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# Facile synthesis and functionalization of fluoranthenes *via* intramolecular [4 + 2] annulations between thiophenes and alkynes

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## ABSTRACT

Fluoranthenes have attracted tremendous attention due to their unique optoelectronic properties and extensive applications. Although several synthetic methodologies have been developed for the preparation of fluoranthene derivatives, it is still unfavorable to functionalize the fluoranthene framework at different positions due to the relatively low selectivity and reactivity. Herein, a catalyst-free intramolecular [4 + 2] annulation between thiophenes and alkynes is developed towards the synthesis of fluoranthenes. Altogether 20 examples have been demonstrated using this method. Various functional groups can be precisely introduced into the fluoranthene skeleton at different positions by simply tuning the substituents on the thiophenes and alkynes. The conjugation of the fluoranthene can be facilely extended through different directions. Furthermore, the feasibility of this [4 + 2] annulation reaction is also investigated by density functional theory calculations. Therefore, this protocol provides not only a synthetic methodology towards fluoranthenes with substituents functionalized at different positions, but also an effective pathway to construct large polycyclic aromatic hydrocarbons containing fluoranthene moieties.

A fluoranthene is composed of a naphthalene and a benzene which are connected by a five-membered ring. Therefore, the fluoranthene is one of the smallest non-alternant polycyclic aromatic hydrocarbons [1–3] and its derivatives always exhibit unique optoelectronic properties [4–6], such as intense photoluminescence (PL) resistance to oxygen quenching, small Stokes shifts, and long PL lifetime. In the past decades, fluoranthenes have attracted increasing interest due to their outstanding applications in organic light-emitting diodes (OLEDs) [7], organic field-effect transistors (OFET) [8,9], perovskite solar cells [10,11], and fluorescent sensors [12]. Until now, a number of synthetic methodologies have been developed for the preparation of fluoranthene and its derivatives [13–15]. To endow the fluoranthene additional optoelectronic properties, substituents are required to extend the $\pi$-conjugation [16,17]. However, it is still unfavorable to functionalize the fluoranthene framework at different positions, most likely due to the relatively low selectivity and reactivity. In view of the intriguing photophysical properties of fluoranthene-containing organic semiconductors, it is still desirable to develop simple methods for the synthesis of fluoranthene derivatives and the extension of the $\pi$-conjugation through different positions.

The Diels-Alder (D-A) reaction is one of the most powerful synthetic approaches for the construction of cyclic compounds [18,19]. Numerous dienes and alkynes have been developed and utilized to produce six-membered aromatic rings *via* [4 + 2] D-A reactions [20–22]. Among the various dienes, thiophenes have been successfully converted to benzene rings *via* intermolecular [4 + 2] annulations, followed by sulfur extrusion reactions [23–25]. However, the intramolecular [4 + 2] annulation between the thiophene and alkyne has been rarely reported. In this paper, a catalyst-free intramolecular [4 + 2] annulation between the thiophene and the alkyne is utilized to construct fluoranthenes (Scheme 1). Various functional groups can be precisely introduced into the fluoranthenes at different positions by simply tuning the substituents on the thiophenes and alkynes. Therefore, this protocol provides a simple pathway to extend the conjugation of the fluoranthene and construct large polycyclic aromatic hydrocarbons.

The straightforward synthetic approach to the fluoranthene started from 1,8-dibromonaphthalene (**1**), as shown in Scheme 1. To prepare the asymmetric precursor **2** with thienyl and alkynyl substituents, palladium-catalyzed Sonogashira [26] and Suzuki [27] coupling reactions were alternately conducted. It should be noted that the sequence of the two-step coupling reactions can be random and the overall yields of the two steps are over 60% in both routes with reversed sequences. Subsequently, *via* catalyst-free intramolecular [4 + 2] annulation between thiophene and alkyne, fluoranthene derivative **3** could be produced.

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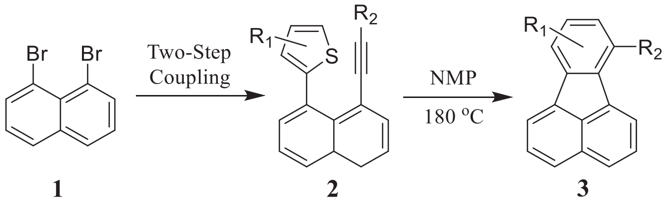
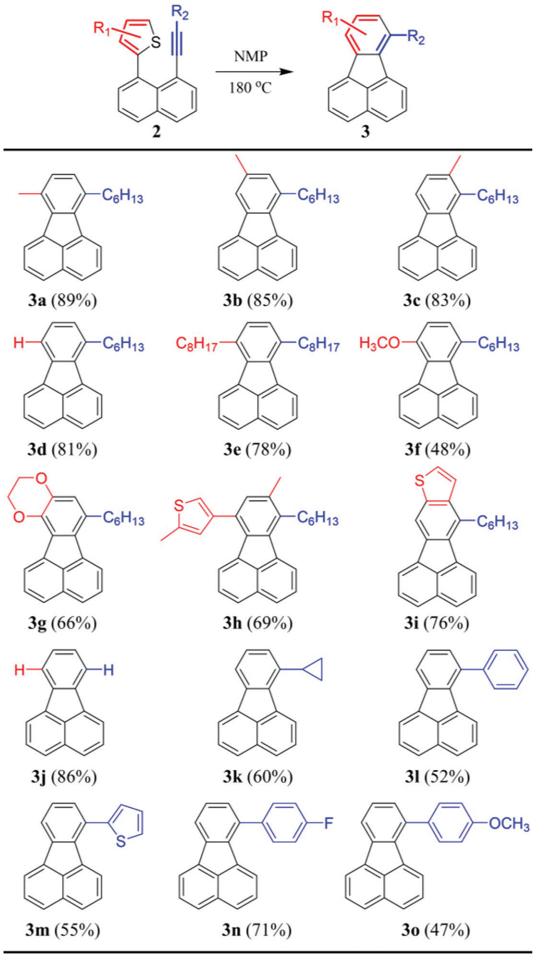


**Scheme 1.** Synthesis of fluoranthene derivatives *via* intramolecular [4 + 2] annulation reactions between thiophenes and alkynes.

The annulation condition was initially investigated using 1-(3-methylthien-2-yl)–8-(1-octynyl)naphthalene (**2a**) as the model starting material. Effects of solvent, temperature, and additive on the isolated yields have been systematically investigated. Firstly, the reactions were carried out by stirring the solutions of **2a** (1.0 mmol) in different solvents (7 mL) at the temperatures around their boiling points (Table S1 in Supporting information, entries 1–6). In the solvents with low boiling points, such as tetrahydrofuran and acetonitrile, no starting material was consumed. With the solvent boiling point increasing, the yields enhanced to 10%, 45% and 54%, in toluene, *N*,*N*-dimethylformamide, and *o*-xylene, respectively. When the reaction was carried out at 180 °C using 1-methyl-2-pyrrolidinone (NMP) as the solvent, the yield dramatically improved to 89%. To figure out whether the reaction was temperature-dependent or solvent-dependent, the annulation reactions were further conducted in NMP at different temperatures (Table S1, entries 6–9). Similar to the results in lower boiling point solvent, the yields gradually decreased to 65%, 10% and 0%, at 160, 120 and 80 °C, respectively. Interestingly, the solvent was not necessary for this annulation reaction. When **2a** was heated at 180 °C without any solvent, **3a** could also be produced but in low yield of 21% (Table S1, entry 10). Since NMP was regarded as a weak base, some basic additives were introduced to verify the possible contribution of a base in this annulation reaction (Table S1, entries 11–18). The results indicated that the introduction of basic additives, such as $K_2CO_3$, triethylamine ($Et_3N$), 4-dimethylaminopyridine (DMAP), and 1,8-diazabicyclo[5.4.0]undec–7-ene (DBU) did not assist the annulation reactions. Therefore, the temperature is crucial for this annulation reaction and further investigation was carried out by stirring the corresponding NMP solutions at 180 °C. It should be noted that no obvious intermolecular reaction could be detected. After the reaction, only two spots, *i.e.*, the desired product and the starting material, could be found on the thin-layer chromatography plate. The relatively lower yields could be attributed to the incompletely consumed starting material.

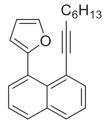
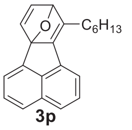
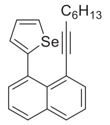
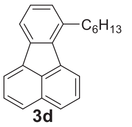
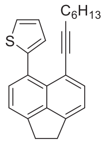
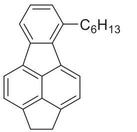
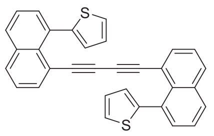
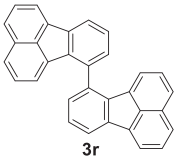
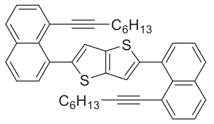
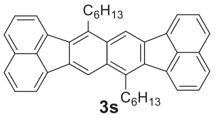
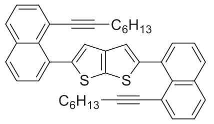
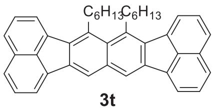
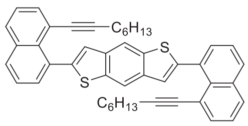
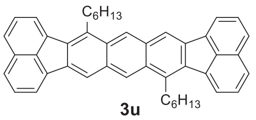
With the optimized reaction condition, the scope of the substituents $R_1$ and $R_2$ on the thienyl and the alkynyl groups, respectively, were evaluated (Scheme 2). Firstly, the substituted positions of $R_1$ on the thiophene ring were studied. When the methyl group was substituted at 3-, 4- and 5-positions of the thiophene ring, products **3a**, **3b** and **3c** with methyl groups substituted at different positions were obtained in high yields over 80%, indicating that the substitution on the 3-, 4- and 5-position of the thiophene group had a negligible effect on the annulation reaction. Moreover, when no substituent was on the thiophene ring or a longer alkyl group was substituted at 3-position, **3d** and **3e** were produced in yields around 80%. Furthermore, electron-donating units, such as 3-methoxylthiophene and 3,4-ethylenedioxythiophene, served as dienophiles and provided **3f** and **3g**, respectively. Additionally, other decorated thiophene derivatives, such as 5,5′-dimethyl-3,3′-bithiophene and thieno[3,2-*b*]thiophene, were also suitable for this [4 + 2] annulation reaction and corresponding products **3h** and **3i** were afforded in high yields. Subsequently, the universality of the alkynes was explored. When both $R_1$ and $R_2$ were hydrogen atoms, fluoranthene **3j** without any substituent was obtained in 86% yield. It is interesting to note that when $R_1$ was 3-hexylthiophene and $R_2$ was a hydrogen atom, compound **3d** could also be produced. In addition to the linear alkyl group, a cyclopropyl substituent with a secondary carbon was introduced on the fluoranthene skeleton (**3k**). Moreover, when the alkyl groups were replaced by aryl groups, phenyl-substituted **3l** and thienyl-substituted **3m** were afforded in moderate yields. Furthermore, electron-withdrawing fluoride and electron-donating methoxyl groups were further attached at the *para*-position of the phenyl groups. Compounds **3n** and **3o** were obtained in yields of 71% and 47%, respectively, which indicates that an electron-deficient substituent is more favorable for this annulation reaction in comparison to an electron-rich group.



**Scheme 2.** Scope of the substituents on the thiophene and the alkyne units.

In addition to the two substituents $R_1$ and $R_2$ on the thiophene and the alkyne units, the scope of the 1-ethynyl-8-thienylnaphthalene skeleton was also investigated. As shown in Table 1, when furan and selenophene derivatives were used as the reactants (Table 1, entries 1 and 2), the [4 + 2] D-A reactions could occur. However, the oxygen could not be extruded and an oxygen bridged product **3p** was obtained. Meanwhile, selenophene-based precursor could be converted to corresponding fluoranthene **3d**, similar to thiophene-based reactant. In view of cost and synthetic feasibility, thiophene derivatives were much more convenient for this annulation reaction in comparison to selenophene analogues. Moreover, when 1,2-dihydroacenaphthalene was used instead of naphthalene, fluoranthene **3q** was provided in 61% yield. Further-

**Table 1**
Scope of the skeletons for the annulation reactions.

| Entry | Reactant | Product | Yield (%) |
|---|---|---|---|
| 1 |  |  **3p** | 84 |
| 2 |  |  **3d** | 88 |
| 3 |  |  **3q** | 61 |
| 4 |  |  **3r** | 75 |
| 5 |  |  **3s** | 67 |
| 6 |  |  **3t** | 71 |
| 7 |  |  **3u** | 66 |

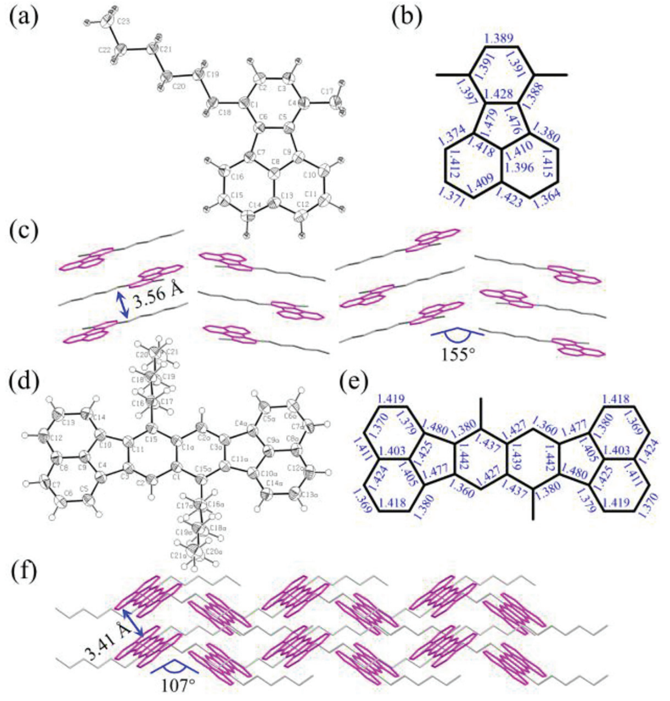


**Fig. 1.** (a, d) ORTEP diagram with ellipsoid contour probability level of 50%, (b, e) bond lengths of the core motifs, and (c, f) molecular packings of **3a** and **3s**.

more, when the precursors were dimerized, single bond linked fluoranthene dimer **3r** was afforded in 75% yield. Interestingly, when thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thiophene were used as building blocks for this annulation reaction, isomeric polycyclic aromatic hydrocarbons **3s** and **3t** were obtained in similar yields of 67% and 71%, respectively. Upon further introduction of a benzene ring, conjugation-extended product **3u** was produced in 66% yield. All these examples demonstrate the universality of this intramolecular [4 + 2] annulation between thiophenes and alkynes towards fluoranthene derivatives.

To gain insight into the molecular conformation, yellow single crystals of **3a** and **3s** suitable for X-ray diffraction were obtained by slow evaporation from mixed solutions of chloroform and methanol at room temperature. As shown in Fig. 1, the bond lengths of the C-C bonds in the benzene rings range from 1.360 Å to 1.439 Å, which are typical C-C bond lengths for delocalized aromatic systems. However, the bonds lengths of the two unshared C-C bonds in the five-membered rings (C5-C9 and C6-C7 in **3a**, and C3-C4 and C10-C11 in **3s**) are in the region of 1.476–1.480 Å, suggesting their single bond characteristics. Moreover, the fluoranthene skeletons in both molecules of **3a** and **3s** are planar. Therefore, relatively small interplane distances of 3.56 and 3.41 Å can be found for **3a** and **3s** which display herringbone packing structures with herringbone angles of 155° and 107°, respectively. Moreover, the shortest C-H···$\pi$ distances are measured to be 2.85 and 3.01 Å for **3a** and **3s** (Fig. S3 in Supporting information), respectively, suggesting the weak intermolecular interactions among the planar fluoranthene molecules.

The mechanism for this intramolecular [4 + 2] annulation reaction between thiophenes and alkynes is proposed and shown in Fig. S4 (Supporting information). First, the 1,3-diene subunit in the thiophene ring reacts with the alkyne unit and produces the intermediate compound **IM** *via* the transition state **TS**, which is similar to the traditional [4 + 2] Diels-Alder reaction. Subsequently, the sulfur atom decomposes to produce the product *via* S-extrusion reaction due to the large ring tension. The feasibility of the [4 + 2] D-A reaction was further verified by density functional theory (DFT) calculations. The reaction pathway and the relative Gibbs free energies for the starting material **SM**, the transition state **TS**, and the S-bridged intermediate **IM** at 453.15 K were calculated using Gaussian 16 program [28] with the B3LYP functional and the 6–31G(d) basis set. As shown in Fig. S5 (Supporting information), although the [4 + 2] D-A reaction is endothermic only at 2.8 kcal/mol, a large energy barrier of 37.3 kcal/mol can be found for the first [4 + 2] D-A reaction, which explains the high temperature condition in this annulation reaction.

The photophysical properties of the as-prepared fluoranthene derivatives were further investigated by measuring their UV–vis absorption and photoluminescence (PL) spectra in toluene solutions (ca. $5 \times 10^{-6}$ mol/L). As shown in Fig. S6 (Supporting information), **3j** displays two absorption bands in the region of 250–300 and 300–400 nm, assigning to the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ electron transitions, respectively. Meanwhile, **3j** exhibits the maximum PL wavelength at 442 nm. Under the same condition, compounds **3r**, **3s** and **3u** with different conjugation skeletons demonstrate absorption maxima at 362, 454 and 478 nm, and PL maxima at 461, 484, and 499 nm, which is obviously due to the extended effective conjugation length. Fig. S7 (Supporting information) shows the photographs of the dilute solutions of **3j**, **3r**, **3s** and **3u** under the irradiation of a UV light. Strong blue or blue-green emissions can be observed, suggesting their intense luminescent characteristics.

In summary, a catalyst-free intramolecular [4 + 2] annulation between thiophenes and alkynes has been established to construct fluoranthene derivatives. Various functional groups can be introduced to the different positions of fluoranthenes by simply tuning the substituents on the 1-ethynyl-8-thienylnaphthalene skeleton. Consequently, the conjugation of the fluoranthene can be facilely extended through different directions. Overall, this work provides not only a synthetic methodology towards fluoranthenes with substituent functionalized at different positions, but also an effective pathway to construct large polycyclic aromatic hydrocarbons containing fluoranthene moieties.

## Declaration of competing interest

The authors declare no competing financial interest

## Acknowledgments

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.06.065.

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