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Selective Oxidative Cyclization by $FeCl_3$ in the Construction of 10*H*-Indeno[1,2-*b*]triphenylene Skeletons in Polycyclic Aromatic Hydrocarbons

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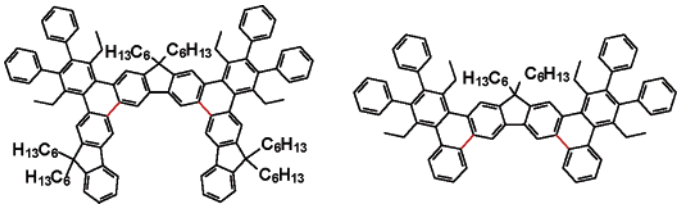

A novel family of polycyclic aromatic hydrocarbons of various shapes based on the 10*H*-indeno[1,2-*b*]-triphenylene skeleton has been synthesized via a reaction sequence of Diels−Alder reaction, decarbonylation, followed by an oxidative cyclization. In particular, the reaction conditions for regioselective oxidative cyclization promoted by $FeCl_3$ are investigated, and this reaction is employed as an effective method to afford the above molecules under mild conditions. Their photophysical properties in dilute solution are also reported.

Introduction

In the past decades, polycyclic aromatic hydrocarbons (PAHs) with well-defined geometry and desired electronic properties have attracted considerable attention. In addition to their applications in the construction of fullerenes and carbon nanotubes and in the assembly of supramolecular architectures, PAHs have been extensively used in electronic and optoelectronic devices, such as photovoltaic cells, liquid crystal displays, organic light-emitting diodes (OLEDs), and organic field effect transistors (OFETs).[1] Studies on these molecular-defined model compounds also enrich the chemistry of PAHs.[2]

Since both the molecular size and the shape of PAHs play very important roles on their electronic properties, energetics, and reactivity, it is necessary to design and synthesize PAHs of diverse structures for systematic investigation of their structure−property relationships and the tuning of molecular properties for specific applications.[1,3] Moreover, the construction of novel nanosized, soluble, planar or helical polycyclic aromatic compounds is of great interest. Thus, elegant synthetic approaches to PAHs with diverse sizes and shapes have been developed.[3,4] In particular, a multibond oxidative coupling

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reaction using $FeCl_3$ has been explored as an efficient methodology in the construction of novel PAHs, including hexa-*peri*-hexabenzocoronene (HBC), sulfur-containing polycyclic aromatics, as well as heterosuperbenzenes.[4] However, to our best knowledge, no selectivity was observed with such oxidative cyclization in the construction of larger HBC derivatives.

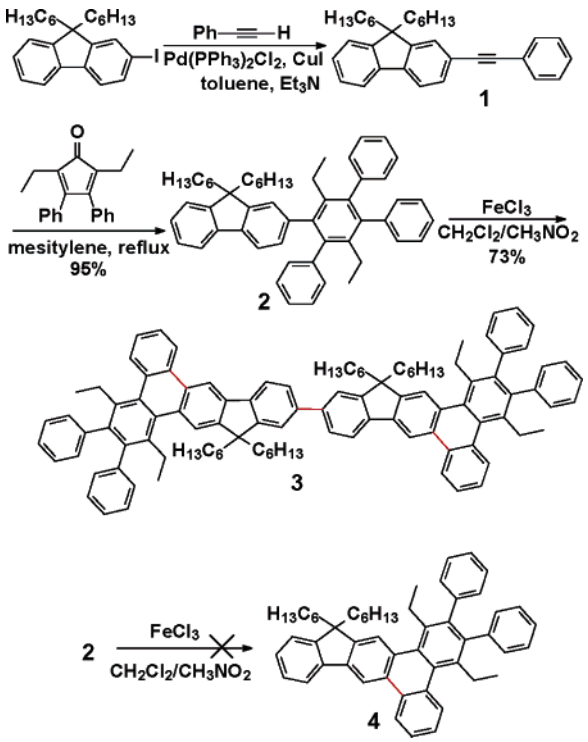
Herein, we report the synthesis of a novel class of PAHs with various shapes, in which the 10*H*-indeno[1,2-*b*]triphenylene moiety served as the basic skeleton. We developed a facile, efficient, and regioselective approach to such molecules via a reaction sequence of Sonogashira cross-coupling, Diels−Alder reaction, decarbonylation, and an oxidative cyclization by $FeCl_3$. Additionally, fluorene units were incorporated as the basic building block for these PAHs because fluorene analogues and polyfluorenes have exhibited desired properties for applications in optoelectronic devices.[5] Due to the presence of a number of alkyl substituents, the accomplished PAHs exhibit good solubility in common organic solvents.

Results and Discussion

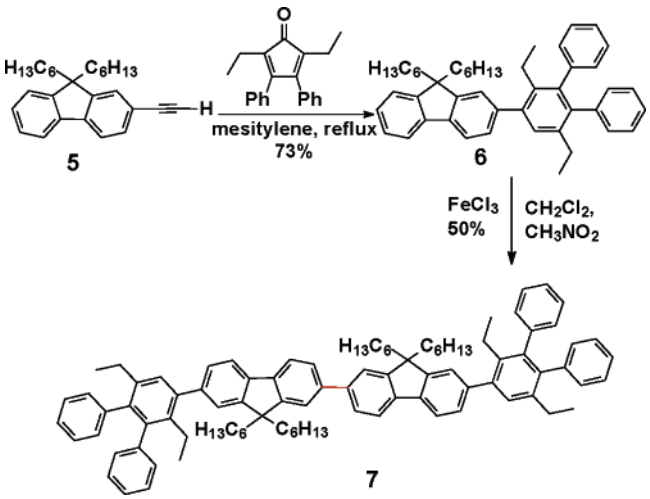
Synthesis. Scheme 1 illustrates the synthetic route to dimer **3**. The Sonogashira coupling reaction of 9,9-dihexyl-2-iodofluorene with phenylacetylene in the presence of Pd catalyst afforded **1** as a white solid in high yield. The Diels−Alder reaction of compound **1** with 2,5-diethyl-3,4-diphenylcyclopentadienone followed by decarbonylation in refluxed mesitylene produced **2** in 95% yield. It is noteworthy that the oxidative cyclization mediated by $FeCl_3$ (8 equiv of $FeCl_3$ per C−C bond formation)[4] afforded dimer **3** rather than the expected **4**. The formation of **3** requires not only the cyclization to afford the expected 10*H*-indeno[1,2-*b*]triphenylene skeleton but also an intermolecular dimerization coupling between the fluorene units. We were not able to isolate any compound **4**. At 0 °C, we did not observe polymerization or other compounds even when an excess amount of $FeCl_3$ (20 equiv per C−C bond formation) was used.

As shown in Scheme 2, to better understand the process of the oxidative cyclization, we applied the same reaction conditions to 9′,9′-dihexyl-2′-fluorenylacetylene **5**.[4i] Compound **5** and 2,5-diethyl-3,4-diphenylcyclopentadienone underwent a Diels−Alder reaction followed by decarbonylation to produce **6**. In comparison with **2**, the phenyl ring in close proximity to the adjacent fluorenyl moiety was absent in compound **6** so that the 10*H*-indeno[1,2-*b*]triphenylene skeleton could not be formed using $FeCl_3$ as the oxidant. To assess the specificity of the oxidative cyclization under such conditions, compound **6** was subjected to $FeCl_3$ oxidation and compound **7** was produced and isolated in 50% yield. For compound **6**, we knew that the 10*H*-indeno[1,2-*b*]triphenylene skeleton could not be constructed using $FeCl_3$ oxidant. We also employed a larger excess of $FeCl_3$ (20 equiv per C−C bond formation) to drive the reaction to completion without polymerization and chlorization. The $FeCl_3$ oxidation has ever been employed to prepare polyfluorene from fluorene derivatives at room temperature.[6] These experimental results suggest that the $FeCl_3$ oxidative coupling might be an effective method for the preparation of oligofluorene derivatives. In addition, as shown in Schemes 1 and 2, we did not observe any products from the C−C bond formation between the benzene rings that are not part of the fluorene units. This result

SCHEME 1



SCHEME 2



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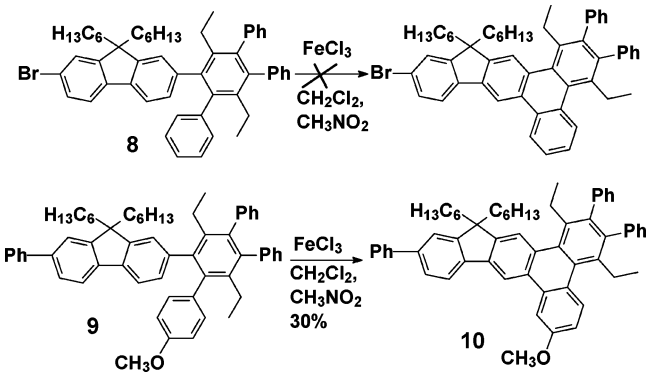
SCHEME 3



is quite different from the preparation of hexa-*peri*-hexabenzocoronene (HBC) derivatives.[4a,b,i]

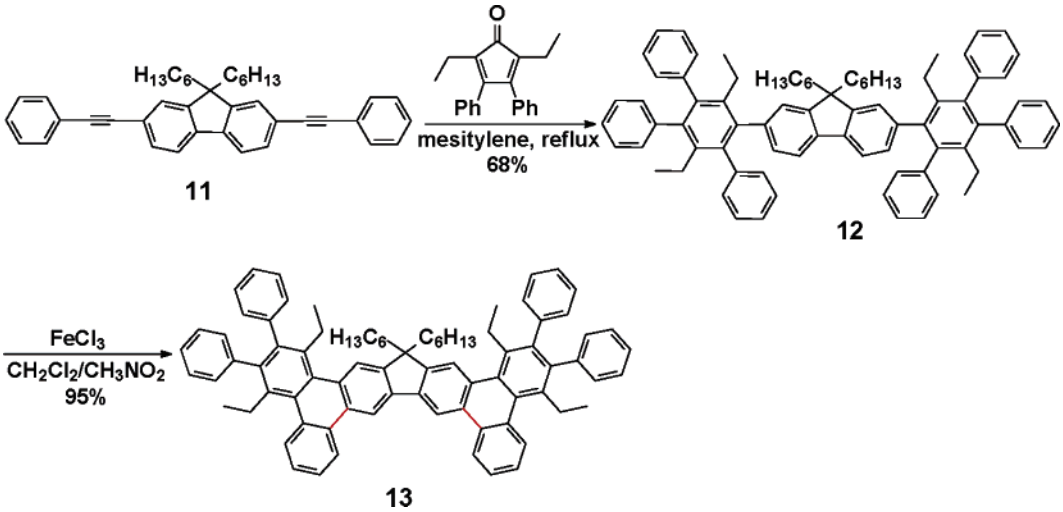
We then optimized the conditions of this oxidative cyclization by examining the amount of $FeCl_3$ added as well as the reaction temperature. It was found that even in the presence of an excess amount of $FeCl_3$ (more than 20 equiv per C−C bond formation), no chlorinated byproducts were produced at 0 °C.[4b,i] Nonetheless, the cyclization was completed in less than 10 min. However, as shown in Scheme 3, when a bromide substituent was introduced at the C7 position of the fluorene unit, the formation of the 10*H*-indeno[1,2-*b*]triphenylene system was not achieved, and we speculated that this might be due to the deactivation effect of the bromide group. Upon introducing a methoxy substituent to enhance the electron density of the phenylene ring, compound **10** was obtained by the oxidative cyclization of **9** in 30% yield.

With these results in hand, we utilized the oxidative cyclization protocol described above to construct larger systems via the fluorenyl−phenyl or fluorenyl−fluorenyl carbon−carbon bond formation. From the corresponding iodide compounds, we prepared 9,9-dihexyl-2,7-bis(2-phenylethynyl)fluorene (**11**) and bis(9,9-dihexyl-2-fluorenyl)acetylene (**14**) through the Sonogashira coupling reaction.[4i,7] As shown in Scheme 4, the Diels−Alder reaction of 9,9-dihexyl-2,7-bis(2-phenylethynyl)fluorene with 2,5-diethyl-3,4-diphenylcyclopentadienone followed by decarbonylation afforded **12** in 68% yield. A double cyclization of **12** by the oxidation of $FeCl_3$ afforded **13** in an optimal yield of 95%. Compound **16** was also obtained via a similar procedure in a good yield (94%), as illustrated in Scheme 5. For this two-fluorene-terminated compound **16** from compound **15**, it was surprising that we did not observe any dimerization, such as in the cyclizations of **3** and **7**, or polymerization at 0 °C. This might be due to the lower cation activity caused by the high delocalization of the whole conjugated structure and the steric hindrance within the structure of **15**. This may allow us to prepare even larger molecules with interesting structures through the formation of multiple C−C bonds utilizing oligofluorenylacetylene derivatives.

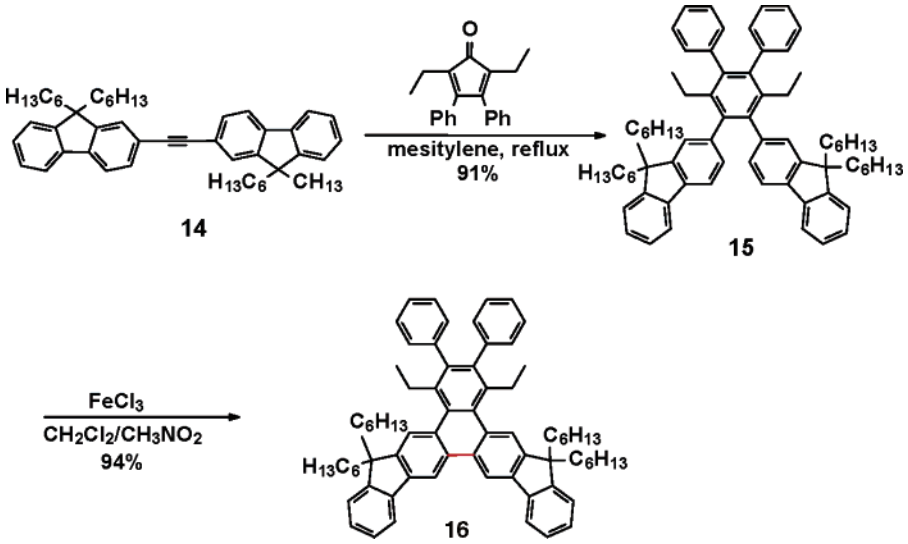
To demonstrate generality of the method, we examined whether extended fluorenyl moieties would affect the cyclization efficiency. We prepared model compound **18** through Diels−Alder reaction and decarbonylation from 2,7-bis[2′-(9″,9″-dihexyl-2″-fluorenylethynyl)]-9,9-dihexylfluorene (**17**) (as shown in Scheme 6). Similar oxidative conditions effectively provided the double-cyclized product **19** in 61% yield. This result suggests that the current protocol may provide an effective method for the preparation of helical polycyclic aromatics.

All herein prepared polycyclic aromatic hydrocarbons readily dissolved in common organic solvents, such as $CHCl_3$ and chlorobenzene, and were characterized by standard spectroscopic measurements. The identity and the purity of all new compounds were confirmed by ^1H and ^{13}C NMR spectra, MALDI-TOF or EI mass spectrum, as well as elemental analysis. ^1H NMR spectra in $CDCl_3$ of all compounds show sharp and well-defined signals at room temperature. For all compounds, the presence of signals at 0.4−0.7 ppm was observed in ^1H NMR spectra. These signals were assigned to methylene groups of the hexyl substituents, and they were more upfield than those of the methyl group and the methylene groups in other structures. Such behaviors had actually also been observed by us and by others in the extensively investigated 9,9-dialkylfluorene moiety.[8] For all cyclized compounds, in the aromatic range of ^1H NMR spectra, both sharp singlet signals belonging to the triphenylene system moved downfield to 8.3 ppm from less than 8.0 ppm after the cyclization. Spectroscopic measurements also confirm the C_2 symmetry of these polycyclic molecules. Likely due to the hexyl substituents,[9] fused compounds **13** and **16** with such large planar π-systems did not exhibit concentration-dependent chemical shifts in the ^1H NMR spectra, although their favorable cofacial interactions could induce aggregation within the system.

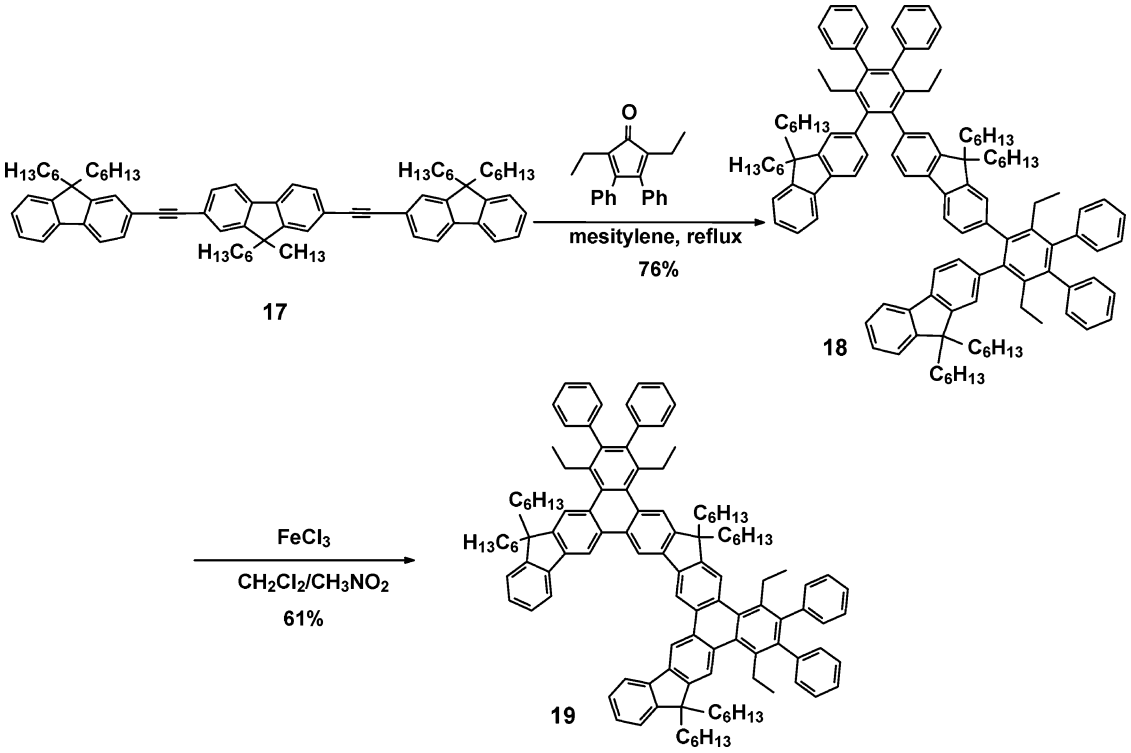
SCHEME 4



SCHEME 5



SCHEME 6



Photophysical Properties. The basic photophysical properties of these 10*H*-indeno[1,2-*b*]triphenylene derivatives in dilute THF solutions (10^{-5} mol L^{-1}) were first investigated, and their absorption spectra are shown in Figure 1. Table 1 summarizes the photophysical properties of these compounds. The typical absorption feature of the triphenylene moiety was at ~250−260 nm.[10] For most of our compounds studied, a slight red shift was observed in their absorption spectra (270 nm for **3**, 276 nm for **10**, 276 nm for **13**, and 281 nm for **16**), except for compound **7** because no 10*H*-indeno[1,2-*b*]triphenylene skeleton existed in this compound structure. We also observed the strong absorption behaviors at ~300−310 nm for another five com-

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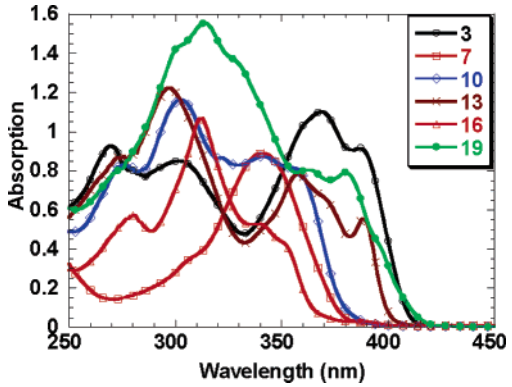

FIGURE 1. The absorption spectra of new compounds in dilute THF solutions (10^{-5} mol L^{-1}) at room temperature.

TABLE 1. Photophysical Properties of New Compounds in Dilute THF Solutions (10^{-5} mol L^{-1})

compound	absorption λ_{max} (nm)	ϵ ($\times 10^5$ M^{-1} cm^{-1})	emission λ_{max} (nm)
3	302	0.90	393
	369	1.2	417
7	341	0.73	386
10	303	0.93	412
	341	0.70	
13	297	1.1	383
	357	0.70	403
	388	0.50	
16	312	0.97	406
19	313	0.77	397
	363	1.4	
	380	1.5	

pounds. Compounds **3**, **10**, and **13** exhibited similar absorption peaks in this region (302 nm for **3**, 303 nm for **10**, and 297 nm for **13**), while compounds **16** and **19** showed the similar absorption feature (312 nm for **16** and 313 nm for **19**). The molar extinction coefficients (ϵ) of these peaks for these five compounds were around $\sim 10^5$ M^{-1} cm^{-1}.

Normally, oligofluorene and polyfluorene derivatives show strong $\pi-\pi^*$ electron absorption bands in the visible region, which is progressively red-shifted with increasing chain length. For compound **3**, the maximum absorption peaked, λ_{max}, at 369 nm with a shoulder at 387 nm. For compound **7**, its absorption, λ_{max}, was at 341 nm, which was close to that of the corresponding oligofluorene derivatives.[11] In comparison with compound **7** ($\lambda_{max} = 341$ nm), compound **3** exhibited the obvious red shift, which might be due to the increasing effective conjugation length by the 10*H*-indeno[1,2-*b*]triphenylene units. Similar behaviors were also observed from the absorption spectra of compounds **10** and **13**. In comparison with compound **16**, compound **19** exhibited a broad absorption spectrum. Moreover, its onset red-shifted from about 370 nm for compound **16** to 410 nm. These observations suggested the formation of a highly extended π-delocalized system in compound **19**.

Figure 2 illustrates the photoluminescent (PL) spectra for these compounds in dilute THF solutions, and all compounds showed similar behaviors and a maximum with a well-defined

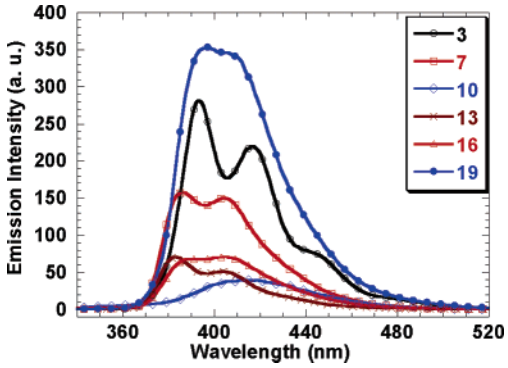

FIGURE 2. The emission spectra of new compounds in dilute THF solutions (10^{-5} mol L^{-1}) at room temperature.

vibronic feature. The PL behaviors of these compounds show a red shift in comparison to their corresponding absorption. The emission behavior of compound **3** peaked at 393 nm with a vibronic emission at 417 nm. We also observed the maximum emissions at 386 nm for compound **7**, at 412 nm for compound **10**, at 406 nm for compound **16**, and at 397 nm for compound **19**. From the PL feature of compound **13**, both peaks at 383 and 403 nm showed almost the same emission intensity.

Conclusion

In conclusion, we have successfully developed a highly effective, regioselective oxidative cyclization method to construct a series of polycyclic aromatic hydrocarbons containing a 10*H*-indeno[1,2-*b*]triphenylene skeleton. The synthesis described herein is generally accomplished in four steps: Sonogashira coupling, Diels−Alder reaction, decarbonylation, and finally the $FeCl_3$ oxidative cyclization. Compared with the work,[3,4] the replacement of 2,3,4,5-tetraphenylcyclopentadienone with 2,5-diethyl-3,4-diphenylcyclopentadienone not only efficiently enhances the solubility of the desired polycyclic aromatics but also provides an alternative synthetic route to prepare PAH derivatives with interesting structures. Moreover, we do not observe any C−C bond formation arising from coupling of a pair of benzene rings in which both are not parts of the fluorene unit. The utilization of this chemistry to construct larger PAHs indicates that the scope of such oxidative cyclization by $FeCl_3$ could be extended beyond simple fluorene derivatives. The ease of synthesizing these large polycyclic aromatics with interesting structures and their aromatic precursors with the current method has allowed us to expand the pool of cyclization strategies and to better understand the structure−property relationship within such structures. The investigation of photophysical properties also demonstrates the increase of effective conjugated length after cyclization. These results indicate that the derivatives of **13** and **16** might be suitable for organic field effect transistor (OFET) applications. Detailed studies on the photophysical properties of these new polycyclic aromatics and their applications in optoelectronic devices are currently underway in our laboratory.

Experimental Section

The ethynylene derivatives **1**, **5**, **8**, **11**, **14**, and **17** have been prepared by the literature procedures.[4i,7]

Compound 2. A dry flask with a magnetic stirrer was loaded with **1** (0.42 g, 0.97 mmol), commercially available 2,5-diethyl-3,4-diphenylcyclopentadienone (0.56 g, 1.93 mmol), and mesitylene

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(15 mL). The mixture was refluxed for 24 h. After the evaporation of the solvent under vacuum, the residue was purified by column chromatography (petroleum ether/dichloromethane = 15:1) to give 0.64 g (95%) of **2**. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.61−7.63 (1H, m), 7.49−7.51 (1H, d, J = 7.8 Hz), 7.19−7.30 (4H, m), 7.01−7.19 (16H, m), 2.32−2.37 (4H, m), 1.85−1.97 (4H, m), 0.54−1.26 (28H, m). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 150.7, 149.5, 141.4, 141.21, 141.18, 141.0, 140.94, 140.91, 140.0, 138.8, 137.7, 137.6, 130.6, 130.54, 130.50, 130.4, 129.0, 127.1, 127.0, 126.94, 126.88, 126.54, 126.48, 125.73, 125.67, 125.2, 122.6, 119.4, 118.3, 54.8, 40.7, 40.6, 31.55, 31.48, 29.9, 29.6, 24.5, 23.7, 23.4, 22.7, 22.4, 15.23, 15.1, 13.9, 13.7. MS (EI, *m*/*z*): 694 (M^+, 100%), 609 ($M^+ - 85$). Anal. Calcd for $C_{53}H_{58}$: C, 91.59; H, 8.41. Found: C, 91.19; H, 8.57.

Compound 3. Compound **2** (0.14 g, 0.20 mmol) was dissolved in 100 mL of dry dichloromethane in a dry flask. A constant stream of nitrogen was bubbled into the solution through a glass capillary. A solution of $FeCl_3$ (0.39 g, 2.4 mmol) in 5 mL of CH_3NO_2 was then added dropwise via syringe at 0 °C. The reaction mixture was stirred for 10 min and quenched by adding 50 mL of methanol. The reaction mixture was added to 100 mL of water and extracted with dichloromethane. After the evaporation of the solvents, the residue was purified by column chromatography (petroleum ether/dichloromethane = 10:1) to give 0.10 g (73%) of **3** as a light yellow solid. ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 8.87 (2H, s), 8.68−8.72 (2H, d, J = 8.0 Hz), 8.42−8.45 (2H, d, J = 8.0 Hz), 8.36 (2H, s), 8.04−8.08 (2H, d, J = 8.0 Hz), 7.54−7.81 (8H, m), 7.10−7.26 (20H, m), 3.20−3.27 (8H, m,), 2.14−2.17 (8H, m), 0.70−1.37 (56H, m). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 152.2, 149.1, 141.5, 141.4, 141.2, 141.16, 141.0, 140.3, 139.8, 135.2, 135.1, 133.4, 132.7, 131.4, 131.2, 131.1, 131.0, 130.6, 130.3, 128.6, 127.2, 126.6, 126.4, 125.9, 123.7, 122.7, 121.7, 120.4, 114.0, 55.3, 40.9, 31.4, 29.7, 27.0, 26.8, 23.9, 22.5, 15.4, 15.3, 13.9. MALDI-TOF MS, *m*/*z*: 1383 (M^+). Anal. Calcd for $C_{106}H_{110}$: C, 91.99; H, 8.01. Found: C, 91.61; H, 7.95.

Compound 6. Compound **6** was prepared by a procedure similar to that used to prepare **2**. Thus, the reaction between 9′,9′-dihexyl-2′-fluorenylacetylene (0.50 g, 1.4 mmol) and 2,5-diethyl-3,4-diphenylcyclopentadienone (0.80 g, 2.8 mmol) in mesitylene (15 mL) gave 0.63 g (73%) of **6** as a white solid after purification by column chromatography (petroleum ether/dichloromethane = 15:1). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.72−7.79 (2H, m), 7.33−7.44 (6H, m), 7.01−7.12 (10H, m), 2.40−2.50 (4H, m), 1.95−1.99 (4H, m), 0.65−1.13 (28H, m). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 150.8, 150.3, 141.9, 141.7, 141.3, 141.0, 140.9, 140.5, 139.7, 139.1, 137.3, 130.4, 130.2, 129.2, 127.9, 127.2, 127.1, 126.9, 126.7, 125.8, 124.0, 122.7, 119.6, 119.2, 55.1, 40.6, 31.5, 29.7, 26.7, 23.7, 23.6, 22.5, 15.5, 15.2, 13.2. MS (EI, *m*/*z*): 618 (M^+, 100%), 533 ($M^+ - 85$). Anal. Calcd for $C_{47}H_{54}$: C, 91.21; H, 8.79. Found: C, 91.01; H, 8.97.

Compound 7. This compound was prepared following a procedure similar to that used to prepare compound **3**. Thus, the reaction between **6** (0.12 g, 0.20 mmol) in dry dichloromethane (100 mL) and $FeCl_3$ (0.39 g, 2.4 mmol) in 5 mL of CH_3NO_2 gave 0.060 g (50%) of **7** as a white solid after product purification by column chromatography (petroleum ether/dichloromethane = 10:1). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.80−7.86 (2H, dd, J = 8.0 Hz, 3.6 Hz), 7.67−7.72 (2H, m), 7.43−7.49 (2H, dd, J = 8.0 Hz, 3.6 Hz), 7.29 (1H, s), 7.02−7.26 (10H, m), 2.44−2.50 (4H, m), 2.07−2.10 (4H, m), 0.69−1.26 (28H, m). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 151.6, 150.7, 141.9, 141.7, 141.5, 141.4, 140.9, 140.54, 140.52, 140.4, 140.2, 139.4, 139.1, 137.3, 130.4, 130.2, 129.2, 128.0, 127.2, 127.1, 126.1, 125.8, 124.1, 121.3, 119.8, 119.2, 55.2, 40.5, 31.5, 29.7, 26.7, 23.8, 23.7, 22.50, 22.47, 15.4, 15.2, 14.0, 13.9. MALDI-TOF MS, *m*/z: 1235 (M^+). Anal. Calcd for $C_{94}H_{106}$: C, 91.35; H, 8.65. Found: C, 91.09; H, 8.71.

Compound 9. This compound was prepared following procedures similar to those used to prepare compound **2**. Thus, the reaction between 9,9-dihexyl-2-(2-(4-methoxylphenyl)ethynyl)-7-phenyl-9*H*-fluorene (0.76 g, 1.4 mmol) and 2,5-diethyl-3,4-diphenylcyclopentadienone (0.80 g, 2.8 mmol) in mesitylene (15 mL) gave 0.90 g (80%) of **9** as a white solid after purification by column chromatography (petroleum ether/dichloromethane = 15:1). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.65−7.69 (2H, d, J = 8.0 Hz), 7.43−7.56 (5H, m), 7.35−7.39 (1H, d, J = 8.0 Hz), 7.00−7.25 (15H, m), 6.65−6.69 (1H, dd, J = 2.4 Hz, 8.6 Hz), 6.55−6.59 (1H, dd, J = 2.4 Hz, 8.6 Hz), 3.64 (3H, s), 2.24−2.28 (4H, m), 1.86−1.95 (4H, m), 0.52−1.07 (28H, m). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 157.5, 151.4, 149.87, 141.83, 141.80, 141.21, 141.17, 140.9, 140.6, 140.3, 139.7, 138.3, 138.1, 137.6, 133.4, 131.5, 131.4, 130.57, 130.50, 129.0, 128.8, 127.3, 127.2, 127.1, 127.05, 125.8, 125.1, 121.3, 119.7, 118.7, 112.7, 112.3, 54.9, 54.7, 40.6, 31.5, 29.9, 29.6, 24.5, 23.6, 23.4, 22.8, 22.4, 15.2, 15.1, 14.0, 13.9. MS (EI, *m*/*z*): 800 (M^+, 100%), 715 ($M^+ - 85$). Anal. Calcd for $C_{60}H_{64}O$: C, 89.95; H, 8.05. Found: C, 89.55; H, 8.23.

Compound 10. This compound was prepared following procedures similar to those used to prepare compound **3**. Thus, the reaction between **9** in 100 mL of dry dichloromethane (0.14 g, 0.17 mmol) and $FeCl_3$ (0.28 g 1.7 mmol) in 5 mL of CH_3NO_2 gave 0.041 g (30%) of **10** as a white solid after product purification by column chromatography (petroleum ether/dichloromethane = 8:1). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 8.78 (1H, s), 8.37−8.41 (1H, d, J = 9.2 Hz), 8.36 (1H, s), 8.11−8.13 (1H, d, J = 2.4 Hz), 8.02−8.06 (1H, d, J = 8.0 Hz), 7.44−7.77 (8H, m), 7.11−7.24 (10H, m), 4.10 (3H, s), 3.19−3.25 (4H, q, J = 5.5 Hz), 2.08−2.16 (4H, m), 0.70−1.28 (28H, m). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 158.3, 152.1, 149.1, 141.7, 141.31, 141.29, 141.24, 140.7, 140.6, 140.2, 139.7, 135.1, 134.3, 132.8, 132.7, 132.3, 131.1, 131.0, 130.0, 128.9, 127.3, 127.1, 126.3, 125.9, 125.4, 122.7, 121.7, 120.3, 114.0, 113.7, 106.7, 55.5, 55.3, 40.9, 31.4, 29.7, 27.0, 26.8, 23.9, 22.5, 15.4, 15.1, 13.9. MS (EI, *m*/*z*): 798 (M^+, 100%), 713 ($M^+ - 85$). Anal. Calcd for $C_{60}H_{62}O$: C, 90.18; H, 7.82. Found: C, 90.00; H, 7.92.

Compound 12. This compound was prepared following procedures similar to those used to prepare compound **2**. Thus, the reaction between 9,9-dihexyl-2,7-bis(2-phenylethynyl)fluorene (0.54 g, 1.0 mmol) and 2,5-diethyl-3,4-diphenylcyclopentadienone (1.2 g, 4.0 mmol) in mesitylene (10 mL) gave 0.72 g (68%) of **12** as a white solid after product purification by column chromatography (petroleum ether/dichloromethane = 10:1). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.34−7.38 (2H, d, J = 8.0 Hz), 7.01−7.10 (34H, m), 2.20−2.28 (8H, m), 1.74−1.78 (4H, m), 0.57−1.00 (34H, m). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 149.43, 149.40, 141.4, 141.3, 141.10, 141.03, 140.88, 140.85, 140.78, 139.6, 138.7, 137.7, 137.6, 137.5, 130.5, 128.7, 127.1, 125.7, 124.8, 118.3, 54.6, 41.1, 31.9, 31.7, 31.6, 30.0, 24.5, 23.3, 22.8, 22.4, 15.3, 15.2, 14.3, 14.1, 13.9. MALDI-TOF MS, *m*/*z*: 1055 (M^+). Anal. Calcd for $C_{81}H_{82}$: C, 92.17; H, 7.83. Found: C, 91.90; H, 7.82.

Compound 13. This compound was prepared following a procedure similar to that used to prepare compound **3**. Thus, the reaction between **12** (0.11 g, 0.10 mmol) in 100 mL of dry dichloromethane and $FeCl_3$ (0.26 g, 1.6 mmol) in 5 mL of CH_3NO_2 gave 0.10 g (95%) of **13** as a white solid after purification by column chromatography (petroleum ether/dichloromethane = 10:1). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 9.07 (2H, s), 8.80−8.82 (2H, d, J = 7.2 Hz), 8.44−8.46 (2H, d, J = 7.2 Hz), 8.37 (2H, s), 7.67−7.72 (2H, t, J = 7.2 Hz), 7.50−7.60 (2H, t, J = 7.2 Hz), 7.11−7.21 (20H, m), 3.20−3.28 (8H, m), 2.12−2.17 (4H, m), 0.82−1.06 (28H, m), 0.64−0.39 (6H, t, m). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 149.2, 141.4, 141.3, 141.1, 141.0, 139.8, 135.12, 135.07, 133.3, 132.7, 131.3, 131.2, 131.02, 130.95, 130.3, 128.5, 127.1, 126.6, 125.9, 123.7, 122.7, 114.3, 55.4, 41.5, 31.5, 29.8, 29.7, 27.0, 26.9, 24.1, 22.5, 15.5, 15.3, 13.9. MALDI-TOF MS, *m*/*z*: 1051 (M^+). Anal. Calcd for $C_{81}H_{78}$: C, 92.52; H, 7.48. Found: C, 92.12; H, 7.60.

Compound 15. This compound was prepared following procedures similar to those used to prepare compound **2**. Thus, the reaction between 1,2-bis(9′,9′-dihexylfluoren-2′-yl)ethyne (0.80 g,

1.2 mmol), 2,5-diethyl-3,4-diphenylcyclopentadienone (0.69 g, 2.4 mmol), and mesitylene (15 mL) gave 1.0 g (91%) of **15** as a white solid after product purification by column chromatography (petroleum ether/dichloromethane = 20:1). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.48−7.51 (2H, m), 7.39−7.43 (2H, d, J = 8.0 Hz), 6.99−7.23 (20H, m), 2.28−2.36 (4H, m), 1.79−1.86 (8H, m), 0.25−1.11 (50H, m). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 150.5, 149.6, 141.4, 141.1, 141.0, 140.9, 140.0, 138.7, 137.7, 130.6, 130.4, 129.7, 128.7, 127.1, 126.6, 126.5, 125.7, 125.2, 123.2, 122.4, 119.4, 118.9, 118.3, 54.8, 40.7, 31.6, 31.5, 30.0, 29.7, 24.5, 23.6, 23.4, 22.8, 22.5, 15.2, 14.0, 13.9. MALDI-TOF MS, *m*/*z*: 951 (M^+). Anal. Calcd for $C_{72}H_{86}$: C, 90.89; H, 9.11. Found: C, 90.77; H, 9.07.

Compound 16. This compound was prepared following a procedure similar to that used to prepare compound **3**. Thus, the reaction between **15** (95 mg, 0.10 mmol) in 50 mL of dry dichloromethane and $FeCl_3$ (0.19 g 1.2 mmol) in 5 mL of CH_3NO_2 gave 0.089 g (94%) of **16** as a white solid after product purification by column chromatography (petroleum ether/dichloromethane = 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.92 (2H, s), 8.31 (2H, s), 8.01−8.03 (2H, d, J = 7.2 Hz), 7.35−7.43 (6H, m), 7.02−7.18 (10H, m), 3.19−3.21 (4H, m), 2.05−2.11 (8H, m), 1.05−1.12 (30H, m), 0.67−0.80 (20H, m). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 151.3, 148.4, 141.15, 141.11, 141.0, 140.1, 134.8, 133.4, 131.0, 130.5, 130.4, 127.4, 127.1, 126.9, 125.8, 123.0, 122.5, 120.1, 113.9, 55.2, 40.9, 31.5, 29.8, 27.2, 23.9, 22.5, 15.4, 14.0. MALDI-TOF MS, *m*/*z*: 949 (M^+). Anal. Calcd for $C_{72}H_{84}$: C, 91.08; H, 8.92. Found: C, 90.87; H, 9.00.

Compound 18. This compound was prepared following procedures similar to those used to prepare compound **2**. Thus, the reaction between 9,9-dihexyl-2,7-bis(2-(9″,9″-dihexylfluoren-2″-yl)ethynyl)fluorene (0.21 g, 0.2 mmol), 2,5-diethyl-3,4-diphenylcyclopentadienone (0.23 g, 0.8 mmol), and mesitylene (5 mL) gave 0.24 g (76%) of **18** as a white solid after purification by column chromatography (petroleum ether/dichloromethane = 15:1). ^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.43−7.46 (2H, m), 7.32−7.36 (2H, d, J = 7.8 Hz), 6.97−7.18 (36H, m), 2.22−2.29 (8H, m), 1.80−1.90 (12H, m), 0.17−1.09 (78H, m). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 150.5, 149.48, 149.43, 141.43, 141.35, 141.12, 141.07, 140.8, 140.0, 139.5, 138.8, 138.6, 137.8, 137.6, 130.6, 130.4, 128.7, 128.5, 127.0, 126.5, 126.5, 125.7, 125.2, 124.8, 124.4, 119.4, 118.3, 54.8, 54.6, 41.1, 40.8, 40.6, 31.7, 31.6, 31.2, 30.1, 29.7, 24.5, 23.6, 23.3, 22.8, 22.7, 22.5, 15.2, 14.01, 13.98, 13.92. MALDI-TOF MS, *m*/*z*: 1567 (M^+). Anal. Calcd for $C_{119}H_{138}$: C, 91.13; H, 8.87. Found: C, 91.01; H, 8.91.

Compound 19. This compound was prepared following a procedure similar to that used to prepare compound **3**. Thus, the reaction between **18** (0.18 g, 0.11 mmol) in 100 mL of dry dichloromethane and $FeCl_3$ (0.43 g, 2.6 mmol) in 10 mL of CH_3NO_2 gave 0.11 g (61%) of **19** as a white solid after product purification by column chromatography (petroleum ether/dichloromethane = 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.19 (2H, s), 9.10 (2H, s), 8.37 (2H, s), 8.34 (2H, s), 8.21−8.24 (2H, d, J = 7.5 Hz), 7.52−7.56 (2H, m), 7.40−7.42 (4H, m), 7.07−7.20 (20H, m), 3.22−3.24 (8H, m), 2.04−2.09 (12H, m), 1.03−1.17 (48H, m), 0.47−0.94 (30H, m). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 151.4, 149.1, 148.6, 141.25, 141.18, 141.17, 141.14, 140.2, 140.0, 134.90, 134.89, 133.5, 133.4, 131.0, 130.9, 130.8, 130.60, 130.59, 127.5, 127.14, 127.07, 125.9, 123.1, 122.7, 122.6, 120.4, 114.5, 114.3, 55.3, 55.2, 41.5, 41.0, 31.51, 31.47, 29.82, 29.80, 29.71, 29.67, 27.2, 24.1, 23.9, 22.6, 22.5, 15.4, 14.0, 13.9. MALDI-TOF MS, *m*/*z*: 1563 (M^+). Anal. Calcd for $C_{119}H_{134}$: C, 91.37; H, 8.63. Found: C, 91.07; H, 8.58.

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Supporting Information Available: ^{1}H and ^{13}C NMR, MS spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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