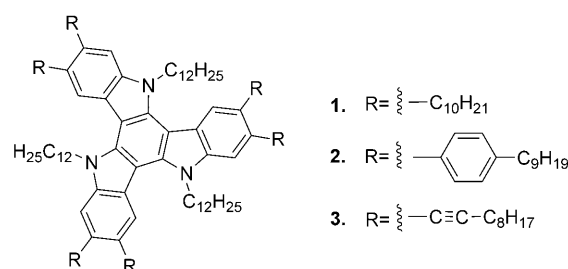# High Charge Mobility in Discotic Liquid-Crystalline Triindoles: Just a Core Business?**

Eva M. García-Frutos, Upendra K. Pandey, Roberto Termine, Ana Omenat, Joaquín Barberá, José L. Serrano, Attilio Golemme,* and Berta Gómez-Lor*

A key parameter in the performance of organic electronics devices is the mobility of charges. On the macroscopic level, it has been demonstrated that the highest charge carrier mobilities are obtained in highly ordered single-crystalline materials.[1] However, the inherent fragility of single crystals poses serious technological problems, thus considerably limiting their practical applications. An interesting alternative is offered by discotic mesogens, which are typically composed of a central aromatic core substituted with flexible alkylic chains.[2] Cores tend to form columnar stacks, maximizing π-orbital overlap between adjacent molecules and thus favoring a one-dimensional migration of charge carriers.[3] Furthermore, the inherent fluidity of liquid crystals induces advantageous properties, such as the ability to self-heal structural defects and easier alignment and processing from the isotropic phase. However, fluidity is also associated with intrastack dynamism of the functional units that reduces carrier mobility in the bulk. Therefore, the preferred strategy for improving mobility in discotic mesophases has been the enhancement of the intermolecular order within the stacks. To achieve this goal, different approaches have been explored: 1) linking the cores to peripheral alkylic chains through bulky moieties;[4] 2) introducing functional groups providing directional interactions[5] (e.g. hydrogen bonds); or even 3) inducing helical columnar arrangements that provide a higher degree of order.[4a,6,7] Herein, we present an experimental study on new triindole mesogens, one of them exhibiting very high hole mobility ($\mu \approx 1.4\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$). We show how carrier mobility in such compounds does not depend only on the degree of intracolumnar order along the columns by itself, but also, as in most π-conjugated organic semiconductors, on the stacking distance between molecules, which usually decreases with increasing order.[8] Moreover, results show how intracolumnar molecular distance can be controlled by a suitable choice of the spacers between the aromatic core and the peripheral chains, underlining the promising role of ethynyl moieties as linkers in high-mobility columnar phases.

Heptacyclic 10,15-dihydro-5H-diindolo[3,2-*a*:3′,2′-*c*]carbazole (triindole) was recently introduced as a new core for discotic mesogens.[9] Attachment of six decyl chains (compound **1** in Scheme 1) resulted in columnar hexagonal

Scheme 1. Structures of compounds 1–3 used in this study.

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mesophases, although no stacking periodicity was observed. Despite the intracolumnar disorder, **1** has a high hole mobility $\mu = 0.02\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ in the mesophase. In an attempt to raise the mobility values by increasing intracolumnar order, we have investigated the effect of sterically demanding phenyl (compound **2**) and rigid alkyne (compound **3**) spacers between the peripheral alkyl chains and the central triindole core.

The synthesis of **2** and **3** is described in the Supporting Information. Both compounds are obtained as crystalline solids. On heating, they show mesomorphic behavior between room temperature and about 150 °C, which is a significantly broader temperature range when compared with compound **1** (see Table 1). In particular, distancing the disordered alkylic chains from the central core with phenyl (compound **2**) or alkyne linkers (compound **3**) does not significantly influence the melting points but drastically increases the clearing point of these materials. Both **2** and **3** exhibit a hysteresis phenomenon in the crystallization process upon cooling,

Table 1: Phase transition temperatures [°C] and corresponding enthalpy values (in brackets, [kJ mol⁻¹]), of compounds **1**, **2**, and **3**, and lattice constants [Å] of the hexagonal columnar mesophase determined by XRD and charge carrier mobility μ.

Compd.	Thermal properties[a]	Lattice constants[b]	μ [cm² V⁻¹ s⁻¹][b]
1	C 38.9 (51.2) Col$_h$ 67.3 (0.5) I	$a = 27.7$	0.02 ± 0.005
2	C 39.3 (39.7) Col$_{ho}$ 153–160 I	$a = 29.4$ $c = 4.4$	$6 \times 10^{-4} \pm 0.0004$
3	C 43.5 (51.2) Col$_{ho}$ 150–165 I	$a = 29.0$ $c = 3.9$	1.4 ± 0.3

[a] Corresponding to the first heating scan (DSC). The temperature range for the transition Col$_{ho}$-I of **2** and **3** has been determined by POM (polarizing optical microscopy). C crystal, Col$_h$ hexagonal columnar mesophase, Col$_{ho}$ ordered hexagonal columnar. [b] **1** (45 °C), **2** (25 °C), **3** (25 °C).

showing a supercooled state that maintains the structural features of the mesophases (Supporting Information, Figure S2). This behavior favors the structural characterization of the compounds at room temperature.[10]

The mesophases of **2** and **3** were identified as ordered hexagonal columnar (Col$_{ho}$) on the basis of the typical pseudo focal conic fan-shaped textures observed by POM (polarizing optical microscopy) (see Figure 1) and of their X-ray dif-
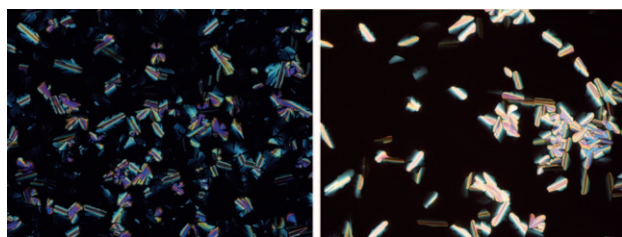

Figure 1. Polarizing optical photomicrographs of **2** (left) and **3** (right) obtained at 105 °C and 117 °C, respectively, on cooling from the isotropic liquid.

fractograms (Table 1). The X-ray diffraction patterns obtained for these compounds show a diffuse halo at 4.5 Å that is typical of the liquid-like order of the aliphatic chains. The diffraction patterns of **2** and **3**, in contrast to that observed for compound **1**, present an additional diffuse maximum with intensity reinforcement in the meridian region in the oriented pattern of **2** (an oriented pattern of **3** could not be obtained). This maximum corresponds to the periodic stacking of the cores, indicating the higher order achieved by distancing the disordered alkylic chains from the central core. It is interesting to note that this scattering peak is broader for **2** than for **3** and this gives evidence of a larger correlation length for the last compound. From the peak width it can be concluded that, whereas the π–π stacking involves a few molecules in the case of **2**, it extends to several nanometers in the case of **3**.

Bulky phenyl linkers have been previously shown to efficiently interlock molecules within the columns.[4a] However, in the case of **2**, the high steric demand of these

connecting groups induces large stacking periodicities ($c = 4.4$ Å). The alternative strategy of distancing the alkylic chains from the central core by rigid ethynyl groups results instead in closer adjacent disks ($c = 3.9$ Å) for **3** (Table 1). It should be noted that while phenyl[4a] or phenylethynyl moieties[11] have often been used as linkers between the flexible chains and the aromatic core, the direct attachment of the pendant side chains through an alkyne spacer has been rarely described.[12, 13]

Charge carrier (hole) mobility of **2** and **3** was measured by the steady-state space charge limited current (SCLC) technique,[14] which has been widely used to obtain values of mobility in organic compounds. The current–voltage characteristics typically exhibit a linear region at low applied voltages, where the behavior is ohmic. However, at higher voltages, where the current becomes space-charge-limited, an approximately quadratic dependence can be observed. In this regime the current depends only on the carrier mobility, assuming contacts to be ohmic and the material to be trap-free, and the Mott–Gurney[15] equation applies:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \tag{1}$$

where J is the measured current density, μ is the charge mobility, ε_0 is the free-space permittivity, ε_r is the dielectric constant of the material, V is the applied voltage, and d is the thickness of the device. As all of the other parameters in the equation are measurable, charge mobility can be easily obtained. Figure 2 shows a typical result of current–voltage measurements for compound **3**.

The measured values of mobility were highly dependent on the alignment of each particular sample, and even on the alignment of different areas within the same sample (see the Supporting Information). Well-aligned samples of **2** could be obtained, but for **3** alignment was poor or, in the best samples, incomplete. In the best cases, the measured hole mobilities at room temperature were $\mu \approx 6 \times 10^{-4}$ cm² V⁻¹ s⁻¹ for **2** and $\mu \approx 1.4$ cm² V⁻¹ s⁻¹ for **3** (Table 1). Such values correlated well with the degree of alignment estimated by optical microscopy and decreased even by one order of magnitude when the
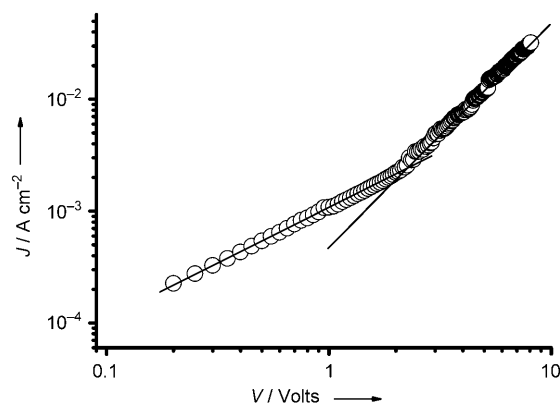

Figure 2. Typical current–voltage curve obtained for compound **3** at room temperature. The two straight lines, with slopes of 1 and 2, represent ideal ohmic and SCLC behavior, respectively.

alignment was particularly poor. Moreover, as the SCLC technique is sensitive not only to orientational order defects but also to the charge injection effectiveness at the electrodes, this should be considered as a lower limit for the hole mobility of **3**. To our knowledge, the hole mobility of **3** is the highest ever reported for discotic phases.[16–18] This result is particularly relevant as the columnar phases with the highest hole mobility generally exhibit shorter stacking distances (around 3.4 Å) and considerably more extended π systems. Furthermore, from what is known on similar model compounds,[19] the core of **1–3** is expected to be non-planar, although examples of columnar phases with high mobility obtained from mesogens with non-planar cores are known.[20]

In the compounds under investigation, the correlation length of the intracolumnar order increases in the sequence **1 < 2 < 3**. However, hole mobility increases in steps of two orders of magnitude in the sequence **2 < 1 < 3**, underlining the minor role of intracolumnar order in determining charge mobility. On the other hand, compound **2**, where the value of the stacking distance ($c = 4.4$ Å) is higher than in **3** ($c = 3.9$ Å), shows the lowest charge mobility, underlining the importance of the stacking distance.

The role of ethynyl linkers is then twofold: increasing the order within the column and at the same time reducing the stacking distances. However, the possible contributions to the charge transport of a larger π-orbital overlap and/or of a variation of the relative orientation of adjacent molecules induced by the alkyne spacers could also be important. A computational study aimed at clarifying this point is in progress.

In conclusion, the strategy of introducing alkyne spacers has been shown to efficiently increase the supramolecular order in the discotic mesophases, thus simultaneously reducing the distance between molecules in the stack, resulting in the discotic liquid crystalline material with the highest hole mobility reported to date. The fact that the stacking distance and the extent of π conjugation are far from ideal shows the importance of triindole as a core for high-mobility columnar phases. We have also shown that even though higher order has been often claimed as a fundamental factor for improving mobility in discotic liquid crystals, at least in this particular case the stacking distance between molecules seems to be even more important. This result can be of general relevance for many columnar phases, as it points out the specific role of chain linkers, within molecular periphery, in determining stacking distances.[21] The recognition of such an important structure–function relationship can certainly guide future work aimed at obtaining columnar phases with high charge mobility.

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