

# Tetraalkoxyphenanthrene: A New Precursor for Luminescent Conjugated Polymers

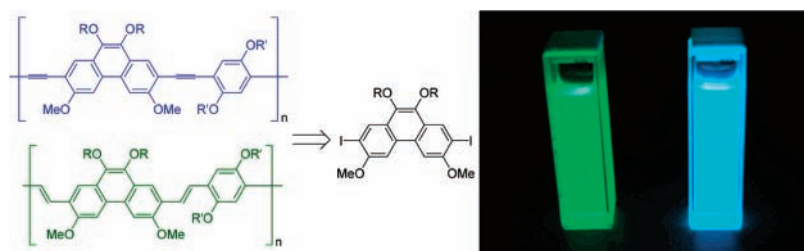
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## ABSTRACT



We have developed a convenient synthesis of tetraalkoxyphenanthrene derivatives and demonstrated their use to form luminescent conjugated oligomers and polymers. Palladium-catalyzed cross-coupling reactions of 2,7-diiodo-3,6-dimethoxy-9,10-di(2-ethylhexyloxy)phenanthrene produced high molecular weight poly(*p*-phenylene ethynylene)s and low molecular weight poly(*p*-phenylene vinylene)s. These new polymers, which are luminescent in the solid state and in solution, may be useful for developing LED or solar cell devices, or in chemical sensors.

Conjugated polymers, such as polythiophene, poly(*p*-phenylene vinylene) (PPV), poly(*p*-phenylene), and poly(*p*-phenylene ethynylene) (PPE), have remarkable electronic and optical properties as a consequence of electron delocalization within  $\pi$ -orbitals.<sup>1,2</sup> These semiconducting properties, when combined with the processibility and purification of organic

polymers, make these materials useful for flexible display and solar cell technologies.<sup>3</sup> Luminescent polymers, particularly PPV and its derivatives (e.g., MEH-PPV), are being commercialized for application in organic light emitting diodes (LEDs) and chemical sensors.<sup>4</sup> Fluorene-based polymers have been shown to emit blue light with high quantum yields while having good processability and interesting solid-state behavior,<sup>5</sup> and similar results have been observed for poly(2,7-carbazole).<sup>6</sup> Although the many derivatives of conjugated polymers now available offer a broad spectrum

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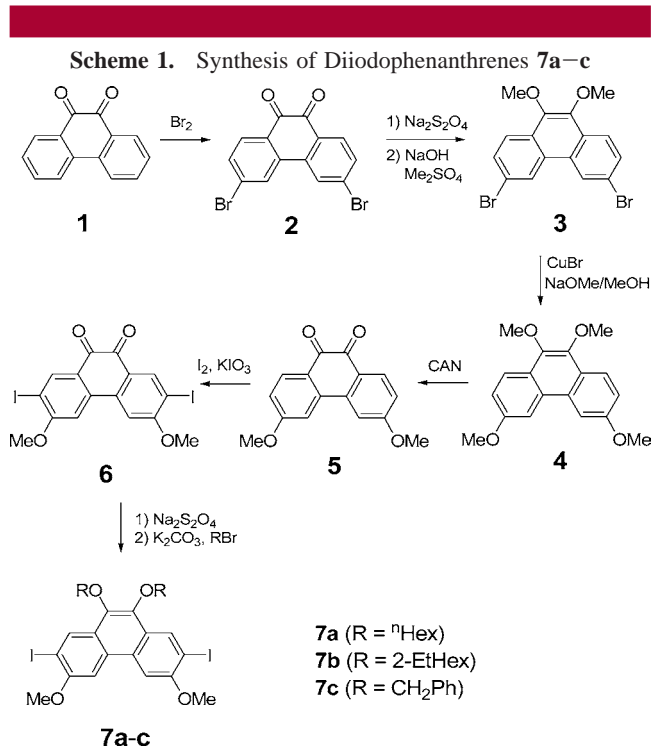
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of color tunability, the continued development of polymers with improved stability, better quantum yields, and modified optical properties is important.

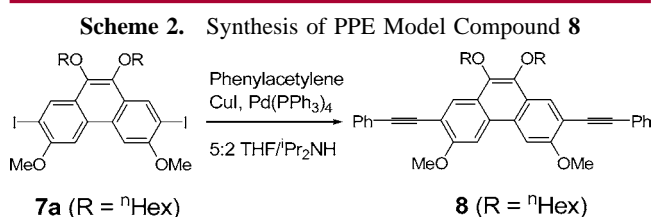
Though PPEs may be too unstable for semiconductor devices, they have been exploited for use in chemical sensors.<sup>7,8</sup> Modification of the side chains in this polymer may permit control over solubility and may incorporate additional functionality.<sup>9</sup> We and others have been investigating the effect of extending the conjugation between the alkyne groups in the polymer. By incorporating zinc salphen moieties, for instance, we have observed dramatic red shifting of the luminescence of the polymer with a resulting diminution of fluorescence intensity.<sup>10</sup> Adding triphenylene to the backbone of PPEs can modulate the fluorescence lifetimes and can increase intrachain exciton migration.<sup>11</sup> The incorporation of other conjugated species, such as phenanthrene, into PPEs and PPVs is still an underdeveloped area of exploration.<sup>12</sup> A recent report suggests that phenanthrene may be a useful moiety for incorporation into conjugated polymers for electroluminescent devices.<sup>13</sup> Unfortunately, the lack of suitable phenanthrene precursors has limited its utility in conjugated polymers. Here we report a simple route to new tetraalkoxyphenanthrenes. Further, we demonstrate that these are convenient precursors to highly luminescent conjugated PPEs and PPVs, as well as model compounds.

We identified compounds **7**, the first 3,6,9,10-tetraalkoxyphenanthrenes, as useful precursors to incorporate into conjugated polymers. Compounds **7a** and **7b** were prepared in six steps from phenanthrenequinone **1** as shown in Scheme 1. Free-radical bromination of **1** afforded 3,6-dibromophenanthrenequinone **2** in good yield.<sup>14</sup> It was necessary to protect the quinone by reduction and methylation prior to substituting the bromides with methoxy groups. Attempts to convert **2**



directly to **5** were unsuccessful. Starting with **3**, however, **4** could be prepared in high yield by Cu(I)-catalyzed nucleophilic aromatic substitution with sodium methoxide.<sup>15</sup> Subsequent iodination of **4** failed to yield **7** (R = Me), producing instead only phenanthrenequinone **5** as the product. Compound **5** could be rapidly prepared in excellent yield by treating **4** with cerium ammonium nitrate (CAN). Iodination of **5** afforded compound **6** selectively in good yield. Afterward, the alkyl or branched alkyl derivatives **7a** and **7b** were prepared by the in situ reduction and alkylation of **6** with 1-bromohexane and 1-bromo-2-ethylhexane, respectively, in the presence of base. To illustrate the generality of this approach, benzyl-functionalized derivative **7c** was also prepared by an analogous procedure.

This route is simple, requires little chromatography, and can be easily scaled up to multigram quantities. Compound **2** is typically prepared on a 10–20 g scale and subsequent steps could be done on a large scale. Compound **3** is prepared from compound **2** in a separatory funnel. The other steps are all fast (5 min to 16 h) and give good yields (44%, 86–98%). Surprisingly, compound **7b** can be purified by recrystallization, even though it is present as a mixture of diastereomers arising from the stereocenters in the branched



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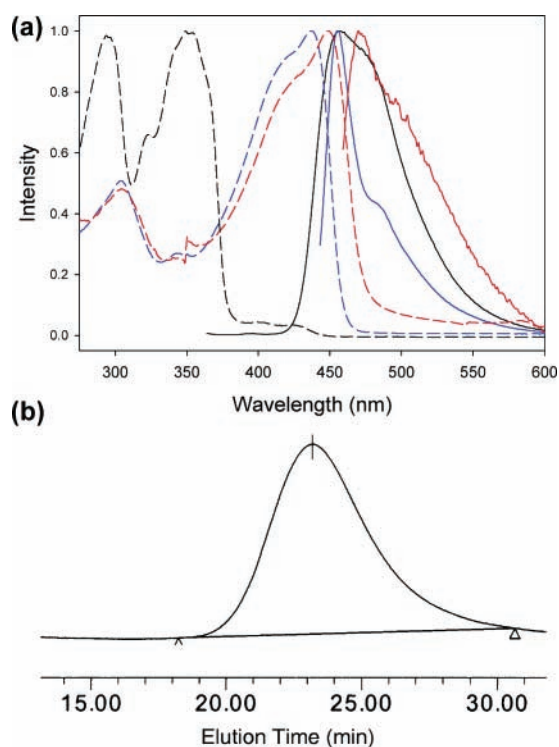
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alkyl substituents. This purification step is important to access high molecular weight polymers by step growth mechanisms.

To test and optimize Sonogashira coupling conditions, model compound **8** was prepared, Scheme 2. Compound **8** could be prepared in nearly quantitative yield by Sonogashira–Hagihara Pd(0)-catalyzed cross-coupling of **7a** with phenylacetylene. Figure 1a shows the absorption and emis-

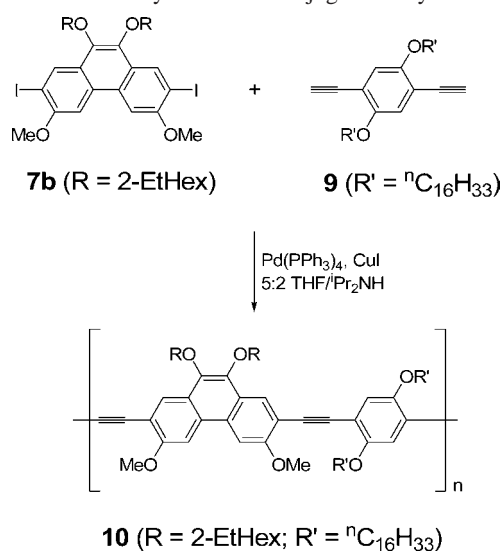


**Figure 1.** (a) UV–vis (dashed line) and fluorescence (solid line) spectra of model compound **8** (black) and polymer **10** in dichloromethane (blue) and in the solid state (red). (b) GPC analysis of polymer **10**.

sion spectrum of compound **8** in solution. The absorption maximum at 353 nm is assigned to the  $\pi$ – $\pi^*$  transition of the conjugated chain. It also exhibits blue fluorescence ( $\lambda_{em} = 456$  nm) that is red-shifted by ca. 100 nm from the maximum absorbance. This is consistent with the Stokes shift typically observed for phenanthrene.<sup>16</sup>

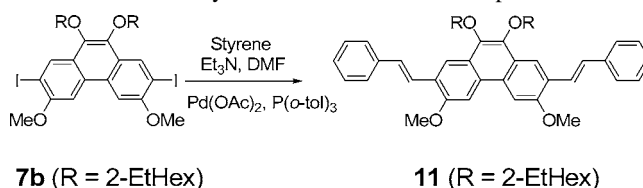
To demonstrate the utility of the new tetraalkoxyphenanthrenediiodides for the preparation of conjugated polymers, we prepared PPEs incorporating this moiety, Scheme 3. Polymer **10** was prepared by the Pd(0)-catalyzed cross-coupling reaction of **7b** with **9**. The structure of the polymer was verified by elemental analysis and <sup>1</sup>H NMR spectroscopy. Gel permeation chromatography (GPC) of polymer samples showed monomodal distributions with number-average molecular weights ( $M_n$ ) between  $5 \times 10^4$  and  $1.5 \times 10^5$ , Figure 1b. The yellow polymer is fluorescent in solution ( $\lambda_{em} = 455$  nm; QY = 70%) and in the solid state, Figure

### Scheme 3. Synthesis of Conjugated Polymer **10**



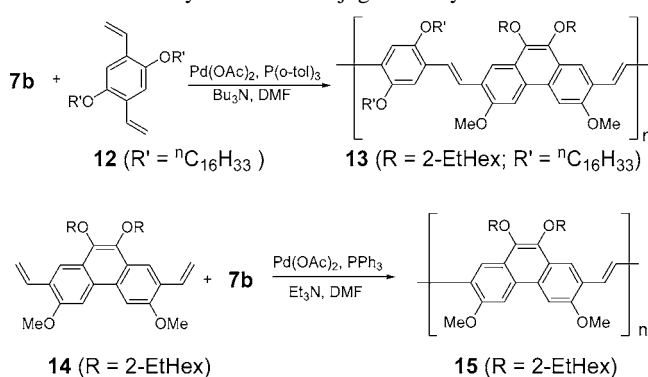
1a. The solid-state fluorescence is only slightly red-shifted from the polymer in solution, but is significantly broadened, which may be due to additional  $\pi$ – $\pi$  interactions or conformational rigidity in the solid state.

### Scheme 4. Synthesis of PPV Model Compound **11**

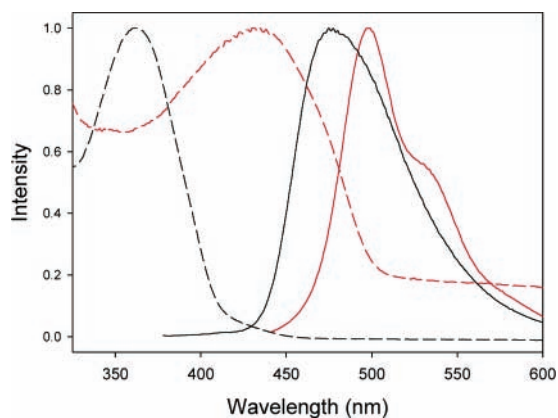


In an effort to develop PPV analogues, model compound **11** was prepared by the Heck coupling of styrene with **7b**. This compound exhibits green fluorescence at 475 nm. By reacting compound **7b** with divinylbenzene **12** under similar conditions, low molecular weight ( $M_n = 4400$ ) conjugated polymers **13** were formed, Scheme 5. The optical properties

### Scheme 5. Synthesis of Conjugated Polymers **13** and **15**



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**Figure 2.** Optical spectroscopy of **11** (black) and **13** (red). UV-vis spectra (dashed line) and fluorescence spectra (solid line).

of compound **11** and polymer **13** are illustrated in Figure 2. The fluorescence spectrum of **13** shows emission at 499 nm (green) in solution, considerably blue-shifted from the photoluminescence of MEH-PPV (ca. 600 nm) as a consequence of the rigid biphenyl linkages introduced by the phenanthrene moieties.<sup>17</sup>

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To prepare an analogue of PPV incorporating only tetraalkoxyphenanthrene, we first prepared 2,7-divinyl-3,6-dimethoxy-9,10-di(2-ethylhexyloxy)phenanthrene **14** by the Stille coupling of vinyltributylstannane with compound **7b**. Heck coupling of **7b** with **14** was undertaken, Scheme 5, but GPC of the product showed only oligomeric material **15**. Work is underway to prepare high molecular weight analogues of PPV incorporating the tetraalkoxyphenanthrene moieties.

In summary, we have developed a simple procedure for the preparation of new 3,6,9,10-tetraalkoxyphenanthrenes and their diiodide derivatives. These compounds are excellent precursors to luminescent conjugated polymers that incorporate phenanthrene moieties. The rigid biphenyl unit within phenanthrene reduces the emission wavelength of the polymer, while simultaneously offering 4 sites to modify solubility and functionality. These conjugated polymers may be useful for polymer-based LEDs and for chemical sensors, and we are now investigating their properties.

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**Supporting Information Available:** Experimental procedures, spectroscopic data, and <sup>1</sup>H and <sup>13</sup>C NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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