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New indole trimers as precursors for molecular electronic materials**

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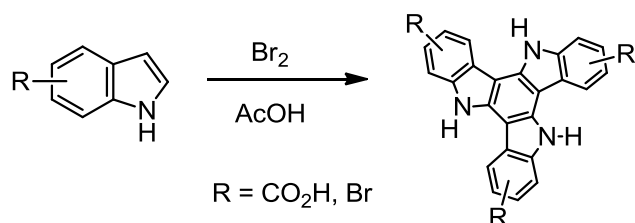
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Triazatruxene; DFT; Electrochemistry; Fluorescence; Transistor; FET

Abstract

We have prepared two new C_3 -symmetric, substituted-triazatruxene molecules using a facile one-pot trimerisation of 5-carboxyindole and 6-bromoindole in acetic acid using Br_2 , 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 solubility^{1,3} 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 $1.13 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.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 Br_2 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 molecules^{18,20} 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 C_3 -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.

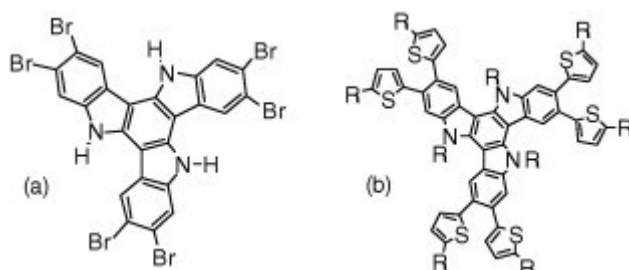
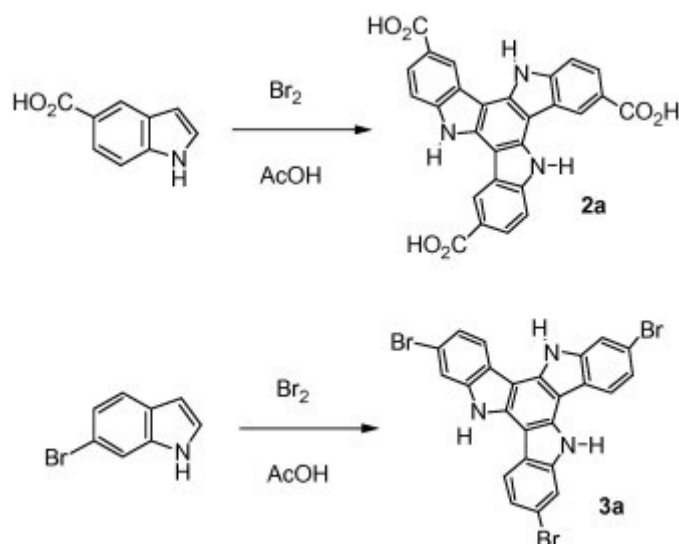


Figure 1. (a) hexabromotriazatruxene (**1**) and (b) examples of derivatives prepared from **1**¹⁶

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).

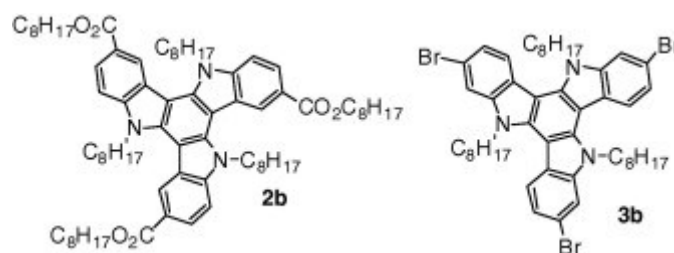


Figure 2. Alkylated compounds **2b** and **3b**.

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**.

Compound	Reduction	1 st oxidation	2 nd oxidation
2a ^c	-1.084 ^a	0.959 ^a	
2b ^c	-1.035 ^a	1.054 ^a	
3a ^c	-0.728 ^a	1.010 ^a	
3b ^d	-0.847 ^a	1.107 ^b	1.631 ^a

^apeak potential of chemically-irreversible process

^b $E_{1/2}$ value of chemically-reversible process

^cDimethylformamide solvent, 0.1 M TBABF₄ electrolyte

^dDichloromethane solvent, 0.3 M TBABF₄ 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,⁷ 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**.

Compound	λ_{\max} /nm ($\epsilon/M^{-1}cm^{-1} \times 10^3$)				
2a	269 (13.7) ^a	288 (18.7) ^a	322 (21.8) ^a	339 (8.9) ^a	354 (7.3) ^a
2b	281 (79.3)	299 (99.8)	332 (117.0)	351 (42.2)	365 (33.4)
3a		279 (24.9)	317 (80.3)	331 (44.6)	349 (17.9)
3b		287 (40.2)	324 (112.0)	341 (54.2)	359 (21.7)

^aMolar 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**,⁵ 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).

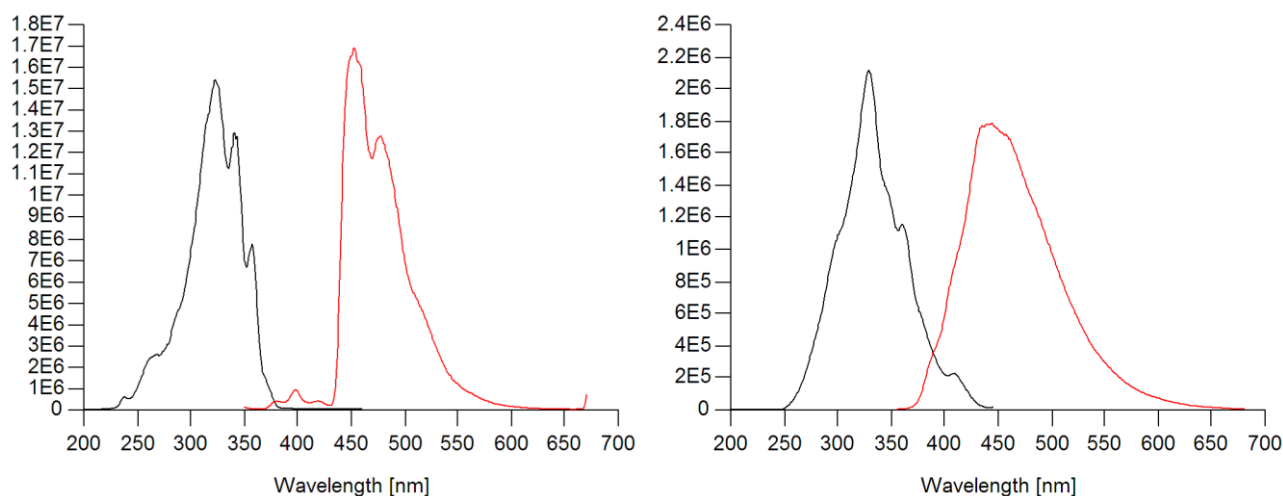


Figure 3. Emission spectra of **2b** at RT (left) and **3b** at 77 K (right) the latter showing strong phosphorescence and also weak fluorescence signals.

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)).

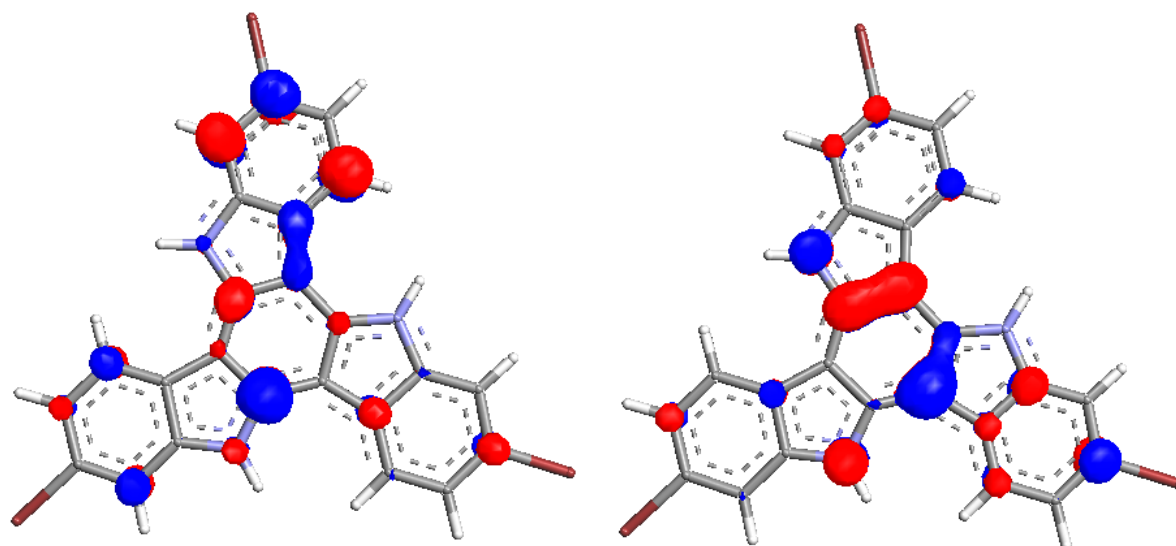


Figure 4. LUMO (left) and HOMO (right) of **3a**

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

	HOMO-1	HOMO	LUMO	LUMO+1
2a	-5.602	-5.601	-1.504	-1.504
2b	-5.196	-5.193	-1.206	-1.188
3a	-5.466	-5.465	-1.046	-1.045
3b	-5.230	-5.213	-0.979	-0.953

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 $^{\circ}\text{C}$ 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 2.1×10^4 and the hole mobility as $1.43 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (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 Br_2 (1.1 mmol) in AcOH (20 ml) was added dropwise over 5 mins. The solution was left to stir overnight, filtered and the solid product washed with CH_3CN .

2a – Yield 44%; $\text{C}_{27}\text{H}_{15}\text{O}_6\text{N}_3 \cdot 2\text{H}_2\text{O}$ – Calcd C 63.15, H 3.70, N 8.19, Found C 63.47, H 4.63, N 7.38 – ^1H -NMR (DMSO-d_6) 12.76 (3H, s), 9.42 (3H, s), 8.14 (3H, d $J = 14$ Hz), 7.87 (3H, s)

3a – Yield 61%; $\text{C}_{24}\text{H}_{12}\text{N}_3\text{Br}_3 \cdot \text{H}_2\text{O}$ – Calcd C 48.00, H 2.33, N 7.00, Found C 48.03, H 1.93, N 6.96 – ^1H -NMR (DMSO-d_6) 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, 0.01 mol), $[\text{CH}_3(\text{CH}_2)_3]_4\text{N}(\text{HSO}_4)$ (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 CH_2Cl_2 and washed with 10% aqueous HCl (3.5 equiv). The solution was dried over MgSO_4 and the solvent evaporated. The remaining solid was triturated with CH_3CN to give a pale yellow solid – Yield 2.09%; $\text{C}_{75}\text{H}_{111}\text{O}_6\text{N}_3$ – Calcd C 78.28, H 9.67, N 3.66, Found C 78.03, H 9.59, N 3.54 – ^1H -NMR (DMSO-d_6) 9.01 (3H, s), 8.13 (3H, d $J = 14$ Hz), 7.59 (3H, d $J_{\text{H-H}} 0.035$), 4.93 (6H, t $J_{\text{H-H}} 0.035$), 4.37 (6H, t $J_{\text{H-H}} 0.035$), 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), $[\text{CH}_3(\text{CH}_2)_3]_4\text{N}(\text{HSO}_4)$ (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 CH_2Cl_2 and washed with 10% aqueous HCl (3.5 equiv). The solution was dried over MgSO_4 and the solvent evaporated. The remaining solid was triturated with CH_3CN to give a pale yellow solid – Yield 14%; $\text{C}_{48}\text{H}_{60}\text{N}_3\text{Br}_3$ – Calcd C 62.75, H 6.59, N 4.61, Found C 62.72, H 6.49, N 4.42 – ^1H -NMR (DMSO-d_6) 7.94 (3H, d $J_{\text{H-H}} 0.035$), 7.63 (3H, s), 7.34 (3H, d $J_{\text{H-H}} 0.035$), 1.93 (6H, m), 1.04 (36H, m), 0.87 (9H, m) – FAB-MS: m/z 917(M^+)

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