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Synthesis of Conjugated Oligomers Having Aromatic and Enediyne Units Alternately in the Backbone that Show Intense Fluorescence Emission

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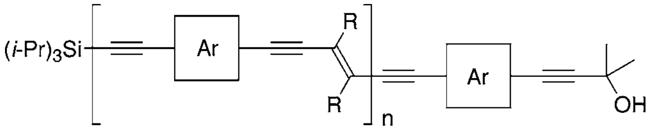
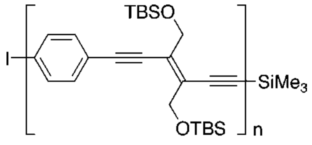
ABSTRACT



Ar = phenyl, pyridyl, thienyl
n = 1, 2, 3

Synthesis and fluorescence properties of π-conjugated compounds having alternately an aromatic ring such as benzene, pyridine, and thiophene and an enediyne unit in the backbone are described.

Linearly π-conjugated oligomers and polymers having an enediyne-scaffold, i.e., oligo- and poly(triacetylene)s, have attracted much interest as advanced materials for electronic and photonic applications.[1,2] Recently, Diederich and co-workers have shown that the introduction of aromatic spacers into oligo- or poly(triacetylene)s results in significant modulation of their optical properties. They synthesized highly fluorescent hybrid polymers by inserting biphenyl moieties into poly(triacetylene)s.[2] They also prepared a comprehensive series of hybrid oligomers by insertion of different aromatic rings between two enediyne moieties and investigated their optical and electronic properties compared to those of the corresponding homotrimer, highlighting the enhancement of the emission properties.[3] Most recently, they prepared (phenylene enediyne)-monomer, -dimer, -trimer, and -tetramer of type **1** ($n = 1{-}4$) shown in Figure 1 using Sonogashira coupling on solid support as a key reaction.



1
n = 1, 2, 3, 4

Figure 1.

Interestingly, the dimer and, in particular, the trimer and tetramer display intense fluorescence emission, with the highest quantum yield, $\Phi_F = 0.69$, being measured for the trimer.[4,5] We therefore were interested in the fluorescence property of oligo(arylene enediyne)s that have an aromatic

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(1) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377.

(2) Edelmann, M. J.; Odermatt, S.; Diederich, F. *Chimia* **2001**, *55*, 132−138.

(3) (a) Martin, R. E.; Wytko, J. A.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1999**, *82*, 1470−1485. (b) Edelmann, M. J.; Raimundo, J.-M.; Utesch, N. F.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **2002**, *85*, 2195−2213.

(4) Utesch, N. F.; Diederich, F. *Org. Biomol. Chem.* **2003**, *1*, 237−239.

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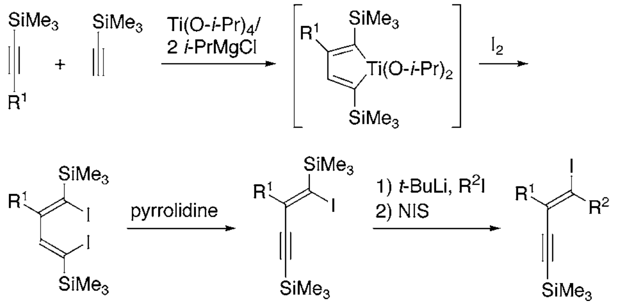
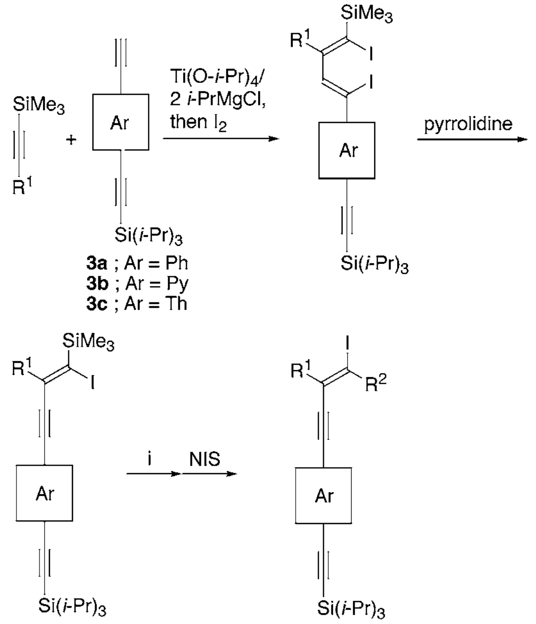
Scheme 1



group other than a phenyl group. The synthetic method of Diederich, however, only allowed access to oligo(phenylene enediyne), and thus, a new synthetic method was needed. We have now succeeded in developing a general method for preparing oligo(arylene enediyne)s.

Previously, we reported a synthetic method for preparing *trans*-1-iodo-4-(trimethylsilyl)but-1-en-3-yne derivatives starting from 1-trimethylsilyl-1-alkynes and ethynyltrimethylsilane according to the procedure shown in Scheme 1. The iodoenynes thus prepared were effectively used as building blocks for synthesizing conjugated oligomers having an enyne or enediyne unit.[6] Applying the protocol shown in Scheme 1, we have now succeeded in preparing vinyl iodo compounds **2** easily. Thus, as shown in Scheme 2, compounds **2**, where Ar is a phenyl (**2a**), pyridyl (**2b**), or thienyl group (**2c**), were prepared in 32–38% overall yield by starting with, respectively, diynes **3a**–**c** instead of ethynyltrimethylsilane. Compounds **2** thus obtained proved to serve as building blocks for synthesizing the corresponding oligo(arylene enediyne)s (vide infra). Meanwhile, the starting compounds **3a**–**c** were readily prepared in good overall yield according to the conventional reaction sequences as shown in Scheme 3.[7] As also shown in Scheme 3, we prepared

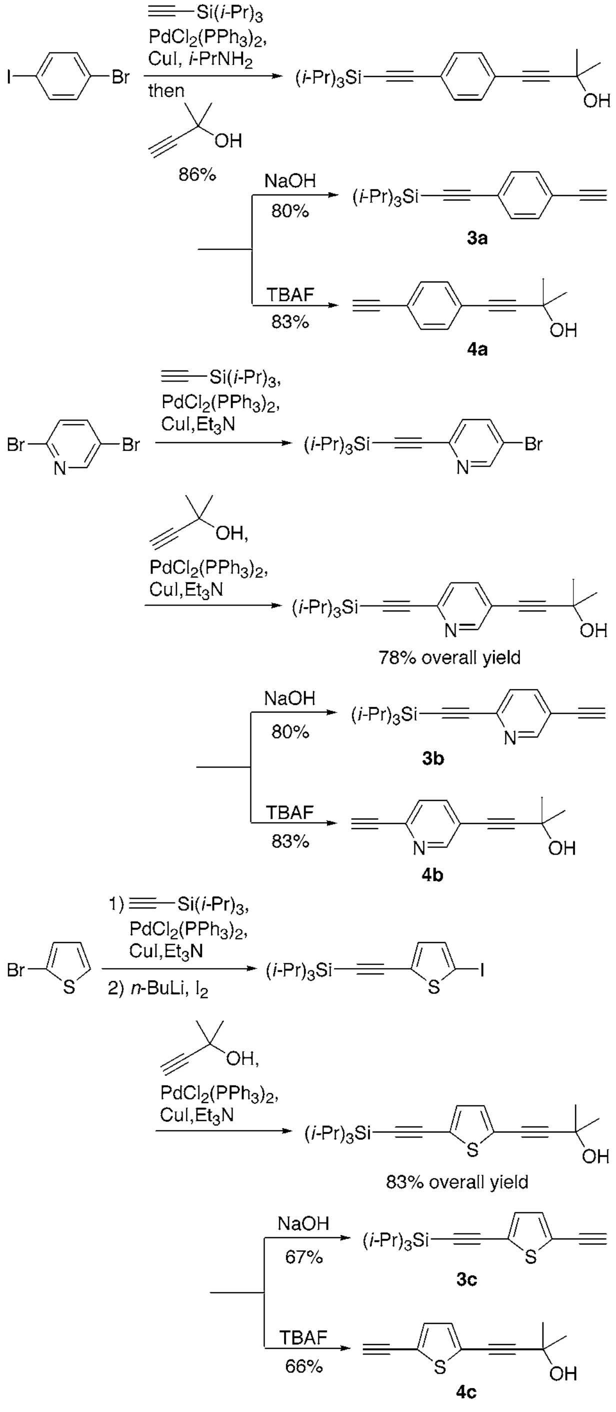
Scheme 2[a]



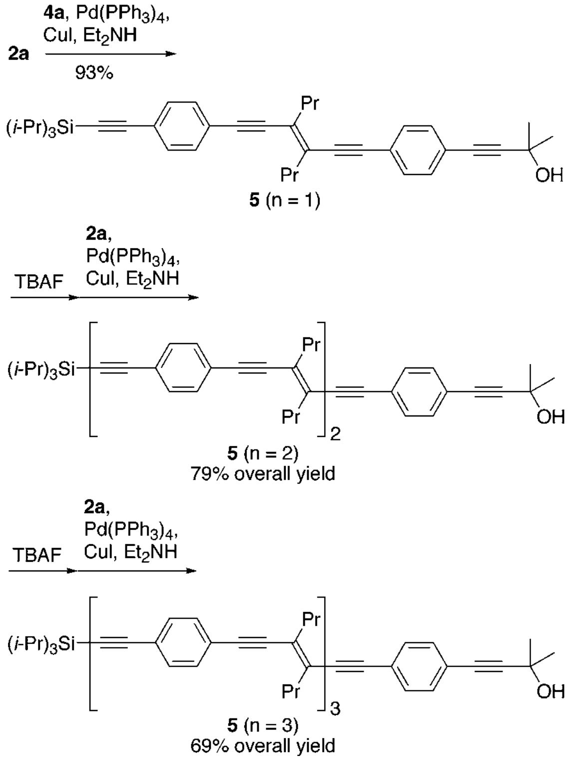
2a ; Ar = Ph, $R^1 = R^2 = Pr$
37% overall yield from **3a**
2b ; Ar = Py, $R^1 = Pr$, $R^2 = Bu$
32% overall yield from **3b**
2c ; Ar = Th, $R^1 = R^2 = Pr$
38% overall yield from **3c**

[a] Reagents: (i) For Ar = Ph, Th; *t*-BuLi, PrI. For Ar = Py; Bu(PhS)CuLi.

Scheme 3



Scheme 4



diacetylenes **4a**−**c**, which can be utilized as the terminal unit for synthesizing oligo(arylene enediyne)s.

Using **2a** and **4a** thus prepared, we synthesized conjugated oligomers **5** having alternately a phenyl and an enediyne unit according to essentially the same synthetic method for preparing conjugated oligomers having an enyne scaffold[6] (Scheme 4). Thus, Sonogashira coupling of **2a** with **4a** afforded **5** ($n = 1$) in 93% yield. Treatment of **5** ($n = 1$) with TBAF and Sonogashira coupling of the resulting desilylated compound with **2a** furnished the dimer **5** ($n = 2$) in 79% overall yield, which in turn was converted to the trimer **5** ($n = 3$) by desilylation and coupling with **2a**.

Similarly, oligomers **6** ($n = 1-3$) and **7** ($n = 1-3$), which contain a pyridyl or thienyl group and enediyne units alternately, were synthesized starting from, respectively, **2b** and **4b** and **2c** and **4c** as shown in Scheme 5.

The electronic absorption and fluorescence spectra of the oligo(arylene enediyne)s **5**−**7** thus prepared are summarized in Table 1. It can be seen from Table 1 that, in all cases, the longest-wavelength absorption maxima λ_{max} are bathochromically shifted with increasing conjugation length as expected.[4] While the position of the λ_{max} differs little between the oligomer having a phenyl or pyridyl group as the arylene unit, it shifts about 30 nm to lower energy for the thiophene-containing oligomers **7** in comparison with **5** and **6**, presumably due to the electron-rich character of the thiophene ring.

As reported by Diederich, the oligomers having a phenyl group and an enediyne unit alternately show very intense fluorescence emission. The fact that the oligomers **5** possess somewhat higher fluorescence quantum yield compared with the Diederich oligomer **1** with similar conjugated length seems to be attributable to a heavy-atom effect of the terminal iodine group in **1**. While the fluorescence intensity and the emission maxima of the pyridine-containing oligomer **6** are similar to those of **5**, thiophene derivative **7** shows a weaker but yet intense fluorescence emission with a significantly larger bathochromic shift in the emission maxima compared with **5** and **6**.

Scheme 5

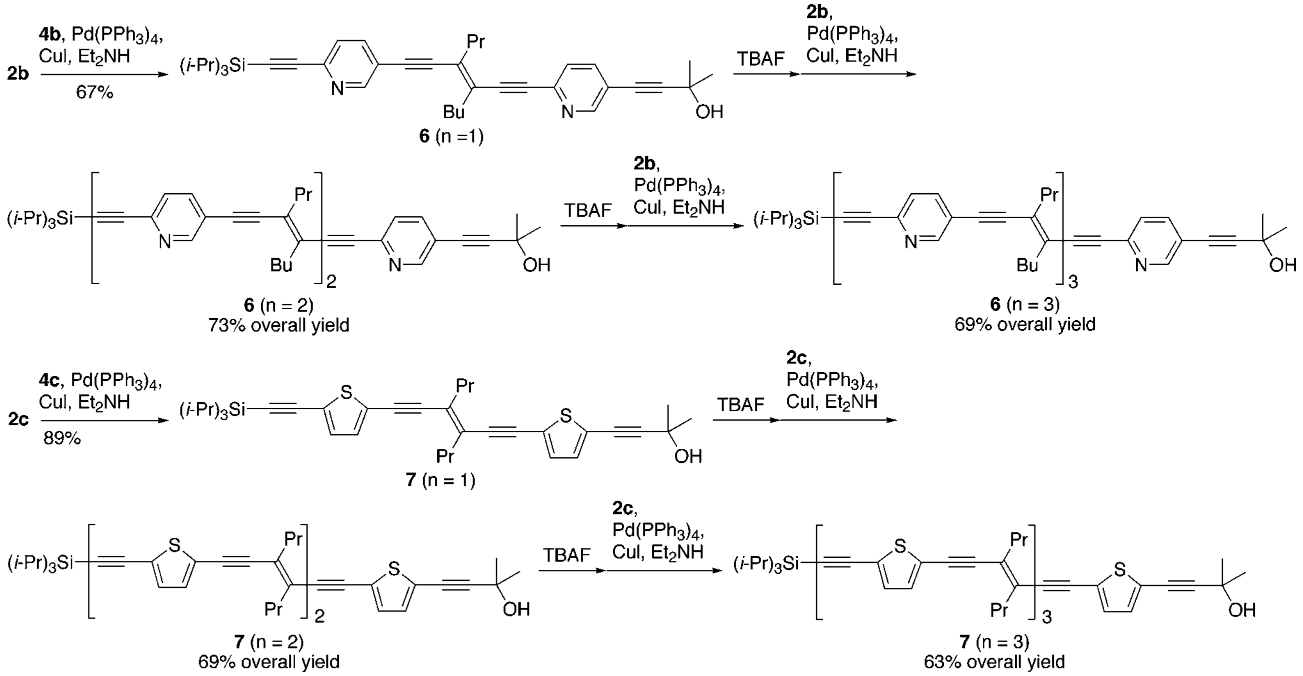


Table 1. Electronic Absorption and Emission Data of Oligo(arylene enediyne)s[a]

oligo(arylene enediyne)s		absorption $\lambda_{\max}$ [nm][b] (ϵ [M^{-1} cm^{-1}][c])	emission	
	n		$\lambda_{\max}$ [nm][d]	Φ_F[e]
5	1	355 (49 000)	398	0.83
	2	379 (91 600)	429	0.85
	3	390 (122 000)	442	0.76
6	1	359 (53 100)	405	0.84
	2	384 (94 200)	436	0.78
	3	394 (158 000)	447	0.81
7	1	385 (23 400)	434	0.58
	2	407 (52 000)	477	0.30
	3	427 (58 200)	494	0.34

[a] Spectra were recorded at room temperature in $CHCl_3$. [b] Longest-wavelength absorption maximum. [c] Molar extinction coefficient. [d] Fluorescence emission maximum. [e] Fluorescence quantum yield, determined by using Quinine sulfate ($\Phi_F = 0.577$) as reference compound.

In conclusion, we have developed a general and efficient method for preparing monodisperse π-conjugated oligomers having aromatic and enediyne units alternately in the backbone. All the oligo(arylene enediyne)s thus synthesized show intense fluorescence emission. Investigation on the utility of these oligomers as organic light-emitting diodes is now in progress in our group.

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Supporting Information Available: Experimental procedures, spectroscopic data, and physical properties of **2**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) (a) Takayama, Y.; Delas, C.; Muraoka, K.; Sato, F. *Org. Lett.* **2003**, *5*, 365−368. (b) Takayama, Y.; Delas, C.; Muraoka, K.; Uemura, M.; Sato, F. *J. Am. Chem. Soc.* **2003**, *125*, 14163−14167.

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