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Four Iodine-Mediated Electrophilic Cyclizations of Rigid Parallel Triple Bonds Mapped from 1,8-Dialkynylnaphthalenes

Xiaopeng Chen, Ping Lu,* and Yanguang Wang*[a]

Abstract: Four different types of fused arenes, including fluoranthene, indeno[2,1-*a*]phenalene, (8*H*)cyclopenta[*a*]acenaphthylene, and pyridine[*a*]acenaphthylene, were efficiently constructed through iodine-mediated electrophilic cyclizations of 1,8-dialkynyl naphthalenes in a single step. Theoretical calculations supported our hypothesis that these reactions had high regioselectivity. Oxidative coupling of the fluoranthene skeleton, followed by aromatization, effectively synthesized perylene derivative **14**, which emitted light at 597 nm in dichloromethane with an emission efficiency of 0.81 referred to 5,6,11,12-tetraphenylnaphthacene as a standard.

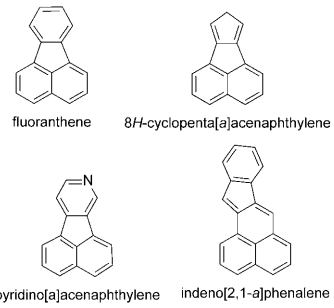
Keywords: fluorescence · heterocyces · iodocyclization · parallel diynes · tandem reactions

Introduction

Iodine-mediated electrophilic cyclization has attracted much attention in recent years because this methodology is efficient in the construction of fused rings with a broad output of heterocyclic or carbocyclic skeletons.[1] When the heteroatom (i.e. N,[2]O,[3] S,[4] or Se[4b,5]) nucleophilically attacks the electron-deficient triple bond, which is activated by iodine, compounds with a heterocyclic skeleton could thereby be constructed. Aromatic hydrocarbons or aryl iodide could be obtained through a similar mechanism when an electron-rich double bond was used as the nucleophile.[6] By using this strategy, Swager and co-workers[7] elegantly designed and synthesized a variety of rigid carbocyclic platforms that might be applied in the fields of optoelectronic devices due to the highly conjugated systems.

There are two types of parallel triple bonds. When heteroatom and/or sp^3-hybridized carbon hold two triple bonds together as the bridge, the backbone of this type of diyne is flexible. Molecular movement could make these two triple bonds in a parallel state. These flexible parallel triple bonds have been extensively used as substrates in many reactions, typically in cascade reactions, in which one of the triple bonds is activated by Lewis acid or metal ion, then a nucleophilic attack occurs subsequently to form a variety of functionalized compounds.[8] However, when two triple bonds occupy 1- and 8- positions of naphthalene, these two triple bonds become rigid parallel. With different chemical behavior, rigid parallel triple bonds are highly reactive towards either nucleophiles or electrophiles due to the fact that the two triple bonds are bent in the structure resulting from the repulsion strain between π electrons.[9] For instance, a C=C double bond could be easily inserted into one of the rigid parallel triple bonds to derive an enyne.[9e] Another example, reported by our group recently, was the cascade reaction between 1,8-diiodonaphthalene and propargylic alcohols, involving the in situ formation of rigid parallel triple bonds through Pd-catalyzed Sonogashira coupling, subsequent Pd-catalyzed hydration, aldol condensation, Pd-catalyzed allylic oxidation, and Pd-catalyzed C–H activation.[9a]

Polycyclic aromatic hydrocarbons (PAHs) have been intensively explored due to their utilities in many fields. Fused five or six carbocyclic rings are the key substructures of coannulenes or higher fullerenes, such as C_{60} and its analogues. Fluoranthene, as a typical example, has been utilized as a synthetic precursor of coannulenes and as a model of fluorescent compounds for its high emission efficiency.[10] However, (8*H*)cyclopenta[*a*] acenaphthylene, pyridino[*a*]acenaphthylene, and indeno[2,1-*a*]phenalene are seldom explored because their structures could not easily be constructed.



To enrich our ongoing research on the fluorescent structure–property relationship[11] and synthetic materials for or-

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ganic light-emitting diodes,[12] we were interested in developing a new strategy for the construction of PAHs from 1,8-dialkynylnaphthalenes that contained the rigid parallel triple bonds. To our surprise, it was found that the iodocyclization of 1,8-dialkynylnaphthalenes furnished fluoranthene, (8*H*)cyclopenta[*a*]acenaphthylene, pyridino[*a*]acenaphthylene, and indeno[2,1-*a*]phenalene with high selectivity, depending on the structure of the substrates and the solvents used for reaction. We herein report the details of these efforts.

Results and Discussion

Iodine-mediated tandem reaction of 1,8-bis(hydroxypropargyl) naphthalene: We first examined the reaction of 1,8-bis(hydroxypropargyl)naphthalene (**1a**) with iodine in dichloromethane. Fluoranthene (**2a**)[13] was effectively constructed under mild conditions. To obtain a greater understanding of this transformation, optimization of reaction conditions was carried out by using **1b** as a substrate (Table 1). 1,2-Dichloroethane was found to be the most suitable solvent for this reaction (Table 1, entries 1 and 5–10). Dichloromethane resembled dichloroethane in yield (entries 1 and 5). Other organic solvents were proved to be relatively ineffective because of the relatively lower yields. Either refluxing or freezing the reaction mixture would decrease the yield significantly (entries 1 and 4). We thereby selected dichloroethane as the solvent and ran the reaction at room temperature for 8 h.

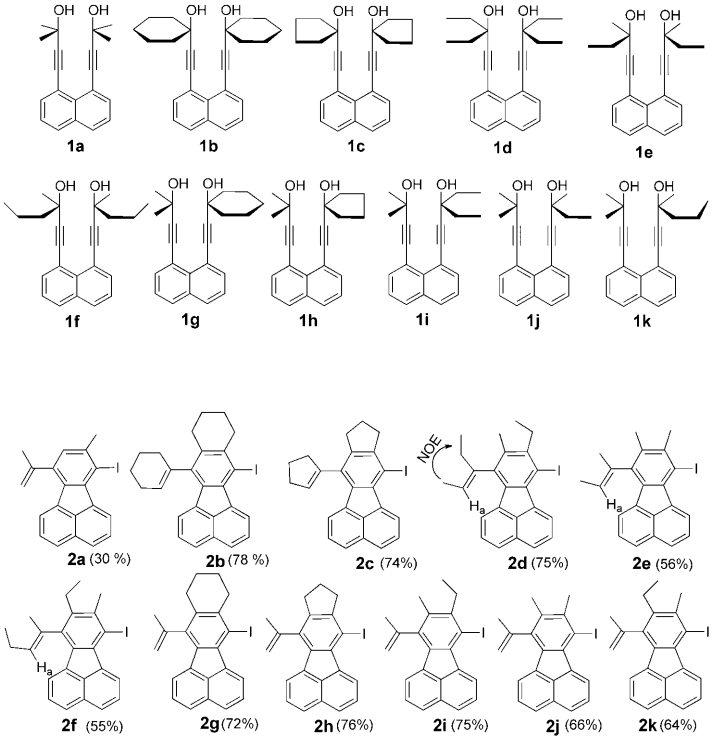
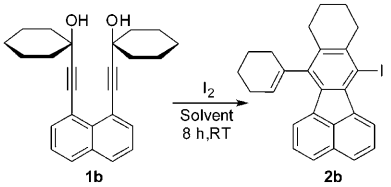


Table 1. Optimization of reaction conditions for the preparation of **2b**.[a]



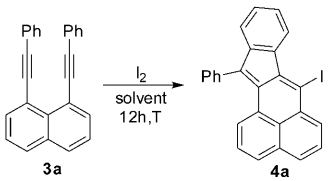
Entry	Solvent	*T* [°C]	Yield [%][b]
1	dichloroethane	RT	78
2	dichloroethane	0	64
3	dichloroethane	50	58
4	dichloroethane	reflux	23
5	CH_2Cl_2	RT	72
6	$CHCl_3$	RT	38
7	CCl_4	RT	32
8	CH_3CN	RT	29
9	THF	RT	20
10	1,4-dioxane	RT	<5

[a] Reaction conditions: **1b** (186 mg, 0.5 mmol), I_2 (140 mg, 0.55 mmol), solvent (10 mL), RT, 8 h. [b] Isolated yield.

Under the optimized reaction conditions, we tested for the substrate diversity. A series of 7-iodofluoranthenes **2a–k** were synthesized and the isolated yields varied from 30 to 78% as indicated in parentheses. Structures of products **2a–k** were fully characterized by NMR spectroscopy and HRMS (see the Supporting Information). X-ray analysis of **2c**[13] further confirmed the 7-iodofluoranthene skeleton. For **1a–d**, molecules with a symmetrical plane and two identical alkyl groups attached to the carbon substituted by hydroxyl **2a–d** were constructed. Compound **2d** presented an *E* configuration that was established by an NOE between methyl and ethyl groups (see Figure S7 in the Supporting Information). For **1e**, with a symmetrical plane but two different alkyl groups attached to the carbon substituted by hydroxyl, **2e** was isolated as a major product, which was in good accordance with the Saytzeff rule[14] that the elimination reaction would give the most substituted alkene as the major product. A similar situation was found when **1f** was used as the substrate. Moreover, both **2e** and **2f** possessed *E* configurations by comparing the chemical shifts of H_a in **2d**, **2e**, and **2f** ($\delta = 5.65$, 5.59, and 5.52 ppm, respectively). For **1g–k**, without symmetrical planes, the reaction was highly regioselective to afford **2g–k** as major products, respectively.

Iodine-mediated tandem reaction of 1,8-diarenynylnaphthalene: Then we moved our attention to 1,8-diarenynyl naphthalenes. By treatment of **3a** with three molar equivalents iodine in dichloromethane for 12 h, a new carbocyclic skeleton was afforded in 29% yield. Based on the X-ray analysis, the structure of the product was unassailably determined to be 7-iodo-12-phenylindeno[2,1-*a*]phenalene (**4a**).[15] Promoted by this result, we tried to optimize the reaction conditions for this transformation (Table 2). Yield was significantly increased by raising the reaction temperature to 40°C (Table 2, entries 1 and 2). Compound **4a** could also be afforded in moderate yields by changing the solvent to other

Table 2. Optimization of reaction conditions for the preparation of **4a**.[a]

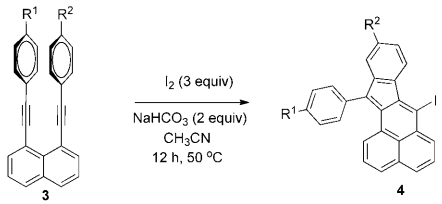


Entry	Solvent	T [°C]	Yield [%][b]
1	CH_2Cl_2	RT	29
2	CH_2Cl_2	40	56
3	$CHCl_3$	50	41
4	CCl_4	50	43
5	dichloroethane	50	18
6	THF	50	36
7	1,4-dioxane	50	33
8	EtOH	50	59
9	CH_3CN	50	61
10[c]	CH_3CN	50	92
11[c,d]	CH_3CN	50	76

[a] Reaction conditions: **3a** (33 mg, 0.1 mmol), I_2 (76 mg, 0.3 mmol), solvent (1 mL), room temperature, 12 h. [b] Isolated yield. [c] $NaHCO_3$ (17 mg, 0.2 mmol) was added, 12 h. [d] I_2 (50.8 mg, 0.2 mmol), 48 h.

halogenated solvents, such as chloroform, carbon tetrachloride, or dichloroethane (entries 2–5). THF or 1,4-dioxane worked for this transformation, but in relatively lower yield (entries 6 and 7). Yield was slightly increased by using polar protic solvent (entry 8) or by using polar aprotic solvent (entry 9). To our delight, **4a** was isolated in 92% yield after the reaction was performed for 12 h in acetonitrile at 50°C when two equivalents of $NaHCO_3$ were added (entry 10).[6b,16] Addition of $NaHCO_3$ did improve the yield dramatically. Meanwhile, reducing the amount of iodine to two molar equivalents would result in an incomplete reaction, which was shown by TLC tracking after 48 h (entry 11).

With the optimized reaction conditions, we tested other 1,8-diarenynyl naphthalenes **3b–j** for this iodocyclization reaction (Scheme 1). 7-Iodo-indeno[2,1-*a*]phenalenes **4a–d** were constructed from the corresponding starting materials **3a–d**. Influence of electron effect on this reaction was not apparent. Either electron-withdrawing (−F) or electron-donating ($-OCH_3$) groups attached on the phenyl rings worked for this iodocyclization. Compounds **3e** and **3f** did not afford the desired products. Unsymmetrical 1,8-diarenynylnaphthalenes **3g–j** lost their regioselectivity although the reaction proceed well according to ^1H NMR spectroscopic analysis (see the Supporting Information).

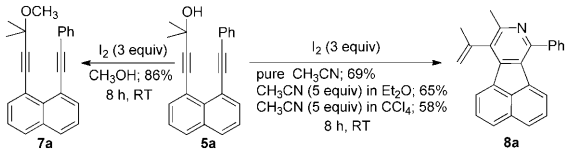


3a: R^1=R^2=H
3b: R^1=R^2=F
3c: R^1=R^2=CH_3
3d: R^1=R^2=OCH_3
3e: R^1=R^2=$COCH_3$
3f: R^1=R^2=CN
3g: R^1=H, R^2=F
3h: R^1=H, R^2=Br
3i: R^1=H, R^2=CH_3
3j: R^1=H, R^2=OCH_3

4a: R^1=R^2=H; 92%
4b: R^1=R^2=F; 86%
4c: R^1=R^2=CH_3; 94%
4d: R^1=R^2=OCH_3I; 95%
4ea (R^1=H, R^2=F)+**4eb**(R^1=F, R^2=H): 80%
4fa (R^1=H, R^2=Br)+**4fb**(R^1=Br, R^2=H): 72%
4ga (R^1=H, R^2= CH_3)+**4gb**(R^1= CH_3, R^2=H): 88%
4ha (R^1=H, R^2= OCH_3)+**4hb**(R^1= OCH_3, R^2=H): 91%

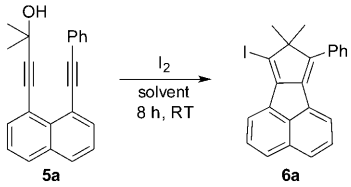
Scheme 1. Iodocyclization of **3** to **4**.

Iodine-mediated tandem reaction of 1-arenynyl-8-hydroxypropargyl naphthalene: We finally moved our attention to the reaction of iodine with 1-arenynyl-8-hydroxypropargyl naphthalenes **5**. Reaction of **5a** with iodine in dichloromethane led to the formation of a new carbocyclic skeleton, that is, (8*H*)cyclopenta[*a*]acenaphthylene (**6a**). Structure of **6a** was comparatively determined by X-ray diffraction analysis of **6c**[17] (Scheme 3). Delighted by this result, we optimized reaction conditions by using **5a** as a substrate. The reaction was initially tested with three equivalents of iodine in dichloromethane at room temperature for 8 h. In this way, **6a** was prepared in 58% yield (Table 3, entry 1). The best yield (72%) was achieved in dichloroethane (entry 2). Yield was decreased in chloroform (45%), carbon tetrachloride (15%), and 1,4-dioxane (12%). Starting material **5a** was recovered in a certain amount in these cases (entries 3–5). The reaction did not occur in the solvent of diethyl ether (entry 6). Although the reaction occurred in THF or nitro-



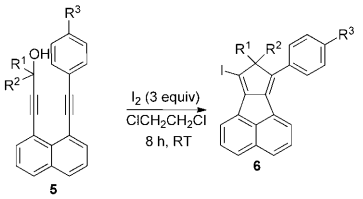
Scheme 2. Reaction of **5a** with iodine in acetonitrile or methanol.

Table 3. Optimization of reaction conditions for the preparation of **6a**.[a]



Entry	Solvent	Yield **6a** [%][b]	Yield **5a** [%][b]
1	CH_2Cl_2	58	<5
2	dichloroethane	72	<5
3	$CHCl_3$	42	36
4	CCl_4	15	76
5	1,4-dioxane	12	54
6	Et_2O	0	92
7	THF	0[c]	<5
8	CH_3NO_2	0[c]	<5
9	CH_3OH	0[d]	<5
10	CH_3CN	12[e]	<5

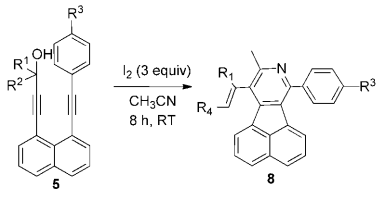
[a] Reaction conditions: **5a** (31 mg, 0.1 mmol), I_2 (0.3 mmol), solvent (1 mL), RT, 8 h. [b] Yield of **6a** and the recovery of **5a** were determined after column chromatography. [c] No main product was isolated. [d] Compound **7a** was isolated in a yield of 86%. [e] Compound **8a** was isolated in a yield of 69%.



5a: R^1=R^2=CH_3, R^3=H
5b: R^1=R^2=CH_3, R^3=CH_3
5c: R^1=R^2=CH_3, R^3=OCH_3
5d: R^1=R^2=CH_3, R^3=F
5e: R^1=R^2=CH_3, R^3=Br
5f: R^1=R^2=CH_3, R^3=CN
5g: R^1=R^2=CH_3, R^3=$COCH_3$
5h: R^1=CH_3, R^2=C_2H_5, R^3=H
5i: R^1=CH_3, R^2=nC_3H_7, R^3=H
5j: R^1=R^2=C_2H_5, R^3=H
5k: R^1,R^2= -C_4H_{8-}, R^3=H
5l: R^1,R^2= -C_5H_{10-}, R^3=H

6a: R^1=R^2=CH_3, R^3=H; 72%
6b: R^1=R^2=CH_3, R^3=CH_3; 68%
6c: R^1=R^2=CH_3, R^3=OCH_3; 55%
6d: R^1=R^2=CH_3, R^3=F; 53%
6e: R^1=R^2=CH_3, R^3=Br, 42%
6f: R^1=CH_3, R^2=C_2H_5, R^3=H; 64%
6g: R^1=CH_3, R^2=nC_3H_7, R^3=H; 58%
6h: R^1=R^2=C_2H_5, R^3=H; 55%

Scheme 3. Synthesis of (8*H*)cyclopenta[*a*]acenaphthylenes **6**.



5a: R^1=R^2=CH_3, R^3=H
5b: R^1=R^2=CH_3, R^3=CH_3
5c: R^1=R^2=CH_3, R^3=OCH_3
5d: R^1=R^2=CH_3, R^3=F
5e: R^1=R^2=CH_3, R^3=Br
5f: R^1=R^2=CH_3, R^3=CN
5g: R^1=R^2=CH_3, R^3=$COCH_3$
5h: R^1=CH_3, R^2=C_2H_5, R^3=H
5i: R^1=CH_3, R^2=nC_3H_7, R^3=H
5j: R^1=R^2=C_2H_5, R^3=H
5k: R^1,R^2= -C_4H_{8-}, R^3=H
5l: R^1,R^2= -C_5H_{10-}, R^3=H

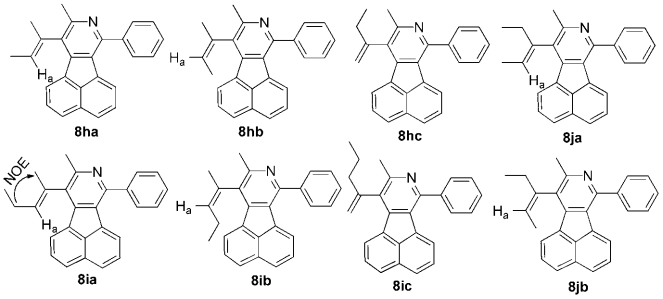
8a: R^1=CH_3, R^3=H, R^4=H; 69%
8b: R^1=CH_3, R^3=CH_3, R^4=H; 62%
8c: R^1=CH_3, R^3=OCH_3, R^4=H; 50%
8d: R^1=CH_3, R^3=F, R^4=H; 62%
8e: R^1=CH_3, R^3=Br, R^4=H; 48%
8f: R^1=CH_3, R^3=CN, R^4=H; 28%
8g: R^1=CH_3, R^3=$COCH_3$, R^4=H; 35%
8ha/8hb/8hc = 4:1:0.18; 70%
8ia/8ib/8hc = 4:1:0.44; 78%
8ja/8jb = 3:1; 76%
8k: R^1,R^4= -C_3H_{6-},R^3=H; 76%
8l: R^1,R^4= -C_4H_{8-}, R^3=H; 82%

Scheme 4. Reactions of **5** with iodine in acetonitrile.

methane as shown by the disappearance of **5a** by TLC tracking, too many spots were observed and the desired product **6a** could not be isolated in a significant amount (entries 7 and 8). When the reaction ran in methanol, an ether **7a** (Scheme 2) was obtained in a yield of 86% (entry 9). To our surprise, when acetonitrile was used as the solvent, the major product was isolated and determined to be a pyridino[*a*]acenaphthylene derivative **8a** in addition to the minor formation of **6a** (entry 10). The structure of **8a** was confirmed by X-ray diffraction analysis[18] Acetonitrile did participate in the formation of **8a**. When acetonitrile was fed in five molar equivalents to **5a** in a solution of either carbon tetrachloride or diethyl ether, **8a** could also be obtained in yields of 58 and 65%, respectively (Scheme 2).

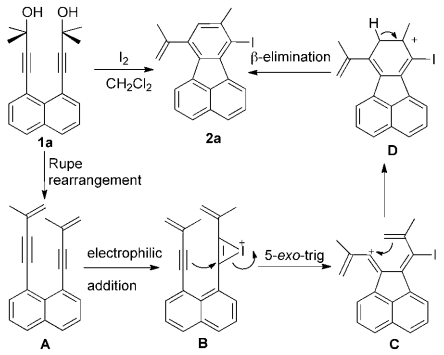
With the optimized conditions in hand, various substrates **5a–l** were investigated and the results were summarized in Scheme 3. 1-Arenynyl-8-hydroxypropargyl naphthalenes, in which the arenynyl part was attached with different functional groups, such as methyl (**5b**), methoxy (**5c**), fluoro (**5d**), and bromo (**5e**), readily underwent cyclization to afford **6b–e** in moderate yields (42–68%). No major product was obtained when the substrate was **5f** or **5g**. Substrates with different propargyls (**5h–j**) also worked for this reaction and constructed **6f**, **6g**, and **6h** in yields of 64, 58, and 55%, respectively. No desired product was isolated when either cyclopentyl (**5k**) or cyclohexyl (**5l**) was used as substrate although **5k** or **5l** completely disappeared by TLC tracking after 8 h.

Alternatively, encouraged by the reaction of **5a** with iodine in pure acetonitrile (Scheme 2), we investigated the tolerance of this transformation with various substrates **5a–l** (Scheme 4). A series of substituted pyridino[*a*]acenaphthylenes **8a–g** were readily constructed from 1-arenynyl-8-hydroxypropargyl naphthalenes **5a–g** and yields varied from 69 to 28%. Compounds **5f** and **5g** also worked for this transformation, but in relatively lower yields. Relatively higher yields could be approached when **5k** or **5l** were used. When **5h** was tested for this cyclization, **8ha** was isolated in a yield of 56% and a mixture of **8hb** and **8hc** was obtained

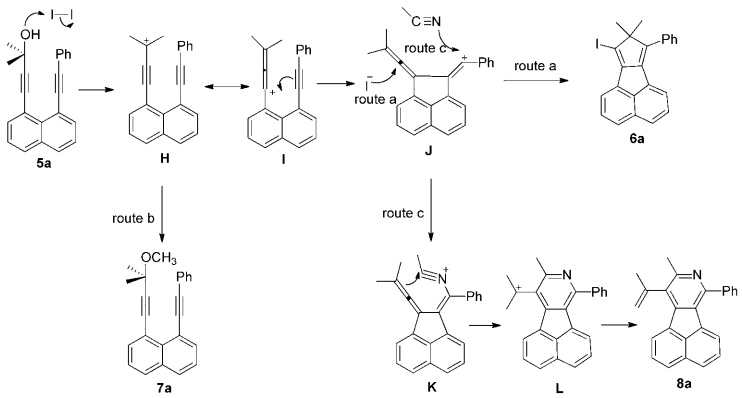


in a yield of 14% and in an 1:0.18 ratio based on the analysis of ^{1}H NMR spectra. The chemical shifts for H_a in **8ha** and **8hb** were determined to be $\delta = 5.64$ and 5.93 ppm, respectively. A similar situation was observed when **5i** was used as substrate. It was not surprising because of the fact that the β-elimination occurred in the final step of this conversion and it obeyed the Saytzeff rule[14] with regioselectivity. In the case of **5j**, **8ja** and **8jb** were isolated in yields of 57 and 19%, respectively.

Proposed mechanism and computational simulation: Three different 1,8-dialkylnylnaphthalenes with rigid parallel triple bonds afforded four different fused rings when they reacted with iodine as we described above. Mechanisms for these transformations must be impressive because of the high regioselectivity for each one. In the case of the conversion from **1a** to **2a**, a working mechanism was proposed and illustrated according to the substrate survey and literature processes (Scheme 5). Firstly, propargylic alcohol (**1a**) was converted to enyne **A** through Rupe-type elimination,[19] which was catalyzed by iodine. Electrophilic addition of iodine to one of triple bonds of **A** led to the formation of iodonium intermediate **B**.[20] The 5-*exo*-trig cyclization[21] was thus performed by addition of an adjacent triple bond on iodonium and a vinylic carbocation **C**[22] was generated. Intramolecular cyclization led to the formation of a more stable carbocation **D**. Finally, β-elimination of **D** afforded bicyclized product **2a**.

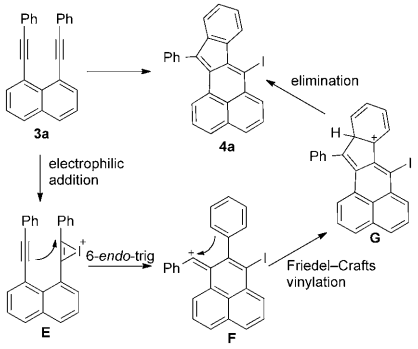


Scheme 5. Possible mechanism for **2a** formation.



Scheme 7. Possible mechanism for the formation of **6a**, **7a**, and **8a**.

In the case of the formation of the indeno[2,1-*a*]phenalene skeleton (**4**) from 1,8-diarenynyl naphthalenes (**3**), based on the investigation of the substrate diversity and the reaction conditions, an iodocyclization reaction mechanism was also proposed (Scheme 6). One of the triple bonds was

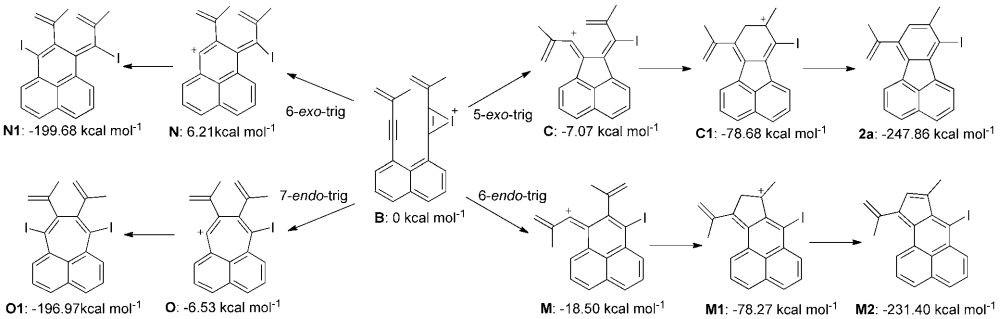


Scheme 6. Possible mechanism for **4a** formation.

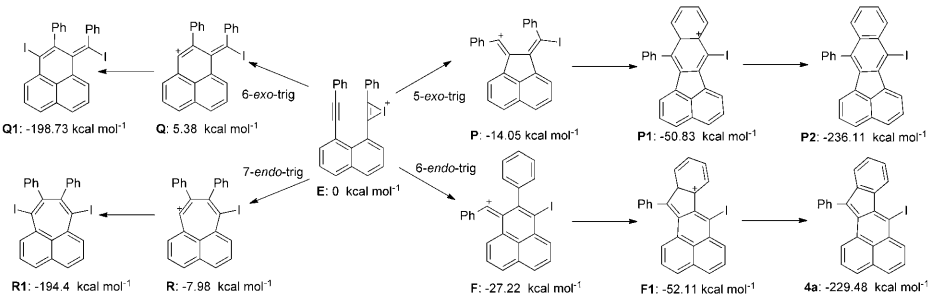
converted to iodonium intermediate **E**, which could be electrophilically attacked by the side triple bond to produce a vinylic carbocation **F** by a feasible 6-*endo*-trig process.[23] By a normal aromatic electrophilic addition–elimination, a Friedel–Crafts vinylation[24] occurred and **4a** was obtained.

By comparing reaction conditions for the above two transformations, a preliminary impression could be concluded that the triple bond in the hydroxypropargyl part was more reactive than the one in the arenynyl part because of the different reaction temperatures used in dichloromethane (Table 1, entry 5, and Table 2, entry 1). When **5a** was reacted with iodine, the hydroxyl was firstly activated by iodine (Scheme 7). Cooperated with iodine, a relatively stable propargyl carbocation **H** formed, which could be resonated with allenic carbocation **I**.[25] By overlapping the π orbital of C≡C and sp^2 orbital of the allenic carbocation, a vinylic carbocation **J** was generated. In those solvents without nucleophilicity, the iodide anion attacked the internal carbon atom of allene and afforded a cyclized product **6a** (route a in Scheme 7). Methanol, with the lone-pair electron, functioned as a nucleophile and trapped the intermediate **H** to afford **7a** successfully (route b in Scheme 7). In comparison with methanol, acetonitrile exhibited relatively weaker nucleophilicity. It hooked intermediate (**J**) by a Ritter-type reaction[26] and smoothly yielded intermediate **K** (route c in Scheme 7). Subsequently, intramolecularly nucleophilic attack of allene on the electron-deficient carbon atom brought a stable carbocation **L**, which finally fulfilled the reaction by β-elimination. Thus, pyridino[*a*]acenaphthylene **8a** was constructed effectively.

Route to **2a** involved the primary formation of a five-membered ring and was followed by the second cyclization. However, a six-membered ring was firstly fused in the formation of **4a**. To explain this unique regioselectivity, we anticipated all fates of the carbocations **B** and **E**. As we expected, **B** would have four opportunities to afford **C**, **M**, **N**, and **O** intermediates (Scheme 8) by 5-*exo*-trig, 6-*endo*-trig, 6-*exo*-trig, and 7-*endo*-trig, respectively. All of these ring closures should be the favored processes according to Baldwin's rule.[27] As indicated in Scheme 8, routes through 6-*exo*-trig and 7-*endo*-trig to **N** and **O** could be ignored because of the relatively higher potential energies of their final outcomes, **N1** and **O1**, respectively (calculated by the PM3 method in the program of Guassian 03). Although intermediate **M** was relatively stable compared with intermediate **C** (the energy difference between **M** and **C** was calculated to be 11.43 kcal mol^{-1}), **2a** was much more stable than **M2** (the energy difference between **2a** and **M2** was calculated to be 16.26 kcal mol^{-1}). Therefore, the route through 5-*exo*-trig leading to the formation of **2a** was indeed a thermodynamically controlled reaction. A similar situation happened to intermediate **E**, with four carbocations **F**, **P**, **R**, and **Q** postulated. Routes to **Q** and **R** could be neglected due to the higher potential energies of **Q1** and **R1** (Scheme 9). The route from **E** to **4a** had the higher priority over the route from **E** to **P2**. In this case, the energy difference between **P** and **F** was calculated to be 13.17 kcal mol^{-1} and **F** was more stable, whereas the energy difference between **P2** and **4a** was only 7.63 kcal mol^{-1} and **P2** was more stable. Therefore, the reaction from **E** to **4a** was indeed a kinetically controlled reaction and **4a** was finally constructed.

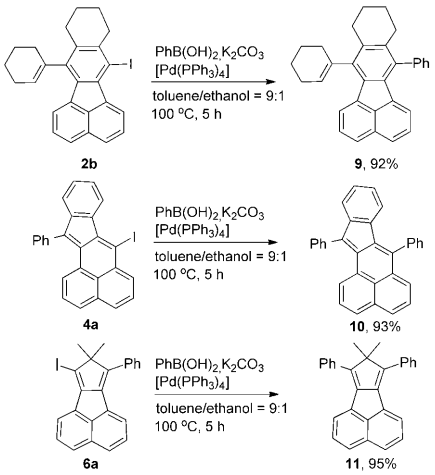


Scheme 8. Fates of carbocations **B** and their relative potential energies.



Scheme 9. Fates of carbocations **E** and their relative potential energies.

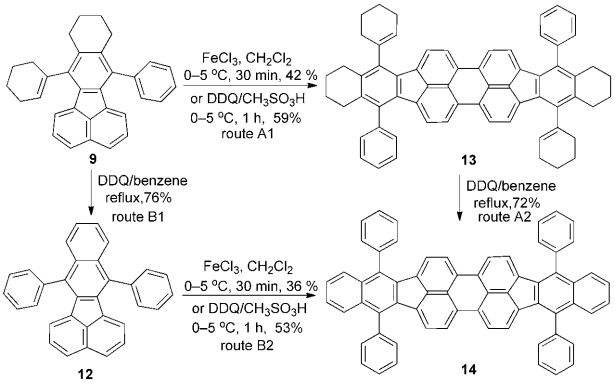
Synthetic extension of this work: Aryl iodides played a key role in the construction of polycyclic aromatic hydrocarbons that had been utilized as the traditional candidates in the optoelectronic fields,[6g,28] such as organic field effect transistors, organic light-emitting diodes, nonlinear optics, organic photovoltaics, and so on. The reason was obvious that aryl iodides were versatile starting materials in many palladium and/or copper-catalyzed coupling reactions, such as Sonogashira coupling,[29] Suzuki coupling,[30] and Ullman coupling.[31] A higher and rigid π-conjugation system could thereafter be extended in such way. As an example, we tested the Suzuki coupling of the synthesized **2b**, **4a**, and **6a** with phenylboronic acid. The corresponding products **9**, **10**, and **11** were prepared in high yields (Scheme 10).



Scheme 10. Extension of aryl iodides **2b**, **4a**, and **6a** to PAHs **9**, **10**, and **11** by Suzuki coupling.

Further extension of **9** to perylene derivative **14** was shown in Scheme 11. By route A, the direct treatment of **9** with either $FeCl_3$ or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)/CH_3SO_3H in the dry dichloromethane under a nitrogen atmosphere, **13** was isolated as major product by a Scholl reaction.[32] The structure of **13** was established by crystal analysis.[33] Dehydrogenation of **13** by using DDQ in benzene afforded the aromatized product **14**[34] in a yield of 72%. Alternatively, as the sequence of the individual reaction was changed to dehydrogenation and subsequent oxidative coupling (route B in Scheme 11), **14** could also be approached in moderate yield. Many efforts from **12** to coannulene skeleton failed.

Photophysical properties of PAHs 8a and 9–14: Now we have seven chromophores in hand, those were pyridino[*a*]acenaphthylene (**8a**), fluoranthene (**9**), indeno[2,1-*a*] phenalene (**10**), (8*H*)cyclopenta[*a*]acenaphthylene (**11**), benzo[*k*]-fluoranthene (**12**), diindeno[1,2,3*cd*:1′,2′,3′-*lm*]perylene (**13**),



Scheme 11. Construction of perylene skeletons **13** and **14**.

Table 4. Photopysical data of **8a** and **9**–**14** with different chromophores.

Compd.	Abs.[a] λ_{max} ($\varepsilon/10^4$)	Em.[a] λ_{em} (λ_{ex})	Stokes	Φ	HOMO [eV]/ LUMO [eV][d]	Eg [eV]
8a	365 (2.65)	450 (370)	85	0.16[b]	−5.75/−1.85	3.91
9	327 (0.57), 358 (0.79), 374 (0.79)	463, 475 (373)	89	0.54[b]	−5.49/−1.47	4.01
10	388 (1.20), 417 (1.21)	434, 449 (413)	17	0.01[b]	−4.94/−2.13	2.81
11	383 (5.08)	469 (398)	86	0.91[b]	−4.99/−1.33	3.66
12	367 (0.83), 387 (1.63), 409 (1.72)	424, 447 (410)	15	1.00[b]	−5.28/−1.53	3.75
13	481 (1.51), 515 (2.96), 555 (3.85)	580 (558)	25	0.05[c]	−4.81/−2.21	2.60
14	504 (0.54), 542 (1.71), 587 (2.73)	597, 643 (588)	10	0.81[c]	−4.75/−2.27	2.48

[a] Measured in CH_2Cl_2 solution, $c = 1\times10^{-5}$ M. [b] Quantum yields (Φ) were calculated based on 9,10-diphenylanthracene ($\Phi = 0.90$ in cyclohexane). [c] Φ was calculated based on 5,6,11,12-tetraphenylnaphthacene ($\Phi = 0.98$ in benzene). [d] Calculated by the B3LYP/6-31G(d) method on Guassian 03 program.

and benzo[5,6]indeno[1,2,3*cd*]benzo[5,6]indeno[1,2,3*lm*]perylene (**14**). Absorption and emission spectra of **8a** and **9**–**14** were measured in dilute CH_2Cl_2 with a concentration of 10^{-5} M, respectively. Emission spectra were recorded when the individual solution was excited at a certain wavelength (λ_{ex} listed in Table 4). Their photophysical data were summarized in Figure 1 and Table 4. Maximum absorption wavelengths of **8a** and **9**–**12** fell within a range of 365–417 nm, whereas **13** and **14** absorbed light at lower-energy bands (555 and 587 nm, respectively), assigned to the π–π* transition of the perylene skeleton. All of these compounds showed large molar absorptivities as indicated in the parenthesis in Table 4. Dehydroaromatization of **9** afforded **12** and the maximum absorption wavelength shifted from 374 to 409 nm, which indicated the extension of the conjugation. Oxidative coupling from **9** to **13** extended the efficient conjugation as well and the maximum absorption wavelength shifted from 374 to 555 nm. A similar situation was observed for the conversion from **12** to **14**, the maximum absorption wavelength changed from 409 to 587 nm. Emission spectra of **8a** and **9**–**12** emitted light in a range of 447 to 475 nm, whereas **9** showed the largest Stokes shift with the biggest energy loss. Compounds **13** and **14** emitted light at 580 and 597 nm, respectively. Most of these compounds emitted intense light with high quantum yields.

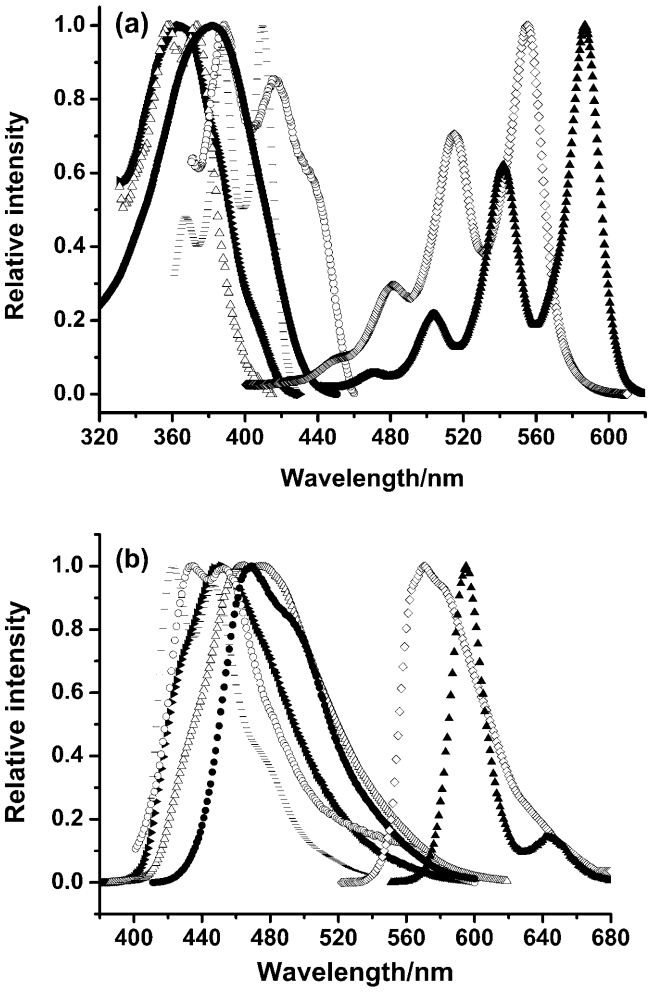


Figure 1. Absorption (a) and emission (b) of **8a** and **9**–**14** in CH_2Cl_2, $c = 1\times10^{-5}$ M (▶ = **8a**, △ = **9**, ○ = **10**, ● = **11**, – = **12**, ◇ = **13**, ▲ = **14**).

Conclusion

Fluoranthene, (8*H*)cyclopenta[*a*]acenaphthylene, pyridino[*a*]acenaphthylene, and indeno[2,1-*a*]phenalene have been synthesized by the iodine-mediated cyclization of the rigid parallel triple bonds mapped from 1,8-dialkynyl naphthalenes. High regioselectivity for cyclization largely relied on the substrates and the solvents and could be understood by the theoretical calculation. All reactions were efficient and provided relatively short-cut routes to conjugated polyaromatic hydrocarbons. Further, large molar absorptivities and high emission efficiencies of these polyaromatic compounds indicated that these fused compounds might be used as optoelectronic materials in the future.

Experimental Section

Typical procedure for the synthesis of 7-iodo-8-methyl-10-(prop-1-en-2-yl)fluoranthene (2a): In a 25 mL round-bottomed flask, **1a** (146 mg, 0.5 mmol) was dissolved in dichloroethane (10 mL). Iodine (140 mg, 0.55 mmol) was added to the solution in one portion at room temperature. The solution turned in color to a brownish red, and finally to a deep brown. After complete consumption of starting material **1a** as tracked by TLC, the solution was washed with aqueous $Na_2S_2O_3$ (3×15 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent solvent: hexane). Compound **2a** (57 mg, 30%) was obtained as a yellow solid. M.p. 123.4–124.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS; see Figure S1 in the Supporting Information): δ = 9.08 (d, ^3J(H,H) = 7.1 Hz, 1H), 8.09 (d, ^3J(H,H) = 7.1 Hz, 1H; CH), 7.89 (d, ^3J(H,H) = 8.1 Hz, 1H; CH), 7.84 (d, ^3J(H,H) = 8.1 Hz, 1H; CH), 7.72

(t, ^3J(H,H) = 7.7 Hz, 1H; CH), 7.60 (t, ^3J(H,H) = 7.7 Hz, 1H; CH), 7.05 (s, 1H; CH), 5.41 (s, 1H; CH), 5.19 (s, 1H; CH), 2.60 (s, 3H; CH_3), 2.25 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS; see Figure S2 in the Supporting Information): δ = 144.4, 141.9, 141.0, 140.2, 137.7, 135.3, 134.8, 132.8, 129.8, 128.5, 127.7, 127.6, 127.0, 126.7, 123.5, 122.7, 115.2, 95.7, 28.9, 23.8 ppm; EIMS: *m*/*z* (%): 382 (79.29) [M^+], 240 (100); HRMS: *m*/*z*: cacld for $C_{20}H_{15}I$: 382.0219 [M^+]; found: 382.0223.

Typical procedure for the synthesis of 7-iodo-12-phenylindeno[2,1-a]phenalene (4a): In a 10 mL round-bottomed flask, **3a** (164 mg, 0.5 mmol) and $NaHCO_3$ (84 mg, 1.0 mmol) were dissolved in CH_3CN (5 mL). Iodine (380 mg, 1.5 mmol) was added to the solution in one portion after the temperature was raised to 50 °C. The solution turned in color to a brownish red. After complete consumption of the starting material **3a** as tracked by TLC, the solution was washed with aqueous $Na_2S_2O_3$ (3× 15 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent solvent: hexane). Compound **4a** (209 mg, 92%) was obtained as a reddish brown solid. M.p. 180.6–181.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS; see Figure S24 in the Supporting Information): δ = 9.08 (m, 1H; CH), 8.21 (d, ^3J(H,H) = 7.5 Hz, 1H; CH), 7.76 (d, ^3J(H,H) = 7.5 Hz, 1H; CH), 7.71 (d, ^3J(H,H) = 7.8 Hz, 1H; CH), 7.66 (d, ^3J(H,H) = 7.8 Hz, 1H; CH), 7.58 (m, 2H; CH), 7.55–7.45 (m, 4H; CH), 7.34 (m, 2H; CH), 7.23 (t, ^3J(H,H) = 8.0 Hz, 1H; CH), 7.04 ppm (m, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS; see Figure S25 in the Supporting Information): δ = 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, 127.5, 126.6, 126.5, 126.0, 125.7, 124.5, 123.9, 120.6, 105.1 ppm; HRMS: *m*/*z*: calcd for $C_{26}H_{15}I$: 454.0219 [M^+]; found: 454.0207.

Typical procedure for the synthesis of 7-iodo-8,8-dimethyl-9-phenyl(8-*H*)cyclopenta[*a*]acenaphthylene (6a): In a 10 mL round-bottomed flask, **5a** (155 mg, 0.5 mmol) was dissolved in dichloroethane (5 mL). Iodine (380 mg, 1.5 mmol) was added in one portion to the solution at room temperature. The solution turned in color to a light green, and finally to a deep brown. After complete consumption of the starting material (**5a**) as tracked by TLC, the solution was washed with aqueous $Na_2S_2O_3$ (3× 15 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent solvent: hexane). Compound **6a** (151 mg, 72%) was obtained as a yellow solid. M.p. 74.6–76.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS; see Figure S36 in the Supporting Information): δ = 8.11 (d, ^3J(H,H) = 7.0 Hz, 1H; CH), 7.77 (d, ^3J(H,H) = 8.0 Hz, 1H; CH), 7.69 (d, ^3J(H,H) = 7.4 Hz, 1H; CH), 7.60 (m, 3H), 7.49 (t, ^3J(H,H) = 7.6 Hz, 2H), 7.47–7.39 (m, 3H), 1.38 ppm (s, 6H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS; see Figure S37 in the Supporting Information): δ = 148.8, 147.4, 144.3, 143.0, 136.7, 132.4, 132.3, 131.7, 128.6, 128.1, 127.82, 127.78, 127.6, 125.9, 125.2, 118.7, 118.4, 100.2, 65.5, 23.9 ppm; HRMS: *m*/z: calcd for $C_{23}H_{17}I$: 420.0375 [M^+]; found: 420.0374.

Typical procedure for the synthesis of 7-phenyl-9-methyl-10-(prop-1-en-2-yl)acenaphtho[1,2-*c*]pyridine (8a): In a 10 mL round-bottomed flask, **5a** (155 mg, 0.5 mmol) was dissolved in CH_3CN (5 mL). Iodine (380 mg, 1.5 mmol) was added in one portion to the solution at room temperature. The solution turned in color to a light green, and finally to a deep brown. After complete consumption of starting material (**5a**) as tracked by TLC, the solution was washed with aqueous $Na_2S_2O_3$ (3×15 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent solvent: CH_2Cl_2/hexane 1:5). Compound **8a** (115 mg, 69%) was obtained as yellow solid. M.p. 102.8–103.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS; see Figure S54 in the Supporting Information): δ = 8.25 (d, ^3J(H,H) = 7.2 Hz, 1H), 7.93 (d, ^3J(H,H) = 8.2 Hz, 1H; CH), 7.81 (m, 3H), 7.65 (t, ^3J(H,H) = 8.0 Hz, 1H; CH), 7.57 (m, 3H), 7.45 (m, 2H), 5.60 (s, 1H; CH), 5.24 (s, 1H; CH), 2.72 (s, 3H; CH_3), 2.30 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS; see Figure S55 in the Supporting Information): δ = 154.3, 152.8, 143.7, 142.3, 140.6, 134.7, 134.5, 132.9, 132.6, 130.0, 129.2, 129.0, 128.65, 128.60, 127.92, 127.87, 126.8, 124.7, 123.0, 116.6, 23.1, 22.1 ppm; HRMS: *m*/*z*: calcd for $C_{25}H_{19}N$: 333.1517 [M^+]; found: 333.1518.

Typical procedure for the synthesis of 7-cyclohexenyl-12-phenyl-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene (9): [$Pd(PPh_3)_4$] (58 mg, 0.05 mmol) was added to a solution of **2b** (462 mg, 1 mmol), $PhB(OH)_2$ (146 mg, 1.2 mmol), and K_2CO_3 (690 mg, 5 mmol) in toluene and ethanol (toluene/ethanol 9:1, 30 mL) at ambient temperature. The reaction mixture was purged with nitrogen for 10 min. Then the sealed flask was heated at 100 °C for about 5 h. After complete consumption of **2b**, determined by TLC, toluene and ethanol were removed and the residue was dissolved in diethyl ether. The solution was washed with water and dried over anhydrous Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent solvent: hexane). Compound **9** (379 mg, 92%) was obtained as a yellow solid. M.p. 227.9–229.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS; see Figure S83 in the Supporting Information): δ = 8.02 (d, ^3J(H,H) = 7.0 Hz, 1H; CH), 7.73 (d, ^3J(H,H) = 8.1 Hz, 1H; CH), 7.65 (d, ^3J(H,H) = 8.2 Hz, 1H; CH), 7.56 (t, ^3J(H,H) = 7.7 Hz, 3H; CH), 7.50 (dd, ^3J(H,H) = 8.4, 6.1 Hz, 1H; CH), 7.39 (dd, ^3J(H,H) = 5.4, 1.9 Hz, 2H; CH), 7.29–7.22 (m, 1H; CH), 6.37 (d, ^3J(H,H) = 7.1 Hz, 1H; CH), 5.83 (s, 1H; CH), 3.00 (dt, ^3J(H,H) = 17.0, 6.4 Hz, 1H; CH), 2.74 (dt, ^3J-(H,H) = 12.3, 5.8 Hz, 1H; CH), 2.45 (dt, ^3J(H,H) = 59.5, 14.8 Hz, 6H), 2.05–1.68 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS; see Figure S84 in the Supporting Information): δ = 140.5, 139.6, 137.2, 136.63, 136.56, 134.9, 134.8, 134.6, 133.6, 133.1, 129.7, 129.2, 129.1, 129.0, 127.7, 127.5, 127.2, 125.9, 125.71, 125.66, 122.1, 122.0, 28.6, 28.5, 27.1, 25.6, 23.4, 23.2, 22.3 ppm; EIMS: *m*/*z* (%): 438 (100) [M^+]; HRMS: *m*/z: calcd for $C_{32}H_{28}$: 412.2191 [M^+]; found: 412.2192.

Typical procedure for the synthesis of 7,12-diphenylbenzo[*k*]fluoranthene (12): Route B1: DDQ (1362 mg, 6 mmol) was added to a solution of **9** (412 mg, 1 mmol) in benzene (80 mL) at ambient temperature. The reaction mixture was purged with nitrogen for 10 min. Then the sealed flask was heated at 80 °C for about 48 h. After complete consumption of **9**, as determined by TLC, benzene was removed and the residue was dissolved in diethyl ether. The solution was washed with water and dried over anhydrous Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent solvent: hexane). Compound **12** (307 mg, 76%) was obtained as a yellow solid. M.p. > 350 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS; see Figure S89 in the Supporting Information): δ = 7.70–7.61 (m, 10H), 7.56 (d, ^3J(H,H) = 7.6 Hz, 4H; CH), 7.39 (dd, ^3J(H,H) = 6.2, 3.1 Hz, 2H; CH), 7.32 (t, ^3J(H,H) = 7.6 Hz, 2H; CH), 6.62 ppm (d, ^3J(H,H) = 7.1 Hz, 2H; CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS; see Figure S90 in the Supporting Information): δ = 138.9, 136.6, 135.6, 134.9, 134.8, 132.9, 130.1, 130.0, 129.2, 128.0, 127.8, 126.8, 125.9, 125.8, 122.2 ppm; EIMS: *m*/*z*: 4 404 (100) [M^+]; HRMS: *m*/*z*: calcd for $C_{32}H_{20}$: 404.1565 [M^+]; found: 404.1563.

Typical procedure for the synthesis of dibenzo{[*f*,*f*′]-4,7′-diphenyl4′,7- dicyclohexenyl-}diindeno[1,2,3*cd*:1′,2′,3′-*lm*]perylene (13)

Route A1 method A:[32b] $FeCl_3$ (325 mg, 2 mmol) was added to a solution of **9** (206 mg, 0.5 mmol) in dry CH_2Cl_2 (50 mL) at ambient temperature. The reaction mixture was purged with nitrogen for 10 min. Then the sealed flask was stirred at 0–5 °C for about 1 h. After complete consumption of **9** as determined by TLC, the solution was washed with water and dried over Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent solvent: CH_2Cl_2/hexane 1:15). Compound **13** (86 mg, 42%) was obtained as a red solid.

Route A1 method B:[32a] DDQ (136 mg, 0.6 mmol) was added to a solution of **9** (206 mg, 0.5 mmol) in CH_2Cl_2 (50 mL) containing CH_3SO_3H (10% v/v) at 0–5 °C. The reaction mixture was purged with nitrogen for 10 min. Then the sealed flask was stirred at 0–5 °C for about 1 h. After complete consumption of **9**, as determined by TLC, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (100 mL). After filtration, the filtrate was distilled under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent solvent: CH_2Cl_2/hexane 1:15). Compound **13** (119 mg, 56%) was obtained as a red solid. M.p. > 350 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS; see Figure S91 in the Supporting Information): δ = 8.17 (d, ^3J(H,H) = 7.7 Hz, 1H; CH), 8.04 (d, ^3J(H,H) = 7.7 Hz, 1H; CH), 7.96 (d, ^3J(H,H) = 7.6 Hz,

1H; CH), 7.91 (d, ^3J(H,H) = 7.7 Hz, 1H; CH), 7.84 (d, ^3J(H,H) = 7.8 Hz, 1H; CH), 7.71 (d, ^3J(H,H) = 7.7 Hz, 1H; CH), 7.63–7.49 (m, 6H; CH), 7.44–7.35 (m, 4H), 6.32 (d, ^3J(H,H) = 7.7 Hz, 1H; CH), 6.28 (d, ^3J(H,H) = 7.7 Hz, 1H; CH), 5.85–5.79 (m, 2H; CH_2), 3.03–2.91 (m, 2H; CH_2), 2.77–2.60 (m, 2H; CH_2), 2.57–2.27 (m, 12H), 2.06–1.69 ppm (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS; see Figure S92 in the Supporting Information): δ = 140.6, 140.0, 137.3, 137.0, 136.7, 135.2, 135.1, 134.9, 134.4, 134.0, 130.3, 130.2, 129.52, 129.50, 129.44, 129.42, 129.3, 127.5, 126.2, 125.4, 123.3, 123.2, 121.8, 121.6, 30.0, 28.8, 27.4, 25.90, 25.87, 23.7, 23.4, 22.5 ppm; TOF EIMS: *m*/*z* (%): 820.4 (100) [M^+]; HRMS: *m*/*z*: calcd for $C_{64}H_{52}$: 820.4069 [M^+]; found: 820.4072.

Typical procedure for the synthesis of dibenzo{[*f*,*f*′]-4,4′,7,7′-tetraphenyl}-diindeno-[1,2,3 *cd*:1′,2′,3′-*lm*]perylene (14)

Route B2 method A: The reaction of **12** (202 mg, 0.5 mmol) with $FeCl_3$ (325 mg, 2 mmol) in dry CH_2Cl_2 (50 mL) at 0–5 °C afforded **14** (72 mg) as a purple/black solid in a yield of 36% (eluent solvent: CH_2Cl_2/hexane 1:10)

Route B2 method B: The reaction of **12** (202 mg, 0.5 mmol) with DDQ (136 mg, 0.6 mmol) in dry CH_2Cl_2 (50 mL) containing CH_3SO_3H (10% v/v) at 0–5 °C afforded **14** (106 mg) as a purple/black solid in a yield of 53% (eluent solvent: CH_2Cl_2/hexane 1:10).

Route A2: The reaction of **13** (410 mg, 0.5 mmol) with DDQ (1362 mg, 6 mmol) in benzene (80 mL) at 80 °C afforded **14** (289 mg) as a purple/black solid in a yield of 76% (eluent solvent: CH_2Cl_2/hexane 1:10). M.p. > 350 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS; see Figure S93 in the Supporting Information): δ = 7.75 (d, ^3J(H,H) = 7.8 Hz, 4H; CH), 7.66–7.58 (m, 16H), 7.47 (m, 8H), 7.38 (m, 4H), 6.51 ppm (d, ^3J(H,H) = 7.8 Hz, 4H; CH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS; see Figure S94 in the Supporting Information): δ = 139.0, 136.7, 136.3, 135.3, 134.9, 133.1, 130.3, 130.2, 129.5, 128.2, 127.1, 126.1, 125.6, 123.2, 121.8 ppm; TOF EIMS: *m*/*z* (%): 804.3 (46.8) [M^+], 117 (100); HRMS: *m*/*z*: calcd for $C_{64}H_{36}$: 804.2817 [M^+]; found: 804.2812.

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