

Syntheses and Structures of Novel Heteroarene-Fused Coplanar π -Conjugated Chromophores

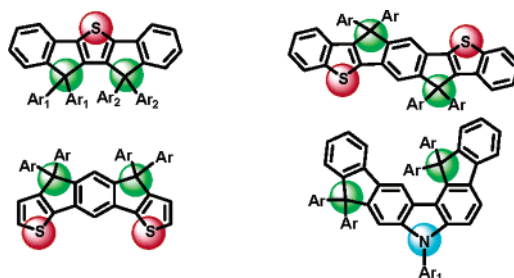
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ABSTRACT



We have synthesized a series of novel coplanar chromophores in which heteroarenes, namely, thiophene, benzothiophene, and carbazole, were fused to neighboring phenylene ring(s) through intramolecular annulation via sp^3 -hybridized carbon atoms bearing two *p*-tolyl groups as peripheral substituents. The molecular configurations of the π -conjugated backbones were determined by X-ray crystallographic analysis; the heteroarene-fused molecular frameworks of these novel molecules exhibit nearly coplanar conformations.

Polymeric and oligomeric π -conjugated materials possessing coplanar π -conjugated backbones, such as the ladder-type poly(*p*-phenylene)s (LPPPs),¹ have become the subject of a considerable degree of interest for their use in optoelectronics applications because of their enhanced degree of π -conjugation,² highly efficient photoluminescence, and remarkable hole mobility.³ The superior physical properties of LPPPs can be ascribed to the conformational rigidity of the coplanar molecular backbone that is obtained through intramolecular annulation. More importantly, the physical properties of ladder-type materials can be tailored by changing the degree of coplanarity between consecutive backbone units or, more effectively, by flattening the π -conjugated molecular framework by incorporating heteroatoms, such as silicon,⁴ sulfur,⁵ selenium,⁶ boron,⁷ and nitrogen,⁸ as bridging atoms. Alter-

natively, the physical behavior of π -conjugated materials can be modulated, often dramatically, by incorporating heteroarenes directly as constituents of the conjugated backbones, facilitating ready manipulation of the electronic structures.⁹ In this Letter, we report the syntheses and solid-state structures of novel coplanar chromophores featuring embedded heteroarenes as constituents of coplanar conjugated

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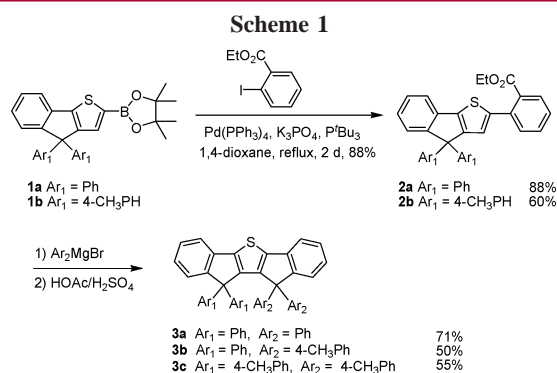
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backbones. Because of their intrinsic coplanarity, ladder-type materials usually exhibit strong intermolecular π - π interactions, and hence, they tend to be crystalline. Unfortunately, non-homogeneous crystalline systems that feature grain boundaries of various sizes often cause problems in device applications. In our present approach, the introduction of aryl groups as peripheral substituents of the coplanar backbone impedes the intermolecular interactions between the molecules quite efficiently, leading to their exhibiting amorphous morphologies, which is crucial for practical applications in organic light-emitting diodes (OLEDs).

Scheme 1 depicts the syntheses of three thiophene-implanted coplanar chromophores that feature aryl substituents.



The pinacol boronates of the diaryl-substituted indenothiophenes⁹ **1** were reacted with ethyl 2-iodobenzoate in the presence of catalytic amounts of Pd(PPh₃)₄ and co-catalyst *t*-Bu₃P to yield the coupling products **2** in good yields. The additions of excess amounts of aryl Grignard reagents, which we prepared in advance from the corresponding aryl bromides, onto the ester group of compounds **2** gave the corresponding alcohols as intermediates. Without further purification, these crude alcohols were subjected to acid-catalyzed intramolecular annulation to afford the coplanar phenylene-thiophene-phenylene systems **3** in good isolated yields. The flexibility of this synthetic sequence allowed us to introduce different aryl substituents, which we expected to exert subtle influences on the molecular morphologies and physical properties.

We characterized the molecular structure of **3c** using X-ray crystallography (Figure 1). The π -conjugated molecular plane

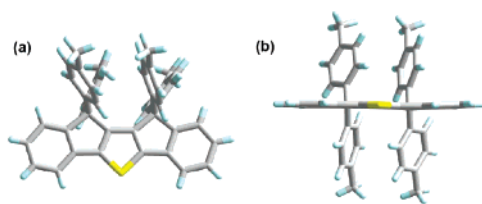
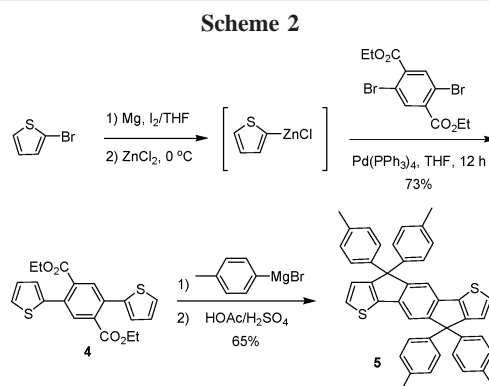


Figure 1. (a) Top and (b) side views of the solid-state structure of **3c**.

bridged by the two sp³-hybridized carbon atoms was almost coplanar. The *p*-tolyl groups occupying the top and bottom faces of the molecular plane were arranged with a dihedral angle of ca. 15.3°.¹⁰

The acid-mediated intramolecular ring closure between a tertiary hydroxyl group and adjacent arene(s) is a useful reaction for establishing the coplanarity of a conjugated backbone. This versatile synthetic strategy provides the flexibility to introduce various heteroarenes as constituent parts of the conjugated backbone to effectively manipulate the energy levels, as well as the electronic behavior, of the resulting coplanar molecules. Along this line, Pd-catalyzed Negishi coupling reaction of diethyl 2,5-dibromoterephthalate with 2-thienyl zinc chloride, which was generated in situ through transmetalation of a corresponding 2-thienyl Grignard reagent with ZnCl₂, afforded the doubly coupled product **4** in 73% yield (Scheme 2).¹¹



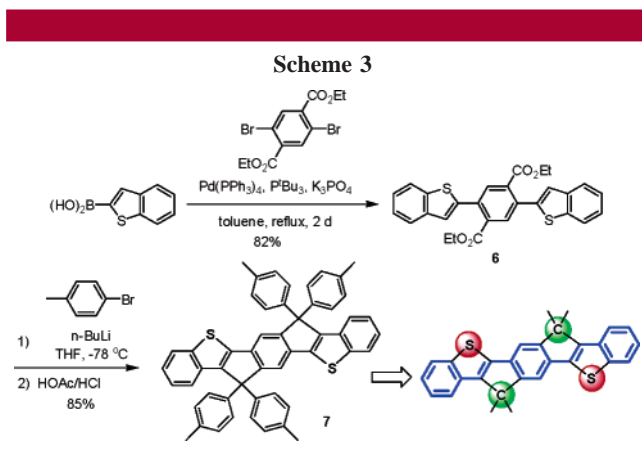
After the double addition and acid-promoted intramolecular cyclization reaction sequence, we isolated a new chromophore, *p*-thiophene-phenylene-thiophene (**5**), in 65% yield (Scheme 2); we confirmed its coplanar structure through X-ray crystallographic analysis (Figure S-1, Supporting Information).¹⁰

The degree of π -conjugation can be extended effectively by increasing the degree of coplanarity of a backbone unit. Thus, the Suzuki coupling of diethyl 2,5-dibromoterephthalate with benzothiophene boronic acid afforded the bis-(benzothienyl)phenylene **6** in excellent yield. A subsequent ring-closure strategy provided the new coplanar chromophore **7**, which can be regarded as a coplanar distyryl-*p*-phenylene flattened through the incorporation of two different bridging atoms (i.e., carbon and sulfur) (Scheme 3). This compound serves as a new member of the family of coplanar oligo-(phenylenevinylene) (OPV) derivatives that contain bridging silicon and silicon,⁴ silicon and carbon,¹² and sulfur and carbon^{5b} atoms.

(10) Crystal packing diagrams and the analyses of possible intermolecular interactions of molecules **3c**, **5**, **7**, **9**, and **15** are provided in the Supporting Information.

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X-ray crystallographic structural analysis of **7** confirmed the relative coplanarity of this molecule's backbone (Figure 2).

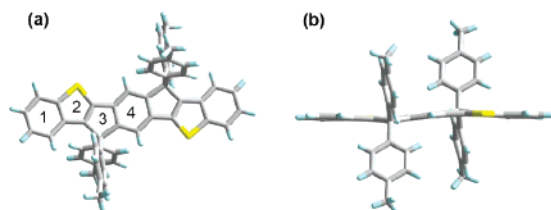


Figure 2. (a) Top and (b) side views of the solid-state structure of **7**.

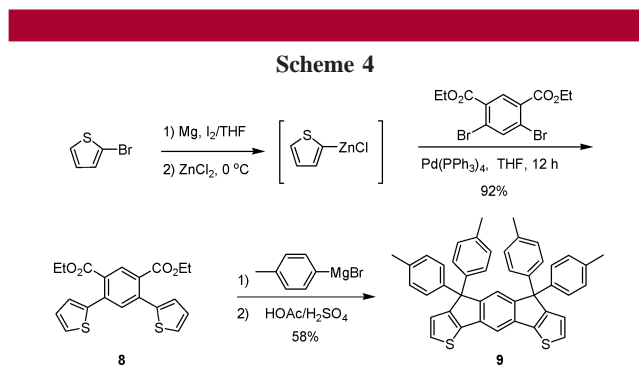
Interestingly, the bridging carbon atoms appear somewhat deviated from the planar structure, leading to a slightly twisted molecular plane having a dihedral angle of 6.7° between the central and terminal phenylene units (rings 1 and 4).¹⁰

Both theoretical calculations¹³ and practical examples¹⁴ have indicated that the energy levels, as well as the electronic properties, of π -conjugated molecules can be modulated when they adopt different molecular geometries. Using a similar synthetic pathway (Scheme 4), we synthesized the *m*-thiophene–phenylene–thiophene **9** as a novel coplanar molecule to serve as a counterpart when determining the physical properties of the linear isomer **5**. Negishi coupling of thienyl zinc chloride and diethyl 4,6-dibromoisophthalate afforded the diester **8** in excellent yield. Subsequent addition of a *p*-tolyl Grignard reagent onto the ester groups of **8**, followed by intramolecular annulation, gave the target product **9** in an isolated yield of 58%.¹⁵

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(15) The coplanar molecules **5** and **9** may serve as useful core structures for developing potential π -conjugated oligomers or polymers because halogenations can be performed readily at the C2 positions of terminal thiophene moieties. We are currently investigating such reactions.



We confirmed the nearly flat molecular structure of **9** using X-ray crystallography (Figure 3); the two fused thiophene

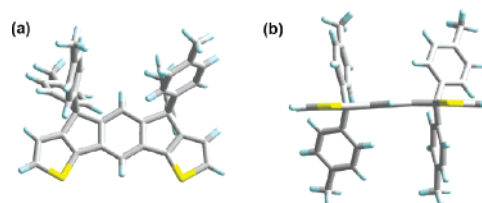


Figure 3. (a) Top and (b) side views of the solid-state structure of **9**.

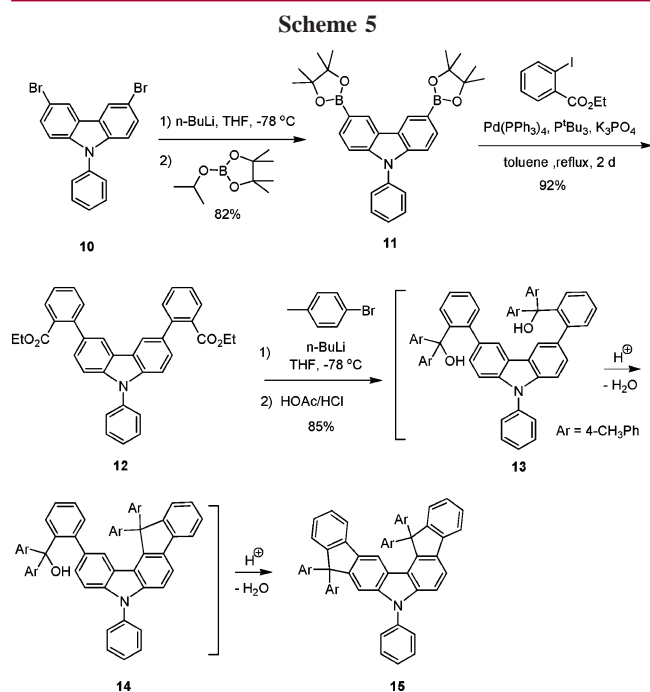
rings were twisted by 5.6 and 2.2° , respectively, in relation to the central phenylene ring.¹⁰

Carbazole-based conjugated oligomers and polymers are often used as hole-transporting materials, as well as host materials,¹⁶ in organic light-emitting devices (OLEDs). Much research effort has been exerted toward the realization of carbazole derivatives for optoelectronic applications. We applied our present synthetic protocol to the synthesis of coplanar chromophores containing carbazole units as core structural features. Recently, interesting carbazole-based coplanar molecules were reported that featured phenylene substituents at the C2 and C7 positions of their carbazole units; their molecular planes were subsequently flattened at the electron-rich sites (e.g., C3 and C6) of the carbazole moiety.¹⁷ We became intrigued to extend the π -conjugation of carbazole in a different manner—through intramolecular ring closure of aryl substitutions at the C3 and C6 positions. This approach led us to prepare the interesting carbazole-containing coplanar chromophore **15** (Scheme 5).

The electron-rich C3 and C6 positions of carbazole are functionalized quite readily; thus, we treated 3,6-dibromo-

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9-phenylcarbazole with *n*-BuLi at -78°C , followed by quenching of the dilithiated intermediate with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, to obtain the bis(pinacolato boronate) **11** in 82% yield. Suzuki coupling of the diboronate **11** with ethyl 2-iodobenzoate afforded the diester **12** in excellent isolated yield (92%). Subsequent double addition of aryl lithium onto the ester groups of **12**, followed by acid-mediated intramolecular annulation, gave the novel coplanar carbazole-cored chromophore **15** having two bridging carbon atoms attached to the C4 and C7 positions, respectively, of the central carbazole moiety. We confirmed the structure of **15** through X-ray crystallographic analysis (Figure 4). We believe that the acid-promoted intramolecular Friedel–Crafts alkylation of the diol **13** occurred initially at the C4 position of the carbazole to form the alcohol **14**. The presence of the two *p*-tolyl groups attached to the bridging carbon atom presents a sterically congested environment that inhibits the second ring closure from occurring at the C5

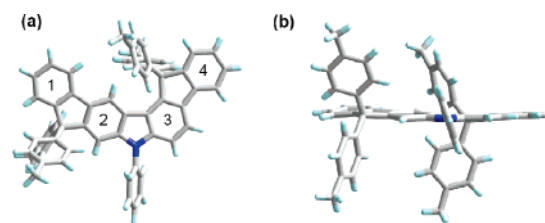


Figure 4. (a) Top and (b) side views of the solid-state structure of **15**.

position of the carbazole and, sequentially, forces the second annulation to occur at the C7 position. In Figure 4, we observe that the terminal phenylene rings are twisted slightly from the molecular plane of **15**, leading to a nearly flat structure having dihedral angles of 6.7° (between rings 1 and 2), 6.8° (rings 2 and 3), and 2.0° (rings 3 and 4).¹⁰

In summary, we have achieved an efficient syntheses of a series of novel coplanar chromophores that feature phenylene ring(s) fused to heteroarenes, namely, thiophene, benzothiophene, and carbazole. The carbon atoms bearing the two *p*-tolyl groups flatten their respective phenylene(s) and adjacent heteroarene(s) units to afford nearly coplanar molecular configurations of the conjugated backbones, which we confirmed through X-ray crystallography. The structure–property relationships and potential applications in OLEDs of these new compounds are currently under investigation and will be reported in due course.

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Supporting Information Available: Detailed experimental procedures; spectroscopic characterization and NMR spectra of new compounds; crystal data, crystal packing, and crystal CIF files of compounds **3c**, **5**, **7**, **9**, and **15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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