

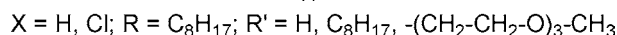
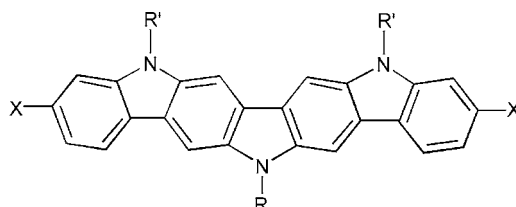
Synthesis of Diindolocarbazoles by Ullmann Reaction: A Rapid Route to Ladder Oligo(*p*-aniline)s

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ABSTRACT



New and facile synthesis of symmetric diindolocarbazoles was developed using the copper-catalyzed Ullmann reaction. The key step is a double-intramolecular cyclization reaction realized on *N*-alkyl-3,6-dibromo-2,7-bis(2'-aminophenyl)carbazole derivatives which offers the desired symmetric ladder oligo(*p*-aniline)s. Depending upon the nature of the side- and/or end-groups, well-defined thin films and/or semiladder polymers could be obtained. These electroactive ladder oligomers may have great potential in organic electronics.

Organic semiconducting materials including polymers, oligomers, and small molecules are a subject of high interest as potential active materials in electronic devices.¹ In the particular area of *p*-type organic field-effect transistors (OFETs), the best candidates are regioregular polythiophenes,² oligothiophenes,³ oligofluorenes,⁴ oligo(*p*-phenylevinylene)s,⁵ oligo(2,6-anthrylene)s,⁶ and fused aromatic compounds such

as pentacene.⁷ Of all organic semiconducting materials reported so far, the highest charge mobilities have been recorded with pentacene (about 5 cm² V⁻¹ s⁻¹ with on–off current ratios up to 10⁸ in some cases).^{7de} Although pentacene shows impressive performances, it is not clear whether this molecule will ultimately be used in organic electronics.^{4,8} In fact, pentacene suffers from facile atmospheric degradation, insolubility, and sensitivity to visible light.⁹ Therefore, novel organic semiconductors combining high environmental

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stability, processability and appropriate charge carrier mobility are still required. One potentially interesting approach is the development of pentacene-like oligomers which would show a similar coplanar structure and favorable packing geometry together with improved stability and processability. Synthetic ladder-type π -conjugated molecules having optimized chemical, physical, and structural properties could be excellent candidates for such improvements. Short linear fused ring compounds such as benzodithiophene¹⁰ and dithieno[3,2-*b*:2',3'-*d*]thiophene¹¹ have been explored as a building block for the synthesis of a variety of planar structures, especially dimers. However, only a few examples of longer ladder conjugated oligomers, usually containing fused-ring thiophenes, have been reported but without any test of their performances in electronic devices.¹² Substituted anthradithiophenes were also prepared by Laquindanum et al.⁹ This synthetic approach gives a mixture of syn and anti isomers, but these molecules show better solubility and solution stability when compared to pentacene. However, no attempt was made to characterize or separate the isomers. Dibenzothienobisbenzothiophene (DBTBT) was also synthesized by Sirringhaus et al.¹³ via an intramolecular coupling, but an inseparable mixture of different regioisomers was obtained. Poor FET performances are observed when DBTBT films contain a mixture of different isomers. These results prove that isomeric purity is of first importance for achieving high charge-transport mobility.

In this regard, we have recently reported^{14,15} a new class of pentacene-like semiconducting organic materials (see Figure 1). Symmetric indolocarbazole¹⁴ **1** and diindolocar-

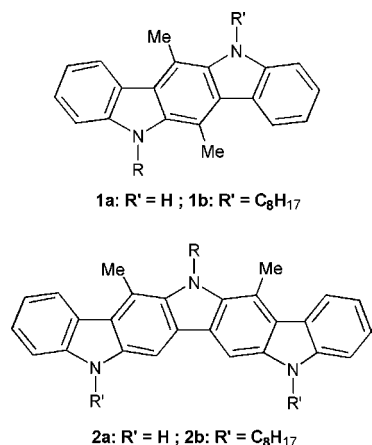


Figure 1. Indolocarbazoles and diindolocarbazoles.

bazole¹⁵ **2** derivatives were indeed prepared by the Cadogan ring-closure reaction using *N*-alkyl-substituted carbazole precursors. These oligomers are soluble in common organic

solvents and stable under ambient conditions. X-ray analyses of a single crystal of 5,11-dioctyl-6,12-dimethylindolo[3,2-*b*]carbazole **1b** showed a coplanar molecular structure with an interesting π -stacking arrangement of the molecules. This type of organization is very important to enhance charge carrier mobility along the π - π stacking.^{1c,11,16}

As we previously reported, Cadogan ring closure is not regioselective, and the use of carbazole precursors with methyl protective groups is necessary to obtain the desired isomers.¹⁵ We report here a more rapid and regioselective (or direct) synthetic approach for the synthesis of symmetric diindolocarbazoles using the copper-catalyzed Ullmann reaction for the intramolecular ring-closure reactions. Interestingly, a diindolocarbazole with amphiphilic side chains was also prepared. This kind of molecule has the potential to lead to well-defined thin films through Langmuir–Blodgett processing, which allows fine control of both the orientation and the thickness of the film.¹⁷ Moreover, a 3,10-dichloro-diindolocarbazole was synthesized for further development of semiladder poly(3,10-diindolocarbazole)s.

The symmetric diindolocarbazoles were generated in a four-step synthetic sequence starting from *N*-octyl-2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole **3**.¹⁵ As shown in Scheme 1, a double Suzuki cross-coupling reaction of compound **3** with 1-bromo-2-nitrobenzene or 1-bromo-4-chloro-2-nitrobenzene using palladium catalyst gives compounds **4**¹⁵ and **5** in good yields. Interestingly, it is possible to introduce regioselectively the bromine atoms at the 3- and 6- positions on the carbazole unit of compounds **4** and **5** by using 2 equiv of *N*-bromosuccinimide in acetone. Thus, compounds **6** and **7** were obtained after a simple recrystallization in methanol, with excellent yields.

The nitro groups were then reduced to amine moieties with the use of SnCl₂ according to a procedure developed by Bellamy et al.¹⁸ to lead to compounds **8** and **9** with good yields. It is important to notice that peaks of some protons of the ¹H NMR spectrum and of some carbon atoms of the ¹³C NMR spectrum of compounds **6** to **9** were doubled. This can be explained by a phenomenon of atropisomerism¹⁹ due to a limited (hindered) rotation around the aryl–aryl bond (between phenyl and carbazole moieties). To obtain the trimer **10**, we first attempted the palladium-catalyzed ami-

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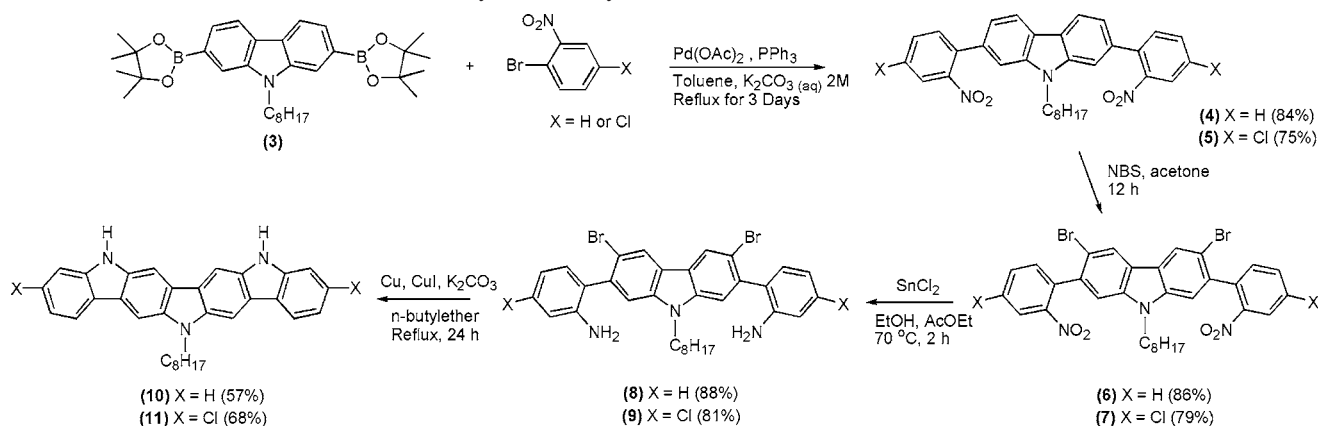
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Scheme 1. Synthesis of Symmetric Diindolocarbazoles **10** and **11**



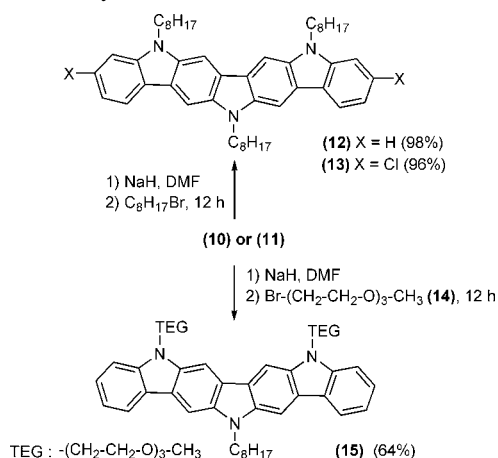
nation reaction pioneered by Hartwig²⁰ and Buchwald.²¹ Different reaction conditions using $\text{Pd}(\text{dba})_2$,^{20b} $\text{Pd}(\text{OAc})_2$,^{22a} or $\text{Pd}(\text{PPh}_3)_4$ ^{22b} were tested in diluted conditions to avoid the intermolecular coupling, but we were unable to obtain the desired product **10** via this type of reactions. To achieve the double-intramolecular cyclization, copper-catalyzed Ullmann reaction was then performed using conditions reported by Field et al.²³ Compounds **10** and **11** were successively obtained with interesting isolated yields (57% and 68%, respectively). By comparison with the reductive Cadogan ring-closure reaction,¹⁵ this methodology is more straightforward and leads to the symmetric diindolocarbazoles in higher yields. As we reported earlier, these compounds are excellent intermediates to develop different kinds of diindolocarbazoles depending upon the nature of the substituents. To obtain totally symmetric diindolocarbazoles, compounds **10** and **11** were alkylated with 1-bromooctane in the presence of sodium hydride as described in Scheme 2. Thus, com-

to offer the amphiphilic diindolocarbazole **15** in a 64% isolated yield.

All of these substituted diindolocarbazoles are soluble in common organic solvents as THF, CH_2Cl_2 , toluene, etc., and their ^1H NMR and ^{13}C NMR analyses are in good agreement with their chemical structures.

The UV–vis absorption and electrochemical properties of compound **12** were also studied. The UV–vis absorption spectrum of **12** in CH_2Cl_2 displays two absorption maxima in the visible range, at 439 and 466 nm (Figure 2).

Scheme 2. Synthesis of Diindolocarbazoles **12**, **13**, and **15**



pounds **12** and **13** were isolated in excellent yields. Diindolocarbazole **10** was also alkylated with bromotriethylene glycol monomethyl ether **14** according to a similar procedure

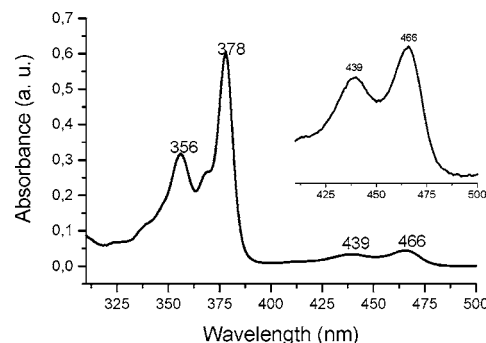


Figure 2. UV–vis spectrum of compound **12**.

Cyclovoltammetric measurements on of diindolocarbazole **12** in THF solution (with 0.1 M tetrabutylammonium perchlorate) show that the oxidation at 0.67 V (vs SCE) and the reduction at -2.22 V (vs SCE) are reversible (see Figure

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3). Interestingly, the band gap calculated from electrochemical data (2.69 eV) is in excellent agreement with the one obtained from UV-vis spectroscopy (2.59 eV).

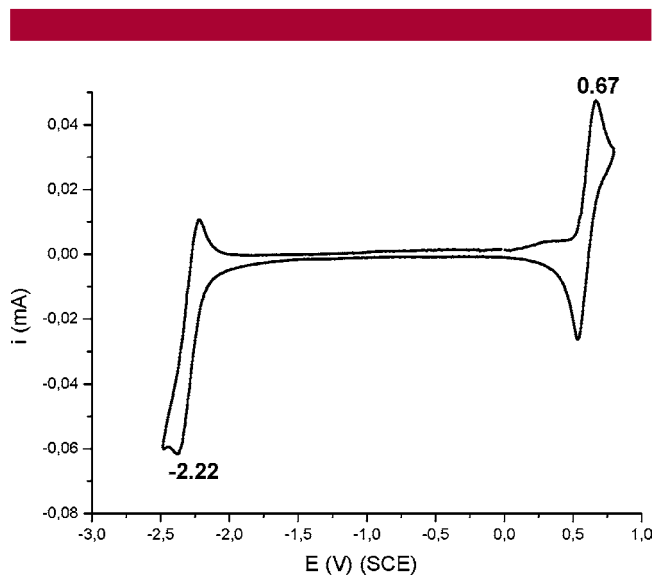


Figure 3. Cyclic voltammogram of compound **12**.

In conclusion, we have described a new and straightforward approach for the synthesis of symmetric diindolocarbazoles via the copper-catalyzed Ullmann reaction as the

ring-closure reaction. Starting from *N*-octyl-2,7-diboronic ester carbazole **3**, the symmetric diindolocarbazoles **10** and **11** were generated in four steps with overall yields of about 35%. This synthetic approach offers the opportunity to prepare rapidly a large variety of diindolocarbazoles by the appropriate choice of end-groups and side chains. For instance, 3,10-dichlorodiiindolocarbazole **13** was prepared as a precursor to semiladder poly(3,10-diindolocarbazole)s. Amphiphilic diindolocarbazole **15** was also prepared. This kind of molecule has the potential to lead to well-defined thin films through Langmuir–Blodgett processing. Preliminary studies of the spectroscopic and electrochemical properties of the diindolocarbazole **12** are particularly promising for the utilization of this class of materials in organic field-effect transistors. For instance, hole mobility of $0.001 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{\text{on}}/I_{\text{off}}$ ratio of 10^5 were already reported with indolocarbazoles¹⁴ and the present longer conjugated oligomers should lead to even better performances. All these physical studies are currently in progress.

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Supporting Information Available: Detailed experimental procedures and ^1H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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