

## Oxidative Cyclization of Bis(biaryl)acetylenes: Synthesis and Photophysics of Dibenzo[*g,p*]chrysene-Based Fluorescent Polymers

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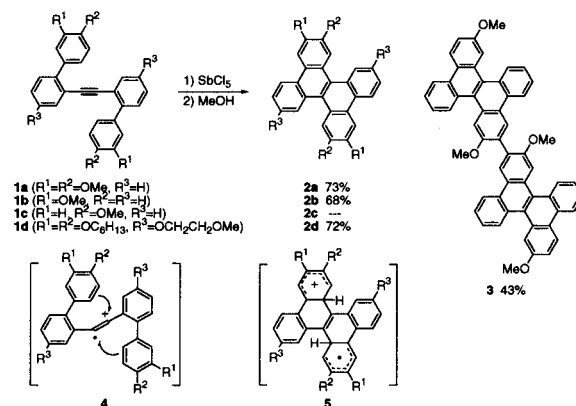
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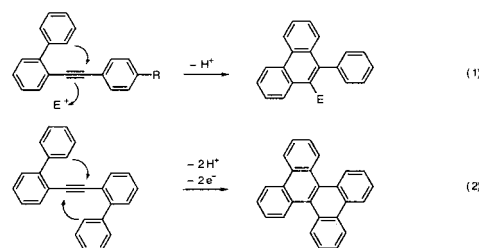
Annulation of  $\pi$ -conjugated frameworks has proved to be an effective way to enhance conjugation in  $\pi$ -conjugated polymers by eliminating conformational disorder. Upon the basis of this approach a number of ladder polymers having small band gaps and intense fluorescence have been developed.<sup>1–3</sup> Similarly isolated fused polycyclic aromatics also serve as attractive building units.<sup>4</sup> Considering their rigid structures and symmetrically forbidden or weakly allowed transitions,<sup>5</sup> the incorporation of these units into  $\pi$ -conjugated main chains would realize unique fluorescence properties such as small Stokes shifts and extended excited-state lifetimes. These features may allow for long-range, through-bond exciton migration, a key requisite for amplified sensing of ultra-trace analytes such as 2,4,6-trinitrotoluene (TNT),<sup>6</sup> using the molecular-wire approach.<sup>7,8</sup> As a proof of this concept, we have recently reported investigations of a series of triphenylene-based polymers.<sup>9</sup> As an extension, we have been interested to incorporate dibenzo[*g,p*]chrysene, recognized as a benzeno-annulated stilbene, into conjugated polymers. However, the conventional routes to this skeleton have been limited to only a few types of classical syntheses.<sup>10</sup> We report herein a conceptually new oxidative acetylene cyclization method that provides a facile and versatile route to dibenzo[*g,p*]chrysenes and a demonstration of the utility of the chromophore in the design of novel  $\pi$ -conjugated polymers.

Our group has previously reported powerful routes to fused polycyclic aromatics as shown in eq 1, where the electrophilic 6-endo mode cyclization directed by electron-donating substituents provides a variety of phenanthrene derivatives.<sup>11</sup> To construct a

Scheme 1



dibenzo[*g,p*]chrysene skeleton, we have extended this scheme to a double intramolecular cyclization as shown in eq 2. The



difficulty of this type of cyclization was how to achieve the doubly selective 6-endo mode cyclization. Our strategy was to oxidize the acetylene moiety, which may change the hybridization of the acetylene carbons from  $sp$  to  $sp^2$ , facilitating the subsequent electrophilic and radical cyclization in 6-endo mode. We find that this unusual cyclization proceeds well with the use of  $SbCl_5$  as an oxidant,<sup>12</sup> as shown in Scheme 1.

The addition of 1.5 mol amount of  $SbCl_5$  (1.0 M  $CH_2Cl_2$  solution) to a  $CH_2Cl_2$  solution of bis(biaryl)acetylene **1a** at room temperature immediately produced a deep purple solution. Quenching the reaction with methanol followed by chromatography gave the desired dibenzo[*g,p*]chrysene derivative **2a** in 73% yield.<sup>13</sup> Considering the optimized stoichiometry of  $SbCl_5$  as an oxidant,<sup>12</sup> the principle skeleton-forming reaction likely proceeds by a one-electron oxidation. Other one-electron oxidants such as  $FeCl_3$  and  $NOSbF_6$  also produced **2a** but resulted in lower yields (21 and 50%, respectively). As for other substrates, dimethoxy-substituted **1b** also underwent this cyclization to give a desired product **2b** in good yield. However, the use of **1c** with isomeric methoxy groups afforded an unexpected dimerized product **3** as the sole characterizable product (vide infra).

Considering our observations, a plausible mechanism of the present cyclization involves a one-electron oxidation of the diphenylacetylene moiety of **1** to form the acetylene cation radicals **4**. Subsequent electrophilic and radical cyclization with the biaryl moieties produces radical cation intermediate **5**. A PM3 calcula-

(12)  $SbCl_5$  is an excellent oxidant for the preparation of aromatic cation radicals according to the following equation:  $2Ar + 3SbCl_5 \rightarrow 2Ar^{+\bullet} + SbCl_6^- + SbCl_3$  (b) Matuura, A.; Nishinaga, T.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 10007. (c) Blomgren, G. E.; Kommandeur, J. *J. Chem. Phys.* **1961**, *35*, 1636.

(13) X-ray crystal structural analysis of **2a** has revealed its significantly twisted structure. For the detail, see the Supporting Information. A similar structure has been reported for parent dibenzo[*g,p*]chrysene: Herbstein, F. H. *Acta Crystallogr.* **1979**, *B35*, 1661. Despite this twisted structure, the dibenzo[*g,p*]chrysene monomer **2** and polymers **7** still have high fluorescence quantum yields.

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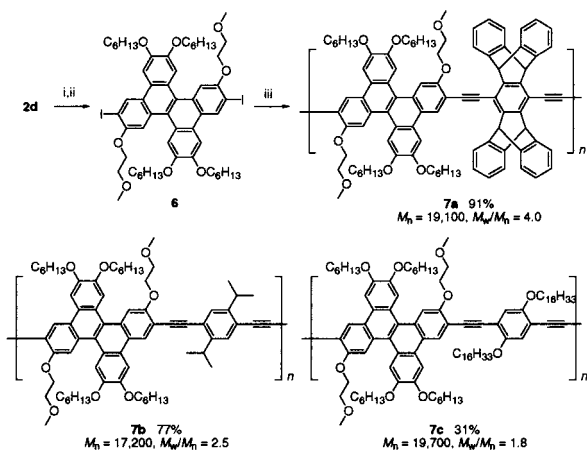
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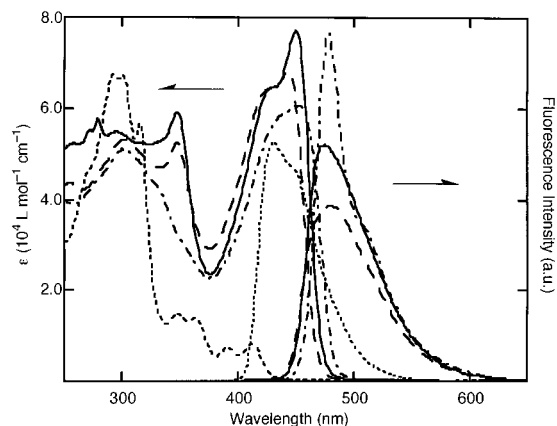
Scheme 2<sup>a</sup>

<sup>a</sup> Reagents and conditions: i) *t*-BuLi, Et<sub>2</sub>O, rt; ii) ICH<sub>2</sub>CH<sub>2</sub>I, -78 °C; iii) appropriate diethynylarene, Pd(PPh<sub>3</sub>)<sub>4</sub>/CuI, toluene/*i*-Pr<sub>2</sub>NH.

tion showed that the highest occupied molecular orbital of **1** is localized on the central diphenylethyne, suggesting that the initial oxidation occurs at this moiety. The formation of the radical cation **5** is supported by the exclusive formation of dimer **3** in the case of **1c** which has no substituents at the R<sup>1</sup> positions. This scheme represents a new approach to polycyclic aromatic compounds, and this reaction is, to our knowledge, the first example of an oxidative acetylene cyclization. However, if this reaction is considered as an acetylene-extended version of oxidative aryl-aryl coupling for the biaryl synthesis,<sup>14</sup> an alternative mechanism involving the oxidation of one of the biaryl moieties followed by the cascade electrophilic or radical cyclization to form **5** is possible.

To incorporate the dibenzochrysenes into  $\pi$ -conjugated polymer chain, we need to introduce reactive functional groups into its skeleton. The introduction of an ortho-directing group for lithiation affords the functionalized dibenzochrysenes as shown in Scheme 2. Thus, 2-methoxyethoxy-substituted dibenzochrysenes **2d** prepared by the above cyclization was dilithiated using *tert*-BuLi followed by the treatment with 1,2-diiodoethane to give diiododibenzochrysenes **6** in 47% yield. Novel  $\pi$ -conjugated polymers **7** are synthesized as air-stable yellow solids by Pd/Cu-catalyzed cross-coupling reactions<sup>15</sup> of **6** with diethynylbenzene monomers, including a diethynylpentiptycene monomer recently developed for TNT sensing.<sup>6ab</sup>

The dibenzochrysenes-based polymers **7** are highly fluorescent and their spectra are shown in Figure 1 and summarized in Table 1 together with the data for monomer. Monomeric dibenzochrysenes show their longest absorption maxima around 390–412 nm with moderate intensity and the polymers exhibit intense absorption maxima around 444–453 nm. The red-shift from monomer **2d** to polymers **7** and the significant increase in molar extinction coefficients suggest an extension of  $\pi$ -conjugation along the polymer main chain. In the fluorescence spectra, the polymers show intense emission bands around 474–480 nm with high quantum yields comparable to those of monomeric compounds **2**.<sup>13</sup> These polymers show small Stokes shifts of only 24–36 nm



**Figure 1.** UV-vis absorption spectra and fluorescence spectra of dibenzo[*g,p*]chrysenes monomer and polymers: **2d** (dotted line), **7a** (solid line), **7b** (broken line), **7c** (broken-dotted line).

**Table 1.** Photophysical Data for Dibenz[*g,p*]chrysenes Derivatives and Polymers<sup>a</sup>

compd	UV-vis absorption		fluorescence	
	$\lambda_{\max}/\text{nm}^b$	$\log \epsilon$	$\lambda_{\max}/\text{nm}^c$	$\Phi_f^d$
<b>2a</b>	397	3.63	415	0.24
<b>2b</b>	394	3.73	423	0.30
<b>2d</b>	412	3.91	431	0.29
<b>7a</b>	450	4.89 <sup>e</sup>	474	0.31
<b>7b</b>	444	4.83 <sup>e</sup>	480	0.25
<b>7c</b>	453	4.78 <sup>e</sup>	478	0.35

<sup>a</sup> In dichloromethane. <sup>b</sup> Only the longest  $\lambda_{\max}$  are given. <sup>c</sup> Excited at the absorption maximum wavelengths. <sup>d</sup> Determined with quinine sulfate as a standard. <sup>e</sup> Per monomer unit.

despite the involvement of the phenylene-vinylene structure in the  $\pi$ -conjugated framework. Most importantly, these polymers have considerably longer fluorescence lifetimes (**7a**, 2.5 ns; **7b**, 2.6 ns; **7c**, 1.4 ns) than the subnanosecond lifetimes typical of  $\pi$ -conjugated polymers such as poly(*p*-phenyleneethynylene)s and poly(*p*-phenylenevinylene)s.

In summary, we report a new oxidative cyclization method to dibenzo[*g,p*]chrysenes and demonstrate their utility in the synthesis of novel  $\pi$ -conjugated polymers. The polymers thus prepared show attractive fluorescence properties such as high quantum yields, small Stokes shifts, and long excited-state lifetimes. These features make them promising candidates for sensory applications. As an initial proof of this fact, we have conducted preliminary experiments indicating that polymer **7a** displays higher sensitivity to TNT than the triphenylene- or pentiptycene-based polymers under investigation in our group.<sup>6ab,9</sup> Further comprehensive study on the relationships of the structure-sensing abilities for these polymers is now in progress.

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**Supporting Information Available:** Experimental procedures and data for all new compounds and crystal structural data for **2a** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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