# Star-Shaped and Linear Nanosized Molecules Functionalized with Hexa-*peri*-hexabenzocoronene: Synthesis and Optical Properties

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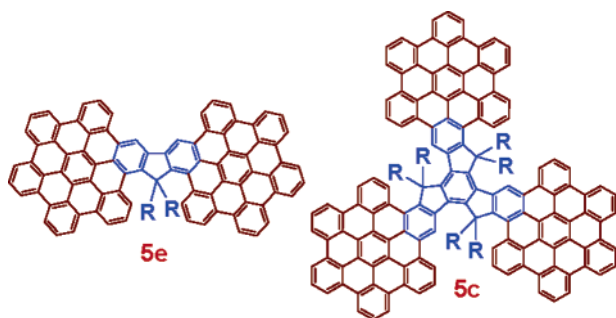
A synthetic strategy promising the establishment of a new star-shaped and linear polycyclic aromatic hydrocarbons (PAHs) family with distinct molecular topologies has been developed. The Sonogashira reaction between the iodide derivatives **2a**−**e** and phenylacetylene catalyzed with Pd(0) affords **3a**−**e** in high yields. The Diels−Alder and decarbonylation reactions between **3a**−**e** and tetraphenylcyclophentadiene following the oxidation by FeCl₃ produce the star-shaped and linear PAHs **5a**−**e** containing a five-membered ring. The structural analysis and the optical properties of all new compounds are performed by a combination of MALDI-TOF mass spectrometry, UV−vis, and fluorescence spectrometry. The electronic and photophysical properties are studied by orthogonal comparisons of the absorption and fluorescence spectra in THF solutions, which not only give insight into the interactions among aromatic submoieties in each molecule and the effects of meta-conjugation and para-conjugation on electronic delocalization, but also indicate effective conjugation length variations from oligophenylacetylenes **3a**−**e** to oligophenylene dendrimers **4a**−**e** and PAHs **5a**−**e**. The star-shaped **5c** exhibits the highest aggregation in excited states compared with the other four hexa-*peri*-hexabenzocoronene (HBC) derivatives.

Introduction

The well-defined geometric structures and fascinating electronic properties of polycyclic aromatic hydrocarbons (PAHs) have promoted their extensive use in liquid crystalline materials, electronics and optoelectronics, fullerenes and carbon nanotubes, and supramolecular architectures, as well as theoretically interesting molecules.[1] Such molecularly defined graphite model compounds enrich the chemistry of polycyclic aromatic hydrocarbons.[2] "Fully benzenoid" hexa-*peri*-hexabenzocoronene (HBC) (as shown in Chart 1) and its larger homologues developed by Müllen represent an intriguing PAH family.[3] HBCs exhibit liquid crystalline properties

CHART 1
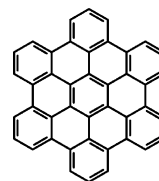
and hole transport capabilities and also emit light over a broad range of wavelengths, paving the way for organic photonic and electronic devices such as organic light-emitting diodes(OLEDs), field effect transistors (FETs), and solar cells.[4]

Recently, the breakthrough made by Müllen has provided an elegant approach to PAHs with diverse size and shape in a straightforward manner.[5] Since both

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molecular size and boundary shape of PAHs influence the electronic structures, energetics, and reactivities, it is necessary to design and synthesize novel PAHs for the thorough investigation of their structure−property relationships and the tuning of molecular properties toward specific applications.[6] Substituted monomeric HBCs self-assemble in a face-to-face manner to form columnar stacks with requisite nanophase separation of the side chains.

During the past decades, truxene has been recognized as a starting material for the construction of large polyarenes and bowl-shaped fragments of the fullerenes, liquid crystals, and C_3 tripod materials in asymmetric catalysis and chiral recognition.[7] We prepared a series of star-shaped oligothiophene-functionalized truxene derivatives and novel π-conjugated dendrimers based on truxene, which exhibited unique NMR behaviors, optical properties, and electroluminescence.[8] Moreover, among organic π-conjugated materials with large energy band gaps including poly-*p*-phenylene (PPP)[9] and ladder-poly-*p*-phenylene (LPPP),[10] polyfluorene (PF)[11] and oligofluorene[12] derivatives have been considered as the most promising blue-light emitters due to their high photoluminescence (PL) efficiency, good charge transport ability, thermal stability, and facile tunability of physical properties through chemical modification. Herein, we describe a strategy to selectively functionalize one, two, or three sides of both truxene and fluorene moieties. The elec-tronic properties are investigated by orthogonal comparisons of the absorption and fluorescence spectra in dilute solutions, which not only give insight into the interactions among aromatic submoieties in each molecule, as well as the effects of meta-conjugation and para-conjugation on electronic delocalization, but also shed light on distinct effective conjugation length variations from **3a**−**e** to **4a**−**e** as well as **5a**−**e**.

Results and Discussion

Synthesis. Scheme 1 illustrates that the selective iodination of each branch of truxene and fluorene rings from readily available hexahexyl-substituted truxene derivative **1** afforded their corresponding iodides **2a**−**e** according to a procedure to that found in the literature.[13] We usually employed the iodide derivatives since they readily undergo the Sonogashira reaction. We obtained the iodides **2a**−**e** in good yields by controlling the amount of H_5IO_6 and I_2.

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SCHEME 1[a]

R = *n*-C₆H₁₃

SCHEME 2[a]
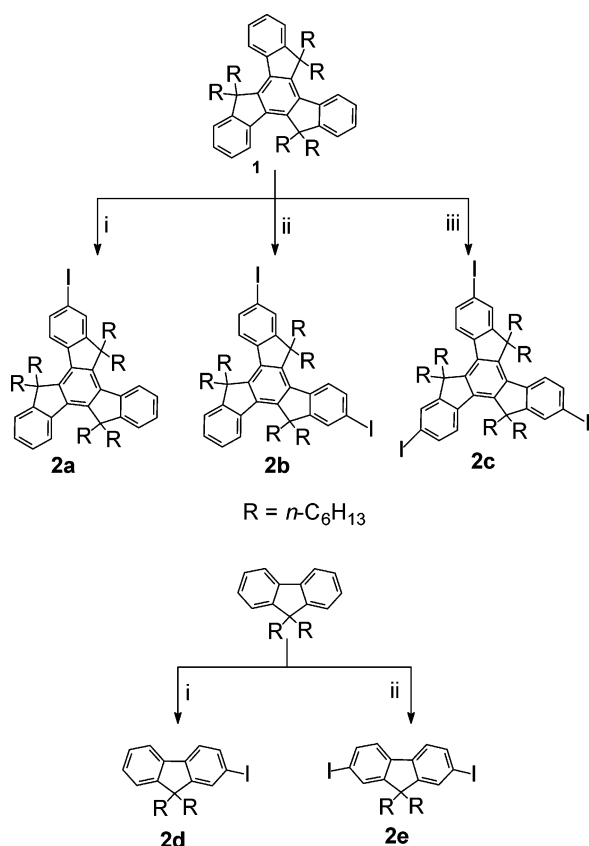
[a] Reagents and conditions: (i) H₅IO₆ (1/3 equiv), I₂ (1/3 equiv), CH₃COOH/H₂SO₄/H₂O (100:20:3), 60 °C; (ii) H₅IO₆ (2/3 equiv), I₂ (2/3 equiv), CH₃COOH/H₂SO₄/H₂O (100:20:3), 60 °C; (iii) H₅IO₆ (1 equiv), I₂ (1 equiv), CH₃COOH/H₂SO₄/H₂O (100:20:3), 60 °C.

The subsequent Sonogashira reaction between **2a** and phenylacetylene afforded **3a** with one phenylacetylene arm at the truxene moiety as shown in Scheme 2. We also got **3b** with two phenylacetylene arms and star-shaped **3c** with three phenylacetylene arms at the truxene moiety. The linear compounds **3d** and **3e** with one or two phenylacetylene arms at the fluorene moiety were also obtained according to the same procedure in good yields. The Diels−Alder reactions of **3a−c** with excess commercially available tetraphenylcyclopentadienone following the decarbonylation generated the desired oligophenylene dendrimers **4a−c**, respectively (Scheme 3).[2b] The same procedure also produced the linear oligophenylene compounds **4d** and **4e**. Although crude products in this reaction exhibited very deep color, the pure white solids **4a−e** were obtained after repeated washing with hot methanol.

The final oxidative cyclodehydrogenation of dendrimers **4a−e** with FeCl₃ in CH₂Cl₂ furnished target PAHs **5a−e** in quantitative yields (Scheme 4). Due to the existence of five-membered rings which makes a significant difference between our molecules and the Müllen-type PAHs, a small amount of FeCl₃ did not oxidize the 3D skeleton to form the PAH plane. We found that longer reaction time and greater amounts of FeCl₃ (more than 20 equiv per C−C bond) were keys to promote the conversions in this step, especially for **5b** and **5c**. Unfortunately, the excess FeCl₃ sometimes produced some chlorinated byproducts although such byproducts
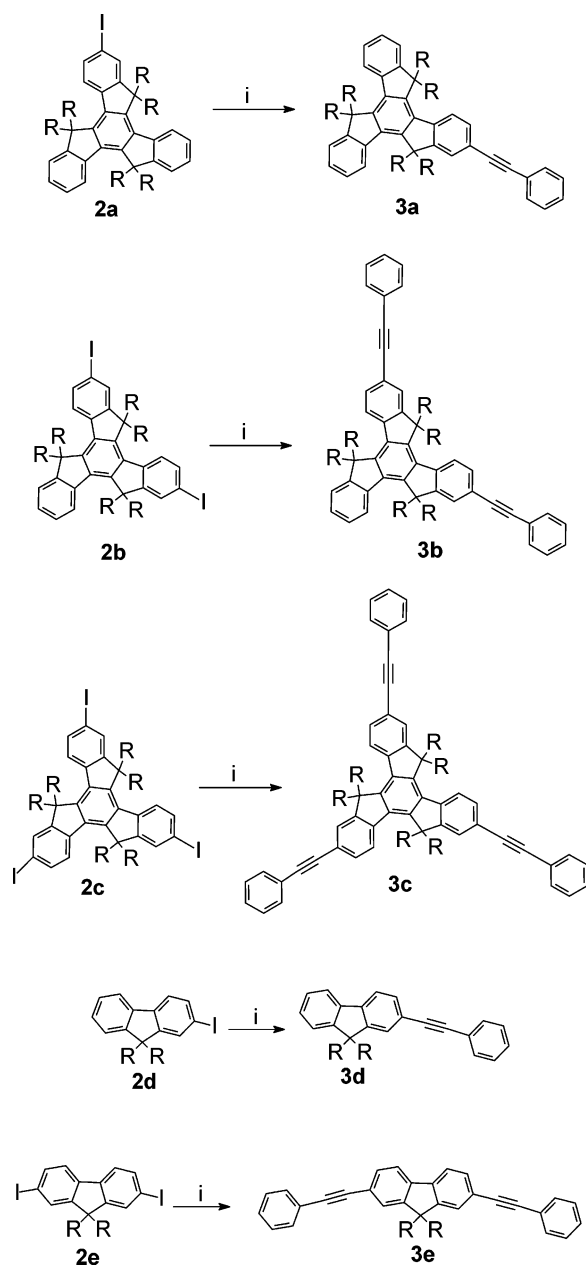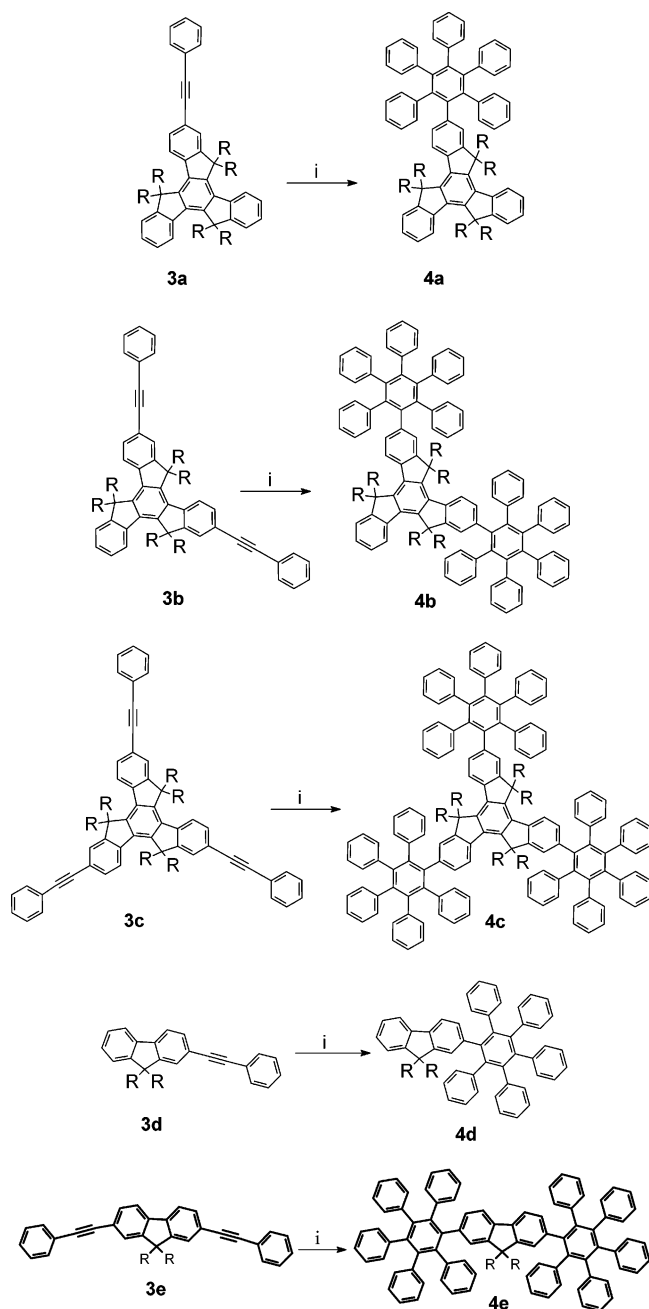
[a] Reagents and conditions: (i) phenylacetylene, Pd(PPh₃)₄, CuI, NEt₃, toluene.

did not affect the properties of desired materials (see the Supporting Information).[14]

The structure of all intermediate compounds has been confirmed by ¹H and ¹³C NMR, MALDI-TOF MS characterizations, as well as elemental analysis after purified by standard column chromatography. The target PAHs derivatives **5a−e** were characterized by MALDI-TOF MS spectroscopy. From MALDI-TOF MS spectra, we observed the exact loss of 12 hydrogen atoms for **5a** and **5d**, 24 for **5b** and **5e**, and 36 for **5c**, respectively.

UV−vis and Photoluminescence Properties in Solution. The UV−vis absorption and fluorescence spectra of the novel intermediate and target compounds

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SCHEME 3[a]

[a] Reagents and conditions: (i) tetraphenylcyclopentadienone, diphenyl ether, reflux.

were measured in THF. The solution concentration of all compounds was about 1.0×10^{-6} M. Table 1 summarizes the optical properties of all new compounds. Figure 1 presents the combined absorption and fluorescence spectra of PAHs **5a–e** in dilute THF solutions, while the orthogonal comparisons of those of compounds **3–5** are recorded in Figures 2 and 3. From Figures 2 and 3, we observed that both absorption and fluorescence spectra of the oligophenylene dendrimers **4a–e** were slightly blue-shifted in comparison with the corresponding oligophenyl acetylenes **3a–e** as shown in Figure 4, while significant red-shift was observed when these precursors were planarized to PAHs **5a–e** in accordance with the change of effective conjugation length. In comparison

with the absorption spectra of **3a–e**, with the increase of phenylacetylene substituents, we observed that the absorption λ_{max} increased accordingly for both truxene and fluorene derivatives. It would be interesting to investigate the spectra of truxene derivatives (**3–5c**) and fluorene derivatives (**3–5e**), which represented meta-conjugation and para-conjugation on electronic delocalization, respectively. Although **3c** contained three functionalized phenylacetylene groups, its absorption λ_{max} was slightly blue-shifted in comparison with that of **3e** (two phenylacetylene groups). Similar results were observed from the absorption spectra between **4c** and **4e**. However, the spectrum of **5e** was very similar to that of **5c** except for some small shoulders, which were due to the dominating HBC skeletons. These results indicated that the para-conjugation in the structure was more helpful for the extension of effective conjugation length than star-shaped meta-conjugation. The UV–vis absorption spectra of **5a**, **5b**, and **5d** peaked at 367, 370, and 363 nm, respectively. Those of **5c** and **5e** were less structured, with a red shift to 373 nm, and became broad. The absorption spectra of **5a–e** exhibited the characteristic profile of HBCs, which were almost the same as the Müllen-type HBC derivatives. It is clear that the aromatic chromophores are mainly HBC moieties and their intramolecular π-electronic conjugation is not effective. This observation is distinct from the current size-absorption λ_{max} relationship for all-benzenoid analogues.

From the emission spectra, we observed that the maximum peak of **5e** (373 nm) slightly red-shifted in comparison with that of **5d** (363 nm). For the series of truxene HBC derivatives, the peak at about 490 nm obviously amplified with the increase of HBC segments in their emission spectra while decreased at about 370 nm. **5c** gave a broad less-structured emission with the maximum peak at about 491 nm in comparison with the other four compounds and *n*-alkyl-substituted HBCs, which indicated that a higher degree of aggregation existed in **5c** than those of others; **5c** exhibited unique optical properties in comparison with Müllen-type HBCs. The investigation of the optical properties of all compounds also demonstrated that a novel series of HBCs derivatives with fused five-membered rings were successfully prepared.

Conclusion

In conclusion, the initial utilization of truxene and fluorene moieties as basic building blocks to construct a novel large PAH family containing HBC chromophores has been presented. The thorough investigation of the photophysical properties of acetylenes **3**, oligophenylene dendrimers **4**, and PAHs **5** in THF solutions indicates unique π-electron delocalization among intramolecular chromophores for our compounds. The star-shaped truxene-cored HBC **5c** exhibits the highest degree of aggregation in solution in comparison with the other four HBCs, and such aggregation is enhanced with the increase of the HBC moiety. The difference between the effects of meta-conjugation and para-conjugation on electronic delocalization are demonstrated. We have opened versatile opportunities to create novel large PAHs with completely distinct molecular topologies as well as unique electronic and photoelectronic properties, suggesting the

SCHEME 4[a]
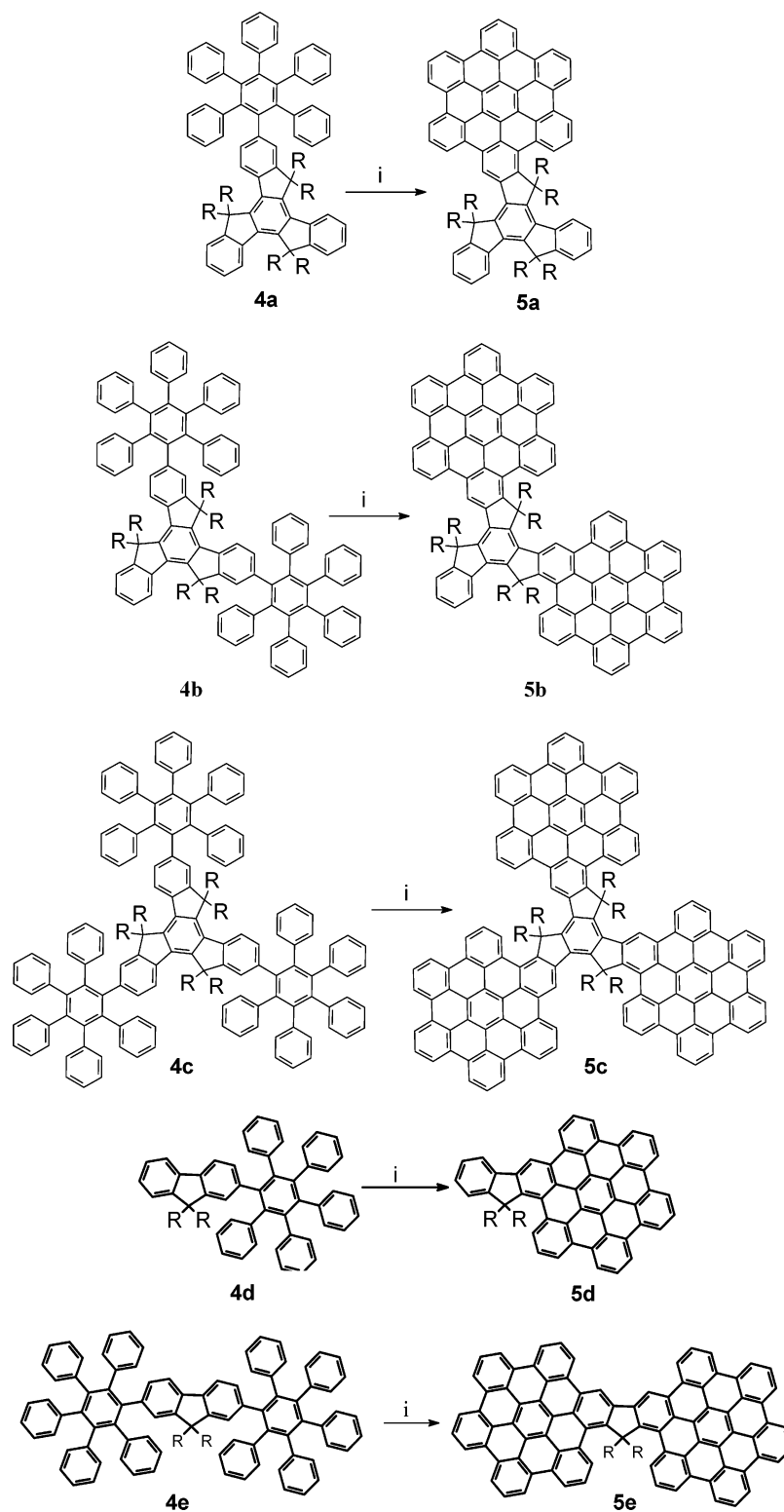
[a] Reagents and conditions: (i) FeCl$_3$ (3 eq/H), CH$_2$Cl$_2$/CH$_3$NO$_2$.

potential utility of these materials in electronic and optoelectronic devices.

Experimental Section

General Methods. All commercial chemicals were used as received. ^{1}H and^{13}C NMR spectra were recorded on a 200, 300,

or 400 MHz spectrometer using CDCl$_3$ or CD$_2$Cl$_2$ as solvent in all cases. In the NMR assignments, Fr and Tr present fluorene and truxene groups, respectively. UV−vis spectra were recorded on a UV−vis spectrometer. PL spectra were carried out on a luminescence spectrometer. MALDI-TOF mass spectra were recorded on a time-of-flight (TOF) mass spectrometer using a 337 nm nitrogen laser with CCA as matrix.

TABLE 1. Photophysical Properties of Compounds 3a–5e in THF Solutions

molecules	molecular weight (g/mol)	absorbance λ_{max} (nm)	emission λ_{max} (nm)	ϵ^a (10^5 L/mol·cm)
3a	947.5	349, 331, 310, 295	348, 365	1.1
3b	1047.6	332, 350	357, 374	2.0
3c	1147.7	334, 351	362, 381	1.6
3d	434.6	338, 323	330, 344	0.44
3e	534.8	349	359, 378, (403)	1.1
4a	1304.0	309, 296	343, 359	1.4
4b	1760.5	318, 311	347, 363	1.2
4c	2217.1	322	351, 367	1.6
4d	791.1	314	336, 339	0.29
4e	1247.7	324	345	0.65
5a	1291.9	415, 397, 367, 351	459, 469, 479, 490, 513, 526	0.86
5b	1736.4	419, 400, 370	460, 480, 490, 512, 524	1.7
5c	2180.8	373	461, (470), 491, 512	1.4
5d	779.0	412, 394, 363, 346	460, 474, 490, 515, 525	1.0
5e	1223.5	437, 373	464, 496	1.4

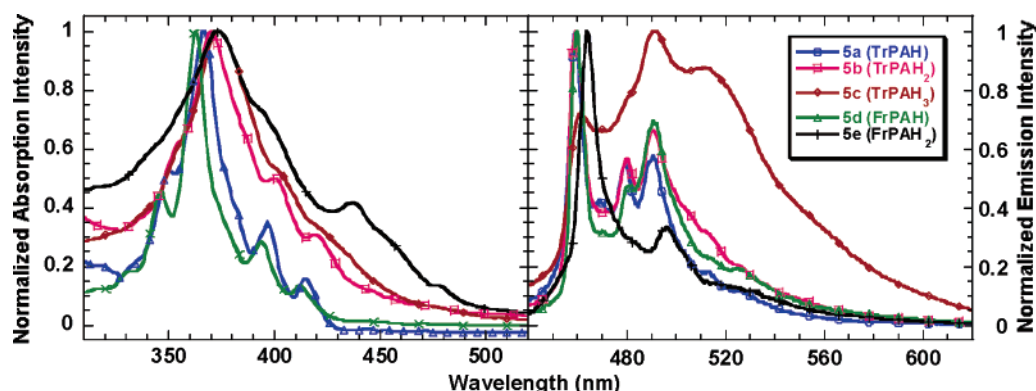^{a} The solution concentration of all compounds was about 1.0×10^{-6} M.

FIGURE 1. Absorption (left) and photoluminescence spectra (right) of PAHs in THF solutions at room temperature.
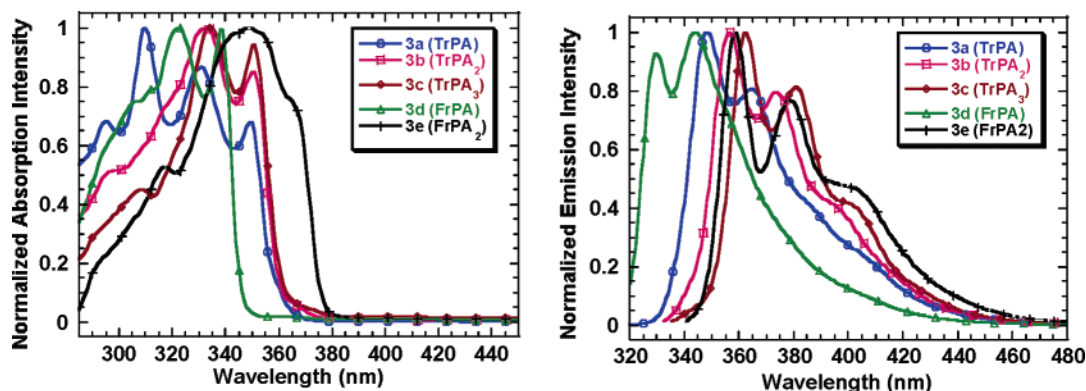

FIGURE 2. Absorption (left) and photoluminescence spectra (right) of **3a–e** in THF solutions at room temperature.

2d and **2e** were synthesized according to a procedure similar to that found in the literature.[13]

2a. A mixture of compound **1** (5.00 g, 5.91 mmol) and 10 mL of solvent mixture ($CH_3COOH/H_2SO_4/H_2O = 100:20:3$) was heated to 60 °C with vigorous stirring, followed by adding H_5IO_6 (0.23 g, 0.98 mmol) and I_2 (0.50 g, 1.97 mmol). The mixture was stirred at 80 °C under nitrogen atmosphere. After the elementary iodine almost disappeared (for **2a**, it took about 2 d), the mixture was cooled to room temperature and 150 mL water was added. The whole mixture was extracted with ether, and the organic phase was washed with water, 2 M aqueous Na_2CO_3, 5% $Na_2S_2O_3$ aqueous solution, and saturated NaCl solution and dried over $MgSO_4$. After removal of the solvent, the product was purified by recrystallization twice from ethanol to afford **2a** (4.77 g, 83%) as a colorless crystal. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm, δ): 8.35–8.37 (2H, d, $J = 6.6$

Hz), 8.08–8.11 (1H, d, $J = 8.7$ Hz), 7.76–7.77 (1H, d, $J = 1.5$ Hz), 7.69–7.72 (1H, dd, $J = 8.7$ Hz, $J = 1.5$ Hz), 7.38–7.47 (6H, m), 2.90–2.99 (6H, m), 2.01–2.08 (6H, m), 0.85–0.90 (36H, m), 0.46–0.63 (30H, m). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm, δ): 153.6, 153.6, 153.4, 145.5, 144.9, 144.8, 144.1, 140.3, 140.1, 140.1, 140.0, 138.6, 138.3, 137.3, 135.0, 131.4, 126.5, 126.3, 126.07, 126.0, 125.9, 124.7, 124.6, 124.6, 124.5, 122.2, 122.1, 55.9, 55.7, 55.6, 55.6, 37.0, 36.9, 36.9, 36.7, 31.5, 31.4, 31.4, 29.5, 29.4, 29.4, 23.9, 23.8, 22.2, 13.8.

2b. A mixture of compound **1** (5.00 g, 5.91 mmol) and 10 mL of solvent mixture ($CH_3COOH/H_2SO_4/H_2O = 100:20:3$) was heated to 60 °C with vigorous stirring, followed by adding H_5IO_6 (0.46 g, 1.96 mmol) and I_2 (1.00 g, 3.94 mmol). The mixture was stirred at 80 °C under nitrogen atmosphere. After the elementary iodine almost disappeared (for **2b**, it took about 2 d), the mixture was cooled to room temperature and 150 mL
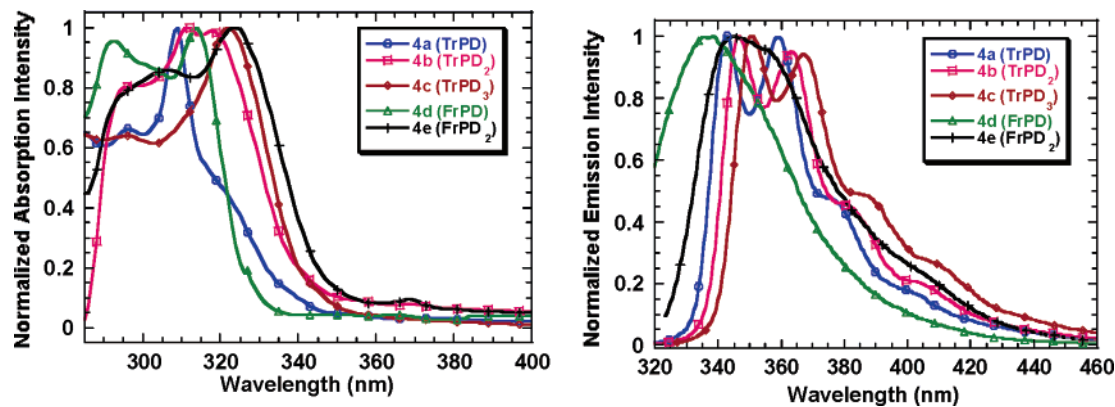
FIGURE 3. Absorption (left) and photoluminescence spectra (right) of **4a**−**e** in THF solutions at room temperature.
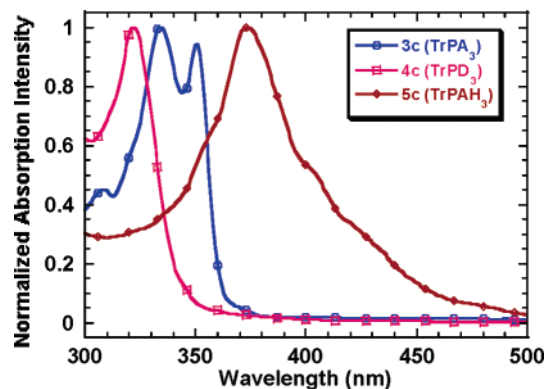

FIGURE 4. Comparison of the absorption spectra of **3c**−**5c** in THF solutions at room temperature.

water was added. The whole mixture was extracted with ether, and the organic phase was washed with water, 2 M aqueous Na_2CO_3, 5% $Na_2S_2O_3$ aqueous solution, and saturated NaCl solution and dried over $MgSO_4$. After removal of the solvent, the product was purified by recrystallization several times from ethanol to afford crude **2b** (4.54 g, 70%) as a colorless solid, which contained a slight amount of **2a**, and used directly.

2c. A mixture of compound **1** (5.00 g, 5.91 mmol) and 15 mL of solvent mixture ($CH_3COOH/H_2SO_4/H_2O = 100:40:3$) was heated to 60 °C with vigorous stirring, followed by addition of 3 mL of $CHCl_3$, H_5IO_6 (1.15 g, 4.9 mmol), and I_2 (2.50 g, 9.85 mmol). The mixture was stirred at 80 °C under nitrogen atmosphere. A small amount of H_5IO_6 was added to the mixture until ^1H NMR indicated that the reaction was completd (for **2c**, it took about 5 d), the mixture was cooled to room temperature, and 150 mL of water was added. The brown precipitate was filtered and purified by recrystallization three times from ethanol to afford **2c** (6.51 g, 90%) as a white solid. ^1H NMR ($CDCl_3$, 300 MHz, ppm, δ): 7.92−8.14 (3H, d, $J = 12$ Hz), 7.72−7.80 (3H, s), 7.64−7.72 (3H, d, $J = 12$ Hz), 2.72−2.98 (6H, m), 1.88−2.16 (6H, m), 0.76−1.08 (36H, m), 0.59−0.76 (18H, t, $J = 9.0$ Hz), 0.29−0.58 (12H, m). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm, δ): 155.9, 145.0, 139.5, 137.6, 135.3, 131.5, 126.2, 92.6, 55.9, 36.7, 31.4, 29.3, 23.8, 22.2, 13.8.

3a. A flame-dried flask with a magnetic stirrer was loaded with **2a** (4.00 g, 4.12 mmol), $Pd(PPh_3)_4$ (95.2 mg, 0.0824 mmol), and CuI (31.7 mg, 0.1648 mmol). Under nitrogen atmosphere, dry toluene (150 mL) and triethylamine (30 mL) were added, and the mixture was stirred for 20 min, yielding a yellow transparent solution. Phenylacetylene (0.91 mL, 8.24 mmol) was then added via a syringe, and the flask was closed. The reaction mixture, which turned to yellow-orange suspension over 30 min, was stirred vigorously for 2 d. The suspension was filtered, and the filtrate was concentrated under vacuum. The residue was purified by flash column chromatography

using petroleum as eluent to afford a colorless solid (3.33 g, 85%). ^1H NMR ($CDCl_3$, 500 MHz, ppm, δ): 8.34−8.37 (3H, m), 7.62−7.63 (1H, d, $J = 1.5$ Hz), 7.60−7.62 (2H, dd, $J = 8.0$ Hz, $J = 1.5$ Hz), 7.57−7.59 (1H, dd, $J = 8.0$ Hz, $J = 1.5$ Hz), 7.45−7.47 (2H, m), 7.35−7.41(7H, m), 2.86−3.01 (6H, m), 2.07−2.13 (6H, m), 0.85−0.90 (36H, m), 0.58−0.62 (18H, m), 0.45−0.55 (12H, m). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm, δ): 153.7, 153.6, 153.5, 145.4, 145.0, 140.7, 140.1, 140.1, 138.5, 138.4, 137.7, 131.6, 129.7, 128.3, 128.1, 126.4, 126.0, 125.2, 124.6, 124.6, 124.4, 123.5, 122.1, 120.6, 90.3, 89.5, 55.6, 55.6, 37.0, 36.9, 36.8, 31.4, 29.4, 23.8, 22.2, 13.8. MS (MALDI-TOF): calcd for $C_{71}H_{94}$ m/z 946.74 (100.0), 947.74 (80.4), 948.74 (30.7), 949.75 (8.3), 950.75 (1.6), 948.75 (1.1), found 946.61 (100.0), 947.62 (85.5), 948.62 (31.8), 949.63 (9.3). Anal. Calcd for $C_{71}H_{94}$: C, 90.00; H, 10.00. Found: C, 89.78; H, 10.15.

3b. The procedure is analogous to that described for **3a** (yield: 81%). ^1H NMR ($CDCl_3$, 500 MHz, ppm, δ): 8.33−8.37 (3H, m), 7.63 (2H, s), 7.60−7.62 (4H, dd, $J = 8.0$ Hz, $J = 1.5$ Hz), 7.58−7.59 (2H, d, $J = 8.5$ Hz), 7.46−7.48 (1H, m), 7.36−7.41 (8H, m), 2.90−3.02 (6H, m), 2.07−2.12 (6H, m), 0.82−0.95 (36H, m), 0.59−0.63 (18H, m), 0.45−0.51 (12H, m). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm, δ): 153.6, 153.5, 145.6, 145.3, 140.5, 140.4, 139.9, 138.6, 137.9, 137.7, 131.6, 129.8, 128.3, 128.2, 126.6, 126.1, 125.2, 124.6, 124.5, 123.4, 122.2, 120.8, 90.2, 89.6, 55.7, 37.0, 36.8, 31.4, 31.4, 29.4, 23.9, 22.2, 22.2, 13.8. MS (MALDI-TOF): calcd for $C_{79}H_{98}$ m/z 1046.77 (100.0), 1047.77 (89.3), 1048.77 (38.1), 1049.78 (11.5), 1050.78 (2.5), 1048.78 (1.3), found 1047.10 (100.0), 1048.10 (85.8), 1049.10 (37.2), 1050.10 (11.4). Anal. Calcd for $C_{79}H_{98}$: C, 90.57; H, 9.43. Found: C, 90.18; H, 9.75.

3c. The procedure is analogous to that of **3a** (yield: 87%). ^1H NMR ($CDCl_3$, 200 MHz, ppm, δ): 8.33−8.37 (3H, d, $J = 8.4$ Hz), 7.58−7.64 (12H, m), 7.37−7.44 (9H, m), 2.87−3.01 (6H, m), 2.04−2.18 (6H, m), 0.87−0.99 (36H, m), 0.58−0.65 (18H, t, $J = 6.5$ Hz), 0.47−0.51 (12H, m). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm, δ): 155.0, 153.6, 145.8, 140.2, 137.9, 131.6, 129.9, 128.3, 128.2, 125.2, 124.5, 123.3, 121.0, 116.0, 90.1, 89.8, 55.8, 36.9, 31.4, 29.4, 23.9, 22.2, 13.8. MS (MALDI-TOF): calcd for $C_{87}H_{102}$ m/z 1146.80 (100.0), 1147.80 (98.3), 1148.80 (46.3), 1149.81 (15.3), 1150.81 (3.6), 1148.81 (1.5), found 1146.52 (100.0), 1147.51 (92.9), 1148.44 (49.0), 1149.49 (19.3), 1150.48 (9.5). Anal. Calcd for $C_{87}H_{102}$: C, 91.04; H, 8.96. Found: C, 90.85; H, 9.05.

3d. The procedure is analogous to that of **3a** (yield: 84%). ^1H NMR ($CDCl_3$, 500 MHz, ppm, δ): 7.68−7.70 (1H, dd, $J = 8.0$ Hz, $J = 1.5$ Hz), 7.66−7.68 (1H, d, $J = 7.5$ Hz), 7.56−7.58 (2H, dd, $J = 8.0$ Hz, $J = 1.5$ Hz), 7.51−7.53 (1H, dd, $J = 7.5$ Hz, $J = 1.5$ Hz), 7.50 (1H, d, $J = 1.5$ Hz), 7.31−7.38 (6H, m), 1.95−1.98 (4H, t, $J = 8.5$ Hz), 1.09−1.13 (4H, q, $J = 7.0$ Hz), 1.00−1.08 (8H, m), 0.75−0.78 (6H, t, $J = 7.5$ Hz), 0.57−0.65 (4H, m). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm, δ): 151.0, 150.7, 141.4, 140.4, 131.5, 130.6, 128.3, 128.1, 127.4, 126.8, 125.9, 123.4, 122.8, 121.3, 119.9, 119.5, 90.5, 89.2, 55.1, 40.3, 31.5, 29.7, 23.7, 22.5, 13.9. MS (MALDI-TOF): calcd for $C_{33}H_{38}$ m/z

434.30 (100.0), 435.30 (37.3), 436.30 (6.5), found 434.24 (100.0), 435.21 (55.1), 436.21 (8.9). Anal. Calcd for $C_{33}H_{38}$: C, 91.19; H, 8.81. Found: C, 90.89; H, 8.91.

3e. The procedure is analogous to that of **3a** (yield: 80%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 7.66−7.68 (2H, d, J = 8.0 Hz), 7.56−7.58 (4H, dd, J = 8.0 Hz, J = 1.5 Hz), 7.52−7.54 (2H, dd, J = 7.5 Hz, J = 1.0 Hz), 7.50−7.51 (2H, d, J = 1.0 Hz), 7.34−7.39 (6H, m), 1.97−2.00 (4H, m), 1.09−1.14 (4H, q, J = 7.0 Hz), 1.01−1.07 (8H, m), 0.76−0.78 (6H, t, J = 7.5 Hz), 0.58−0.64 (4H, m). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, δ): 151.0, 140.6, 131.6, 130.7, 128.3, 128.2, 125.9, 123.3, 121.9, 119.9, 90.3, 89.7, 55.2, 40.4, 31.5, 29.7, 23.7, 22.6, 13.9. MS (MALDI-TOF): calcd for $C_{41}H_{42}$ m/z 534.33 (100.0), 535.33 (46.2), 536.34 (10.4), 537.34 (1.5); found 534.12 (100.0), 535.07 (70.1), 536.07 (21.0), 537.06 (3.9). Anal. Calcd for $C_{41}H_{42}$: C, 92.08; H, 7.92. Found: C, 92.21; H, 7.57.

4a. Compound **3a** (1.00 g, 1.06 mmol), tetraphenyl cyclopentadienone (0.61 g, 1.59 mmol), and 10 mL of diphenyl ether were deoxygenated and then heated to reflux under nitrogen atmosphere overnight. After being cooled to room temperature, the diphenyl ether was removed under reduced pressure and the residue was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ = 5:1) to afford a yellow solid, which was further purified by recrystallization from methanol to give a white powder (1.32 g, 96%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 8.30−8.32 (1H, d, J = 8.0 Hz), 8.25−8.26 (1H, m), 7.77−7.78 (1H, d, J = 8.0 Hz), 7.29−7.41 (6H, m), 6.96−6.97 (2H, m), 6.74−6.87 (25H, m), 2.88−2.94 (2H, m), 2.68−2.76 (4H, m), 1.98−2.04 (2H, m), 1.90−1.95 (2H, m), 1.62−1.67 (2H, m), 0.81−0.97 (36H, m), 0.17−0.72 (30H, m). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, δ): 153.6, 153.5, 151.9, 145.0, 144.4, 144.2, 140.7, 140.6, 140.4, 140.3, 140.2, 138.8, 138.2, 138.0, 137.3, 131.6, 131.4, 126.5, 126.3, 126.1, 125.8, 125.4, 125.2, 125.1, 124.6, 124.5, 122.9, 122.0, 122.0, 55.3, 55.2, 36.5, 36.8, 31.7, 31.5, 31.4, 29.6, 29.4, 29.4, 23.7, 23.5, 22.3, 22.3, 13.9, 13.8. MS (MALDI-TOF) (CCA + AgTFA): calcd for $C_{99}H_{114}^+$ m/z 1303.90 (100.0), 1302.89 (92.3), 1304.90 (53.7), 1305.90 (18.3), 1306.91 (5.0), 1307.91 (1.0), found 1304.30 (100.0), 1303.31 (97.8), 1305.36 (64.5); calcd for [M + Ag]$^+$ $C_{99}H_{114}Ag^+$ m/z 1411.80 (100.0), 1410.80 (73.1), 1412.80 (67.9), 1409.80 (65.4), 1413.80 (36.5), 1412.81 (14.8), 1414.81 (14.5), 1413.81 (5.2), 1415.81 (3.7), 1411.81 (1.2), found 1412.34 (100.0), 1410.34 (80.9), 1413.30 (79.0), 1411.31 (74.1), 1414.47 (41.4), 1415.37 (27.8); calcd for [M − C_6H_{13}]$^+$ $C_{93}H_{101}^+$ m/z 1218.79 (100.0), 1217.79 (96.7), 1219.80 (52.7), 1220.80 (18.0), 1221.80 (4.3), 1218.80 (1.5), found 1219.31 (100.0), 1218.29 (96.0), 1220.32 (51.0), 1221.34 (17.1), 1222.36 (6.8). Anal. Calcd for $C_{99}H_{114}$: C, 91.19; H, 8.81. Found: C, 91.08; H, 8.47.

4b. Compound **3b** (1.00 g, 0.955 mmol), tetraphenyl cyclopentadienone (1.10 g, 2.87 mmol), and 12 mL of diphenyl ether were deoxygenated and then heated to reflux under nitrogen atmosphere overnight. After being cooled to room temperature, the diphenyl ether was removed under reduced pressure and the residue was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ = 4:1) to afford a yellow solid, which was further purified by recrystallization from methanol to give a white powder (1.65 g, 98%). ^{1}H NMR (CDCl$_3$, 200 MHz, ppm, δ): 8.19−8.21 (m, 1H), 7.70−7.74 (2H, m), 7.25−7.32 (2H, m), 6.72−6.96 (55H, m), 2.60−2.70 (4H, m), 2.45−2.55 (2H, m), 1.83−1.85 (2H, m), 1.42−1.60 (4H, m), 0.85−0.98 (12H, m), 0.59−0.78 (48H, m), 0.08−0.42 (18H, m). ^{13}C NMR (CDCl$_3$, 50 MHz, ppm, δ): 153.4, 151.8, 144.6, 143.8, 140.6, 140.6, 140.4, 140.3, 140.2, 138.6, 137.9, 137.7, 137.3, 131.5, 131.4, 129.2, 126.5, 126.3, 125.2, 125.1, 55.0, 36.8, 31.6, 31.5, 29.6, 29.4, 23.7, 23.5, 22.4, 22.3, 14.0, 13.9. MS (MALDI-TOF) (CCA + AgTFA): calcd for [M + Ag]$^+$ $C_{135}H_{138}Ag^+$ m/z 1866.99 (100.0), 1868.99 (92.9), 1867.99 (75.5), 1869.99 (70.2), 1865.98 (65.7), 1867.98 (61.0), 1869.00 (37.8), 1870.99 (33.7), 1870.00 (14.1), 1872.00 (13.1), 1871.00 (5.6), 1873.00 (3.9), 1872.01 (1.0), found 1867.83 (100.0), 1868.79 (99.6), 1866.79 (79.8), 1869.75 (66.4), 1865.75 (57.1), 1870.79 (39.9), 1871.76 (22.7); calcd for [M − C_6H_{13}]$^+$ $C_{129}H_{125}$ m/z 1674.98 (100.0), 1675.98 (70.3), 1673.98

(68.8), 1676.99 (34.4), 1677.99 (12.2), 1678.99 (3.2), 1675.99 (1.9); found 1674.83 (100.0), 1673.85 (71.8), 1675.88 (70.1), 1676.87 (35.8), 1677.85 (14.6), 1678.83 (7.3). Anal. Calcd for $C_{135}H_{138}$: C, 92.10; H, 7.90. Found: C, 92.43; H, 7.85.

4c. Compound **3c** (1.00 g, 0.872 mmol), tetraphenyl cyclopentadienone (1.51 g, 3.92 mmol), and 15 mL of diphenyl ether were deoxygenated and then heated to reflux under nitrogen atmosphere overnight. After the mixture was cooled to room temperature, the diphenyl ether was removed under reduced pressure and the residue was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ = 2:1) to remove some of the rest tetraphenyl cyclopentadienone, which was further purified by recrystallization from methanol six to eight times to give a light pale powder (1.74 g, 90%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 7.62−7.63 (3H, d, J = 8.0 Hz), 6.90−6.92 (3H, d, J = 8.0 Hz), 6.80−6.85 (63H, m), 6.70−6.72 (15H, m), 2.42−2.48 (6H, m), 1.41−1.47 (6H, m), 0.97−1.01 (12H, q, J = 7.0 Hz), 0.75−0.76 (24H, m), 0.69−0.72 (18H, t, J = 7.5 Hz), −0.02 to −0.01 (12H, m). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, δ): 151.8, 144.1, 140.7, 140.6, 140.4, 140.3, 140.1, 138.4, 137.6, 137.4, 131.5, 131.4, 131.4, 129.1, 126.5, 126.5, 126.3, 125.3, 125.2, 125.1, 122.8, 54.9, 36.7, 31.7, 29.5, 23.4, 22.5, 14.0. MS (MALDI-TOF) (CCA + AgTFA): calcd for [M + Ag]$^+$ $C_{171}H_{162}$-Ag$^+$ m/z 2325.18 (100.0), 2323.18 (66.1), 2324.18 (63.2), 2326.18 (58.8), 2327.18 (35.9), 2322.17 (34.3), 2324.17 (31.9), 2328.19 (19.7), 2326.19 (19.0), 2327.19 (8.6), 2329.19 (6.6), 2330.19 (1.9), 2325.19 (1.5), found 2325.25 (100.0), 2324.26 (95.8), 2326.25 (90.3), 2323.27 (73.6), 2327.24 (59.0), 2322.28 (54.9), 2328.32 (39.6); calcd for [M − C_6H_{13}]$^+$ [$C_{165}H_{149}$]$^+$ m/z 2131.17 (100.0), 2132.17 (90.1), 2133.18 (56.5), 2130.17 (53.8), 2134.18 (25.8), 2135.18 (8.8), 2136.19 (2.8), 2132.18 (2.2), found 2131.35 (100.0), 2132.30 (88.9), 2133.33 (55.6), 2130.32 (56.2), 2134.28 (27.7), 2135.31 (12.6). Anal. Calcd for $C_{171}H_{162}$: C, 92.64; H, 7.36. Found: C, 92.28; H, 7.05.

4d. Compound **3d** (1.50 g, 3.45 mmol), tetraphenyl cyclopentadienone (1.99 g, 5.18 mmol), and 20 mL of diphenyl ether were deoxygenated and then heated to reflux under nitrogen atmosphere overnight. After the mixture was cooled to room temperature, the diphenyl ether was removed under reduced pressure and the residue was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ = 5:1) to afford a light yellow solid which was further purified by recrystallization from methanol to give a white powder (2.57 g, 94%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, δ): 7.46−7.47 (1H, m), 7.17−7.21 (3H, m), 6.89−6.91 (1H, d, J = 8.0 Hz), 6.83−6.87 (21H, m), 6.78−6.81 (1H, dd, J = 8.0 Hz, J = 1.5 Hz), 6.75−6.77 (5H, m), 1.71−1.77 (2H, m), 1.57−1.63 (2H, m), 1.11−1.17 (4H, q, J = 7.0 Hz), 0.92−1.04 (8H, m), 0.79−0.82 (6H, t, J = 7.0 Hz), 0.19−0.29 (4H, m). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, δ): 150.6, 149.0, 141.1, 140.7, 140.6, 140.3, 140.3, 139.6, 138.1, 131.4, 131.3, 129.9, 126.5, 126.4, 126.2, 126.0, 125.2, 125.1, 122.4, 119.3, 118.0, 54.5, 40.6, 31.5, 29.8, 23.2, 22.7, 14.0. MS (MALDI-TOF) (CCA + AgTFA): calcd for $C_{61}H_{58}$ m/z 790.45 (100.0), 791.46 (68.7), 792.46 (23.2), 793.46 (5.0), found 790.44 (100.0), 791.45 (74.9), 792.46 (30.5); calcd for [M + Ag]$^+$ $C_{61}H_{58}Ag^+$ m/z 897.36 (100.0), 899.36 (92.9), 898.36 (67.8), 900.36 (63.8), 899.37 (23.2), 901.37 (22.4), 900.37 (5.2), 902.37 (4.8), found 899.34 (100.0), 897.33 (85.0), 900.31 (58.4), 898.31 (58.1), 901.29 (18.2), 902.37 (5.9). Anal. Calcd for $C_{61}H_{58}$: C, 92.61; H, 7.39. Found: C, 92.23; H, 7.48.

4e. Compound **3e** (1.00 g, 1.87 mmol), tetraphenyl cyclopentadienone (2.16 g, 5.61 mmol), and 25 mL of diphenyl ether were deoxygenated and then heated to reflux under nitrogen atmosphere overnight. After the mixture was cooled to room temperature, the diphenyl ether was removed under reduced pressure and the residue was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ = 4:1) to afford a yellow solid, which was further purified by recrystallization from methanol to give a white powder (2.14 g, 93%). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm, δ): 6.95−6.98 (2H, d, J = 7.5 Hz), 6.74−6.82 (52H, m), 6.67−6.70 (2H, d, J = 7.5 Hz), 1.36−1.50 (4H, m), 1.21−1.26 (4H, q, J = 6.9 Hz), 0.95−1.06 (8H, m), 0.96−0.91 (6H, t,

$J = 7.2$ Hz), $-0.22- -0.08$ (4H, m). ^{13}C NMR (CDCl$_3$, 50 MHz, ppm, δ): 148.9, 140.6, 140.6, 140.3, 140.1, 139.0, 138.2, 131.4, 131.3, 129.8, 126.5, 126.4, 125.7, 125.2, 125.0, 117.9, 54.2, 41.0, 31.7, 30.2, 23.2, 22.8, 14.1. MS (MALDI-TOF) (CCA + AgT-FA): calcd for C$_{97}$H$_{82}$ m/z 1247.65 (100.0), 1246.64 (91.6), 1248.65 (54.0), 1249.65 (19.2), 1250.66 (5.1), 1251.66 (1.1), found 1248.11 (100.0), 1247.14 (95.2), 1249.14 (51.6), 1250.11 (22.0), 1251.63 (6.0); calcd for [M + Ag]$^+$ C$_{97}$H$_{82}$Ag$^+$ m/z 1355.55 (100.0), 1354.55 (72.5), 1356.55 (67.4), 1353.55 (66.4), 1357.55 (35.6), 1356.56 (14.0), 1358.56 (13.7), 1357.56 (4.5), 1359.56 (3.4), found 1356.11 (100.0), 1357.06 (74.9), 1355.10 (74.3), 1354.09 (64.4), 1358.07 (39.1), 1359.08 (14.6), 13560.03 (7.8). Anal. Calcd for C$_{97}$H$_{92}$: C, 93.38; H, 6.62. Found: C, 93.07; H, 6.83.

5a. To a flame-dried flask with a magnetic stirrer was added a solution of compound **4a** (100 mg, 0.0767 mmol) in 250 mL of dry dichloromethane. The solution was degassed by bubbling nitrogen for 20 min, and then iron(III) trichloride (1.50 g, 9.20 mmol) dissolved in 15 mL of nitromethane was added dropwise via a syringe. A constant nitrogen stream was carried out during the entire reaction, and the reaction was quenched by adding 300 mL of methanol after 0.5 h. The yellow precipitate was collected and washed repetitively with methanol until the filtrate was colorless. The light yellow powder was dried under vacuum to give **5a** in quantitative yield (99 mg, 100%). MS (MALDI-TOF) (CCA + AgTFA): calcd for C$_{99}$H$_{102}$ m/z 1291.80 (100.0), 1290.80 (89.6), 1292.80 (53.8), 1293.81 (20.2), 1294.81 (5.5), 1292.81 (1.5), 1295.81 (1.1), found 1293.46 (100.0), 1294.45 (96.3), 1291.42 (95.9), 1290.43 (82.9), 1292.41 (78.0), 1289.39 (65.4), 1295.44 (58.1), 1297.36 (36.2), 1298.41 (28.5), 1299.34 (27.2); calcd for [M + Ag]$^+$ C$_{99}$H$_{102}$Ag$^+$ m/z 1400.71 (100.0), 1398.71 (89.1), 1397.70 (79.8), 1399.70 (74.1), 1399.71 (49.2), 1401.71 (45.7), 1402.71 (16.0), 1401.72 (4.9), 1403.72 (4.7), 1402.72 (1.7), found 1400.39 (100.0), 1401.42 (88.9), 1398.40 (77.8), 1399.42 (76.3), 1402.45 (68.9), 1403.41 (50.4), 1397.37 (45.9), 1396.34 (45.9), 1404.44 (37.8); calcd for [M − C$_6$H$_{13}$]$^+$ [C$_{93}$H$_{89}$]$^+$ m/z 1206.70 (100.0), 1205.70 (95.4), 1207.70 (50.5), 1208.71 (17.7), 1209.71 (4.5), 1207.71 (1.3), found 1206.24 (100.0), 1207.26 (95.8), 1208.27 (73.3), 1209.23 (45.3), 1205.23 (28.8).

5b. To a flame-dried flask with a magnetic stirrer was added a solution of compound **4b** (100 mg, 0.0568 mmol) in 250 mL of dry dichloromethane. The solution was degassed by bubbling nitrogen for 20 min, and then iron(III) trichloride (2.21 g, 13.6 mmol) dissolved in 22 mL of nitromethane was added dropwise via a syringe. A constant nitrogen stream was carried out during the entire reaction, and the reaction was quenched by adding 300 mL of methanol after 0.5 h. The yellow brown precipitate was collected and washed repetitively with methanol until the filtrate was colorless. The yellow powder was dried under vacuum to give **5a** in quantitative yield (99 mg, 100%). MS (MALDI-TOF) (CCA): calcd for C$_{135}$H$_{114}$ m/z 1735.90 (100.0), 1736.90 (75.4), 1734.89 (65.8), 1737.90 (37.6), 1738.91 (14.0), 1739.91 (4.1), 1740.91 (1.0), found 1734.75 (100.0), 1735.82 (99.9), 1736.75 (91.9), 1733.75 (82.8), 1737.75 (72.9), 1738.76 (62.2), 1739.69 (58.3); calcd for [M − C$_6$H$_{13}$]$^+$ [C$_{129}$H$_{101}$]$^+$ m/z 1650.79 (100.0), 1651.80 (72.7), 1649.79 (69.7), 1652.80 (34.6), 1653.80 (11.7), 1654.81 (3.4), 1650.80 (1.1), found 1650.69 (100.0), 1651.74 (86.6), 1649.72 (80.9), 1652.72 (53.2), 1653.69 (33.5), 1654.67 (22.4).

5c. To a flame-dried flask with a magnetic stirrer was added a solution of compound **4c** (100 mg, 0.0451 mmol) in 300 mL of dry dichloromethane. The solution was degassed by bubbling nitrogen for 20 min, and then iron(III) trichloride (2.65 g, 16.3 mmol) dissolved in 27 mL of nitromethane was added dropwise via a syringe. A constant nitrogen stream was carried out during the entire reaction, and the reaction was quenched by adding 400 mL of methanol after 4 h. The yellow brown precipitate was collected and washed repetitively with methanol until the filtrate was colorless. The yellow powder was dried under vacuum to give **5c** in quantitative yield (98 mg, 100%). MS (MALDI-TOF) (CCA + AgTFA): calcd for [M − C$_6$H$_{13}$]$^+$ [C$_{165}$H$_{113}$]$^+$ m/z 2094.89 (100.0), found 2097.19 (100.0); calcd for [M − C$_6$H$_{13}$ + Cl]$^+$ m/z 2128.85 (100.0), found 2133.17 (100.0); calcd for [M − C$_6$H$_{13}$ + 3Cl]$^+$ m/z 2198.79 (100.0), found 2201.13 (100.0); calcd for [M − C$_6$H$_{13}$ + 4Cl]$^+$ m/z 2233.76 (100.0), found 2235.07 (100.0); calcd for [M − C$_6$H$_{13}$ + 5Cl]$^+$ m/z 2168.73 (100.0), found 2270.00 (100.0).

5d. To a flame-dried flask with a magnetic stirrer was added a solution of compound **4d** (100 mg, 0.127 mmol) in 250 mL of dry dichloromethane. The solution was degassed by bubbling nitrogen for 20 min, and then iron(III) trichloride (2.47 g, 15.2 mmol) dissolved in 25 mL of nitromethane was added dropwise via a syringe. A constant nitrogen stream was carried out during the entire reaction, and the reaction was quenched by adding 300 mL of methanol after 0.5 h. The yellow brown precipitate was collected and washed repetitively with methanol until the filtrate was colorless. The light yellow powder was dried under vacuum to give **5d** in quantitative yield (98 mg, 100%). MS (MALDI-TOF) (CCA): calcd for C$_{61}$H$_{46}$ m/z 778.36 (100.0), 779.36 (67.8), 780.37 (23.1), 781.37 (5.1), found 778.25 (100.0), 779.21 (72.5), 780.22 (25.9), 781.27 (8.2).

5e. To a flame-dried flask with a magnetic stirrer was added a solution of compound **4e** (100 mg, 0.0801 mmol) in 250 mL of dry dichloromethane. The solution was degassed by bubbling nitrogen for 20 min, and then iron(III) trichloride (3.12 g, 19.2 mmol) dissolved in 31 mL of nitromethane was added dropwise via a syringe. A constant nitrogen stream was carried out during the entire reaction, and the reaction was quenched by adding 300 mL of methanol after 4 h. The yellow brown precipitate was collected and washed repetitively with methanol until the filtrate was colorless. The light yellow powder was dried under vacuum to give **5e** in quantitative yield (98 mg, 100%). MS (MALDI-TOF) (Di): calcd for C$_{97}$H$_{58}$ m/z 1223.46 (100.0), 1222.45 (91.9), 1224.46 (53.8), 1225.46 (18.7), 1226.47 (5.0), 1227.47 (1.1), found 1226.62 (100.0), 1227.65 (81.8), 1225.60 (63.1), 1224.58 (58.5), 1228.61 (45.9), 1229.63 (21.4), 1230.71 (16.4).

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

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