New indole trimers as precursors for molecular electronic materials**

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Abstract

We have prepared two new C₃-symmetric, substituted-triazatruxene molecules using a facile one-pot trimerisation of 5-carboxyindole and 6-bromoindole in acetic acid using Br₂, giving 2a and 3a respectively. These were subsequently modified by the addition of 6 alkyl chains to the N- and carboxyl-positions of 2a giving 2b and 3 alkyl chains to the N-positions of 3a giving 3b. The new molecules were characterised using cyclic voltammetry, UV/Vis and emission spectroscopy, DFT calculations and in the case of 3b, field-effect transistor measurements showing gate-modulated source-drain current. These represent a straightforward route to large polyaromatic molecules with easily-modified side groups and are suitable as building blocks for synthesis of functional molecules for materials.

Main text

Conjugated organic molecules with a large π-system have been intensely studied in the area of organic electronics and optoelectronics. In recent years, much work has used aromatic fragments such as thiophenes, stilbenes, perylenes, porphyrins and others as the basis for larger conjugated systems through well-established coupling reactions. In addition, the nature of any side groups can also play a significant role in the intrinsic properties of the system, offering unusual functionality¹ or the potential for cheaper more readily available solution processing techniques.² Introduction of side-groups may cause an increase in solubility¹,³ and one of the most commonly used moieties is the long-chain alkyl group. Addition of such chains may also benefit the engineering of subsequent devices through the formation of discotic liquid crystalline materials. Fused polyaromatic systems such as pentacene have led to high-mobility field-effect transistors (FET), with for example the hexabenzocoronene derivative HBC-C14 showing a charge mobility of up to 1.13 cm²V⁻¹s⁻¹.⁴ It can remain challenging however, to develop new polyaromatic molecules that are both rapidly synthesized and also where further side-group substitutions can be readily and selectively made.

In this context, we previously reported the formation of 2,3,7,8,12,13-hexabromo-5,10,15-trihydroindolo[3,2-a,3’,2’-c]carbazole (1) (Figure 1, also called hexabromotriazatruxene) by the simple reaction of three equivalents of Br₂ with indole.⁵ This represents a straightforward route to a large, conjugated π-system containing readily-substituted Br and N-H groups and has stimulated much subsequent work to prepare a large number of derivatives (Figure 1),⁶⁻²⁰ studied for their photophysical, liquid crystal and/or charge-transport properties. In particular, such trigonal aromatic molecules offer enhanced opportunities in the formation of dendritic molecules¹⁸,²⁰ or discotic liquid crystalline systems⁹ in comparison with linear analogues.

To date however, published work has been limited to the modification of 1, and new trimerisation reactions to give analogues of 1 have not been pursued. In this work, we further develop the trimerisation of indoles to produce conveniently new C₃-symmetric triindole species, along with further synthesis to modify their side
chains. These materials were studied through a combination of cyclic voltammetry, absorption and emission spectroscopy, DFT calculations and, in one case, FET measurements to demonstrate the potential for use in organic electronics.

Figure 1. (a) hexabromotriazatruxene (1) and (b) examples of derivatives prepared from 1

We have used the reaction of substituted indole molecules with Br₂ to prepare 2a and 3a successfully (Scheme 1). In contrast to the synthesis of 1 in CH₃CN, we used acetic acid as the solvent in this work; the excess acid appears to catalyse the triindole formation also reducing the need for extensive purification of the trimer species.

Scheme 1. Synthesis of 2a and 3a.

Products 2a and 3a were obtained in acceptable purity, as shown by ¹H NMR spectroscopy, directly by precipitation from the reaction mixture. We attempted to extend the trimerisation reaction to other substituted
indoles, however reaction of 5-cyano-, 5-methoxy- and 5-carboxaldehyde-indole resulted in mixtures of species, with no observable triindole product, possibly due to reaction of Br₂ with the added functional group. The reaction of 5-bromindole gave a mixture of products that proved too difficult to separate. The reaction of 5-nitroindole with three equivalents of Br₂ gave a single pure product, however this proved to be a monomeric indole with 2,3-dibromo-substitution. The 2,3-dibromoindole species have long been sought as synthetic intermediates to a range of species.²¹ While the one-step synthesis of a 2,3-dibrominated indole has been achieved for a number of N-alkylated species,²²,²³ it has never previously been successfully achieved in one-step for indoles where the nitrogen is protonated. Polybrominated indole monomers are of interest in a biological context due to their apparent antibacterial and anti-fungal activity, however their material properties make them unsuitable for organic electronic applications and they are not discussed further here.

Alkylation of both 2a and 3a was achieved to give 2b and 3b. For 2b, both the acid protons and the NH protons were replaced to give a hexa-alkylated species, whereas 3b contains only three alkyl chains (Figure 2).

![Figure 2. Alkylated compounds 2b and 3b.](image)

For all the new compounds, we were unable to obtain crystals of sufficient quality for structure solution, possibly due to disorder within the orientation of the trimeric rings and attached alkyl chains.

Cyclic voltammetry was carried out for 2a, 2b, 3a and 3b (Table 1). All the compounds showed a chemically-irreversible reduction, with that of the tribrominated species less negative than that of the acid/ester-containing compounds. The oxidation processes for 2a and 3a were chemically irreversible which is expected due to deprotonation of the NH group and possible N-N bond formation upon oxidation.²⁴ Alkylation of the NH position leads to greater chemical reversibility of the oxidation process for 2b and 3b, although 2b still shows slight chemical irreversibility.

Comparison of 2a and 2b or 3a and 3b indicates that addition of the octyl chains has resulted in little alteration of the oxidation potential. Direct comparison of these systems is problematic however as different
solvents were required due to solubility differences and peak potentials of irreversible processes cannot be directly compared with $E_{1/2}$ values of reversible couples.

**Table 1.** Electrochemical data for 2a, 2b, 3a and 4a.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reduction</th>
<th>1st oxidation</th>
<th>2nd oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a$^a$</td>
<td>-1.084$^a$</td>
<td>0.959$^a$</td>
<td></td>
</tr>
<tr>
<td>2b$^a$</td>
<td>-1.035$^a$</td>
<td>1.054$^a$</td>
<td></td>
</tr>
<tr>
<td>3a$^a$</td>
<td>-0.728$^a$</td>
<td>1.010$^a$</td>
<td></td>
</tr>
<tr>
<td>3b$^b$</td>
<td>-0.847$^a$</td>
<td>1.107$^a$</td>
<td>1.631$^a$</td>
</tr>
</tbody>
</table>

$^a$peak potential of chemically-irreversible process  
$^b$$E_{1/2}$ value of chemically-reversible process  
$^c$Dimethylformamide solvent, 0.1 M TBABF$_4$ electrolyte  
$^d$Dichloromethane solvent, 0.3 M TBABF$_4$ electrolyte

Perhaps surprising is the smaller than expected separation between the first oxidation and the first reduction potentials given the HOMO-LUMO gap indicated by DFT calculations and the optical gap indicated by spectroscopy (*vide infra*). No simple explanation for this can be given other than to note that the irreversible nature of the reductions means these do not necessarily reflect accurately the thermodynamic characteristics of the molecules.

Previous work by Huang *et al* established that a simple N-alkyl substituted triazatruxene, displays two characteristic absorption peaks at 316 nm and 256 nm, with a number of poorly defined shoulder peaks. In the case of 2a, 2b, 3a and 3b, these shoulder peaks become much more clearly defined and a number of new transitions appear (Table 2).

**Table 2.** Absorption peaks of 2a, 2b, 3a and 3b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{max}$/nm ($\varepsilon$/M$^{-1}$cm$^{-1}$ x 10$^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>269 (13.7)$^a$ 288 (18.7)$^a$ 322 (21.8)$^a$ 339 (8.9)$^a$ 354 (7.3)$^a$</td>
</tr>
<tr>
<td>2b</td>
<td>281 (79.3) 299 (99.8) 332 (117.0) 351 (42.2) 365 (33.4)</td>
</tr>
<tr>
<td>3a</td>
<td>279 (24.9) 317 (80.3) 331 (44.6) 349 (17.9)</td>
</tr>
<tr>
<td>3b</td>
<td>287 (40.2) 324 (112.0) 341 (54.2) 359 (21.7)</td>
</tr>
</tbody>
</table>

$^a$Molar extinction coefficients not reliable due to poor solubility.

It is notable that the presence of alkyl chains on the indole nitrogen atoms causes an inductive effect leading to a red-shift observed from 2a and 2b to 3a and 3b. The observed extinction coefficients for 2a were
significantly lower than expected based on the results for 2b. This has been attributed to poor solubility of 2a and difficulty in determining an accurate value. Observed values are given in Table 2 but should be treated with caution.

Compounds 2b and 3b were found to be emissive in EtOH at 293 K, both showing relatively featureless emission spectra with peaks at 450 nm and 401 nm respectively, typical of fluorescent polyaromatic molecules. This contrasts with 1, which was found to be non-emissive at room temperature, due to the large number of bromine atoms in the hexabrominated species, causing an increase in the heavy-atom effect, hence a greater proportion of intersystem crossing into the triplet excited state. In the case of 3b the rate of intersystem crossing caused by the heavy atom effect is sufficiently slow that the system is still fluorescent at room temperature. The emission and excitation spectra observed for 3b at 77 K are closely related to those observed for a frozen EtOH solution of 1 and show phosphorescence peaks at 453 and 477 nm, much more intense than the small fluorescence peak which is still visible (Figure 3).

**Figure 3.** Emission spectra of 2b at RT (left) and 3b at 77 K (right) the latter showing strong phosphorescence and also weak fluorescence signals.

DFT calculations based on a B3LYP functional and 6-31G* basis set have been carried out for all triindole species (Table 3, Figure 4, Figure S1 (see supporting data)).
Figure 4. LUMO (left) and HOMO (right) of 3a

Table 3. Calculated energies in eV of the frontier orbitals of 2a, 2b, 3a and 3b

<table>
<thead>
<tr>
<th></th>
<th>HOMO-1</th>
<th>HOMO</th>
<th>LUMO</th>
<th>LUMO+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>-5.602</td>
<td>-5.601</td>
<td>-1.504</td>
<td>-1.504</td>
</tr>
<tr>
<td>2b</td>
<td>-5.196</td>
<td>-5.193</td>
<td>-1.206</td>
<td>-1.188</td>
</tr>
<tr>
<td>3a</td>
<td>-5.466</td>
<td>-5.465</td>
<td>-1.046</td>
<td>-1.045</td>
</tr>
<tr>
<td>3b</td>
<td>-5.230</td>
<td>-5.213</td>
<td>-0.979</td>
<td>-0.953</td>
</tr>
</tbody>
</table>

Apparent from Table 3 is the degeneracy of the HOMO-1 and HOMO levels as well as the LUMO and LUMO+1 levels for each molecule. Given the inherent symmetry of the triazatruxene system it might be expected that this degeneracy would extend to the HOMO-2 and LUMO+2 as well. This is not the case however, with HOMO-2 energies of -6.499 eV, -5.985 eV, -6.440 eV and -6.099 eV and LUMO+2 energies of -1.354 eV, -0.614 eV, -1.019 eV and -0.535 eV for 2a, 2b, 3a and 3b respectively. The calculated HOMO-LUMO gap decreases from non-alkylated to alkylated systems from 4.10 eV for 2a to 3.99 eV for 2b and from 4.42 eV for 3a to 4.23 eV for 3b. This broadly agrees with the UV/Vis spectroscopy results.

The presence of the acid and ester groups results in a significant change in the unoccupied frontier molecular orbitals, with 28% of the LUMO and LUMO+1 character residing specifically on the acid groups of 2a and 38% of the LUMO and LUMO+1 on the ester groups of 2b. This is in stark contrast to the 15% Br character in the LUMO and LUMO+1 of both 3a and 3b.
As discussed above, the family of triazatruxenes has shown excellent potential for application as semiconducting materials and to confirm the potential of the new molecules in this regard, FET measurements were carried out using 3b. The material was spin coated onto an FET substrate with gold source and drain electrodes with a gap and width of 2 μm and annealed at 120 °C for 15 minutes under a stream of nitrogen. Although the performance was not exceptional, a distinct positive channel field effect was observed leading to threshold voltage estimated as -31 V, the on/off ratio as 2.1 x10^4 and the hole mobility as 1.43 x10^-6 cm^2 V^-1 s^-1 (Figures S2-3).

We have achieved the facile synthesis of large polyaromatic systems with easily-functionalised groups from commercial precursors in one pot. These present versatile new intermediates in the pursuit of both novel organic electronic materials and discotic liquid crystals.

General synthetic procedure for 2a and 3a: The substituted indole (0.5 mmol) was dissolved in AcOH (30 ml) and Br₂ (1.1mmol) in AcOH (20 ml) was added dropwise over 5 mins. The solution was left to stir overnight, filtered and the solid product washed with CH₃CN.

2a – Yield 44%; C₂₂H₁₅O₆N₄•2H₂O – Calcd C 63.15, H 3.70, N 8.19, Found C 63.47, H 4.63, N 7.38 – ^1H-NMR (DMSO-d₆) 12.76 (3H, s), 9.42 (3H, s), 8.14 (3H, d J = 14 Hz), 7.87 (3H, s)

3a – Yield 61%; C₂₂H₁₅N₃Br₂•2H₂O – Calcd C 48.00, H 2.33, N 7.00, Found C 48.03, H 1.93, N 6.96 – ^1H-NMR (DMSO-d₆) 12.35 (3H, s), 8.81 (3H, d J = 14 Hz), 8.06 (3H, s), 7.75 (3H, d J = 14 Hz) – FAB-MS: m/z 580(M⁺)

2b – Compound 2a, (238 mg, 0.5 mmol), KOH (560 mg, 0.01mol), [CH₃(CH₂)₃]₄N(HSO₄) (12 mg, 0.025 mmol) and 1-iodooctane (2.2 ml, 12 mmol) were dissolved in acetone (50 ml) and heated under reflux for 24 h. Once cool the solvent was removed and the residue dissolved in CH₂Cl₂ and washed with 10% aqueous HCl (3.5 equiv). The solution was dried over MgSO₄ and the solvent evaporated. The remaining solid was triturated with CH₃CN to give a pale yellow solid – Yield 2.09%; C₇₁H₁₁₁O₆N₃ – Calcd C 78.28, H 9.67, N 3.66, Found C 78.03, H 9.59, N 3.54 – ^1H-NMR (DMSO-d₆) 9.01 (3H,s), 8.13 (3H,d J = 14 Hz), 7.59 (3H,d J₆₋₃ 0.035), 4.93 (6H, t J₆₋₃ 0.035), 4.37(6H, t J₆₋₃ 0.035), 1.91 (6H, m), 1.79 (6H, m), 1.49-1.06 (60H, m), 0.84 (9H, m), 0.71 (9H, m) – FAB-MS: m/z 1148(M⁺)

3b – Compound 3a (582 mg, 1.02 mmol), KOH (1.12 g,0.02 mol), [CH₃(CH₂)₃]₄N(HSO₄) (24 mg, 0.05 mmol) and 1-iodooctane (2.2 ml, 12 mmol) were dissolved in acetone (50 ml) and heated under reflux for 24 h. Once cool the solvent was removed and the residue dissolved in CH₂Cl₂ and washed with 10% aqueous HCl (3.5 equiv). The solution was dried over MgSO₄ and the solvent evaporated. The remaining solid was triturated with CH₃CN to give a pale yellow solid – Yield 14%; C₄₈H₆₀N₃Br₃ – Calcd C 62.75, H 6.59, N 4.61, Found C 62.72, H 6.49, N 4.42 – ^1H-NMR (DMSO-d₆) 7.94 (3H, d J₆₋₃ 0.035), 7.63 (3H, s), 7.34 (3H, d JH-H 0.035), 1.93(6H, m), 1.04(36H, m), 0.87(9H, m) – FAB-MS: m/z 917(M⁺)
References and notes


[16] Luo, J.; Zhao, B; Shao, J.; Lim, K. A.; Chan, H. S. O.; Chi, C., J. Mater. Chem., 2009, 19, 8327


