

Synthesis, Structures, and Physical Properties of Benzo[*k*]fluoranthene-Based Linear Acenes**

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Abstract: This work describes the syntheses, crystal structures, photophysical properties, and electro-chemical analyses of benzo[*k*]fluoranthene-based linear acenes, together with ab initio density functional theory computations on them. The molecules were prepared in generally moderate to good yields through Pd-catalyzed cycloadditions between 1,8-diethynylnaphthalene de-

rivatives and aryl iodides. This protocol is simpler and more efficient than conventional methods. The scope and limitations of this reaction were examined. The structures of compounds **4hb**,

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15ac, **17ab**, **19ac**, and **24je** were determined by X-ray analysis; they are either bent or twisted, rather than planar. The photophysical and electro-chemical properties of these cycloadducts were also investigated and compared with computational predictions based on density functional theory.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) might be the largest class of organic molecules.^[1,2] They exhibit a wide range of molecular sizes and structural forms, causing them to have versatile physical properties and allowing them to be employed as organic materials, including as liquid crystals,^[3]

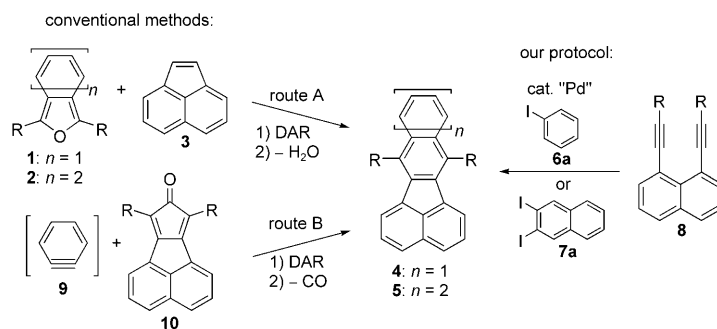
in optoelectronics,^[4] as conducting materials,^[5] in solar cells,^[6] and in other functions. The benzo[*k*]fluoranthenes **4** (Scheme 1) have recently stimulated our interest because of their special properties: modifications by peripheral functional groups can allow compounds **4** to act as luminescent materials,^[7] useful molecular sensors,^[8] or organic semiconductors.^[9] The unsubstituted benzo[*k*]fluoranthene **4** (R = H)^[10] and naphtha[2,3-*k*]fluoranthene **5** (R = H)^[11] are commercially available and numerous approaches for preparing them have been described. However, the methods for generating their functionalized derivatives are relatively few. Two protocols based on the Diels–Alder reaction have been developed (Scheme 1). Reactions between the reactive dieno-

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Scheme 1. Conventional and new methods for the synthesis of benzo[*k*]fluoranthenes (**4**) and naphtho[2,3-*k*]fluoranthenes (**5**).

phile acenaphthylene (**3**)^[7,12] and either the isobenzofurans **1** or the naphtho[2,3-*c*]furans **2**, followed by aromatization under acidic conditions, yield the desired products **4** or **5**, respectively (Route A, or Bergmann's protocol).^[13] The convenience and efficiency of this protocol are heavily dependent on the furan derivatives **1** and **2**. 1,3-Diphenylisobenzofuran (**1**, R=Ph), for example, is commercially available, whereas other substituted furan derivatives, such as 5,6-dimethyl-1,3-diphenylisobenzofuran^[14] or 1,3-diphenylnaphtho[2,3-*c*]furan (**2**, R=Ph),^[15] have to be prepared by lengthy synthetic processes. 7,10-Diphenylbenzo[*k*]fluoranthene (**4**, R=Ph)^[7] is hence easily accessible, but the synthesis of other substituted derivatives such as 9,10-dimethyl-7,12-diphenylbenzo[*k*]fluoranthene^[16] or 7,14-diphenylnaphtho[2,3-*k*]fluoranthene^[15b] is inconvenient.

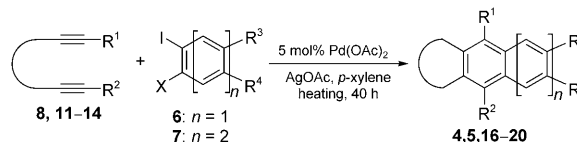
Benzo[*k*]fluoranthenes **4** can also be obtained through cycloadditions between the cyclopenta[*a*]acenaphthylene-8-ones **10** and benzyne (**9**) with subsequent elimination of carbon monoxide (Route B, or Allen's protocol).^[17] The cyclopentadienone derivatives **10** are generated either through the Knoevenagel condensation from acenaphthenequinone and a ketone^[18] or by the metal-catalyzed carbonylation of diynes **8**.^[19] The former method cannot be employed with simple ketones such as acetone or butan-2-one^[17] or with ketones that contain acid- or base-sensitive functional groups. The metal-catalyzed carbonylation of diynes **8** can more readily be performed when bulky silyl substituents are present as the R moieties.^[19]

Fluoranthenes can be prepared through Rh^I-catalyzed [(2+2)+2] cycloadditions between 1,8-diethynylnaphthalenes **8** (Scheme 1) and norbornadiene or a molecule of an alkyne.^[20] Similarly, the replacement of an alkyne with a benzyne derivative in this reaction should yield a benzo[*k*]fluoranthene **4**. Benzyne, however, is very active, and it reacts with 1,8-diethynylnaphthalene (**8**, R=H) to yield benzo[*a*]pyrene in the absence of metal catalysts, even at room temperature.^[21] Accordingly, stabilized benzyne or *pre-benzyne*s are suitable starting materials in the protocol designed here. Fortunately, in the presence of Pd catalysts, iodobenzenes^[22] and 1,2-diiodobenzenes^[23] can be formally treated as *pre-arynes*, which have been utilized in the synthesis of highly substituted naphthalenes through cycloaddition with two alkyne units. In the light of these metal-catalyzed protocols, the target molecules **4** and **5** were observed to be obtainable through Pd-catalyzed cycloadditions between 1,8-diethynylnaphthalenes **8** and either iodobenzene (**6a**) or 2,3-diiodonaphthalene (**7a**), respectively. Here this reaction is elucidated for the construction of benzo[*k*]fluoranthene-based linear acenes. Their structures and physical properties are analyzed and compared with corresponding computational results.

Results and Discussion

Synthesis: Upon heating of diynes **8** or **11–14** with aryl iodides **6** or **7** in the presence of catalytic amounts of Pd-

(OAc)₂,^[24] numerous benzo[*k*]fluoranthene-based linear acenes—such as the benzo[*k*]fluoranthenes **4**, the naphtho[2,3-*k*]fluoranthenes **5**, the 1,2-dihydrobenzo[*k*]cyclopenta[*cd*]fluoranthenes **15**, the 9,10-dihydrocyclopenta[*cd*]naphtho[2,3-*k*]fluoranthenes **16**, the benzo[*k*]indeno[1,2,3-*cd*]fluoranthenes **17–19**, and the indeno[1,2,3-*cd*]naphtho[2,3-*k*]fluoranthenes **20**—are generated in moderate to good yields (Scheme 2 and Table 1). A



Scheme 2. Preparation of benzo[*k*]fluoranthene-based linear acenes. For details see Table 1.

diyne and an aryl iodide provide a four-carbon building block and a two-carbon building block, respectively, and these undergo formal [(2+2)+2] cycloaddition. The aryl iodides **6** and **7** reacted here as “*pre-arynes*”. In this newly developed protocol, many substituents can easily be introduced into these cycloadducts through variation of R¹, R², R³, and R⁴. This feature can be exploited for screening and tuning of the photophysical properties of the desired molecules. Some functional groups, including aryl bromides, esters, and ethers, can be tolerated under the reaction conditions. Except in the case of diynes **4**, reactions performed in toluene or in *p*-xylene at 110 or 130 °C do not differ significantly. The amounts of AgOAc used in these reactions depend on the number of iodo substituents in the aryl iodides: one equivalent for iodobenzene and two equivalents for diiodoarenes. The presence of an additional triphenylphosphine ligand makes the reaction inefficient. The reactivities of several aryl iodides in cycloadditions either with 1,8-bis(phenylethynyl)naphthalene (**8a**) or with 5,6-bis(phenylethynyl)acenaphthalene (**11a**) were examined. Unlike *o*-diiodoarenes, monoiodoarenes could not be utilized in this reaction because they afforded the products in unsatisfactory yields and with low regioselectivities. 3-Iodotoluene, for example, produced a mixture of 8- and 9-methyl-7,12-diphenylbenzo[*k*]fluoranthenes in low yields (less than 10%). 9-Iodophenanthrene was also only poorly active in this reaction, giving the cycloadduct **21** in 9% yield (entry 25 in Table 1). Fortunately, the expensive 1,2-diiodobenzene^[25] can be replaced with iodobenzene (**6a**). 1,2-Diiodo-4,5-dimethylbenzene (**6b**), 1,2-diiodo-4,5-dimethoxybenzene (**6c**), and 2,3-diiodonaphthalene (**7a**) generated the corresponding cycloadducts in moderate yields (entries 2, 3, and 6, Table 1).

1,2,4,5-Tetraiodobenzene (**6e**) was able to undergo two-fold cycloadditions; treatment of the diyne **11a** with excess 1,2,4,5-tetraiodobenzene (**6e**) furnished the diiodo-substituted benzo[*k*]fluoranthene **15ae**, which was used to prepare the cycloadduct **22** in 65% yield (entries 11 and 26, Table 1).

Table 1. Preparation of benzo[*k*]fluoranthene-based linear acenes.^[a]

Entry	Diyne	Aryl iodide	T [°C]	Product	Yield [%]
1	8a : R ¹ = Ph	6a : X = R ² = R ³ = H	110/85	4aa	73/85
2	8a	6b : X = I; R ² = R ³ = Me	110	4ab	48 ^[b]
3	8a	6c : X = I; R ² = R ³ = OMe	110	4ac	62 ^[c]
4	8b : R ¹ = 2-Br-C ₆ H ₄	6a	110	4ba	55
5	8c : R ¹ = SiMe ₃	6b	110	4cb : R ¹ = H	33
6	8a	7a : X = I; R ² -R ³ = C ₄ H ₄	110	5aa	58 ^[b]
7	11a : R ¹ = R ² = Ph	6a : X = R ³ = R ⁴ = H	130/110	15aa	61/55
8	11a	6b : X = I; R ³ = R ⁴ = Me	130	15ab	53
9	11a	6c : X = I; R ³ = R ⁴ = OMe	130	15ac	64
10	11a	6d : X = Br; R ³ = OMe, R ⁴ = H	130	15ad	traces
11	11a	6e : X = R ³ = R ⁴ = I	110	15ae	56 ^[d]
12	11d : R ¹ = R ² = 4-OMe-Ph	6b	110	15db	84
13	11d	6c	110	15dc	75
14	11e : R ¹ = 4-OMe-Ph, R ² = 4-CO ₂ Me-Ph	6b	110	15eb	69
15	11e	6c	110	15ec	63
16	11a	7a : X = I; R ³ -R ⁴ = C ₄ H ₄	130	16aa	52
17	12a : R ¹ = Ph, R ² = Me, R ³ = H	6b : X = I; R ⁴ = R ⁵ = Me	130	17ab	47
18	12a	6c : X = I; R ⁴ = R ⁵ = OMe	130	17ac	58
19	13a : R ¹ = R ² = R ³ = Ph	6a : X = R ⁴ = R ⁵ = H	110	18aa	< 33
20	13f : R ¹ = 4-O-C ₆ H ₁₇ -Ph, R ² = R ³ = Ph	6c : X = I; R ⁴ = R ⁵ = OMe	110	18fc	39
21	14a : R ¹ = Ph, R ² = Me, R ³ = CO ₂ Me	6a : X = R ⁴ = R ⁵ = H	130	19aa	60
22	14a	6b : X = I; R ⁴ = R ⁵ = Me	130	19ab	51
23	14a	6c : X = I; R ⁴ = R ⁵ = OMe	130/110	19ac	68/71
24	14a	7a : X = I; R ⁴ -R ⁵ = C ₄ H ₄	130/110	20aa	63/61
25	11a		130	21	9 ^[e]
26	8a	15ac	110	22	65

[a] Diynes (0.25 mmol), iodoarenes (0.50 mmol), Pd(OAc)₂ (12.5 μmol, 5 mol %), AgOAc (0.50 mmol; 0.25 mmol for iodobenzene), and *p*-xylene (or toluene, 4 mL) were used in this reaction, if not otherwise mentioned. The isolated yields are based on the diynes. [b] Acetonitrile was used as the solvent. [c] The reaction was carried out in a mixture of *p*-xylene (3 mL) and acetonitrile (1 mL). [d] 1,2,4,5-Tetraiodobenzene (0.75 mmol) was used. [e] Compound **11a** (36%) was recovered.

Unlike the *o*-diiodoarenes, 3-bromo-4-iodoanisole (**6d**) did not yield the desired cycloadduct (entries 10, Table 1).^[26] 1,2,3,4-Tetrafluoro-5,6-diiodobenzene, 3,6-dichloro-1,2,4,5-tetraiodobenzene, and 2-iodopyridine also did not undergo cycloadditions.

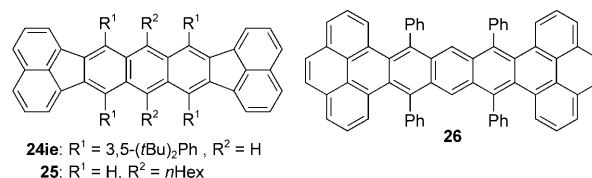
Unlike other diynes, the 1,8-bis(arylethynyl)naphthalenes **8** easily undergo cyclization to form the corresponding 7-phenylbenzo[*k*]fluoranthene products,^[27] presumably be-

cause of the short distances between the pairs of parallel alkynyl moieties in compounds **8**.^[28] 7,8,9,10-Tetraphenyl-3,4-bis(phenylethynyl)fluoranthene (**13a**) gave the cycloadduct **18aa** in low yield; its low solubility in common organic solvents makes its purification difficult (entry 19, Table 1). This inconvenience was overcome by using the dioctoxy-substituted diyne **13f** (entry 20, Table 1).

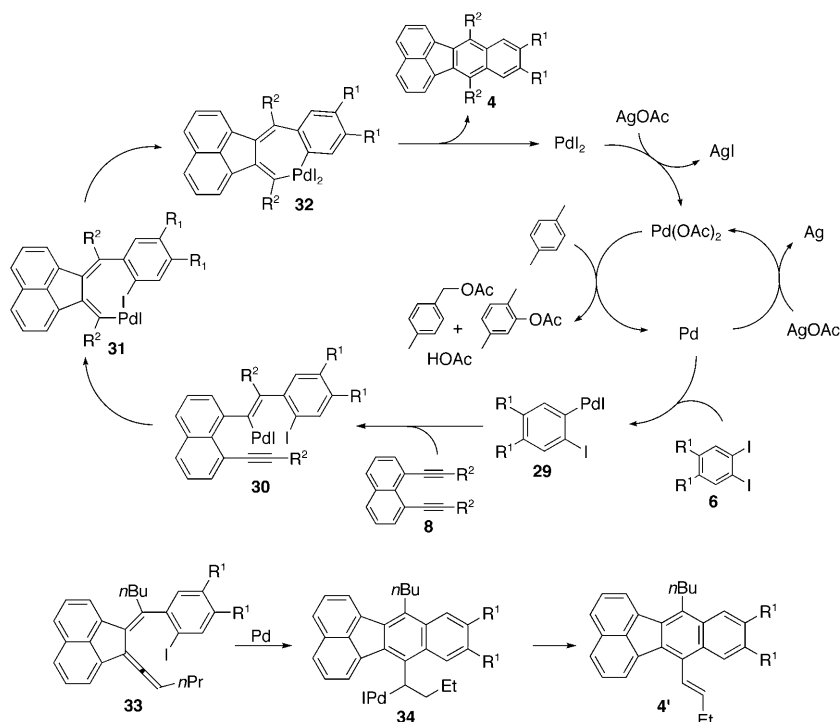
Diaryl-substituted diynes appear to be more suitable than trimethylsilyl- and alkyl-substituted analogues for use in this reaction. The cycloaddition between the sterically congested 1,8-bis(trimethylsilylethynyl)naphthalene (**8c**) and 1,2-diiodo-4,5-dimethylbenzene (**6b**) formed a mixture of mono- and bis(trimethylsilyl)-substituted cycloadducts in low yield. These two compounds were converted into 9,10-dimethylbenzo[*k*]fluoranthene (**4cb**) by treatment with acetic acid (entry 6, Table 1).

The reactions of the alkyl-substituted 1,8-diethynyl-naphthalenes **8g** and **8h** with diiodoarenes **6** were inefficient (Table 2), although 1,2,3,4-tetra(*n*-propyl)naphthalene can be obtained in excellent yield from 1,2-diiodobenzene and oct-4-yne under the same reaction conditions.^[23] The diynes **8g** and **8h** generated the desired cycloadducts **4**, accompanied by the byproducts **4'** and the fluoranthenes **23**.^[29] The low yields of the alkyl-substituted benzo[*k*]fluoranthenes **4** and **4'** perhaps follow from poor stability of one intermediate in this reaction (Scheme 3). Notably, the **4**/**4'** ratio is dependent on the substituents in the diynes **8** and the *o*-diiodoarenes **6**, with the former being more important than the latter. The amounts of **4'** became significant when the dialkyl-substituted diyne **8g** was utilized. Use of a lower reaction temperature (80 °C) did not improve the selectivity of the formation of **4gc** and **4'gc**. Separation of compounds **4** from compounds **4'** was very difficult, so the byproducts **4'** were converted into compounds **4** by palladium-catalyzed hydrogenation. Hydrogenation in methanol was unsuccessful, because of the low solubilities of compounds **4'** under these conditions, but addition of dichloromethane to the reaction mixtures ensured excellent yields.

As mentioned above, the asymmetric benzo[1,2-*k*:4,5-*k'*]difluoranthene derivative **22** was prepared by the developed protocol in a two-step process (entries 11 and 26, Table 1). The symmetric benzo[1,2-*k*:4,5-*k'*]difluoranthenes **24** and their analogues are important molecules because they are (potential) photoelectronic materials^[30,31] and exhibit interesting conformations on metal surfaces.^[32] Syntheses of 7,9,16,18-tetraphenylbenzo[1,2-*k*:4,5-*k'*]difluoranthene (**24ae**),^[30] 7,9,16,18-tetrakis[3,5-di(*tert*-butyl)phenyl]ben-



zo[1,2-*k*:4,5-*k'*]difluoranthene (**24ie**),^[33] 8,17-di-*n*-hexylbenzo[1,2-*k*:4,5-*k'*]difluoranthene (**25**),^[34] and 6,8,15,17-tetraphenyl-1,18,4,5,9,10,13,14-tetrabenzoheptacene (**26**)^[35] have been reported elsewhere. Compounds **24ie** and **25** were prepared by a lengthy synthetic process and the method for the generation of 7,9,16,18-tetraphenylbenzo[1,2-*k*:4,5-*k'*]difluoranthene (**24ae**) has not been clearly elucidated. Elaboration of the presented protocol offers the potential for the synthesis of symmetric benzo[1,2-*k*:4,5-*k'*]difluoranthene derivatives through twofold cycloadditions between 1,2,4,5-tetraiodobenzene (**6e**) and diynes **8**, **11**, or **13** in a one-pot procedure (Table 3). A test was performed with diyne **11a** (2.5 equiv) in the presence of $\text{Pd}(\text{OAc})_2$ (10 mol %) and AgOAc (4 equiv) [Variant A, entry 5 in Table 3]. Unfortunately, the desired product **27ae** was obtained in only 35% yield, accompanied by the monoadduct **15ae** (37%). The results were almost identical, however, when the reaction was performed either under more dilute conditions or with more catalyst (40 mol %), as well as for a longer reaction time (three days). Increasing the amount of AgOAc to 6 equiv slightly improved the yield of **27ae** (46%), but **15ae** (17%) was also obtained, possibly indicating that the lower solubilities of **6e** and **15ae** under these conditions made the cycloadditions inefficient and caused some of the AgOAc to be degraded (Scheme 3). This problem could be resolved by addition of two equal portions of

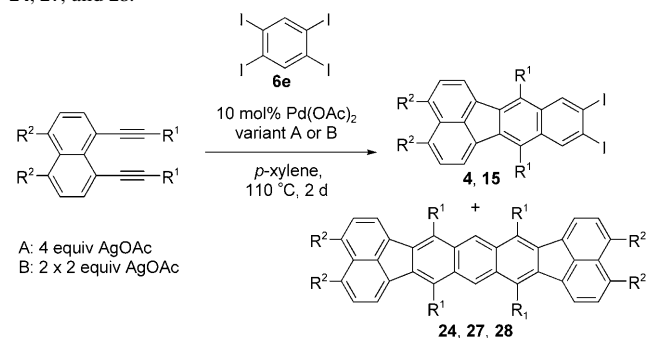


Scheme 3. Proposed reaction mechanism for the formation of cycloadducts **4** and **4'**.

Table 2. Reactions between the alkyl-substituted 1,8-diethynynaphthalenes **8** and the diiodoarenes **6**.^[a]

Entry	Diyne	R ¹	Aryl iodide	R ²	Product	Ratio (4/4') ^[b]	Yield [%] ^[c]
1	8g	<i>n</i> Bu	6b	Me	4gb+4'gb	50:50	22 (92)
2	8g	<i>n</i> Bu	6c	OMe	4gc+4'gc	52:48	39 (94)
3	8h	Ph	6b	Me	4hb+4'hb	79:21	24 (89)
4	8h	Ph	6c	OMe	4hc+4'hc	83:17	34 (90)

[a] The cycloaddition reactions were carried in thick-walled sealable tubes. Diynes (0.25 mmol), diiodoarenes (0.50 mmol), Pd(OAc)₂ (12.5 μmol), AgOAc (0.50 mmol), and toluene (4 mL) were used in these reactions. [b] Determination by ¹H NMR analysis. [c] Isolated yields for the mixtures of **4** and **4'**. Yields for hydrogenation are reported in parentheses.

Table 3. Preparation of the benzo[1,2-*k*:4,5-*k'*]difluoranthene derivatives **24**, **27**, and **28**.^[a]

Entry	Diyne	Variant	Product (yield, %)
1	8a : R ¹ =Ph, R ² =H	A	4ae (35) ^[b] + 24ae (31)
2	8a	B	4ae (35) ^[b] + 24ae (33)
3	8j : R ¹ =4- <i>n</i> Bu-Ph, R ² =H	A	4je (36) ^[b] + 24je (30)
4	8j	B	4je (38) ^[b] + 24je (31)
5	11a : R ¹ =Ph, R ² -R ² =(CH ₂) ₂	A	15ae (39)+ 27ae (34)
6	11a	A ^[c]	15ae (17)+ 27ae (46)
7	11a	B	15ae (0)+ 27ae (61)
8	13a : R ¹ =Ph, R ² -R ² =C(CPh) ₃ C	B	28ae (<23)
9	13f : R ¹ =4-O- <i>n</i> C ₈ H ₁₇ -Ph, R ² -R ² =C-(CPh) ₃ C	B	28fe (25)

[a] Variant **A**: diynes (0.48 mmol), tetraiodobenzene (0.19 mmol), Pd(OAc)₂ (19.0 μmol), AgOAc (0.76 mmol), and *p*-xylene (4 mL) were used in this reaction. Variant **B**: similar to Variant **A**, but AgOAc (0.38 × 2 mmol) was added in two equal portions at a 24 h interval. [b] An inseparable mixture of the 7-arylbenzo[*k*]fluoranthene and the compound **4** was obtained. The yield of the latter is calculated from ¹H NMR analysis. [c] AgOAc (6 equiv) was used.

AgOAc (2 × 2 equiv) at an interval of 24 h apart; **27ae** was then isolated in 61 % yield (Variant **B**, entry 7 in Table 3). Under these optimized conditions, the more extended linear acenes **28** were straightforwardly prepared through reactions between the 3,4-diethynylfluoranthenes **13** and **6e** (entries 8 and 9 in Table 3). Like that of **18aa**, the separation of cycloadduct **28ae** from impurities is difficult because it is only weakly soluble in common organic solvents, but the tetraacetoxy-substituted cycloadduct **28fe** can be purified. In the synthesis of cycloadducts **24**, however, the reactions performed with Variants **A** and **B**

did not differ significantly. The unsatisfactory results arise from competition between the cycloaddition and the cyclization of diynes **8**. Crystals of **24ae** could not be grown, and so the tetrakis(*n*-butylphenyl)-substituted derivative **24je** with higher solubility in organic solvents was synthesized for X-ray structural analysis.

Scheme 3 presents a putative literature-based mechanism for the generation of the benzo[*k*]fluoranthenes **4**. Initially, Pd(OAc)₂ oxidizes *p*-xylene to produce 2,5-dimethylphenyl acetate and 4-methylbenzyl acetate.^[36,37] The thus-generated palladium(0) species undergoes oxidative addition with the *o*-diiodobenzene **6** to give the complex **29**. A *syn*-addition of the Ar–Pd bond in **29** to one triple bond of the diyne **8** yields the alkenylpalladium derivative **30**. This process is followed by the insertion of the other alkynyl moiety to afford the arylbutadienylpalladium intermediate **31**. Cyclization of **31** would furnish the palladabenzocycloheptatriene **32**,^[38] which would subsequently undergo reductive elimination to produce the benzo[*k*]fluoranthene **4** and PdI₂. Pd(OAc)₂ is eventually regenerated by the reaction of PdI₂ with the additional AgOAc. However, when the diiodoarene [or 1,2,4,5-tetraiodobenzene (**6e**)] is inactive under these reaction conditions, AgOAc can be consumed oxidizing Pd⁰ species. This reduction/oxidation cycle is responsible for the inefficiency of the twofold cycloadditions. As stated above, the dialkyl-substituted diyne **8** (R²=*n*Bu) yielded the desired cycloadducts **4**, as well as the byproducts **4'** (Table 2). Compound **31** (R²=*n*Bu) in a crowded environment preferentially undergoes β-hydride elimination to generate the allene **33**, rather than ring-closure to form the complex **32** (R²=*n*Bu). Palladium-catalyzed cyclization of **33** gives the byproducts **4'** after β-hydride elimination. The low stability of the allene intermediate **33** under the reaction conditions here might be the cause of the unsatisfactory yields of these alkyl-substituted cycloadducts.

X-ray crystallographic structures: X-ray-quality crystals of **4hb**, **15ac**, **17ab**, **19ac**, and **24je** were obtained by slow evaporation of CH₂Cl₂/MeOH solvent mixtures at ambient temperature (Table 4).^[39] In the solid state, these molecules have either bent or twisted conformations. The degree of bending can be determined by analyzing the dihedral angle between the two peripheral benzene or naphthalene planes along the longest axis of the molecule. Compounds **4hb**, **15ac**, **17ab**, and **19ac**^[40] have bent structures, with angles of bending of 7.7°, 8.9°, 10.2°, and 15.9°, respectively. These angles of bending increase with the molecular length. However, compound **24je**,^[41] the longest molecule in Table 4, is twisted rather than bent in the solid state (Figure 1). The torsion angle of the central anthracene core, measured at C7–C7A–C13A–C13, and the dihedral angle associated with the two naphthalene planes in **24je** are 12.4° and 21.1°, respectively, whereas 8,17-di-*n*-hexylbenzo[1,2-*k*:4,5-*k'*]difluoranthene (**25**) has an almost planar structure.^[34] π – π stacking is an usual intermolecular interaction in PAHs.^[42] In the five compounds listed in Table 4, the skeletons and substituents display different forms of packing and only **17ab** exhibits significant π – π interaction. Molecules of **17ab** form two nonequivalent π -stacks in a cross-herringbone-like packing pattern. The slightly bent structure of **17ab** causes the molecules to pack in a concave-convex manner and to exhibit four intermolecular interactions, the associated distances of which are in the 3.54–3.91 Å range.^[43] Notably, molecules of **4hb** are not well organized, and each reveals the presence of three alkyl– π interactions.^[44]

Photophysical properties: The photophysical properties of numerous acenes were measured (Figure 2 and Table 5),^[45] and the effects of the substituents and of the extension of the aromatic system were analyzed. The effects of the latter exceed those of the former. Increasing extension of the aromatic π system should cause the absorption bands to shift bathochromically, and the results here support this expectation with shifts in the order **4** < **5** < **24** < **28**. Compounds **5aa**

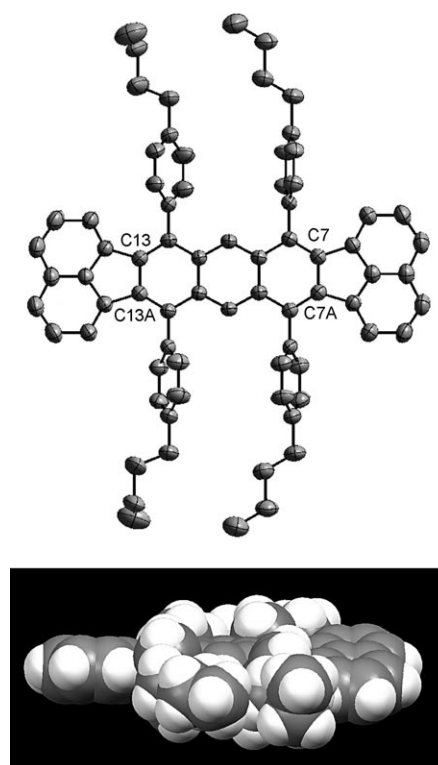


Figure 1. Molecular structure of cycloadduct **24je**: top) showing 50% probability ellipsoids, and bottom) in space-filling mode.

and **17ac/18fc** are all benzoannulated cycloadducts of **4aa**, in which an additional benzo ring is present at the 9,10-positions and at the 3,4-positions, respectively. Their absorption spectra, but not their emission bands, are very similar.

Geometrically, cycloadducts **24** and **28fe** can be regarded as quasi-dimeric molecules of **4aa** and **18fc**, respectively. The shapes of their absorption bands are very similar to those of their “monomers”, but their positions are bathochromically shifted to approximately 90–100 nm. Compounds **17ac** and **18fc** are weakly fluorescent, as revealed by the low quantum yields. Notably, dilute solutions of **24ae** and **24je** are brightly green-fluorescent even under ambient lighting.

The substituents in these cycloadducts can be grouped into two classes: those directly attached to the central aromatic core and those in the phenyl side arm. The former class has a greater influence over photophysical properties than the latter. The two methoxy groups in **4ac** and the ethylene bridge in **15aa**, for example, slightly red-shift the absorption and emission bands and increase the quantum yields

Table 4. Crystal structure data for cycloadducts **4hb**, **15ac**, **17ab**, **19ac**, and **24je**.

	4hb	15ac	17ab	19ac	24je
formula	C ₃₂ H ₂₈	C ₇₂ H ₅₂ O ₄	C ₄₂ H ₃₀	C ₇₀ H ₄₈ O ₉	C ₃₇ H ₃₃
<i>M_w</i>	412.54	981.14	534.66	1033.08	477.63
solvent	CH ₂ Cl ₂ /MeOH	CH ₂ Cl ₂ /MeOH	CH ₂ Cl ₂ /MeOH	CH ₂ Cl ₂ /MeOH	CH ₂ Cl ₂ /MeOH
<i>T</i> [K]	296(2)	296(2)	295(2)	296(2)	296(2)
crystal system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> ₁	<i>P</i> ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbcm</i>	<i>C</i> 2/ <i>c</i>
<i>Z</i>	2	2	4	8	8
unit cell dimensions					
<i>a</i> [Å]	10.6072(3)	10.3250(5)	16.167(3)	17.2064(13)	17.8939(6)
<i>b</i> [Å]	10.6637(3)	11.8629(6)	8.4914(14)	23.5573(18)	20.3823(8)
<i>c</i> [Å]	11.8750(4)	23.5306(11)	22.917(4)	31.957(2)	15.5372(6)
α [°]	89.211(2)	104.513(3)	90	90	90
β [°]	75.182(2)	100.927(3)	91.398(3)	90	105.478(2)
γ [°]	61.934(2)	91.007(3)	90	90	90
<i>V</i> [Å ³]	1136.86(6)	2733.1(2)	3145.1(9)	12953.2(16)	5461.2(4)
conformation (°)	bent (7.5) ^[a]	bent (7.7) ^[a]	bent (10.2) ^[a]	bent (15.9) ^[a]	twisted (21) ^[a]

[a] Determination from the dihedral angle between two peripheral benzene or naphthalene planes along the longest axis of the molecules.

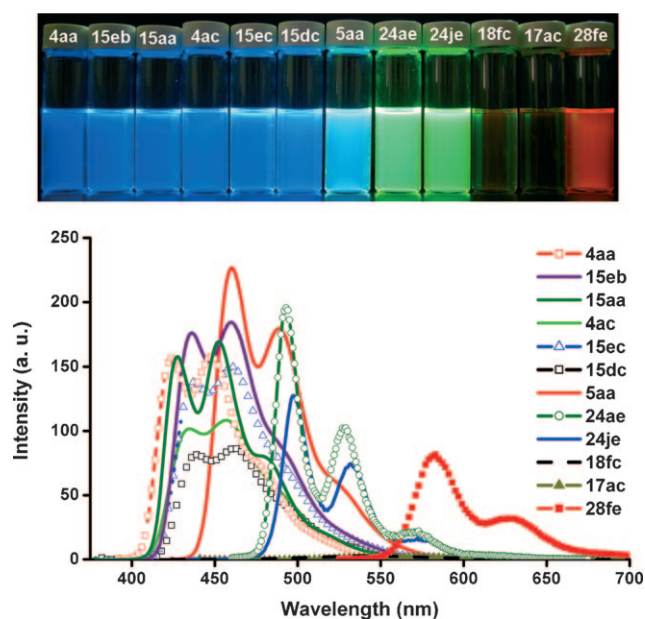


Figure 2. Photoluminescence spectra of benzo[*k*]fluoranthene-based linear acenes (ca. 10^{-5} M) in CH_2Cl_2 .

Table 5. Photophysical properties of benzo[*k*]fluoranthene-based linear acenes.^[a]

Entry	Cpd	λ_a [nm]	λ_f [nm]	Φ_f [%] ^[b]
1	4aa	300, 311, 330, 354, 368, 387, 410 [310, 330, 345, 375, 385, 408] ^[c]	424, 448 [418, 444] ^[d]	48
2	4ac	307 (s), 320, 340 (s), 391, 413	435, 457	86
3	5aa	323, 338, 372 (s), 395, 419, 445	460, 489, 528 (s)	61
4	15aa	306, 318, 373, 394, 417	429, 452, 482 (s)	75
5	15dc	311, 324, 375 (s), 397, 419	439, 462	73
6	15eb	308, 321, 376, 397, 420	439, 462, 493 (s)	83
7	15ec	313 (s), 326, 396, 417	437, 460, 493 (s)	54
8	17ac	317 (s), 331, 412, 436, 464	547, 567	7
9	18fc	324 (s), 340, 419, 446, 473	544	6
10	24ae	343 (s), 359, 426, 454, 485	494, 529, 570 (s)	52 ^[e]
11	24je	343 (s), 359, 429, 456, 488	496, 531, 574 (s)	44
12	28fe	310, 373, 393, 425 (s), 450 (s), 486, 522, 564	580, 626 (s)	35

[a] All samples (ca. 10^{-5} M) measured in CH_2Cl_2 . Only absorption bands over 300 nm are listed in this table. Excitation and emission maxima are italicized. Shoulders are indicated by (s). [b] Standards for the determination of quantum yields: quinine sulfate for entries 1–7; rhodamine 110 for entries 8–11; rhodamine 101 for compound **28fe**. [c] Measurement in acetonitrile from ref. [46]. [d] Measurement in benzene from ref. [7b]. [e] Because of its low solubility in common organic solvents, the purity of this compound was not determined by HPLC.

relative to **4aa**. The effects of the substituents in the phenyl side arms should not be important because the X-ray structures demonstrate that the two phenyl rings are twisted from the central aromatic core. This prediction is verified by comparing compounds **15dc/15ec** and **24ae/24je**, which all exhibit essentially identical absorption and fluorescence spectra, but different quantum yields (Figure 2). The addition of functional groups in products **4** and **15** did not significantly change their photophysical properties, except for quantum yields, and so offers the potential for fine-tuning of their electroluminescence properties.

Electrochemistry: The redox properties of the benzo[*k*]fluoranthene-based linear acenes were characterized by

cyclic voltammetry and are summarized in Table 6.^[47,48] The first oxidation potentials are dependent on the substituents and the extension of the aromatic systems in the central cores. As was determined with regard to the photophysical properties, substituents directly bound to the central aromatic cores have a stronger effect on redox properties than those in the phenyl side arms. The two methoxy groups in **4ac** (0.91 V) and the ethylene bridge in **15aa** (0.83 V) result in lower oxidation potentials than in the case of **4aa** (1.06 V vs. Fc/Fc^+). Substituents in the two side-arm phenyl moieties can also slightly change the electrochemical properties, as revealed by comparison of **15dc** (0.69 V) with **15ec** (0.75 V) and of **24ae** (0.62 V) with **24je** (0.58 V). The extension of the π system in the central aromatic core typically reduces the oxidation potential of the compound—the order **4** > **5** > **24** > **28** is consistent with this fact—but the potentials of **24je** (0.58 V) and **28fe** (0.59 V) are very similar to each other. Moreover, the first oxidation potentials of compounds **5** and **17/18**, which all are benzo-annulated cycloadducts of **4aa**, differ: that of **5aa** (0.73 V) is significantly less than those both of **17ac** (1.03 V) and of **18fc** (0.87 V). These unusual results can be explained by analysis of the isosurface distribution of the HOMOs (see DFT calculations and Figure 4, below).

DFT calculations: Density functional theory (DFT) calculations were performed to investigate the effects of substituents and the conjugation lengths of the aromatic systems on their electronic properties. The geometric optimizations and frequencies of the molecules were calculated at the B3LYP/6–31G** level with the aid of the Gaussian 03 program.^[49] The octoxy groups of compounds **18fc** and **28fe** were all simplified by treating them as methoxy groups. More reliable energy levels of the

highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) were obtained at the B3LYP/6–311+G**//B3LYP/6–31G** level.^[50] In Figure 3 the redox potentials determined by CV are compared with the HOMO and LUMO levels generated from the DFT computations, and they exhibit similar tendencies. To provide insight into the effects of substituents and conjugation lengths of the aromatic systems on the electrochemical properties, Figure 4 plots the HOMO and LUMO surfaces of some important compound classes. The optimized structure of compound **4aa** has a planar backbone with a frontier orbital that is distributed throughout the benzo[*k*]fluoranthene framework but not on the two perpendicular phenyl rings.

Table 6. Cyclic voltammetric (CV) analyses for benzo[*k*]fluoranthene-based linear acenes.^[a]

Entry	Cpd	Oxidation potential (E_{pa}) ^[b]	Reduction potential (E_{pa}) ^[b]
1	4aa	1.06 (E_p) [1.42 vs. SCE] ^[c]	−2.36
2	4ac	0.91	−2.41
3	5aa	0.73	−2.36
4	15aa	0.83, 1.19 (E_p)	−2.50
5	15dc	0.69, 1.08 (E_p)	−2.56
6	15eb	0.78, 1.17 (E_p)	−2.52, −2.73 (E_p)
7	15ec	0.75, 1.08 (E_p)	−2.51, −2.78
8	17ac	1.03	−1.96, −2.32
9	18fc	0.87	−1.94, −2.27
10	24ae	0.62	−2.38 (E_p), −2.60 (E_p), −2.98 (E_p)
11	24je	0.58, 0.91 (E_p)	−2.35 (E_p), −2.60 (E_p), −3.01 (E_p)
12	28fe	0.59	−1.87 (E_p), −2.30 (E_p), −2.57 (E_p)

[a] Experimental conditions: compounds (concentration ca. 10^{-3} M) in background electrolyte solution of TBAPF₆ (tetrabutylammonium hexafluorophosphate, 0.1 M) in benzene/acetonitrile (9:1). Working electrode: glass carbon (GC) electrode, reference electrode: Ag/AgNO₃ [AgNO₃ (0.1 M) and N(*n*Bu)₄ClO₄ (0.1 M) in acetonitrile], counter electrode: platinum wire. Scan rate: 50 mV s^{−1}. Internal standard: ferrocene. [b] Units: volt vs. Fc/Fc⁺. [c] Measurement in benzene/acetonitrile (1:1) from ref. [7b].

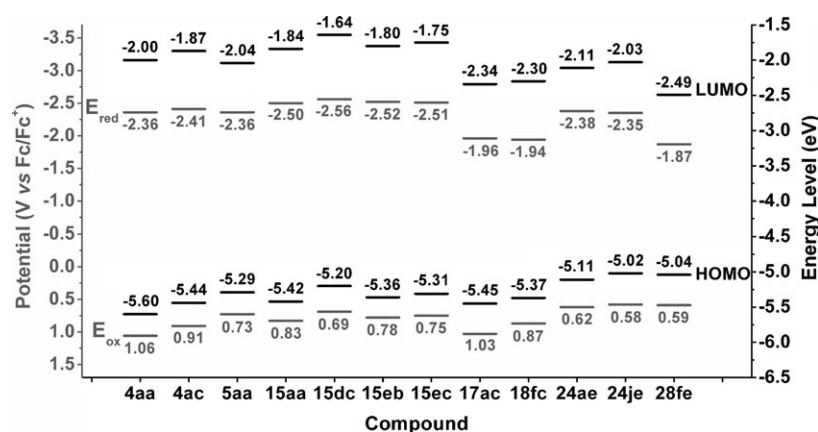


Figure 3. Redox potentials determined by CV (in gray) and HOMO and LUMO levels generated from the DFT computations (in black).

Substituents that are directly bound to the central aromatic core therefore influence the photophysical and electrochemical properties more strongly than those positioned in the phenyl side arm. However, with increasing conjugation length of the central aromatic core, some π orbitals are not

extended as efficiently as might be expected (see rectangle in Figure 4). The nonbonding characteristics of, for example, the LUMOs (indicated by the arrow can see one for **24ae** but not for **5aa**) of **5aa** and **24ae** suggest that the effective lengths of the isosurface distributions of their LUMOs correspond to those of anthracene and quasi-benzo[*k*]fluoranthene, respectively, and their LUMO potentials are analogous to that of **4aa**. Similarly, the isosurface and the potential of the HOMO of **17ac** are very close to those of **4ac**. Moreover, the HOMO and LUMO of **28fe** are not distributed throughout the entire skeleton; its HOMO is like that of benzo[1,2-*k*;4,5-*k'*]difluoranthene **24ae** and its LUMO is akin to that of **17ac**. Qualitatively, these computational analyses of the HOMOs and/or LUMOs of compounds **5**, **17**, **24**, and **28** fit with the results obtained by CV.

Conclusion

The Pd-catalyzed formal [(2+2)+2] cycloadditions between diynes and aryl iodides offer a simple method for preparing highly substituted benzo[*k*]fluoranthene-based linear acenes. The advantages of the developed synthetic protocols include: 1) relatively small numbers of synthetic steps, 2) easy introduction of functional groups, and 3) linear extension of aromatic cores.

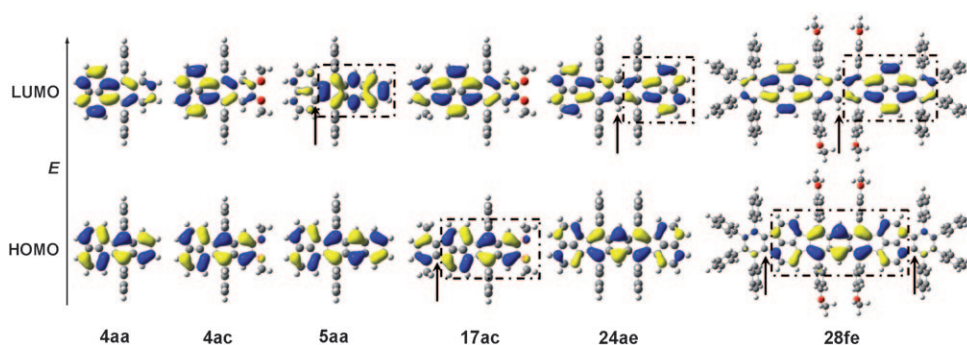


Figure 4. Isosurface plots of the frontier orbitals of **4aa**, **4ac**, **5aa**, **17ac**, **24ae**, and **28fe** calculated at the B3LYP/6-311+G**//B3LYP/6-31G** level. Rectangles and arrows indicate the effective lengths of frontier orbital distributions and nonbonding characteristic, respectively.

Although cycloadducts **4** and **15** exhibit identical blue fluorescence, their quantum yields and HOMO potentials differ. These differences might be useful for screening for efficient electroluminescence materials. Further studies of the electroluminescence of these molecules are currently underway, because such molecules could potentially be used as organic light emitting diodes (OLEDs).^[51]

Experimental Section

Instruments: ¹H and ¹³C NMR: Bruker 300 (300 and 75.5 MHz) and 400 (400 and 100 MHz). MS: Bruker Daltonics Apex II30. X-ray crystal structure determination: the data were collected with a Stoe-Siemens-AED diffractometer. Melting points were determined with a Büchi B545 melting point apparatus and are uncorrected. The purities (>97%) of samples for photophysical studies were determined by HPLC [Shimadzu LC-20AT/SPD-20AV or Dionex UltiMate 3000; Column: Alltech Partsil PAC54 (250×4.6 mm); mobile phase: hexane/EtOH (95:5); flow rate: 1 mL min⁻¹]. UV spectra were recorded with a HP 8453 instrument. Photoluminescence experiments were accomplished with Jasco FP-6300 and Cary Eclipse fluorescence spectrophotometers. Quinine sulfate ($\Phi = 0.546$),^[52] rhodamine 110 ($\Phi_f = 0.95$)^[53] and rhodamine 101 ($\Phi_f = 0.96$)^[54] were used as the standards for the determination of quantum yields. The electrochemical experiments were accomplished with a Princeton Applied Research Corporation (PAR) model 263 A potentiostat controlled by PAR model 270 software. A three-electrode cell was used for the electrochemical experiments. Computation: the geometry optimizations and frequencies of selected compounds were calculated by use of the B3LYP functional^[52] and a 6-31G (d,p) basis set with the Gaussian 03 Program.^[49] The HOMO and LUMO levels and orbital surfaces were obtained at the B3LYP/6-311+G(d,p) theory level from the structures optimized at the B3LYP/6-31G(d,p) theory level. The HOMO and LUMO orbital surfaces (isodensity value = 0.025) were generated with the GaussView 4.1.2 program.^[55]

General procedure for palladium-catalyzed cycloaddition of diynes with aryl iodides: A mixture of the appropriate diyne (0.25 mmol), the aryl iodide (0.50 mmol), AgOAc (0.50 mmol, 0.25 mmol for iodobenzene), Pd(OAc)₂ (12.5 μ mol), and *p*-xylene, toluene, or acetonitrile (4 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was heated at 110 or 130 °C for 40 h. After cooling to room temperature, the suspension was filtered through a 3 cm thick layer of Celite, and the Celite was rinsed well with CH₂Cl₂ (30 mL). The solvents were removed under reduced pressure, and the residue was subjected to chromatography on silica gel. Elution with hexane/CH₂Cl₂ afforded the coupling product.

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