

# Conjugated Polymers Containing Large Soluble Diethynyl Iptycenes

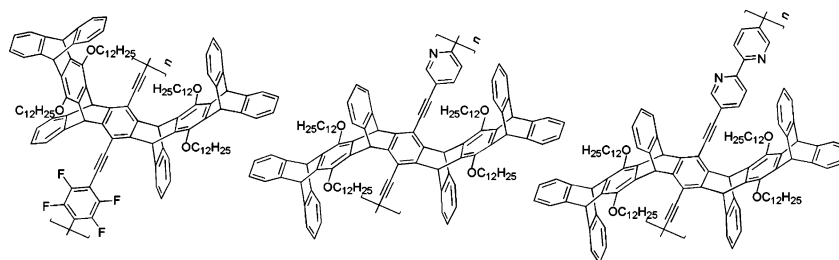
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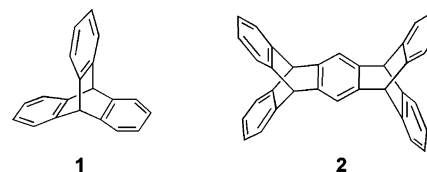
## ABSTRACT



An efficient synthesis of large iptycenes appended with alkoxy and ethynyl substituents is reported. The rigid shape-persistent iptycene scaffold prevents interactions between the polymer backbones and can be used to solubilize polymers containing less soluble but readily accessible comonomers to prepare functional, solution-processible poly(*p*-phenyleneethynylene) (PPE)-conjugated polymers. These polymers are highly emissive in thin films without significant excimer/excimer formation as a result of the effective chain isolation enforced by the iptycene units.

Iptycenes refer to a large family of compounds wherein a number of arene units are joined together to form the bridges of [2.2.2] bicyclic ring system(s).<sup>1</sup> A prefix denotes the number of the separated arene planes within the molecules. Accordingly, triptycene (**1**) and pentyptycene (**2**) each contain three and five phenyl rings, respectively. The simplest member of the family, triptycene **1**, was first synthesized by Bartlett et al. in 1942,<sup>2</sup> and in recent decades a great number of complex iptycenes have been synthesized with diversified arenes to include naphthalenes, anthracenes, thiophenes, pyrroles, phthalocyanines, etc.<sup>1,3–7</sup> The unique

geometrical and structural characteristics of iptycenes have inspired investigations in a range of fields, including intramolecular charge transfer,<sup>8</sup> atropisomer studies,<sup>9</sup> and molecular gear devices.<sup>10</sup>



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Our laboratory has focused on the utility of iptycenes, particularly triptycene and pentyptycene derivatives, for the creation of new materials.<sup>7,11–14</sup> Conjugated polymers containing these rigid, three-dimensional scaffolds display improved photoluminescent stability and quantum yields in the solid state, and these enhancements are the results of a spatial isolation of the polymer backbones that significantly reduces interchain excimer/excimer formation in the con-

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densed phase.<sup>7b,11,12</sup> The large free volume inherent to the iptycene scaffolds has also been exploited to achieve enhanced chromophore and liquid crystal alignments.<sup>13</sup> Further applications of these structures involve incorporating them into materials to bring about improved or emergent electronic or mechanical properties.<sup>14</sup>

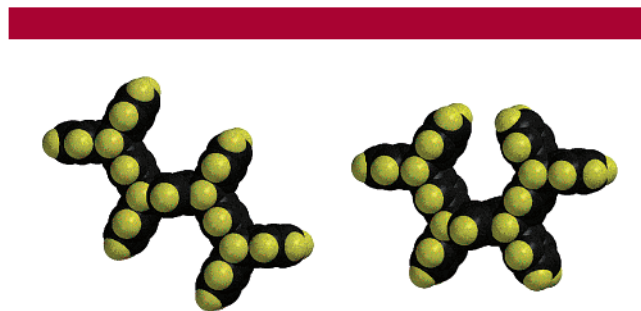
As triptycene and pentiptycene have demonstrated utility in a wide range of applications, we became interested to expand the scope of materials incorporating this functionality. In particular we have been interested to produce new PPEs containing high electron affinity monomers such as fluorinated phenylenes and bipyridyls. The affinity of these aromatic monomers for donor substituted aromatic rings generally leads to less soluble and less emissive aggregated polymers. Given our previous success with pentiptycenes, we initially set out to produce solublized iptycene derivatives and synthesized a stereoisomeric mixture of compound **7**.

The synthesis of **7** begins with a D–A reaction between 6,13-bis(triisopropylsilyl)ethynylpentacene<sup>15</sup> and 1,4-benzoquinone. Even though the diethynyl pentacene derivative has two potential sites to react with dienophiles, no product corresponding to the structure containing two equivalent quinone-derived fragments was detected, even under the conditions that a large excess of quinone was present. The mono-quinone-pentacene adduct was isolated and identified as a mixture of two stereoisomers, which was carried on to subsequent reactions without separation. In the presence of sodium hydride and 1-iodohexane, both isomers undergo a one-pot tautomerization and alkylation to give iptycene **4a**, with one of the arene planes being an anthracene unit. This intermediate iptycene was then able to react with another equivalent of *p*-benzoquinone, again followed by tautomerization and alkylation to afford stereoisomeric pentiptycenes

**5a** and **6a**, which were only partially separable via flash column chromatography. The triisopropylsilyl (TIPS) groups were then cleaved using tetrabutylammonium fluoride to afford **7** as a stereoisomer mixture. This synthesis route has the virtue of allowing the incorporation of two different side chains (*R'* groups in Scheme 1) in a stepwise manner to produce more polar, ionic, or amphiphilic iptycenes.

Unfortunately, pentiptycene **7** did not show the expected high solubility, and its polymerization with 1,4-diiodotetrafluorobenzene was not successful. Even when 1,4-diiodobenzene was used as the comonomer, only very low molecular weight oligomers (mostly dimers and trimers) were generated, indicating that the solubility of **7** was inadequate for the copolymerization of these less soluble comonomers.

We speculated that larger iptycenes such as **8** and **9** may be more efficient in breaking up the crystal lattice and will display higher solubility due to their more extended structures. Subsequently, stereoisomeric noniptycenes **8a** and **9a** were synthesized via the same synthetic route as that generating **7**, with the difference that triptycenequinone<sup>7b</sup> **3b** was used in the place of *p*-benzoquinone. Nonetheless, in this case stereoisomers **5a** and **6a** were successfully separated by column chromatography, most likely due to their more distinct difference in structural geometry and thus polarity. The absolute structure of this pair of stereoisomers was assigned on the basis of <sup>13</sup>C NMR spectroscopy. Compounds **5a** and **6a** give very similar proton and carbon NMR spectra. The only conspicuous distinction, besides the slight differences in chemical shift, is that one of the peaks in the aliphatic region of the <sup>13</sup>C NMR spectra is a doublet for one of the isomers and appears as a singlet for the other (details shown in the SI). This peak is assigned to the methyl carbons in the TIPS moieties, and the splitting is attributed to an atropisomeric effect.<sup>9</sup> We have recently observed similar behavior in the <sup>13</sup>C NMR spectra in a related set of stereoisomers, the absolute configuration of which was determined by X-ray crystal structures.<sup>16</sup> On the basis of the similar correlations between the structures and the spectra, the configurations of **5a** and **6a**, and thus **8a** and **9a**, were assigned (see space-filling structures in Figure 1).



**Figure 1.** Space-filling models of iptycenes **8** and **9**. Alkoxy side chains are omitted for clarity.

As expected, the size and configuration of the iptycene scaffold greatly affect the properties of the molecules.

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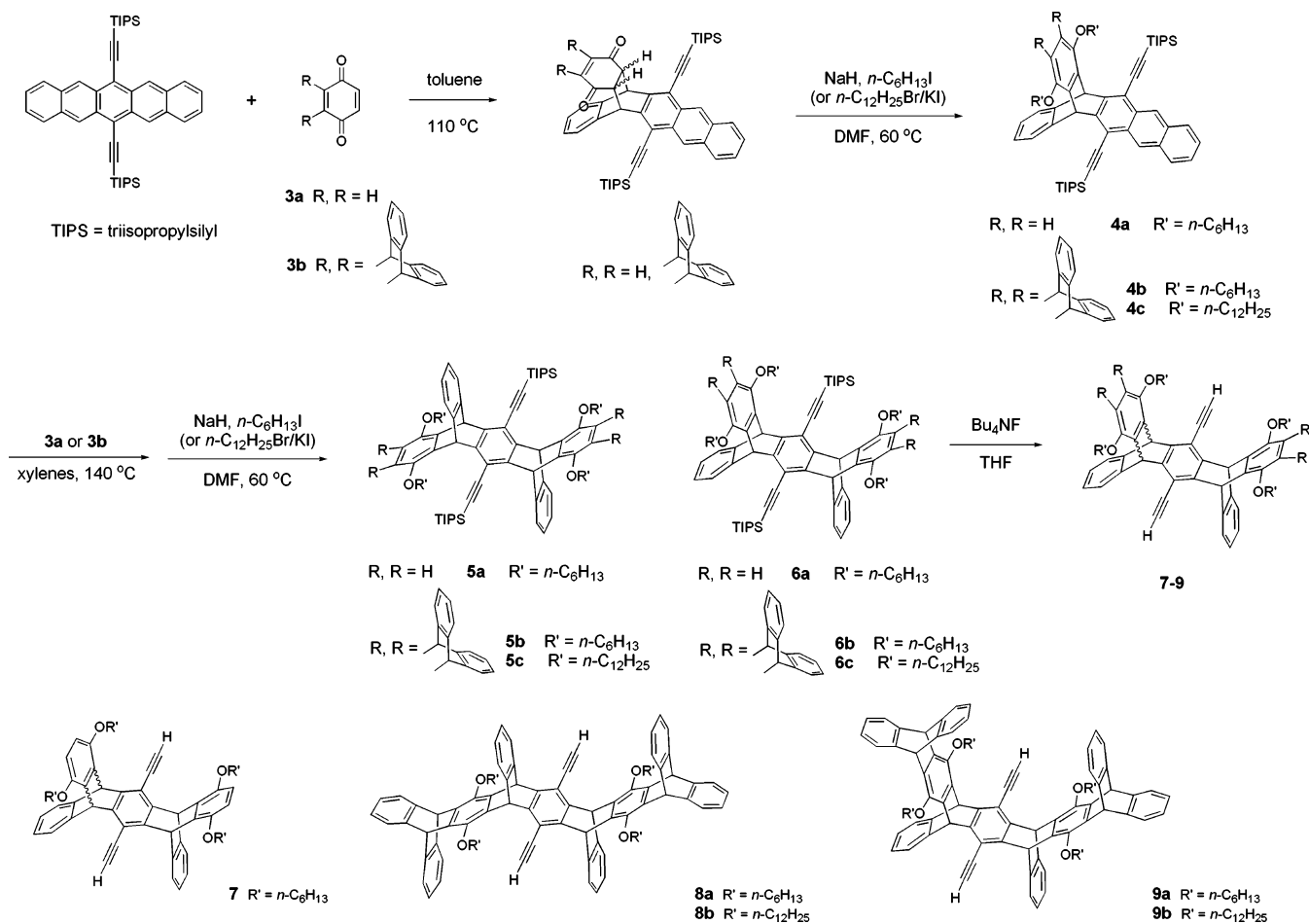
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**Scheme 1.** Syntheses of Diethynyl Iptycenes



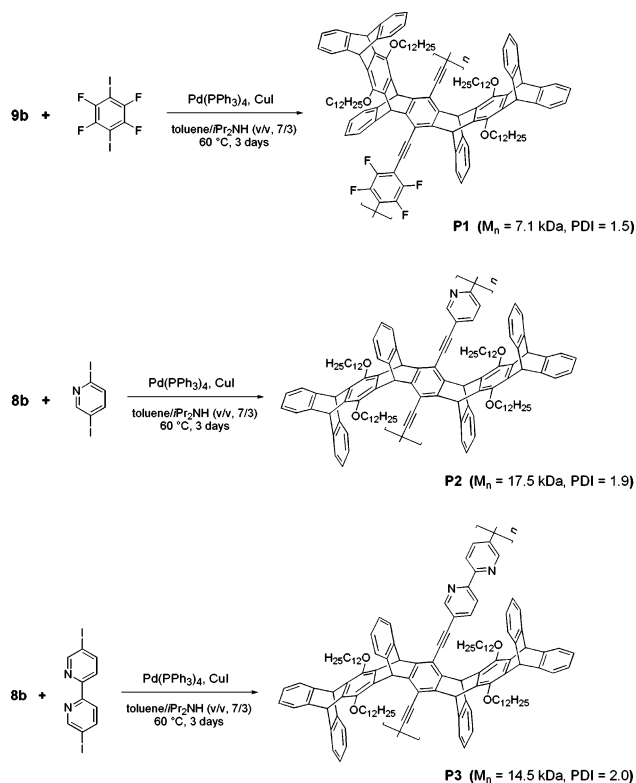
Specifically, iptycenes **8a** and **9a** having larger and extended scaffolds show higher solubility than their analogue **7**. Moreover, the *syn* isomer **9a** is more soluble and less prone to crystallize relative to the *anti* isomer **8a**. It appears that a lack of  $C_2$  symmetry factor in the *syn* isomers favors solubility. However, although these larger iptycences possess improved solubilities compared to **7**, their copolymerizations with less soluble monomers such as 1,4-diiodotetrafluorobenzene were still unsuccessful at generating polymers. Further efforts toward making soluble PPEs were made at extending the length of the side chains in the iptycenes, as a typical practice for enhancing the solubility. Finally, iptycenes **8b** and **9b** having *n*-dodecyloxy side chains were attained. They exhibited the desired high solubility and were proven adequate in the subsequent polymerizations.

Comonomers that have been tested for the formation of PPEs under standard Sonogashira coupling conditions include 2,5-diiodopyridine, 5,5'-diiodo-2,2'-bipyridine, and 1,4-diiodotetrafluorobenzene (Scheme 2). The strong tendency of these monomers to  $\pi$ -stack with other electron-rich phenyl rings causes aggregation and low solubility. The initial members of this family of materials shown in Scheme 2 were synthesized with acceptable molecular weights and are all freely soluble in common organic

solvents such as chloroform, methylene chloride, and tetrahydrofuran. Preliminary photophysical studies indicate the iptycenes prevent interactions between conjugated backbones even in spin-cast thin films of the PPEs. Particularly, the fluorescence spectra of these films showed no signature of exciplex-like complexes, thereby indicating that the large iptycenes effectively prevented interactions between the conjugated backbones (Figure 2). Additional characterization of these molecules will be reported in due course. The polymerizations shown here are merely a demonstration of the great utility of the reported iptycenes for polymerization with diverse commoners, circumventing elaborate synthetic endeavors that would have otherwise been needed to produce soluble materials.

In summary, a new series of diethynyl iptycene monomers bearing alkoxy side chains have been synthesized. Owing to the excellent solubility these compounds can be used to produce highly soluble and highly emissive PPEs with monomers that typically give low solubility materials. As stated earlier our interest in iptycenes revolves around their rigid, three-dimensional structures. Linking these noncompliant scaffolds into polymers produces materials with large free volume, low density, and high permeability by virtue

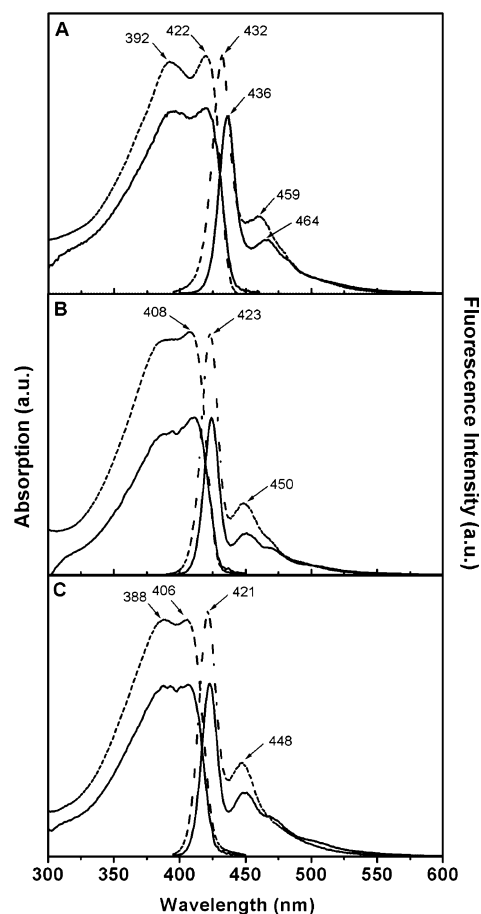
## Scheme 2. Polymer Syntheses



of their molecular-dimension cavities.<sup>17</sup> The *syn* isomer **9** possesses a well-defined gallery confined by five phenyl rings, which can potentially impart selective molecular recognition properties.

**Acknowledgment.** This work has been supported by National Science Foundation, TSA, TSWG, and Sandia National Laboratories.

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**Figure 2.** Absorption and fluorescence spectra of **P1** (A), **P2** (B), and **P3** (C) in chloroform (dash line) and thin films (solid line).

**Supporting Information Available:** Experimental procedures for syntheses and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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