A Sm(II)-Mediated Cascade Approach to Dibenzoindolo[3,2-b]carbazoles: Synthesis and Evaluation

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ABSTRACT: Previously unstudied dibenzoindolo[3,2-b]carbazoles have been prepared by two-directional, phase tag-assisted synthesis utilizing a connective-Pummerer cyclization and a SmI₂-mediated tag cleavage—cyclization cascade. The use of a phase tag allows us to exploit unstable intermediates that would otherwise need to be avoided. The novel materials were characterized by X-ray, cyclic voltammetry, UV−vis spectroscopy, TGA, and DSC. Preliminary studies on the performance of OFET devices are also described.

Supporting Information

Indolo[3,2-b]carbazoles, nitrogen containing analogues of pentacene, have been shown to be promising organic semiconductors with mobilities as high as 1 cm² V⁻¹ s⁻¹, with the advantage that the nitrogen atom allows for easy structural modification either to alter electronic properties or enhance solubility allowing for solution processing of devices (Figure 1A).1 Larger acenes beyond pentacene are less well studied owing to the decreased stability as the conjugation length is increased.2 Various methods have been employed to enhance the stability of the larger acenes to allow for a more detailed study of their properties, mainly via either extensive functionalization of the aromatic core or the inclusion of heteroatoms such as sulfur or nitrogen into the structure.3 Herein we describe the synthesis, optical and electrochemical properties, and preliminary transistor performances of dibenzoindolo[3,2-b]carbazoles [DBICs], a previously unknown class of aza-heptacenes based on an extended indolo[3,2-b]carbazole framework (Figure 1B). The first synthesis of DBICs involves the utilization of a two-directional Pummerer⁴-type cyclization and a two-directional radical cascade mediated by SmI₂.⁵ Crucially, these two key steps incorporate the introduction and removal of a phase tag that facilitates the purification of unstable intermediates that would otherwise have to be avoided. Attractively, the use of tag introduction/cyclization and tag cleavage/cyclization⁶ delivers a route in which the use of a phase tag adds no strategically redundant steps to the synthesis.

We have previously employed Pummerer-type cyclizations⁷ in the synthesis of a range of different targets including bis-oxindole-based monomers for use in semiconducting polymers,⁸ and benzo[1]carbazole end-capped oligothiophenes for preliminary evaluation as semiconductors.⁹ Here we report an extension of this methodology in the first synthesis of dibenzoindolo[3,2-b]carbazoles.

Bis-hydroxyamides 1, synthesized according to previously described procedures,⁶,⁷ underwent oxidation and selective double Pummerer-type cyclization upon capture of a fluorous
thiol \( \text{HS}(\text{CH}(_2)_3(\text{CF}(_2))_7\text{CF}_3 \) to give linear regioisomers (>5:1) \( 2 \) as a 1:1 mixture of diastereoisomers after rapid purification by fluoruous \(^{10}\) solid phase extraction (FSPE) \(^{11}\) (Scheme 1).

Scheme 1. Two Directional, Tag-Assisted Synthesis of DBICs\(^{a}\)

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\begin{align*}
\text{DBIC-1} & \quad R^1 = \text{CH}_2\text{CH}((\text{CH}_2)_3\text{C}_{10}H_{21})_2, \quad R^2 = H, \quad 17\% \text{ (5 steps from 1; step avg. 70\%)} \\
\text{DBIC-2} & \quad R^1 = \text{C}_{10}H_{21}, \quad R^2 = H, \quad 16\% \text{ (5 steps from 1; step avg. 69\%)} \\
\text{DBIC-3} & \quad R^1 = \text{C}_{10}H_{21}, \quad R^2 = \text{Me}, \quad 10\% \text{(5 steps from 1; step avg. 63\%)} \\
\end{align*}
\]

\(^{a}R^2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_3\). FSPE = fluoruous solid phase extraction. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

Depronatonation and alkylation of \( 2 \) using LDA and a dibromo-alkylating agent gave key intermediates 3 that proved highly unstable toward conventional chromatography. Fortunately, purification by FSPE (rapid filtration through fluoruous silica gel, eluting with a fluorophilic solvent) gave 3 with little decomposition. Finally, treatment of 3 with SmI\(_2\) and a proton source at 60 \(^\circ\)C triggered cleavage \(^{12}\) of both fluoruous tags and a double cyclization to give the desired DBICs after oxidation of the product mixture with \( p \)-benzoquinone (\( p \)-BQ). The novelaza-heptacenes were obtained in overall yields of 10–70\% from known and readily accessible hydroxymides 1 (Scheme 1).

Slow evaporation from THF delivered crystals of DBIC-2 and DBIC-3 suitable for X-ray crystallographic analysis (Figure 2). \(^{13}\) DBIC-2 was found to pack in a lamellar-type structure (with the aromatic cores arranged in layers separated by regions of aggregated alkyl chains with an interlamellar spacing of 15 Å) in which the aromatic cores pack in a herringbone-like manner similar to pentacene but offset along the long axis of the molecule such that only three rings from each molecule are overlapping in the edge-to-face orientation. Each molecule is surrounded by six others via a shortest carbon–carbon distance of 3.5 Å, two in a completely offset parallel face-to-face arrangement and four in an edge-to-face manner.

DBIC-3 was found to pack in a herringbone motif, and segregation of the alkyl chains is again observed with an interlayer spacing of 16 Å (Figure 2). Each molecule is surrounded by six others in the same manner observed for DBIC-2 (except with only two rings on each adjacent molecule overlapping in the edge-to-face orientation) via a shortest carbon–carbon distance of 3.7 Å, four of these in an edge-to-face arrangement and two in a completely offset parallel face-to-face arrangement. The crystal structures of DBIC-1 and DBIC-2 show twisting of the alkyl chains, which implies that the packing structure is being dominated by the aromatic cores, with the alkyl chains twisting to accommodate the packing of the aromatic core.

DSC traces for compounds DBIC-2 and DBIC-3 both showed single melting point transitions at 194 and 229 \(^\circ\)C, respectively. DBIC-1, with the longer branched alkyl chain, forms two mesophases, identified by polarized optical microscopy, that were observed at 100 and 104 \(^\circ\)C before the material melted into an isotropic liquid at 106 \(^\circ\)C.\(^{14}\)

The HOMO energy levels of DBIC-1 and DBIC-2 suggest that devices should operate under ambient conditions (Table 1).\(^{15}\) The introduction of methyl groups onto the backbone (DBIC-3) raises the HOMO energy level by 0.2 eV. All HOMO energy levels are raised relative to those reported for indolo[3,2-b]carbazoles in the literature and better match the work function of gold which should allow for effective charge injection (see Supporting Information (SI)). UV–vis spectroscopy showed an onset of absorption at around 515 nm for all three compounds, significantly red-shifted relative to indolo[3,2-b]carbazoles \((\lambda_{\text{onset}} \approx 450 \text{ nm})\)\(^{16}\) as a consequence of the extended conjugation length (see SI).

Preliminary OFET devices were fabricated by vacuum sublimation of DBIC-2 and DBIC-3 onto OTS treated SiO\(_2\)/Si\(^{17}\) wafers, while fabrication of devices based on DBIC-1 was performed by spin coating from a 0.5% w/w solution in THF. DBIC-1 and DBIC-2 were found to show good transfer characteristics and similar mobilities of \( 2.6 \times 10^{-3} \) and \( 4.0 \times 10^{-3} \) \((\pm 1 \times 10^{-3})\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively, whereas DBIC-3 exhibited a mobility 2 orders of magnitude lower \((3.1 \times 10^{-5})\). This is possibly a consequence of the tighter crystal packing of DBIC-2 relative to DBIC-3. Fabrication of devices based on DBIC-2 using substrates maintained at 25 \(^\circ\)C did not exhibit normal transfer characteristics making it difficult to obtain accurate values for the devices’ performance. It was found that when a heated substrate \((100 \ ^{\circ}\text{C})\) was used during the evaporation, this problem was alleviated. Transfer and output curves for DBIC-2 are shown in Figure 3.

Analysis by powder-XRD indicates that the orientation of DBIC-2 on the two different temperature substrates is almost identical. A primary diffraction peak is observed at \( 2\theta = 5.70^\circ \) \((100 \ ^{\circ}\text{C})\) (Figure 4) and \( 5.72^\circ \) \((25 \ ^{\circ}\text{C})\), with second-, third-,
Table 1. Summary of Optical and Electronic Properties

|     | HOMO/ eV | LUMO/ eV | HOMO calc$^a$ | LUMO calc$^a$ | $λ_{max}$ / nm | $E_{onset}$ / eV | $\mu$/cm$^2$ V$^{-1}$ s$^{-1}$ | $I_{on}/I_{off}$ | $V_t$/eV | $\lambda$ (opt)/ eV$^0$
|-----|----------|----------|---------------|---------------|----------------|----------------|-----------------------------|----------------|----------|---------------
| DBIC-1 | −5.13 | −2.72 | − | − | 515 | 2.41 | 2.6 × 10$^{-3}$ ($\pm 5 \times 10^{-3}$)$^d$ | 1 × 10$^3$ | −1 | − |
| DBIC-2 | −5.19 | −2.79 | −5.70 | −0.77 | 516 | 2.40 | 4.0 × 10$^{-3}$ ($\pm 1 \times 10^{-3}$)$^c$ | 4 × 10$^4$ | −19 | 0.11 | 0.076 |
| DBIC-3 | −4.99 | −2.57 | −5.52 | −0.67 | 513 | 2.42 | 3.1 × 10$^{-3}$ ($\pm 2.8 \times 10^{-3}$)$^c$ | 4 × 10$^3$ | −13 | 0.05 | 0.074 |

$^a$Estimated from cyclic voltammetry using the equation: $E_{FOMO}$ (eV) = $(5.1 - F_{max} + E_{1/2(Fc)})$.$^b$Estimated from cyclic voltammetry (HOMO) and optical band gap. $^c$See SI for computational method. $^d$Estimated from cyclic voltammetry using the equation: $E_{FOMO}$ (eV) = $(5.1 - F_{max} + E_{1/2(Fc)})$.$^e$Fabricated by vacuum evaporation onto OTS−SiO$_2$. $^f$Fabricated by vacuum evaporation onto OTS−SiO$_2$ at 25 °C.

Figure 3. Transfer (top) and output characteristics (bottom) for DBIC-2.

Figure 4. Powder-XRD for DBIC-2 and DBIC-3.

and fourth-order diffraction peaks visible in both cases. The primary diffraction peaks correspond to a $d$-spacing of 15.5 Å: this matches closely with the predicted (1,0,0) reflection from the single crystal data obtained, which gives a $d$-spacing of 15.7 Å. This hints that the compound may be adopting an orientation in which the alkyl chains are pointing both downward toward the substrate and upward away from the substrate, with the aromatic core laid with its longest axis parallel to an angle of $\sim 35^\circ$ relative to the substrate. DBIC-3 displays a primary diffraction peak of 6.39Å, corresponding to a $d$-spacing of 13.8 Å. This matches with the predicted primary diffraction peak at 6.56Å (0,1,−1), estimated from the single crystal data, suggesting the aromatic core of the compound may be adopting a conformation with its long axis at an angle of $\sim 50^\circ$ relative to the substrate. Using the coordinates from the crystal structures, we estimated both transfer integrals ($t$) and reorganization energies ($\lambda$) for transport through DBIC-2 and DBIC-3. Using semiclassical Marcus hopping theory, the rates of charge transfer (hole) were then calculated to be 0.22 and 0.02 s$^{-1}$.$^{16}$ The calculated reorganization energies are low and close in value (0.076 and 0.074 eV), with the source of the differing rates being derived from the large difference in the respective transfer integrals.

In summary, we have synthesized the previously unstudied dibenzoindolo[3,2-f]carbazoles by a novel, tag-assisted approach involving a two-directional Pummerer-type reaction and a two-directional SmI$_2$-mediated radical cascade. The use of a phase tag allows us to exploit intermediates that are unstable to purification by conventional chromatography and would otherwise need to be avoided. Dibenzoindolo[3,2-f]carbazoles show good ambient stability, with HOMO levels between $-5.0$ and $-5.1$ eV. The compounds were found to pack in a lamellar “herring bone-type” structure. Preliminary OFET devices were fabricated and found to provide modest mobilities of up to 4.0 $\times$ 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$.

The optimization of device performance is currently underway in our laboratories.

**ASSOCIATED CONTENT**

**Supporting Information**

Experimental details for the preparation of compounds and devices, $^1$H and $^{13}$C NMR spectra for new compounds, DSC and CV traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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