# Directed Electrophilic Cyclizations: Efficient Methodology for the Synthesis of Fused Polycyclic Aromatics

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**Abstract:** A versatile method for the synthesis of complex, fused polycyclic aromatic systems in high chemical yield is described. Construction is achieved using a general two-step synthetic sequence. Pd-catalyzed Suzuki and Negishi type cross-coupling chemistries allow for the preparation of nonfused skeletal ring systems in yields consistently >80%. The critical ring-forming step, which generally proceeds in very high to quantitative yield, utilizes 4-alkoxyphenylethynyl groups and is induced by strong electrophiles such as trifluoroacetic acid and iodonium tetrafluoroborate. The reaction in essence produces phenanthrene moieties which are integrated into extended polycyclic aromatic structures. Fused polycyclic benzenoids as well as benzenoid/thiophene systems may be prepared utilizing this methodology. The scope of the described cross-coupling/cyclization chemistry including mechanistic insights and problematic side reactions are described.

## Introduction

The availability of rigid molecular platforms is critical to advances in a number of areas of chemical research. Examples include host−guest chemistry where rigid molecules often serve as substrate-specific receptors,[1−6] liquid crystal chemistry wherein molecules posessing a rigid core are required to achieve mesomorphic behavior,[7−10] and even biochemical studies of synthetic peptides wherein carefully designed rigid segments serve as $\beta$-turn mimics.[11−13] The utility of such rigid molecular structures can be altered and even enhanced if, in addition to being highly rigid, the molecules are extensively conjugated. Rigid conjugated materials are the key components in a number of advanced technologies utilizing nonlinear optical (NLO),[14−16] photo- and electroluminescent,[17−20] and molecule-based sensory devices.[21−27] These materials function as a result of their highly conjugated $\pi$ electron systems, which can transform an applied bias or optical input to a desired response. Examples of these advanced materials include substituted polyphenylenes, polythiophenes, and push-pull NLO materials which are inherently rigid as a result of their highly unsaturated frameworks. It is commonly believed that the degree of conjugation and hence properties in such systems can be enhanced if they can be rigidified to eliminate conformational disorder which lowers conjugation.[28] Fused polycyclic aromatics are an obvious chemical structural class which would meet this requirement while maintaining conjugation.

While a number of methodologies are presently available for the direct preparation of fused polycyclic aromatic systems, most are plagued by some type of limitation. The most widely employed and direct method is the Mallory photochemical cyclization.[29] This method is the most versatile route as the cyclization can be performed on a variety of frameworks

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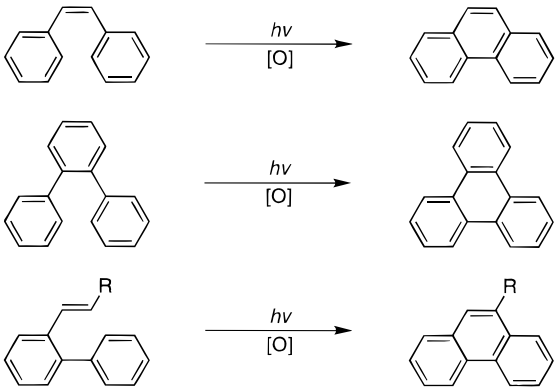
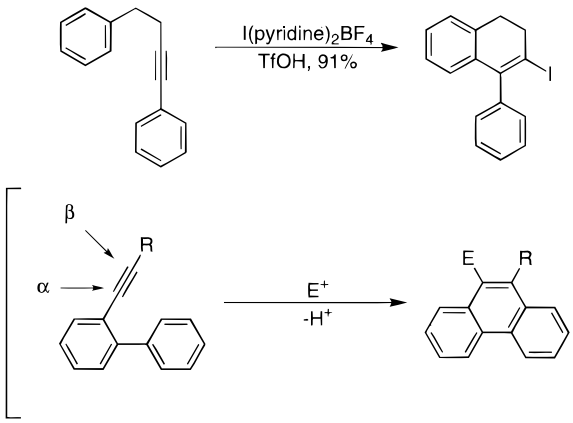
**Scheme 1**




including *cis*-substituted stilbenes to give phenanthrene type subunits, *o*-terphenyl systems to give triphenylene type structures, and 2-olefinic biphenyls to produce substituted phenanthrene systems (Scheme 1). The primary limitation of the photochemical route is the necessarily dilute conditions ($\sim 10^{-3}$ M) under which the reaction must be run, limiting it to the preparation of only analytical quantities of material.

Another direct route to fused polycyclic aromatics is the [2 + 2] cyclization of thioketones which is followed by sulfur elimination to give the aromatic product.[30] This method, while proceeding in very high yield is limited in its versatility as it requires structurally specific and synthetically challenging precursor structures. Another well-explored approach to the construction of polycyclic aromatics is the utilization of Diels−Alder chemistry to provide access to precusor ring systems which may be aromatized upon further chemical treatment. Miller has oxidatively converted partially saturated precursor ring systems to linear polyacenequinoids,[31] while Schlüter has used oxidation[32,33] and dehydration[33,34] protocols to prepare fused aromatic ladder polymers. In another case, Katz has prepared [5]- and [6]helicenes by Diels−Alder reaction of α-substituted divinylnapthalenes with *p*-benzoquinone.[35] Complete aromatization is achieved by reductive trapping of the quinoidal product.[36] Longitudinally twisted polycyclic aromatics have been prepared by Pascal using a thermally induced Diels−Alder/elimination protocol.[37] Additional routes to fused polycyclic aromatic systems include annulation strategies which often employ metal carbene[38−43] and/or vinyl ketene[44−47] intermediates. While these methodologies allow access to highly functionalized materials, the lower yields and multistep syntheses necessary for the preparation of precursor compounds make these methodologies more amenable to complex molecule synthesis than to the synthesis of topologically interesting molecules in useful quantities.

**Scheme 2**




With the goal of ultimately preparing *polymeric* fused polycyclic aromatic systems,[48] we first endeavored to develop versatile, high-yielding synthetic routes to their corresponding *molecular* analogues. Of interest was a report wherein Barluenga used iodonium tetrafluoroborate ($IBF_4$), a highly electrophilic source of iodonium ion, to cyclize 1,4-diphenylbut-1-yne to the corresponding iododihydronapthalene (Scheme 2, top).[49] We desired to modify this system such that cyclization would produce a fused polycyclic aromatic. In order to exclusively form 6-membered rings, it was necessary to convince the majority of positive charge—resulting from initial electrophilic attack—to reside on the carbon atom labeled as $\beta$ (Scheme 2, bottom). Hence, it was necessary to chose a group R which could provide more favorable positive charge stabilization than the phenyl group attached to carbon atom labeled α. To accomplish this, R was chosen to be an electron-rich *p*-alkoxyphenyl group, which provides resonance stabilization of the positive charge at the $\beta$ carbon.

This electrophile-direction strategy proved successful, and in this paper, we describe our studies of this novel cyclization reaction including synthetic and mechanistic implications. In addition, we describe the preparation of the cyclization precursor systems utilizing Pd-catalyzed cross-coupling chemistry. This tandem cross-coupling/cyclization approach is highly effective and hence constitutes a new high-yielding, versatile methodolgy for the synthesis of fused polycyclic aromatic systems.[50]

## Results and Discussion

The general structural requirement for the precursor systems, in addition to the carbocation directing group, is that the alkynyl group and the aromatic ring undergoing electrophilic substitution (Ar′) must be *ortho*-substituted. All systems reported contain a central ring to which two (*p*-alkoxyphenyl)ethynyl−Ar′ pairs are attached. We have studied symmetric systems in which the two Ar′ partners are configured *para*, *meta*, and *ortho* to each other (Figure 1).

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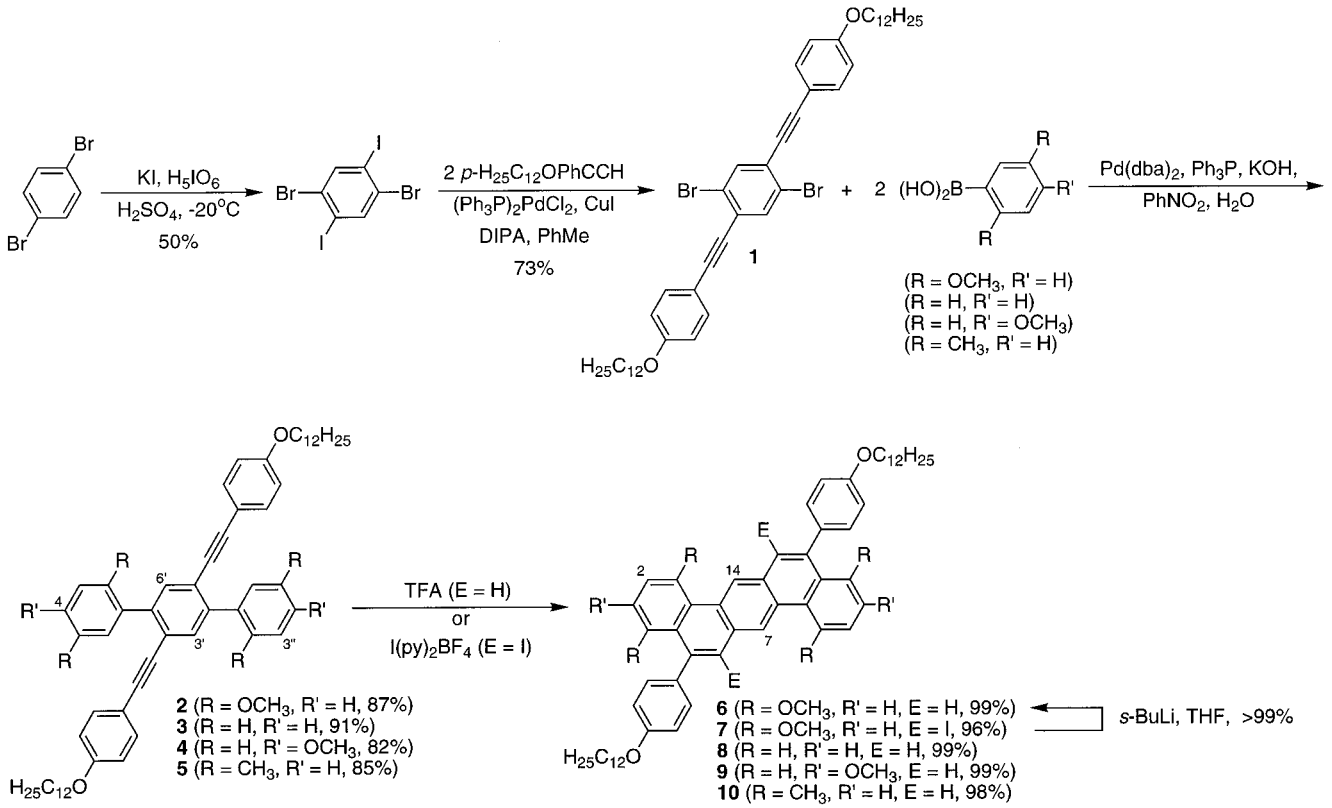
**Scheme 3**



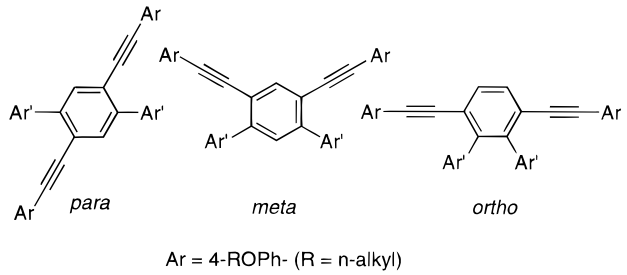




**Figure 1.** General topology of precyclized structures investigated.

***Para*-Substituted Systems.** With a general design concept in mind, we have prepared precursor systems with the general structures **2**−**5**. This was accomplished in short order starting with 1,4-dibromobenzene. Utilizing a modified version of an iodination procedure developed by Mattern,[51] 1,4-dibromo-2,5-diiodobenzene was produced in 50% yield (Scheme 3). Although the yield is modest, starting materials are relatively inexpensive and quantities on the order of 2−300 g can be easily prepared. This intermediate is a versatile building block since coupling at the iodide positions can be effected with complete chemoselectivity using Pd-catalyzed cross-coupling reactions, leaving the bromide positions available for further cross-coupling under more aggressive conditions. The tetrahalide was reacted with 2 equiv of 4-(dodecyloxy)phenylacetylene, prepared in three steps from 4-iodophenol (87% overall), using standard Pd(0)/Cu(1) cocatalysis to produce the dibromide **1** (73%).[52,53]

Treatment of the dibromide **1** with a variety of substituted phenylboronic acids under modified Suzuki cross-coupling conditions[54] produced the substituted terphenyls **2**−**5**. These compounds are obtained as colorless solids and may be crystallized from a variety of common organic solvents. The highly soluble nature of these materials is attributed to the presence of the dodecyloxy groups which provide an entropic driving force for solubilization. In our optimization of these coupling reactions, we found several parameters to be critical. In agreement with the work of Kim and Webster,[55] we found nitrobenzene to be a more effective solvent than toluene and dimethoxyethane (DME), which are more commonly used. In addition, employing smaller amounts of catalyst (0.3%) was generally more effective than larger amounts (2−5%). This result may be attributable to unwanted Heck type reactions with the dibenzylideneacetone (dba) ligands and a reduction in the tendency of the catalyst to deactivate prematurely by forming Pd black.[56,57] We cannot attribute the improved yields with low catalyst ratios to the inhibition or reduction of aryl exchange reactions which have been previously observed,[58−63] since higher ligand to metal ratios (>15:1) had virtually no effect on the reaction. Lower ligand to metal ratios (4:1) were detrimental, as the catalyst rapidly precipitated out of solution as inactive Pd black.

Initial cyclization attempts were conducted on compound **2** using the protocol reported by Barluenga.[49,64,65] Treatment of $I(pyr)_2BF_4$ with 2 equiv of triflic acid (TfOH) precipitates

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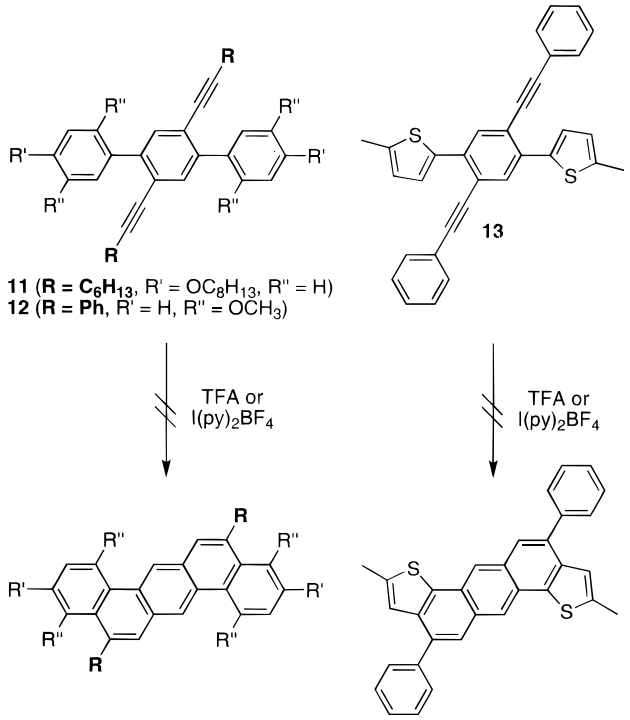
pyridine as its triflate salt and liberates free $IBF_4$. However, use of this procedure resulted in mixtures of cyclization products. We reasoned that $H^+$ from unreacted TfOH or from the acid produced during the cyclization was competing with $I^+$. Consistent with this reasoning, treatment of **2** with TfOH alone produces the substituted dibenz[*a*,*h*]anthracene product **6** exclusively, in quantitative yield. We have found that the same transformation can be effected under much milder conditions employing trifluoroacetic acid (TFA) in place of TfOH. Reduction of the TfOH/$I(pyr)_2BF_4$ ratio from 2:1 to 1:1 resulted in the exclusive formation of **7** (96%), since 1 equiv of pyridine (pyr) was still available to react with the acid produced during the reaction. The versatility of the cyclization reaction is apparent as substrates with a variety of substitution patterns (**6**−**10**) were prepared.

The conversion of substituted *p*-terphenyls (**2**−**5**) to dibenz[*a*,*h*]anthracene systems (**6**−**10**) was accompanied by consistent and diagnostic spectral changes. All substituted *p*-terphenyls were obtained as colorless materials and were converted to yellow to bright yellow materials on cyclization. The UV−vis spectra of these materials, on cyclization, exhibit a characteristic bathochromic shift for the onset of absorption and a hypsochromic shift for $\lambda_{max}$. Compound **2**, for example, displays an absorption maximum ($\lambda_{max}$) at 342 nm ($\epsilon$ = 59 900) with a shoulder at 364 nm ($\epsilon$ = 51 000). On conversion to **6**, $\lambda_{max}$ shifts to 318 nm ($\epsilon$ = 55 600) and lower intensity absorptions appear at 280 ($\epsilon$ = 37 500), 356 ($\epsilon$ = 24 600), 374 ($\epsilon$ = 24 000), 406 ($\epsilon$ = 12 100), and 430 ($\epsilon$ = 14 400) nm. These optical properties, particularly the observation of low-intensity absorptions (relative to $\lambda_{max}$) on the low-energy side of $\lambda_{max}$, are similar to those observed for similar polycyclic aromatic hydrocarbons.[66] The $^1$H NMR spectra of these materials also display characteristic changes. The singlet assigned to the 3′ and 6′ protons of compound **2** appears at 7.59 ppm and shifts downfield to 10.10 ppm on conversion to **6** where they are located at the 7 and 14 positions. Such downfield signals are characteristic of bay region protons. The new singlet present for **6** at 7.78 ppm corresponds to the protons at the 6 and 13 positions. Four additional aromatic resonances are present in the $^1$H NMR spectrum of **6**, all doublets. Two of these doublets (6.94 and 7.34 ppm) correspond to the protons on the *p*-alkoxyphenyl moieties, while the other two doublets (7.03 and 7.18 ppm), with an integrated area 50% of the first two doublets, correspond to the protons on the terminal rings of the dibenz[*a*,*h*]anthracene ring system. In the $^{13}$C NMR spectra, the conversion from **2** to **6** is accompanied by the disappearance of acetylenic resonances (88.11 and 93.31 ppm) for **2** and an increase from 13 to 15 for the number of aromatic resonances. This change is attributable to the conversion of the acetylene carbons to aromatic carbons. Compounds **2**−**10** all display high-resolution mass spectra (HRMS) in agreement with the proposed structures, and the low-resolution mass spectrum (LRMS) of the diiodide **7** ($M^+$ = *m/z* 1170.4) displays signals at *m/z* 1044 and 918, corresponding to the loss of the two iodides. As additional structure proof, the diiodide **7** was treated with *s*-BuLi and the reaction was quenched with 2-propanol. The $^1$H NMR spectrum of the compound obtained (>99% by NMR) is identical to the spectrum obtained following the direct treatment of **2** with TFA, providing additional support for the structure **6**. The spectral trends observed for the conversions of compounds **3**−**5** to **8**−**10** were consistent with those described for the conversion of **2** to **6** and **7** and are in complete agreement with the reported structures.

**Scheme 4**




To further investigate the scope of the reaction, we prepared **11**−**13** (Scheme 4), which lack the *p*-alkoxy directing groups present in **2**−**5**. Compound **11** contains simple alkyl directing groups in place of *p*-alkoxyphenyl groups. Treatment of these systems with TFA resulted in the complete recovery of starting material. Exposure to $I(pyr)_2BF_4$ produced complex mixtures of products, most likely due to competitive aryl ring iodination. These results indicate that the *p*-alkoxy group on the phenylethynyl moiety is indeed *critical* to the success of the reaction. In addition, the presence of the electron-activating methoxy groups as in **2** and **12** is not necessary as evidenced by the quantitative formation of **8**. Regarding solvent, the reaction has proven successful only in halogenated (polar, non-nucleophilic) solvents such as methylene chloride, 1,2-dichloroethane, and 1,2,3-trichloropropane. The reaction fails in hydrocarbon solvents (hexane and pentane) and ethereal solvents (THF and diethyl ether). These results support our assertion that the reaction proceeds through a carbocationic intermediate species, as is shown in Scheme 5. Selective electrophilic attack at the acetylenic carbon attached to the central ring of the terphenyl moiety is driven by resonance stabilization provided by the *p*-alkoxy directing group. Ring closure may then occur by electrophilic attack on the outer rings of the terphenyl moiety in a Friedel−Crafts type manner. This ring closure is accompanied by loss of a proton, making the reaction catalytic. However, for kinetic purposes a large excess of acid was usually employed. In addition, we believe that ring protonation occurs, necessitating the use of excess acid. This claim is based on the deep green color which was observed during the cyclization of more electron-rich systems. In fact, treatment of compound **9** with TFA-*d* overnight resulted in extensive substitution of deuterium for hydrogen on the aromatic ring system.

As is evident from the structure of **13**, we were interested in preparing fused polycyclic aromatic heterocycles as well as aromatic hydrocarbons. As a first example we investigated Ar′

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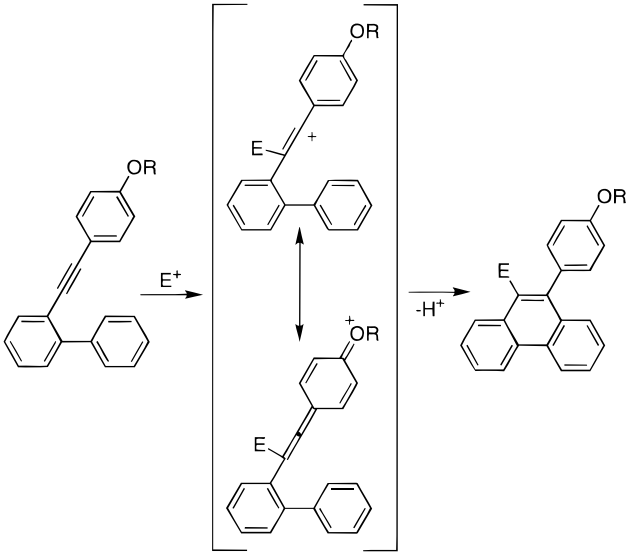
**Scheme 5**




groups (Figure 1) incorporating fused heterocyclic linkages. 4-Dibenzothiopheneboronic acid was prepared by metalation of dibenzothiophene with *n*-BuLi in THF followed by a $B(OMe)_3$ quench and acidic (5% HCl) hydrolysis.[2] Two equivalents of the boronic acid were coupled with 1 equiv of **1** to produce cyclization precursor **14** in 86% yield (Scheme 6). The colorless compound **14** was treated with TFA in $CH_2Cl_2$ at room temperature (rt), and after approximately 10 min, a bright yellow crystalline compound precipitated from the solution. The product was exclusively the biscyclized compound **15**, indicating the monocyclized product displays much greater solubility.

On conversion of the colorless **14** to the bright yellow **15**, an approximately 60 nm bathochromic shift is observed for the onset of absorption ($\lambda_{onset}$ (**14**) $\approx$ 390 nm, $\lambda_{onset}$ (**15**) $\approx$ 450 nm) in the UV−vis spectrum. Consistent with the observations made for compounds **2**−**10**, a hypsochromic shift is observed for $\lambda_{max}$ following cyclization ($\lambda_{max}$ (**14**) = 346 nm, $\lambda_{max}$ (**15**) = 340 nm), while lower intensity absorptions appear on the low-energy side of $\lambda_{max}$ (372, 392, 404, and 430 nm). In the $^1$H NMR spectrum of **14**, the protons assigned to the 3 and 6 positions of the central ring appear as a singlet at 7.98 ppm and shift downfield to 9.88 ppm on conversion to **15**, where they are now bay region protons (10 and 20). The chemical shifts of the two doublets attributed to the *p*-alkoxyphenyl moiety appear at 6.66 and 6.99 ppm for compound **14**, as they are shielded by the dibenzothiophenyl moiety, which is permitted to freely rotate. On cyclization to **15**, rotation is eliminated; hence, shielding is reduced and the two doublets are shifted downfield to 7.12 and 7.60 ppm. These aromatic shielding effects are not as dramatic in systems **2**−**10**, as the terminal aryl groups (substituted phenyls), physically much smaller than the dibenzothiophenyl groups, are not able to shield as effectively. Two additional doublets appear at 8.12 and 8.31 ppm in the $^1$H NMR spectrum of **15** and correspond to the protons at the 6/16 and 7/17 positions (not assigned). The presence of these doublets confirms the conversion of the ABC spin systems present on the dibenzothiophenyl moieties of **14** to AB spin systems on cyclization to **15**. The $^{13}$C NMR spectrum of compound **14** displays two acetylenic resonances (87.25 and 95.05 ppm) and 17 aromatic resonances (19 expected), while no acetylene resonances and 21 aromatic resonances (21 expected) are observed for **15**. Accurate HRMS data and satisfactory combustion analyses were obtained for both **14** and **15**.

We have found that the cyclization may also be performed directly onto a thiophene moiety. The cyclization precursor **16** was prepared (Scheme 7) in quantitative yield using a Negishi type coupling,[67,68] utilizing the dibromide **1** with 2 equiv of 2-(chlorozincio)-5-methylthiophene. Cyclization of the precursor **16** becomes problematic, however, as a 5/6 mixture of products **17** and **18** was obtained. While the two structural isomers have proven inseparable, their $^1$H NMR (500 MHz, $CDCl_3$) resonances are easily discernible due to the asymmetric nature of **18**. Changes in chemical shifts due to shielding/deshielding effects of the migrated phenyl proved critical in identifying structure **18**. The methyl resonance of **17** appears at 2.64 ppm, and on conversion to **18**, the methyl in the relatively unchanged environment appears at 2.65 ppm while the methyl on the side of the migrated phenyl, now deshielded, moves downfield to 2.70 ppm. More diagnostic is the effect on the thienyl proton which appears at 7.19 ppm for **17**. On conversion to **18**, the thienyl proton in the nearly unchanged environment appears at 7.20 ppm while the deshielded thienyl proton appears at *7.83 ppm*. The thienyl protons are easily identifiable as they appear as apparent doublets due to a weak coupling ($J$ = 0.8−1.2 Hz) with the adjacent methyl groups. The $^1$H NMR spectrum of **17** displays four aromatic resonances in addition to the thienyl resonance just discussed. Two of these resonances appear as doublets and correspond to the protons on the *p*-alkoxyphenyl groups. The remaining two resonances appear as singlets and correspond to the pseudo bay protons (8.55 ppm) and the 5/11 protons (7.75 ppm). There are no resonances detected which display the distinctive coupling constant ($J$ = 3.6 Hz) attributed to a 3,4-thienyl spin system,[69] as was evident in **16**. Compound **18**, in addition to the two thienyl resonances, displays four singlets and three doublets in the aromatic region. Two of the singlets correspond to the pseudo bay region protons (8.57 and 8.76 ppm) while the remaining two singlets correspond to the 5 and 10 protons (7.77 and 7.78 ppm). One doublet (broad) appears at 7.04 ppm and corresponds to four hydrogens of the *p*-alkoxyphenyl groups, while the remaining two doublets (7.59 and 7.74 ppm) correspond to two protons each. Additional support that the two compounds exist as structural isomers comes from mass spectral and combustion data. In the low-resolution mass spectrum, the only signals present are for the molecular ion (*m/z* 838) and for the loss a dodecyl side chain (*m/z* 670), while the HRMS data obtained are accurate to 1 ppm.

As shown in Scheme 7, product **18** forms by phenyl migration of the "correct" cyclization product **17**, presumably through a phenonium ion.[70] The occurrence of this event is not surprising as it has been previously reported that biphenyl, $^{13}$C-enriched at the *ipso* (1) position, undergoes rearrangement at 50 °C with $AlCl_3/H_2O$ in $C_6H_6$ to give biphenyl which is $^{13}$C-enriched at the 2, 3, and 4 positions.[71] The observation that migration is occurring in our system under much milder conditions is not surprising as it has been reported that *p*-methoxyphenyl undergoes migration approximately 500−880 times faster than phenyl in the pinacol rearrangement.[72,73] Treatment of **16** with an iodonium source should prevent aryl migration, as $I^+$ addition

(67) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821.
(68) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.
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(70) Lowery, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; pp 434−446.
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(72) Bachmann, W. E.; Ferguson, J. W. *J. Am. Chem. Soc.* **1934**, *56*, 2081.
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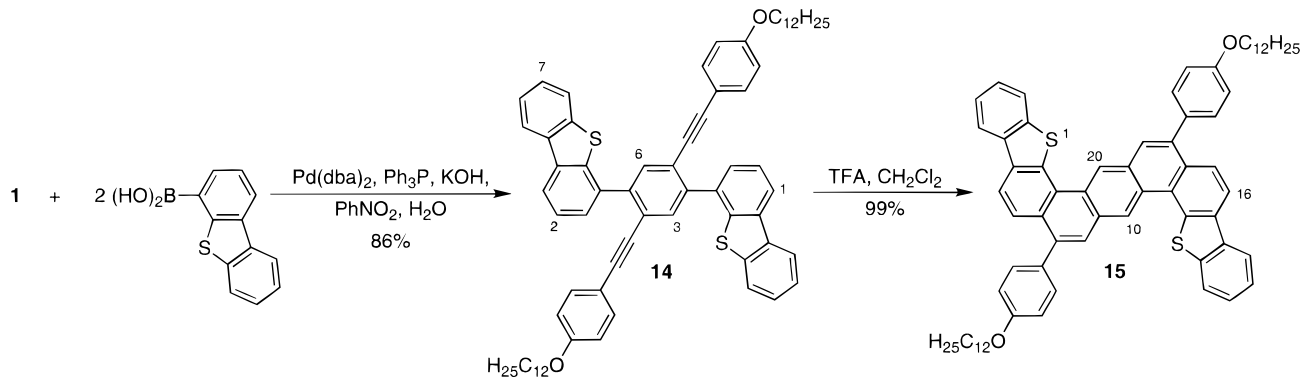
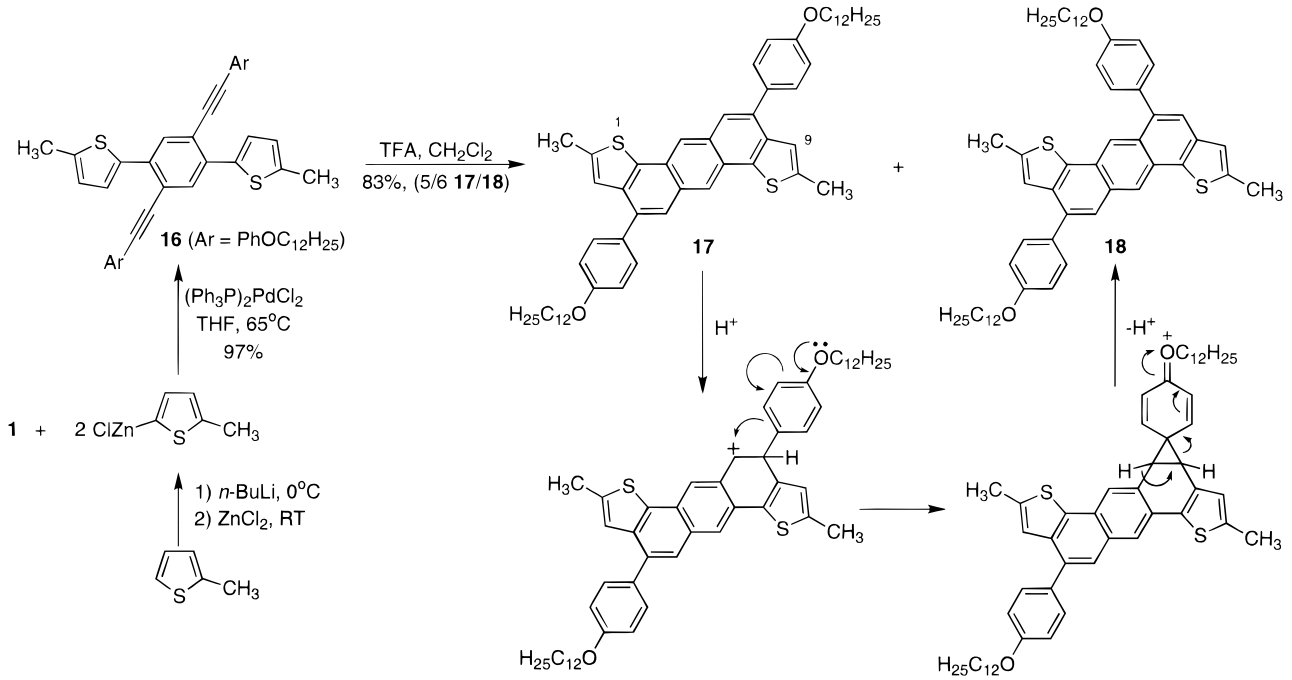
**Scheme 6**




**Scheme 7**



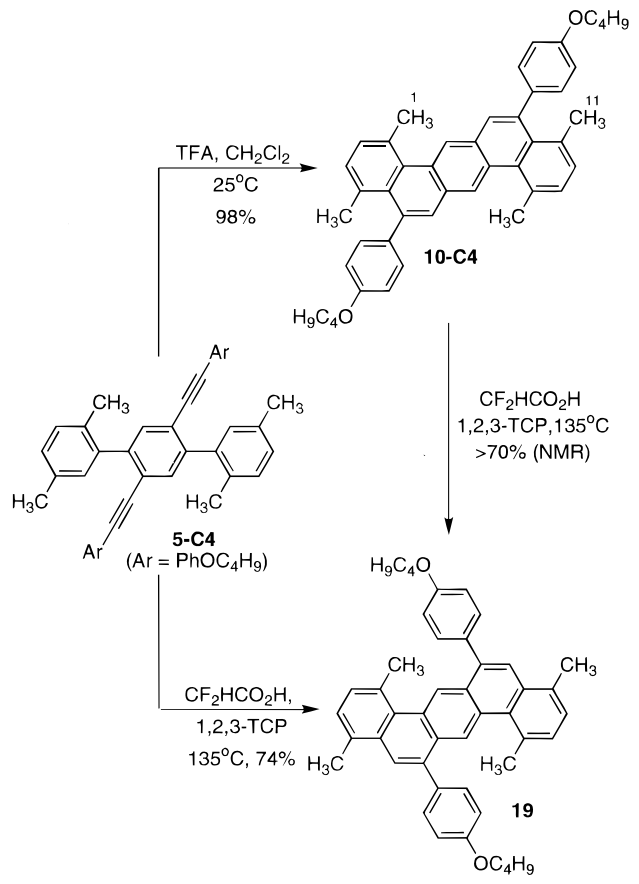

at the phenyl juncture should be energetically unfavorable. However, this approach was precluded by the rapid oxidation of **16** on exposure to iodonium.

To examine the phenyl migratory event more closely, one of the original model systems was reexamined. Compound **5-C4** (butoxy replaces dodecyloxy) when treated under standard cyclization conditions (TFA, $CH_2Cl_2$, rt) produced the expected product **10-C4** (Scheme 8). However, when heated to 135 °C overnight using difluoroacetic acid in 1,2,3-trichloropropane (1,2,3-TCP), the bismigrated product **19** was obtained exclusively (74%). Alternately, **19** can be prepared from the intermediate **10-C4** using the identical conditions. While compounds **10-C4** and **19** show identical coupling patterns, their structural assignments are supported by their diagnostic chemical shifts, particularly those of the methyl groups. In the precyclized system **5-C4**, the two methyl resonances appear at 2.24 and 2.36 ppm. On cyclization to **10-C4**, the 4/11 methyl resonances shift upfield to 2.04 ppm as a result of shielding from the *p*-butoxyphenyl groups located at the 5 and 12 positions. The 1/8 methyl protons, deshielded by the dibenz[*a*,*h*]anthracene ring system move downfield to 3.18 ppm. Following rearrangement to **19**, the two methyl resonances appear at 2.70 and 2.79 ppm. The 4/11 methyls, no longer shielded by the *p*-butoxyphenyl groups which have migrated to the 6 and 13 positions, move downfield while the 1/8 methyls now move upfield as a result of slight shielding from the migrated *p*-butoxyphenyl groups: the one methyl is shielded by the 13 *p*-butoxyphenyl and the 8 methyl is shielded by the 6 *p*-butoxyphenyl. The low-resolution mass spectrum of **19** displays a lone signal corresponding to the molecular ion (*m*/*z* 630.4) while the HRMS reading is accurate to 1 ppm. The exclusive formation of the bismigrated product **19** under thermodynamic conditions is not surprising as it relieves the strain caused by the two *peri* interactions present in **10-C4**. In fact, AM1 calculations[74] show a 10.9 kJ/mol higher $\Delta H_f$ for **10-C4** ($\Delta H_f$ = 69.4 kJ/mol) than for **19** ($\Delta H_f$ = 58.5 kJ/mol).

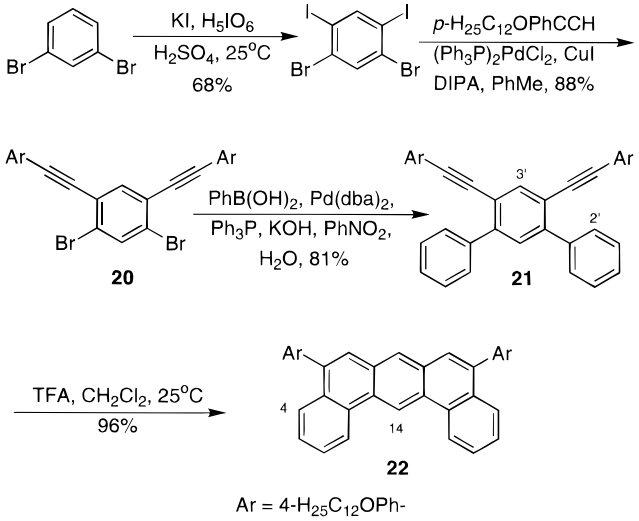
***Meta*-Substituted Systems.** Systems in which the Ar′ (Figure 1) substituents are oriented *meta* to each other were prepared following the general synthetic methodology used to prepare the *para*-substituted systems reported above. Iodination of 1,3-dibromobenzene (Scheme 9) produced 1,5-dibromo-2,4-diiodobenzene in 68% yield. The preparation of this tetrahalide was operationally simpler than the preparation of its "*para*" structural isomer as the reaction is not plagued by overiodinated side products and can therefore be run between 0 and 25 °C (<30 min reaction time). Compound **20**, the "*meta*" structual isomer of **1**, was prepared in an analogous fashion in 88% yield utilizing standard Pd(0)/Cu(1) cocatalysis. Reaction of **20** with

(74) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

**Scheme 8**




**Scheme 9**

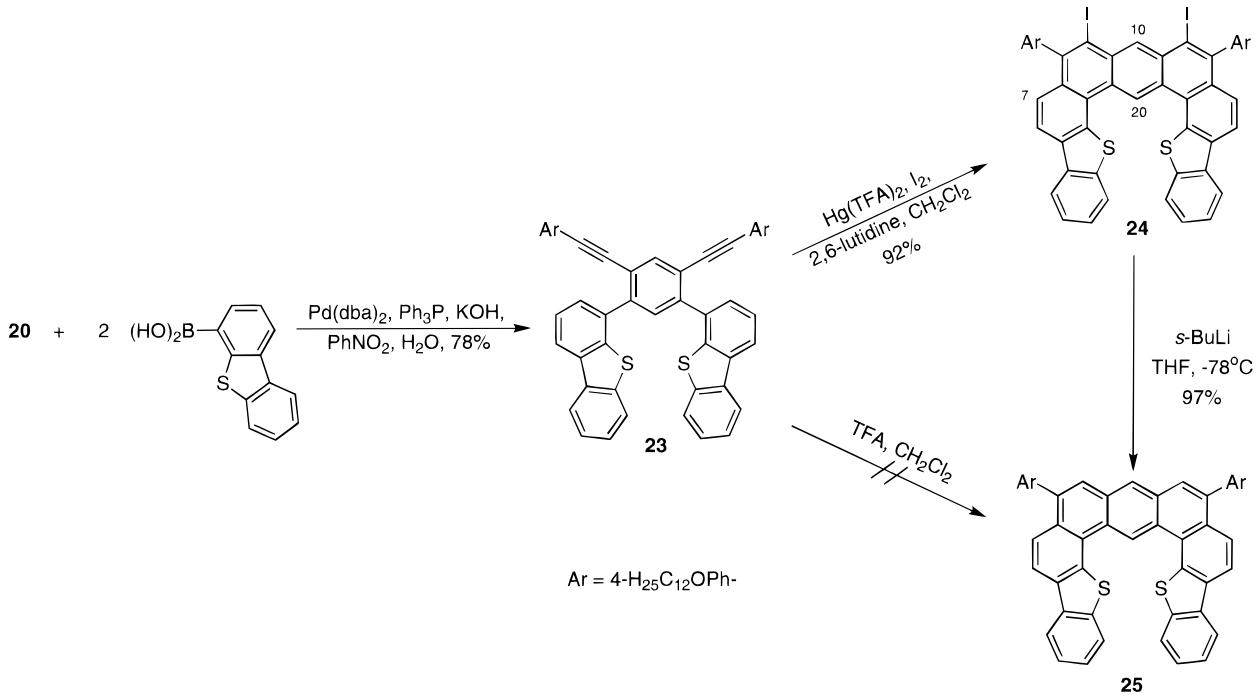



2 equiv of phenylboronic acid produced the *m*-terphenyl **21** in 81% yield as an off-white solid. TFA-induced cyclization provided the substituted dibenz[*a*,*j*]anthracene **22** (96%) as a light yellow solid. The $^1$H NMR spectrum of this compound displays two downfield resonances corresponding to the three bay region protons of **22**: a doublet at 9.08 (2H) and a singlet at 10.06 (1H) ppm. In the $^{13}$C NMR spectra, cyclization from **21** to **22** is accompanied by loss of the acetylenic resonances at 87.26 and 93.11 ppm and an increase in the number of aromatic resonances from 12 to 16. The increase of four aromatic carbons can be accounted for by the conversion of acetylenes to components of the aromatic ring structure and desymmetrization of the first and third rings of the *o*-terphenyl moiety on cyclization. The effects on the optical properties observed for the conversion of **21** to **22** are not as great as those observed in the *para*-oriented systems. Changes in the onset and maximum of absorption are shifted by no more than 10 nm in either direction on cyclization, while the overall spectral shapes are, qualitatively, very similar. Both **21** and **22** display accurate HRMS data and give satisfactory combustion analyses.

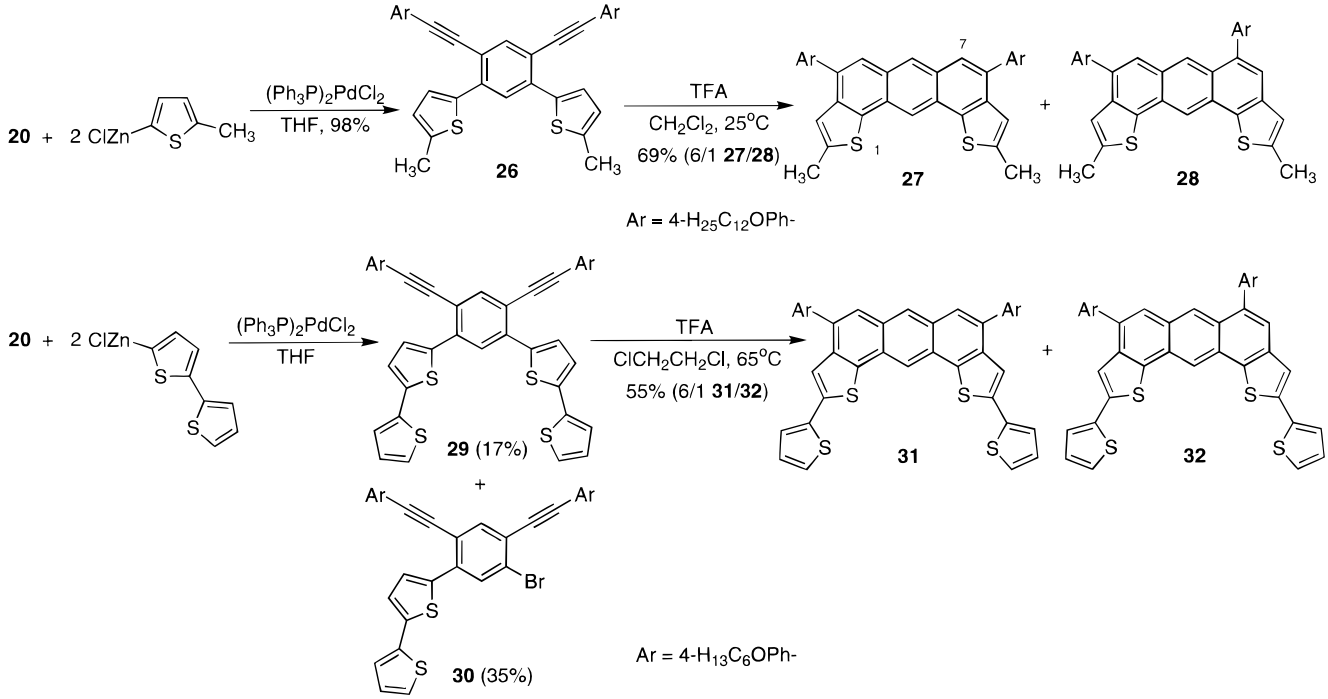
The cyclization of such *meta*-substituted systems provides fused ring systems with an different overall shape than their *para* analogues. For example, compound **22** is "U shaped". To generate analogs with a cavity, we prepared the extended bis(dibenzothiophenyl) compound **23** (Scheme 10). On treatment with TFA, an inseparable mixture of cyclized products was obtained. Keeping in mind our previous experience with phenyl migration, we sought to circumvent the problem with the use of iodonium, which should block the adjacent position and prevent migration. This strategy proved successful as a single compound **24** was isolated as a bright yellow solid in 92% yield. The reaction was conducted using iodonium generated in situ by reaction of $Hg(TFA)_2$ with $I_2$ in the presence of 2,6-lutidine. This procedure proved to be operationally simpler than using the bis(pyridine)iodonium tetrafluoroborate reagent, since the addition of 2,6-lutidine may be carefully controlled, precluding the addition of small quantities of TfOH. The reaction using this procedure was rapid and usually complete after only 10−20 min. The bay region proton (20) now appears at 11.12 ppm, while the proton (10) sandwiched between the two iodides appears at 9.67 ppm. These protons appeared as singlets at 7.95 and 8.01 ppm prior to cyclization, i.e., for compound **23**. Similar shielding effects were observed for the two doublets attributed to the *p*-alkoxyphenyl rings as were observed for their counterparts in the conversion of **14** to **15**. These doublets appear at 6.69 and 7.03 ppm for **23** and shift downfield to 7.10 and 7.27 ppm after cyclization to **24**. This effect is not as dramatic as in the *para* case as a result of shielding provided by the iodides. Compound **24** displays two additional doublets (7.66 and 8.23 ppm) which result from the conversion of the ABC spin systems on the dibenzothiophenyl moieties of **23** to AB systems on cyclization, consistent with the observations made for the conversion of **14** to **15**. The $^{13}$C NMR of **23** displays two acetylenic resonances and 19 aromatic resonances (20 expected), while for **24**, no acetylene resonances are present and 22 aromatic resonances (22 expected) are observed. The most upfield aromatic carbon resonance, present at 107.14 ppm, most likely corresponds to the aryl carbons bearing the iodides, which are known to dramatically shield the carbons to which they are attached. Compound **24** gave a HRMS accurate to 2.5 ppm and satisfactory combustion analysis.

The iodides of **24** may be easily replaced by protons using *s*-BuLi-mediated lithium−halogen exchange followed by a 2-propanol quench. The reduced product **25** was again isolated as a bright yellow solid (97%). The $^1$H NMR spectrum of **25** displays an additional resonance not observed for **24**, a singlet at 7.75 ppm attributed to the replacement of iodides with protons. Interestingly, the two doublets assigned to the *p*-alkoxyphenyl group now appear at 7.02 and 7.45 ppm. While the downfield shift of one doublet due to removal of the shielding iodides is expected, the reason for the slight upfield shift of the other doublet is not apparent. The $^{13}$C NMR spectrum of **25** displays 22 aromatic carbons (22 expected), and the resonance which appeared at 107.12 ppm for **24** and was assigned to the iodide bearing carbons is no longer observed, with the most upfield aromatic resonance appearing at 114.37 ppm. The loss of the iodides is also reflected in the HRMS which is accurate to within 1 ppm and in the combustion

**Scheme 10**




**Scheme 11**




analysis. In the UV−vis spectra, the wavelength of maximum absorption $\lambda_{max}$ is shifted hypsochromically on cyclization, from 318 nm for **23** to 286 and 280 nm for **24** and **25**, respectively. Again the onset of absorption is shifted bathochromically from ca. 380 nm for **23** to ca. 440 nm for both **24** and **25**. It should be noted that comparison of the $^1$H NMR spectrum of **25** with spectra of materials obtained by the direct reaction of **23** with TFA showed no overlap, thereby indicating that extensive acid-promoted rearrangements/migrations were occurring.

As demonstrated earlier, we were interested in performing cyclizations directly onto heterocyclic rings. The *meta*-substituted bisthienyl compound **26** was prepared (Scheme 11) in an analogous fashion to its *para* analogue **16**. TFA promoted cyclization now proceeds more cleanly, providing a 6:1 mixture of the correct cyclization product **27** to its inseparable phenyl-migrated isomer **28**. In accord with the proposed structure **27**, three singlets were observed in the aromatic region at 8.65 (1H), 8.43 (1H), and 7.70 (2H) ppm, corresponding to the 12, 6, and 5/7 protons, respectively. Again, the thienyl proton of **27** is observed as an apparent doublet at 7.20 ppm due to weak coupling ($J$ = 0.9 Hz) with the adjacent methyl group. This proton appeared at 6.80 ppm as a doublet of doublets ($J$ = 3.6, 0.9 Hz) prior to cyclization, i.e., for **26**. Note also that the doublet at 7.58 ppm ($J$ = 3.6 Hz) for **26** is no longer present in the spectrum of **27** as this resonance corresponds to the proton which is eliminated after the initial cyclization. The shielding effects on the *p*-alkoxyphenyl are less dramatic than in the conversion of **23** to **24** as the methylthienyl group is physically

smaller than the dibenzothiophenyl group and not able to shield as well. These *p*-alkoxyphenyl doublets appear at 6.88 and 7.47 ppm for **26** and shift to 7.03 and 7.57 ppm on conversion to **27**. The cyclization is again accompanied by loss of the acetylene resonances ($^{13}$C NMR, appearing at 87.62 and 94.61 ppm for **26**) and an increase in the number of aromatic resonances from 12 (12 expected) for **26** to 14 (14 expected) for **27**. Due to the small amount present and the overlap of resonances with **27**, the structure **28** may only be *tentatively* assigned; however, strong evidence exists in support of this assignment. Minor resonances present in the $^1$H NMR spectrum occur at 8.86 (s), 8.44 (s), and 7.92 (s) ppm and most likely correspond to the 12, 6, and 9 protons of **28**, respectively. The 7.92 ppm resonance qualitatively displays very similar line shape to the resonance at 7.20 assigned to the 3 and 9 thienyl protons and may correspond to the thienyl resonance on the "side" of the molecule which has undergone phenyl migration. This dramatic downfield shift from 7.20 to 7.92 ppm is consistent with the analogous shift observed in the **17**/**18** system (7.19 to 7.83 ppm) and is again attributed to deshielding of the thienyl proton. Additional signals appear at 7.71 and 7.73 and may correspond to the 5/8 protons of **28**, recalling that the 5/7 protons of **27** appear at 7.70 ppm. The remaining resonances, i.e., those of the *p*-alkoxyphenyl groups and the thienyl resonance in the nearly unchanged environment are obscured by the resonances attributed to **27**. Interestingly, heating the mixture **27**/**28** with TFA in 1,2-dichloroethane at 75 °C for 2 h improved the product ratio from 6:1 to 10:1. This observation strongly supports the assertion that **28** exists as a structural isomer which forms as the result of an isomerization process from **27**. Additional support that **28** exists as a structural isomer comes from mass spectral evidence. In the LR mass spectrum only two signals are observed, corresponding to $M^+$ (*m/z* 838.5) and ($M^+ - C_{12}H_{25}$) (*m/z* 670), while the HRMS agrees to within 1.5 ppm of the calculated value.

The preparation of more complex structures was easily accomplished by coupling of bithiophene to the dibromide **20**. In an effort to prepare conjugated polymers with helical architectures, we were interested in preparing the bromide **30** by reaction of 1 equiv of 5-(chlorozincio)-2,2′-bithiophene with 1 equiv of **20**. Homopolymerization of **30** using conditions developed by McCullough[75] would produce the desired polymers. The coupling reaction to produce **30** afforded a statistical mixture of products as the desired product **30** was obtained in 35% yield, while the disubstituted product **29** was obtained in 17% yield. The attempted cyclization of **29** using standard conditions ($CH_2Cl_2$, 25 °C) resulted in the recovery of only starting material. Heating the reaction to 65 °C in the higher boiling solvent 1,2-dichloroethane produced a 6:1 mixture of the product **31** and its phenyl-migrated structural isomer **32**.

In the aromatic region of the $^1$H NMR spectrum of **31** a 2,3,4-thienyl spin system is clearly present, as are the doublets attributed to the *p*-(hexyloxy)phenyl groups. The remaining four signals in the aromatic region are all singlets. The singlet at 8.72 (1H) corresponds to the pseudo bay region proton (12) while the singlet at 8.42 (1H) corresponds to the proton at the 6 position. The remaining singlets at 7.58 and 7.72 ppm (2H each) correspond to the 5/7 protons and the 3/9 thienyl protons. The presence of thienyl rather than methyl groups at the 2/10 positions precludes splitting of the 3/9 thienyl protons, however, the protons analogous to the 5/7 protons in **31** appear at 7.75 and 7.70 ppm in **17** and **27**, respectively, implying that the 7.72 ppm resonance corresponds to the 5/7 protons and the 7.58 ppm resonance corresponds to the 3/9 thienyl protons. The conversion of **29** to **31** is accompanied by loss of the acetylene resonances (87.59 and 95.72 ppm) in the $^{13}$C NMR and an increase in the number of aromatic carbons from 16 (16 expected) for **29** to 18 (18 expected) for **31**. Again, due to the small amount present and the overlap of resonances with **31**, the structure **32** may only be *tentatively* assigned. The positions of the minor resonances ascribed to **32** relative to the resonances ascribed to **31** reveal a trend consistent with the relative positions observed for the **27**/**28** system. Minor resonances present in the $^1$H NMR spectrum occur at 8.95 (s), 8.46 (s), and 8.29 (s) ppm and correspond to the 12, 6, and 9 protons of **32**, respectively. The 8.29 ppm resonance qualitatively displays very similar line shape to the resonance at 7.58 assigned to the 3 and 9 thienyl protons and may correspond to the thienyl resonance on the side of the molecule which has undergone phenyl migration. This downfield shift from 7.58 to 8.29 ppm is consistent with the analogous shift observed in the **27**/**28** system (7.20 to 7.92 ppm) and is again attributed to deshielding of the thienyl proton. The relative downfield positioning of the signals is attributed to the deshielding effect of replacing a methyl group with a thienyl group. Additional weak signals appear at 7.73 and 7.75 and may correspond to the 5/8 protons of **32**. The remaining resonances are all obscured by the resonances attributed to **31**. The low-resolution mass spectrum of the **31**/**32** mixture does display two signals at *m/z* 798 and 823 at 10% the intensity of the molecular ion (*m/z* 806, 100); however, satisfactory combustion analysis was obtained providing additional support that **32** exists as a structural isomer. Interestingly, the conversion is accompanied by a narrowing of features in the UV−vis absorption spectrum of **31**/**32** relative to **29**. Compound **29** displays a *broad* absorption from 450 to 290 nm ($\lambda_{max} = 366$ nm). Following cyclization, low-intensity absorptions appear at 440 and 406 nm, while the absorption corresponding to $\lambda_{max}$ (370 nm) begins at 390 and ends at 280 nm with relatively sharp features. This narrowing effect is attributed to a reduction in the number of accessible conformations available to the molecule upon rigidification of the ring system.

***Ortho*-Substituted Systems.** To extend the electrophilic cyclization strategy beyond the *meta* and *para* systems, we decided to explore the more sterically demanding *ortho*-substituted system (where the aryl groups undergoing electrophilic cyclization are *ortho* to each other; see Figure 1). If this methodology were to be successful, it would provide entry to a host of interesting helical structures.

To determine the efficacy of the cyclization for the *ortho*-substituted systems, we targeted the *o*-terphenyl **35**. This proves an ideal substrate to study since the parent pentahelicene of the cyclization product **37** is a known compound and its NMR is available in the literature.[76−78] Compound **35** was synthesized, in a manner similar to that employed for the *meta* and *para* systems, as outlined in Scheme 12.

The synthesis commenced with the readily available (two steps from *o*-xylene) 3,4-dibromo-2,5-diiodo-*o*-xylene. Chemoselective Pd(0)/Cu(I)-catalyzed coupling with 4-(butyloxy)phenylacetylene provided the substituted dibromide **33** in good yield. Unlike the *meta* and *para* systems, Suzuki coupling on the dibromide **33** was unsuccessful. To increase the reactivity,

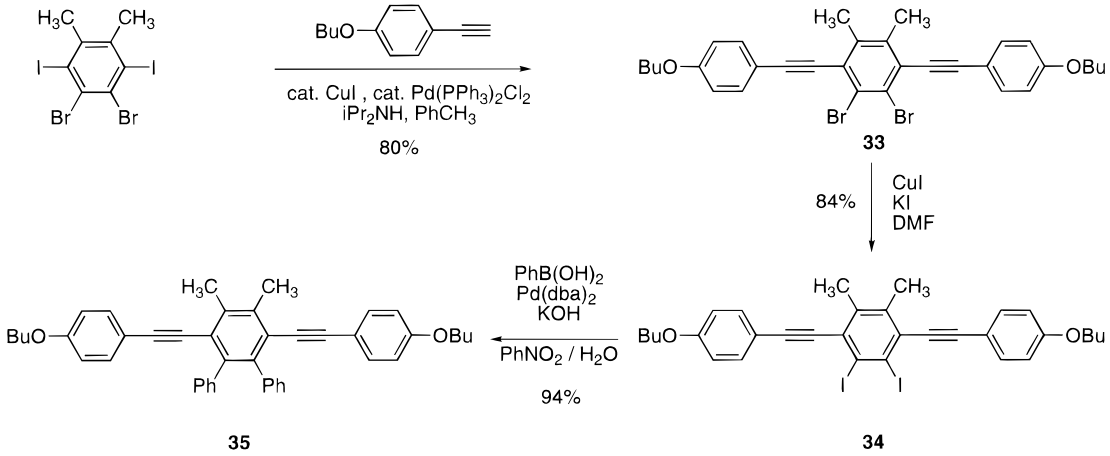
(75) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.

(76) Martin, R. H.; Defay, N.; Figeys, H. P.; Flammang-Barbieux, M.; Cosyn, J. P.; Gelboke, M.; Schurter, J. J. *Tetrahedron* **1969**, *25*, 4985.

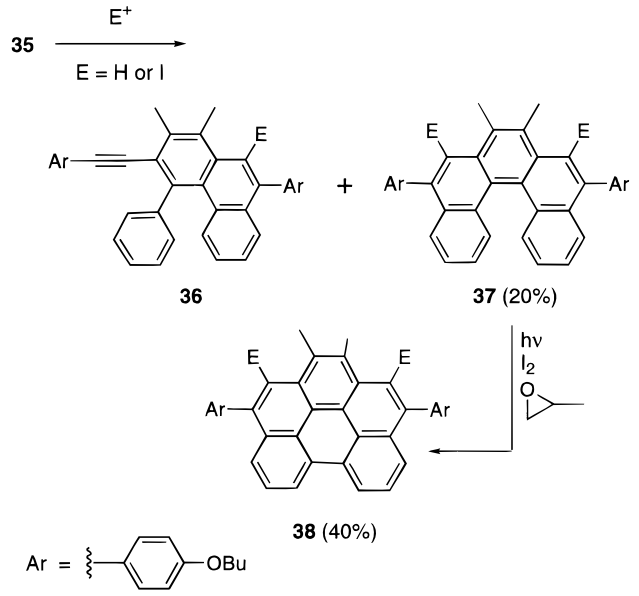
(77) Matthews, R. S.; Jones, D. W.; Bartle, K. D. *Spectrochim. Acta A* **1971**, *27*, 1185.

(78) Defay, N.; Zimmerman, D.; Martin, R. H. *Tetrahedron Lett.* **1971**, 1871.

**Scheme 12**




**Scheme 13**




the bromines were replaced by iodine by prolonged treatment of **33** with large excesses of both CuI and KI in hot (ca. 145 °C) DMF. The diiodide **34** could be converted in very high yield to the target terphenyl **35** under the modified Suzuki coupling conditions (used for the *meta* and *para* systems), so long as a large excess (about 10 equiv) of the phenylboronic acid was used.

With the target terphenyl **35** in hand, attempts were made to induce the cyclization which would lead to a pentahelicene. Initial attempts focused on the acid-catalyzed cyclization. The protocol employed in the previous cases (*meta* and *para*) failed to work in this instance. $^1$H NMR and TLC indicated a complex and nearly inseparable mixture of products had been formed. A careful analysis of the $^1$H NMR of the crude reaction mixture indicated that in most cases one of the major products was most likely the monocyclized compound **36** (see Scheme 13). There also appeared to be a somewhat smaller amount of the expected product **37**. Since the cyclization appeared to have gone at least partway, we decided to use more aggressive reaction conditions. The solvent and reagents were switched to the higher boiling 1,2,3-trichloropropane and trichloroacetic acid. Refluxing at higher temperatures or using a stronger acid (triflic acid, −78 °C to room temperature) proved unsuccessful, and in most cases, we obtained complex mixtures wherein the major identifiable component was usually the monocyclized product **36**.

Cyclization using $I^+$ as the electrophile prepared from mercury(II) trifluoroacetate and $I_2$ was successfully employed for the *meta* system. This approach resulted in the starting material **35** being recovered in almost quantitative yield. We reasoned that perhaps a more reactive form of $I^+$ was required, and therefore, the earlier protocol was altered by replacing the mercury(II) trifluoroacetate with silver triflate. There was also a question in our mind as to the effect of added base, which may reduce the reactivity of the $I^+$. Compound **35** was subjected to the iodine/silver triflate mixture in the presence of only half an equivalent of base (2,6-dimethylpyridine), and the result was encouraging. One of the distinguishing features of the $^1$H NMR of the parent pentahelicene was the downfield shift (8.34 ppm) of the innermost (bay) protons. The $^1$H NMR of the crude reaction mixture indicated a doublet at 8.43 ppm. By integrating the signals for the methyl peaks on the aromatic rings, it was observed that the crude mixture contained approximately equal amounts of **35** and what we believed was the expected cyclized helicene **37** along with some decomposition products. This seemed to suggest that the base was indeed interfering with the reaction. In all subsequent runs, the base was omitted. It was observed that the order of mixing had a very pronounced effect on the reaction. The addition of **35** to a mixture of silver triflate and iodine gave a complex mixture of products, whereas addition of iodine to a mixture of **35** and silver triflate gave a much cleaner reaction.

Optimized conditions gave **37** in 20% yield. Pure samples of **37** were isolated, and to our surprise, characterization by mass spectroscopy, $^1$H NMR, and $^{13}$C NMR indicated that the product did not contain any iodine! We were able to confirm, on the basis of COSY, $^1$H NMR, and $^{13}$C NMR, along with careful comparison of the $^1$H NMR reported for the parent pentahelicene,[76−78] that the iodine/silver triflate protocol actually provided us with **37** (E = H). To further confirm the identity of **37** it was subjected to the Mallory photocyclization reaction[29] to form the corresponding benzo[*ghi*]perylene **38** (see Scheme 13) whose $^1$H NMR agreed quite well with that of the parent benzo[*ghi*]perylene.[79]

We have considered that the iodine actually played no role in the reaction. To test this hypothesis, a sample of **35** was treated with silver triflate and then divided into two parts; one part was treated with iodine, while the other was allowed to stir for the appropriate amount of time and subjected to the usual workup conditions. It was observed that the aliquot which had not been treated with iodine gave a complex mixture of products,

(79) *The Aldrich Library of $^{13}$C and $^1$H FT NMR Spectra*, 1st ed.; Pouchert, C. J., Behnke, J., Eds.; Aldrich Chemical Co.: Milwaukee, WI, 1994; Vol. 2, p 58C.

whereas that which had been treated with iodine gave **37** (E = H). Furthermore, the substitution of sliver trifluoroacetate or mercury trifluoroacetate for silver triflate led to complex mixtures.

## Conclusion

We have described a versatile method for the synthesis of complex, fused polycyclic aromatic systems in high chemical yield. Construction is achieved using a general two-step synthetic sequence. Pd-catalyzed Suzuki and Negishi type cross-coupling chemistries allow for the preparation of nonfused skeletal ring systems in yields consistently >80%. The critical ring-forming step, which generally proceeds in very high to quantitative yield in the *meta* and *para* cases (but not in the *ortho* case), utilizes 4-alkoxyphenylethynyl groups and is induced by strong electrophiles such as trifluoroacetic acid (TFA) and iodonium tetrafluoroborate. Fused polycyclic benzenoids as well as benzenoid/thiophene systems have been prepared utilizing this methodology. We have studied symmetric systems which contain two ethynyl−Ar′ partners. When the ethynyl groups and the aryl groups undergoing electrophilic substitution (Ar′) are situated *para* to each other, the resulting cyclization products are substituted bisaryl[*a*,*h*]anthracenes. In the case where the ethynyl−Ar′ partners are situated *meta* to each other, cyclization provides substituted bisaryl[*a*,*j*]anthracenes. When the ethynyl−Ar′ partners are situated *para* to each other and the aryl groups undergoing electrophilic cyclization are *ortho* to each other, the product is a helicene. Unfortunately, the *ortho* system does not work as well as the *meta* and *para* cases. The forcing conditions and low yields of this method render it of limited synthetic utility for the preparation of helicenes. Our ongoing studies will focus on applying this methodology to the design and construction of graphite ribbons (rigid aromatic polymeric systems) and other electronic polymers.[48]

## Experimental Section

**General Methods.** NMR spectra ($^1$H and $^{13}$C) were obtained on Bruker AC-100, AC-250, and AMX-500 spectrometers. Chemical shifts are reported in ppm relative to residual protio solvent (chloroform 7.24 ppm ($^1$H), 77.0 ppm ($^{13}$C); DMSO 2.49 ppm ($^1$H)). Microanalyses and mass spectra were obtained at the University of Pennsylvania instrumentation center. UV−vis spectra were recorded in $CHCl_3$ on a Hewlett Packard 8452A diode array spectrophotometer. Luminescence spectra were recorded in $CHCl_3$.

All solvents were distilled by vacuum transfer. THF was stored over $CaH_2$ before being distilled from sodium benzophenone ketyl. Toluene was distilled from sodium metal. Nitrobenzene and methylene chloride were distilled from $P_2O_5$. Nitrobenzene was stored in the dark. Diisopropylamine (DIPA) was distilled from solid KOH pellets.

Synthetic manipulations were performed under an argon atmosphere in oven-dried glassware using standard Schlenk techniques.

**1,4-Dibromo-2,5-diiodobenzene.** To a 3000 mL three-neck round bottom flask equipped for mechanical stirring was added concentrated $H_2SO_4$ (1500 mL) and periodic acid (66.6 g, 0.292 mol). After dissolution of the periodic acid, KI (145.6 g, 0.880 mol) was added in small portions over 40 min to produce a deep purple solution. The temperature was then lowered to −30 °C and 1,4-dibromobenzene (138 g, 0.585 mol) was added over approximately 5 min. An additional 600 mL portion of $H_2SO_4$ was added to facilitate stirring. The mixture was stirred for 24 h while maintaining the temperature between −30 and −20 °C. The entire mixture was then poured over approximately 9000 g of ice and filtered on a glass frit. The solid was taken up in $CHCl_3$, washed with 5% NaOH (2×) and $H_2O$, and dried ($MgSO_4$), and the solvent was removed in vacuo. Following recrystallization from THF (1×) and $CHCl_3$ (2×), 1,4-dibromo-2,5-diiodobenzene (142.1 g, 49.8%) was obtained as a white crystalline solid (mp 159−161 °C, lit.[80] 161−163 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 8.02 (s, 2H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 101.5, 129.2, 142.3. HRMS (CI $CH_4$, positive ion): found *m/z* 485.6646 ($M^+$); calcd for $C_6H_2Br_2I_2$ *m/z* 485.6613 ($M^+$). Anal. Calcd for $C_6H_2Br_2I_2$: C, 14.78; H, 0.41. Found: C, 14.58; H, 0.43.

**1,4-Dibromo-2,5-bis((4-(dodecyloxy)phenyl)ethynyl)benzene (1).** To a 500 mL flask charged with 1,4-dibromo-2,5-diiodobenzene (16.0 g, 0.0328 mol), $(Ph_3P)_2PdCl_2$ (0.461 g, 0.657 mmol), CuI (0.656 g, 3.44 mmol), and $(C_4H_9)_4NBr$ (0.634 g, 1.97 mmol) were added 75 mL of toluene, 75 mL of DIPA, and 50 mL of THF. 4-(Dodecyloxy)-phenylacetylene (19.74 g, 0.0689 mol) dissolved in 25 mL of THF was added dropwise at 25 °C generating a noticeable amount of heat. After 2 h of stirring without any external source of heat, the mixture was diluted with 200 mL of $CHCl_3$ and washed with 5% HCl (3 × 50 mL), $H_2O$ (50 mL), 5% $NH_4OH$ (2 × 50 mL), and $H_2O$ (2 × 50 mL). MeOH was added to precipitate the compound as a yellow solid. After crystallization from THF/MeOH, **1** (19.17 g, 73%) was obtained as small colorless plates (mp 108−110 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.86 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.77 (m, 4H), 3.95 (t, 4H, $J$ = 6.5 Hz), 6.86 (d, 4H, $J$ = 8.9 Hz), 7.47 (d, 4H, $J$ = 8.7 Hz), 7.71 (s, 2H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.1, 22.7, 26.0, 29.2, 29.4, 29.6, 31.9, 68.1, 85.8, 96.9, 114.1, 114.6, 123.4, 126.3, 133.3, 135.7, 159.9. Anal. Calcd for $C_{46}H_{60}O_2Br_2$: C, 68.65; H, 7.51. Found: C, 68.28; H, 7.46.

**General Coupling Procedure for Preparation of *p*-Terphenyls 2−5. 2′,5′-Bis((4-(dodecyloxy)phenyl)ethynyl)-2,2″,5,5″-tetramethoxy-[1,1′:4′,1″]terphenyl (2).** A 25 mL Schlenk tube was charged with **1** (0.089 g, 0.111 mmol), 2,5-(dimethoxy)phenylboronic acid (0.043 g, 0.234 mmol), $Pd(dba)_2$ (0.0004 g, $6.66 \times 10^{-4}$ mmol), triphenylphosphine (0.0026 g, $9.99 \times 10^{-3}$ mmol), and KOH (0.131 g, 2.34 mmol). To the mixture was added $H_2O$ (1 mL) followed by $PhNO_2$ (4 mL). The heterogeneous mixture was purged with a rapid stream of argon for 20 min before being placed in an oil bath (85 °C). After 16 h of heating at the stated temperature, the solution was allowed to cool, diluted with $CHCl_3$ (4 mL), washed with 5% NaOH (2 × 4 mL), $H_2O$, 5% HCl (3 × 4 mL) and $H_2O$, and dried ($Na_2SO_4$). The solvent was removed at 85 °C under high vacuum (0.01 Torr), and the solid residue was chromatographed on silica gel (1:1 hexanes/toluene) to afford **3** (0.089 g, 86.9%) as a colorless solid (mp 158−159 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.87 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.74 (m, 4H), 3.75 (s, 6H), 3.78 (s, 6H), 3.90 (t, 4H, $J$ = 6.5 Hz), 6.75 (d, 4H, $J$ = 8.6 Hz), 6.92 (s, 4H), 7.00 (s, 2H), 7.13 (d, 4H, $J$ = 8.7), 7.59 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 14.08, 22.67, 25.99, 29.16, 29.32, 29.35, 29.54, 29.57, 29.61, 29.63, 31.90, 55.80, 56.37, 68.03, 88.11, 93.31, 112.27, 114.39, 114.42, 115.44, 116.83, 122.76, 129.97, 132.81, 133.34, 139.51, 151.38, 153.21, 159.07. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 364 (sh, 51 000), 342 (59 800), 258 (27 300) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 376 (1), 392 (0.96) nm. HRMS (FAB): found *m/z* 918.5783 ($M^+$); calcd for $C_{62}H_{78}O_6$ *m/z* 918.5798 ($M^+$). Anal. Calcd for $C_{62}H_{78}O_6$: C, 81.01; H, 8.55. Found: C, 80.64; H, 8.48.

**2′,5′-Bis((4-(dodecyloxy)phenyl)ethynyl)[1,1′:4′,1″]terphenyl (3).** Compound **3** was prepared as described for compound **2**, substituting phenylboronic acid for 2,5-(dimethoxy)phenylboronic acid. Compound **3** was obtained as a colorless solid in 91.3% yield (mp 102−104 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.87 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.83 (m, 4H), 3.92 (t, 4H, 6.6 Hz), 6.79 (d, 4H, $J$ = 8.8 Hz), 7.25 (d, 4H, $J$ = 8.8 Hz), 7.45 (m, 6H), 7.68 (s, 2H), 7.74 (d, 4H, $J$ = 7.5 Hz). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.1, 22.7, 26.0, 29.1, 29.3, 29.6, 31.9, 68.0, 87.9, 93.9, 114.5, 115.1, 121.6, 127.6, 127.9, 129.3, 132.8, 133.5, 139.6, 142.0, 159.2. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 366 (sh, 53 400), 348 (57 200), 286 (43 700) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 382(1), 398 (0.81) nm. HRMS (FAB): found *m/z* 799.5463 (M + $H^+$); calcd for $C_{58}H_{71}O_2$ *m/z* 799.5454.

**2′,5′-Bis((4-(dodecyloxy)phenyl)ethynyl)-4,4″-dimethoxy[1,1′:4′,1″]terphenyl (4).** Compound **4** was prepared as described for compound **2**, substituting 4-(methoxy)phenylboronic acid for 2,5-(dimethoxy)phenylboronic acid. Compound **4** was obtained as a colorless solid in 82.2% yield. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.87

(80) Hart, H.; Harada, K.; Chi-Jen, F. D. *J. Org. Chem.* **1985**, *50*, 3104.

(t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.75 (m, 4H), 3.87 (s, 6H), 3.93 (t, 4H, $J$ = 6.70 Hz), 6.80 (d, 4H, $J$ = 8.66 Hz), 7.00 (d, 4H, $J$ = 8.66 Hz), 7.28 (d, 4H, $J$ = 8.66 Hz), 7.63 (s, 2H), 7.67 (d, 4H, $J$ = 8.63 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 14.12, 22.68, 26.00, 29.18, 29.37, 29.58, 29.62, 31.91, 55.35, 68.10, 88.19, 93.73, 113.38, 114.54, 115.25, 121.51, 130.47, 132.21, 132.85, 133.44, 141.24, 159.26, 159.27. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 368 (sh, 40 100), 344 (44 600), 298 (50 000) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 382 (1), 398 (0.83) nm. HRMS (FAB): found *m/z* 858.5549 ($M^+$); calcd for $C_{60}H_{74}O_2$ *m/z* 858.5587.

**2′,5′-Bis((4-(dodecyloxy)phenyl)ethynyl)-2,5,2″,5″-tetramethyl-[1,1′:4′,1″]terphenyl (5).** Compound **5** was prepared as described for compound **2**, substituting 2,5-(dimethyl)phenylboronic acid for 2,5-(dimethoxy)phenylboronic acid. Compound **5** was obtained as a white solid in 85.4% yield (mp 164−167 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.88 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.75 (m, 4H), 2.26 (s, 6H), 2.37 (s, 6H), 3.90 (t, 4H, $J$ = 6.53 Hz), 6.75 (d, 4H, $J$ = 8.80 Hz), 7.07 (d, 4H, $J$ = 8.75), 7.11−7.21 (m, 6H), 7.49 (s, 2H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.12, 19.57, 20.97, 22.68, 25.98, 29.14, 29.35, 29.58, 31.91, 68.00, 87.73, 93.83, 114.40, 115.12, 112.57, 128.28, 129.57, 130.59, 132.32, 132.81, 133.34, 134.56, 139.81, 143.02, 159.14. UV−vis (**5-C4** (butoxy replaces dodecyloxy), $CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$) 364 (sh, 61 200), 342 (63 900) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 372 (1), 390 (0.77) nm. HRMS (FAB): found *m/z* 854.6008 ($M^+$); calcd for $C_{62}H_{78}O_2$ *m/z* 854.6002.

**General Acid-Induced Cyclization Procedure. 5,12-Bis(4-(dodecyloxy)phenyl)-1,4,8,11-tetramethoxydibenz[*a*,*h*]anthracene (6).** In a 100 mL Schlenk flask, **2** (0.500 g, 0.544 mmol) was dissolved in 50 mL of $CH_2Cl_2$. To the solution was added trifluoroacetic acid (1.5 mL, 19.5 mmol) in one portion at room temperature. The solution turned in color first to a light red, then to a yellow brown, and finally to a deep green. After 45 min, $^1$H NMR indicated the reaction was complete. The solution was washed with 10% $NaHCO_3$ solution (3 × 10 mL) and $H_2O$ (2 × 15 mL) and dried ($Na_2SO_4$). After removal of the solvent under reduced pressure, the crude product was recrystallized from benzene. Compound **6** was obtained (0.498 g, 99.6%) as bright yellow needles (mp 209−211 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.87 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.83 (m, 4H), 3.43 (s, 6H), 4.03 (t, 4H, $J$ = 6.5 Hz), 4.13 (s, 6H), 6.94 (d, 4H, $J$ = 8.6 Hz), 7.03 (d, 2H, $J$ = 8.8 Hz), 7.18 (d, 2H, $J$ = 9.0 Hz), 7.34 (d, 4H, $J$ = 8.5 Hz), 7.78 (s, 2H), 10.10 (s, 2H). $^{13}$C NMR (25 MHz, $CDCl_3$): $\delta$ 14.0, 22.7, 26.2, 29.3, 29.5, 29.6, 31.9, 56.5, 57.0, 68.4, 110.0, 111.1, 113.3, 122.8, 124.7, 128.0, 128.1, 129.1, 131.1, 132.7, 135.7, 138.9, 151.8, 154.1, 157.5. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 430 (14 400), 406 (12 100), 374 (24 000), 356 (24 600), 318 (55 600), 280 (37 500) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 438 (1), 462 (0.53) nm. HRMS (FAB): found *m/z* 918.5841 ($M^+$); calcd for $C_{62}H_{78}O_6$ *m/z* 918.5798 ($M^+$). Anal. Calcd for $C_{62}H_{78}O_6$: C, 81.01; H, 8.55. Found: C, 80.66; H, 8.65.

**5,12-Bis(4-(dodecyloxy)phenyl)-6,13-diiodo-1,4,8,11-tetramethoxydibenz[*a*,*h*]anthracene (7).** To a 50 mL Schlenk tube wrapped with aluminum foil to omit light and containing $I(pyr)_2BF_4$ (0.250 g, 0.672 mmol) was added $CH_2Cl_2$ (25 mL), followed by $CF_3SO_3H$ (60 $\mu$L, 6.78 × $10^{-4}$ mmol). The solution was allowed to stir at room temperature for 15 min before being cooled to −40 °C. After this time, **2** (0.300 g, 0.326 mmol) dissolved in $CH_2Cl_2$ (10 mL) was added in one portion. The solution was allowed to warm from −40 to −30 °C over 30 min and then from −30 to 10 °C over 1.5 h. To the solution were added 50 mL saturated aqueous thiosulfate solution and 50 mL of $CHCl_3$. The organic layer was washed with an additional portion of thiosulfate (50 mL) and $H_2O$ (2 × 50 mL) and dried ($MgSO_4$). After removal of solvent under reduced pressure, the crude solid was recrystallized from THF/MeOH to afford **7** (0.368 g, 96.3%) as a yellow solid (mp 232−233 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.88 (t, 6H, $J$ = 6.7 Hz), 1.1−1.5 (36 H), 1.84 (m, 4H), 3.29 (s, 6H), 4.04 (t, 4H, $J$ = 6.6 Hz), 4.19 (s, 6H), 6.97 (d, 4H, $J$ = 8.5 Hz), 6.99 (d, 2H, $J$ = 8.7), 7.12 (d, 4H, $J$ = 8.5 Hz), 7.21 (d, 2H, $J$ = 8.7 Hz), 10.13 (s, 2H). $^{13}$C NMR (25 MHz, $CDCl_3$): $\delta$ 14.0, 22.7, 26.2, 29.7, 31.9, 57.3, 57.5, 68.3, 111.4, 111.8, 113.4, 113.5, 122.5, 125.7, 128.7, 129.9, 132.2, 134.9, 142.6, 143.9, 151.1, 153.1, 157.8. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 436 (14 100), 410 (11 000), 380 (16 900), 362 (20 100), 328 (58 800), 284 (42 600) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 374 (0.58), 442 (1) nm (very low intensity). HRMS (FAB): found *m/z* 1170.3802 ($M^+$); calcd for $C_{62}H_{76}O_6I_2$ *m/z* 1170.3731. Anal. Calcd for $C_{62}H_{76}O_6I_2$: C, 63.59; H, 6.54. Found: C, 63.51; H, 6.59.

**Preparation of 5,12-Bis(4-(dodecyloxy)phenyl)-1,4,8,11-tetramethoxydibenz[*a*,*h*]anthracene (6) from 5,12-Bis(4-(dodecyloxy)-phenyl)-6,13-diiodo-1,4,8,11-tetramethoxydibenz[*a*,*h*]anthracene (7).** A solution of **7** (0.005 g, 0.004 mmol) in 3 mL of THF was cooled to −78 °C, and *s*-BuLi (0.10 mL, 1.53 M, 0.153 mmol) was added. After 5 min of stirring, the golden yellow solution was quench by the rapid addition of 1 mL of MeOH. The mixture was diluted with $CHCl_3$ (30 mL), washed with 5% HCl (2 × 10 mL) and $H_2O$ (10 mL), and dried ($Na_2SO_4$) before removing the solvent in vacuo. The product **6** (>95% by NMR) exhibited a $^1$H NMR spectrum identical to material prepared via TFA-induced cyclization of the terphenyl **2**.

**5,12-Bis(4-(dodecyloxy)phenyl)dibenz[*a*,*h*]anthracene (8).** Compound **8** was prepared as described for compound **6**, using **3** as the starting material. Species **8** was isolated as a pale yellow solid in 99.4% yield (mp 146−149 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.87 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.83 (m, 4H), 4.06 (t, 4H, $J$ = 6.5 Hz), 7.06 (d, 4H, $J$ = 8.6 Hz), 7.52 (d, 4H, $J$ = 8.6 Hz), 7.56 (t, 2H, $J$ = 7.9 Hz), 7.70 (t, 2H, $J$ = 7.9 Hz), 7.88 (s, 2H), 7.97 (d, 2H, 8.1 Hz), 8.91 (d, 2H, $J$ = 8.3 Hz), 9.14 (s, 2H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.1, 22.7, 26.2, 29.4, 29.7, 31.9, 68.2, 114.4, 122.0, 123.1, 126.6, 126.8, 127.1, 127.9, 129.0, 130.4, 130.6, 131.1, 131.7, 132.9, 138.5, 158.7. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 408 (1390), 366 (16 500), 350 (16 600), 314 (55 400), 304 (51 100) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 412 (1), 436 (0.61) nm. HRMS (FAB): found *m/z* 799.5452 (M + $H^+$); calcd for $C_{58}H_{71}O_2$ *m/z* 799.5454.

**5,12-Bis(4-(dodecyloxy)phenyl)-3,10-dimethoxydibenz[*a*,*h*]anthracene (9).** Compound **9** was prepared as described for compound **6**, using compound **4** as the starting material. Species **9** was isolated as a yellow solid in 98.7% yield (mp 151−154 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.89 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.85 (m, 4H), 3.81 (s, 6H), 4.04 (t, 4H, $J$ = 6.40 Hz), 7.04 (d, 4H, 8.72 Hz), 7.30 (dd, 2H, $J$ = 8.94, 2.62 Hz), 7.37 (d, 2H, $J$ = 2.55 Hz), 7.50 (d, 4H, $J$ = 8.67 Hz), 7.81 (s, 2H), 8.77 (d, 2H, $J$ = 9.06), 8.95 (s, 2H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.13, 22.70, 26.13, 29.38, 29.48, 29.65, 31.92, 55.32, 68.12, 108.70, 114.39, 115.78, 121.19, 124.59, 124.70, 128.35, 128.52, 129.82, 130.90, 132.93, 132.98, 138.05, 158.37, 158.61. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 410 (2800), 370 (18 100), 322 (98 100), 286 (46 600) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 414 (1), 438 (0.55) nm. HRMS (FAB): found *m/z* 858.5596 ($M^+$); calcd for $C_{60}H_{74}O_2$ *m/z* 858.5587.

**5,12-Bis(4-(dodecyloxy)phenyl)-1,4,8,11-tetramethyldibenz[*a*,*h*]-anthracene (10).** Compound **10** was prepared as described for **6**, using compound **5** as the starting material. Species **10** was isolated as a bright yellow solid in 98.2% yield (mp 180−184 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.89 (t, 6H, $J$ = 6.83 Hz), 1.1−1.6 (36H), 1.82 (m, 4H), 2.04 (s, 6H), 3.18 (s, 6H), 4.03 (t, 4H, $J$ = 6.52 Hz), 6.96 (d, 4H, $J$ = 8.67 Hz), 7.25 (d, 2H, $J$ = 7.50 Hz), 7.33 (d, 4H, $J$ = 8.56 Hz), 7.42 (d, 2H, $J$ = 7.50 Hz), 7.69 (s, 2H), 9.06 (s, 2H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.15, 22.72, 25.16, 26.14, 26.70, 29.39, 29.48, 29.66, 30.33, 31.95, 68.14, 114.05, 125.53, 127.03, 129.42, 129.57, 130.07, 130.32, 130.89, 131.98, 132.12, 133.22, 133.87, 137.71, 138.43, 158.19. UV−vis (**10-C4** (butoxy replaces docecyloxy), $CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 418 (2500), 378 (28 800), 364 (27 300), 310 (71 200) nm. Luminescence spectrum (**10-C4** (butoxy replaces docecyloxy), $CHCl_3$) $\lambda_{max}$ (rel intensity): 426 (1), 448 (0.64) nm. HRMS (FAB): found *m/z* 854.6031 ($M^+$); calcd for $C_{62}H_{78}O_2$ *m/z* 854.6002.

**1,4-Bis(dibenzo[*b*,*d*]thiophen-4-yl)-2,5-bis((4-(dodecyloxy)-phenyl)ethynyl)benzene (14).** Compound **14** was prepared as described for compound **2**, substituting 4-dibenzothiopheneboronic acid for 2,5-(dimethoxy)phenylboronic acid. The crude product was crystallized from $CHCl_3$/EtOH. Compound **14** was obtained as a colorless solid in 86.3% yield (mp 168−169 °C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.86 (t, 6H, $J$ = 6.8 Hz), 1.2−1.42 (36H), 1.70 (m, 4H), 3.85 (t, 4H, $J$ = 6.60 Hz), 6.66 (d, 4H, $J$ = 8.79 Hz), 6.99 (d, 4H, $J$ = 8.81 Hz), 7.47 (m, 4H), 7.61 (t, 2H, $J$ = 7.66 Hz), 7.73 (dd, 2H, $J$ = 7.37, 1.03 Hz), 7.84 (m, 2H), 7.98 (s, 2H), 8.23 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$, partial): $\delta$ 14.10, 22.67, 25.95, 29.12, 29.33, 29.53, 29.56, 29.61, 31.90, 68.00, 87.25, 95.05, 114.37, 114.84, 120.93, 121.69, 122.63, 122.75, 124.29, 126.73, 128.32, 132.85, 133.06, 134.82, 135.84,

135.93, 139.81, 141.70, 159.25. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 368 (52 900), 346 (56 500), 290 (37 900) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 388 nm. HRMS (FAB): found *m/z* 1010.5111 ($M^+$); calcd for $C_{70}H_{74}O_2S_2$ *m/z* 1010.5130. Anal. Calcd for $C_{70}H_{74}O_2S_2$: C, 83.12; H, 7.37. Found: C, 83.22; H, 7.53.

**8,18-Bis(4-(dodecyloxy)phenyl)bis(dibenzo[*b,d*]thiophene)[4,3-*a,h*]-anthracene (15).** To a solution of **14** (0.205 g, 0.203 mmol) in 55 mL of $CH_2Cl_2$ was added 1 mL of TFA. After 30 min, a bright yellow product precipitated out of solution. Stirring was allowed to continue for an additional 20 min. The solution was diluted with 50 mL of $CHCl_3$, and the organic layer washed with 5% NaOH (2 × 20 mL) and $H_2O$. The solvent was dried ($MgSO_4$) and removed under reduced pressure. The solid was crystallized from benzene to afford the product **15** as bright yellow needles (0.202 g, 98.5%) (mp > 290 °C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.88 (t, 6H, $J$ = 6.8 Hz), 1.2−1.4 (m, 32H), 1.55 (quint, 4H, $J$ = 7.73 Hz), 1.89 (quint, 4H, $J$ = 7.15 Hz), 4.11 (t, 4H, $J$ = 6.45 Hz), 7.12 (d, 4H, $J$ = 8.55 Hz), 7.54 (m, 4H), 7.60 (d, 4H, $J$ = 8.54 Hz), 8.05 (m, 2H), 8.14 (d, 2H, $J$ = 8.62 Hz), 8.19 (s, 2H), 8.28 (m, 2H), 8.35 (d, 2H, $J$ = 8.66 Hz), 9.88 (s, 2H). $^{13}$C NMR (125 MHz, $CD_2Cl_4$, 100 °C): $\delta$ 13.74, 22.38, 25.98, 29.06, 29.23, 29.33, 29.39, 31.67, 68.51, 114.88, 120.00, 121.43, 122.10, 124.61, 124.67, 126.07, 126.40, 126.60, 128.08, 128.76, 131.06, 131.30, 132.29, 133.36, 134.76, 134.91, 135.81, 139.32, 139.51, 158.92. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 430 (18 000), 404 (21 400), 392 (28 000), 372 (24 400), 340 (89 900), 324 (77 100), 260 (63 100) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 438 (1), 462 (0.50) nm. HRMS (FAB): found *m/z* 1010.5116 ($M^+$); calcd for $C_{70}H_{74}O_2S_2$ *m/z* 1010.5130. Anal. Calcd for $C_{70}H_{74}O_2S_2$: C, 83.12; H, 7.37. Found: C, 83.41; H, 7.38.

**2,5-Bis((4-(dodecyloxy)phenyl)ethynyl)-1,4-bis(5-methylthiophen-2-yl)benzene (16).** To a cooled (0 °C) solution of 2-methylthiophene (140 $\mu$L, 1.45 mmol) dissolved in 10 mL of THF was added *n*-BuLi (0.67 mL, 1.75 M, 1.17 mmol). After 25 min, a solution of $ZnCl_2$ (0.507 g, 3.72 mmol) dissolved in 8 mL of THF was added to the 2-methyl-5-lithiothiophene solution. The mixture was allowed to stir for 20 min and then was cannulated into a separate flask containing **1** (0.25 g, 0.311 mmol) and $(Ph_3P)_2PdCl_2$ (0.0087 g, 0.012 mmol). The reaction was refluxed for 4 h and, after cooling to room temperature (rt), carefully quenched with MeOH. The mixture was diluted with diethyl ether ($CHCl_3$ for shorter side chain derivatives), washed with 5% HCl and $H_2O$, and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the product was purified by silica gel chromatography (15:1 hexanes/THF eluent) to afford **16** as a yellow/orange solid (0.254 g, 97.4%) (mp 160−162 °C). Species **16-C4** was purified by recrystallization from $CHCl_3$/*i*-PrOH. Compound **16**. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.88 (t, 6H, $J$ = 7.04 Hz), 1.24−1.47 (36H), 1.78 (m, 4H), 2.54 (app s, 6H), 3.96 (t, 4H, $J$ = 6.59 Hz), 6.77 (app dd, 2H, $J$ = 3.60, 0.97 Hz), 6.87 (d, 4H, $J$ = 8.71 Hz), 7.45 (d, 4H, $J$ = 8.70 Hz), 7.52 (d, 2H, $J$ = 3.58 Hz), 7.75 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 14.10, 15.40, 22.68, 26.02, 29.19, 29.34, 29.38, 29.57, 29.59, 29.63, 31.92, 68.13, 88.17, 95.25, 114.63, 115.18, 120.15, 125.61, 126.85, 132.91, 133.14, 133.90, 138.80, 140.64, 159.47. UV−vis (**16-C4** (butoxy replaces dodecyloxy), $CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 358 (41 900), 326 (78 200) nm. Luminescence spectrum (**16-C4** (butoxy replaces dodecyloxy), $CHCl_3$) $\lambda_{max}$ (rel intensity): 422 nm. HRMS (FAB): found *m/z* 838.4802 ($M^+$); calcd for $C_{56}H_{70}O_2S_2$ *m/z* 838.4817. Anal. Calcd for $C_{40}H_{38}O_2S_2$ (**16-C4**, butoxy replaces dodecyloxy): C, 78.14; H, 6.23. Found: C, 78.51; H, 6.32.

**4,10-Bis(4-(dodecyloxy)phenyl)-2,8-dimethylbisthien[2,3-*a,h*]anthracene (17) and 4,11-Bis(4-(dodecyloxy)phenyl)-2,8-dimethylbisthien[2,3-*a,h*]anthracene (18).** Compounds **17** and **18** were prepared using the standard TFA-induced cyclization conditions. Chromatography on silica gel (4:3:1 hexanes/toluene/$CHCl_3$) provided a 6:5 mixture of the inseparable structural isomers **17**/**18** (82.5%). As compound **18** is asymmetric, its proton resonances are easily discernible from those of **17**. Compound **17**. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.88 (t, 6H, $J$ = 7.07 Hz), 1.24−1.47 (36H), 1.84 (quint, 4H), 2.64 (d, 6H, $J$ = 0.93 Hz), 4.04 (t, 4H, $J$ = 6.56 Hz), 7.036 (d, 4H, $J$ = 8.76 Hz), 7.192 (d, 2H, $J$ = 1.14 Hz), 7.58 (d, 4H, $J$ = 8.62 Hz), 7.75 (s, 2H), 8.55 (s, 2H). Compound **18**. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.88 (t, 6H, $J$ = 7.07 Hz), 1.24−1.47 (36H), 1.84 (quint, 4H), 2.65 (d, 3H, 1.02 Hz), 2.70 (d, 3H, $J$ = 0.89 Hz), 4.04 (t, 4H, $J$ = 6.56 Hz), 7.042 (br d, 4H, $J$ = 8.64 Hz), 7.199 (d, 1H, $J$ = 1.25 Hz), 7.59 (d, 2H, $J$ = 8.60 Hz), 7.74 (d, 2H, $J$ = 8.66 Hz), 7.770 (s, 1H), 7.775 (s, 1H), 7.83 (d, 1H, $J$ = 1.07 Hz), 8.57 (s, 1H), 8.76 (s, 1H). UV−vis (**17**/**18**, $CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 408 (10 700), 384 (18 700), 362 (24 600), 326 (142 000) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 426 nm. HRMS (FAB): found *m/z* 838.4823 ($M^+$); calcd for $C_{56}H_{70}O_2S_2$ (**17**/**18**) *m/z* 838.4817. LRMS (FAB): 838 (100, $M^+$), 670 (10, $M^+ - C_{12}H_{25}$), 460 (10). Anal. Calcd for $C_{56}H_{70}O_2S_2$ (**17**/**18**): C, 80.14; H, 8.41. Found: C, 79.68; H, 8.55.

**6,13-Bis(4-butoxyphenyl)-1,4,8,11-tetramethyldibenz[*a,h*]anthracene (19).** A 250 mL Schlenk flask was charged with **5** (butyloxy replaces dodecyloxy) (0.300 g, 0.476 mmol), 1,2,3-trichloropropane (150 mL), and difluoroacetic acid (15 mL). The mixture was subjected to three freeze−pump−thaw cycles and was then heated at 130 °C for 12 h. The mixture was allowed to cool and was diluted with 150 mL of $CH_2Cl_2$ before being washed with 5% NaOH (2 × 75 mL) and $H_2O$. The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure to provide a crude product which was purified by silica gel chromatography (1:1 hexanes/toluene). Crystallization from $CHCl_3$/*i*-PrOH provided compound **19** as a light yellow solid (0.222 g, 74.0%).

Alternately, the cyclized compound **10** (butoxy replaces dodecyloxy) may be exposed to identical conditions to provide **19** (>70% by NMR). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.07 (t, 6H, $J$ = 7.40 Hz), 1.60 (m, 4H), 1.89 (quint, 4H), 2.71 (s, 6H), 2.81 (s, 6H), 4.11 (t, 4H, $J$ = 6.50), 7.11 (d, 4H, $J$ = 8.55 Hz), 7.33 (d, 2H, $J$ = 7.48 Hz), 7.35 (d, 2H, $J$ = 7.65 Hz), 7.57 (d, 4H, $J$ = 8.51 Hz), 7.85 (s, 2H), 9.31 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 13.92, 19.33, 20.15, 26.51, 26.83, 31.43, 67.93, 114.52, 124.02, 126.42, 127.86, 129.69, 129.88, 129.93, 130.39, 131.17, 131.62, 132.57, 133.18, 133.69, 138.42, 158.69. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 410 (2230), 374 (20 600), 358 (20 600), 340 (17 300), 318 (72 200), 304 (77 300) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 412 (1), 436 (0.60) nm. HRMS (FAB): found *m/z* 630.3494 ($M^+$); calcd for $C_{46}H_{46}O_2$ *m/z* 630.3498.

**1,5-Dibromo-2,4-diiodobenzene.** Periodic acid (36.95 g, 0.162mol) was allowed to dissolve in 150 mL of concentrated $H_2SO_4$. To the colorless solution was slowly added KI (80.75 g, 0.487 mol), and the mixture was cooled to 0 °C. 1,3-Dibromobenzene (75 g, 0.318 mol) was quickly added in one portion, and the reaction mixture was allowed to stir for 30 min. The entire reaction was poured onto ice and filtered (glass frit), and the crude product was crystallized two times from THF/MeOH. 1,3-Dibromo-4,6-diiodobenzene was obtained as a colorless crystalline solid (155.04 g, 68.1%) (mp 164−165 °C, lit.[80] 166−167 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 7.81 (s, 1H), 8.26 (s, 1H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 100.40, 130.47, 135.30, 149.46. HRMS ($CH_4$ CI, positive ion): found *m/z* 485.6635 ($M^+$); calcd for $C_6H_2Br_2I_2$ *m/z* 485.6613. Anal. Calcd for $C_6H_2Br_2I_2$: C, 14.78; H, 0.41. Found: C, 15.16; H, 0.53.

**1,5-Dibromo-2,4-bis((4-(dodecyloxy)phenyl)ethynyl)benzene (20).** Compound **20** was prepared in an analogous fashion to compound **1** only replacing 1,4 dibromo-2,5-diiodobenzene with 1,5-dibromo-2,4-diiodobenzene. The compound was isolated by removing ca. three-fourths of the reaction solvent under reduced pressure and diluting the remaining solvent with benzene. The organics were washed with 5% HCl, $H_2O$, 5% $NH_4OH$, and $H_2O$ before being dried ($MgSO_4$). The solvent was reduced to ca. one-third volume, and the crude product was precipitated by the addition of MeOH/acetone. The solid was filtered and recrystallized two times from *n*-hexane. Compound **20** was obtained as an off-white amorphous solid (88.3%) (mp 111−112 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.89 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.78 (m, 4H), 3.94 (t, 4H, $J$ = 6.25 Hz), 6.86 (d, 4H, $J$ = 8.45 Hz), 7.48 (d, 4H), $J$ = 8.37 Hz), 7.65 (s, 1H), 7.83 (s, 1H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.14, 22.71, 26.01, 29.08, 29.39, 29.65, 31.93, 68.06, 85.53, 95.60, 114.23, 114.55, 124.50, 125.07, 133.20, 135.49, 135.93, 159.75. HRMS ($CH_4$ CI, positive ion): found *m/z* 634.1090 ($M^+$); calcd for $C_{34}H_{36}O_2Br_2$ (side chains = -$OC_6H_{13}$) *m/z* 634.1082.

**4′,6′-Bis((4-(dodecyloxy)phenyl)ethynyl)[1,1′:3′,1″]terphenyl (21).** Compound **21** was prepared in an analogous fashion to compound **3** only replacing 2,5-dibromo-1,4-bis((4-(dodecyloxy)phenyl)ethynyl)-benzene (**1**) with 1,5-dibromo-2,4-bis((4-(dodecyloxy)phenyl)ethynyl)-benzene (**20**). Purification by silica gel chromatography (15:1 hexanes/THF) provided **21** as an off-white solid in 80.9% yield (mp 65−68

°C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.91 (t, 6H, $J$ = 7.12 Hz), 1.26−1.47 (m, 36H), 1.78 (m, 4H), 3.95 (t, 4H, $J$ = 6.54 Hz), 6.83 (d, 4H, $J$ = 8.74 Hz), 7.30 (d, 4H, $J$ = 8.74 Hz), 7.41 (t, 2H, $J$ = 7.47 Hz), 7.48 (t, 4H, $J$ = 7.72 Hz), 7.51 (s, 1H), 7.75 (d, 4H, $J$ = 7.18 Hz), 7.91 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 14.12, 22.68, 26.00, 29.17, 29.35, 29.37, 29.57, 29.60, 29.63, 31.92, 68.06, 87.26, 93.11, 114.51, 115.20, 120.96, 127.66, 127.90, 129.30, 130.54, 132.82, 136.72, 140.01, 142.88, 159.26. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 314 (74 400) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 388 nm. HRMS (FAB): found *m/z* 798.5395 ($M^+$); calcd for $C_{58}H_{70}O_2$ *m/z* 798.5376. Anal. Calcd for $C_{58}H_{70}O_2$: C, 87.17; H, 8.83. Found: C, 87.45; H, 8.97.

**5,9-Bis(4-(dodecyloxy)phenyl)dibenz[*a,j*]anthracene (22).** Compound **22** was prepared in an analogous fashion to compound **6**, using compound **21** as the starting material. Purification by silica gel chromatography (20:1 hexanes/THF) provided **22** as a yellow solid in 95.7% yield. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.90 (t, 6H, $J$ = 7.05 Hz), 1.23−1.42 (32H), 1.48−1.54 (m, 4H), 1.82−1.88 (m, 4H), 4.05 (t, 4H, $J$ = 6.56 Hz), 7.05 (d, 4H, $J$ = 8.60 Hz), 7.50 (d, 4H, $J$ = 8.58), 7.58 (td, 2H, $J$ = 7.60, 1.05 Hz), 7.75 (td, 2H, $J$ = 7.60, 1.05 Hz), 7.77 (s, 2H), 7.98 (dd, 2H, $J$ = 8.20, 1.00 Hz), 8.29 (s, 1H), 9.08 (d, 2H, $J$ = 8.07 Hz), 10.06 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 14.11, 22.70, 26.14, 29.38, 29.46, 29.64, 29.69, 31.94, 68.16, 114.38, 116.08, 123.05, 126.62, 126.70, 127.21, 127.26, 127.30, 128.40, 130.78, 131.05, 131.13, 131.70, 132.87, 138.76, 158.71. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 400 (1270), 380 (2820), 350 (23 700), 318 (85 200), 266 (44 300) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 410 (1), 432 (0.69) nm. HRMS (FAB): found *m/z* 798.5360 ($M^+$); calcd for $C_{58}H_{70}O_2$ *m/z* 798.5376. Anal. Calcd for $C_{58}H_{70}O_2$: C, 87.17; H, 8.83. Found: C, 87.18; H, 8.88.

**1,5-Bis(dibenzo[*b,d*]thiophen-4-yl)-2,4-bis((4-(dodecyloxy)-phenyl)ethynyl)benzene (23).** Compound **23** was prepared as described for compound **2**, substituting 4-dibenzothiopheneboronic acid for 2,5-(dimethoxy)phenylboronic acid and **20** for **1**. The crude product was crystallized once from THF/MeOH and once from acetone/$CHCl_3$. Compound **23** was obtained as a colorless solid in 78.4% yield (mp 165−169 °C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.87 (t, 6H, $J$ = 7.01 Hz), 1.24−1.42 (m, 40H), 1.72 (quint, 4H, $J$ = 7.75 Hz), 3.87 (t, 4H, $J$ = 6.56 Hz), 6.70 (d, 4H, $J$ = 8.81 Hz), 7.03 (d, 4H, $J$ = 8.80 Hz), 7.43 (m, 4H), 7.58 (t, 2H, $J$ = 7.61 Hz), 7.73 (dd, 2H, $J$ = 7.40, 0.92 Hz), 7.80 (dd, 2H, $J$ = 6.80, 2.32 Hz), 7.95 (s, 1H), 8.01, (s, 1H), 8.18 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$, partial): $\delta$ 13.98, 22.68, 25.97, 29.13, 29.34, 29.57, 29.64, 31.91, 68.04, 86.66, 94.08, 114.42, 114.88, 120.91, 121.64, 122.73, 122.96, 124.23, 126.68, 128.35, 130.02, 132.88, 135.00, 135.78, 135.92, 136.32, 139.75, 139.79, 141.53, 159.27. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 318 (73 800), 298 (58 400) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 394 nm. HRMS (FAB): found *m/z* 842.3267 ($M^+$); calcd for $C_{58}H_{50}O_2S_2$ (**23-C6**) *m/z* 842.3252. Anal. Calcd for $C_{58}H_{50}O_2S_2$ (**23-C6**): C, 82.62; H, 5.98. Found: C, 82.24; H, 6.04. Anal. Calcd for $C_{70}H_{74}O_2S_2$: C, 83.12; H, 7.37. Found: C, 83.30; H, 7.37.

**8,12-Bis(4-(dodecyloxy)phenyl)-9,11-diiodobis(dibenzo[*b,d*]-thiophene)[4,3-*a*:3′,4′-*j*]anthracene (24).** To a 50 mL Schlenk tube containing $I_2$ (0.40 g, 1.57 mmol) was added 14.56 mL of a $Hg(TFA)_2$/$CH_2Cl_2$ solution (0.03 M, 0.437 mmol) followed by 2,6-lutidine (50 $\mu$L, 0.429 mmol). The mixture was cooled to 0 °C and allowed to stir for 15 min before a solution of **23** (0.16 g, 0.190 mmol) dissolved in 5 mL of $CH_2Cl_2$ was added. After 20 min of stirring, maintaining the temperature at 0 °C, the reaction was quenched with 5% NaOH (15 mL). The mixture was diluted with $CHCl_3$, washed with additional 5% NaOH (2 × 30 mL), $H_2O$, 5% HCl (2 × 30 mL), and $H_2O$, and dried ($Na_2SO_4$), and the solvent was removed in vacuo. The crude product was chromatographed on silica gel (1:1 hexanes/toluene) to provide **24** as a bright yellow solid (0.192 g, 92.3%) (mp 202−204 °C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.89 (t, 6H, $J$ = 7.10 Hz), 1.24−1.44 (m, 36H), 1.54 (quint, 4H, $J$ = 7.72 Hz), 1.88 (quint, 4H, $J$ = 7.93 Hz), 4.10 (t, 4H, $J$ = 6.53 Hz), 7.11 (d, 4H, $J$ = 8.64 Hz), 7.27 (d, 4H, $J$ = 8.59 Hz), 7.50 (m, 4H), 7.66 (d, 2H, $J$ = 8.55 Hz), 7.94 (ddd, 2H, $J$ = 7.35, 1.99, 0.94 Hz), 8.23 (d, 2H, 8.68 Hz) overlapping with 8.23 (dd, 2H, $J$ = 7.38, 2.05 Hz), 9.67 (s, 1H), 11.12 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 14.12, 22.71, 26.21, 29.38, 29.45, 29.51, 29.66, 31.94, 68.15, 107.14, 114.45, 120.73, 121.71, 122.16, 122.45, 124.79, 126.45, 126.54, 126.91, 128.98, 131.14, 132.69, 133.15, 134.98, 135.05, 135.34, 138.02, 140.01, 141.33, 146.55, 158.96. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 432 (5070), 402 (18 400), 384 (26 400), 356 (57 600), 338 (48 900), 286 (106 000), 258 (72 000) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 436 (1), 462 (0.63) nm (very low intensity). HRMS (FAB): found *m/z* 1094.1161 ($M^+$); calcd for $C_{58}H_{48}I_2O_2S_2$ (**24-C6**) *m/z* 1094.1184. Anal. Calcd for $C_{58}H_{48}I_2O_2S_2$ (**24-C6**): C, 63.62; H, 4.42. Found: C, 63.84; H, 4.96.

**8,12-Bis(4-(dodecyloxy)phenyl)bis(dibenzo[*b,d*]thiophene)[4,3-*a*:3′,4′-*j*]anthracene (25).** Compound **24** (0.110 g, 0.100 mmol) was dissolved in 35 mL of THF and cooled to −78 °C. To the solution was added *s*-BuLi (1.5 mL, 1.53 M, 0.98 mmol) resulting in the formation of a deep green solution. After 4 min of stirring, the reaction was quenched by the rapid addition of 3 mL of MeOH. The mixture was diluted with 100 mL of $CHCl_3$, and the organic layer was washed with 5% HCl (2 × 30 mL) and $H_2O$ and dried ($Na_2SO_4$) before removal of the solvent in vacuo. The residue was purified by silica gel chromatography (7:7:1 hexanes/toluene/$CHCl_3$) to afford **25** as a bright yellow solid (0.082 g, 96.8%) (mp 194−195 °C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.91 (t, 6H, $J$ = 7.05 Hz), 1.37−1.44 (m, 36H), 1.52 (quint, 4H, $J$ = 6.75 Hz), 1.85 (quint, 4H, $J$ = 8.02 Hz), 4.03 (t, 4H, $J$ = 6.56 Hz), 7.02 (d, 4H, $J$ = 8.57 Hz), 7.45 (d, 4H, $J$ = 8.53 Hz), 7.52 (m, 4H), 7.75 (s, 2H), 8.03 (m, 2H) overlapped with 8.04 (d, 2H, $J$ = 8.58 Hz), 8.25 (m, 2H), 8.285 (d, 2H, $J$ = 8.67 Hz), 8.290 (s, 1H), 11.01 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 14.12, 22.71, 26.17, 29.39, 29.41, 29.50, 29.67, 29.72, 31.95, 68.16, 114.37, 119.94, 121.55, 121.88, 122.36, 124.57, 124.61, 126.59, 127.22, 127.45, 127.67, 127.84, 130.99, 131.14, 132.05, 133.23, 134.49, 135.09, 135.47, 139.58, 139.85, 158.72. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 430 (4440), 380 (28 200), 350 (71 200), 334 (51 100), 296 (63 800), 280 (85 300), 266 (67 200) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 434 nm. HRMS (FAB): found *m/z* 1010.5088 ($M^+$); calcd for $C_{70}H_{74}O_2S_2$ *m/z* 1010.5130. Anal. Calcd for $C_{70}H_{74}O_2S_2$: C, 83.12; H, 7.37. Found: C, 83.24; H, 7.45.

**2,4-Bis((4-(dodecyloxy)phenyl)ethynyl)-1,5-bis(5-methylthiophen-2-yl)benzene (26).** Compound **26** was prepared as described for **16**, substituting the dibromide **20** for **1**. The crude product was purified by silica gel chromatography (6:1 hexanes/ethyl acetate) to afford **26** as a yellow solid in 98.4% yield. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.86 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.77 (m, 4H), 2.55 (app s, 6H), 3.96 (t, 4H, $J$ = 6.53 Hz), 6.80 (dd, 2H, $J$ = 3.60, 0.89 Hz), 6.88 (d, 4H, 8.77 Hz), 7.47 (d, 4H, $J$ = 8.76 Hz), 7.58 (d, 2H, $J$ = 3.59 Hz), 7.74 (s, 1H), 7.82 (s, 1H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.12, 15.39, 22.68, 26.00, 29.17, 29.37, 29.62, 31.91, 68.02, 87.62, 94.61, 114.52, 115.18, 118.59, 125.69, 127.05, 127.85, 132.79, 135.08, 138.50, 139.20, 140.88, 159.31. HRMS (FAB): found *m/z* 838.4839 ($M^+$); calcd for $C_{56}H_{70}O_2S_2$ *m/z* 838.4817.

**4,8-Bis(4-(dodecyloxy)phenyl)-2,10-dimethylbisthien[2,3-*a*:3′,2′-*j*]anthracene (27) and 4,7-Bis(4-(dodecyloxy)phenyl)-2,10-dimethylbisthien[2,3-*a*:3′,2′-*j*]anthracene (28).** Compounds **27** and **28** were prepared using standard acid cyclization conditions. Silica gel chromatography (3:2 hexanes/toluene) provided a 6:1 mixture (69%) of the inseparable structural isomers **27**/**28**. Due to the small amount present and the apparent overlap of several resonances with **27**, the structure **28** can only be *tentatively* assigned. Compound **27**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.86 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (36H), 1.83 (m, 4H), 2.67 (app s, 6H), 4.03 (t, 4H, $J$ = 6.55 Hz), 7.03 (d, 4H, $J$ = 8.60 Hz), 7.20 (d, 2H, $J$ = 0.87 Hz), 7.57 (d, 4H, $J$ = 8.57), 7.70 (s, 2H), 8.43 (s, 1H), 8.65 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 16.18, 22.67, 26.09, 29.33, 29.41, 29.60, 31.90, 68.14, 114.50, 115.63, 123.29, 124.62, 126.87, 128.23, 129.43, 130.13, 133.27, 135.19, 136.38, 137.18, 139.57, 158.74. UV−vis (**27**/**28**, $CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 416 (6130), 392 (8800), 370 (8680), 328 (103 000). Luminescence spectrum (**27**/**28**, $CHCl_3$) $\lambda_{max}$ (rel intensity): 426 (1), 452 (0.65) nm. HRMS (FAB): found *m/z* 838.4826 ($M^+$); calcd for $C_{56}H_{70}O_2S_2$ (**27**/**28**) *m/z* 838.4817.

**2,4-Bis((4-(hexyloxy)phenyl)ethynyl)-1,5-bis(2,2′-bithiophene-5-yl)benzene (29) and 1-Bromo-2,4-bis((4-(hexyloxy)phenyl)ethynyl)-5-(2,2′-bithiophene-5-yl)benzene (30).** To a cooled (−50 °C) solution of 2,2′-bithiophene (0.330 g, 1.98 mmol) dissolved in 10 mL of THF was added n-BuLi (1.28 mL, 1.55 M, 1.98 mmol). After 20 min of stirring, a solution of $ZnCl_2$ (0.338 g, 2.48 mmol) in 10 mL of THF

was added via cannula. The solution was allowed to warm to room temperature and stir for an additional 10 min before being transferred to another flask containing 1,5-dibromo-2,4-bis((4-(hexyloxy)phenyl)-ethynyl)benzene ($C_6$ side chain version of **20**) (1.25 g, 1.97 mmol) and $(Ph_3P)_2PdCl_2$ (0.028 g, 0.040 mmol) predissolved in 10 mL of THF. The reaction was allowed to stir at rt for 14 h before being carefully quenched with MeOH. The mixture was diluted with diethyl ether, washed with $H_2O$, and dried ($MgSO_4$), and the solvent was concentrated under reduced pressure. The crude mixture was separated by column chromatography using alumina as the stationary phase (12:1 hexanes/EtOAc) to provide two major fractions. The first fraction was further purified by performing a second column using the same conditions to afford compound **30** as a yellow solid (0.49 g, 34.7%) (mp 97−100 °C). The second fraction from the first column was further purified by performing a second column using alumina as the stationary phase (8:1 hexanes/EtOAc eluent). Compound **29** was isolated as a yellow solid (0.276 g, 17.4%) (mp 108−111 °C). Compound **29**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.89 (t, 6H, $J$ = 6.30 Hz), 1.1−1.5 (12H), 1.75 (m, 4H), 3.91 (t, 4H, $J$ = 6.55 Hz), 6.84 (d, 4H, $J$ = 8.82 Hz), 6.99 (dd, 2H, $J$ = 5.03, 3.66 Hz), 7.17 (m, 6H), 7.44 (d, 4H, $J$ = 8.72 Hz), 7.62 (d, 2H, $J$ = 3.87 Hz), 7.76 (s, 1H), 7.77 (s, 1H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.04, 22.59, 25.68, 29.15, 31.57, 68.05, 87.59, 95.72, 114.58, 115.00, 119.08, 123.71, 123.82, 124.50, 127.40, 127.76, 127.90, 132.87, 134.32, 137.37, 138.04, 138.54, 140.14, 159.44. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 366 (60 300), 258 (31 500) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 446 nm. HRMS (FAB): found *m/z* 806.2367 ($M^+$); calcd for $C_{50}H_{46}O_2S_4$ *m/z* 806.2381. Anal. Calcd for $C_{50}H_{46}O_2S_4$: C, 74.40; H, 5.74. Found: C, 74.30; H, 5.82. Compound **30**. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.88 (t, 6H, $J$ = 6.8 Hz), 1.1−1.5 (12H), 1.72 (m, 4H), 3.87 (t, 4H, $J$ = 6.50 Hz), 6.81 (br d, 4H, $J$ = 8.69 Hz), 6.96 (t, 1H, $J$ = 3.75 Hz), 7.13 (m, 3H), 7.42 (d, 2H, $J$ = 8.38 Hz), 7.45 (d, 2H, $J$ = 8.28 Hz), 7.54 (d, 1H, $J$ = 3.94 Hz), 7.65 (s, 1H), 7.76 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 14.00, 22.58, 25.68, 29.15, 31.56, 68.12, 86.20, 86.97, 95.42, 95.93, 114.58, 114.61, 114.70, 114.78, 119.54, 123.84, 123.89, 124.32, 124.70, 124.75, 127.94, 128.08, 131.41, 132.91, 133.23, 133.27, 135.30, 137.21, 137.39, 138.63, 139.00, 159.65, 159.69. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 380 (35 200), 328 (60 300), 262 (30 100) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 436 nm. HRMS (FAB): found *m/z* 720.1748 ($M^+$); calcd for $C_{42}H_{41}O_2BrS_2$ *m/z* 720.1731.

**4,8-Bis(4-(hexyloxy)phenyl)-2,10-bis(thiophen-2-yl)bisthien[2,3-*a*:3′,2′-*j*]anthracene (31) and 4,7-Bis(4-(hexyloxy)phenyl)-2,10-bis-(thiophen-2-yl)bisthien[2,3-*a*:3′,2′-*j*]anthracene (32).** A 200 mL Schlenk flask was charged with **29** (0.100 g, 0.124 equiv) and 110 mL of 1,2-dichloroethane. The solution was subjected to two freeze−pump−thaw cycles before TFA (1.5 mL) was added and the solution was heated to 65 °C. After 4 h, the reaction was allowed to cool to rt and was diluted with 50 mL of $CHCl_3$. The organics were washed with 5% NaOH (2 × 40 mL) and $H_2O$ (40 mL), dried ($Na_2SO_4$), and concentrated in vacuo. Silica gel chromatography (1:1 hexanes/$CHCl_3$) afforded a 6:1 mixture of the inseparable structural isomers **31**/**32** as a bright yellow solid (0.055 g, 55.0%). Due to the small amount present and the apparent overlap of resonances with **31**, the structure **32** can only be *tentatively* assigned. Compound **31**. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.93 (t, 6H, $J$ = 7.08 Hz), 1.37 (m, 8H), 1.51 (m, 4H), 1.85 (quint, 4H), 4.06 (t, 4H, $J$ = 6.54 Hz), 7.06 (d, 4H, $J$ = 8.67 Hz), 7.08 (dd, 2H, $J$ = 5.03, 3.66 Hz), 7.29 (dd, 2H, $J$ = 5.09, 1.10 Hz), 7.35 (dd, 2H, $J$ = 3.55, 1.07 Hz), 7.58 (s, 2H), 7.59 (d, 4H, $J$ = 8.61), 7.72 (s, 2H), 8.42 (s, 1H), 8.72 (s, 1H). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 14.10, 22.66, 25.81, 29.34, 31.66, 68.08, 114.49, 115.66, 120.97, 124.55, 125.00, 126.29, 127.91, 128.17, 129.35, 129.67, 130.11, 132.76, 135.08, 136.11, 136.30, 137.14, 137.60, 158.74. UV−vis (**31**/**32**, $CHCl_3$) $\lambda_{max}$ ($\epsilon$, $cm^{-1}$ $M^{-1}$): 440 (8120), 406 (28 200), 370 (93 000), 358 (92 800), 340 (75 400), 322 (67 100) nm. Luminescence spectrum ($CHCl_3$) $\lambda_{max}$ (rel intensity): 452 (1), 480 (0.70) nm. HRMS (FAB): found *m/z* 806.2350 ($M^+$); calcd for $C_{50}H_{46}O_2S_4$ (**31**/**32**) *m/z* 806.2381. LRMS (FAB): 823 (10), 806 (100, $M^+$), 798 (10), 460. Anal. Calcd for $C_{50}H_{46}O_2S_4$ (**31**/**32**): C, 74.40; H, 5.74. Found: C, 74.12; H, 5.94.

**1,2-Dibromo-3,6-bis((4-butoxyphenyl)ethynyl)-4,5-dimethylbenzene (33).** A mixture of 3,4-dibromo-2,6-diiodo-*o*-xylene (5.171 g, 10.0 mmol, 1 equiv), bis(triphenylphosphino)palladium(II) chloride (130 mg, 0.19 mmol, 19 mol %), and cuprous iodide (65 mg, 0.34 mmol, 3.4 mol %) in a 200 mL Schlenk flask was evacuated and back-filled with argon. Toluene (100 mL) was added with vigorous stirring followed by diisopropylamine (4.5 mL, 32 mmol, 3.2 equiv). The mixture was allowed to stir for about 5 min during which time it became progressively more red. 4-(Butyloxy)phenylacetylene (4.20 g, 24 mmol, 2.4 equiv) was added dropwise over a period of about 10 min. The reaction was heated at 70 °C for 24 h, cooled, and filtered through silica gel using chloroform (300 mL). The solvent was removed under reduced pressure, and the resulting black sludge was stirred with ether (125 mL), filtered, and washed with ether to give **34** (4.879 g, 80%) as a pale yellow powder which was essentially pure. An analytically pure sample was obtained by recrystallization from THF/MeOH (mp 136−137 °C). $^1$HNMR (250 MHz, $CDCl_3$): $\delta$ 0.99 (t, 6H, $J$ = 7.32 Hz), 1.50 (m, 4H), 1.79 (m, 4H), 2.51 (s, 6H), 3.99 (t, 4H, $J$ = 6.50 Hz), 6.90 (d, 4H, $J$ = 8.77 Hz), 7.51 (d, 4H, $J$ = 8.77 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 13.82, 19.21, 19.28, 31.23, 67.84, 87.44, 99.50, 114.66, 114.78, 125.38, 126.54, 133.10, 138.59, 159.74. HRMS (FAB): found *m/z* 606.0777 ($M^+$); calcd for $C_{32}H_{32}O_2Br_2$ *m/z* 606.0768.

**1,2-Diiodo-3,6-bis((4-butoxyphenyl)ethynyl)-4,5-dimethylbenzene (34).** A mixture of cuprous iodide (22.3 g, 117 mmol, 23 equiv), potassium iodide (45 g, 270 mmol, 54 equiv), and **34** (3.03 g, 5 mmol) in a 500 mL Schlenk flask was evacuated and back-filled with argon. DMF (200 mL) was added with vigorous stirring, and the mixture was heated to 145−150 °C for 90 h. After cooling, a significant portion (150−170 mL) of the DMF was removed under reduced pressure, and the mixture was diluted with chloroform (500 mL) and filtered through silica gel, which was washed with more chloroform (500 mL). The combined filtrate and washings were washed with concentrated ammonium hydroxide (4 × 800 mL), and the solvent was removed under reduced pressure. The yellow black sludge was stirred with ether (125 mL), filtered, and washed successively with ether, water, and cold acetone to give **35** (2.96 g, 84%) as a pale yellow solid which was essentially pure. A single recrystallization from THF/MeOH provided analytically pure compound (mp 174−176 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.98 (t, 6H, $J$ = 7.39 Hz), 1.50 (m, 4H), 1.79 (m, 4H), 2.53 (s, 6H), 3.99 (t, 4H, $J$ = 6.53 Hz), 6.89 (d, 4H, $J$ = 8.79 Hz), 7.51 (d, 4H, $J$ = 8.71 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 13.82, 19.21, 20.00, 31.23, 67.84, 92.95, 98.06, 112.19, 114.66, 114.77, 130.62, 132.96, 138.71, 159.75. HRMS (FAB): found *m/z* 702.0403 ($M^+$); calcd for $C_{32}H_{32}I_2O_2$ *m/z* 702.0410.

**3′,6′-Bis((4-butoxyphenyl)ethynyl)-4′,5′-dimethyl[1,1′:2′,1″]terphenyl (35).** A mixture of diiodide **34** (545 mg, 0.78 mmol), phenylboronic acid (1.03 g, 8.4 mmol, 11 equiv), palladium bis-(dibenzylideneacetone) (28 mg, 0.05 mmol, 6 mol %), potassium hydroxide powder (2.15 g, 38 mmol, 49 equiv), and triphenylphosphine (0.29 g, 1.1 mmol, 1.4 equiv) in a 200 mL Schlenk flask was evacuated and back-filled with argon. Nitrobenzene (40 mL) was added with vigorous stirring followed by water (12 mL). The reaction mixture was purged with argon for about 30 min and then heated to 100 °C for 16 h. After cooling, the reaction was diluted with ether (250 mL). The organic layer was washed with 2 M potassium hydroxide (2 × 100 mL) and 10% hydrochloric acid (2 × 100 mL) and filtered through silica gel which was washed with ether (150 mL). The solvents were removed under reduced pressure, and the brown sludge was dissolved in chloroform (10 mL) and filtered to remove insolubles. The filtrate was diluted with methanol (300 mL), and the product precipitated. This was filtered and washed with methanol. The filtrate and washings were evaporated under reduced pressure. The brown solid was coated onto silica gel from methylene chloride, loaded onto a silica gel column, and eluted with 60% hexane/40% toluene mixture. The solid was then dissolved in chloroform (1 mL), diluted with methanol (30 mL), filtered, and washed with methanol. This gave **35** (441 mg, 94%) as a pale yellow solid which was essentially pure (mp 149−151 °C). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.95 (t, 6H, $J$ = 7.42 Hz), 1.46 (m, 4H), 1.74 (m, 4H), 2.62 (s, 6H), 3.92 (t, 4H, $J$ = 6.57 Hz), 6.73 (d, 4H, $J$ = 8.75 Hz), 7.00 (d, 4H, $J$ = 8.78 Hz), 7.16 (s, 10H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 13.82, 18.61, 19.19, 31.21, 67.72, 87.80, 98.40, 114.38, 115.55, 123.25, 126.20, 127.04, 130.81, 132.62, 137.09, 140.48, 141.23, 159.04. HRMS (FAB): found *m/z* 602.3193 ($M^+$); calcd for $C_{44}H_{42}O_2$ *m/z* 602.3185.

**1,6-Bis(4-butoxyphenyl)-3,4-dimethyldibenzo[*c*,*g*]phenanthrene (37).** To a solution of 120 mg of **35** (0.2 mmol) in 50 mL of $CH_2Cl_2$

contained in a flask wrapped in aluminium foil was added 140 mg of silver triflate (0.54 mmol). After 4 h, 0.6 g of iodine (2.4 mmol) was added, and the reaction was allowed to stir for a further 8 h. The reaction was quenched by addition of 10 mL each of 2 M KOH and saturated $NH_4Cl$ solutions. The organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo yielding 130 mg of a black solid. Silica gel chromatography (65:35 hexanes/toluene) gave **37** as a bright yellow solid (24 mg, 20%) (mp 186−189 °C). $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.43 (d, 2H, $J$ = 8.5 Hz, H(1)), 8.08 (s, 2H, H(6)), 7.96 (dd, 2H, $J$ = 7.7, 0.5 Hz, H(4)), 7.62 (d, 4H, $J$ = 8.5 Hz, OC═CHC*H*), 7.38 (dd, $J$ = 7.1, 7.1 Hz, H(3)), 7.20 (dd, 2H, $J$ = 7.1, 7.1 Hz, H(2)), 7.10 (d, 4H, $J$ = 8.5 Hz, OC═C*H*), 4.08 (t, 4H, $J$ = 6.5 Hz, OC$H_2$), 2.78 (s, 6H, C═C$CH_3$), 1.88−1.82 (m, 4H, OC$H_2$$CH_2$), 1.59−1.51 (m, 4H, $CH_3$C$H_2$), 1.03 (t, 6H, $J$ = 7.4 Hz, $CH_2$C$H_3$). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 158.72, 138.52, 133.28, 131.61, 131.20, 130.99, 130.61, 130.55, 130.07, 125.92, 125.69, 124.90, 124.25, 122.6, 114.47, 67.86, 31.44, 19.33, 15.97, 13.89. HRMS (FAB): found *m/z* 602.3178 ($M^+$); calcd for $C_{44}H_{42}O_2$ *m/z* 602.3185.

**4,11-Bis(4-butoxyphenyl)-1,2-dimethylbenzo[*ghi*]perylene (38).** To a solution of **37** (12.5 mg, 0.02 mmol, 1 equiv) in benzene (500 mL) were added iodine (94 mg, 0.37 mmol, 18.5 equiv) and propylene oxide (2 mL, 28 mmol, 1400 equiv). The solution was irradiated through pyrex for 2 h and then evaporated under reduced pressure. The crude material was filtered through a plug of silica gel using a 1:1 toluene/hexane solution. Careful chromatography on silica gel with 3:1 hexane/toluene gave **38** (5 mg, 40%) as a yellow solid (mp 207−209 °C). $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 9.06 (d, 2H, $J$ = 8.1 Hz), 8.33 (s, 2H), 8.25 (d, 2H, $J$ = 7.8 Hz), 7.94 (dd, 2H, $J$ = 8, 8 Hz), 7.65 (d, 4H, $J$ = 9 Hz), 7.13 (d, 4H, $J$ = 8.7 Hz), 4.12 (t, 4H, $J$ = 6.3 Hz), 3.05 (s, 6H), 1.90−1.83 (m, 4H), 1.62−1.50 (m, 4H), 0.86 (t, 6H, $J$ = 7.7 Hz). HRMS (EI): found *m/z* 600.3024 ($M^+$); calcd for $C_{44}H_{40}O_2$ *m/z* 600.3028.

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**Supporting Information Available:** Synthetic procedures and spectral data for the synthesis of 4-(dodecyloxy)phenylacetylene including UV, emission, $^1$H NMR, and $^{13}$C NMR spectra of most of the compounds reported (105 pages). See any current masthead page for ordering and Internet access instructions.

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