# Synthesis of Decaarylanthracene with Nine Different Substituents

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Supporting Information Placeholder

ABSTRACT: A synthesis of decaarylanthracene with nine different substituents has been accomplished by a coupling/ring-transformation strategy. The oxidation of tetraarylthiophenes with four different substituents to the corresponding thiophene *S*-oxides, and a [4+2] cycloaddition with a double benzyne precursor afforded a multiply arylated naphthalene derivative. Subsequently, the naphthalene derivative was converted into a naphthalyne, and then a [4+2] cycloaddition of another thiophene *S*-oxide provided decaarylanthracenes with nine different aryl groups.

Decaarylanthracene (DAA) with Nine Different Substituents
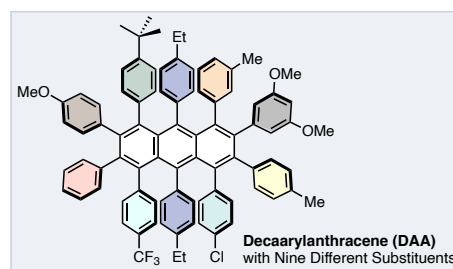
■ INTRODUCTION

Acenes are linearly fused aromatic rings that are classified as polycyclic aromatic hydrocarbons (PAHs). These highly conjugated structures have excellent optical and organic electronic properties, and have been well-studied for two decades[1] Particularly, acenes with multiple aromatic rings are organic electronic materials for everyday societal use (Figure 1). For example, oligoanthracene, which have three anthracenes connected to each other, is utilized as an organic field-effect transistor (OFET).[2] Additionally, dinaphthylanthracene, which has two naphthalene groups bonded to an anthracene unit, is well-known as an organic light-emitting diode (OLED).[3] Rubrene, which has four benzene substituents on a central tetracene core, is also used in OLEDs, OFETs, and organic semiconductors.[4] Another OLED material is known: fused anthracene, in which eight of the hydrogens on anthracene are substituted with aryl groups.[5] Therefore, the development of efficient methods to introduce multiple aryl groups onto acenes is necessary, and in turn gives us the opportunity to create innovative functional molecules.[6]

Specifically, anthracene has been synthesized from dihydroanthracene using oxidative methods, and from anthraquinones using reductive methods, as well as by retrocyclization.[7] However, these methods are limited in the number of substituents that can be introduced. Another known method is the synthesis of anthracene derivatives by the cycloaddition of benzynes. For example, Pascal and co-workers have successfully synthesized decaphenylanthracene (DPA) using a [4+2] cycloaddition of benzynes (Figure 2A).[8] This synthesis involved the cycloaddition of a substituted benzyne, which was generated from tetraphenylanthranilic acid, with hexaphenylisobenzofuran. This pioneering synthetic strategy can be applied to other polyphenylacenes as well.[9] However, the substituents introduced in this manner are limited to only phenyl groups, and there are no examples of decaarylanthracenes that have different aromatic substituents.
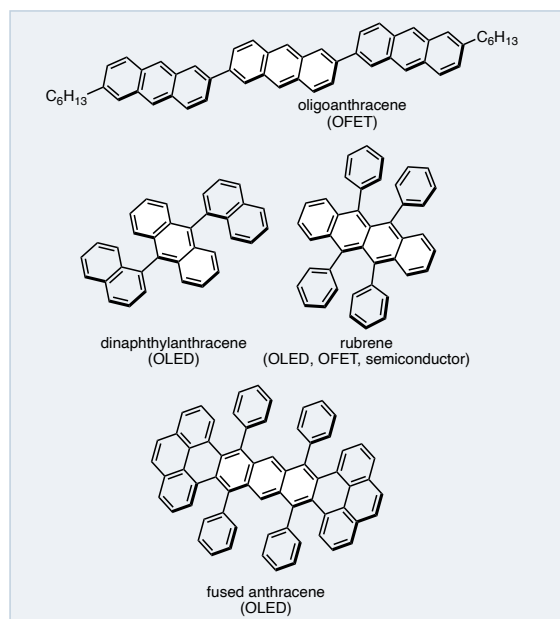

Figure 1. Multiply arylated acenes in organic materials.

Meanwhile, in 2015, we developed a coupling/ring transformation strategy and applied it to the first synthesis of hexaarylbenzenes (HABs) with five and six different aryl groups (Figure 2A).[10] Our HAB synthesis commenced with cross-coupling reactions (involving C–H arylations) of 3-methoxythiophene to give tetraarylthiophenes with four different aryl groups (Figure 2B). Oxidation of the thiophenes, then [4+2] cycloaddition/desulfonation of the resulting tetraarylthiophene *S*-oxides with diarylalkynes, afforded the HABs. This demonstrated a net ring transformation from a thiophene to a benzene, and this general strategy has been applicable for the synthesis of multi-arylated azines, heteroles, and acenes (Figure 2C). As such, we have achieved the synthesis of pentaarylpyridine (PAP),[11a] hexaarylindole (HAI),[11c] hexaarylisoquino
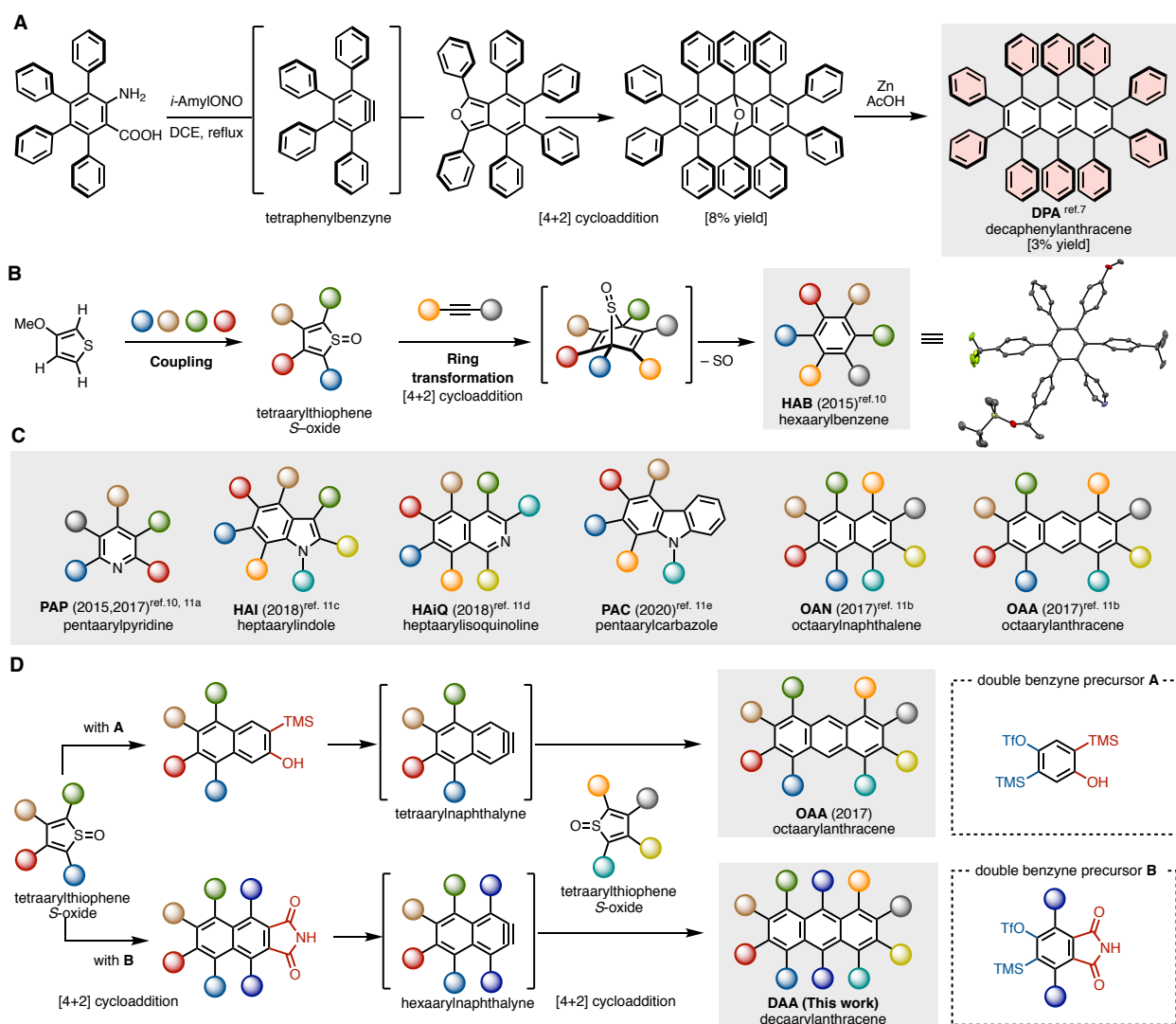
Figure 2. (A) A pioneering synthesis of decaphenylanthracene (DPA) by Pascal and co-workers. (B) A synthesis of hexaarylbenzenes through a coupling/ring transformation strategy. (C) Syntheses of multi-arylated heteroarenes, heteroles and acenes by using the coupling/ring transformation strategy. (D) Previously synthesized octaarylanthracene (OAA), and synthesis of decaarylanthracene (DAA; this work).

line (HAiQ),[11d] and pentaarylcarbazole (PAC),[11e] as well as octaarylnaphthalene (OAN) and octaarylanthracene (OAA).[11b] In the synthesis of OAA,[11b] the target molecule was divided into three units: two tetraarylthiophene *S*-oxides and a double benzyne precursor **A** (Figure 2D).[5,12] First, the tetraarylthiophene *S*-oxide was reacted with a benzyne (which was generated from a double benzyne precursor **A** with an appropriate base) via [4+2] cycloaddition to afford the desired adduct. Thereafter, generation of a tetraarylnaphthalyne in the presence of another tetraarylthiophene *S*-oxide produced OAA through another [4+2] cycloaddition. Although we accomplished OAA by using a coupling/ring transformation strategy, the synthesis of decaarylanthracene (DAA), which would be a highly crowded assembly of 10 aryl groups onto the anthracene core, was not achievable with the same route. To realize the synthesis of DAA, a double benzyne precursor **B**, with two additional aryl groups on the benzene core, was designed. Precursor **B** has an imide group and an *o*-trimethylsilylaryl triflate, which enables the sequential generation of benzyne intermediates under different conditions. Herein, we report the first synthesis of DAA us-

ing double benzyne precursor **B** and hexaarylnaphthalyne as key units.

■ RESULTS AND DISCUSSION

Synthesis of a Double Benzyne Precursor.

To synthesize precursor **B**, which is in itself a highly substituted benzene core, C–H arylation and [4+2] cycloaddition of 3-methoxythiophene (**1**) were envisaged to be effective tools. The synthesis of precursor **B** commenced with C–H arylations of 3-methoxythiophene with 4-iodoethylbenzene in the presence of catalytic PdCl₂/bipy and Ag₂CO₃ to provide 2,5-diaryl-3-methoxythiophene **2** in 66% yield (Scheme 1).[13] After C4-bromination of thiophene **2**, the resulting product was oxidized to the corresponding thiophene *S*-oxide **3** to enhance the reactivity of thiophene as a diene. A subsequent [4+2] cycloaddition with dimethyl acetylenedicarboxylate provided the corresponding benzene **4** in moderate yield. In the presence of aqueous HBr, demethylation of the methoxy group and hydrolysis of the ester proceeded

smoothly. After acid anhydride formation, phthalimide **5** was formed in 90% yield (over three steps). Finally, the bromophenol moiety of **5** was readily converted to *o*-trimethylsilylaryl triflate by a three-step sequence (silylation, lithiation, retro-Brook rearrange-ment followed by triflation) to afford double benzyne precursor **6** (as the equivalent unit of double benzyne precursor **B** in Figure 2D).

Scheme 1. Synthesis of a double benzyne precursor.

double benzyne precursor **6**
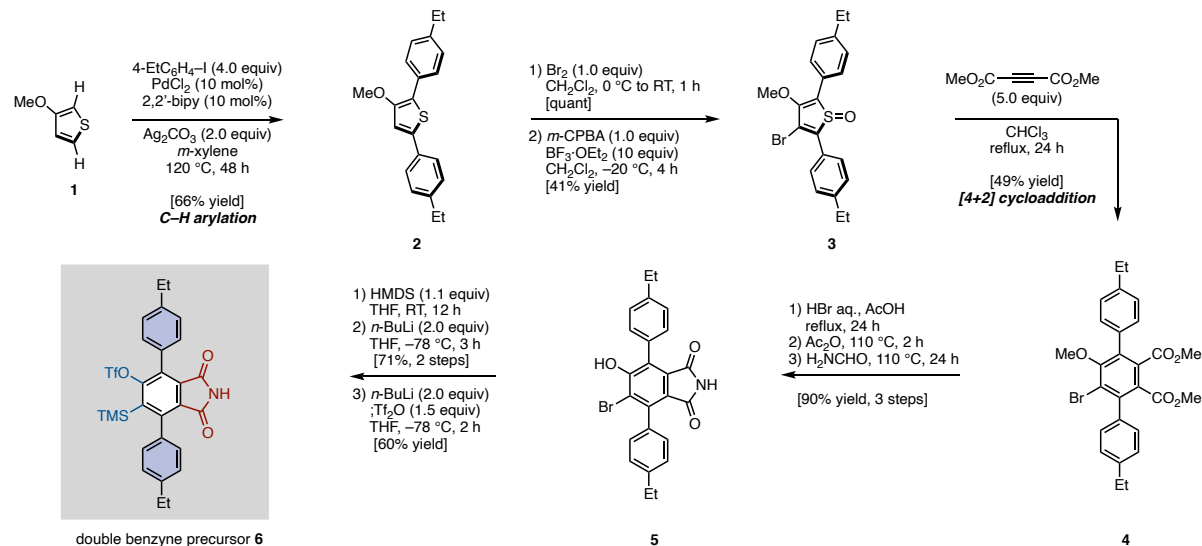
[4+2] Cycloaddition Between the Double Benzyne Precursor and Tetraarylthiophene *S*-Oxide.

With precursor **6** in hand, the synthesis of DAA was attempted by a [4+2] cycloaddition with tetraarylthiophene *S*-oxide **7a** (Scheme 2A). **7a** was readily prepared from 3-methoxythiophene (**1**) using our previously reported method in seven steps.[11b] Initially, the [4+2] cycloaddition of **6** with **7a** under fluoride conditions to generate benzyne was examined.[14] When tetrabutylammonium fluoride (TBAF), which is used for generating benzyne from *o*-trimethylsilylaryl triflate, was applied, [4+2] cycloadduct **8** was not detected. Instead of the desired product **8**, unprecedented 8-membered ring **9** and 5,5-fused ring system **10** were formed as primary products of the reaction (Scheme 2B). Treatment with CsF using a CH₃CN/DCE solvent mixture only caused side reactions as well. However, when the reaction was run in DCE and toluene, **8** was detected. Tetrabutylammonium difluorotriphenylsilicate (TBAT), which is a soluble fluoride source in toluene, showed no positive effect on the yield of **8**. Other inorganic fluoride sources such as KF and NH₄F gave no reaction. Finally, when the reaction was scaled up using CsF in toluene, in addition to the desired 6-membered ring **8** (6% yield), the undesired 8-membered products **9** and 5,5-membered ring systems **10** were also isolated in 22% yield and 9% yield, respectively. Although a rigorous screening of reaction conditions (solvent, temperature, concentration and stoichiometry) was conducted, the yield of **8** unfortunately could not be improved.

Next, to determine the structure of [4+2] product **8**, the imide moiety was derivatized. Treatment of **8** with methyl iodide in the presence of K₂CO₃ provided *N*-methylated imide **Me-8** in 73% yield. **Me-8** was crystallized from CHCl₃/pentane solution and characterized by X-ray crystallographic analysis. The X-ray crystal structure of **Me-8** showed that the naphthalene skeleton is largely distorted, and that the steric repulsion forces the surrounding aryl groups to avoid each other by being out of plane with respect to the naphthalene core. Additionally, from the mixture of **9**, isomer **9a** was isolated and *N*-methylated to give **Me-9a**; from the mixture of **10**, isomer **10b** was isolated and derivatized by demethylation, TBS protection and *N*-methylation to give **TBSMe-10b**. **Me-9a** and **TBSMe-10b** were crystallized from CHCl₃/pentane or 1,2-dichloroethane/hexane solution and characterized by X-ray crystallographic analysis to reveal their unexpected structures.

Based on the structures of **Me-9a** and **TBSMe-10b**, two plausible reaction mechanisms are shown in Scheme 2C. These unexpected reactions could be initiated by nucleophilic addition of **7a** to the sterically hindered aryne formed from **6**. When the resulting carbanion attacks the C2 position of thiophene, a 5,5-fused ring system **10** would be formed (red arrow). On the other hand, addition of the carbanion to the sulfur atom would provide 8-membered ring **9** via carbon–sulfur bond cleavage (blue arrow). Regarding the formation of the 8-membered ring, the reaction with cyclic sulfilimines/sulfoxides and arynes afforded thiazocine/oxathiocine derivatives in a similar fashion by Hosoya, Yoshida and coworkers.[15] Since these unexpected products were not observed in the reaction with thiophene *S*-oxide **3** and double benzyne precursor **A** in our previous report,[11b] the steric hindrance on the periphery of the aryne appears to cause the preference for nucleophilic addition over [4+2] cycloaddition. The solvent effect (the difference between toluene and other solvents) in this reaction might be explained as follows. When using polar solvents, nucleophilic addition would be preferred due to stabilization of the ionic intermediate, and therefore the 5,5-fused ring system **10** and the 8-membered ring **9** would predominate. On the other hand, when a nonpolar solvent is used, 6-membered ring **8** formation proceeds in a slightly preferential manner.

Scheme 2. (A) [4+2] cycloaddition of a double benzyne precursor and tetraarylthiophene *S*-oxide. (B) Structural determination of the side products **9** and **10**. (C) Plausible reaction mechanisms for the formation of the 5,5-fused ring system and the 8-membered ring. In the ORTEP drawing of **Me-8**, **Me-9a** and **TBSMe-10a**, hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at 50% probabilities.
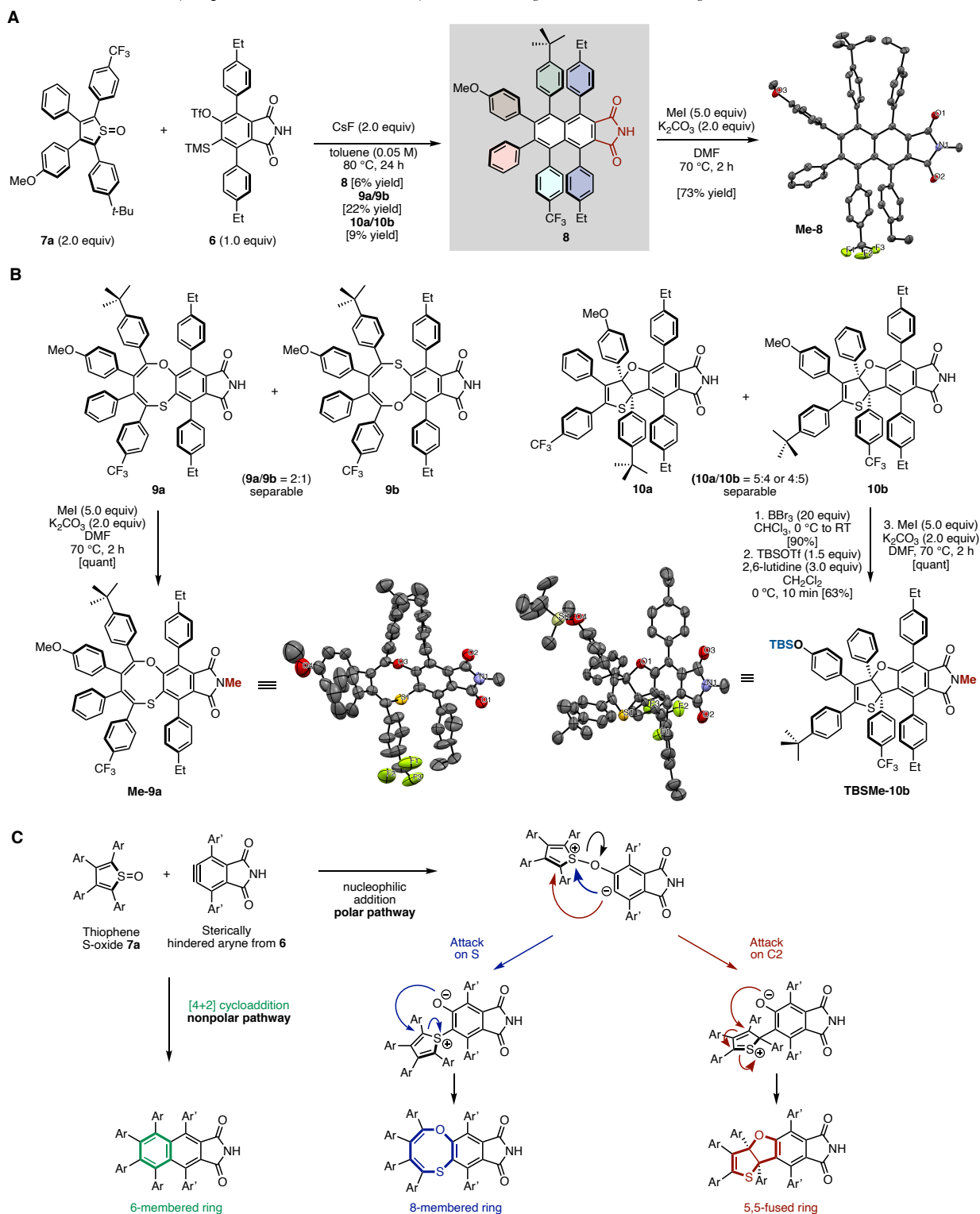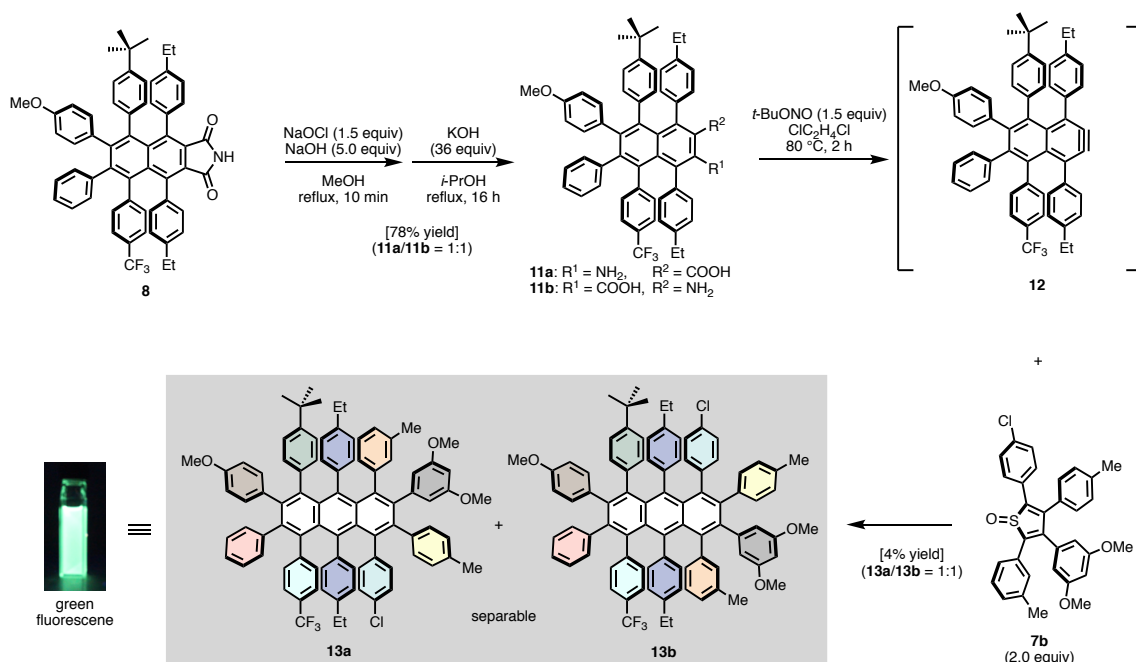

Synthesis of Decaarylanthracene (DAA).

To complete the synthesis of DAA, Hofmann rearrangement of **8**, followed by hydrolysis, was conducted to provide hexaarylnaphtha-

lyne precursor **11** as a mixture of regioisomers (**11a**/**11b** = 1:1) in 78% combined yield (Scheme 3). Finally, treatment of this mixture with *tert*-butyl nitrite to give hexaarylnaphthalyne **12**, followed by reaction with thiophene *S*-oxide **7b**, produced decaarylanthracene (DAA: **13**) as a mixture of regioisomers (**13a**/**13b** = 1:1) in 4% combined yield. These regioisomers were separable by preparative thin-layer chromatography.

Next, the absorption and fluorescence of the two isomers of DAA **13** were measured.[16] The absorption and fluorescence of the parent decaphenylanthracene (DPA) was already reported by Pascal and coworkers, in which DPA has an absorption maximum at 429 nm and emission maxima at 486 and 512 nm (in cyclohexane).[8] Compared with the synthesized DAAs **13**, there are no large differences in photophysical properties between symmetrical DPA and highly unsymmetrical DAAs **13**.

Scheme 3. Synthesis of decaarylanthracene (DAA).

■ CONCLUSIONS

In summary, a general synthetic method toward decaarylanthracene (DAA) has been developed by employing a [4+2] cycloaddition of tetraarylthiophene *S*-oxides with a series of multiply arylated arynes. The present study also shows the versatility of tetraarylthiophene *S*-oxides in [4+2] cycloaddition. Conveniently, all synthetic units (**6**, **7a** and **7b**) are accessible from 3-methoxythiophene (**1**) as the starting material. Therefore, DAAs **12** can be synthesized by a combination of coupling and [4+2] cycloaddition of 3-methoxythiophene (**1**). Moreover, different aryl groups could be installed onto the C2 and C5 positions of 3-methoxythiophene by C–H arylation developed in our group,[17] which would lead to the synthesis of double benzyne precursor **B** with two different aryl groups. Although the yield and regioselectivity in the [4+2] cycloaddition steps require improvement, this methodology, in principle, allows access to decaarylanthracenes with substituents that are all different. With the development of a new method that can synthesize previously unattainable molecular structures, the discovery of new functional materials can be expected.

■ ASSOCIATED CONTENT

The Supporting Information is available free of charge.
Experimental procedures and spectroscopic data for compounds including ^{1}H, ^{13}C NMR spectra (PDF)

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Notes

No competing financial interests have been declared.

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(14) For details regarding screening conditions, see the Supporting Information.

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(16) The measured absorption and fluorescence wavelength of DAAs **13** (in dichloromethane) are summarized, and the measured spectra are shown in the Supporting Information.

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