dissolved in a 1:1 mixture of THF/ Et_3N (10 mL). The catalyst mixture, $Pd(PPh_3)_2Cl_2$ (0.028 g, 0.039 mmol) and CuI (0.015 g, 0.008 mmol), was added to this solution to give an orange suspension. Phenylacetylene (0.120 g, 1.18 mmol) was added dropwise over 5 min to give a dark brown mixture. Once the addition was complete, the mixture was heated to 60 °C for 24 h. The dark brown suspension was cooled, CH_2Cl_2 was added, and the mixture was filtered through Celite. The filtrate was reduced to give a black viscous liquid. The product, a white solid (mp 118–120 °C), was isolated by flash column chromatography (neat hexanes, $R_f = 0.3$). Yield: 0.227 g (68%). HRMS $C_{22}H_{14}S_2$ calcd (found): 426.0199 (426.0189). 1H NMR: δ 7.13 (dd, 2H, $^3J_{HH} = 3.6$, $^3J_{HH} = 5.0$), 7.35 (dd, 2H, $^3J_{HH} = 5.0$), 7.41 (m, 5H), 7.63 (m, 2H), 7.70 (pd, 2H), 7.80 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 88.9, 90.3, 123.2, 123.5, 124.1, 124.8, 125.7, 128.1, 128.4, 128.6, 128.8, 132.0, 135.5, 143.3.

1-Ferrocenyl-3,5-bis(2'-thienyl)benzene (14). In a 100 mL three-neck flask, a dark red solution of tributylstannylferrocene (0.612 g, 1.3 mmol) in THF (2 mL) was added to a colorless solution of **7^{Br}** (0.278 g, 0.865 mmol) in THF (30 mL) to give an orange mixture. Following the addition of $PdCl_2(dppf)$ (0.018 g, 0.026 mmol), the mixture was brought to reflux for 2 d. The resulting dark brown solution was cooled under a stream of Ar. The reaction was quenched with H_2O (10 mL), solid KF (2 equiv) was added, and the mixture was stirred for 2 h. Ether (15 mL) was then added and the aqueous layer was extracted with the same solvent (2×15 mL). The combined organic fractions were washed with H_2O (10 mL), dried over $MgSO_4$, and reduced to give a dark red liquid. The crude product was purified by flash column chromatography (20:1 hexanes/ CH_2Cl_2) to obtain the desired product as a dark orange liquid. Yield: 0.033 g (8%). HRMS $C_{24}H_{18}FeS_2$ calcd (found): 426.0199 (426.0189). 1H NMR: δ 4.10 (s, 5H), 4.37 (pt, 2H), 4.72 (pt, 2H), 7.14 (dd, 2H, $^3J_{HH} = 3.6$, $^3J_{HH} = 5.2$), 7.34 (dd, 2H, $^3J_{HH} = 5.2$, $^4J_{HH} = 1.2$), 7.41 (dd, 2H, $^3J_{HH} = 3.6$, $^4J_{HH} = 1.2$), 7.63 (pd, 2H), 7.67 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 67.1, 69.4, 70.0, 85.0, 121.7, 123.3, 123.7, 125.3, 128.3, 135.3, 141.2, 144.3 (two quaternary carbon atoms not observed).

1-Phenyl-3,5-bis(5'-(2',2''-bithienyl)benzene (15). This compound and **10** were made similarly. Thus, reaction of phenylmagnesium bromide in Et_2O (3.0 M, 0.173 mL, 0.519 mmol), $PdCl_2(dppf)$ (0.008 g, 0.010 mmol) and **8^{Br}** (0.100 g, 0.346 mmol) in THF (20 mL) gave, after workup and purification by flash column chromatography (neat hexanes, $R_f = 0.1$), the desired product as a pale yellow solid (mp. 134–138 °C). Yield: 0.109 g (68%). HRMS $C_{28}H_{18}S_4$ calcd (found): 482.0291 (482.0285). 1H NMR: δ 7.05 (dd, 2H, $^3J_{HH} = 5.2$, $^3J_{HH} = 3.6$), 7.20 (d, 2H, $^3J_{HH} = 3.6$), 7.24 (m, 4H), 7.35 (d, 2H, $^3J_{HH} = 3.6$), 7.42 (t, 1H, $^3J_{HH} = 7.2$), 7.50 (t, 2H, $^3J_{HH} = 7.2$), 7.67 (d, 2H, $^3J_{HH} = 7.2$), 7.71 (pd, 2H), 7.79 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 121.9, 124.0, 124.1, 124.6, 124.7, 124.8, 127.5, 128.1, 128.2, 129.1, 135.5, 137.4, 137.5, 140.7, 142.6, 143.1.

1-(4'-Methoxyphenyl)-3,5-bis(5'-(2',2''-bithienyl)benzene (16). This compound and **11** were made similarly. Thus, reaction of **8^{Br}** (0.146 g, 0.5 mmol), 4-methoxyphenylmagnesium bromide in THF (0.5 M, 1.52 mL, 0.758 mmol), and $PdCl_2(dppf)$ (0.011 g, 0.015 mmol) in THF (20 mL) gave, following workup and purification by flash column chromatography (3:1 hexanes/ CH_2Cl_2 , $R_f = 0.2$), the desired product as a pale yellow solid (mp 144–147 °C). Yield: 0.090 g (35%). HRMS $C_{29}H_{20}OS_4$ calcd (found): 512.0397 (512.0390). 1H NMR: δ 3.89 (s, 3H), 7.04 (m, 4H), 7.19 (d, 2H, $^3J_{HH} = 3.8$), 7.24 (m, 4H), 7.33 (d, 2H, $^3J_{HH} = 3.8$), 7.61 (m, 2H), 7.67 (pd, 2H), 7.74 (pt, 1H). $^{13}C\{^1H\}$ NMR: δ 55.6, 110.0, 114.6, 121.4, 123.6, 124.0, 124.5, 124.7, 124.8, 128.1, 128.5, 133.1, 135.4, 137.4, 137.6, 142.6, 142.7.

1-(4'-Fluorophenyl)-3,5-bis{5''-(2'',2''''-bithienyl)}benzene (17). This compound and **12** were made similarly. Thus, reaction of **8^{Br}** (0.100 g, 0.346 mmol), 4-fluorophenylmagnesium bromide in THF (0.5 M, 1.04 mL, 0.519 mmol), and PdCl₂(dppf) (0.008 g, 0.010 mmol) in THF (20 mL) gave, following workup and purification by flash column chromatography (10:1 hexanes/CH₂Cl₂, *R_f* = 0.3), the desired product as a pale yellow solid (mp 154–157 °C). Yield: 0.123 g (71%). HRMS C₂₈H₁₇FS₄ calcd (found): 500.0197 (500.0208). ¹H NMR: δ 7.05 (dd, 2H, ³J_{HH} = 5.2, ³J_{HH} = 3.6), 7.19 (d, 4H), 7.26 (m, 4H), 7.34 (d, 2H, ³J_{HH} = 3.6), 7.64 (m, 4H), 7.77 (pt, 1H). ¹³C{¹H} NMR: δ 116.0 (d, ¹J_{CF} = 85.6), 121.9, 123.8, 124.1, 124.7, 124.8, 128.2, 129.1, 129.2, 135.6, 136.8, 137.5, 137.6, 142.1, 142.4.

1,1',3,3'-Tetra(2''-thienyl)-5,5'-biphenyl (18). This compound was isolated as a byproduct of the synthesis of **9**. A dedicated synthesis was as follows: **7^{Br}** (0.600 g, 1.86 mmol) was dissolved in THF (20 mL), and solid Pd(dppf)Cl₂ (0.014 g, 0.019 mmol) was added to give an orange mixture. Magnesium turnings (0.022 g, 0.931 mmol) and a few crystals of I₂ were then added. After holding the mixture at reflux overnight, MeI (100 μL, 0.309 mmol) was added, which caused the Mg turnings to dissolve within minutes. The reaction mixture was heated to reflux for 18 h before being quenched on ice with H₂O (10 mL). Workup was the same as outlined for **1**. The desired product, a white solid (mp 148–155 °C), was obtained following flash column chromatography (neat

hexanes, *R_f* = 0.1). Yield: 0.112 g (25%). HRMS C₂₈H₁₈S₄ calcd (found): 482.0291 (482.0290). ¹H NMR: δ 7.15 (dd, 4H, H, ³J_{HH} = 5.0, ³J_{HH} = 3.6), 7.36 (dd, 4H, ³J_{HH} = 5.0, ⁴J_{HH} = 1.0), 7.45 (dd, 4H, ³J_{HH} = 3.6, ⁴J_{HH} = 1.0), 7.77 (pd, 4H), 7.90 (pt, 2H). ¹³C{¹H} NMR: δ 123.2, 124.1, 124.4, 125.7, 128.4, 135.9, 142.4, 143.9.

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Supporting Information Available: General experimental considerations, details and additional results of density functional calculations, including Cartesian coordinates and energies for **1–4** and **9–17**, ¹H and ¹³C NMR spectra, summary table of crystallographic data for compounds **4** and **12**, and full data in CIF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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