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Intramolecular Domino Electrophilic and Thermal Cyclization of *peri*-Ethynylene Naphthalene Oligomers

Xiaobo Huang,[a, b] Lintao Zeng,[a] Zebing Zeng,[a] and Jishan Wu*[a]

Abstract: The intramolecular electrophilic or thermal cyclization of arylene ethynylene precursors recently became a powerful method for the synthesis of new polycyclic aromatic hydrocarbons (PAHs). In this work, we investigated in detail the synthesis and intramolecular cyclization reaction of a series of *peri*-ethynylene naphthalene oligomers in which the ethynylene units are fixed in close proximity within the naphthalene framework. The high reactivity of these precursors led to simultaneous thermal cyclization reactions, even during their syntheses. Electrophilic cyclizations with iodine were also undertaken. Several new PAHs containing five-membered rings, for example, indeno[2,1-*a*]phenalene, acenaphtho[1,2-*a*]pyrene, and benzo- or naphtho-annulated fluoranthene derivatives, were synthesized and their structures were unambiguously determined by X-ray crystallographic analysis. Plausible mechanisms were proposed and it was demonstrated that oligomers most probably underwent intramolecular domino cyclization via either radical or cationic intermediates. The photophysical and electrochemical properties of these new PAHs were investigated and some of them displayed amphoteric redox behavior, due to the existence of five-membered rings.

Keywords: cyclization · domino reactions · fluoranthenes · hydrocarbons · polycycles

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have attracted much interest due to their unique optoelectronic and self-assembly properties. They can be used as active components in organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), solar cells, and near-infrared dyes.[1] Since the first half of the 20th century, the groups of Scholl, Clar, and Zander have made significant contributions to the synthesis and structural characterization of PAHs,[2] and now more and more organic chemists, encouraged by their wide use, focus on developing novel methods to prepare well-defined PAHs. There are some general methods for the construction of PAH ring systems, such as intra- and intermolecular Diels–Alder reactions,[3] flash-vacuum pyrolysis,[4] inter- or intramolecular coupling,[1c,5] photocyclization,[6] and transition-metal-catalyzed annulation.[7]

Arylene ethynylene derivatives, with the ethynylene unit located close to another aryl or ethynylene unit, recently became useful precursors for the synthesis of PAHs through an electrophilic or thermal cyclization reaction or a transition-metal-catalyzed annulation reaction. For example, the electrophilic cyclization of precursor **1** with iodine gives iodophenanthrene and this type of reaction has been used to prepare a series of fused PAHs by Swager et al.[8] When two ethynylene groups are located at the *ortho* positions of a benzene ring or an ethene unit, a Bergman-type thermal cyclization can take place to generate a new benzenoid ring.[9] Similarly, when the ethynylene units are strategically positioned in enforced proximity within a macrocyclic entity (e.g., in **2**) the molecule readily undergoes thermal polymerization.[10] The treatment of **2** with iodine affords an antiaromatic indenofluorene derivative with 20 π electrons, as reported by Swager et al.[10] and Haley et al.[11] When two ethynylene units are *peri*-fixed between two naphthalene rings in a macrocyclic structure, for example, in **3**, the compound has high reactivity and tends to undergo intramolecular thermal cyclization to relieve the severe steric congestion between the *peri* triple bonds.[12] Tobe et al.[13] and our group[14] recently reported the synthesis of stable zethrene derivatives by taking advantage of the simultaneous transannular cyclization of **3**. Additionally, we demonstrated that a higher-order analogue of **3**, an octadehydronaphtho[14]annulene in which two naphthalene rings were bridged by two diacetylene units, also underwent simultaneous thermal cyclization to give a heptazethrene derivative with a singlet biradical character in the ground state.[15] 1,8-Bis(2-phenylethynyl)naphthalene (**4**) has a similar structure to **3**, but with less tension because of its acyclic nature. The thermal[16] and electrophilic cyclization[17] of **4** have been studied and various PAH structures have been obtained. Recently, Lu et al. reported the synthesis of several fused arenes by iodine-mediated electrophilic cyclizations of different 1,8-dialkynyl-

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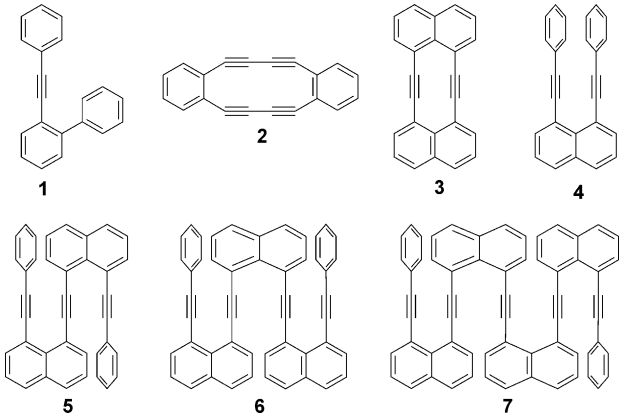
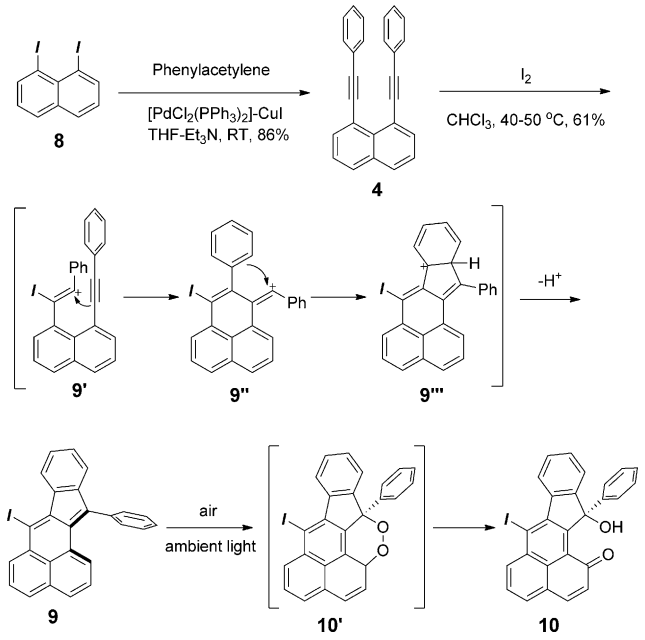
naphthalenes.[18] Transition-metal-mediated cycloaromatization of the *peri*-diyne in **4** with external alkynes was reported by Siegel et al. to provide a general route to indenofused PAHs.[19]



So far, studies on reactions of *peri*-ethynylene units have mostly focused on compounds with two parallel triple bonds, but attempts to further elongate the arylene ethynylene oligomeric chain have seldom been reported[20] because of difficulties such as complicated reactions and challenging separation and structural determination of the products. We have been working on the synthesis of novel PAHs by various methodologies in the past few years.[21] Herein, we report in detail the synthesis and intramolecular cyclization of a series of *peri*-ethynylene naphthalene oligomers **4**–**7** through an interesting domino cyclization process via either radical or cationic intermediates. Various PAHs containing five-membered rings were obtained and their structures determined by X-ray crystallographic analysis. Their photophysical and electrochemical properties were also investigated.

Results and Discussion

Synthesis and intramolecular cyclization of compounds 4–7: We first investigated the simplest compound, **4** (Scheme 1). Precursor 1,8-diiodonaphthalene (**8**) was obtained from 1,8-diaminonaphthalene according to published procedures.[22] Compound **4** was then synthesized in 86% yield by the Pd-catalyzed Sonogashira–Hagihara coupling of **8** and phenylacetylene at room temperature. Treatment of **8** with I_2 in $CHCl_3$ at 40–50°C afforded 7-iodo-12-phenylindeno[2,1-*a*]phenalene (**9**) in 61% yield. The structure of **9** was verified by single-crystal X-ray diffraction analysis (Figure 1).[23] We hypothesized that **9** was produced through a domino intramolecular electrophilic cyclization mechanism (Scheme 1): At the outset, I^+ attacks the terminal of the ethynylene unit adjacent to the naphthalene ring to initialize the reaction and give intermediate **9′**. Subsequently, the electrophilic cyclization between the newly generated cation



Scheme 1. Iodine-mediated electrophilic cyclization of compound **4** and subsequent oxidation.

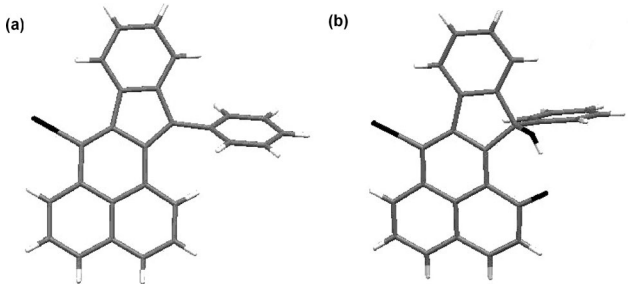


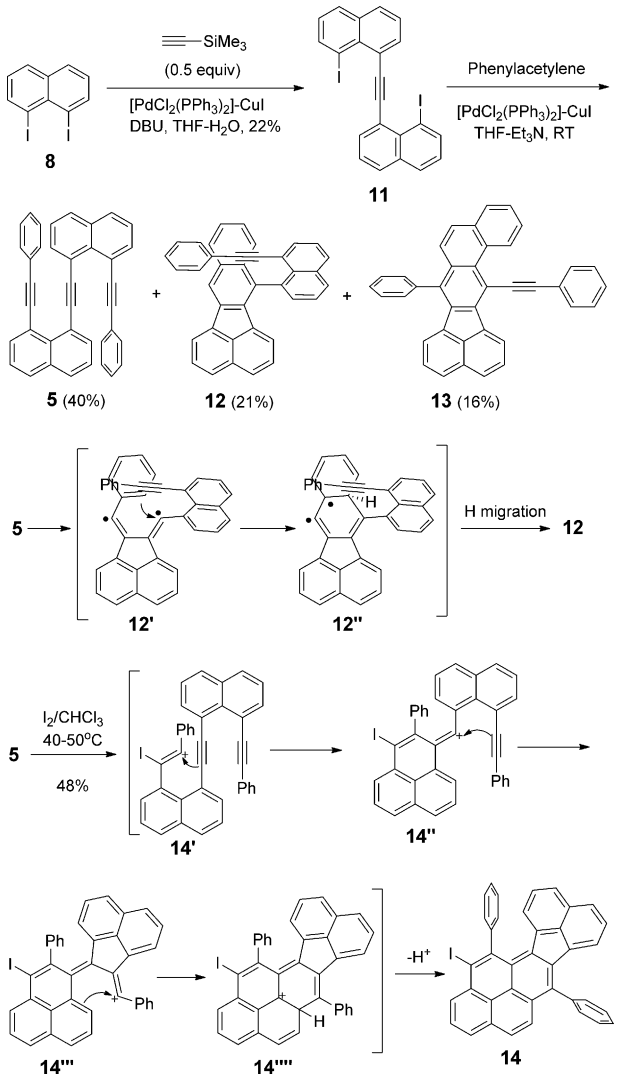
Figure 1. Single-crystal structures of compounds **9** (a) and **10** (b).

and the second ethynylene unit affords intermediate **9″**. Again, electrophilic attack takes place on the C≡C terminal close to the naphthalene ring. The electrophilic cyclization between the electron-rich phenyl ring and the positive cation then occurs to give a new five-membered ring in **9‴**. The deprotonation/aromatization of **9‴** provides the final product **9**. The overall process is analogous to the traditional cationic polymerization of a vinylene monomer, which typically involves initialization, chain propagation, and termination steps. The difference is that the reaction of **4** with iodine proceeds through a succession of rapid intramolecular cyclization reactions.

An unexpected yellow compound, 12-hydroxy-7-iodo-2-phenylindeno[2,1-*a*]phenalen-1(12*H*)-one (**10**), was generated when the solution of **4** in chloroform was exposed to ambient air and light for weeks. A single crystal of **10** was obtained by slow evaporation of the solvent ($CHCl_3$/CH_3OH) and the structure was identified by X-ray crystallographic analysis (Figure 1).[24] A plausible mechanism for the generation of **10** is shown in Scheme 1. Compound **9** most probably

possesses diene characteristics (marked in bold) and allows a Diels–Alder cycloaddition reaction with singlet oxygen in atmospheric air. The cycloadduct **10′** then undergoes rearrangement to give the oxidized product **10**. The thermal cyclization of **4** to give phenylbenzo[*k*]fluoranthene in solution has been thoroughly studied[16] and our reinvestigation revealed the same results.

We then investigated the synthesis and intramolecular cyclization of compound **5**, which contains three *peri*-ethynylene units (Scheme 2). We, first, prepared 1,2-bis(8-iodonaphthalen-1-yl)ethyne (**11**) by the Sonogashira–Hagihara coupling of **8** and 0.5 equivalents of trimethylsilylacetylene, according to a one-pot procedure.[25] The yield was relatively low (22%) because of the formation of side products (e.g., 1,4-bis(8-iodonaphthalen-1-yl)buta-1,3-diyne) through the homocoupling of terminal alkyne moieties.[26] Compound **5** was then synthesized in 40% yield by the Sonogashira–Hagihara coupling between **11** and phenylacetylene. We also separated a benzofluoranthene derivative (**12**) in 21% yield and a naphthofluoranthene derivative (**13**) in 16% yield. The structures of both compounds were elucidated by single-crystal X-ray diffraction analysis (Figure 2).[27]



Scheme 2. Synthesis of compound **5** and its intramolecular cyclization reactions.

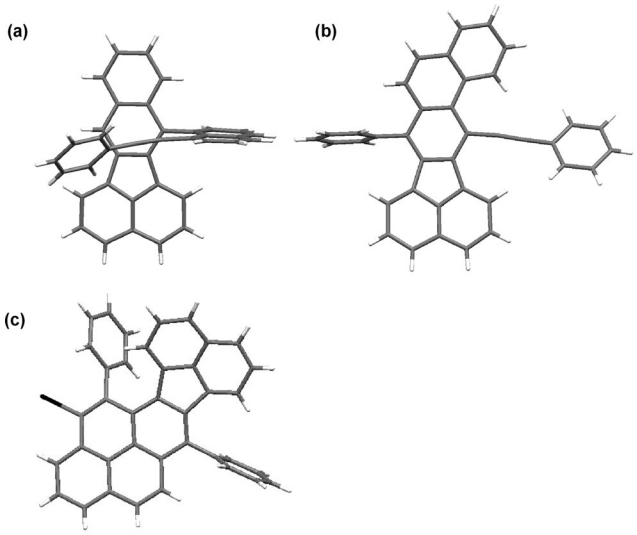
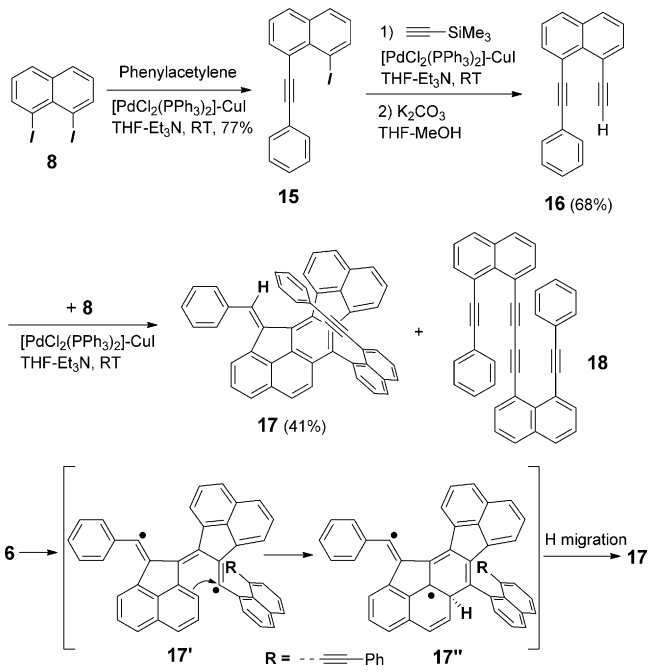


Figure 2. Single-crystal structures of compounds **12** (a), **13** (b), and **14** (c).

The formation of **12** from **5** can be rationalized by envisioning an intramolecular domino radical cyclization process (Scheme 2). Thermal cyclization takes places between two ethynylene units in **5** to generate the diradical intermediate **12′**, which contains a five-membered ring. Intramolecular radical cyclization in **12′** then affords another biradical intermediate, **12″**. Subsequent hydrogen migration in **12″** gives the final product **12**. Such a process mimics the traditional radical polymerization of olefins, although, in this case, the initialization, propagation, and termination processes take place in an intramolecular fashion. The role of the Pd catalyst in the cyclization reaction should be taken into account because Pd catalysts usually are known to facilitate intramolecular cyclizations. The formation of isomer **13** was unexpected and was attributable to unforeseen rearrangements during the thermal cyclization of **5**. The electrophilic cyclization of **5** with iodine was tested under experimental conditions similar to those used for the cyclization of **4**. Interestingly, an acenaphtho[1,2-*a*]pyrene derivative, 14-iodo-6,13-diphenylacenaphtho[1,2-*a*]pyrene (**14**), was generated in 48% yield and its structure was confirmed by X-ray crystallographic analysis (Figure 2).[28] Similar to **9**, the generation of **14** can be explained by a five-step intramolecular domino electrophilic cyclization process that involves intermediates **14′**–**14′′′′** (Scheme 2).

The synthetic success of **4** and **5** encouraged us to further study the synthesis and reaction of higher-order *peri*-ethynylene naphthalene oligomers **6** and **7**. For that, the intermediate compound 1-ethynyl-8-(2-phenylethynyl)naphthalene (**16**) was prepared (Scheme 3). The Sonogashira–Hagihara coupling between **8** and one equivalent of phenylacetylene



Scheme 3. Attempted synthesis of compound **6** and its intramolecular cyclization reaction.

gave 1-iodo-8-(2-phenylethynyl)naphthalene (**15**) in 77% yield. Subsequent coupling of **15** with trimethylsilylacetylene followed by desilylation gave the terminal alkyne **16** in 68% yield in two steps. Compound **6** can theoretically be obtained by a Sonogashira–Hagihara coupling reaction between **8** and **16**. After the reaction, however, instead of the desired product **6**, we isolated the acenaphtho[1,8-*jk*]fluoranthene derivative **17** in 41% yield, the structure of which was verified by X-ray crystallography (Figure 3).[29] Compound **17** possibly arose from the unstable compound **6** in a sequence of cyclization reactions via the diradical intermediates **17′** and **17″** followed by hydrogen migration (Scheme 3). In addition, the homocoupling product of **16**, 1,4-bis[8-(2-phenylethynyl)naphthalen-1-yl]buta-1,3-diyne (**18**), was also separated from the reaction mixture and its structure was determined by X-ray crystallographic analysis (Figure 3).[30]

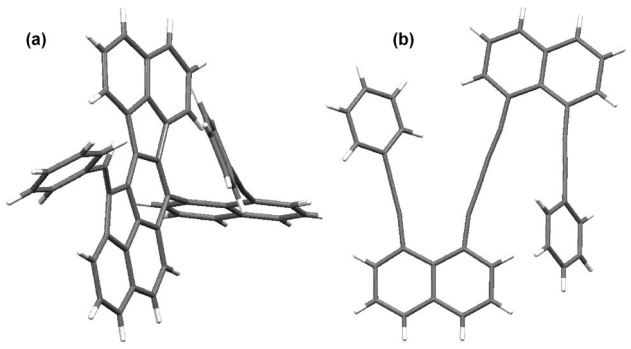
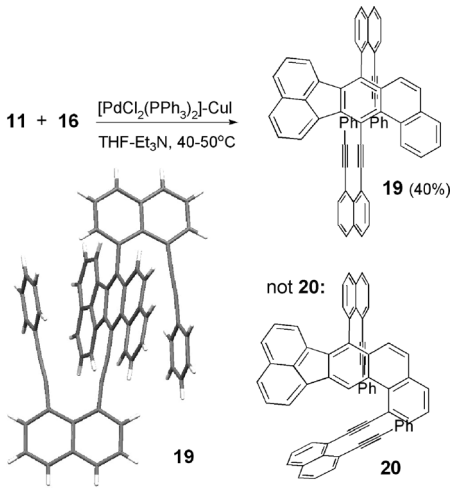


Figure 3. Single-crystal structures of compounds **17** (a) and **18** (b).

Similarly, Sonogashira–Hagihara coupling reaction between **11** and **16** did not give the expected product **7**, but instead a complicated mixture was obtained. An unexpected naphtho[2,1-*k*]fluoranthene derivative (**19**) was produced in 40% yield (Scheme 4). The structure of **19** was determined



Scheme 4. Attempted synthesis of compound **7** and crystallographic structure of cyclization compound **19**.

by X-ray diffraction analysis (Scheme 4).[31] We theorized that the formation of compound **19** was mediated by the highly reactive species **7** given that they have identical molecular compositions. However, the expected thermal cyclization product **20** could not be isolated from the mixture. Compound **19** could also undergo thermal cyclization/re-arrangement similar to that of **13** because they have the same naphtho[2,1-*k*]fluoroanthene framework. The high reactivity of **6** and **7** and the overall complexity of the product mixture limited further studies on the synthesis, reactivity, and properties of higher-order oligomers and even polymers.

Photophysical properties of new PAHs: All of the cyclized products contain a five-membered ring. It has been demonstrated that such compounds usually possess interesting photophysical and electrochemical properties.[32] Compounds **9**, **12**, **13**, **14**, **17**, and **19** have good solubility in common organic solvents, such as $CHCl_3$, CH_2Cl_2, and THF. Their UV/Vis absorption and fluorescence spectra recorded in chloroform are shown in Figures 4 and 5, respectively, whereas corresponding data are compiled in Table 1. These compounds have well-resolved absorption bands and high molar absorption coefficients in the region from 300 to 550 nm, due to the effective π–π^* transition of the π-conjugated structures. Compound **9** exhibits the highest maximum absorption wavelength (515 nm). Compounds **13** and **19** have similar absorption spectra because they possess an identical naphtho[2,1-*k*]fluoranthene core. Both **9** and **14** show low quantum yields, due to the existence of the iodine atom, which quenches fluorescence (Table 1). Compounds **12**, **13**, and **19** emit strong blue or yellow–green light with moderate

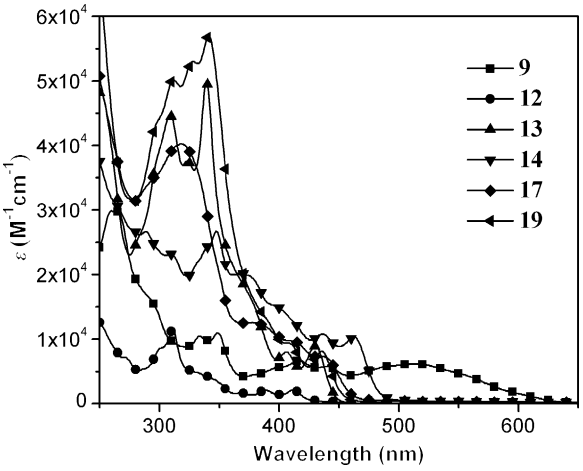


Figure 4. UV/Vis absorption spectra of compounds **9**, **12**, **13**, **14**, **17**, and **19** in chloroform ($c = 1.0 \times 10^{-5}$ M).

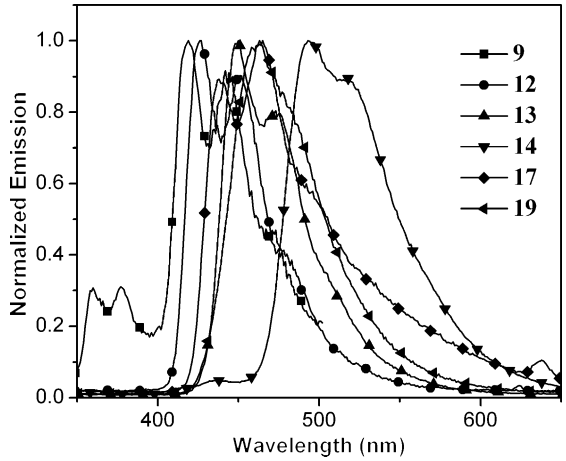


Figure 5. Fluorescence spectra of compounds **9**, **12**, **13**, **14**, **17**, and **19** in chloroform (excitation at the absorption maximum of respective absorption spectra).

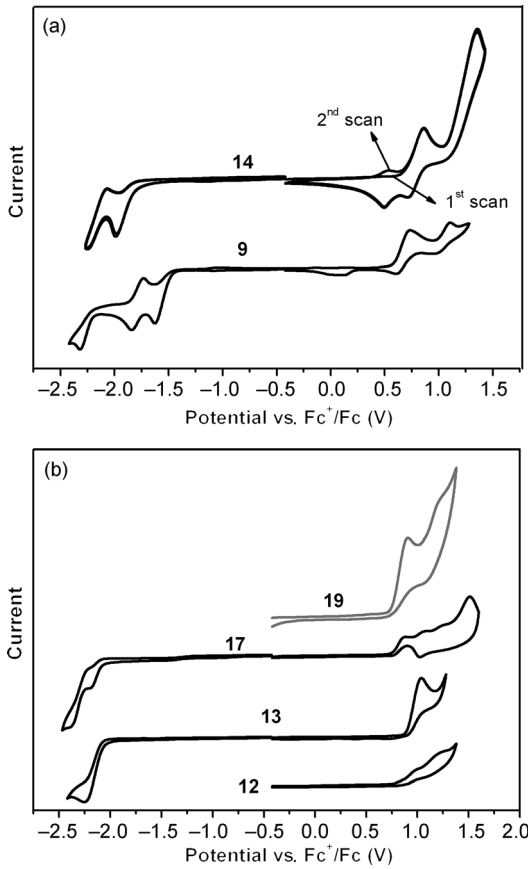


Figure 6. Cyclic voltammograms of solutions of compounds **9** and **14** (a) and **12**, **13**, **17**, and **19** (b) in dry dichloromethane (1 mM) with tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte. A three-electrode electrochemical cell was used with a gold disc electrode as the working electrode, a platinum wire as the counter electrode, and AgCl/Ag (in 3 M aq KCl) as the reference electrode. Scan rate = 0.05 V s^{-1}.

quantum yields, whereas compound **17** emits weak yellow–green light in chloroform. Compounds **12**, **13**, **17**, and **19** have absorption and emission properties analogous to the benzo[*k*]fluoroanthene derivatives reported by Yan and coworkers, due to skeletal similarities.[32a]

Table 1. Summary of photophysical and electrochemical properties of compounds **9**, **12**, **13**, **14**, **17**, and **19**. E_{ox}^1, E_{ox}^2, E_{red}^1, and E_{red}^2 are the half-wave potentials for respective redox waves with E (Fc^+/Fc) as the reference. The ferrocene couple (Fc^+/Fc) was used as the internal reference and under our experimental conditions, E (Fc^+/Fc) = 0.42 V versus Ag/AgCl.

	UV/Vis [nm]	λ_{em} (λ_{ex}) [nm]	Cyclic voltammetry				HOMO [eV][a]	LUMO [eV][b]	E_g[c] [eV]	Φ_{PL}[f]
			E_{ox}^1	E_{ox}^2	E_{red}^1	E_{red}^2				
9	349, 417, 441, 515	360, 377, 418, 443 (260)	0.67	1.02	−1.55	−1.79	−5.38	−3.33	2.05	0.003
12	311, 389, 412	427, 452 (311)	0.92	–	–	–	−5.56	−2.67[e]	2.89[d]	0.890
13	309, 339, 406, 430	450, 473 (339)	0.89	–	−2.17	–	−5.70	−3.19	2.51	0.400
14	348, 437, 464	494, 516 (348)	0.79	1.25	−1.90	−2.16	−5.48	−2.99	2.49	0.050
17	318, 383, 437	439, 463 (318)	0.81	–	−2.13	−2.31	−5.56	−2.72	2.84	0.008
19	341, 436	463 (341)	0.82	–	–	–	−5.54	−2.81[e]	2.73[d]	0.310

[a] The HOMO energy level was calculated from the onset of oxidation wave. [b] The LUMO energy level was calculated from the onset of the first reduction wave. [c] The energy levels were calculated by using the following equations: HOMO = −(4.8+E_{ox}^{onset}), LUMO = −(4.8+E_{red}^{onset}), E_g = LUMO − HOMO. [d] The energy levels were calculated from the absorption of UV/Vis spectra: band gap energy [eV] = 1240/wavelength [nm]. [e] The LUMO energy level was calculated by using the following equations: LUMO = E_g + HOMO. [f] Quantum yields were determined with 9,10-diphenylanthracene as the fluorescence reference in chloroform (Φ = 0.91).

Electrochemical properties of the new PAHs: Cyclic voltammetry (CV) analyses of compounds **9**, **12**, **13**, **14**, **17**, and **19** in dry dichloromethane were undertaken to examine their electrochemical behavior and measure their energy levels (Figure 6 and Table 1). All compounds can be oxidized into the corresponding cationic species (i.e., radical cation and dication), which are partially stabilized by the extended π-conju-

gation. Due to the existence of a five-membered ring, quasi-reversible or irreversible reduction waves were also observed for some of these compounds (**9**, **13**, **14**, **17**) because the reduced cyclopentadiene anion is aromatic and can be further stabilized by delocalization along the whole fused π system. Such an amphoteric redox behavior is common among five-membered-ring-containing PAHs. However, no clear reduction waves were observed for **12** and **19** in the measuring range. Compounds **9** and **14** both show lower first oxidation potentials and higher first reduction potentials than the other compounds due to their more extended π-conjugation, as also evidenced by their UV/Vis absorption spectra. Multiple redox waves were observed for both compounds. It is noteworthy that the first and second oxidation scans of **14** are different, that is, an additional oxidation peak at 0.52 V (vs. Fc^+/Fc) appeared after the first scan (Figure 6a), indicating that the first scan actually resulted in the formation of a cationic species that can undergo subsequent chemical reaction (intramolecular or intermolecular coupling) towards a new entity with more extended π conjugation.

Conclusion

We investigated the synthesis and intramolecular cyclization reaction of a series of *peri*-ethynylene naphthalene oligomers. Our research demonstrated that these oligomers had high reactivity due to the close proximity and parallel alignment of ethylene units. In such systems, intramolecular domino thermal cyclization reactions via diradical intermediates readily take place and, thus, several benzo- or naphtho-annulated fluoroanthene derivatives (**12**, **13**, **17**, and **19**) were obtained and identified by crystallographic analysis. The electrophilic cyclization of **4** and **5** with iodine proceeded through an analogous domino cyclization process and afforded cyclized derivatives **9** and **14**, respectively. All of the newly formed PAH molecules serve as UV/Vis absorption/emission chromophores. It is noteworthy that some of these five-membered-ring-containing PAHs exhibit amphoteric redox behavior and have potential applications as ambipolar semiconductors. Our detailed studies also provide a wealth of data that will prove useful for the synthesis of new PAHs from arylene ethynylene precursors in the future.

Experimental Section

Synthesis of 4: Compound **8** (308 mg, 0.810 mmol), $[PdCl_2(PPh_3)_2]$ (28 mg, 0.040 mmol), CuI (15 mg, 0.081 mmol), PPh_3 (21 mg, 0.081 mmol), and phenylacetylene (0.35 mL, 3.260 mmol) were added to a mixture of Et_3N (15 mL) and THF (15 mL). The resulting solution was degassed and stirred at room temperature for 12 h under a N_2 atmosphere. The solvent was removed under reduced pressure and the residue was extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and evaporated to dryness in vacuum. The residue was purified by flash column chromatography through silica gel with hexane/chloroform (20:1) as the eluent to give compound **4** as a yellow solid (228 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.88$ (d, $J = 7.0$ Hz, 2H), 7.84 (d, $J = 8.5$ Hz, 2H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 4H), 7.22–7.19 (m, 2H), 7.14–7.11 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 134.9$, 134.2, 131.6, 131.5, 129.6, 127.92, 127.85, 125.6, 123.8, 120.9 ppm; MS (EI): m/z: 328.1 $[M]^+$.

Synthesis of 9: A solution of compound **4** (220 mg, 0.67 mmol) and I_2 (423 mg, 1.68 mmol) in $CHCl_3$ (20 mL) was stirred under a N_2 atmosphere at 40–50 °C for 12 h. Afterwards, the reaction mixture was cooled and a saturated aqueous solution of sodium thiosulfate was added. Subsequently, the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then evaporated to dryness in vacuum. The residue was purified by flash column chromatography through silica gel with hexane as the eluent to give compound **9** as a red solid (186 mg, 61%). M.p. 170–171 °C; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): $\delta = 9.11$–9.10 (m, 1H), 8.25 (d, $J = 6.5$ Hz, 1H), 7.84 (d, $J = 8.5$ Hz, 1H), 7.74 (t, $J = 8.5$ Hz, 2H), 7.63–7.57 (m, 3H), 7.53–7.49 (m, 3H), 7.39–7.38 (m, 2H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.09–7.08 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 146.0$, 144.0, 136.8, 136.4, 135.2, 134.8, 132.9, 132.6, 131.2, 130.8, 129.9, 128.9, 128.5, 128.1, 127.4, 126.6, 126.5, 126.0, 125.7, 124.5, 123.9, 120.6, 105.1 ppm; MS (EI): m/z: 454.0 $[M]^+$; HRMS (EI): m/z calcd for $C_{26}H_{15}I_2$: 454.0219; found: 454.0219.

Synthesis of 11: 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), trimethylsilyl acetylene (0.18 mL, 1.320 mmol), and H_2O (1 mL, 1.050 mmol) were successively added to a solution of compound **8** (1.0 g, 2.630 mmol), $[PdCl_2(PPh_3)_2]$ (110.7 mg, 0.158 mmol), and CuI (50 mg, 0.263 mmol) in toluene (15 mL). The reaction mixture was stirred at 50–60 °C for 18 h under an Ar atmosphere. The solution was then cooled to room temperature and the solvent was removed under reduced pressure. Subsequently, the residue was extracted with ethyl ether. The organic layer was washed with an aqueous solution of HCl (10%), and then with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness in vacuum. The residue was purified by flash column chromatography through silica gel (hexane) to give compound **11** as an orange solid (300 mg, 22%). M.p. 182–183 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.31$ (dd, $^4J = 1.5$ Hz, $^3J = 7.5$ Hz, 2H), 8.18 (dd, $^4J = 1.2$ Hz, $^3J = 7.2$ Hz, 2H), 7.88–7.82 (m, 4H), 7.52 (t, $J = 7.8$ Hz, 2H), 7.13 ppm (t, $J = 7.6$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 142.4$, 135.0, 134.2, 132.0, 130.2, 130.0, 127.1, 125.8, 123.9, 100.6, 92.7 ppm; MS (EI): m/z: 530.0 $[M]^+$; HRMS (EI): m/z calcd for $C_{22}H_{12}I_2$: 529.9029; found: 529.9026.

Synthesis of 5, 12, and 13: Compound **11** (106 mg, 0.20 mmol), $[PdCl_2(PPh_3)_2]$ (7 mg, 0.01 mmol), CuI (1. mg, 0.01 mmol), and phenylacetylene (0.11 mL, 1.00 mmol) were added to a mixture of Et_3N (15 mL) and THF (15 mL). The resulting solution was stirred at room temperature for 12 h under a N_2 atmosphere. The solvent was removed under reduced pressure and the residue was extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and evaporated to dryness in vacuum. The residue was purified by flash column chromatography through silica gel with hexane/chloroform (40:1) as the eluent to give compounds **5**, **12**, and **13**.

Compound **5** was obtained as pale yellow solid (38 mg, 40%). M.p. 111–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.79$–7.61 (m, 8H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.20–7.17 (m, 4H), 7.09 (t, $J = 7.5$ Hz, 2H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.81 ppm (t, $J = 7.4$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 134.6$, 134.5, 134.0, 131.6, 131.3, 129.3, 129.1, 127.5, 127.4, 125.3, 125.2, 123.8, 121.6, 121.1, 97.1, 96.6, 89.9 ppm; MS (EI): m/z: 476.3 $[M-2H]^+$; HRMS (EI): m/z calcd for $C_{38}H_{22}$: 478.1722; found: 478.1709.

Compound **12** was obtained as a pale yellow solid (20 mg, 21%). M.p. 186–187 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.15$ (dd, $^4J = 1.5$ Hz, $^3J = 8.0$ Hz, 1H), 8.06 (dd, $^4J = 1.5$ Hz, $^3J = 8.0$ Hz, 1H), 7.98 (s, 1H), 7.91 (d, $J = 7.0$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.73 (t, $J = 7.0$ Hz, 1H), 7.87–7.58 (m, 4H), 7.51–7.43 (m, 3H), 7.35–7.32 (m, 1H), 7.16 (t, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.93 (t, $J = 7.5$ Hz, 2H), 6.35 (dd, $J_1 = 1.5$ Hz, $J_2 = 8.0$ Hz, 2H), 6.15 ppm (d, $J = 6.5$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 137.3$, 137.2, 136.9, 136.5, 136.4, 135.5, 135.2, 134.75, 134.72, 134.5, 133.3, 131.3, 131.0, 130.3, 129.7, 129.4, 128.7, 128.2, 127.8, 127.2, 127.1, 127.0, 126.5, 125.96, 125.87, 125.5, 123.1, 121.6, 120.5, 120.4, 118.8, 95.2, 89.2 ppm; MS (EI): m/z: 478.2 $[M]^+$; HRMS (EI): m/z calcd for $C_{38}H_{22}$: 478.1722; found: 478.1711.

Compound **13** was obtained as a yellow solid (15 mg, 16%). M.p. 246–247°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.56 (d, J = 8.5 Hz, 1H), 9.09 (d, J = 7.5 Hz, 1H), 7.91 (dd, ^4J = 2.0 Hz, ^3J = 8.0 Hz, 2H), 7.86 (dd, ^4J = 1.5 Hz, ^3J = 7.0 Hz, 2H), 7.81–7.64 (m, 8H), 7.59–7.49 (m, 6H), 7.36 (t, J = 6.5 Hz, 1H), 6.57 ppm (d, J = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.0, 139.1, 136.7, 136.6, 135.6, 135.5, 134.9, 133.1, 131.8, 131.5, 131.2, 130.2, 129.9, 129.8, 129.2, 128.8, 128.7, 128.3, 128.2, 128.1, 127.8, 127.6, 127.2, 127.1, 126.9, 126.6, 125.7, 125.2, 124.0, 123.8, 122.7, 113.6, 99.3, 91.7 ppm; MS (EI): m/z: 478.2 $[M]^+$; HRMS (EI): m/z calcd for $C_{38}H_{22}$: 478.1722; found: 478.1712.

Synthesis of 14: A solution of compound **5** (42.4 mg, 0.089 mmol) and I_2 (56.3 mg, 0.220 mmol) in $CHCl_3$ (15 mL) was stirred under a N_2 atmosphere at 40–50°C for 12 h. A saturated aqueous solution of sodium thiosulfate was poured into the cooled reaction mixture and the organic layer was washed with brine and dried over anhydrous Na_2SO_4, and then evaporated in vacuum to dryness. The residue was purified by silica gel column chromatography (hexane) to give compound **14** as a yellow solid (26 mg, 48%). M.p. 284–285°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.81 (d, J = 7.5 Hz, 1H), 8.18 (d, J = 7.5 Hz, 1H), 8.02 (t, J = 7.5 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.86 (d, $J_=$9.0 Hz, 1H), 7.73 (dd, ^4J = 1.5 Hz, ^3J = 8.0 Hz, 2H), 7.71–7.68 (m, 4H), 7.59–7.55 (m, 3H), 7.39–7.34 (m, 3H), 7.28 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.55 ppm (d, J = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 146.9, 143.5, 139.3, 137.5, 137.2, 136.1, 134.7, 134.1, 133.7, 133.5, 132.8, 132.2, 130.7, 130.3, 130.2, 129.8, 129.3, 129.2, 128.8, 128.3, 128.1, 127.6, 127.5, 127.4, 127.1, 126.79, 126.76, 126.73, 126.2, 126.1, 125. 7, 124.8, 123.3, 111.7 ppm; MS (EI): m/z: 604.1 $[M]^+$; HRMS (EI): m/z calcd for $C_{38}H_{21}I$: 604.0688; found: 604.0691.

Synthesis of 15: Compound **8** (1.86 g, 4.900 mmol), $[PdCl_2(PPh_3)_2]$ (114 mg, 0.160 mmol), CuI (62 mg, 0.326 mmol), PPh_3 (85 mg, 0.324 mmol), and phenylacetylene (0.35 mL, 3.26 mmol) were dissolved in a mixture of Et_3N (30 mL) and THF (30 mL). The resultant solution was stirred at room temperature for 18 h under a N_2 atmosphere. The solvent was removed under reduced pressure and the residue was extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and evaporated to dryness in vacuum. The residue was purified by flash column chromatography through silica gel (hexane) to give compound **15** as a pale yellow oil (886 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (dd, ^4J = 1.5 Hz, ^3J = 7.2 Hz, 1H), 7.94 (dd, ^4J = 1.5 Hz, ^3J = 7.2 Hz, 1H), 7.85–7.79 (m, 2H), 7.69–7.66 (m, 2H), 7.47–7.38 (m, 4H), 7.10 ppm (t, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.6, 135.9, 134.9, 131.8, 130.8, 130.4, 130.1, 128.4, 128.3, 127.1, 125.4, 124.0, 122.8, 100.8, 92.9, 89.2 ppm; MS (EI); m/z: 354.0 $[M]^+$, 277.1, 226.1, 113.1, 72.1, 59.1; HRMS (EI): m/z calcd for $C_{18}H_{11}I$: 353.9906; found: 353.9911.

Synthesis of 16: Compound **15** (0.92 g, 2.60 mmol), $[PdCl_2(PPh_3)_2]$ (91 mg, 0.13 mmol), CuI (50 mg, 0.26 mmol), PPh_3 (68 mg, 0.26 mmol), and trimethylsilyl acetylene (1.76 mL, 13.0 mmol) were dissolved in a mixture of Et_3N (20 mL) and THF (20 mL). The resultant solution was stirred at room temperature for 12 h under a N_2 atmosphere. The solvent was removed under reduced pressure and the residue was extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and evaporated to dryness in vacuum. The residue can be used without further purification. The residue was dissolved in a mixture of CH_3OH (30 mL) and THF (30 mL) and then K_2CO_3 (1.79 g, 13.0 mmol) was added. The resultant solution was stirred at room temperature for 5 h. The reaction mixture was poured into water (50 mL) and extracted with $CHCl_3$ (3×50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated to dryness in vacuum. The crude product was purified by flash column chromatography through silica gel with hexane as the eluent to afford compound **16** as a pale yellow viscous liquid (446 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.81 (m, 4H), 7.65–7.62 (m, 2H), 7.49–7.36 (m, 5H), 3.53 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.9, 134.4, 134.0, 131.8, 131.0, 130.2, 129.7, 128.4, 128.2, 125.6, 125.4, 124.1, 120.5, 119.6, 96.2, 89.9, 83.9, 83.8 ppm; MS (EI): m/z: 252.1 $[M]^+$; HRMS (EI): m/z calcd for $C_{20}H_{12}$: 252.0939; found: 252.0941.

Synthesis of 17: Compound **8** (57 mg, 0.150 mmol), compound **16** (113 mg, 0.450 mmol), $[PdCl_2(PPh_3)_2]$ (5.3 mg, 0.075 mmol), and CuI (1.4 mg, 0.0075 mmol) were dissolved in a mixture of Et_3N (10 mL) and THF (10 mL). The resultant solution was stirred at room temperature for 18 h under a N_2 atmosphere. The solvent was removed under reduced pressure and the residue was extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and evaporated to dryness in vacuum. The residue was purified by flash column chromatography through silica gel with hexane/chloroform (30:1) as the eluent to give compound **17** as a yellow solid (38 mg, 41%). M.p. 283–284°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.45–8.43 (m, 2H), 8.18 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 2H), 7.85–7.48 (m, 15H), 7.40–7.35 (m, 2H), 7.16 (t, J = 7.2 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.62 (t, J = 7.8 Hz, 2H), 6.19 (d, J = 7.5 Hz, 1H), 6.08 ppm (dd, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.32, 139.30, 137.8, 137.2, 137.0, 136.5, 136.4, 136.1, 136.0, 135.0, 134.8, 134.7, 134.4, 134.3, 133.3, 132.4, 131.5, 130.4, 130.2, 130.1, 129.7, 129.6, 129.5, 128.6, 128.3, 128.0, 127.7, 127.6, 127.1, 127.0, 126.8, 126.7, 126.6, 125.7, 125.6, 125.1, 124.7, 124.4, 123.4, 122.8, 122.2, 120.8, 120.5, 114.1, 95.3, 90.0 ppm; MS (EI): m/z: 628.3 $[M]^+$; HRMS (EI): m/z calcd for $C_{50}H_{28}$: 628.2176; found: 628.2203.

Synthesis of 19: Compound **11** (81 mg, 0.150 mmol), compound **16** (113 mg, 0.450 mmol), $[PdCl_2(PPh_3)_2]$ (5.3 mg, 0.0075 mmol), and CuI (1.4 mg, 0.0075 mmol) were dissolved in a mixture of Et_3N (10 mL) and THF (10 mL). The resultant solution was stirred at 40–50°C for 12 h under a N_2 atmosphere. The solvent was removed under reduced pressure and the residue was extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and evaporated to dryness in vacuum. The residue was purified by flash column chromatography through silica gel with hexane/chloroform (20:1) as the eluent to give compound **19** as a yellow solid (47 mg, 40%). M.p. 190°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.48–10.46 (m, 1H), 9.00 (d, J = 7.5 Hz, 1H), 8.19 (dd, ^3J = 8.5 Hz, ^4J = 1.0 Hz, 1H), 8.08 (dd, ^3J = 8.5 Hz, ^4J = 1.0 Hz, 1H), 8.03–7.98 (m, 2H), 7.96 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1H), 7.85 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H), 7.81–7.76 (m, 3H), 7.68 (q, J = 8.7 Hz, 2H), 7.59–7.48 (m, 8H), 7.38 (d, J = 8.5 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.80 (t, J = 8.0 Hz, 2H), 6.66–6.63 (m, 1H), 6.58 (dd, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 2H), 6.35 (t, J = 7.5 Hz, 2H), 6.27 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 2H), 6.01 ppm (d, J = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.8, 137.06, 137.03, 136.5, 135.9, 135.8, 134.9, 134.72, 134.69, 134.5, 134.46, 134.40, 133.3, 132.8, 131.7, 131.4, 130.9, 130.6, 129.9, 129.8, 129.7, 129.66, 129.63, 129.56, 129.52, 128.1, 127.9, 127.40, 127.39, 127.31, 127.25, 127.1, 126.9, 126.6, 126.5, 126.4, 126.2, 125.9, 125.84, 125.81, 125.6, 125.5, 125.4, 124.4, 122.9, 122.7, 121.8, 121.6, 121.3, 120.6, 115.2, 99.8, 98.5, 98.2, 95.7, 89.7, 89.0 ppm; MS (EI): m/z: 778.4 $[M]^+$; HRMS (EI): m/z calcd for $C_{62}H_{34}$: 778.2661; found: 778.2677.

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[23] Compound **9**: $C_{26}H_{15}I$; $M_w = 454.28$; triclinic; $0.60 \times 0.36 \times 0.10$ mm; $P\bar{1}$; $a = 8.076(2)$, $b = 9.744(3)$, $c = 12.179(3)$ Å; $\alpha = 71.459(5)$, $\beta = 80.860(5)$, $\gamma = 83.201(5)°$; $V = 894.6(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.686$ mg m^{-3}; collected 11545; independent 4102; parameters 244; $R_1 = 0.0246$; $wR_2 = 0.0659$ ($I > 2\sigma(I)$); GOF = 1.117. CCDC-831273 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. X-ray quality crystals of this compound can be obtained by slow evaporation of the solution in $CHCl_3/CH_3OH$.

[24] Compound **10**: $C_{27}H_{16}Cl_3IO_2$; $M_w = 605.65$; triclinic; $0.72 \times 0.32 \times 0.28$ mm; $P\bar{1}$; $a = 8.6263(3)$, $b = 9.4280(3)$, $c = 16.2156(6)$ Å; $\alpha = 84.4880(10)$, $\beta = 75.2080(10)$, $\gamma = 68.2880(10)°$; $V = 1184.63(7)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.698$ mg m^{-3}; collected 15531; independent 5436; parameters 330; $R_1 = 0.0315$; $wR_2 = 0.0798$ ($I > 2\sigma(I)$); GOF = 1.084. CCDC-831272 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Yellow solid; m.p. 280–281 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 9.21$ (d, $J = 8.0$ Hz, 1H), 8.69 (d, $J = 8.5$ Hz, 1H), 7.81 (d, $J = 7.0$ Hz, 1H), 7.75–7.71 (m, 3H), 7.48–7.40 (m, 3H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.18–7.13 (m, 3H), 6.61 ppm (d, $J = 9.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 187.3$, 159.3, 151.6, 144.8, 143.3, 142.1, 137.7, 137.4, 135.6, 132.5, 130.8, 129.1, 128.3, 128.2, 127.9, 127.8, 127.7, 127.0, 125.2, 124.8, 124.1, 104.6, 83.4 ppm; MS (EI): m/z: 486.0 [M^+]; HRMS (EI): m/z calcd for $C_{26}H_{15}O_2I$ 486.0117: found: 486.0104. X-ray quality crystals of this compound can be obtained by slow evaporation of a solution of **10** in a mixture of $CHCl_3$ and CH_3OH.

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[26] This compound was characterized by NMR spectroscopy and MS. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.52$ (dd, $^3J = 7.6$ Hz, $^4J = 1.3$ Hz, 2H), 7.98 (dd, $^3J = 7.6$ Hz, $^4J = 1.3$ Hz, 2H), 7.83 (d, $J = 8.2$ Hz, 4H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.12 ppm (t, $J = 7.6$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 142.8$, 137.8, 134.8, 132.7, 131.2, 130.2, 127.3, 125.4, 121.9, 93.5, 88.0, 83.2 ppm; MS (EI): m/z: 554.0 [M]$^+$.

[27] Compound **12**: $C_{38}H_{22}$; $M_w = 478.56$; monoclinic; $0.40 \times 0.30 \times 0.14$ mm; $P21/n$; $a = 15.5297(13)$, $b = 15.5775(14)$, $c = 10.6412(10)$ Å; $\alpha = 90$, $\beta = 104.436(2)$, $\gamma = 90°$; $V = 2493.0(4)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.275$ mg m^{-3}; collected 17635; independent 5711; parameters 343; $R_1 = 0.0672$; $wR_2 = 0.1336$ ($I > 2\sigma(I)$); GOF = 1.080. CCDC-831275 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Compound **13**: $C_{38}H_{22}$; $M_w = 478.56$; monoclinic; $0.60 \times 0.22 \times 0.06$ mm; $P21/n$; $a = 9.6169(15)$, $b = 22.307(3)$, $c = 11.2104(17)$ Å; $\alpha = 90$, $\beta = 90.961(4)$, $\gamma = 90°$; $V = 2404.6(6)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.322$ mg m^{-3}; collected 17063; independent 5517; parameters 343; $R_1 = 0.0765$; $wR_2 = 0.1588$ ($I > 2\sigma(I)$); GOF = 1.040. CCDC-831276 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. X-ray quality crystals of both these two compounds can be obtained by slow evaporation of the solution in $CHCl_3/CH_3OH$.

[28] Compound **14**: $C_{38}H_{21}I$; $M_w = 604.45$; triclinic; $0.60 \times 0.60 \times 0.50$ mm; $P\bar{1}$; $a = 9.8841(5)$, $b = 10.9360(5)$, $c = 12.5535(6)$ Å; $\alpha = 100.9490(10)$, $\beta = 93.2250(10)$, $\gamma = 105.9390(10)°$; $V = 1272.54(11)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.577$ mg m^{-3}; collected 8967; independent 5775; parameters 352; $R_1 = 0.0307$; $wR_2 = 0.0832$ ($I > 2\sigma(I)$); GOF = 1.093. CCDC-831269 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. X-ray quality crystals of this compound can be obtained by slow evaporation of the solution in $CHCl_3/CH_3OH$.

[29] Compound **17**: $C_{50}H_{28}$; $M_w = 628.72$; monoclinic; $0.38 \times 0.30 \times 0.26$ mm; $P21/n$; $a = 10.8735(9)$, $b = 21.800(2)$, $c = 13.6272(12)$ Å; $\alpha = 90$, $\beta = 96.901(3)$, $\gamma = 90°$; $V = 3206.9(5)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.302$ mg m^{-3}; collected 22939; independent 7361; parameters 451; $R_1 = 0.0504$; $wR_2 = 0.1180$ ($I > 2\sigma(I)$); GOF = 1.029. CCDC-831270 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. X-ray quality crystals of this compound can be obtained by slow evaporation of the solution in $CHCl_3/CH_3OH$.

[30] Compound **18**: $C_{40}H_{22}$; $M_w = 502.58$; monoclinic; $0.60 \times 0.46 \times 0.20$ mm; $C2/c$; $a = 27.253(3)$, $b = 12.1238(13)$, $c = 18.2854(19)$ Å; $\alpha = 90$, $\beta = 118.828(3)$, $\gamma = 90°$; $V = 5293.0(10)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.261$ mg m^{-3}; collected 18481; independent 6077; parameters 361: $R_1 = 0.0462$; $wR_2 = 0.1115$ ($I > 2\sigma(I)$); GOF = 1.036. CCDC-831271 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. X-ray quality crystals of this compound can be obtained by slow evaporation of a solution of **18** in a mixture of $CHCl_3$ and hexane. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.86-7.81$ (m, 10H), 7.52 (dd, $^3J = 7.0$ Hz, $^4J = 1.5$ Hz, 2H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.21–7.16 ppm (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 136.4, 134.8, 134.0, 132.0, 131.9, 130.3, 129.5, 128.10, 128.06, 127.99, 125.8, 125.35, 125.33, 123.8, 121.0, 119.7, 97.7, 89.3, 83.7, 82.6 ppm; MS (EI): m/z: 502.2 $[M]^+$.

[31] Compound **19**: $C_{62}H_{34}$; $M_w = 778.89$; monoclinic; $0.70 \times 0.60 \times 0.20$ mm; $P21/n$; $a = 10.6144(10)$, $b = 27.343(3)$, $c = 14.4095(14)$ Å; $\alpha = 90$, $\beta = 106.393(2)$, $\gamma = 90°$; $V = 4012.0(7)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.290$ mg m^{-3}; collected 51615; independent 9206; parameters 559; $R_1 = 0.0695$; $wR_2 = 0.0878$ ($I > 2\sigma(I)$); GOF = 1.099. CCDC-831274 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. X-ray quality crystals of this compound can be obtained by slow evaporation of the solution in $CHCl_3/CH_3OH$.

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