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Combining Furan Annulation, Heck Reaction, and Sonogashira Coupling for the Synthesis of Oligoaryls

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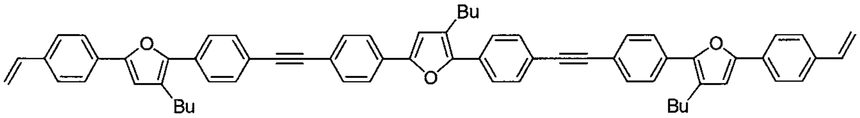
ABSTRACT



A variety of benzene–furan–alkene/alkyne conjugated oligomers of precise length and constitution were synthesized iteratively by combining furan annulation, Heck reaction, and Sonogashira coupling.

Oligoaryls and their vinylene or acetylene homologues of desired conjugation length have been widely investigated because of their potential optoelectronic applications.[1] There has been extensive uses of heteroaromatic rings such as thiophene in these applications.[1] Interestingly, studies on furan derivatives for these applications have been rare.[2−5] We recently reported a convenient one-pot synthesis of symmetric oligoaryls **2** containing two furan moieties (eq 1).[6,7] These oligoaryls are thermally stable and exhibit bright fluorescence in the blue light region. It is noteworthy that **2a** has been shown to be a highly efficient non-amine-based hole-transporting material in electroluminescent devices.[7] The basic synthetic strategy shown in eq 1 involves the reaction of a thiolato-substituted allenyl anion **3**, generated in situ from **1** and BuLi, with a dialdehyde followed by the acid-catalyzed ring closure. Since both vinyl and alkynyl substituents are stable under the reaction conditions,[6] it is envisaged that substrates containing such functionalities can undergo Heck[8] and Sonogashira[9] reactions, respectively, to extend the chain length while incorporating the aldehyde functionality at both ends of the oligoaryl chain. Further annulation leading to furan rings can then proceed to yield the homologues of oligoaryls. In this paper, we report a bidirectional iterative synthesis of furan-containing oligoaryls by combining furan annulation, Heck reaction, and Sonogashira coupling.

Treatment of **1c** with BuLi yielded the corresponding allenyllithium **3b**, which was allowed to react with **5a** followed by acid treatment, affording **4b** in 52% yield. Removal of the TMS group was achieved by treating **4b** with K_2CO_3 in methanol−THF to give **4c** in 98% yield. In a manner similar to that described in eq 1, reaction of **3a** with **6** gave **7** in 45% yield.

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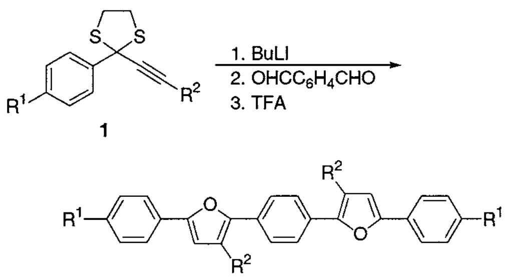
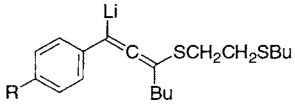


1

2

(1)

a R^1 = H, R^2 = Ph
b R^1 = H, R^2 = Bu
c R^1 = TMSC≡C, R^2 = Bu
d R^1 = H$_2$C=CH, R^2 = Bu



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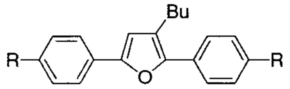

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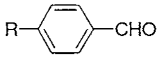
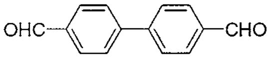
a R = H$_2$C=CH- **b** R = TMSC≡C- **c** R = HC≡C-



5a R = TMSC≡C-
5b R = Br



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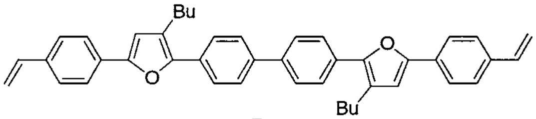

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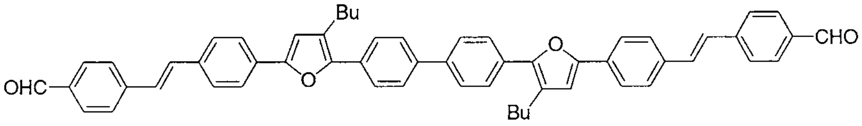
Table 1. Photophysical Properties of Oligoaryls

substrate	λ_{max} (nm)^b	λ_{em} (nm)^b	Φ_f
8	350, 399	508	0.45
9	340, 400	486	0.81
10	397	484	0.91
11	348, 412	507	0.64

The presence of double bonds and triple bonds in **7** and **4c**, respectively, is essential for the Heck or Sonogashira reaction. Thus, treatment of **7** with 4 equiv of **5b** in the presence of 5 mol % Pd(OAc)$_2$, Ph$_3$P, and K$_2$CO$_3$ under an argon atmosphere for 48 h resulted in the formation of **8** in 75% yield. In a similar manner, the Sonogashira reaction was employed to enable the coupling of **4c** with **5b** in the presence of CuI, Ph$_3$P, Et$_3$N, and a catalytic amount of PdCl$_2$(PPh$_3$)$_2$ in MeCN. Oligoaryl **9** was isolated in 63% yield.

Annulation of **9** with **3a** generated in situ from the reaction of **1d** and BuLi afforded **10** in 38% yield. In a similar manner, reaction of **8** with **3b** gave **11** in 42% yield. Both oligoaryls **10** and **11** have either double bonds or triple bonds at both ends of the conjugated system. Accordingly, further elaboration would be possible by repeating the same procedures leading to higher homologues of oligoaryls, which can be used as molecular wires. Although the yields of the annulation are moderate, compounds **8**−**11** were easily precipitated by the addition of methanol to the CH$_2$Cl$_2$ solutions of the crude products.

The photophysical properties of **8**−**11** were briefly examined, and the results are summarized in Table 1. These oligoaryls exhibited a bluish green emission in CHCl$_3$ solution with high quantum efficiency. Compound **11** was somewhat unstable, with slow decomposition observed when the CHCl$_3$ solution was exposed to ambient light. As



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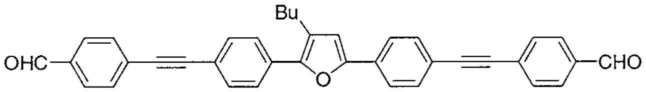

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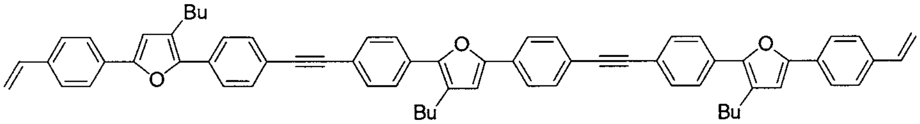

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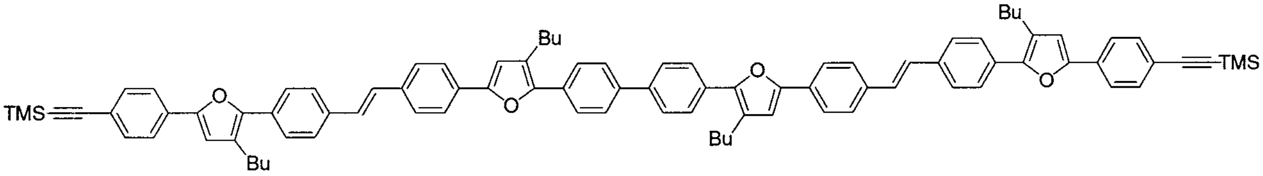

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illustrated in Table 1, the conjugation lengths in **8−11** already reached saturation and essentially the λ_{max} values for each of these oligoaryls remained similar.

In summary, we have demonstrated a new convenient route by combining furan annulation and Heck and Sonogashira reactions for the synthesis of a variety of benzene−furan−alkene/alkyne conjugated oligomers of precise length (up to 6 nm) and constitution. Further extension by using this iterative strategy will be feasible leading to the synthesis of oligoaryls of well-defined conjugation lengths.

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Supporting Information Available: Experimental procedures for the preparation of **4b**,**c** and **8−11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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