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Synthesis and characterization of unsymmetrical phenylene–ethynylene trimers and tetramers with different chromophores as blue-light-emitters

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ABSTRACT

A series of highly fluorescent *p*-phenylene–ethynylene π-conjugated oligomers (trimers and tetramers) with different chromophore substituents have been synthesized stepwise under oxygen-free Sonogashira conditions. The emission wavelengths range from 400 to 455 nm for the series. All four trimers and tetramers have visible blue emission under sunlight especially for the case of the pyrene-substituted trimer and tetramer. All oligomers also exhibit very high quantum yields (0.9–1.1), which suggest that these types of compounds could be used as blue-light-emitters.

Phenylene–ethynylene-conjugated linear materials have attracted much interest in recent years, for example as potential molecular wires. Also significant progress has been made in the application of this type of organic compound for fabricating organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), solar cells, and chemosensors.[1] The study of conjugated organic polymers in general is popular since polymers often possess good mechanical properties and are easily processable;[2] however, the investigation of phenylene–ethynylene conjugated oligomers is specifically attractive due to their well-defined structures, high purities, and freedom from structural defects.[3] In contrast, phenylene–ethynylene polymers usually do not have well-defined structures; they are often polydisperse and contain some diyne units,[4] which disturb the conjugation and adversely affect the polymers' solubilities and optical properties. In addition, for oligomers the fine-tuning of emission wavelengths and the study of structure–optical property relationships can be achieved by adding additional repeat units or by introducing different chromophores as the end units of the conjugated system.[5] For example, conjugated oligomers with defined lengths containing various fluorescent chrompohores have been synthesized and used as functional components of organic electronic devices.[6]

In this Letter, we describe the synthesis of phenylene–ethynylene linear trimers and tetramers with different fluorescent chromphores as end groups. Chemical structure–optical property relationships (emission maxima and efficiencies) are presented in this work.

In order to synthesize linear trimers and tetramers with different chromophores as end units, it is first necessary to synthesize unsymmetrical mono-iodo-substituted key compounds. The synthesis of phenylene–ethynylene trimers 3a–d is shown in Scheme 1. Ethynylbenzene was coupled with an excess of 1, 4-dibutoxy-2, 5-diiodobenzene to give mono-iodo-substituted compound 2, followed by coupling with various terminal alkynes a through d to afford unsymmetrical trimers 3a–d. For the synthesis of tetramers as shown in Scheme 2 the previously synthesized terminal alkyne, 1, 4-dibutoxy-2-ethynyl-5-(phenylethynyl) benzene, was coupled with an excess of 1, 4-dibutoxy-2, 5-diiodobenzene to make mono-iodo oligomer 5, which was then reacted with various terminal alkynes a through d to yield tetramers 6a–d. The yields for products 3a–d and 6a–d decrease with increasing size of the aromatic group on the terminal alkyne, despite the use of oxygen-free Sonogashira coupling conditions. Thus, it is observed that terminal alkynes with larger substituent groups contribute to higher proportions of homo-coupling products. In addition, even when n-butyl groups are introduced into the conjugated system, the resulting oligomers' solubilities still decrease with increasing conjugation length. For example, the solubility of tetramers with four n-butyl groups is lower than for the corresponding trimers with two n-butyl groups. This means that any increase in solubility due to the butyl groups cannot offset the decrease in solubility due to the increased rigid-rod conjugation length. It is concluded that even with butoxy chains on all central units, this series of phenylene–ethynylene oligomers will become completely insoluble when the conjugated system reaches some critical length.

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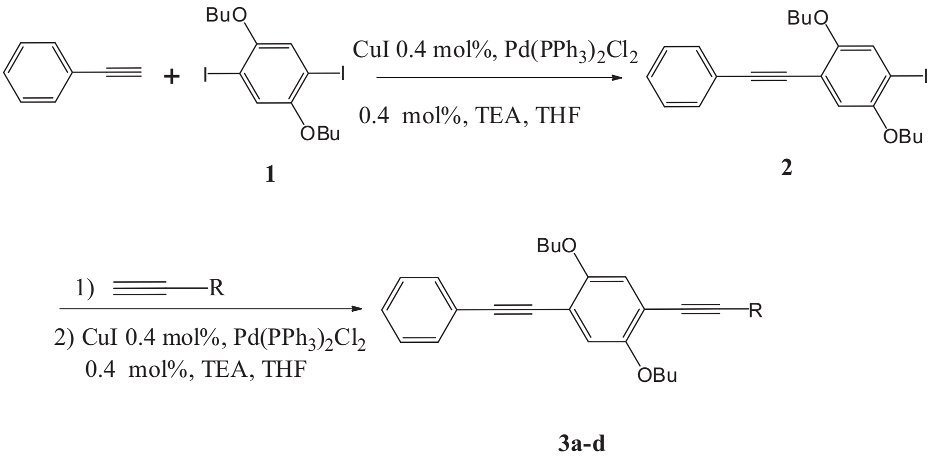
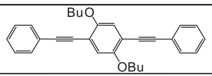
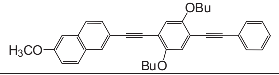
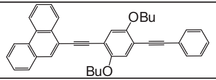
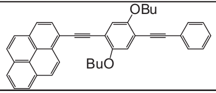
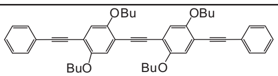
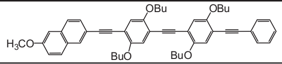
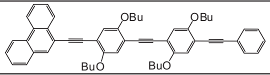
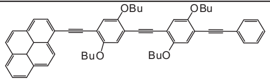
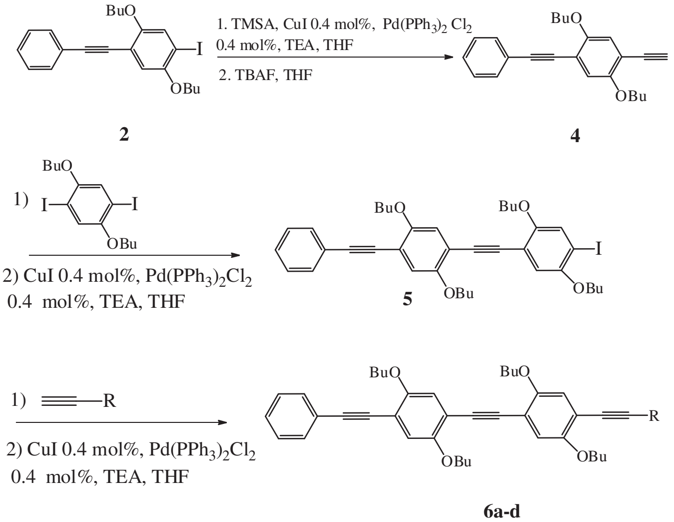


Scheme 1. Synthesis of phenylene–acetylene trimers with various fluorescent chromophores.

Entry	Product **3a-d**	Yield
3a		97%
3b		92%
3c		85%
3d		70%

Entry	Product **6a-d**	Yield
6a		95%
6b		90%
6c		86%
6d		68%



Scheme 2. Synthesis of phenylene–acetylene tetramers with various fluorescent chromophores.

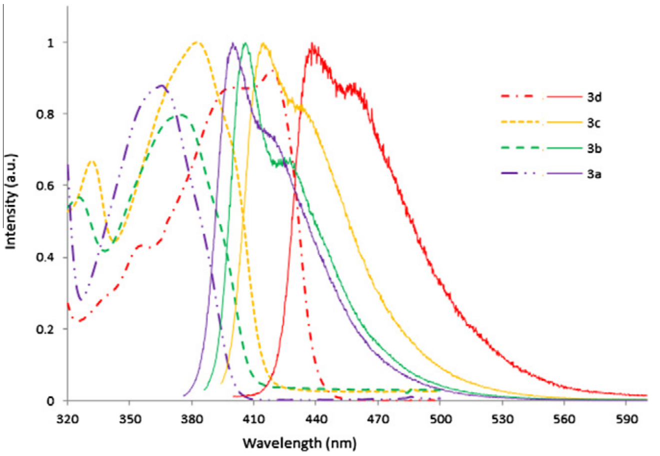


Figure 1. UV–vis and fluorescence spectra of trimers **3a**–**d** in CH_2Cl_2 solution. The dashed line represents the UV–vis spectrum and the solid line represents the fluorescence spectrum.

Absorption and emission spectra of the oligomers **3a–d** shown in Figure 1 have been measured in dichloromethane. The oligomers exhibit significant conjugation-dependent UV/vis bathochromic shifts in their absorption spectra. For example, the absorption maxima of trimers **3a–d** are 366, 374, 384, and 418 nm, respectively. This series of oligomers exhibits the same red shift trend in their emission maxima, with **3a** (benzene end group) emitting at 400 nm, and **3d** (pyrene end group) emitting at 438 nm, as shown in Figure 1. A shoulder on right of the emission peaks for all four oligomers **3a–d** indicates that there could be a relaxation of these series of compounds from the high energy excited state to a lower energy excited state preceding emission; this relaxation appears more subdued in the spectra of **6a–d**.

The absorption spectra for **6a–d** are shown in Figure 2 (dashed line). For tetramers **6a–d** (as chromophores vary from benzene to pyrene), the absorption peaks shift gradually from 390 nm to

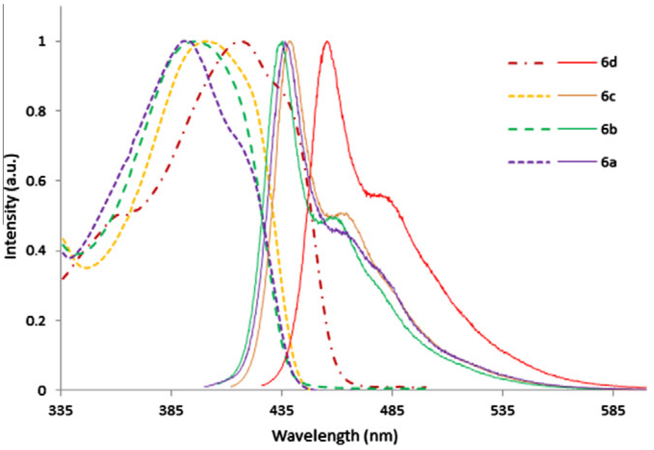


Figure 2. UV–vis and fluorescence spectra of tetramers **6a–d** in CH_2Cl_2 solution. The dashed line represents the UV–vis spectrum and the solid line represents the fluorescence spectrum.

Table 1
Spectroscopic data for oligomers **3a–d** and **6a–d** in CH_2Cl_2 solution

Oligomer	$\lambda_{\max}$ (nm)	λ_{em} (nm)	Stokes shift (nm)	Φ_f
3a	366	400	34	0.97
3b	374	406	32	0.93
3c	384	415	31	1.08
3d	418	438	20	0.97
6a	390	436	46	0.91
6b	396	435	39	1.15
6c	402	439	37	1.04
6d	416	455	39	1.00

416 nm. In addition, tetramers' absorption maxima display red shifts compared to their corresponding trimers, except for tetramer **6d** which has approximately the same absorption maximum as trimer **3d**. A comparison of the absorption maxima of tetramers with those of trimers indicates that repeat-unit dependent red shifts become smaller as chromophores become more conjugated. Thus, as shown in Table 1, the red shift is 24 nm for **3a**–**6a**, 22 nm for **3b**–**6b**, 16 nm for **3c**–**6c**, and 2 nm for **3d**–**6d**.

As for samples **3a**–**3d**, the emission maxima also shift to longer wavelengths from **6a**–**6d**. (Fig. 2). The main emission peak is at approximately the same position for oligomers **6a**, **6b**, and **6c**, but **6b** and **6c** have higher quantum yields than **6a**. In contrast, while the absorption maxima for **3d** and **6d** are nearly the same, the emission maximum for **6d** is at a longer wavelength (455 nm) than that of **3d** (438 nm), probably because of the more subdued influence of relaxation from the high energy excited state to a lower energy excited state preceding emission.

In summary, a series of sp–sp^2-conjugated oligomers including more than 10 new compounds with phenylene–ethynylene backbones were synthesized. Their UV–vis absorption and fluorescence emission spectra show red shift trends consistent with the theory. Optical properties of these oligomers can be tuned by introducing a variety of fluorescent chormophores and by adding repeat units. Their high quantum yields for emission of blue light under ambient conditions make these oligomers interesting technologically. The oligomer with the pyrene chromophore and more repeating units has the best emission efficiency as a blue-light-emitter.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.01.076.

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