New Electrode-Friendly Triindole Columnar phases with High Hole Mobility

Mara Talarico,[†] Roberto Termine,[†]
Eva M. García-Frutos,[‡] Ana Omenat,[§] José L. Serrano,[§]
Berta Gómez-Lor,*[,‡] and Attilio Golemme*[,†]

Centro di Eccellenza CEMIF.CAL, LASCAMM CR-INSTM, Licryl CNR-INFM, Dipartimento di Chimica, Università della Calabria, 87036 Rende, Italy, Instituto de Ciencia de Materiales de Madrid, CSIC Cantoblanco, 28049 Madrid, Spain, and Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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In recent years, the search for low-cost electronic devices with flexible and easy to process components motivated the interest in organic electronic technology.[1] Among the various classes of materials developed in such area, discotic mesophases show intriguing properties: their ability to self-assemble into columnar stacks with aromatic cores surrounded by saturated hydrocarbon peripheral chains gives rise to an insulated, coaxial structure in which one-dimensional transport of charge is possible via the π-electronic conjugated systems of the molecules. This makes discotic liquid crystals particularly suitable as organic charge transport layers in many different devices, such as light emitting diodes, field effect transistors, and photovoltaic cells.[2] An important transport layer property that can heavily influence a device performance is charge mobility, often a limiting factor with amorphous organics but relatively high in ordered mesophases.[3] The search for mesomorphic materials with good mobility is therefore of high relevance in order to obtain devices with improved performance. The mobility of many types of discotic mesogens, with different cores (e.g., triphenylene,[4] hexaazatriphenylene,[5] porphyrin,[6] perylene,[7] phthalocyanine,[8] perihexabenzocoronene[9]), was characterized by using different methods, such as time-of-flight (TOF),[10] pulse radiolysis-time resolved microwave conductivity (PR-TRMC),[11] space charge limited current (SCLC),[12] and field effect transistor (FET)[13]techniques, obtaining in some cases very high charge mobilities[9a] (even approaching the value $\mu \approx 3$ cm^2 V^{-1} s^{-1}, found for the intersheet mobility in graphite).

Still unexplored within this context, is the potential of derivatives of 10,15-dihydro-5*H*-diindolo[3,2-*a*:3′,2′-*c*]carbazole (triindole), a disk-like molecule with C_3-symmetry that can be considered as an extended π-system in which three carbazole units share an aromatic ring. The chemical structure resemblance with the well-known hole transporter carbazole, together with the π-extended structure, renders triindoles attractive candidates in the search of new systems for organic electronics, as charge transport active layers. This work presents results of charge mobility performed in the discotic and crystalline phases of mesogenic compounds with an heptacyclic triindole core. Such a central core represents an innovation in discotic liquid crystals[14a] and its inherent electron-rich nature is expected to bestow favorable HOMO

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* Correspoding authors. E-mail: bgl@icmm.csic.es (B.G.-L.); a.golemme@unical.it. (A.G.).

[†] Università della Calabria.

[‡] Instituto de Ciencia de Materiales de Madrid.

[§] Universidad de Zaragoza-CSIC.

(1) (a) Stingelin-Stutzmann, N.; Smits, E.; Wondergem, H.; Tanase, C.; Blom, P.; Smith, P.; De Leeuw, D. *Nat. Mater.* **2005**, *4*, 601. (b) McCulloch, I. *Nat. Mater.* **2005**, *4*, 583. (c) Sobel, A. *Nat. Mater.* **2003**, *2*, 643. (d) Gelinck, G. H.; Huitema, H. E. A.; Van Veenendaal, E.; Cantatore, E.; Schrijnemakers, L.; Van der Putten, J.; Geuns, T. C. T.; Beenhakkers, M.; Giesbers, J. B.; Huisman, B. H.; Meijer, E. J.; Benito, E. M.; Touwslager, F. J.; Marsman, A. W.; Van Rens, B. J. E.; De Leeuw, D. M. *Nat. Mater.* **2004**, *3*, 106.

(2) (a) Sergeyev, S.; Pisula, W.; Geerts, H. *Chem. Soc. Rev.* **2007**, *36*, 1902. (b) Freudenmann, R.; Behnisch, B.; Hanack, M. *J. Mater. Chem.* **2001**, *11*, 1618. (c) Bayer, A.; Zimmermann, S.; Wendorff, J. H. *Mol. Cryst. Liq. Cryst.* **2003**, *396*, 1. (d) van de Craats, A. M.; Stutzmann, N.; Bunk, O.; Nielsen, M. M.; Watson, M.; Müllen, K.; Chanzy, H. D.; Sirringhaus, H. H.; Friend, R. *Adv. Mater.* **2003**, *15*, 495. (e) Katsuhara, M.; Aoyagi, I.; Nakajima, H.; Mori, T.; Kambayashi, T.; Ofuji, M.; Takanishi, Y.; Ishikawa, K.; Takezoe, H.; Hosono, H. *Synth. Met.* **2005**, *149*, 219. (f) Nelson, J. *Science* **2001**, *293*, 1059. (g) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119.

(3) (a) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685. (b) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. *Appl. Phys. Lett.* **2000**, *77*, 406.

(4) (a) Adam, D.; Schuhmacher, P.; Simmerer, J.; Haussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141. (b) Paraschiv, I.; Giesbers, M.; Van Lagen, B.; Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Marcelis, A. T. M.; Zuilhof, H.; Sudhoelter, E. J. R. *Chem. Mater.* **2006**, *18*, 968.

(5) (a) Gearba, R. I.; Lehmann, M.; Levin, J.; Ivanov, D. A.; Koch, M. H. J.; Baberá, J.; Debije, M. G.; Piris, J.; Geerts, Y. H. *Adv. Mater.* **2003**, *15*, 1614. (b) Lehmann, M.; Kestemont, G.; Goméz Aspe, R.; Buess-Herman, C.; Koch, M. J. H.; Debije, M. G.; Piris, J.; de Haas, M. P.; Warman, J. M.; Watson, M. D.; Lemaur, V.; Cornil, J.; Geerts, Y. H.; Gearba, R.; Ivanov, D. A. *Chem.—Eur. J.* **2005**, *11*, 3349.

(6) (a) van de Craats, A. M.; Schouten, P. G.; Warman, J. M. *EKISHO, J. Jpn. Liq. Cryst. Soc.* **1998**, *2/1*, 12. (b) Schouten, P. G.; Warman, J. M.; de Haas, M. P.; Fox, M. A.; Pan, H. L. *Nature* **1991**, *353*, 736.

(7) An, Z.; Yu, J.; Jones, S. C.; Barlow, S.; Yoo, S.; Domercq, B.; Prins, P.; Siebbeles, L. D. A.; Kippelen, B.; Marder, S. R. *Adv. Mater.* **2005**, *17*, 2580.

(8) (a) Iino, H.; Takayashiki, Y.; Hanna, J.; Bushby, R. J. *Jpn. J. Appl. Phys.* **2005**, *44*, L1310. (b) Iino, H.; Hanna, J.; Bushby, R. J.; Movaghar, B.; Whitaker, B. J.; Cook, M. J. *Appl. Phys. Lett.* **2005**, *87*, 132102.

(9) (a) van de Craats, A. M.; Warman, J. M.; Fechtenkötter, A.; Brand, J. D.; Harbison, M. A.; Müllen, K. *Adv. Mater.* **1999**, *11*, 1469. (b) Paraschiv, I.; Giesbers, M.; van Lagen, B.; Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Marcelis, A. T. M.; Zuilhof, H.; Sudhölter, E. J. R. *Chem. Mater.* **2006**, *18*, 968.

(10) Simmerer, J.; Glusen, B.; Paulus, W.; Kettner, A.; Schuhmacher, P.; Adam, D.; Etzbach, K. H.; Siemensmeyer, K.; Wendorff, J. H.; Ringsdorf, H.; Haarer, D. *Adv. Mater.* **1996**, *8*, 815.

(11) (a) Warman, J. M. In *Pulse Radiolysis*; Tabata, Y., Ed; CRC Press: Boca Raton, FL, 1991. (b) van de Craats, A. M.; Warman, J. M.; Müllen, K.; Geerts, Y.; Brand, J. D. *Adv. Mater.* **1998**, *10*, 36.

(12) (a) Rose, A. *Phys. Rev.* **1955**, *97*, 1538. (b) Blom, P. W. M.; de Jong, M. J. M.; van Munster, M. G. *Phys. Rev. B* **1997**, *55*, R656. (c) Reynaert, J.; Arkhipov, V. I.; Borghs, G.; Heremans, P. *Appl. Phys. Lett.* **2004**, *85*, 603. (d) M. Blom, P. W.; Tanase, C.; de Leeuw, D. M.; Coehoorn, R. *Appl. Phys. Lett.* **2005**, *86*, 092–105.

(13) Shimizu, Y.; Oikawa, K.; Nakayama, K.; Guillon, D. *J. Mater. Chem.* **2007**, *17*, 4223.

(14) (a) Gómez-Lor, B.; Alonso, B.; Omenat, A.; Serrano, J. L. *Chem. Commun.* **2006**, *48*, 5012. (b) García Frutos, E. M.; Gómez-Lor, B. *J. Am. Chem. Soc.* **2008**, *130*, 9173.

10.1021/cm8020512 CCC: $40.75

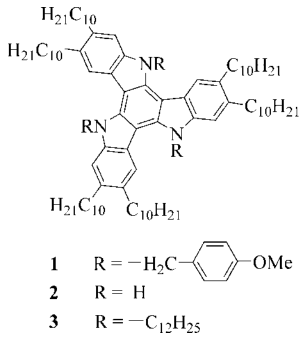

Figure 1. Chemical structures of triindoles **1−3**.

Table 1. Phase Transitions Temperatures and Mobilities

	1	**2**	**3**
phase transition temperatures (°C)[a]	C 84.7 $\mathrm{Col_h}$ 151.5 I	C 76.0 $\mathrm{Col_h}$ 154.8 I	C 38.9$\mathrm{Col_h}$ 67.3 I
μ ($\mathrm{cm^2\ V^{-1}\ s^{-1}}$)[b] $T = 22$ °C	0.011 ± 0.002	0.09 ± 0.02	0.05 ± 0.01
μ ($\mathrm{cm^2\ V^{-1}\ s^{-1}}$)[b] $T_M + 10$ °C	$4\ 10^{-3} \pm 0.001$	0.03 ± 0.01	0.02 ± 0.005

[a] The reported transition temperature data have been collected during the first heating scan (DSC). C, crystal; $\mathrm{Col_h}$, hexagonal columnar mesophase; I, isotropic liquid. [b] Mobilities were measured at room temperature in the crystalline phase and 10 °C above the crystal-mesophase transition (T_M) of compounds **1**, **2**, **3**.

energy levels on molecules, also inducing electrode-friendly, ohmic contact behavior. In particular, mobility measurements were carried out on the three discotic derivatives of triindole **1−3**, whose chemical structure differs only in the peripheral substituent on the nitrogen atom (Figure 1).

The synthesis of triindoles **1−2** has previously been reported.[14a] Compound **3** was prepared accordingly, by 6-fold Sonogashira cross-coupling of *N*-dodecyl hexabromotriindole[14b] with 1-decyne and subsequent hydrogenation of the triple bonds. All three materials show a stable hexagonal columnar mesophase over a wide range of temperatures (see the Supporting Information for further details). General information on the mesomorphic behavior of **1−3** is given in Table 1. As can be observed, the introduction of three additional alkyl chains at the nitrogen positions in compound **3** has a remarkable influence on its mesomorphic properties, significantly lowering the phase transition temperatures.

Previous cyclovoltammetric studies[14a] on compounds **1** and **2** highlighted the electron-donating nature and the redox stability of these triindole derivatives: in fact, they can be easily oxidized to give stable radical cations and higher cationic charged species. Compound **3** is easier to oxidize than compound **1**, probably reflecting the weak electron donating effect of the alkyl chains on the nitrogen functionalities. In particular, energetic considerations based on the measured HOMO energy levels (4.99 eV for **1**, 4.92 eV for **2** and 4.94 eV for **3**) suggest that **1−3** are likely to be hole transporters, in agreement with the synthetic purposes.

The charge carrier mobilities of **1−3** were obtained by using the SCLC technique.[12] The samples consisted of films (thickness ≈ 5 μm) sandwiched between two glass slides, coated with two different electrodes: Au and indium tin oxide (ITO). The Au work function ($w \approx 5.1$ eV) matches the HOMO levels of **1−3**, ensuring the efficient hole injection necessary in order to avoid major underestimations of mobility values. Current−voltage measurements (Figure 2) exhibit a typical linear region at low voltages,[7,12] where the behavior is ohmic, and a quadratic region at higher voltages, where the current becomes space-charge limited. The Mott−Gurney equation[15] applies in this last regime:

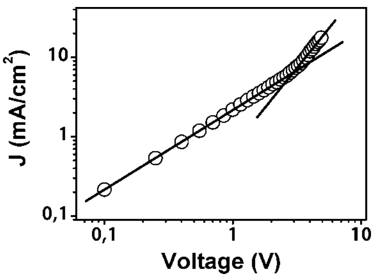

Figure 2. Double logarithmic plot of the current density versus applied voltage measured in a 5 μm thick sample of **2** at room temperature, after annealing. Symbols represent experimental data. Two continuous lines with slopes 1 and 2 have been included, representing ideal linear and quadratic regimes of the current as a function of the applied voltage.

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

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. Because all the other parameters in the equation are measurable, charge mobilities for the three discotic materials can be easily obtained. Results are summarized in Table 1.

In current−voltage measurements performed with the ITO electrode as the anode, currents several orders of magnitude lower were measured. This is expected, as the ITO work function[16a] $w \approx 4.4$−4.5 eV is too different from the HOMO levels of **1−3** to form ohmic contacts, the more so given the treatment with a base that was performed during substrate cleaning (see the Supporting Information), which is known[16b] to further decrease the work function. For all the compounds, from the data obtained it was not possible to measure a dependence of mobility on the applied electric field. Within the range of applied field used ($E \leq 1$−2 V/μm), the mobility is constant within the experimental error.

Mobilities were first measured at room temperature, with the samples in the crystal phase, after they were subjected to an annealing process in order to improve the quality of their alignment (see the Supporting Information), because this is one of the factors that can greatly influence charge mobility in discotic liquid crystals. Annealing was effective in all three cases and observations at the optical microscope revealed that even in the crystal phase, a relatively good homeotropic alignment was maintained. In measurements performed on samples not annealed, but simply cooled rapidly from the isotropic phase, mobility was lower by a factor of 2−3.

The mobility of **1−3** was also measured at different temperatures and in the columnar mesophases. The mobility

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(15) Lampert, M. A.; Mark, P. *Current Injection in Solids*; Academic Press: New York, 1970.

(16) (a) Park, Y.; Choong, V.; Gao, Y.; Hsieh, B. R.; Tang, C. W. *Appl. Phys. Lett.* **1996**, *68*, 2699. (b) Nüesch, F.; Forsythe, E. W.; Le, Q. T.; Gao, Y.; Rothberg, L. J. *J. Appl. Phys.* **2000**, *87*, 7973.

decreased with increasing temperature and in the mesophase it was lower by a factor 3−4 when compared to the values at room temperature, as summarized in Table 1. Such behavior is commonly attributed to the higher motional freedom of the side chains, which determines an increase of the structural disorder within the columns in the mesophase.[9a,17] The final result is a reduction of the efficiency of the charge transfer process. Mobility remained relatively constant throughout the liquid crystalline phase.

Charge mobilities in these new triindole derivatives are quite high, especially if one considers that the SCLC technique is sensitive to the structural defects of the macroscopic alignment and to the charge injection effectiveness at the electrodes: the measured values of mobility can in this sense be considered as a lower limit. In addition, these new triindole columnar phases also exhibit excellent photoconductive properties, even for wavelengths in the visible where absorption is low (see Figures S1 and S2 in the Supporting Information). Moreover, **1**−**3** represent the first discotic liquid crystals with a triindole core and their molecular structure has not yet been optimized. The data presented here show the importance of tuning the electronic and mesomorphic properties of these new liquid crystals upon *N*-substitution. In particular, determining which compound is characterized by the highest mobility can be extremely useful for understanding the relationship between charge transport properties and molecular structure, with the final goal of tuning the functional performance of the materials. Although differences are not dramatic, compound **2** gave the highest mobility among the three triindole derivatives. The difference, which is especially relevant when comparing with compound **1**, could be attributed to the bulky *N*-substitution, that induces a lower degree of planarity in the central core and may contribute to increasing the average intermolecular stacking distance within the columns. As a result, a more efficient intermolecular π-orbital overlap is expected for compound **2**, with a consequent increase in charge mobility. The absence of any X-Ray scattering maximum related to the stacking periodicity indicates that molecules do not stack at a constant distance. However, taking into account the data obtained from the X-Ray diffraction experiments (Table S1 in the Supporting Information) and assuming the same density for the three compounds, it is possible to estimate (see the Supporting Information) that the average distance between molecules within the column follows the relation **2** < **3** < **1**, the same trend as the one observed in the case of charge mobility.

In conclusion, a new class of conducting discotic liquid crystals has been identified in recently synthesized derivatives of heptacyclic triindole. These materials combine the good hole transport properties of the carbazole unit with the supramolecular organization typical of discotic liquid crystals, giving charge mobility values reaching $\mu \approx 0.1$ cm^2 V^{-1} s^{-1}. Such a result is remarkable, considering that the materials studied represent the first discotic liquid crystals with a triindolic core and that their molecular structure has not yet been optimized. Moreover, the particularly high values of the HOMO energy levels make such substances well suitable for all the applications where charge injection from an electrode is required. A comparison among the mobilities of the three investigated materials indicates that bulky substituents on the nitrogen atoms of the core lower the mobility.

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Supporting Information Available: Experimental details, photoconductivity results, characterization data and mesomorphic properties for compound **3**, and X-ray data (PDF). This material is available free of charge via the Internet at http: //pubs.acs.org.

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(17) Schouten, P. G.; Warman, J. M.; de Haas, M. P.; van Nostrum, C. F.; Gelinck, G. H.; Nolte, R. J. M.; Copyn, M. J.; Zwikker, J. W.; Engel, M. K. *J. Am. Chem. Soc.* **1994**, *116*, 6880.