Synthesis of Ethynyl-Substituted Quinquephenyls and Conversion to Extended Fused-Ring Structures†

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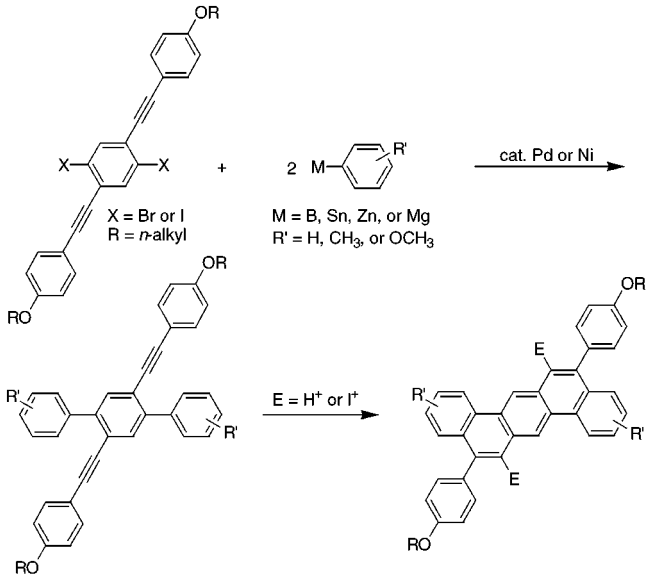
An organometallic coupling, electrophile-induced cyclization strategy for the synthesis of *p*-terphenyl compounds has been extended to the synthesis of *p*-quinquephenyl systems. In this work we report the synthesis of various polycyclic aromatic systems containing nine annelated rings including the synthesis of functionalized polycyclic aromatic systems. An interesting side reaction which leads to an indenyl spiro ring system is also described. This side reaction can be suppressed by changing the electrophile (from H^+ to I^+) or by modification of the cyclization precursor. The UV−vis and fluorescence spectra of several of these polycyclic aromatics and the *p*-quinquephenyl precursors are also reported.

Introduction

Extensively conjugated molecular and polymeric materials are critical components for a large number of advanced technologies. Molecule-based sensory,[1] nonlinear optical,[2] photo- and electroluminescent devices,[3] and photovoltaic devices[4] derive function from highly conjugated materials which can transform an applied bias or optical input to a desired response. Future breakthroughs in molecular electronics will be dependent on the ability to produce conjugated structures with well-defined geometries and functionality. This ability will be aided by improvements in synthetic methodology available for the synthesis of extensively conjugated systems. One structural class of interest is the fused polycyclic aromatics which possess planar structure and are extensively conjugated. These systems provide a rigid well-defined structure which does not display conformational uncertainities.

Recently we have described useful synthetic methodology for the preparation of fused polycyclic aromatics.[5] This method utilizes a two-step protocol wherein *p*-alkoxyphenylethynyl-substituted aromatics are first prepared using metal-catalyzed cross-coupling chemistries. In the key step the ethynyl-substituted precursor compound is transformed to a fused-ring system via an electrophile-induced cyclization reaction. The reaction may be effected with common electrophiles such as trifluoroacetic acid (TFA) or iodonium trifluoroacetate and proceeds under extremely mild conditions (CH_2Cl_2 as solvent, room temperature). This methodology has been used to prepare benzenoid as well as benzenoid/thiophene-containing ring systems. The high-yielding reaction sequence combined with the mild conditions employed during the key ring-forming transformation make this procedure amenable to the preparation of gram quantities of product. This is in contrast to other commonly employed procedures such as photochemical cyclization[6,7] or metal carbene[8−13] and vinyl ketene annulations,[14−17] which require extremely dilute conditions and/or multistep synthetic sequences and are therefore amenable to the production of only limited quantities of material. Hence, this convenient two-step protocol serves as an attractive complement to existing methods used for the synthesis of fused aromatics.



† Part of this work was taken from the thesis of M.B.G. completed at the University of Pennsylvania.

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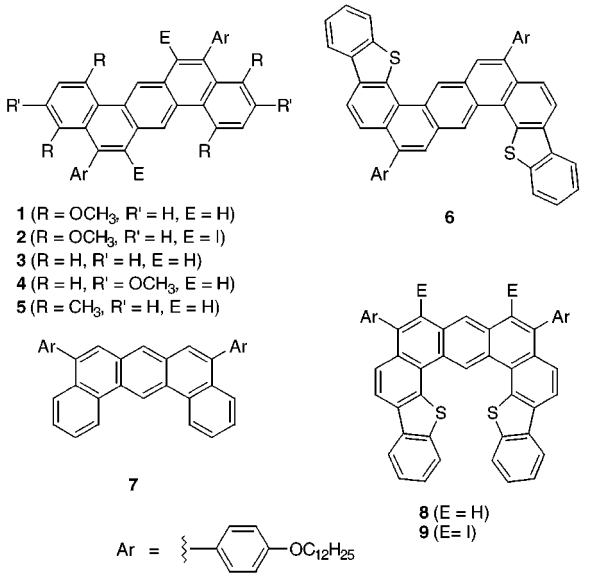
Chart 1



Examples of compounds prepared by the electrophile-induced cyclization reaction are depicted in Chart 1.[5] To date the majority of compounds prepared have been substituted dibenzo[*a*,*h*]anthracene (**1**−**6**) and dibenzo-[*a*,*j*]anthracene (**7**−**9**) ring systems. To further determine the scope of the reaction we have examined several additional structural variants. In one case we have examined the ability to functionalize the iodide positions of **2** and determine whether steric crowding will limit functionalization of iodonium cyclized ring systems. More important, however, we have prepared *p*-quinquephenyl precursor systems in order to prepare compounds with a greater number of annelated rings than formed in previously reported systems. Described below are the syntheses of several *p*-quinquephenyl systems and their cyclization to produce in certain cases compounds containing nine annelated rings. Also described is a side reaction which was observed and produced an interesting indenyl spiro ring system.

Results and Discussion

As part of our efforts to investigate the scope of the cyclization reaction we reexamined the diiodide **2.** When **2** was treated with an excess of *p*-methoxyphenylboronic acid under modified Suzuki cross-coupling conditions, the product **10** was isolated in 95% yield (Scheme 1).[5,18] This result was encouraging as it demonstrated that the dibenzo[*a*,*h*]anthracene ring systems could be highly functionalized to yield sterically crowded products. The effect of the added *p*-methoxyphenyl groups on the dibenzo[*a*,*h*]anthracene ring system was minimal as evidenced by the UV−vis absorption spectra (see Figure 1). Compounds **1**, **2**, and **10** exhibit nearly identical absorption spectra with absorption maxima of 318, 328, and 324 nm, respectively. The presence of low-energy bands on the low-energy side of λ_{max} is unchanged, with the lowest energy transitions appearing at 430, 436, and

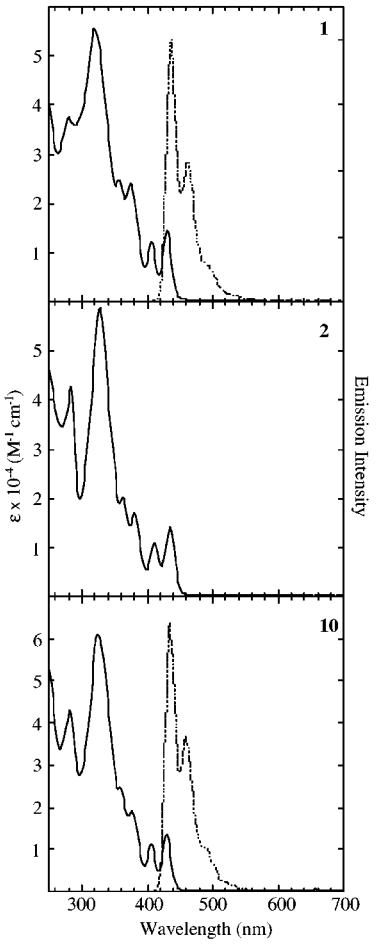
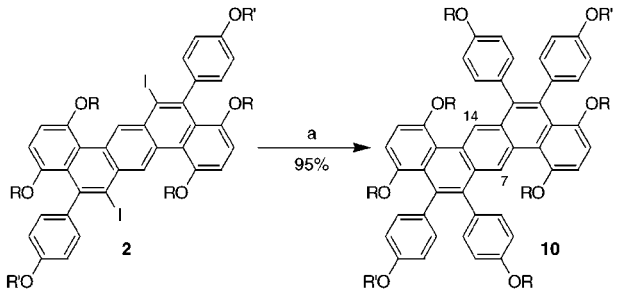


Figure 1. Absorption (solid line) and emission (dashed line) spectra for compounds **10** (bottom), **2** (middle), and **1** (top). Note that **2** does not display any emission under the experimental conditions due to a heavy-atom effect.

Scheme 1



430 nm for **1**, **2**, and **10**, respectively. Compound **10** displays its emission maximum at 436 nm while **1**'s emission maximum is at 438 nm.

Synthesis of *p*-Quinquephenyls. The systems prepared in previous studies (**1**−**9**) contain one bis(4-alkoxyphenylethynyl)phenyl moiety which is involved in the cyclization by electrophilic attack on the terminal rings of the *p*-terphenyl moiety. To increase the number of bis(4-alkoxyphenylethynyl)phenyl moieties to two would require the preparation of a *p*-quinquephenyl ring system. Chemoselective Suzuki cross-couplings at the iodide positions of mixed bromide- and iodide-containing aromatics proved invaluable for the direct synthesis of the functionalized *p*-quinquephenyl systems.

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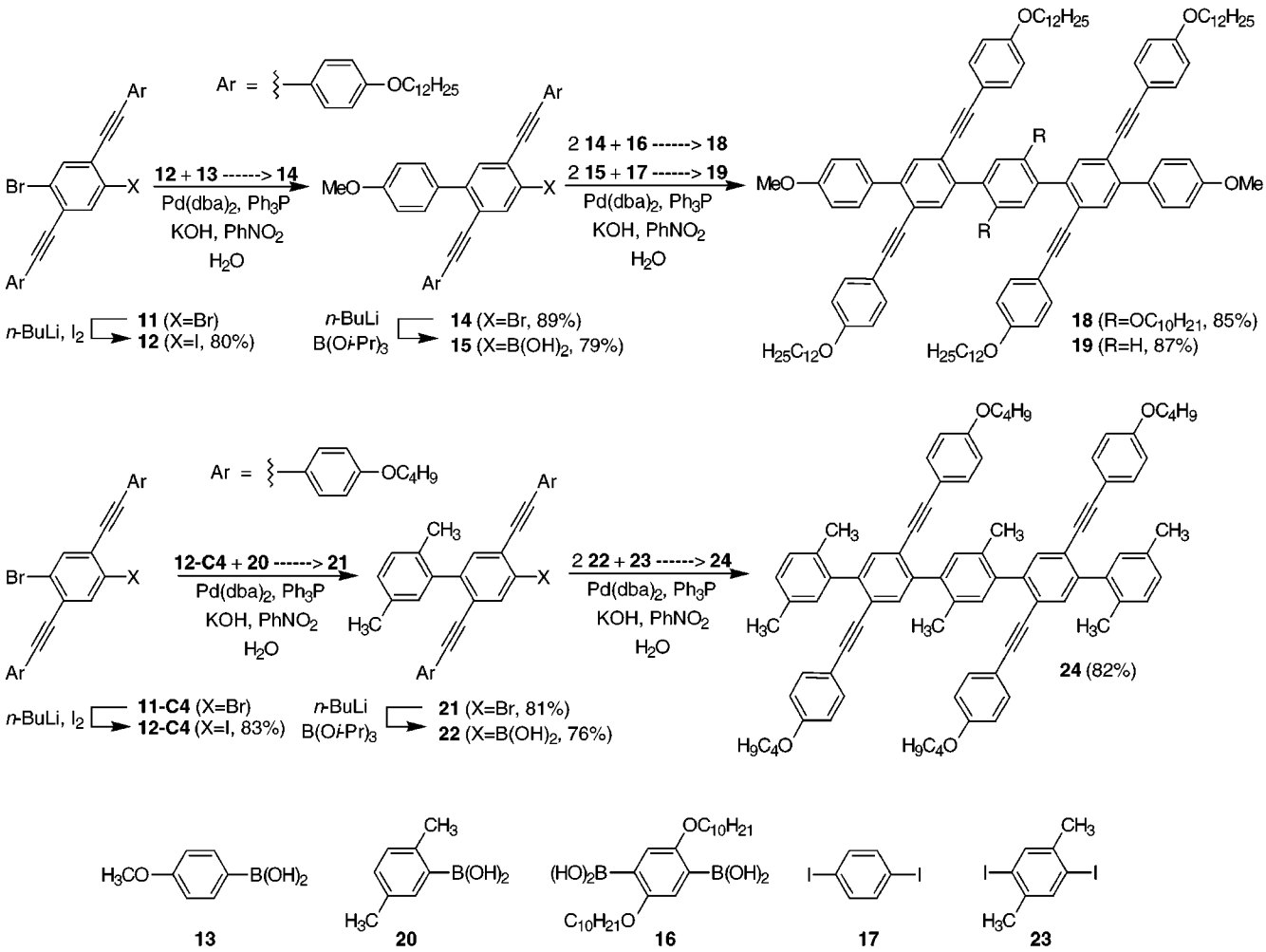
Scheme 2



The mixed iodobromide systems **12** and **12-C4** (butoxy replaces dodecyloxy on the phenylethynyl moiety) were prepared in yields between 80 and 85% by reaction of the corresponding dibromides **11** with 1.15 equiv of *n*-BuLi in THF followed by an I_2 quench (Scheme 2). The reaction of **12** with *p*-methoxyphenylboronic acid **13** provided the substituted bromobiphenyl **14** in 89% yield, while reaction of **12-C4** with 2,5-dimethylphenylboronic acid **20** provided the substituted bromobiphenyl **21** in 81% isolated yield. The conversion of **11** to the iodobromide systems **12** was indeed necessary as reactions employing 1:1 mixtures of its dibromide precursor and boronic acid produced considerable amounts of the *p*-terphenyl systems (confirmed by spectral comparison to authentic samples), as the second coupling is at least as rapid as the first coupling. In fact, the reaction of the mixed halide **12-C4** with 1.03 equiv of **20** produced small amounts (10−15%) of the corresponding *p*-terphenyl even when the reaction temperature was lowered from 85 to 70 °C. The selectivity is higher in the synthesis of **14,** in which the presence of the electron-rich methoxy group situated "para" to the bromide slows down the oxidative addition of Pd(0) to the bromide.

The bromide **14** (2.15 equiv) was reacted with 1,4-didecyloxybenzene-2,5-diboronic acid **16**[19] (1 equiv) to produce the *p*-quinquephenyl **18** in 85% isolated yield. The difficulties associated with the synthesis and purification of simple phenyldiboronic acids made the conversion of the bromo biphenyls **14** and **21** to their respective monoboronic acids **15** and **22**, an operationally simpler approach to the *p*-quinquephenyl systems. These boronic acids could then be reacted with readily available aromatic diiodides. The *p*-quinquephenyl **19** was produced in 87% yield by reaction of **15** with 1,4-diiodobenzene **17,** while the *p*-quinquephenyl **24** was prepared in 82% isolated yield by reaction of 2.2 equiv of the boronic acid **22** with 2,5-diiodo-*p*-xylene. The three *p*-quinquephenyl systems **18**, **19**, and **24** were obtained as colorless solids which could be purified by standard silica gel column chromatography (**18**) or crystallization (**19** and **24**).

The NMR spectra of these materials are straightforward and in complete agreement with the proposed structures. The ^1H NMR spectrum of **18** displays six doublets and three singlets in the aromatic region and triplets at 3.80 (4H) and 3.92 ppm (8H) corresponding to the α methylene groups on the alkoxy side chains and a singlet at 3.88 ppm representing the terminal methoxy groups. The ^{13}C NMR spectrum of **18** displays the expected 21 aromatic resonances and four acetylenic resonances. Compound **19** similarly displays six doublets and three singlets in the aromatic region, with one singlet being twice the intensity of the other two, and triplets at 3.86 (4H) and 3.93 ppm (4H) corresponding to the α methylene groups on the alkoxy side chains and a singlet

(19) Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 7895−6.

at 3.89 ppm for the terminal methoxy groups. The ^{13}C NMR spectrum of **19** displays all four acetylenic resonances but only 16 of the 20 expected aromatic resonances, undoubtedly due to coincidental overlap of some of the signals. In the ^{1}H NMR of compound **24** the signals in the aromatic region corresponding to the pendant *p*-alkoxyphenyl rings show up at 6.75 and 7.08 ppm as non-first-order multiplets. This may be due to slow conformational dynamics. The presence of several low-intensity broad resonances (analytically pure material) lends support to the supposition of conformational dynamics. Also present in the aromatic region are three singlets corresponding to the hydrogens on the middle three rings of the quinquephenyl system and an aryl ABD spin system corresponding to the outermost ring of the quinquephenyl system. All of these signals of **24** are also broad. A lone triplet and a corresponding broad resonance are present at 3.92 and 3.81 ppm, respectively corresponding to the methylenes next to the oxygen on the pendant alkoxy phenyl rings. **24** also displays three singlets at 2.28, 2.32, and 2.38 ppm, corresponding to the three chemically nonequivalent methyl groups. The ^{13}C NMR spectrum of **24** displays three of the four expected acetylene resonances and 17 of 23 expected aromatic resonances. This is again due to coincidental overlap of some of the signals, perhaps as a result of the slow conformational dynamics. Interestingly, compound **18** which displays 21 out of 21 expected resonances in the ^{13}C NMR shows an intense band at 296 nm in its UV−vis absorption spectrum which we ascribe to a relatively high degree of planarity for the *p*-phenylene backbone. Compound **24**, which appears to be conformationally dynamic by ^{1}H NMR, displays only a very weak band at 286 nm, suggesting a less planar structure than **18**. Both **18** and **24** display absorption maxima at 342 nm with shoulders at 364 nm, in agreement with the terphenyl systems reported earlier which serve as precursors to compounds **1**−**5**.[5]

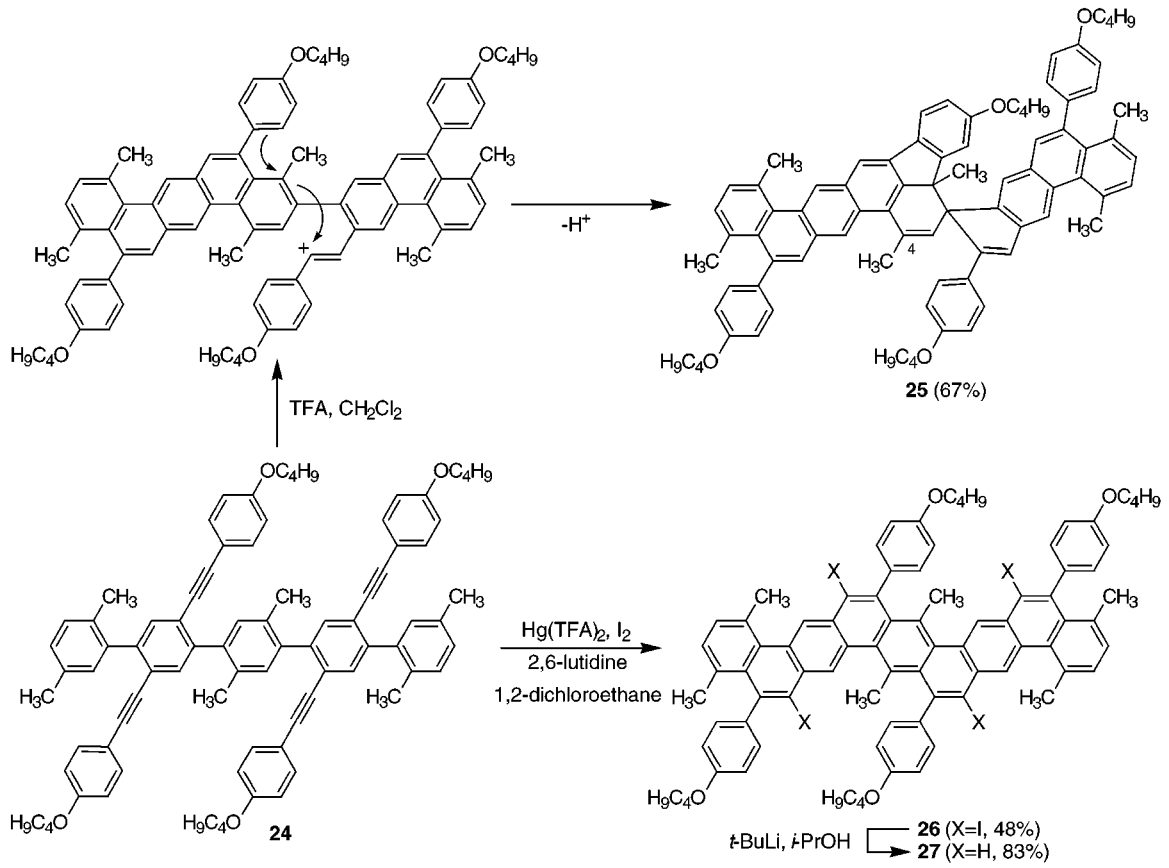
In light of the complications due to the dynamic behavior observed in the NMR, mass spectrometry was key in the structure assignments. Fast atom bombardment mass spectrometry (FAB-MS), typically favored over chemical ionization methods for relatively high molecular weight species, proved to be an inadequate tool for the characterization of the *p*-quinquephenyl model systems. We did obtain positive results, however, by employing laser desorption ionization mass spectrometry (LDI-MS). The measurements were performed without matrix in positive ion mode. Original measurements were made using *p*-quaterphenyl (Aldrich) for molecular weight calibration. Upon successful confirmation of an unknown's molecular weight, that compound then became a member of a pool of molecular weight standards to be used in subsequent measurements. Measurements employing standard peptides for calibration afforded inaccurate results. Extremely clean molecular ion signals were observed for **18**, **19**, and **24**. LDI-MS also provided positive results for the measurements of the boronic acids **15** and **22,** which gave molecular weights corresponding to $3M^{+} - 3H_2O$, indicating the likely formation of cyclotrimers. The mass spectra of the bromides **14** and **21** could be easily measured by FAB-MS.

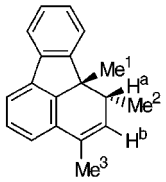
Cyclization of *p*-Quinquephenyl Systems. The terminal methoxy groups of **18** and **19** were appended to simplify the NMR spectra of both the precyclized and cyclized systems and to provide an additional NMR diagnostic. Much to our disappointment, cyclization of the *p*-quinquephenyl systems **18**, **19**, and **24** did not proceed with the same success enjoyed for the *p*-terphenyl systems. These cyclizations often produced mixtures of products whose structures were no longer symmetric, giving rise to complex NMR spectra. In addition, the nature of the cyclized product appeared to be highly dependent on the nature of the appended functionality. We will begin our discussion with the cyclization of compound **24**, as its products have been the most thoroughly characterized.

The acid-catalzyed cyclization of **24** gave as the major isolable product (67% after silica gel chromatography) a yellow solid. LDI-MS showed that this product had the same molecular weight as **24**. A cursory glance at the ^{1}H NMR clearly indicated that the reaction had led to extensive desymmetrization, as indicated by the presence of six nonequivalent methyl signals. Also, there were eight singlets in the aromatic region along with some doublets and more complex (overlapped) multiplets. We were particularly puzzled by the presence of a singlet at 6.82 ppm. On the basis of our experience with compounds of the type **1**−**5** we expected the bay region protons to appear as singlets downfield of about 8 ppm.[5] There were also two doublets in the vinyl region, one at 6.16 ppm, and a rather broad one at 6.20 ppm. In addition, there was a singlet (3H) at 1.21 ppm and a doublet (3H, $J = 1.4$ Hz) at 2.64 ppm. The ^{1}H COSY clearly indicated that the doublet at 2.64 ppm was coupled to the broad doublet at 6.20 ppm. This appeared to indicate the presence of an allylic methyl group. ^{1}H COSY also indicated the presence of an ABD spin system with a doublet of doublets at 6.90 ppm ($J = 2.6$ and 8.5 Hz), and doublets at 6.16 ppm ($J = 2.6$ Hz) and 8.01 ppm ($J = 8.5$ Hz). This implied the presence of a trisubstituted aromatic ring with substitution in the 1, 2, and 4 positions. In the ^{13}C NMR there were four signals between 155 and 160 ppm, indicating the presence of four nonequivalent aromatic carbons attached to oxygen, which again implies desymmetrization. ^{13}C NMR and DEPT showed the presence of two saturated quaternary carbons at 46.28 and 61.36 ppm. The presence of these upfield signals for quaternary carbons along with the methyl singlet at 1.21 ppm in the ^{1}H NMR clearly indicate the interruption of aromaticity. Aryl methyl groups typically appear downfield of 2 ppm. This far upfield shift is unlikely to be due to severe shielding effects, as even the methyl group of 9-methyl-1,8-diphenylanthracene was reported by House to appear between 1.49 and 1.59 ppm in the ^{1}H NMR.[20] On the basis of the above information, we suspected that the major product of the cyclization of **24** was **25** (see Scheme 3). Upon searching the literature, we discovered that Harvey had found that the methyl group of a methylated dihydrophenanthrene system appeared at 1.34 ppm (see Figure 2).[21] The allylic methyl in this same compound appeared at 2.12 ppm ($J = 1.4$ Hz). The singlet at 6.82 ppm in the ^{1}H NMR could now be assigned to the indenyl proton (6.82 ppm in indene).[22] The structure **25** is consistent with all of our observations.

(20) House, H. O.; Hrabie, J. A.; Veer, D. V. *J. Org. Chem.* **1986**, *51*, 921.
(21) Harvey, R. G.; Lindlow, D. F. *Tetrahedron* **1972**, *28*, 2909.

Scheme 3



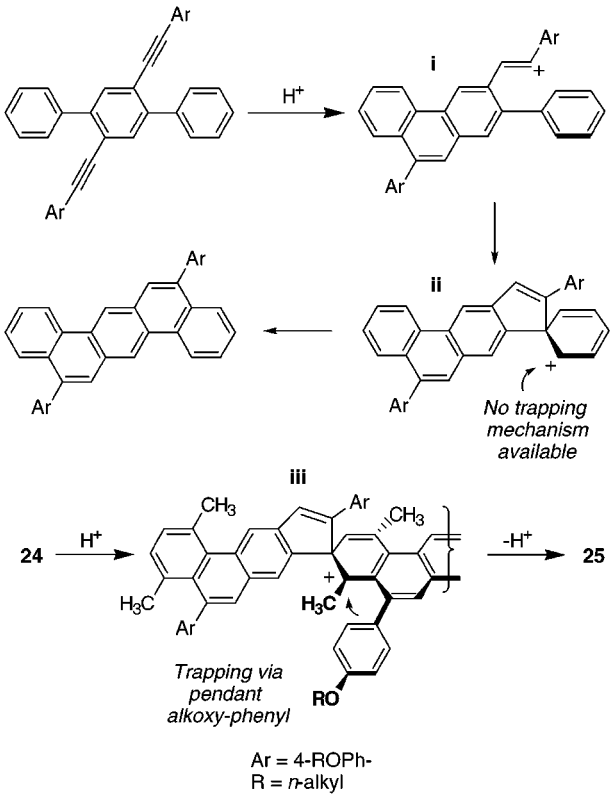


Me^1 (1.34 ppm, s)
Me^2 (0.40 ppm, d, J_{2a} = 7.3 Hz)
H^b (5.84 ppm, dq, J_{ba} = 6.2, J_{b3} = 1.4 Hz)
Me^3 (2.12 ppm, dd, J_{3b} = 1.4, J_{3a} = 0.7 Hz)

Figure 2. ^{1}H NMR data for a dihydrofluoranthene system.

The spiro linkage of **25** presumably forms after one of the "central" phenylethynyl moieties is successfully cyclized. The vinyl carbocation formed from the other "central" phenylethynyl moiety then, instead of attacking the carbon center which would produce a six-membered ring, attacks the ipso position to create a spiro linkage. This intermediate is irreversibly trapped as a result of the ability of the outer phenyl ring to eliminate a proton. This is not entirely unexpected, since it is well-known that, in general, ring closure to form five-member rings is significantly faster than for six-member rings.[23,24] This type of event was not observed in the *p*-terphenyl systems due to the absence of a trapping mechanism, or more specifically the absence of a configuration requiring the cyclization of two phenylethynyl moieties onto the same backbone aryl ring. Electrophilic attack at the ipso position may have indeed been occurring via the vinyl

Scheme 4



cationic intermediate **i** (Scheme 4) which then forms the cationic spiro intermediate **ii**. In the case of the terphenyl systems, there is no trapping mechanism available, thus permitting **ii** to undergo a rearrangement leading

(22) Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. In *Tables of Spectral Data for Structure Determination of Organic Compounds*, 3 ed.; Fresenius, W., Huber, J. F. K., Pugnor, E., Rechnitz, G. A., Simon, W., West, T. S., Eds.; Springer-Verlag: New York, 1989; pp H240.

(23) Carey, F. A.; Sundberg, R. J. In *Advanced Organic Chemistry Part A: Structure and Mechanism*, 3 ed.; Plenum Press: New York, 1990; pp 163−167.

(24) March, J. In *Advanced Organic Chemistry*, 3 ed.; John Wiley & Sons: New York, 1985; p 212.

to the dibenzo[*a*,*h*]anthracene product. In the case of the quinquephenyl system, the corresponding spiro intermediate **iii** is trapped by the pendant alkoxyphenyl moiety, leading to the spiro product **25**.

We were successful in preparing a defect-free cyclization product in modest chemical yield (48%) by employing iodonium as the electrophile. The tetraiodide **26** was prepared as a bright yellow solid by employing iodonium generated in situ by the reaction of mercury(II) trifluoroacetate with I_2 in the presence of 2,6-lutidine.[5] The ^{1}H NMR spectrum of **26** is straightforward and contains four doublets corresponding to the protons on the pendant *p*-alkoxyphenyl groups and two doublets of lower intensity corresponding to the protons on the terminal rings of the fused aromatic system. Also present in the aromatic region are singlets at 9.25 and 9.46 ppm, which represent the two bay region protons. The LDI-MS of this compound displays the molecular ion signal at *m*/*z* 1659 as well as signals at *m*/*z* 1532, 1404, 1277, and 1149, each corresponding to the loss of an iodide. The combination of poor solubility and thermal instability precluded the procurement of a ^{13}C NMR spectrum for **26** and limited the degree to which the material could be purified.

Removal of the iodides of **26** by lithium−halogen exchange followed by a 2-propanol quench provided **27** in 83% isolated yield. The ^{1}H NMR spectrum of **27** displays six aromatic doublets, with two being of lower intensity, but now contains four singlets corresponding to the two bay protons (8.81 and 9.06 ppm) and the two new protons (7.67 and 7.83 ppm) introduced by the reaction. The greater solubility of **27** allowed for the aquisition of a ^{13}C NMR spectrum which displays the expected 27 aromatic resonances and a lack of acetylene carbons and carbons corresponding to the spiro system (46 and 61 ppm) discussed above. LDI-MS displays the molecular ion signal at *m*/*z* 1155, and combustion analysis is accurate to within 0.04% for carbon and 0.24% for hydrogen.

The electronic spectra for **25**−**27** are displayed in Figure 3. Their absorption spectra display the low intensity absorptions on the low energy side of λ_{max} as was observed in systems **1**−**5**.

It is noteworthy to report that the cyclization of the *p*-quinquephenyls **18** and **19** did not exhibit the same behavior as observed for the cyclization of **24**; i.e., there was no evidence of spiro ring junctures. Cyclization of **18** did produce small quantities of a product in which the loss of decyloxy was detected (by LDI-MS). The dominant product, isolated in 38% yield, did not undergo loss of a decyloxy side chain as evidenced by LDI-MS (*m*/*z* 1892). The ^{1}H NMR spectrum of the cyclized product indicates that the molecule has been desymmetrized. However, the spectrum suggests only a minor perturbation from clean cyclization on the basis of the splitting patterns present. Such a perturbation is likely due to 1,2-phenyl migration similar to what we have observed in certain molecular systems.[5] We hesitate however, without X-ray crystallographic evidence, to provide an unambiguous structure assignment. Interestingly, the cyclization product of **18** displays an emission at 476 nm which is closer to **27** (472 nm) than to **25** (438 nm). The products obtained by the TFA-induced cyclization of **19** again appear to be perturbed only slightly from what is to be considered a clean cyclization.

Synthesis and Cyclization of a Modified System. At this juncture it had become clear that blocking the 2 and 6 positions of the pendant 4-alkoxyphenylethynyl moiety could prevent spiro linkages as well as alcohol elimination products. Recall that **18** did not produce any spiro linkages but did give products resulting from elimination of decyl alcohol. Also, **18** did not show any of the conformational dynamics that complicated the NMR spectrum of **24**. Guided by these facts, the target **33** was selected. It was synthesized in a manner analogous to that used for **18** (see Scheme 5).

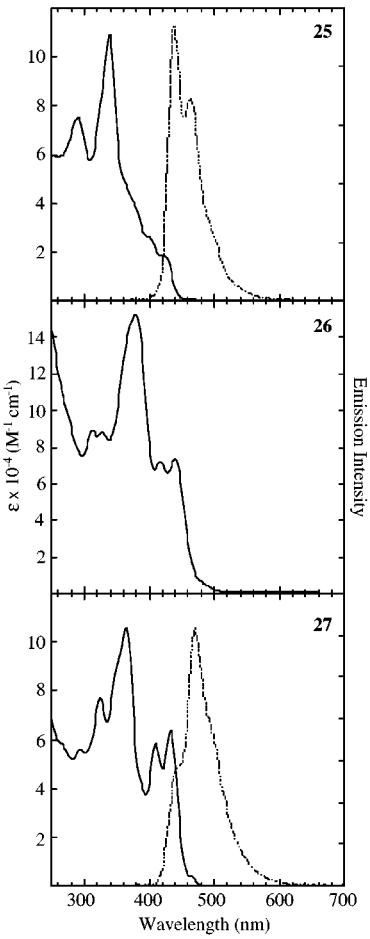
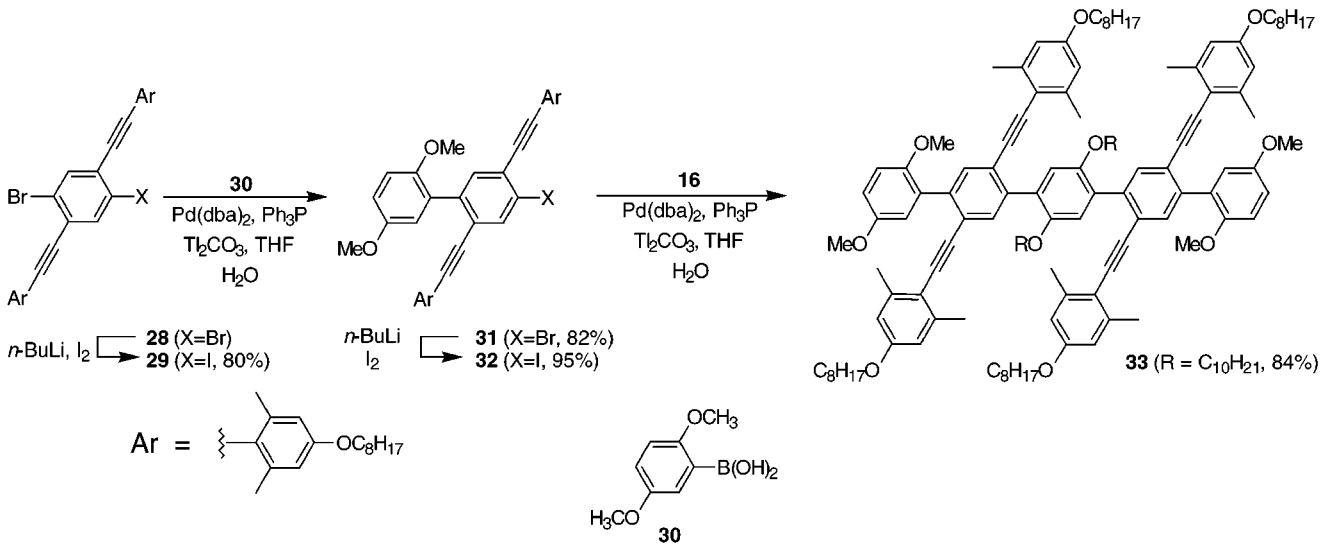


Figure 3. Absorption (solid line) and emission (dashed line) spectra for compounds **25** (top), **26** (middle), and **27** (bottom). Note that **26** does not display any emission under the experimental conditions due to a heavy-atom effect.

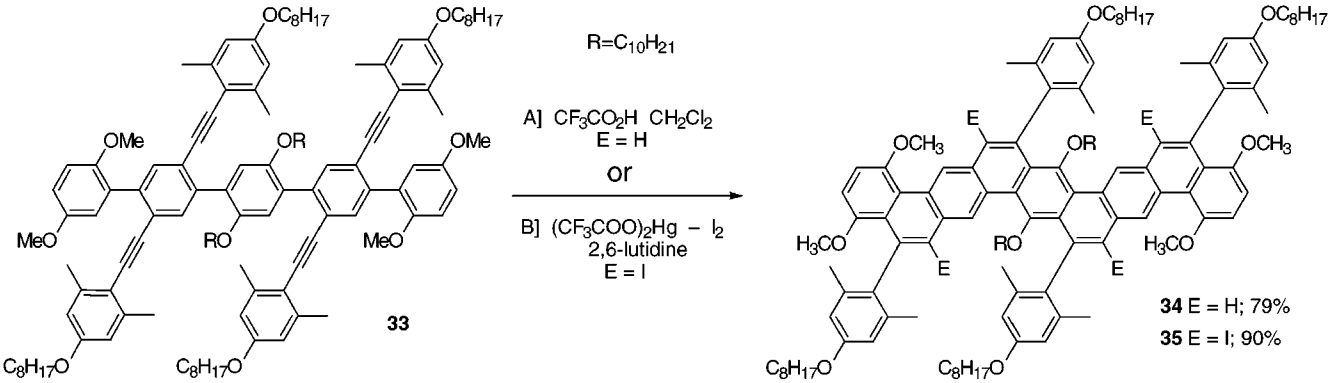
The dibromide **28** (prepared in five steps from 2,6-dimethyl-4-bromophenol and 1,4-diiodo-2,5-dibromobenzene) was converted to the mixed iodobromo compound **29** as detailed earlier for the conversion of **11** to **12**. The introduction of the extra methyl groups on the phenylethynyl moiety made the Suzuki coupling more difficult. The earlier protocol failed completely in this case—most likely due to the greater steric hindrance of the extra methyl groups. This problem was easily overcome by employing the Kishi modification wherein TlOH is used as the base instead of KOH.[25] The more readily available Tl_2CO_3 was also found to work satisfactorily. The use of the thallium protocol conferred another benefit, the reaction could now be run in THF instead of nitrobenzene, and this greatly simplified the problem of solvent removal. Suzuki coupling of **29** with 2,5-dimethoxyphe-

(25) Uenishi, J.-I.; Beau, J.-M.; Armstrong, R. W.; Kishi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 4756.

Scheme 5



Scheme 6



nylboronic acid **30** in the presence of Tl_2CO_3 gave the bromide **31**. The effect of the added bulk of the methyls again manifested itself when we attempted to couple **31** with **16**, which produced no detectable coupling product. Conversion of **31** to the iodide **32** followed by Suzuki coupling (using Tl_2CO_3 in THF as before) with **16** gave **33** in 82% yield. The NMR, UV−vis, and fluorescence spectra of **33** are similar to those of **18**.

Cyclization of **33** with trifluoroacetic acid in methylene chloride gave **34** in 80% yield (see Scheme 6). Unfortunately, this compound is of limited stability and decomposed slowly on silica or after extended (2 days) storage at room temperature. The ^{1}H NMR of this compound is somewhat more complicated than expected. The four singlets and two doublets expected from the aromatic core are seen and are fairly clean. In addition, the two methoxy groups on the aromatic core also show up as two clean singlets, one of which is moved significantly upfield whereas the other has moved downfield by a similar amount relative to their position in **33**. It is thus obvious that the cyclization reaction has not led to any desymmetrization of the molecule. This is also substantiated by the proton-decoupled ^{13}C NMR spectrum. In the region between 150 and 160 ppm there are five lines as expected for the aromatic carbons attached to the various oxygens in **34**. These NMR data are in concordance with those of **27**. The signals from the pendant alkoxy phenyl groups are more complex, most likely due to hindered rotation. If there were free rotation one would expect to see, in the ^{1}H NMR, just two singlets for the pendant aromatic rings and two singlets for the blocking methyl groups (at the 2 and 6 positions of the pendant aromatic ring). However, there are four signals observed for each in the ^{1}H NMR. This appears to suggest that the pendant aromatic rings are conformationally locked with a dihedral angle of between 0° and 90°. The effects of this conformational lock are also evident in the ^{13}C NMR spectrum. In the absence of conformational constraints, one would expect to see 27 peaks in the region downfield of 100 ppm (the aromatic region). If the system were conformationally locked, one would expect to see a total of 31 peaks in the aromatic region. The ^{13}C NMR of **34** shows 30 signals in the aromatic region. Again all 31 signals are not seen 2due to some coincidental overlap. The UV−vis and fluorescence spectra of **34** are similar to those of **27** (see Figure 4).

Recall that iodonium cyclization of **24** led to **26**. The application of the same protocol to **33** gave the tetraiodide **35** in 90% yield. As was observed for **26**, **35** also has very limited stability. In fact, **35** was found to be even less stable than **26**, again making it impossible to obtain a ^{13}C NMR spectrum for a tetraiodinated product. The ^{1}H NMR spectrum of **35** was very similar to that of **34** and is in general concordance with that of **26**. It shows the expected two singlets and two doublets for the aromatic core. The two methoxy groups also exhibited analogous, but more pronounced, shifts. The pendant *p*-alkoxyphenyl groups showed four singlets in the aro-

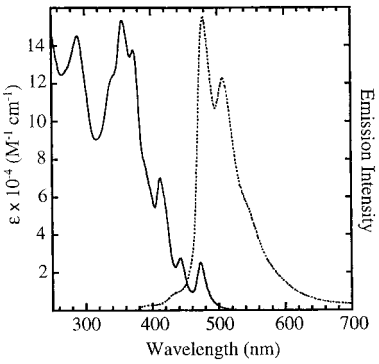


Figure 4. Absorption (solid line) and emission (dashed line) spectra for compound **34**.

matic region and four singlets for the blocking methyl groups, again most likely due to conformational constraints.

Conclusion

We have extended our earlier organometallic coupling strategy to the synthesis of *p*-quinquephenyl systems. We have demonstrated the versatility of and further extended our electrophile-induced cyclization to produce larger planar conjugated systems which have potential applications in many fields. In this work we have shown that this versatile two-step protocol can be used to produce aromatic systems containing nine annelated rings. The reaction conditions are very mild, thus allowing the production of these characteristically relatively sensitive compounds in synthetically useful amounts. Use of iodonium as the electrophile leads to functionalized polycyclic aromatic systems which can undergo further C−C bond forming reactions to yield more complex systems. A side reaction that produces an interesting indenyl spiro ring system has also been described. The use of blocking groups at the 2 and 6 positions of the pendant alkoxyphenylethynyl groups prevents the formation of the indenyl spiro ring system.

Experimental Section

General Methods. NMR spectra (^{1}H and ^{13}C) were obtained on Bruker AC-100, AC-200, AC-250, and AMX-500 spectrometers using $CDCl_3$ as solvent. Chemical shifts are reported in ppm relative to residual protio chloroform (7.24 ppm, ^{1}H; 77.0 ppm, ^{13}C). Microanalyses and high-resolution mass spectra (HRMS) were obtained at the University of Pennsylvania instrumentation center. Silica gel chromatography was performed on 40 μm silica gel (Baker). Infrared spectra were recorded on a Perkin-Elmer 1760-X spectrometer. Samples were prepared by evaporation of solutions of dissolved compounds directly onto KBr plates. UV−vis spectra were recorded in $CHCl_3$ on a Hewlett-Packard 8452A diode array spectrophotometer. Luminescence spectra were recorded in $CHCl_3$ using a Photon Technology International A1010 luminescence spectrometer. Emission measurements were performed in a four-sided quartz cell at room temperature and are uncorrected for detector response. Emission measurements of precyclized and cyclized materials were made at excitation wavelengths of 330 and 365 nm, respectively.

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 using standard Schlenk techniques.

1,4-Didecyloxybenzene-2,5-diboronic Acid (16). 1,4-Didecyloxy-2,5-diiodobenzene (15 g, 0.0233 mol) was dissolved in 200 mL of THF and the solution was cooled to −70 °C. *tert*-BuLi (61.2 mL, 1.64 M) was added and the temperature was allowed to rise to −55 °C over 3 h. The temperature was then brought to −20 °C and allowed to remain there for 45 min. The solution was recooled to −60 °C and $B(OMe)_3$ (15.91 mL, 0.140 mol) was quickly added via syringe in one portion. The solution was stirred at room-temperature overnight and 100 mL of 10% HCl was added. After 90 min the solution was filtered and the solid collected and heated in boiling water. After filtering, the solid was again collected and heated in boiling hexanes to remove monoboronic acid. The insoluble solid was collected and dried in vacuo to afford 9.50 g (85%) of the colorless solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.84 (t, 6H, J = 7.12 Hz), 1.2−1.5 (H28), 1.71 (quint, 4H, J = 7.50 Hz), 3.98 (t, 4H, J = 6.50 Hz), 7.18 (s, 2H), 7.75 (s, 4H). Anal. Calcd for $C_{26}H_{48}O_6B_2$: C, 65.29; H, 10.12. Found: C, 65.29; H, 10.13.

5,12-Bis(4-dodecyloxyphenyl)-1,4,8,11-tetramethoxy-6,13-bis(4-methoxyphenyl)dibenzo[*a,h*]anthracene (10). To a 25 mL Schlenk flask charged with **2** (0.072 g, 0.062 mmol), *p*-methoxyphenylboronic acid (0.093 g, 0.61 mmol), $Pd(dba)_2$ (0.0007 g, 0.001 mmol), triphenylphosphine (0.005 g, 0.019 mmol), and KOH (0.150 g, 2.67 mmol) were added 1.5 mL of H_2O and 4 mL of nitrobenzene. The mixture was heated to 95 °C and allowed to stir for 14 h. After cooling to room temperature the mixture was diluted with ethyl ether (100 mL) and washed with 5% NaOH (3 × 30 mL), H_2O (30 mL), 5% HCl (2 × 40 mL), and H_2O (30 mL). After drying ($MgSO_4$) the ethyl ether was removed using standard rotary evaporation. The remaining nitrobenzene was removed under high vacuum (0.01 Torr) while being heated (95 °C). The crude product was purified by silica gel chromatography (2:2:1 hexanes−ethyl acetate−$CHCl_3$) to provide **10** (mp 168−170 °C) as a bright yellow solid (0.066 g, 94.9%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, 6H, J = 6.77 Hz), 1.26−1.44 (m, 36H), 1.73 (quint, 4H), 3.24 (s, 6H), 3.59 (s, 6H), 3.82 (s, 6H), 3.88 (t, 4H, J = 6.68 Hz), 6.63 (d, 4H, J = 8.65 Hz), 6.84 (d, 4H, J = 8.64 Hz), 6.89 (d, 4H, J = 8.64 Hz), 6.92 (d, 2H, J = 8.84 Hz), 6.98 (d, 2H, J = 8.83 Hz), 7.07 (d, 4H, J = 8.63 Hz), 9.89 (s, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 14.11, 22.68, 26.06, 29.36, 29.62, 31.91, 55.15, 55.35, 57.32, 67.92, 109.12, 111.64, 112.52, 112.84, 114.08, 122.05, 125.34, 127.46, 130.18, 131.60, 132.35, 133.43, 134.34, 137.19, 140.01, 151.75, 153.23, 156.08, 157.57. UV−vis ($CHCl_3$) λ_{max} (ϵ, cm^{-1} M^{-1}): 430 (13 600), 406 (11 300), 376 (19 200), 358 (24 600), 324 (61 100), 282 (43 000) nm. Luminescence spectrum ($CHCl_3$) λ_{max} (rel int): 436 (1), 460 (0.58) nm. HRMS (FAB): found *m/z* 1130.6678 (M^+), calcd for $C_{76}H_{90}O_8$ *m/z* 1130.6635.

1-Bromo-2,5-bis(4-dodecyloxyphenylethynyl)-4-iodobenzene (12). To a 500 mL Schlenk flask containing 1,4-dibromo-2,5-bis-(4-dodecyloxyphenylethynyl)benzene **11**[5] (4.7 g, 5.84 mmol) was added 400 mL of THF. The mixture was cooled to −78 °C and *n*-BuLi (3.95 mL, 1.7 M, 6.72 mmol) was added. The cooling bath was removed until the solution became homogeneous (ca. 10 min), at which time the solution was allowed to stir for an additional 5 min. After recooling to −78 °C, solid I_2 (3 g, 11.8 mmol) was added. Again, the cooling bath was removed and the mixture allowed to stir until homogeneous. After stirring for 5 min the reaction was quenched by the addition of 5% NaOH. The mixture was diluted with 250 mL of ethyl ether (40 mL of $CHCl_3$ was added for solubility), washed with additional 5% NaOH and H_2O, and dried ($MgSO_4$). Removal of the solvent under reduced pressure followed by recrystallization from $CHCl_3$ (2×) provided compound **12** (mp 114−115 °C) as a colorless solid (3.99 g, 80.2%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.86 (t, 6H, J = 7.0 Hz), 1.2−1.5 (36H), 1.77 (m, 4H), 3.95 (t, 4H, J = 6.53 Hz), 6.86 (br d, 4H, J = 7.7 Hz), 7.47 (d, 2H, 8.47 Hz), 7.49 (d, 2H, 8.46 Hz), 7.67 (s, 1H), 7.96 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 14.10, 22.68, 25.98, 29.13, 29.34, 29.58, 31.89, 68.11, 85.53, 89.38, 96.10, 96.88, 98.14, 114.13, 114.62, 124.58, 126.37, 130.67,

133.23, 133.58, 134.76, 141.83, 159.85. HRMS (FAB): found *m/z* 850.2800 (M^+), calcd for $C_{46}H_{60}O_2BrI$ *m/z* 850.2821. HRMS (FAB): found *m/z* 627.0380 ($M^+ + H$), calcd for $C_{30}H_{29}O_2BrI$ (**12-C4**) *m/z* 627.0395. Anal. Calcd for $C_{46}H_{60}BrIO_2$: C, 64.86; H, 7.10. Found: C, 65.00; H, 7.08.

4-Bromo-2,5-bis(4-dodecyloxyphenylethynyl)-4′-methoxy-1,1′-biphenyl (14). A Schlenk flask was charged with **12** (3.65 g, 4.29 mmol), *p*-methoxyphenylboronic acid (0.716 g, 4.71 mmol), $Pd(dba)_2$ (0.025 g, 0.043 mmol), triphenylphosphine (0.168 g, 0.645 mmol), and KOH (2.60 g, 46.3 mmol). H_2O (15 mL) and nitrobenzene (25 mL) were added, and the mixture was heated at 90 °C for 12 h. After cooling to room temperature, the mixture was diluted with 200 mL of ethyl ether and washed with 5% NaOH (2 × 50 mL) and H_2O (40 mL). After removal of the ethyl ether by rotary evaporation, the compound was precipitated by the addition of methanol to the remaining nitrobenzene. Filtration, followed by purification by silica gel chromatography (3:2 $CHCl_3$−hexanes), afforded **14** (mp 80−81 °C) as a colorless solid (3.18 g, 89.3%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.86 (t, 6H, J = 7.0 Hz), 1.2−1.5 (36H), 1.77 (m, 4H), 3.86 (s, 3H), 3.92 (t, 2H, J = 6.67 Hz), 3.95 (t, 2H, J = 6.61 Hz), 6.81 (d, 2H, J = 8.72 Hz), 6.87 (d, 2H, J = 8.76 Hz), 6.98 (d, 2H, J = 8.70 Hz), 7.27 (d, 2H, J = 8.66 Hz), 7.50 (d, 2H, J = 8.70), 7.53 (s, 1H), 7.60 (d, 2H, J = 8.65 Hz), 7.81 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 14.10, 22.67, 25.97, 29.13, 29.35, 29.58, 31.89, 55.24, 68.01, 86.90, 94.85, 95.59, 113.33, 114.48, 122.60, 122.83, 125.16, 130.31, 131.37, 132.87, 133.17, 135.75, 141.83, 159.40, 159.60. HRMS (FAB): found *m/z* 831.4370 ($M^+ + H$), calcd for $C_{53}H_{68}BrO_3$ *m/z* 831.4351. Anal. Calcd for $C_{53}H_{67}BrO_3$: C, 76.51; H, 8.12. Found: C, 76.17; H, 8.03.

2,5-Bis(4-dodecyloxyphenylethynyl)-4′-methoxy-1,1′-biphenyl-4-boronic Acid (15). Compound **14** (2.0 g, 2.41 mmol) was dissolved in 200 mL of THF and the solution cooled to −78 °C. After addition of *n*-BuLi (1.98 mL, 1.7M, 3.37 mmol), the solution was allowed to stir for 15 min before triisopropyl borate (1.55 mL, 6.72 mmol) was rapidly added via syringe. The mixture was allowed to warm to room temperature over 45 min and 5% HCl (50 mL) was added. After stirring for 1 h, the mixture was diluted with 150 mL of ethyl ether. The solvent was washed with H_2O (3 × 75 mL), dried ($MgSO_4$), and removed under reduced pressure. Recrystallization of the crude product from hexane−ethyl acetate (1×) and $CHCl_3$ (1×) provided **15** as a colorless solid (1.52 g, 79.3%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.86 (t, 6H, J = 7.0 Hz), 1.2−1.5 (36H), 1.77 (m, 4H), 3.86 (s, 3H), 3.92 (t, 2H, J = 6.68 Hz), 3.96 (t, 2H, J = 6.64 Hz), 5.93 (br s, 2H), 6.80 (d, 2H, J = 8.85 Hz), 6.88 (d, 2H, J = 8.84 Hz), 6.99 (d, 2H, J = 8.84 Hz), 7.28 (d, 2H, J = 8.79 Hz), 7.45 (d, 2H, J = 8.85 Hz), 7.58 (s, 1H), 7.66 (d, 2H, J = 8.83 Hz), 8.21 (s, 1H). LDI-MS: *m/z* 2338 (10, $3M^+ - 3H_2O$), 1577 (10, $2M^+ - H_2O$), 825 (70), 798 (100), 754 (100), 647 (90).

2″,5″-Bis(decyloxy)-2′,5′,2‴,5‴-tetrakis(4-dodecyloxyphenylethynyl)-4,4⁗-dimethoxy[1,1′:4′,1″:4″,1‴:4‴,1⁗]quinquephenyl (18). A Schlenk flask was charged with the bromide **14** (0.230 g, 0.277 mmol), **16** (0.061 g, 0.128 mmol), $Pd(dba)_2$ (0.0016 g, 0.0028 mmol), triphenylphosphine (0.011 g, 0.042 mmol), and KOH (0.35 g, 6.24 mmol). After adding 2 mL of H_2O and 5 mL of nitrobenzene, the solution was heated to 85 °C and allowed to stir for 12 h. After cooling to room temperature, the mixture was diluted with 20 mL of ethyl ether and washed with 5% NaOH (2 × 10 mL) and H_2O (10 mL). After removal of the ethyl ether by rotary evaporation, the compound was precipitated by the addition of methanol to remove the remaining nitrobenzene. Filtration, followed by purification by silica gel chromatography (3:2 $CHCl_3$−hexanes) provided compound **18** (mp 137−138 °C) as a colorless solid (0.204 g, 84.6%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.86 (t, 18H, J = 7.0 Hz), 1.2−1.5 (100H), 1.5−1.8 (m, 12H), 3.80 (t, 4H, J = 6.60 Hz), 3.88 (s, 6H), 3.92 (t, 8H, J = 6.50 Hz), 6.65 (d, 4H, J = 8.79 Hz), 6.79 (d, 4H, J = 8.82), 7.01 (d, 4H, J = 8.73 Hz), 7.12 (d, 4H, J = 8.67), 7.12 (s, 2H), 7.28 (d, 4H, J = 8.80 Hz), 7.64 (s, 2H), 7.72 (d, 4H, J = 8.71 Hz), 7.73 (s, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 14.10, 22.68, 26.02, 29.10, 29.37, 29.61, 30.32, 31.91, 55.35, 67.97, 69.62, 88.31, 88.41, 93.52, 93.89, 113.35, 114.38, 114.49, 115.23, 115.44, 116.29, 120.79, 123.40, 125.51, 129.49, 130.55, 132.38, 132.49, 132.82, 132.89, 134.69, 139.34, 141.49, 150.22, 159.05, 159.21. UV−vis ($CHCl_3$) λ_{max} (ϵ, cm^{-1} M^{-1}): 364 (92 200), 342 (119 000), 296 (82 100) nm. Luminescence spectrum ($CHCl_3$) λ_{max} (rel int): 422 nm. LDI-MS: *m/z* 1892 (100, M^+), 1784 (15), 1751 (15, $M^+ - C_{10}H_{21}$), 1613 (10). Anal. Calcd for $C_{132}H_{178}O_8$: C, 83.76; H, 9.48. Found: C, 83.85; H, 9.66.

2′,5′,2‴,5‴-Tetrakis(4-dodecyloxyphenylethynyl)-4,4⁗-dimethoxy[1,1′:4′,1″:4″,1‴:4‴, 1⁗]quinquephenyl (19). A Schlenk flask was charged with boronic acid **15** (1.66 g, 2.09 mmol), 1,4-diiodobenzene (0.328 g, 1.00 mmol), $Pd(dba)_2$ (0.011 g, 1.91×10^{-2} mmol), triphenylphosphine (0.078 g, 0.297 mmol), and KOH (1.17 g, 20.9 mmol). Following the addition of 7 mL of H_2O and 20 mL of nitrobenzene, the entire solution was heated to 85 °C. After stirring overnight the solution was allowed to cool to room temperature, at which time it was diluted with 100 mL of $CHCl_3$. After washing with 5% NaOH (2 × 40 mL), H_2O, 5% HCl (2 × 40 mL), and H_2O, the solvent was dried and removed in vacuo. The crude product was crystallized once from $CHCl_3$−*i*-PrOH followed by one crystallization from $CHCl_3$. The *p*-quinquephenyl **19** (mp 157−159 °C) was isolated as a colorless solid (1.38 g, 87.1%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.86 (t, 12H, J = 7.0 Hz), 1.2−1.5 (72H), 1.77 (m, 8H), 3.85 (t, 4H, J = 6.60), 3.89 (s, 6H), 3.93 (t, 4H, J = 6.50 Hz), 6.73 (d, 4H, J = 8.82 Hz), 6.81 (d, 4H, J = 8.84 Hz), 7.02 (d, 4H, J = 8.80), 7.26 (d, 4H, J = 8.87 Hz), 7.31 (d, 4H, J = 8.79 Hz), 7.68 (s, 2H), 7.71 (d, 4H, J = 8.78 Hz), 7.75 (s, 2H), 7.86 (s, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 14.10, 22.67, 25.98, 29.16, 29.34, 29.58, 31.89, 55.33, 68.05, 88.03, 88.14, 93.88, 94.21, 113.37, 114.49, 114.99, 115.17, 121.51, 121.70, 128.87, 130.49, 132.11, 132.87, 133.46, 133.68, 138.96, 141.28, 141.65, 159.26. LRMS (FAB): *m/z* 1578.7 (15, M^+), 1412 (5, $M^+ - PhOCH_3$), 752 (100). LDI-MS: *m/z* 1579 (95, M^+), 1472 (15, $M^+ - PhOCH_3$), 1410 (10, $M^+ - C_{12}H_{25}$), 827 (15), 751 (100), 645 (50).

4-Bromo-2,5-bis(4-butoxyphenylethynyl)-2′,5′-dimethyl-1,1′-biphenyl (21). The bromide **21** was prepared as described for **14** by substituting **20** for **13** and using the butoxy side chain derivative (**12-C4**) of **12**. A small excess of boronic acid was employed (1.03 equiv) and the reaction temperature was kept at 70 °C. Following purification by silica gel chromatography (1:1 hexanes−toluene) **21** (mp 142−144 °C) was isolated as a colorless solid (81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.94 (t, 3H, J = 7.71 Hz), 0.96 (t, 3H, J = 7.66 Hz), 1.46 (m, 4H), 1.70 (m, 4H), 2.16 (s, 3H), 2.33 (s, 3H), 3.91 (t, 2H, J = 6.42 Hz), 3.96 (t, 2H, J = 6.43 Hz), 6.74 (d, 2H, J = 8.73 Hz), 6.85 (d, 2H, J = 8.73 Hz), 7.04 (d, 2H, J = 8.68 Hz), 7.10−7.14 (m, 3H), 7.41 (s, 1H), 7.47 (d, 2H, J = 8.70 Hz), 7.78 (s, 1H). HRMS (FAB): found *m/z* 604.1957 (M^+), calcd for $C_{38}H_{37}O_2Br$ *m/z* 604.1976.

2,5-Bis(4-butoxyphenylethynyl)-2′,5′-dimethyl-1,1′-biphenyl-4-boronic Acid (22). Compound **22** was prepared as described for **15**, employing compound **21** as the starting material. Purification by silica gel chromatography (3:1 hexanes−ethyl acetate) provided **22** as a white solid (76%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.95 (t, 3H, J = 7.79 Hz), 0.97 (t, 3H, J = 7.74 Hz), 1.47 (m, 4H), 1.75 (m, 4H), 2.19 (s, 3H), 2.35 (s, 3H), 3.92 (t, 2H, J = 6.44 Hz), 3.97 (t, 2H, J = 6.41 Hz), 5.97 (s, 2H), 6.76 (d, 2H, J = 8.68 Hz), 6.88 (d, 2H, J = 8.36 Hz), 7.05−7.16 (m, 5H), 7.43 (s, 1H), 7.45 (d, 2H, J = 8.70 Hz), 8.20 (s, 1H). LDI-MS: *m/z* 1658 (10, $3M^+ - 3H_2O$), 1119 (20), 593 (90), 564 (100), 520 (30). Anal. Calcd for $C_{38}H_{39}BO_4$: C, 80.00; H, 6.89. Found: C, 79.48; H, 6.97.

2′,5′,2‴,5‴-Tetrakis(4-butoxyphenylethynyl)-2,5,2″,5″,2⁗,5⁗-hexamethyl[1,1′:4′,1″: 4″,1‴:4‴, 1⁗]quinquephenyl (24). To a 200 mL Schlenk flask charged with **22** (1.70 g, 2.98 mmol), 2,5-diiodo-*p*-xylene (0.485 g, 1.35 mmol), $Pd(dba)_2$ (0.023 g, 0.04 mmol), triphenylphosphine (0.160 g, 0.60 mmol), and KOH (1.67 g, 29.8 mmol) was added 15 mL of H_2O and 45 mL of nitrobenzene. The mixture was allowed to stir for 14 h at 90 °C. After cooling to room temperature the mixture was diluted with 150 mL of ethyl ether and 30 mL of H_2O. The organic layer was washed with additional H_2O, 5% HCl, and saturated NaCl solution. Following removal of ethyl ether

in vacuo, the compound was precipitated by the addition of methanol to the remaining nitrobenzene. After cooling in a refrigerator for 2 h, the product was filtered. Recrystallization from THF−MeOH provided **24** (mp 251−252 °C) as a colorless solid (1.28 g, 82.1%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, 6H, J = 7.43 Hz), 0.95 (t, 6H, J = 7.43 Hz), 1.37−1.50 (m, 8H), 1.64−1.76 (m, 8H), 2.28 (s, 6H), 2.32 (s, 6H), 2.38 (s, 6H), 3.92 (t, 8H, J = 6.57 Hz), 6.75 (d, 8H, J = 8.88 Hz), 7.08 (d, 8H, J = 8.87 Hz), 7.13 (dd, 2H, J = 7.78, 1.63 Hz), 7.17 (br s, 2H), 7.20 (d, 2H, J = 7.79 Hz), 7.29 (s, 2H), 7.52 (s, 2H), 7.57 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.79, 19.18, 19.53, 19.62, 20.99, 31.21, 67.62, 67.74, 87.82, 93.87, 94.26, 114.46, 115.22, 122.60, 122.83, 128.33, 129.62, 130.65, 131.2127, 132.33, 132.49, 132.86, 133.39, 134.61, 139.45, 139.90, 143.15, 159.21. UV−vis ($CHCl_3$) λ_{max} (ϵ, cm^{-1} M^{-1}): 364 (114 000), 342 (127 000) 286 (45900) nm. Luminescence spectrum ($CHCl_3$) λ_{max} (rel int): 374 (1), 394 (0.86) nm. LDI-MS: found m/z 1155 (M^+). Anal. Calcd for $C_{84}H_{82}O_4$: C, 87.31; H, 7.15. Found: C, 87.32; H, 7.25.

8-Butoxy-4,6a-dimethyl-[(5,8-dimethyl-9-(4-butoxyphenyl))phenanthro[2,3-*c*]]spiro[[(2′-(4-butoxyphenyl))(4-(4-butoxyphenyl)-5,8-dimethylnaphtho[1,2-*f*′])]indenyl-1′,6-[6,6a-dihydrofluoranthene]] (25). Compound **25** was prepared following the general TFA cyclization conditions described previously.[5] Following purification by silica gel chromatography (50:1 hexanes−THF) compound **25** (mp 144−145 °C) was isolated as a yellow solid (67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.81 (t, 6H, J = 7.28 Hz), 0.99 (t, 6H, J = 7.42 Hz), 1.21 (s, 3H), 1.20−1.35 (m, 6H), 1.50−1.60 (m, 12H), 1.78−1.88 (m, 6H), 1.99 (s, 3H), 2.05 (s, 3H), 2.64 (app d, 3H, J = 1.40 Hz), 3.12 (s, 3H), 3.21 (s, 3H), 3.63 (t, 2H, J = 6.50 Hz), 3.75 (m, 2H), 4.02 (t, 2H, J = 6.50 Hz), 4.03 (t, 2H, J = 6.50 Hz), 6.16 (q, 1H, J = 1.42 Hz), 6.18 (d, 1H, J = 2.58 Hz), 6.34 (d, 2H, J = 8.77 Hz), 6.65 (d, 2H, 8.63 Hz), 6.80 (s, 1H), 6.86 (dd, 1H, J = 8.48, 2.56 Hz), 6.94 (d, 2H, J = 8.92 Hz), 6.96 (d, 2H, J = 8.90 Hz), 7.20 (d, 1H, J = 7.54 Hz), 7.23 (d, 1H, J = 7.37 Hz), 7.28−7.34 (m, 4H), 7.39 (br d, J = 7.32 Hz), 7.54 (s, 1H), 7.66 (s, 1H), 7.98 (d, 1H, J = 8.46 Hz), 8.01 (s, 1H), 8.03 (s, 1H), 8.57 (s, 1H), 8.62 (s, 1H), 9.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 13.74 (CH_3), 13.90 (CH_3), 17.69 (CH_3), 18.99 (CH_3), 19.09 (CH_2), 19.14 (CH_2), 19.31 (CH_2), 24.97 (CH_3), 25.18 (CH_3), 26.83 (CH_3), 27.06 (CH_3), 29.70 (CH_2), 31.15 (CH_2), 31.21 (CH_2), 31.44 (CH_2), 46.28, 61.36, 67.25 (CH_2), 67.50 (CH_2), 67.81 (CH_2, 2C), 112.22 (CH), 112.83 (CH), 113.64 (CH), 114.07 (CH), 118.87 (CH), 121.15 (CH), 124.79 (CH), 126.21 (CH), 126.41, 126.47 (CH), 127.03, 128.50 (CH), 128.73, 129.54 (CH), 129.83 (CH), 129.92 (CH), 130.01 (CH), 130.13 (CH), 130.24 (CH), 130.28 (CH), 130.32 (CH), 130.47 (CH), 130.53 (CH), 130.61, 130.90 (CH), 131.10, 131.59, 132.09, 132.27, 132.37, 132.59, 132.66, 132.90, 133.22, 133.79, 134.01, 134.93 (CH), 137.68, 137.72, 138.25, 138.55, 139.41, 140.61, 144.44, 145.99, 147.71, 157.76, 158.16, 158.20, 159.50. UV−vis ($CHCl_3$) λ_{max} (ϵ, cm^{-1} M^{-1}): 418 (18 800), 398 (26 500), 370 (43 500), 338 (109 000), 290 (75 200) nm. Luminescence spectrum ($CHCl_3$) λ_{max} (rel int): 438 (1), 462 (0.73) nm. LDI-MS: m/z 1155 (M^+).

5,9,16,20-Tetrakis(4-butoxyphenyl)-6,10,17,21-tetraiodo-1,4,8,12,15,19-hexamethylbis(phenanthro[2,3-*a*,*h*]anthracene) (26). A solution of **24** (0.140 g, 0.121 mmol) in 100 mL of 1,2-dichloroethane was subjected to two freeze−pump−thaw cycles. After warming to room temperature the solution was heated until homogeneous and then allowed to cool to room temperature, remaining homogeneous. To a separate flask charged with I_2 (0.427 g, 1.68 mmol) was added 18.62 mL of a $Hg(TFA)_2$−CH_2Cl_2 solution (0.03 M, 0.559 mmol) followed by 2,6-lutidine (65 μL, 0.558 mmol). After cooling of both solutions to 0 °C, the solution of **24** was cannulated into the iodonium solution over 2 min. After stirring for 15 min, the reaction was quenched with 50 mL of 5% NaOH. Additional washing of the organic layer with 5% NaOH, H_2O, 5% HCl, and H_2O followed by drying ($MgSO_4$) and removal of solvent in vacuo provided the crude product which was crystallized from dilute $CHCl_3$−ethanol (0.96 g, 47.7%). *Note*: It was previously determined that the tetraiodide product **26** is thermally sensitive, therefore strict care was taken to ensure that the product was kept at temperatures below 35 °C during all stages of workup/purification. Thermal instability combined with poor solubility limited the extent to which this product could be purified/characterized. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (t, 6H, J = 7.42 Hz), 1.02 (t, 6H, J = 7.36 Hz), 1.48−1.60 (m, 8H), 1.77−1.87 (m, 8H), 1.83 (s, 6H), 2.51 (s, 6H), 3.23 (s, 6H), 4.02 (t, 4H, J = 6.50 Hz), 4.07 (t, 4H, J = 6.54 Hz), 6.98 (d, 4H, J = 8.70 Hz), 7.07 (d, 4H, J = 8.65 Hz), 7.15 (d, 4H, J = 8.59 Hz), 7.20 (d, 2H, J = 7.50 Hz), 7.42 (d, 4H, J = 8.62 Hz), 7.43 (d, 2H, J = 7.50 Hz), 9.25 (s, 2H), 9.47 (s, 2H). UV−vis ($CHCl_3$) λ_{max} (ϵ, cm^{-1} M^{-1}): 440 (73 300), 418 (71 600), 378 (152 000), 328 (88 400), 312 (89 200) nm. Luminescence spectrum ($CHCl_3$) λ_{max} (rel int): no detectable signal. LDI-MS: m/z 1659 (23, M^+), 1602 (17, $M^+ - C_4H_9$), 1532 (67, $M^+ - I$), 1474 (33, $M^+ - C_4H_9 - I$), 1404 (100, $M^+ - 2I$), 1347 (44, $M^+ - C_4H_9 - 2I$), 1277 (79, $M^+ - 3I$), 1220 (41, $M^+ - C_4H_9$-3I), 1149 (49, $M^+ - 4I$), 1093 (26, $M^+ - C_4H_9 - 4I$). Anal. Calcd for $C_{84}H_{78}O_4I_4$: C, 60.81; H, 4.74. Found: C, 60.15; H, 4.64.

5,9,16,20-Tetrakis(4-butoxyphenyl)-1,4,8,12,15,19-hexamethylbisphenanthro[2,3-*a*,*h*]anthracene (27). To a 500 mL Schlenk flask containing **26** (0.066 g, 0.040 mmol) was added 250 mL of THF. The heterogeneous mixture was cooled to −78 °C and *t*-BuLi (2 mL, 1.46 M, 2.92 mmol) was added. The cooling bath was removed until the solution became homogeneous (ca. 10 min), at which time the solution was allowed to stir for an additional 2 min. After recooling to −78 °C, 5 mL of *i*-PrOH was rapidly added. After allowing to warm to room temperature the mixture was diluted with 150 mL of ethyl ether, washed with 5% HCl (2 × 60 mL) and H_2O, and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. Purification of the crude product by silica gel chromatography (3:2 toluene−hexanes) provided **27** (mp >280 ×a1C) as a bright yellow solid (0.038 g, 82.7%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (t, 6H, J = 7.40 Hz), 1.04 (t, 6H, J = 7.37 Hz), 1.51−1.60 (m, 8H), 1.81−1.90 (m, 8H), 2.05 (s, 6H), 2.75 (s, 6H), 3.22 (s, 6H), 4.06 (t, 4H, J = 6.54 Hz), 4.11 (t, 4H, J = 6.54 Hz), 6.98 (d, 4H, J = 8.66 Hz), 7.11 (d, 4H, J = 8.63 Hz), 7.26 (d, 2H, J = 7.50 Hz), 7.34 (d, 4H, J = 8.61 Hz), 7.43 (d, 2H, J = 7.49 Hz), 7.65 (d, 4H, J = 8.63 Hz), 7.67 (s, 2H), 7.83 (s, 2H), 8.81 (s, 2H), 9.06 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.90, 19.33, 19.36, 25.21, 26.72, 30.16, 31.45, 31.52, 67.84, 67.91, 114.10, 114.75, 127.45, 128.12, 129.31, 129.42, 129.50, 129.89, 130.10, 130.15, 130.20, 130.35, 130.69, 131.98, 132.03, 132.18, 132.35, 133.30, 133.34, 133.92, 134.10, 137.74, 137.86, 138.58, 138.62, 158.08, 158.26. UV−vis ($CHCl_3$) λ_{max} (ϵ, cm^{-1} M^{-1}): 464 (3920), 434 (63 500), 410 (58 500), 364 (106 000), 324 (76 800), 294 (55 800). Luminescence spectrum ($CHCl_3$) λ_{max} (rel int): 472 (1), 444 (0.46) nm. LDI-MS: m/z 1188 (10), 1172 (10), 1155 (100, M^+), 1145 (15), 618 (10). Anal. Calcd for $C_{84}H_{82}O_4$: C, 87.31; H, 7.15. Found: C, 87.27; H, 7.39.

2,5-Bis(4-octyloxy-2,6-dimethylphenylethynyl)-1,4-dibromobenzene (28) was btained as a pale yellow solid (mp 150−152 °C) in 72% yield using the method described for **11**.[5] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.74 (s, 2H, CH═C(Br)), 6.63 (s, 4H, OC═CH), 3.95 (t, 4H, J = 6.5 Hz, OCH_2), 2.52 (s, 12H, C═C(CH_3)), 1.81−1.71 (m, 4H, OCH_2CH_2), 1.30 (br s, 20H, CH_2), and 0.89 (t, 6H, J = 7 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.42, 142.78, 135.67, 126.64, 122.88, 114.31, 113.18, 95.04, 93.80, 67.94, 31.82, 29.34, 29.24, 26.03, 22.66, 21.56, and 14.08. HREIMS: calcd for $C_{42}H_{52}Br_2O_2$ 746.2334, observed 746.2335.

2,5-Bis(4-octyloxy-2,6-dimethylphenylethynyl)-1-iodo-4-bromobenzene (29) was obtained as a pale yellow solid (mp 102−103 °C) in 80% yield by utilizing the same procedure as was used for **12**. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.97 (s, 1H, CH═C(I)), 7.70 (s, 1H, CH═C(Br)), 6.63 (s, 4H, OC═CH), 3.96 (t, 4H, J = 6.5 Hz, OCH_2), 2.55 (s, 6H, C═C(CH_3)), 2.52 (s, 6H, C═C(CH_3)), 1.81−1.71 (m, 4H, OCH_2CH_2), 1.30 (br s, 20H, CH_2), and 0.89 (t, 6H, J = 7 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.40, 142.87, 142.77, 141.88, 135.14, 131.18, 126.76, 124.07, 114.36, 114.25, 113.20, 113.17, 97.11, 96.88, 95.00, 94.29, 93.53, 67.94, 31.81, 29.34, 29.23, 26.03, 22.65,

21.84, 21.57, and 14.08. HREIMS: calcd for $C_{42}H_{52}BrIO_2$ 794.2195, observed 794.2189.

4-Bromo-2,5-bis(4-octyloxy-2,6-dimethylphenylethynyl)-2′,5′-dimethoxy-1,1′-biphenyl (31). A mixture of **29** (166 mg, 0.20 mmol), 2,5-dimethoxyphenylboronic acid (44 mg, 0.09 mmol), $Pd(dba)_2$ (8 mg, 0.014 mmol, 9 mol %), Tl_2CO_3 (381 mg, 0.81 mmol), and triphenylphosphine (160 mg, 0.61 mmol) in a Schlenk flask was evacuated and back-filled with argon thrice. THF (8 mL) and water (1.4 mL) were added, and the mixture was purged with argon for 30 min. The reaction was heated to 60 °C for 40 h, cooled, and filtered through a silica plug with chloroform, and the solvents were removed under reduced pressure. The resulting sticky yellow solid (350 mg) was purified by recrystallization from THF−MeOH to give **31** (139 mg, 82%) as a pale yellow solid (mp 100−102 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.82 (s, 1H, C≡CC═CH), 7.47 (s, 1H, C≡CC═CH), 6.88 (s, 3H, CH_3OC═C*H*C*H*, CH_3OCH), 6.62 (s, 2H, C*H*═C(CH_3)), 6.51 (s, 2H, C*H*═C(CH_3)), 3.95−3.90 (m, 4H, OCH_2), 3.77 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 2.52 (s, 6H, C═CCH_3), 2.13 (s, 6H, C═CCH_3), 1.81−1.70 (m, 4H, OCH_2CH_2), 1.29 (br s, 20H, CH_2), and 0.88 (t, 6H, J = 6 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.12, 158.90, 153.51, 151.06, 142.56, 142.18, 139.30, 135.03, 134.11, 129.78, 125.15, 124.93, 123.00, 116.82, 114.90, 113.10, 112.91, 112.66, 95.00, 94.57, 93.63, 92.44, 67.91, 67.85, 56.45, 55.82, 31.80, 29.70, 29.33, 29.32, 29.25, 29.22, 26.03, 26.01, 22.64, 21.56, 20.87, and 14.06. HREIMS: calcd for $C_{50}H_{61}BrO_4$ 804.3753, observed 804.3781.

4-Iodo-2,5-bis(4-octyloxy-2,6-dimethylphenylethynyl)-2′,5′-dimethoxy-1,1′-biphenyl (32). A solution of **31** (197 mg, 0.24 mmol, 1 equiv) in THF (25 mL) was cooled to −78 °C and a 1.4 M solution of *n*-BuLi in hexane (0.23 mL, 0.32 mmol, 1.3 equiv) was added. After 1 h, a solution of iodine (0.11 g, 0.43 mmol, 1.8 equiv) in THF (10 mL) was added and the reaction was allowed to warm slowly to room temperature and stirred for 12 h at room temperature. Excess iodine was quenched by addition of 2 M KOH (20 mL) and stirring for 30 min. The organic solvents were removed under reduced pressure, and the granular yellow solid was filtered and washed with water. Recrystallization from THF−MeOH gave **32** (194 mg, 95%) as an off-white solid (mp 153−154 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.07 (s, 1H, C≡CC═CH), 7.44 (s, 1H, C≡CC═CH), 6.88 (s, 3H, CH_3OC═C*H*C*H*, CH_3OCH), 6.62 (s, 2H, C*H*═C(CH_3)), 6.51 (s, 2H, C*H*═C(CH_3)), 3.98−3.86 (m, 4H, OCH_2), 3.77 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 2.54 (s, 6H, C═CCH_3), 2.13 (s, 6H, C═CCH_3), 1.81−1.70 (m, 4H, OCH_2CH_2), 1.29 (br s, 20H, CH_2), and 0.88 (t, 6H, J = 6 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.08, 153.47, 150.99, 142.64, 142.15, 141.95, 141.30, 140.07, 133.52, 129.81, 129.67, 124.97, 116.74, 114.91, 114.74, 114.05, 113.09, 112.88, 112.60, 98.07, 97.66, 94.29, 92.90, 92.41, 67.89, 67.82, 56.42, 55.81, 31.80, 29.32, 29.22, 26.02, 22.64, 21.85, 20.88, and 14.08. HREIMS: calcd for $C_{50}H_{61}IO_4$ 852.3574, observed 852.3553.

2′,5′,2‴,5‴-Tetrakis(4-octyloxy-2,6-dimethylphenylethynyl)-2,5,2″,5″,2⁗,5⁗-hexamethoxy[1,1′:4′,1″: 4″,1‴:4‴, 1⁗]quinquephenyl (33) was obtained in 84% yield as a colorless solid (mp 141−143 °C) from **16** and **32** using the same procedure employed for **31**. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.62 (s, 2H, C≡CC═C*H*), 7.59 (s, 2H, C≡CC═C*H*), 7.09 (s, 2H, $H_{21}C_{10}OC$═C*H*), 7.01−6.91 (m, 6H, MeOC*H*, MeOC*H*═C*H*), 6.52 (s, 4H, $H_{17}C_8OC$═C*H*), 6.45 (s, 4H, $H_{17}C_8OC$═C*H*), 3.92−3.83 (m, 12H, OCH_2), 3.81 (s, 6H, OCH_3), 3.76 (s, 6H, OCH_3), 2.20 (s, 12H, C═C(CH_3)), 2.19 (s, 12H, C═C(CH_3)), 1.82−1.56 (m, 12H, OCH_2CH_2), 1.28 (br s, 34H, CH_2), 1.11 (br s, 34H, CH_2), and 0.88−0.79 (m, 18H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.56, 158.51, 153.47, 151.27, 150.05, 141.92, 141.88, 139.34, 138.84, 133.73, 133.26, 130.76, 130.11, 123.34, 122.94, 117.03, 116.69, 115.49, 115.38, 113.84, 112.82, 112.76, 112.70, 96.20, 91.44, 91.00, 69.62, 67.79, 67.74, 56.58, 55.82, 31.89, 29.63, 29.42, 29.37, 29.34, 29.31, 29.26, 29.23, 26.03, 21.06, 20.96, and 14.09. LDI-MS: calcd for $C_{126}H_{166}O_{10}$ 1840.69, observed 1840.32.

5,9,16,20-Tetrakis(4-octyloxy-2,6-dimethylphenyl)-1,4,8,-12,15,19-hexamethylbisphenanthro[2,3-*a*,*h*]anthracene (34). To a solution of **33** (43.4 mg, 24 μmol) in CH_2Cl_2 (15 mL) was added trifluoroacetic acid (0.2 mL, 2.6 mmol, 111 equiv). After 2 h the reaction was diluted with $CHCl_3$ (125 mL) and washed with 2 M KOH (5 × 40 mL). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure to give 43 mg of a brown solid of ∼90% purity by ^{1}H NMR. Silica gel chromatography (1:1 hexanes−$CHCl_3$) gave **34** (34 mg, 79%) as a yellow solid (mp 271−273 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 10.07 (s, 2H), 9.92 (s, 2H), 7.63 (s, 2H), 7.56 (s, 2H), 7.17 (d, 2H, J = 8.9 Hz), 7.00 (d, 2H, J = 8.9 Hz), 6.84−6.68 (m, 8H), 4.16 (s, 6H), 4.14−4.00 (m, 12H), 3.41 (s, 6H), 2.29 (s, 6H), 2.25 (s, 6H), 2.06 (s, 6H), 1.89 (s, 6H), 1.33−1.16 (m, 68H), and 0.93−0.84 (m, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.40, 157.00, 153.72, 151.92, 151.59, 139.39, 138.23, 137.84, 136.49, 135.96, 134.66, 134.29, 134.01, 133.06, 131.33, 130.91, 128.29, 127.53, 127.42, 127.00, 126.14, 125.00, 123.63, 122.29, 112.83, 112.61, 112.39, 112.14, 110.10, 108.86, 74.21, 67.88, 57.14, 56.02, 32.01, 31.91, 31.87, 29.74, 29.69, 29.67, 29.63, 29.56, 29.55, 29.52, 29.46, 29.35, 29.31, 29.26, 26.24, 26.18, 25.71, 22.72, 22.70, 22.69, 21.81, 21.27, 21.18, 20.82, 14.15, and 14.14. LDI-MS: calcd for $C_{126}H_{166}O_{10}$ 1840.69, observed 1543.

5,9,16,20-Tetrakis(4-octyloxy-2,6-dimethylphenyl)-6,-10,17,21-tetraiodo-1,4,8,12,15,19-hexamethylbisphenanthro[2,3-*a*,*h*]anthracene (35). Prepared in 90% yield following the same procedure as was used for **26**. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 10.85 (s, 2H), 10.39 (s, 2H), 7.23 (d, 2H, J = 9.1 Hz), 7.02 (d, 2H, J = 8.9 Hz), 6.76−6.62 (4s, 8H), 4.25 (s, 6H), 4.03−4.00 (m, 12H), 3.34 (s, 6H), 2.29 (s, 6H), 2.00 (s, 6H), 1.94 (s, 6H), 1.85−1.76 (m, 6H), 1.68 (s, 6H), 1.33−1.16 (m, 62H), and 0.93−0.84 (m, 18H).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **10, 12 14, 15, 18, 19, 24−29,** and **31−35** and absorption and emission spectra of compounds **10, 18, 24−27, 33,** and **34** (45 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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