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Thiadiazole fused indolo[2,3-*a*]carbazoles as new building blocks for optoelectronic applications

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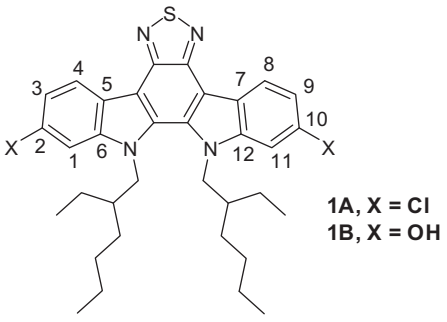
ABSTRACT

New indolo[2,3-*a*][1,2,5]thiadiazolo[3,4-*c*]carbazoles including functional groups (halide or hydroxyl groups) on the meta positions relative to the nitrogen atoms which are known to be the most conjugated, have been synthesized following two synthetic routes. The characterizations of their optical and electrochemical properties evidence their potential as new building blocks for optoelectronic materials.

Great attention has been paid to organic semiconductors (OSCs) over the past two decades. OSCs are very attractive materials for optoelectronic applications as their properties are easily tunable, their synthesis pathway is versatile, and the OSCs based-devices can be flexible. The most investigated OSCs based-devices are Organic Field Effect Transistors (OFETs),[1] Organic Light Emitting Diodes (OLEDs),[2] and Organic Photovoltaic Cells (OPVs).[3] Development of conjugated materials relies on the synthesis of several chemical molecules based on units such as thiophene, carbazole, furan, and fluorene. In particular, the fused-ring heterocyclic aromatic compounds have been widely investigated. Their co-planar structure allows a good molecular organization[4] and a strong π-stacking which are beneficial for high charge carrier mobilities.[5]

Balaji et al. have investigated a new indolo[2,3-*a*]carbazole fused with a benzothiadiazole unit.[6] In addition to the ladder-type nature of this fused heterocyclic aromatic compound, this molecule presents an alternation in the conjugated pathway of electron-rich moieties (indolo[2,3-*a*]carbazole) and electron-deficient units (2,1,3-benzothiadiazole). The concept of alternating electron donor and electron acceptor moieties is well known in the field of low band-gap co-polymers. Indeed, the internal charge transfer (ICT) from the electron-rich to the electron-poor units considerably lowers the co-polymer band-gap. It is one of the most popular strategies to answer to the absorption issue met in bulk heterojunction (BHJ) OPVs.[7] Therefore, several interesting oligomers and co-polymers have been synthesized following this alternation approach and used with success in OSCs.[8,9] Additionally, the facile alkylation of the nitrogen atoms can lead to high solubility and processability of indolocarbazole derivatives and therefore helps to overcome a classical weakness of fused-ring-molecules based materials.

However, since the molecules developed by Balaji et al. are reactive-function free, electropolymerization led only to polyindolocarbazole with a conjugation pathway going through the nitrogen atoms (polymerization through the 3- and 9-positions, see



Scheme 1. Structure of the synthesized molecules.

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Scheme 1). Leclerc et al. showed recently by using a systematic investigation of carbazole- and indolocarbazole-based molecules that a longer conjugation length could be obtained in the case of the *para*-phenylene-like conjugation pathway (polymerization or extension of the conjugation through the 2- and 10-positions) than in the case of the conjugation through the nitrogen atoms.[10] Unfortunately, the reactivity in indolocarbazole or carbazole is decreasing from *para* positions (positions 3 and 9) to *ortho* and *meta* positions (positions 1–11 and 2–10, respectively) of the nitrogen atom. The *meta*-positions cannot be directly functionalized by standard electrophilic aromatic substitution. Therefore a synthetic strategy starting from an initial phenyl derivative including a functional group in the 2- and 10-positions has to be used.

In this Letter, we report two different routes allowing the synthesis of new indolo[2,3-*a*][1,2,5]thiadiazolo[3,4-*c*]carbazole including functional groups (halide or hydroxyl groups) in most conjugated 2- and 10-positions (Scheme 1).

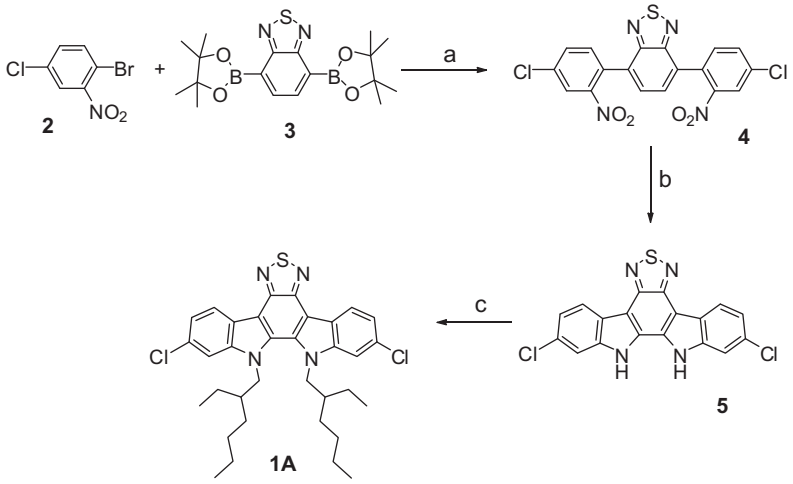
Both routes are based on the cyclization of nitrobiaryl following a Cadogan reaction procedure.[11] Those ring-closures were achieved via reductive deoxygenation of the nitro groups using a slight excess of triethylphosphite.

Scheme 2 displays the synthesis route A, based on the approach used recently by Balaji et al.[6]

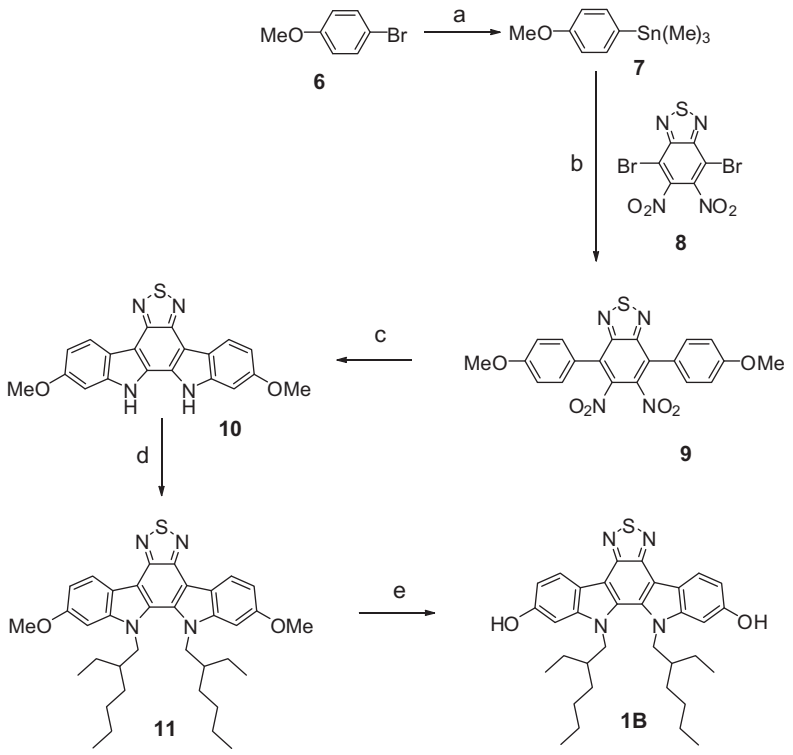
In this route, the nitro groups are carried by the outer phenyl moieties. However, in order to include a functional group in the 2- and 10-positions, we decided to start from the commercially available 2-nitro-4-chloro-bromobenzene in which one halogen (the bromine atom) will be used to achieve a cross-coupling reaction and the other one (the chlorine atom) will be preserved as functional group. Due to the lower reactivity of the chlorine atom in comparison to the bromine atom during cross-coupling reaction, a high regioselectivity could be expected. Thus, the Suzuki condensation of commercially available compounds **2** and **3** leads to the synthesis of bis-adduct compound **4** in 34% yield. The low reaction yield, despite an excess of compound **2**, could be due to the poor purity of initial 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) together with the very low solubility in a THF/water mixture of the mono-adduct intermediate which could precipitate and therefore suspend the reaction. Purification of the product was accomplished by washing thoroughly the crude solid in cyclohexane. Subsequent Cadogan ring-closure in triethylphosphite gave the first thiadiazole fused indolo[3,2-*a*]carbazole compound **5** in 57% yield, similar to the one published by Balaji et al.[12] Several alkylation conditions have been tested. Finally, the dialkyl-product was prepared by the reaction of 2-ethylhexyl bromide with potassium *t*-butoxide as the base and 18-crown-6 (crown ether) as the phase transfer catalyst in dry THF. Compound **1A** has been isolated after purification by column chromatography.[13] Despite these conditions, the alkylation yield remains very low (~10%), in particular in comparison to the yields described by Balaji et al. This could be due to the deactivation of secondary amines in compound **5**, which in turn results from the presence of electronegative chlorine atoms and an electron acceptor benzothiadiazole moiety. However, the recovered monoalkyl and alkyl-free fractions could be used again in order to increase significantly the final yield. The 2-ethylhexyl chains give a very high solubility to the indolo[2,3-*a*]carbazole **1A** in common organic solvents.

Despite the limited amount of synthesis steps (three), route A has been shown to be inefficient especially due to the low yield of the Suzuki cross-coupling reaction. In addition, the 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) compound is relatively expensive. We therefore investigated the alternative route B (Scheme 3) based on the functionalization of 2,7-dibromo-2,1,3-benzothiadiazole with nitro groups on 5- and 6-positions. In this route, the methoxy function is a precursor of the triflate group which is an excellent leaving group used in cross-coupling reactions. We thus decided to start from the aniline unit as outer phenyl ring. The 4,7-dibromo-5,6-dinitro-2,1,3-benthiadiazole has been synthesized following a procedure reported in the literature.[14] Stannylation of bromoanisole gave compound **7** in a high yield. A Stille cross-coupling reaction has been carried out between compound **8** and an excess of compound **7**. The crude product has been washed thoroughly with cyclohexane to give in good yield (61%) compound **9**, which is an orange solid.[15] The following steps are similar to the one used in route A. Cadogan cyclisations in triethylphosphite followed by a dialkylation with 2-ethylhexyl bromide gave compound **11** in a moderate yield. It could be noted that, as expected, the replacement of chlorine atom by electron donor methoxy groups improved the efficiency of the N-alkylation of indolocarbazole **10** with a significantly increased yield (37% compared to 10% in the dichloro-indolocarbazole derivative **5**). Finally, the standard and quasi-quantitative deprotection reaction of methoxy groups using BBr_3 in methylene chloride gave the functionalized dialcohol indolocarbazole derivative **1B**.[16] These hydroxyl groups are precursors of triflate groups that can undergo Stille or Suzuki reactions.

Both routes allowed the synthesis of the targeted indolocarbazole. However, while the route A is shorter and starts from commercially available compounds, it is significantly less efficient than route B with an overall yield of 2%. Route B, with two additional



Scheme 2. Route A for the synthesis of thiadiazole fused indolocarbazole. Reagents and conditions: (a) $Pd(PPh_3)_4$, K_2CO_3 aq 2 M, THF, reflux, 24 h, 34%; (b) $P(OEt)_3$, *o*-DCB, reflux, 24 h, 57%; (c) *t*-BuOK, bromo-2-ethylhexyl, 18-crown-6, dry THF, reflux, 42 h, 12%.



Scheme 3. Route B for the synthesis of thiadiazole fused indolocarbazole. Reagents and conditions: (a) *n*-BuLi, dry THF, $SnMe_3Cl$, −78 °C→RT; (b) $Pd(PPh_3)_4$, THF, reflux, 24 h, 73%; (c) $P(OEt)_3$, *o*-DCB, reflux, 24 h, 61%; (d) *t*-BuOK, bromo-2-ethylhexyl, 18-crown-6, dry THF, reflux, 42 h, 37%; (e) BBr_3, dry CH_2Cl_2, reflux, 12 h, 94%.

steps, has been easier to perform and more efficient. The overall yield of route B (4 steps) is 16%.

The UV–vis absorption spectra of the indolo[2,3-*a*][1,2,5]thiadiazolo[3,4-*c*]carbazoles in solution are shown in Figure 1. Both compounds show similar absorption spectra that are typical of planar conjugated systems,[17] with several maxima.

Successive absorption maxima of both derivatives are centered around 255, 320, and 380 nm with an edge of absorption at 455 and 490 nm for **1A** and **1B**, respectively. The longer conjugation in the case of **1B**, with a fourth maximum around 440 nm, is due to the electron donating nature of the hydroxyl group.

Finally, cyclic voltammetry has been performed on compound **1A** in solution in dry methylene chloride. Oxidation and reduction peaks are observable at 1.25 V and −1.65 V, respectively. HOMO and LUMO levels could be estimated from the oxidation and reduction onsets[18] to 5.49 eV and 3.05 eV, respectively. As expected, the HOMO level is in agreement with the value calculated by Balaji et al. on their molecules (HOMO level of 5.49 eV and 5.53 eV for the derivatives with methyl and hexyl chains as alkyl chains, respectively). The difference between the HOMO and LUMO levels leads to an electrochemical band-gap of 2.44 eV. In addition, the low-lying HOMO level highlights the good air stability of our ladder unit.

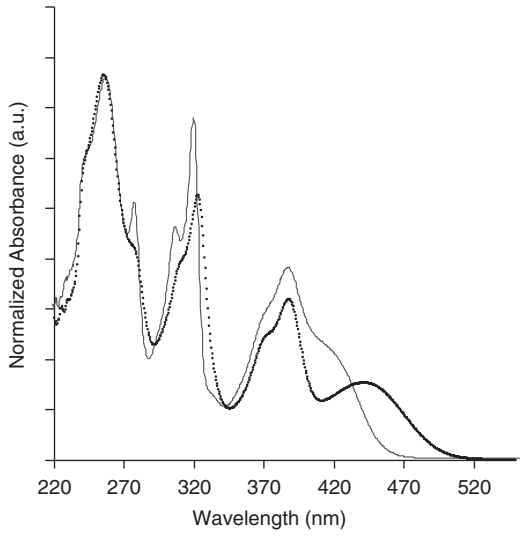


Figure 1. UV–vis absorption of indolocarbazoles **1A** (continuous line) and **1B** (black square) in solution with chloroform was used as the solvent.

In conclusion, we described the synthesis of indolo[2,3-*a*][1,2,5]thiadiazolo[3,4-*c*]carbazoles functionalized, by halide or hydroxyl groups, in 2- and 10-positions following two different routes. Both compounds have shown interesting absorption properties (UV–visible spectroscopy) as well as well-positioned HOMO and LUMO levels (cyclic voltammetry) for optoelectronic applications. In addition, due to the functionalization in the 'meta-positions' (2- and 10-positions) of the nitrogen atoms, these thiadiazole-fused indolocarbazoles can be further extended or polymerized by condensation reactions, such as Suzuki or Stille reactions. Therefore, these new building blocks appear as good candidates for the design and synthesis of new optoelectronic oligomers and polymers.

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12. *Compound* ***5***. A solution of compound **4** (0.2 g, 0.45 mmol) in triethylphosphite (5 mL) and *o*-DCB (2 mL) was refluxed for 24 h. After cooling to RT, solvents were removed by distillation under vacuum and the crude product was purified on column chromatography (60/40:cyclohexane/ethyle acetate as eluent) to give 98 mg of compound **5**. ^{1}H NMR (300 MHz, DMSO d_6, δ, ppm): 12.03 (s, 2H), 8.45 (d, ^3J = 8.5 Hz, 2H), 8.02 (d, ^4J = 1.9 Hz, 2H), 7.44 (dd, ^3J = 8.5 Hz, ^4J = 1.9 Hz, 2H). ^{13}C NMR (75 MHz, DMSO d_6, δ, ppm): 149.21, 139.17, 130.22, 129.88, 123.06, 122.67, 122.59, 113.50, 108.86.
13. *Compound* ***1A***. To a solution of compound **5** (90 mg, 0.23 mmol), *t*-BuOK (65 mg, 0.58 mmol) and 18-crown-6 crown ether (6.2 mg, 2.3×10^{-5} mol) in dry THF (7 mL) was added bromo-2-ethylhexyl (104 μL, 0.58 mmol). The solution was the refluxed for 42 h. After cooling to RT, the reaction was quenched with water, extracted with ethyl acetate and the organic phase was washed with water and dried over sodium sulphate. After solvent evaporation, the crude product was purified on column chromatography (90/10:cyclohexane/ethyl acetate as eluent) to give 17 mg of compound **1A** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.65 (d, ^3J = 8.4 Hz, 2H), 7.61 (d, ^4J = 1.5 Hz, 2H), 7.44 (dd, ^3J = 8.4 Hz, ^4J = 1.7 Hz, 2H), 4.59 (d, ^3J = 7.5 Hz, 4H), 1.89 (t, ^3J = 6.1 Hz, 2H), 0.97 (m, 6H), 0.76 (m, 10H), 0.57 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 149.09, 141.66, 133.16, 130.59, 124.15, 123.07, 122.84, 112.46, 111.91, 52.35, 38.50, 29.59, 27.52, 23.17, 22.65, 13.64, 9.95. Anal. Calcd for $C_{34}H_{40}Cl_2N_4S$: C, 67.20; H, 6.63; Cl, 11.67; N, 9.22; S, 5.28. Found: C, 67.30; H, 6.72; Cl, 11.55; N, 9.17; S, 5.26.
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15. *Compound* ***9***. To a degassed solution of compound **7** (660 mg, 2.43 mmol) and **8** (310 mg, 0.81 mmol) in THF (15 mL), catalytic amount of $Pd(PPh_3)_4$ was added. The solution was then refluxed for 24 h. Then the reaction mixture was cooled down to RT and filtered. The precipitate was then washed thoroughly with cyclohexane to give 259 mg of compound **9** as an orange powder. ^{1}H NMR (300 MHz, DMSO d_6, δ, ppm): 7.57 (d, ^3J = 8.7 Hz, 4H), 7.19 (d, ^3J = 8.7 Hz, 4H), 3.36 (s, 6H). ^{13}C NMR (75 MHz, DMSO d_6, δ, ppm): 160.57, 152.86, 141.13, 130.70, 128.31, 122.65, 114.36, 55.36.
16. *Compound* ***1B***. To a solution of compound **11** (80 mg, 0.134 mmol) in dry dichloromethane (10 mL), BBr_3 1 M in hexane (0.5 mL, 0.5 mmol) was added dropwise. The solution was then refluxed for 12 h. After cooling to RT, the reaction was quenched with methanol and the organic phase was washed with water. After the solvent evaporation under vacuum, the crude product was purified on flash column chromatography (90/10:cyclohexane/ethyl acetate as the eluent) to give 68 mg of compound **1B** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.56 (d, ^3J = 8.3 Hz, 2H), 7.09 (d, ^4J = 1.6 Hz, 2H), 7.01 (dd, ^3J = 8.3 Hz, ^4J = 1.4 Hz, 2H), 5.38 (s, 2H), 4.54 (d, ^3J = 7.3 Hz, 4H), 1.95 (t, ^3J = 6.0 Hz, 2H), 0.97 (m, 6H), 0.77 (m, 10H), 0.56 (m, 12H). ^{3}C NMR (75 MHz, $CDCl_3$, δ, ppm): 153.62, 149.12, 142.48, 133.00, 122.78, 120.14, 111.55, 111.28, 98.69, 52.14, 38.06, 30.18, 27.62, 23.13, 22.67, 13.66, 9.93. Anal. Calcd for $C_{34}H_{42}N_4O_2S$: C, 71.54; H, 7.42; N, 9.82; O, 5.61; S, 5.62. Found: C, 71.48; H, 7.46; N, 9.83; O, 5.59; S, 5.64.
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