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Highly Emissive π-Conjugated Alkynylpyrene Oligomers: Their Synthesis and Photophysical Properties

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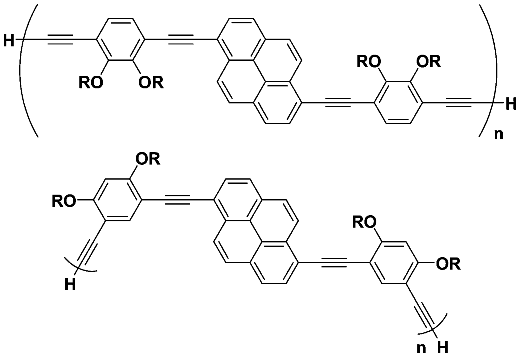

We newly prepared *para*- and *meta*-linked alkynylpyrene oligomers and examined their photophysical properties. Oligomerization of monomeric building blocks was performed by Cu^{I}-promoted oxidative coupling reaction. The resulting oligomers mainly consist of 2-mer to 6-mer that were assigned on the basis of MALDI-TOF mass spectra, and the 2-mer, 3-mer, and 4-mer were isolated and fully characterized. From their absorption and fluorescence spectra, the *para*-linked oligomers were found to be somewhat π-conjugated compared with *meta*-linked ones, and the fluorescence quantum yields decreased with increasing oligomer length ($\Phi_f = 0.79-0.55$).

Size-regulated oligomers sometimes give prospective information for chemical and physical features of the corresponding longer polymers made of the same monomeric building blocks.[1,2] Among the oligomers, π-conjugated ones have been noted for their electrical and optical characteristics, so that the oligomers and polymers have been used for such applications as organic electroluminescent devices[3] and chemical sensors.[4] In designing π-conjugated oligomers, an acetylenic bond is preferably used as a linkage between aromatic nuclei because of its linearity and synthetic advantages.[5] A number of π-conjugated oligomers with acetylene linkers possess benzene,[3b,6] naphthalene,[7] thiophene,[8] and porphyrin[9] as a conventional core. To expand the practicality of π-conjugated oligomers, developments of a new class of π-conjugated oligomers bearing a variety of aromatics are important.

Pyrene and its derivatives have been extensively applied to photonic devices[10] and biological probes[11,12] by virtue of their inherent and novel photophysical characteristics. Thus, pyrene is a fascinating core in fluorescent π-conjugated oligomers and polymers.[13] However, serious drawbacks exist in the photophysical properties of pyrene, which include the relatively short absorption wavelength, the substantial quenching of its fluorescence by the presence of oxygen,[14] and the low fluorescence

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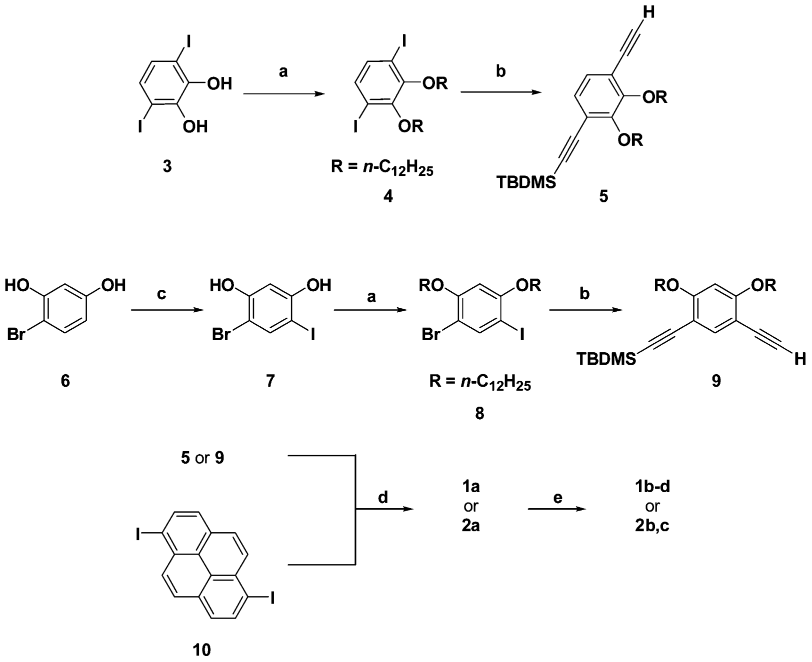
SCHEME 1. Synthetic Schemes for 1a−d and 2a−c[a]



[a] Reagents and conditions: (a) n-$C_{12}H_{25}OH$, DEAD, PPh_3, THF, rt, 1 h; (b) (i) 2-methy-3-butyn-2-ol, $Pd(PPh_3)_4$, CuI, Et_3N, 80 °C, 15 h for **4**, 4 h for **8**, (ii) (*tert*-butyldimethylsilyl)acetylene, $Pd(PPh_3)_4$ for **4**, Pd(*tert*-$Bu_3P)_2$ for **8**, CuI, Et_3N, 80 °C, 2.5 h, (iii) NaH, toluene, reflux, 30 min for **4**, 1.5 h for **8**; (c) ICl, ether, rt, 1 h; (d) (i) $Pd(PPh_3)_4$ for **5**, Pd(*tert*-$Bu_3P)_2$ for **9**, CuI, morpholine, 110 °C, 4 h, (ii) n-Bu_4NF, THF, H_2O, rt, 5 min; (e) CuCl, O_2, TMEDA, THF, acetone, rt, 1 h. DEAD = diethyl azodicarboxylate, THF = tetrahydrofuran, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

quantum yields.[15] Recently, we synthesized various alkynylpyrenes and found that the introduction of alkynyl groups into pyrene nuclei induced effective extension of π-conjugation and a large increase of fluorescence intensities compared with the parent pyrene.[12e] Furthermore, the alkynylpyrenes almost maintain their fluorescence intensities even under aerated conditions, giving rise to an additional useful feature for practical uses. Taking these features into account, we herein report the synthesis and photophysical properties of new acetylene-linked π-conjugated oligomers based on alkynylpyrene skeletons.

Figure 1 shows the chemical structures of alkynylpyrene oligomers **1** and **2**. The monomeric building blocks of the oligomers, **1a** and **2a**, are made up of a pyrene core and two diethynylbenzene derivatives. The structural difference between **1a** and **2a** is the linkage position of terminal acetylene groups on the benzene rings, i.e., *para* for **1a** and *meta* for **2a**. Long alkyl side chains were introduced on the benzene rings to make the alkynylpyrene-based oligomers soluble in common organic solvents. Monomeric building blocks **1a** and **2a** were synthesized by repeating the Sonogashira[16] and deprotection reactions starting from **3**[17] and **6**,[18] respectively. Each oligomer was obtained from the corresponding monomeric building blocks by using a CuCl-TMEDA-promoted oxidative coupling reaction (Scheme 1). In this reaction, the 2-mer (**1b** and **2b**), 3-mer (**1c** and **2c**), and 4-mer (**1d**) were mainly formed, which were separated by recycling preparative gel permeation chromatography (GPC) with $CHCl_3$ as an eluent.

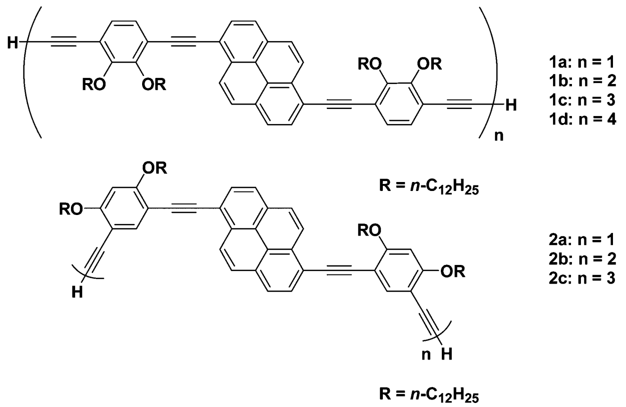


FIGURE 1. Alkynylpyrene oligomers **1a−d** and **2a−c**.

The optical properties of the oligomers were investigated by using $CHCl_3$ as a solvent. When the concentrations of **1a**, **1c**, **2a**, and **2c** were varied, the absorbances at their absorption maxima (λ_{max}) obeyed Beer's law at $\leq 2.0 \times 10^{-5}$ M (Figures S1A and S1B in Supporting Information). Thus, the chromophore aggregation was negligible below that concentration. The electronic absorption spectra of **1a−d** and **2a−c** in $CHCl_3$ are shown in Figure 2. The absorption maximum and its coefficient (log ϵ) of the monomeric building block **1a** are 436 nm and 4.84, respectively (Figure 2a). The absorption maxima of **1b−d** consecutively shifted to longer wavelengths, and their absorption coefficients increased with increasing of oligomer length. The 4-mer **1d** has an absorption maximum at 454 nm,

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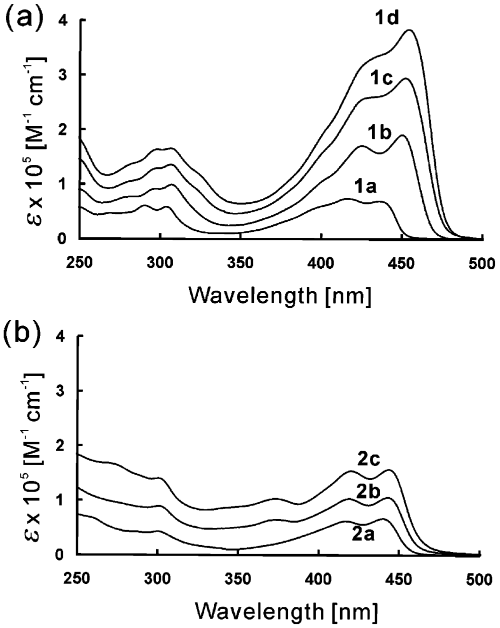

FIGURE 2. Electronic absorption spectra of (a) **1a**−**d** and (b) **2a**−**c** in $CHCl_3$.

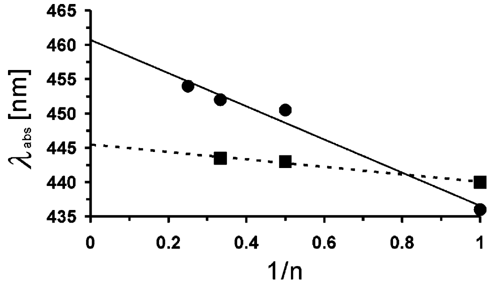

FIGURE 3. Absorption maxima of oligomers **1a**−**d** (circles and solid line) and **2a**−**c** (squares and dashed line) plotted against reciprocal chain length and fitted linearly.

revealing that the magnitude of the bathochromic shift from **1a** to **1d** is ca. 18 nm. In the case of the *meta*-linked oligomers, only a slight bathochromic shift was observed probably because of partial insulation of the π-conjugation on these oligomers (Figure 2b). To anticipate the absorption maxima of the corresponding polymers, each λ_{max} of the oligomers was plotted against the reciprocal chain length 1/*n* (Figure 3).[1b] Although both oligomers have a linear relationship between λ_{max} and 1/*n*, the slope for the *para*-linked oligomers is steeper than that for *meta*-linked ones. In the *para*-linked oligomers, the theoretical absorption maximum for infinite chain length is ca. 460 nm, where the *para*-linked polymers of enough length may absorb. However, the bathochromic shift of the *para*-linked oligomers is not so large possibly because of easy rotation of the benzene ring with respect to the pyrene core.[19] Nevertheless, this finding indicates that the *para*-linkage is preferable for the π-conjugation on alkynylpyrene-based oligomers.

The fluorescence spectra of the oligomers were measured in degassed $CHCl_3$ (Figure 4). In all of the spectra, two strong emission bands are seen in the visible region. The emission maxima of the *para*-linked oligomers **1a**−**d** consecutively shifted to longer wavelengths, in a manner similar to their absorption maxima. On the other hand, the fluorescence spectra for the *meta*-linked oligomers **2a**−**c** scarcely varied in agreement with the electronic absorption spectra. The fluorescence quantum yields (Φ_f) and fluorescence lifetimes (τ_s) of the oligomers were measured in degassed $CHCl_3$ and THF (Table 1). The Φ_f values of the monomers **1a** and **2a** are very high in both the solvents, although the values of the oligomers somewhat decreased, especially for the *meta*-linked ones. Fluorescence quantum yields can be described by the equations $\Phi_f = k_f\tau_s$ and $\Phi_f = k_f/(k_f + k_{isc} + k_{nr})$ under the degassed conditions, in which k_f, k_{isc}, and k_{nr} represent the rate constants for fluorescence radiation, intersystem crossing, and nonradiative decay, respectively. From the experimental values of Φ_f and τ_s, we calculated the values of k_f and $k_{isc} + k_{nr}$. As can be seen in Table 1, the k_f values of the *para*-linked oligomers decrease with increasing oligomer length. The longer the length of the oligomer, the more flexible the structure becomes. Thus, in the longer oligomers, intersystem crossing and nonradiative decay processes might to some extent compete with the fluorescence radiation process. This situation will be responsible for the relationship between the observed Φ_f values and the oligomer lengths. Nevertheless, the oligomers indeed possess high fluorescence quantum yields, and only slight quenching of the fluorescence occurred even under aerated conditions,[22] as in the cases for simple alkynylpyrenes previously

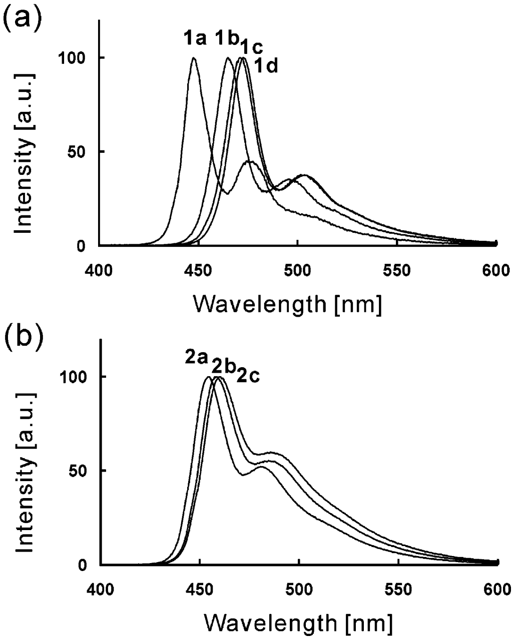

FIGURE 4. Normalized fluorescence spectra of (a) **1a**−**d** and (b) **2a**−**c** in $CHCl_3$ (1.0×10^{-6} M). Excitation wavelength was 436, 451, 452, and 454 nm for **1a**−**d** and 440, 443, and 444 nm for **2a**−**c**, respectively.

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(19) Computational modeling was performed by DFT calculation in order to examine the π-conjugation of the *para*-linked oligomers. The two OR groups on the benzene ring can exist in two conformers, *syn* and *anti*, against the pyrene plane of the oligomers. We assumed that the free rotation of the pyrene and benzene planes on the oligomers may influence the π-conjugation. The structures of the *para*-linked oligomers were simplified as **15**−**18** shown in Supporting Information to make geometry optimization uncomplicated. The ZPE difference between the *syn* and *anti* conformers was calculated to be ≤2.4 kJ/mol on the basis of B3LYP/6-31G(d) level optimized structure. Furthermore, rotational barriers were estimated based on RHF/3-21G(d) level optimized structure (data not shown). The rotational barriers were also very small (*syn* to *anti*, 12 kJ/mol; *anti* to *syn*, 3.1 kJ/mol), implying that the pyrene and benzene planes can easily rotate on the oligomers at room temperature.

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TABLE 1. Photophysical Data of 1a−d and 2a−c[a]

	absorption[b]		fluorescence					
compound	λ_{abs} (nm)	log ϵ (M^{-1} cm^{-1})	$\lambda_{em}{}^{c}$ (nm)	$\Phi_f{}^{d}$ (CHCl$_3$)	$\Phi_f{}^{d}$ (THF)	$\tau_s{}^{e}$ (ns)	$k_f{}^{f}$ ($\times 10^8$) (s^{-1})	$k_{isc} + k_{nr}{}^{f}$ ($\times 10^8$) (s^{-1})
1a	436	4.84	448	0.74	0.79	0.98	8.06	2.14
1b	451	5.28	465	0.67	0.68	1.33	5.11	2.41
1c	452	5.47	470	0.62	0.64	1.48	4.32	2.44
1d	454	5.58	473	0.55	0.55	1.35	4.07	3.34
2a	440	4.82	455	0.70	0.75	1.52	4.93	1.65
2b	443	5.02	459	0.56	0.61	1.11	5.50	3.51
2c	444	5.19	461	0.35	0.44	1.51	2.91	3.71

[a] All measurements were performed under degassed conditions. [b] 1.0×10^{-6} M in CHCl$_3$, λ_{abs} is the absorption band appearing at the longest wavelength. [c] 1.0×10^{-6} M in CHCl$_3$, λ_{em} is the fluorescence band appearing at the shortest wavelength. [d] Fluorescence quantum yield, determined by using 9,10-diphenylanthracene ($\Phi_f = 0.95$ in EtOH)[20] and coumarin102 ($\Phi_f = 0.74$ in EtOH)[21] as reference compound. [e] Fluorescence lifetime, measured at 1.0×10^{-6} M in THF. [f] Calculated by the following equations: $\Phi_f = k_f\tau_s$ and $\tau_s = 1/(k_f + k_{isc} + k_{nr})$.

reported by us.[12e] These findings encouraged us to apply the corresponding polymers as novel electric and photonic materials.

In conclusion, we have developed π-conjugated oligomers based on bis(phenylethynyl)pyrene skeletons. The *para*-linked oligomers showed longer absorption wavelengths and intense fluorescence emissions. These fascinating properties of the alkynylpyrene-based oligomers will facilitate the synthesis of alkynylpyrene polymers and the application to new optical devices. Introduction of extra recognition sites for biological species into our oligomers is also under consideration in order to develop novel chemical sensors.

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Supporting Information Available: Experimental details for the syntheses and analyses, Figures S1A and S1B, ^{1}H NMR spectra, and details of the calculations for **15−18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Integrations of the fluorescence spectra of **1a**−**d** in aerated THF showed that 94%, 93%, 88%, and 85% of the levels observed from the corresponding carefully degassed solutions were maintained, respectively.