Electroactive C_3 symmetric discotic liquid-crystalline triindoles†

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Discotic liquid crystals based on triindole, a novel redox active central core, have been synthesized and their mesomorphic behaviour investigated.
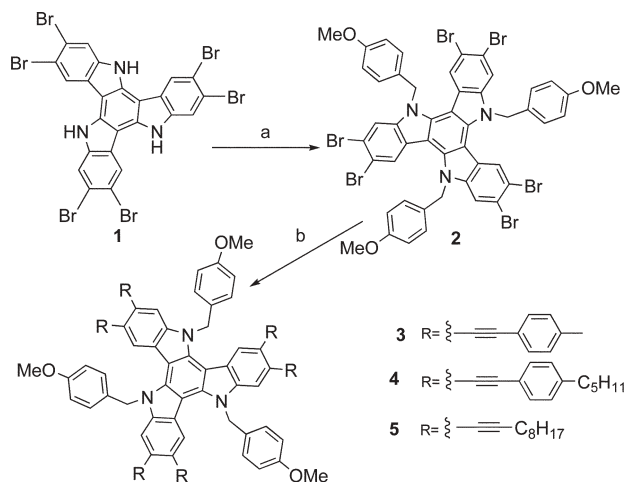
Much effort is being extended to develop organic materials for their use in light emitting diodes,[1] field effect transistors[2] or photovoltaic devices,[3] for which a parameter of prime importance is the mobility of charge within the active organic layer. In this regard, disc-like mesogens are of special interest due to their ability to self-assemble into columnar stacks. The high degree of uniaxial charge-carrier mobility observed in many discotic liquid crystals[4] derived from their columnar arrangement and their self-healing properties are among the most remarkable characteristics of these systems.

Carbazolyl groups have long been recognized in the construction of highly photoconductive amorphous organic materials. They undergo reversible oxidation processes and are able to transport positive charge centers *via* the radical cation species. In fields like xerography, photorefractives and organic light emitting diodes, the photoconductivity or the hole transport properties of the carbazolyl groups are being extensively utilized.[5]

In the search for highly conducting systems some recent attempts have been directed to combine the good hole transport properties inherent to the carbazole unit with the supramolecular organization associated with disc-like mesogens. This objective has been approached by the inclusion of carbazolyl groups in the peripheral lateral chains of well known discotic cores.[6]

In an alternative approach towards the same purpose we propose here the introduction of heptacyclic triindole as a new central core for the construction of discotic liquid crystals. This C_3-symmetric molecule can be considered as an extended π-system in which three carbazole units are sharing an aromatic ring. Surprisingly, while its all-carbon counterpart truxene has been extensively investigated for the construction of extended hydrocarbons,[7] electro-optical devices[8] or liquid crystals,[9] the triindole has been very little studied.[10] In this paper we investigate the electron-rich triindole platform as a novel redox active discotic core. Convenient attachment of flexible side chains leads to hexagonal columnar assemblies in a broad range of temperatures.

The synthesis of the new hexasubstituted triindoles starts from known symmetrical hexabromotriindole[11] **1** followed by Sonogashira coupling reactions in the key step (Scheme 1). Prior to

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a.NaH, PMBCl, THF; b. PdCl$_2$(dppf), RH, CuI, Et$_3$N:THF

Scheme 1 Preparation of hexasubstituted triindoles **3–5**.

the coupling, protection of the amino groups had to be performed, due to the instability of the *N*-unprotected platform under the coupling reaction conditions. Thus, alkylation of **1** with *p*-methoxybenzyl (PMB) chloride in the presence of NaH in THF yielded *N*-PMB protected triindole as a white powder (89%). We chose the six-fold Sonogashira cross-coupling of **2** with *p*-tolylacetylene as a model reaction to screen the catalyst and optimize the reaction conditions, since incomplete coupling is a common problem. Thus, coupling of hexabromo *N*-PMB protected triindole **2** with excess of *p*-tolylacetylene, and air stable PdCl$_2$(dppf) as catalyst led to hexaphenylethynyl triindole **3** in 73% yield. Reaction of **2** with 1-ethynyl-4-pentylbenzene under the same conditions afforded the corresponding hexasubstituted triindole **4** (68%). Coupling of **2** with excess of less reactive 1-decyne led to the hexasubstituted adduct **5** (60%) although a longer reaction time was required in order to avoid incomplete coupling.

Since it is well known that the nature of the flexible side chains has a dramatic influence on the mesomorphic properties, the alkyne groups on **5** were conveniently reduced. Thus, palladium catalyzed transfer hydrogenation, with ammonium formate as the hydrogen donor at reflux yielded **6** (73%) as an orange glassy compound (Scheme 2). Finally, treatment of **6** with AlCl$_3$ in CH$_2$Cl$_2$ led to **7**, obtained as a grey powder in 54% yield.
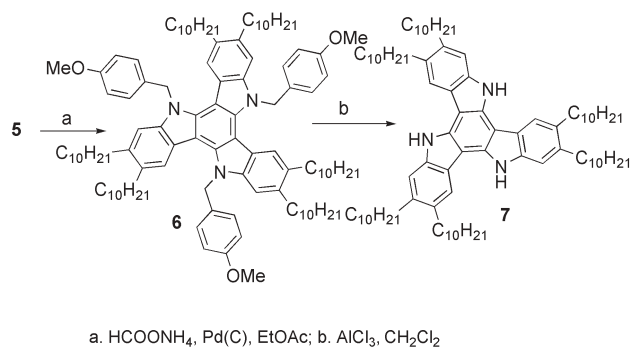
Investigation of the thermal properties of these new compounds indicates that **4** and **5** melt into the isotropic liquid without showing any mesomorphism while compounds **6** and **7** exhibit stable mesophases in a wide temperature range (Table 1).

a. HCOONH$_4$, Pd(C), EtOAc; b. AlCl$_3$, CH$_2$Cl$_2$

Scheme 2 Preparation of hexaalkyl triindoles **6** and **7**.

Table 1 Phase transition temperatures (°C) and corresponding enthalpy values (in brackets, kJ mol^{-1}) of compounds **6** and **7**

Compound	Thermal properties[a]
6	C 84.7 (31.5) Col$_h$ 151.5 (0.7) I
7	C 76.0 (88.7) Col$_h$ 154.8 (1.4) I

[a] Corresponding to the first heating scan (DSC). C: crystal, Col$_h$: hexagonal columnar mesophase, I: isotropic liquid.

The mesophases were assigned as hexagonal columnar on the basis of the typical pseudo focal conic textures observed by polarized optical microscopy (Fig. 1), and this was further confirmed by X-ray diffraction experiments at high temperatures (Table S1).

Curiously, the hexagonal lattice constant *a* deduced from the X-ray measurements (Table S1) is larger for compound **7** (26.9 Å) than for **6** (24.2 Å). This can be accounted for by the bulky *N*-substitution on **6** that presumably shapes thicker central cores resulting in larger average stacking distance and thus in more disordered peripheral hydrocarbon chains reducing the column diameter. In contrast, the expected shorter average stacking distance in compound **7** will probably result in less disordered hydrocarbon chains that can therefore be accommodated within the molecule plane increasing the column diameter.[12] The absence of any scattering maximum related to the stacking periodicity indicates that the molecules do not stack at a constant distance.

It is interesting to note that in spite of the bulky *N*-substitution of compound **6** that prevents planarity of the central core, mesomorphism is not precluded. This evidence introduces the potential of tuning the redox properties of the new liquid crystals
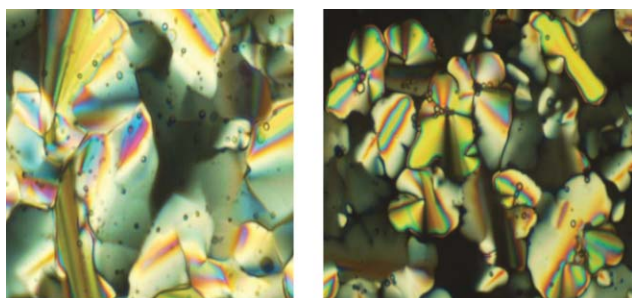
Fig. 1 Polarizing optical photomicrographs of **6** (left) and **7** (right) obtained at 115 °C and 116 °C, respectively on cooling.
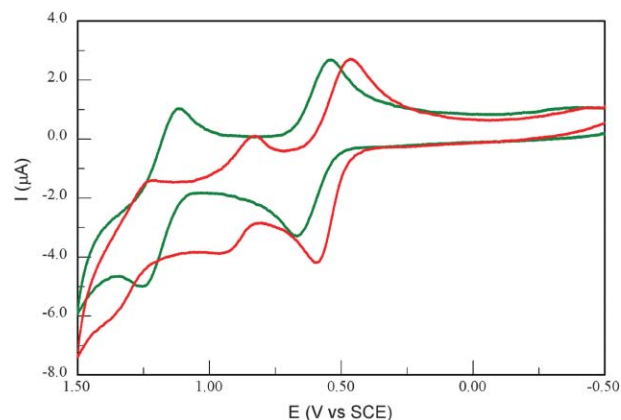
Fig. 2 Cyclic voltammogram of (a) **6** and (b) **7** at c = 10^{-3} mol L^{-1} recorded in CH$_2$Cl$_2$–0.1 M tetrabutylammonium hexafluorophosphate using a Pt working electrode.

by modulating the electronic properties of the platform upon *N*-substitution.

The electron-donating nature and redox stability of the new discotic core have been investigated by cyclic voltammetry of compounds **6** and **7** (Fig. 2). Both compounds can be easily oxidized to stable radical cations and higher cationic charged species. Compound **6** shows two reversible oxidation waves at 640 mV and 1215 mV in the accessible potential window of the solvent. Curiously, compound **7** shows three reversible redox processes at 571 mV, 937 mV, 1330 mV contrary to what would be expected since it has been long recognized that non-alkylated carbazoles are redox instable due to N–N coupling processes.[13] Probably in this case, the higher degree of charge delocalization results in higher stability of the oxidized species. Furthermore, these experiments suggest that non-alkylated triindoles are easier to oxidize than the trialkylated derivatives.

In summary, a novel central core for the construction of redox active liquid crystals, the heptacyclic triindole, has been introduced. Two derivatives showing a stable hexagonal columnar mesophase over a wide range of temperatures have been prepared. The particular relation of triindole to carbazole together with its planar disc-like nature renders this platform an attractive central core in the search for liquid crystals as coaxial hole transport materials. Investigations in this direction are currently in progress.

Notes and references

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12 The free NH groups in compound **7** might also favour an increase of the interaction between the molecular discs, which would result in a shorter stacking distance. However, the FT-IR experiments performed both on the crystal and on the mesophase reveal the presence of one sharp peak at 3467 cm^{-1}, corresponding to the stretching of the non-associated N–H bonds.

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