Making coaxial wires out of Janus dendrimers for efficient charge transport

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ABSTRACT: Highly-conductive coaxial supramolecular wires are prepared by using a new family of *Janus* dendrimers that combines two rigid aromatic parts and two flexible aliphatic parts. The two external regions consist of a promesogenic block based on a third generation Percec-type dendron with four terminal dodecyloxy alkyl chains whereas the two internal regions are formed by one, two or three carbazole units bearing flexible spacers. These functional *Janus* dendrimers self-organize in columnar liquid crystal phases with a strong coaxial segregation within each column. Interestingly, the charge mobility studies revealed that these *Janus* dendrimers displays semiconductor properties with hole mobility values up to 0.5 $cm^2V^{-1}s^{-1}$, depending on the packing within the columns which can be tuned by the number of carbazole functional units. The high hole mobility values measured in these materials are among the highest values reported for columnar liquid crystals.

The field of organic electronics has expanded impressively in the last few years and the first generation devices based on organic semiconductors are commercially available.[1-3] Liquid crystals (LCs) offer an interesting approach for the preparation of these devices, as they self-organize into nanostructured phases which provide properties similar to those of organic single crystals, whereas the molecular dynamics of the LC phases favors the processability of the materials and even the self-healing of structural defects.[4-7] In particular, discotic LC molecules, constituted by a central aromatic core surrounded by flexible alkyl tails, are the most promising candidates as they present excellent charge transport properties.[8-12] The disk-shaped molecules self-assemble into columns favoring the intermolecular interactions of delocalized π-electrons. Thus, columnar LC phases behave as one-dimensional conducting molecular wires that, depending on the π-conjugate nucleus and the degree of order, give high charge mobility values along the direction of the columns (in the 10^{-3}–1 $cm^2V^{-1}s^{-1}$ range).[13-17] Despite these promising properties, given their high viscosity, columnar mesophases still suffer from the difficulty of obtaining the uniformly oriented large domains required in most devices. Percec and collaborators developed an alternative strategy to prepare less viscous high molecular weight columnar LCs. This original and versatile approach was based on the replacement of the discotic molecule by several tapered-shaped dendrons that self-organized in supramolecular columnar structures.[18-22]

The structural versatility of dendrimers, which allow introducing different functional units, makes them an interesting approach for the preparation of materials for optoelectronics.[23-26] For this purpose, *Janus* dendrimers, formed by two different functionalized dendrons attached in the focal point,[27, 28] allow obtaining singular supramolecular organizations with a distribution of functional groups that may facilitate charge transport. Our group has described the preparation of some LC *Janus* dendrimers formed by a mesogenic block based on a 2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) dendronic unit, functionalized with mesogenic units, and an electroactive block with different number of carbazole units. Nevertheless, low values of hole mobility were obtained (≈10^{-8} $cm^2V^{-1}s^{-1}$) due to the flexibility of the bis-MPA dendrons that prevents obtaining well-compacted columnar organizations.[29]

In an attempt to raise the hole mobility values, we have designed a new family of *Janus* dendrimers to obtain coaxial-like molecular wires (**Figure 1a**). In this design, we combine two rigid aromatic parts and two aliphatic flexible parts in order to generate four concentrical regions within the column. The two external regions consist of a mesogenic block based on a third generation Percec-type dendron bearing four terminal dodecyloxy alkyl chains (**Figure 1b**). This dendritic unit was chosen because of its tendency to form stable columnar mesophases due to the high intermolecular interactions among the aromatic rings.[19] The two internal regions are formed by the electroactive block, which contains carbazole units linked to the mesogenic block by a flexible spacer, that favors the carbazole-carbazole interactions within the column. Thus, compound **1** only contains one carbazole unit, whereas compounds **2** and **3** incorporate two carbazole units. In compound

2, these groups are bonded with the mesogenic block by means of a flexible spacer based on a bis-MPA dendron; however, in compound **3**, the linker is based on a rigid benzoic acid. Finally, compound **4** incorporates three carbazole moieties also linked by using a benzoic acid dendron.
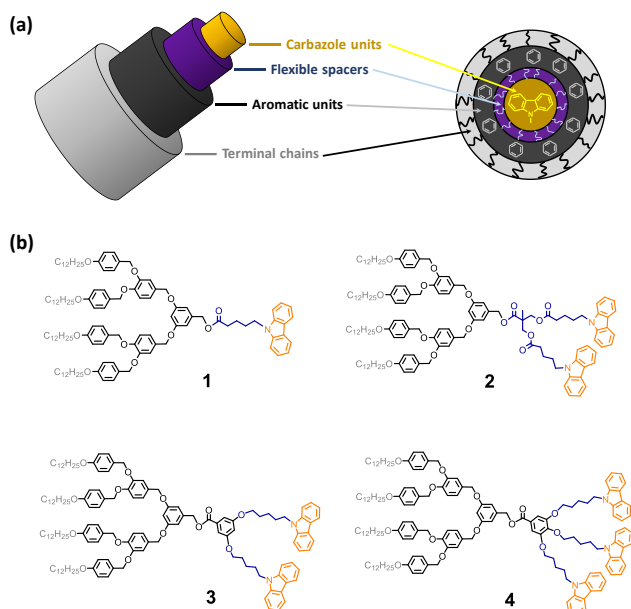
Figure 1. (a) Schematic representation of the supramolecular coaxial wires generated by the columnar LC *Janus* dendrimers, **(b)** chemical structure of the *Janus* dendrimers.

The synthesis of the *Janus* dendrimers is described in the Supporting Information and their chemical structures were confirmed by elemental analysis, IR, NMR and MALDI-TOF mass spectroscopy (see SI Section 2).

The thermal stability of the compounds was studied by thermogravimetric analysis (TGA), indicating that all the *Janus*

dendrimers have good thermal stability. In all cases the clearing point (transition to the isotropic liquid) is well below the 2% weight loss temperature ($T_{2\%}$) (**Table 1**).

The LC properties were studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC), and the results are listed in **Table 1**. All the *Janus* dendrimers showed LC properties with mosaic textures characteristic of columnar mesophases observed by POM (**Figure S1** in the **SI**). The **1**, **3** and **4** *Janus* dendrimers displayed enantiotropic hexagonal columnar LC mesophases, the mesomorphic order freezing in a glassy state at room temperature. On the other hand, compound **2** exhibited two enantiotropic columnar mesophases: a hexagonal arrangement at high temperatures, and a rectangular columnar mesophase at lower temperatures, that vitrified in a glassy state at around 30 ºC, keeping the LC arrangement.

The structures of the liquid crystal phases of the four *Janus* dendrimers were investigated by X-ray diffraction (XRD). Relevant data from this study are collected in **Table 1**. Additional data are gathered in the **SI (Table S1** and **section 3.2)**. The columnar mesomorphism of all the dendrimers is consistent with the X-ray patterns, which contain a set of two or more sharp maxima in the low angle region and a broad, diffuse halo in the high angle region **(Figure S3)**. The high-angle halo is due to the molten hydrocarbon chains and the intracolumnar packing, and its broad, diffuse character indicates that there is no regular stacking along the column axis. The low-angle reflections are assigned to the 2D array of the columns with a hexagonal symmetry for all the dendrimers investigated. The lattice constants a deduced from these spacing for each compound are gathered in **Table 1**. Compound **2** displays an additional mesomorphic phase at lower temperatures, that yields an X-ray diffractogram consistent with a rectangular columnar mesophase with constants a = 78 Å, b = 61 Å.

Table 1. Thermal transitions, XRD parameters, and μ_{hole} values

	$T_{2\%}$ (ºC)	Phase transitions[a]	T (ºC)	Phase	Structural parameters[b]	μ_{hole} [cm²V⁻¹s⁻¹]
1	300	I 74 (5.2) Col$_h$ 22 Col$_{h(g)}$ Col$_{h(g)}$ 27 Col$_h$ 74 (5.2) I	25	Col$_h$	a = 60.2 h = 5.6, Z = 6	[1.3 ± 0.8]·10⁻⁸
2	287	I 51 (5.2) Col$_h$ 37 (3.5) Col$_r$ Col$_{r(g)}$ 30 Col$_r$ 45 (1.7) Col$_h$ 53 (5.0) I	49	Col$_h$	a = 56.7 h = 5.0, Z = 4	–
			25	Col$_r$	a = 78, b = 61 h = 5.6, Z = 4	[5 ± 3]·10⁻⁴
3	305	I 63 (4.4) Col$_h$ 26 Col$_{h(g)}$ Col$_{h(g)}$ 37 Col$_h$ 64 (4.9) I	25	Col$_h$	a = 53.7 h = 5.5, Z = 4	[4.5 ± 2]·10⁻²
4	298	I 55 (3.8) Col$_h$ 26 Col$_{h(g)}$ Col$_{h(g)}$ 34 Col$_h$ 58 (4.3) I	25	Col$_h$	a = 50.3 h = 5.3, Z = 3	[4 ± 3]·10⁻¹

[a] Transition temperatures (ºC) and enthalpies (kJ/mol, in brackets) corresponding to the first cooling and second heating scans, obtained by DSC. Col$_h$: hexagonal columnar mesophase; Col$_r$: rectangular columnar mesophase; Col$_{h(g)}$, Col$_{r(g)}$: glassy phases; I: isotropic liquid.
[b] Structural parameters obtained by XRD. a, b: lattice constants of the columnar phases (Å), h: estimated mean stacking distance (Å), Z: molecules per disk.

It is evident that the molecules of these compounds do not fulfil the expected features to adopt a disk shape. Instead, several molecules must aggregate to fill the whole column cross-section.[18-22] Examining the calculated number Z of molecules per column slice of thickness equal to h in **Table 1** deduced from XRD studies (see **section 3.2** in the SI), it can be observed that the higher the number of carbazole units in the molecule, the lower the number of molecules required to fill the column. Curiously and in agreement with this, the diameter of the column in the Col_h mesophase (lattice constant a) decreases regularly upon increasing the length of the *Janus* dendrimer in its most extended conformation (L) (see **Table S1** and **section 3.2** in the SI). Taking into account the chemical structure of the *Janus* dendrimers, which are constituted by the same mesogenic block based on a third generation Percec-type dendrimer, the regular reduction of the diameter of the column must be related to the number of carbazole units per column stratum. Considering that the mean stacking distance h (column stratum thickness) estimated for the four compounds is almost constant (with a deviation of 6% from the average value), these data suggest that an increasing number of carbazole units in the *Janus* dendrimers is associated with a decrease of the number of mesogenic dendrons per stratum required to produce the molecular organization in the mesophase. Thus compound **1** with $Z = 6$ has six carbazole units per column slice, compounds **2** and **3** with $Z = 4$ have eight carbazole units, and compound **4** with a $Z = 3$ has nine carbazole units per column slice. These data agree with a higher crowding of carbazole rings in the central part of the column, which determines the topology of the rest of the molecule regions, mainly of the two flexible moieties. In particular, the column diameter is affected by the number of dendritic units in the periphery of the column cross-section: six for **1**, four for **2** and **3** and three for **4**. The observed difference in the lattice constant a between compounds **2** and **3**, bearing the same number of carbazole units, could be attributed to the rigidity of the benzoic linker that increases the π-π interactions and, consequently, produces a more compact structure in compound **3**.

Therefore, the results drawn from the X-ray study are consistent with a packing model with a strong segregation within each column in two aromatic regions and two aliphatic regions, as illustrated in Figure 1a. Each column contains the carbazole rings in the center, surrounded by the aliphatic spacers and the dendritic units with their peripheral chains. The above-described kind of arrangement in segregated concentrical regions has also been found for the columnar mesophases of other dendritic molecules with carbazole moieties at the apical position.[20-22] It must be stressed that there is no stacking of discrete disk-shaped aggregates. Thus, several molecules are necessary to fill the cross-section of the columns and these molecules pack with no periodicity in the direction of the column axis. In fact, each column consists of a supramolecular cylinder of indefinite length.

The UV-Vis absorption and fluorescence spectra of the *Janus* dendrimers were recorded on dilute solutions and in thin films at room temperature (Supporting Information, **Figure S4**). Relevant data are collected in **Table S2**. The UV-Vis spectra in solution included the carbazole π-π* and n-π* bands at 295, 330 and 345 nm, and the π-π* bands of the mesogenic blocks at 260 nm. These spectra are a combination of the spectra of

the corresponding building blocks and the presence of new bands was not observed. The fluorescence spectra, recorded with excitation at 295 nm, consisted of two bands (at around 352 and 368 nm) and a shoulder (at around 387 nm), characteristic of *N*-substituted carbazole derivatives. Fluorescence spectra were also collected in thin films and compared to the data from solution; the emission was red-shifted by ca. 5 nm.

To study the possible application of these *Janus* dendrimers in optoelectronics, it is important to investigate their electrochemical properties which can be deduced from cyclic voltammetry (CV) experiments. All the *Janus* dendrimers exhibited similar cyclic voltammograms with an oxidation peak at around 0.8 V in the first CV cycle (**Figure S5** in SI). However, meaningful reduction processes were not detected. The HOMO and LUMO energy values referred to the vacuum level were estimated by combining electrochemical and optical data (**Table S3** in SI). Furthermore, as originally demonstrated by Advincula's research group,[30-32] upon further cycling in CV experiments, it was possible to prepare electropolymerized films due to inter- and intramolecular crosslinking of carbazole-containing dendrimers at the 3,6-positions. The morphology of these electropolymerized films was characterized by using AFM and SEM measurements. It can be observed that the number of electropolymerizable units has a decisive influence on the final size of the spherical particles (**Figure 2**, and **section 3.4** in the SI).


	Diameter [nm]	Height [nm]
1	90±8	5±1
2	70±15	2±0.5
3	115±10	7±0.8
4	150±17	10±1.2
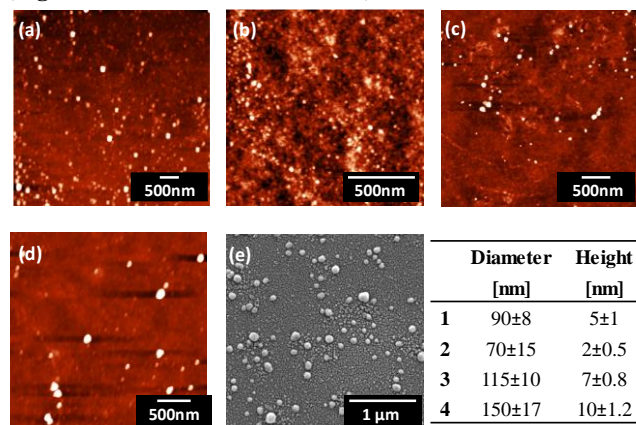
Figure 2. AFM images of: **(a)** compound **1**, (b) compound **2**, **(c)** compound **3** and **(d)** compound **4**. **(e)** SEM image of **3**.

The charge carrier mobility was measured by the space charge-limited current (SCLC) technique. This technique was chosen considering the HOMO energy value of the materials ($E_{HOMO} \approx -5.14$ eV), which matches the work function of Au ($W_{Au} \approx -5.1$ eV) and thus ensures the formation of an ohmic contact. As a counter-electrode, ITO was used because its work function ($W_{ITO} \approx -4.6$ eV) is significantly lower than the estimated LUMO ($E_{LUMO} \approx -1.65$ eV). The SCLC measurements were carried out in films sandwiched between Au- and ITO-coated glass electrodes. All the cells were filled by capillarity by heating the material above the mesophase-isotropic transition. After sample filling, cells were slowly cooled to room temperature. Several thermal treatments were performed in an effort to obtain a uniform alignment of the columns. However, these attempts were not successful, and all measurements were performed on polydomain samples. The details of sample preparation, thermal annealing procedures, and

mobility measurements are included in the Supporting Information.

Figure 3a shows the typical current/voltage curve acquired by connecting the positive pole to the Au electrode and the negative pole to the ITO electrode. As described in the Supporting Information, ionic currents are negligible and their effect can be excluded.
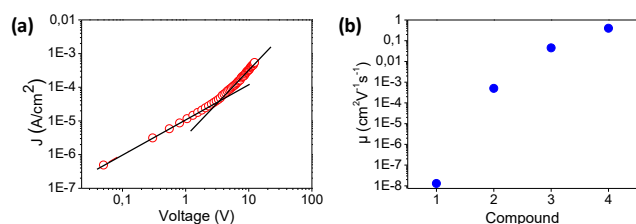
Figure 3. (a) Typical current-voltage curve obtained for compound **4** (red circles represent experimental data and the two black straight lines represent the ideal ohmic and SCLC dependence of J on V). **(b)** Evolution of hole mobility values of the *Janus* dendrimers.

The trend of the hole mobility is particularly informative (**Table 1** and **Figure 3b**). Compound **1** showed a very low mobility value of around 10^{-8} cm^{2}V^{-1}s^{-1}, typical of amorphous phases, while compound **2** exhibited a hole mobility 4 orders of magnitude higher. It can be inferred that the presence of one additional carbazole functional unit in the molecule and the corresponding increase of the number of carbazoles per disk from 6 to 8, introduce additional order and/or a higher volume density of charge transport active units within the inner core of the columns.

Compound **3**, which has the same number of carbazole rings per disk as compound **2**, presented a remarkable increase of hole mobility of two orders of magnitude ($4.5 \cdot 10^{-2}$ cm^{2}V^{-1}s^{-1}), that could be related to the decrease of the conformational mobility of the carbazole moieties that are attached to a rigid benzoic acid dendron. In the case of **2**, the carbazole units (attached to a flexible bis-MPA dendron) are more free to move (larger conformational mobility), the overlapping within the columns (carbazole-carbazole interactions) may be hindered, and consequently the hole mobility decreases.

The hole mobility of **4** ($4 \cdot 10^{-1}$ cm^{2}V^{-1}s^{-1}) was found to be 1 order of magnitude higher than that of **3**, probably because the presence of more transport active units in the molecule leads to a further enhancement of the carbazole-carbazole interactions within the central core of the columns. These hole mobility values are quite high, especially considering that there is a non-regular stacking of carbazole moieties, and that previous works on LCs based on tri-carbazole cores (triindole) reported an increase of charge mobility by reducing the regular π-π stacking distance between the cores within the columns.[14, 16]

In conclusion, we have synthesized a new family of *Janus* dendrimers by the attachment of a third generation Percec-type dendron to different carbazole-containing blocks. These materials combine the good luminescent and charge transport properties of the carbazole unit with the LC organization of the Percec-type dendron. The XRD results revealed the formation of well-ordered columnar superstructures consisting of several molecules filling the column cross-section and nanosegregation in alternated concentric regions within each column. These self-assembled columns are further self-organized into a 2D hexagonal or rectangular lattices. Their semiconducting behavior was studied by the SCLC technique, and charge carrier mobility values from 10^{-8} to 0.5 cm^{2}V^{-1}s^{-1} were ob-

tained. The hole mobility values reported here are comparable with the highest values described to date in the highly ordered hexagonal columnar mesophases.[14, 16] Moreover, an increasing number of carbazole functional units in the molecule leads to an impressive gradual increase in charge carrier mobility, probably *via* a significant enhancement of the packing within the core of the columns. This important structure-function relationship could guide future work aimed to obtain semiconducting soft materials with high charge mobility.

ASSOCIATED CONTENT

Supporting Information. Materials and methods. Experimental procedures. POM, XRD, UV-VIS, CV and SCLC characterization of the *Janus* liquid crystal dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

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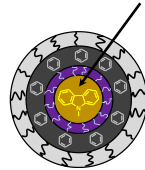(8) Concellón, A.; Marcos, M.; Romero, P.; Serrano, J. L.; Termine, R.; Golemme, A. Not Only Columns: High Hole

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Coaxial supramolecular wires
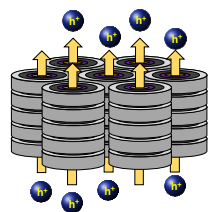
High-conductive region

Nanosegregated columns