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Novel Fluorophores: Efficient Synthesis and Photophysical Study

Gil Tae Hwang, Hyung Su Son, Ja Kang Ku, and Byeang Hyean Kim*

Center for Integrated Molecular Systems, Department of Chemistry,
Division of Molecular Life Science, Pohang University of Science and Technology,
Pohang 790-784, Korea

bhkim@postech.ac.kr

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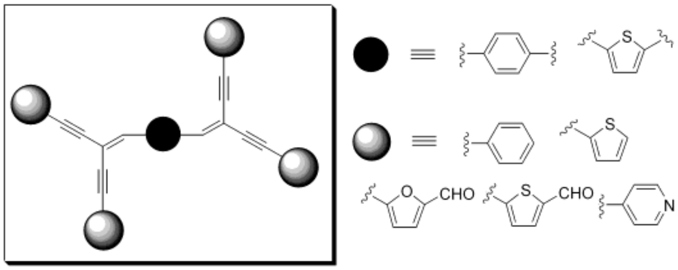
ABSTRACT

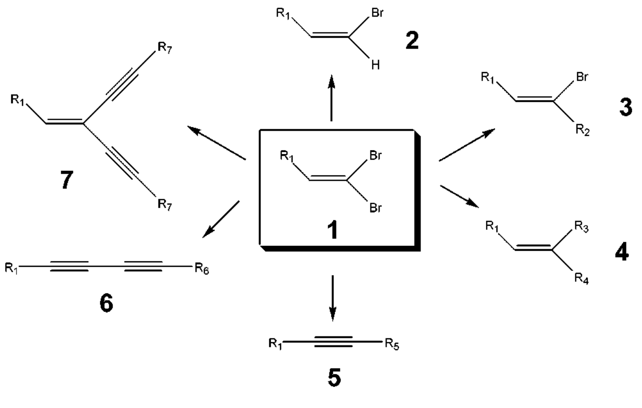


We have synthesized novel fluorophores by using Sonogashira reactions of 1,4-bis(dibromovinyl)benzene and 2,5-bis(dibromovinyl)thiophene with various aromatic bromides. The emission maxima of these fluorophores vary from the indigo blue to the reddish-orange region, depending on the structures of aromatic nuclei and peripheral moieties.

Organic molecules with high photoluminescence efficiencies have recently attracted increasing attention in various research fields as advanced materials for electronic and photonic applications.[1,2] Thus, it is important to synthesize efficiently novel fluorophores that are amenable to further chemical functionalization or modification, which in turn is essential to obtain materials with tunable optoelectronic properties.

1,1-Dibromo-1-alkenes **1** are conveniently prepared by the procedure of Corey and Fuchs.[2] They can be converted to (*Z*)-1-bromo-1-alkenes **2**,[3] (*Z*)-1-aryl(alkenyl)-1-bromo-1-alkenes **3**,[4] 1,1-diaryl(alkenyl)-1-alkenes **4**,[5c] 1-aryl(alkenyl)-1-alkynes **5**,[3,5c] and 1,3-diynes **6**[6] (Scheme 1). However, few studies on the Sonogashira reaction[7] of 1,1-dibromo-1-alkenes have been reported. Furthermore, to the best our knowledge, there is no precedent for the synthesis of fluorophores by using this approach, which may provide

Scheme 1



(R: aliphatic or aromatic groups)

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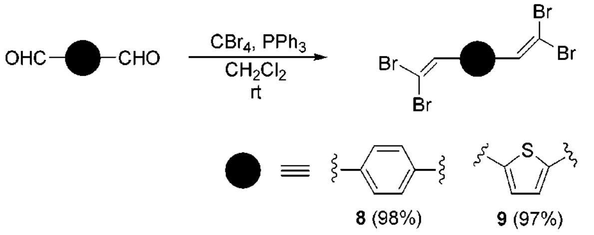
Scheme 2

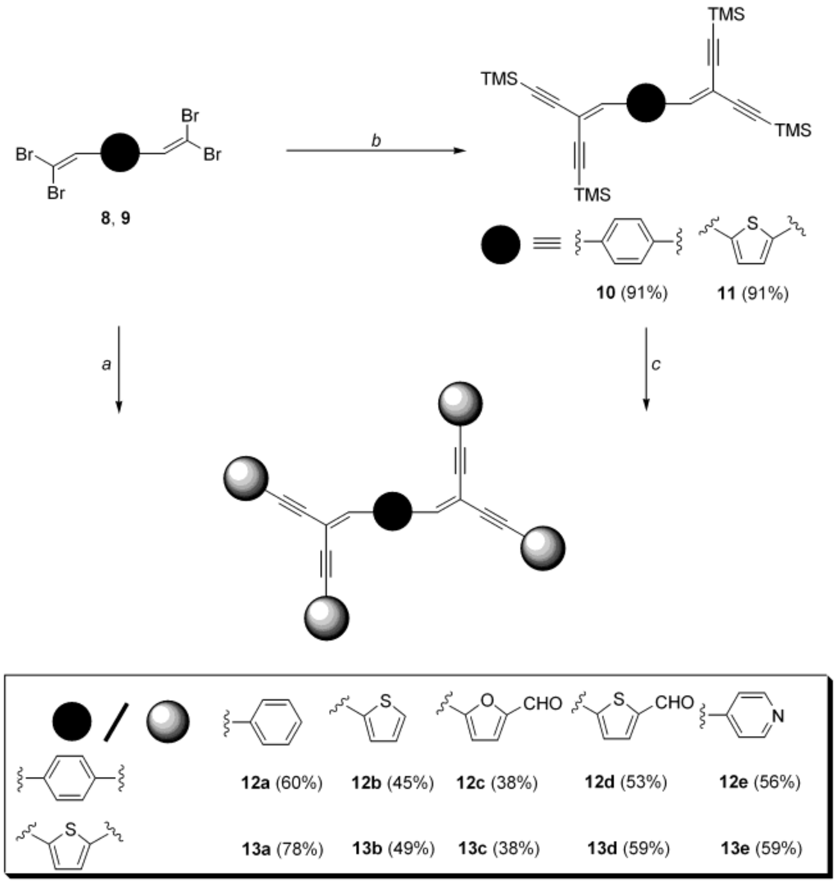


conjugated oligomers and tunable fluorophores through changes in their conjugation length and substitution. Herein, we describe the efficient synthesis of fluorophores via Sonogashira reaction of 1,4-bis(dibromovinyl)benzene **8** and 2,5-bis(dibromovinyl)thiophene **9** (Scheme 2). Treatment of dialdehydes with CBr_4 and PPh_3 under the conditions of Corey and Fuchs[3] gave rise to the dibromo alkenes **8** and **9** in excellent yield. Two complementary methods have been used for the synthesis of fluorophore **12** and **13** (Scheme 3). One is Sonogashira reaction between dibromo alkene **8** or **9** with phenylacetylene (route *a*). Fluorophores **12a** and **13a** were synthesized by this method. The other is modified Sonogashira reaction between TMS-protected tetraalkyne **10** (or **11**) and aromatic bromide (route *b*, *c*).[8] This method consists of in situ liberation of alkyne in the presence of KF from the corresponding TMS-protected compound and coupling with aromatic bromide compounds. Because this approach avoids the TMS deprotection and purification steps, it is highly suitable for coupling of unstable or volatile alkynes. Fluorophores **12b**−**e** and **13b**−**e** were synthesized by this method.

The structures of fluorophores **10**−**13** have been confirmed by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis data.[9] All of the fluorophores **10**−**13** are significantly stable toward air and commonly used organic solvents. The photophysical properties of **10**−**13** in $CHCl_3$ solutions are summarized in Table 1, and their normalized emission spectra are shown in Figure 1.

In the UV−visible absorption spectra, the absorption maxima, ascribed to $\pi-\pi^*$ transition of fluorophores, significantly depend on the central unit of the molecules. A comparison of the absorption maxima of fluorophores **13a**−**e** containing a thiophene nucleus to that of fluorophores **12a**−**e** containing a benzene nucleus shows a substantial red shift. The fluorescence spectra of all fluorophores show two strong

Scheme 3[a]



[a] (*a*) Phenylacetylene, $(PPh_3)_2PdCl_2$, CuI, Et_3N/MeOH, 45−50 °C; (*b*) trimethylsilylacetylene, $(PPh_3)_2PdCl_2$, CuX, Et_3N/MeOH, 45−50 °C; (*c*) ArBr, KF, $(PPh_3)_2PdCl_2$, CuI, Et_2NH/MeOH, 45−50 °C for **12b**, **13b** and Et_3N/MeOH for 45−50 °C for the others, as the CuX, CuI was used for all the fluorophores except **12c** and **13c**, which used CuCl.

Table 1. Photophysical Data of **10**−**13**

compd	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	Φ_F[c]	Φ_F[d]	Φ_F[e]	τ_s[f]
10	412	426, 463	0.01	0.01	0.03	0.6 ± 0.1
12a	416	475, 506	0.19	0.21	0.35	1.2 ± 0.2
12b	438	498, 532	0.29	0.32	0.25	1.6 ± 0.2
12c	450	518, 551	0.10	0.11	0.16	0.6 ± 0.1
12d	456	533, 566	0.08	0.08	0.16	0.8 ± 0.1
12e[g]	420	472, 502	n.d.	n.d.	n.d.	n.d.
11	458	475, 503	0.01	0.01	0.01	0.3 ± 0.1
13a	468	528, 561	0.08	0.09	0.08	0.4 ± 0.2
13b	486	550, 587	0.03	0.03	0.07	0.7 ± 0.2
13c	516	577, 618	0.01	0.01	0.03	0.4 ± 0.1
13d	524	595, 628	0.01	0.01	0.03	0.5 ± 0.1
13e[g]	522	587, 612	n.d.	n.d.	n.d.	n.d.

[a] Only the longest absorption maxima are shown. [b] Emission maximum wavelength excited at the absorption maximum. [c] Quantum efficiencies using quinine sulfate in 1.0 N H_2SO_4 as a standard, λ_{ex} = 366 nm. [d] Quantum efficiencies using 9,10-diphenylanthracene in EtOH as a standard, λ_{ex} = 366 nm. [e] Quantum efficiencies using fluorescein in 0.1 N NaOH as a standard, λ_{ex} = 436 nm. [f] Excited state lifetime (ns) at the emission maximum. [g] Quantum yields are too low to be measured.

emission bands in the visible region. The emission maxima also significantly depend on the aromatic nucleus of the fluorophores and *vary from the indigo blue to the reddish-orange region*. Fluorophores **12** and **13** show a large Stokes shift of about 50−110 nm when compared to the less conjugated fluorophores **10** and **11**. These dramatic emission patterns of fluorophores **12a**, **12d**, **13a**, and **13d** are visualized in Figure 2. The fluorescence quantum yields (Φ_F) of the fluorophores were determined in $CHCl_3$ using quinine sulfate, 9,10-diphenylanthracene, and fluorescein as standards.[10] Fluorophores **12a** and **12b** have a moderate quantum yield and the longest fluorescence lifetime (τ_s) among all the fluorophores, which provides information about the influence of the nature of the substituent and the photophysical property of the fluorophores.

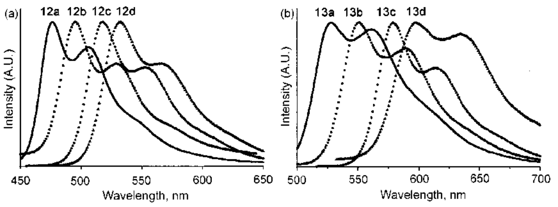


Figure 1. Normalized fluorescence emission spectra of (a) **12** and (b) **13** in $CHCl_3$ at room temperature. Emission spectra were obtained upon excitation at the absorption maximum.

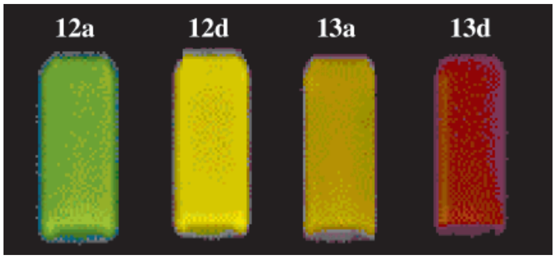


Figure 2. Emissive **12a**, **12d**, **13a**, and **13d**.

In summary, we have synthesized novel fluorophores via Sonogashira reactions of 1,4-bis(dibromovinyl)benzene **8** and 2,5-bis(dibromovinyl)thiophene **9** with different aromatic bromides. Dramatic absorption and emission spectral changes show that they can be used as tunable fluorophores. These unique properties of fluorophores are of interest for electronic and photonic applications. On the basis of the results obtained so far, we are currently designing and synthesizing novel fluorophores with higher quantum yield, and investigation of the electronic properties of fluorophores is currently under way in our laboratory.

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Supporting Information Available: Synthetic details and characterization data of fluorophores **10**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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