Helically Arranged Chiral Molecular Nanographenes

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ABSTRACT: A benchtop solution-phase synthesis of molecular nanographenes composed of two orthogonal dibenzo[fg,ij]phenanthro-[9,10,1,2,3-pqrst]pentaphene (DBPP) moieties covalently connected through a tetrafluorobenzene ring is described. The helical arrangement of these three covalently linked molecular fragments leads to the existence of a chiral axis which gives rise to a racemic mixture, even with the molecular moieties being symmetrically substituted. X-ray diffraction studies show that both enantiomers cocrystallize in a single crystal, and the racemic mixture can be resolved by chiral HPLC. Asymmetric substitution in DBPP moieties affords a pair of diastereoisomers whose rotational isomerization has been studied by 1H NMR. Additionally, the electrochemical and photophysical properties derived from these new molecular nanographenes reveal an electroactive character and a significant fluorescent behavior.

INTRODUCTION

The groundbreaking discovery of 2D graphene as a new nanoform of carbon by A. Geim and K. Novoselov in 2004 had an extraordinary impact in the field of materials science.1 Actually, it paved the way for the development of unprecedented monolayer materials involving other chemical elements of the periodic table, thus starting the emergent age of 2D materials.2 Despite the outstanding chemical and physical properties of pristine graphene, the zero bandgap between its conduction (CB) and valence (VB) bands has limited its use in the search for optoelectronic properties and applications such as field-effect transistors,3 sensing,4 or photovoltaics,5 just to name a few.

In contrast to pristine graphene, the quantum confinement of electrons in smaller C(sp²) lattice structures, the so-called carbon nanoribbons and nanographenes (NGs) or graphene quantum dots (GQDs), increases the HOMO−LUMO gap, thus broadening the range of potential applications.6

Initially, carbon flakes without size control were formed from graphene by using an oxidative top-down approach. More recently, bottom-up synthesis of molecular nanographenes by accessing the realm of modern organic reactions allows the precise control of morphology and size and, therefore, the fine-tuning of electronic properties at will.8 In this way, this bottom-up approach has led to the preparation of NGs with a wide variety of shapes, namely planar nanographenes,9 bilayers,10 bowls,11 saddles,12 helical nanographenes,13 nanoribbons,14 nanobelts,15 and propellers.16

In the past few years, the introduction of chiral elements in nanographenes synthesized by the bottom-up approach and the study of their chiroptical properties have shown a special relevance.17

Chirality in molecular nanographenes is a consequence of morphological defects in the hexagonal honeycomb structure, namely stemming from (i) the presence of helicene moieties and/or (ii) the presence of nonhexagonal rings, which leads to either positive Gaussian curvature (five-membered or smaller rings) and/or negative Gaussian curvature (seven-membered or larger rings).18

Recently, our research group described the formation of molecular nanographenes with chirality derived from the presence of one or both aforementioned morphological defects (Chart 1).19 Herein, we describe the synthesis of a new family of chiral molecular nanographenes 1a−c lacking both helicene and curvature features. Interestingly, nanographene 1a is symmetrically substituted, and its chirality stems from a chiral axis formed as a result of the helical arrangement of the different moieties of the molecule.20 Actually, the kinetics of the racemization in 1a is related to the sterical rotational barriers existing between the two polyaromatic fragments and also with the central tetrafluorobenzene ring, resulting in a singular new type of orthogonally arranged chiral molecular nanographenes.

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RESULTS AND DISCUSSION

Synthetic Procedure. Our synthetic strategy is based on three main synthetic steps involving Sonogashira coupling, Diels–Alder cycloaddition plus retrochelotropic reaction with carbon monoxide extrusion, and a final Scholl cyclodehydrogenation to achieve the graphitized molecular structures 1a−c (Scheme 1).

The first step involves a double Pd-catalyzed Sonogashira cross-coupling reaction of two equivalents of a suitably substituted phenylacetylene 2a−c and 1,4-dibromotetrafluorobenzene. The resulting bis[aryl(ethynyl)]tetrafluorobenzenes 3a−c are able to undergo a 2-fold [4 + 2] cycloaddition reaction with cyclopentadienone 4 endowed with tert-butyl groups in order to improve solubility, thus affording polyaromatic compounds 5a−c in good yields. The final step is the Scholl cyclodehydrogenation of polyphenylenes 5a−c by reaction with dichlorodicyanobenzquinone (DDQ) in the presence of triflic acid at 0 °C, which provides the graphene-like shape by forming eight aryl–aryl bonds in a single reaction step to afford 1a−c in very good yields.

All final products and nonpreviously described intermediates have been characterized by 1H and 13C NMR, 19F-NMR, FT-IR, and high-resolution mass spectrometry. NMR spectra of 1a reveal only three 'Bu groups with 2:2:1 relative intensities and only one 19F signal (see Figure S7 in the Supporting Information). These signals correspond to a quarter of the molecule, revealing its highly symmetric nature with three orthogonal C2 rotational axes. Because of the lack of symmetry planes and inversion centers, this compound is framed in the chiral space-group of symmetry D2h. Moreover, NMR spectra of 1b and 1c (see SI, figures S15 and S22) show a 1:1 mixture of isomers. The presence of four 1:1:1:1 Bu signals for each isomer that correspond to a half molecule indicates a loss of symmetry compared to 1a. These compounds have two C2 rotational axes. As they have neither symmetry planes nor inversion points, they are included in the chiral space-group of symmetry C2h.

Additionally, the structure of 1a has been unequivocally established by single-crystal X-ray diffraction (see section 4 of the Supporting Information). Crystals of 1a with accicular habit (see Figure 1a) were obtained from a dichloroethane solution. The compound crystallizes in the centrosymmetric monoclinic C2/c space group, with one molecule in the asymmetric unit surrounded by several solvent ones (dichloroethane and water) displaying various degrees of disorder. As discussed before, 1a displays chirality (Figure 1c,d) because of the disposition of the two DBPP moieties around the central tetrafluorobenzene ring, with dihedral angles of 54.04° (C1−C6 with C7−C12) and 50.87° (C1−C6 with C63−C68). Additionally, the DBPP fragments deviate greatly from the planarity (Figure 1b), adding also helicity to the structure. The supramolecular arrangement of the molecules is achieved by C−H···π interactions, as the presence of the bulky tert-butyl substituents prevents the formation of π−π stacking (see Table S3 and Figures S31 and S32 for details).

Density functional theory (DFT) calculations on the model system 1a′, where the bulky tert-butyl groups were replaced by methyl groups (see section 9 in the Supporting Information), reveal the occurrence of stabilizing noncovalent C−H···π interactions in this novel nanographene. As clearly shown in Figure 2, there exist significant attractive interactions (greenish surfaces) between the central C6P4 fragment and the closest C−H bonds of the adjacent DBPP moieties. According to the second order perturbation theory (SOP) of the natural bond order (NBO) method, this attractive interaction results from the π(C=C) → σ*(C−H) and σ(C−H) → π*(C=C) electronic delocalizations, whose associated stabilization energies, ∆E(2), amount to −1.04 and −0.68 kcal/mol, respectively. The occurrence of these (4-fold) interactions is key for the stereoisomerism found in these species (see below).

Stereoisomerism of Nanographenes 1a−c. Despite the apparent lack of the typical asymmetry elements of chiral
nanographenes, namely chiral centers, helixes, or curvature, nanographenes 1a−c are chiral molecules. The existence of rotational barriers between the central tetrafluorobenzene ring and the two DBPP moieties and between both DBPPs generates a chiral axis around which the three planes containing each of the three components of the DBPP−C₆F₄−DBPP fragment are disposed in a helical arrangement. The symmetrical substitution pattern of the central C₆F₄ ring does not allow the application of the Cahn−Ingold−Prelog rules to set the priority of the substituents. Therefore, nanographenes 1a−c cannot be formally considered as atropoisomeric molecules endowed with two chiral axes, as in the case of terphenyl derivatives atropoisomerism.21

The rotational barrier involving the two DBPPs is hampered by the occurrence of additional noncovalent interactions between the closest aryl groups of both DBPPs (see Figure 2), which lock these moieties in an orthogonal array. Furthermore, the existence of additional rotational barriers between the central C₆F₄ ring and each DBPP unit by steric hindrance enforces the tetrafluorobenzene ring to adopt a +45 or −45° angle, thus giving rise to the existence of stereoisomers for nanographenes 1a−c (Figure 3). In this way,

Figure 1. (a) Aggregate of crystals of 1a (left) and individual needle with fluid inclusion (right); (b) X-ray crystal structure of 1a; (c) view of the cores of two adjacent enantiomers related by an inversion center (in red); and (d) superimposed cores of both enantiomers of 1a. Hydrogen atoms and solvent molecules have been omitted for clarity.

Figure 2. Contour plots of the reduced density gradient isosurfaces (density cutoff of 0.04 au) for compound 1a'. The greenish surfaces indicate attractive noncovalent interactions (for different orientations, see Figure S45 in the Supporting Information).

Figure 3. Newman-like projections of 1a, 1b, and 1c (priorities from front to rear, blue numbers; absolute configurations, green arrows). (a) Both 1a enantiomers absolute configuration. (b) 1b and 1c anti and syn stereoisomers.
	nanographene 1a has two enantiomeric structures that could be resolved by chiral HPLC (see Figure S39). By establishing priorities from front to rear, the absolute configuration of these enantiomers can be described by the “helical” arrangement of the fragments around the chiral axis, i.e., P if DBPP−C₆F₄−DBPP planes have clockwise rotation or M in the opposite scenario (Figure 3a). The presence of a substituent different from the 'Bu group in each DBPP (1b, R = OMe; 1c, R = H) results in the appearance of two new stereoisomers: anti when the substituents are placed in different sides of the C₆F₄ plane, and syn when they are located at the same side (Figure 3b). Interestingly, nanographenes 1b and 1c were isolated as a 1:1 isomeric mixture, determined by 'H NMR, when the Scholl reaction was performed at 0 °C. DFT calculations on a model of 1c indicate that the corresponding syn and anti isomers are nearly degenerate (ΔΔE = 0.8 kcal/mol, favoring 1c′-syn),
which is consistent with the experimental results. The 90° rotation of the central C₆F₄ ring from +45° to −45° leads to the racemization of nanographene 1a (Figure 3a). However, the same 90° rotation in nanographenes 1b and 1c gives rise to the anti−syn isomerization with a change in the absolute configuration, but not involving racemization (Figure 3b).

Symmetrically substituted nanographenes with axial chirality have previously been described by Campana et al.²³ and Wang et al.²⁵ In these examples, chirality stems from the strain arising from their planar conformation which forces these nanoribbons to twist around the chiral axis. Additionally, the absolute configuration of these twisted nanoribbons has been assigned by the presence of helicenes in their respective structures. However, axial chirality of nanographenes 1a−c arises from rotational barriers between DBPP−C₆F₄−DBPP fragments, and it represents the first example of “atropoisomeric-like” chirality in symmetrically substituted nanographenes.

**1H NMR Study of the anti−syn Isomerization (C₆F₄ Ring Orthogonal Arrangement).** As previously mentioned, compound 1c (R = H) was isolated as 1:1 anti−syn isomeric mixture when the Scholl reaction of polyphenylene 5c was carried out at 0 °C. However, at −65 °C, the Scholl reaction of 5c led to a 70:30 anti−syn isomeric mixture (assigned by 2D NMR, see section 5 of the Supporting Information) with noncomplete racemization (see Figure S34). After workup to remove the DDQ, the mixture was warmed at 40 °C and monitored by 1H NMR every 10 min approximately. Under these conditions, the ratio of isomers decreases over time until reaching 50:50 at equilibrium (Figure 4a). The kinetic constants determined for the anti−syn isomerization are kᵣ = kₛ = 1.08 × 10⁻⁴ s⁻¹. According to the Eyring equation, the rotational barrier of the C₆F₄ central ring is ΔG° = 24.6 kcal/mol at 40 °C with a half-life of t₁/₂ = 107 min (Figure 4b,c).

Moreover, when the Scholl reaction of 5c was carried out at −78 °C, it led to a unique compound 6 (Figure 5), characterized by ¹H, ¹³C, ¹⁹F, and 2D NMR (see Figure S25). The lack of stereogenic elements in 6 is because the C−C bond involving the unsubstituted phenyl group was not formed in any DBPP, allowing the free rotation of the three DBPP−C₆F₄−DBPP fragments. In this case, the most stable conformation calculated by DFT (Figure 5) shows a nonchiral orthogonal arrangement, in contrast to the helical arrangement of chiral isomers 1c.

**Electrochemical Properties of Nanographenes 1a−c.** The electrochemical properties of nanographenes 1a−c were explored by cyclic voltammetry in toluene/acetonitrile 4:1 mixture with tetrabutylammonium hexafluorophosphate as supporting electrolyte and Ag/AgNO₃ as reference electrode at room temperature. Table 1 shows their respective reduction and oxidation potentials vs Fc/Fc⁺ compared to hexa-tert-butylhexa-peri-hexabenzocoronene (Bu-HBC).

| compound | E°red (V) | E°ox (V) |
|----------|----------|----------|
| 'Bu-HBC  | −2.26    | 0.80     |
| 1a       | −2.42    | 0.92     |
| 1b       | −2.39    | 0.94     |
| 1c       | −2.34    | 0.97     |

*Measurements carried out in toluene/acetonitrile 4:1 mixture at room temperature using tetrabutylammonium hexafluorophosphate as supporting electrolyte, a glassy carbon as working electrode, platinum wire as counter electrode, and Ag/AgNO₃ as reference electrode.

Molecular nanographenes 1a−c show nonreversible first reduction waves at −2.42, −2.39, and −2.34 V vs Fc/Fc⁺, respectively, and quasi-reversible first oxidation waves at 0.92, 0.94, and 0.97 V vs Fc/Fc⁺. Compared to 'Bu-HBC, these compounds are poorer electron acceptors and electron donors as a consequence of the more π-extended structure of 'Bu-HBC. This fact suggests that the conjugation between the DBPP−C₆F₄−DBPP is hampered as a result of the noncoplanarity of these fragments. The observed electrochemical trend nicely correlates with the DFT-computed energy of the corresponding HOMO (the orbital from which the electron is released): −5.54 eV (1a') < −5.21 eV ('Bu-HBC), thus showing that a more stabilized HOMO (i.e., more negative) is translated into a higher oxidation potential.

**Spectroscopic Properties of Nanographenes 1a−c:** Absorption, Fluorescence, and Optical Energy Gap. The UV−vis absorption and emission spectra of molecular nanographenes 1a−c are shown in Figure 6. The wavelengths
of the absorption and emission maxima are collected in Table 2.

![Figure 6. Normalized absorption (solid lines) and emission (dashed lines) spectra of 1a–c in CHCl₃ recorded at room temperature.](image)

| compound | absorption λ_{abs}^{max} (nm) | emission λ_{em}^{max} (nm) | E_{0→0} (eV) |
|----------|-------------------------------|-----------------------------|--------------|
| 1a       | 317, 356, 378, 395, 419, 444 | 446, 474, 505               | 2.79 (2.79)  |
| 1b       | 320, 357, 380, 397, 419, 445 | 448, 476, 507               | 2.77 (2.78)  |
| 1c       | 318, 354, 377, 395, 419, 444 | 446, 473, 504               | 2.79 (2.79)  |
| 'Bu-HBC  | 344, 360, 390, 439, 441, 444 | 493, 519, 553               | 2.65 (2.69)  |

*Measurements carried out in CHCl₃ at room temperature. °Data extracted from ref 19b. *Values within parentheses are the energy gaps calculated from the corresponding intersections between the normalized absorption and emission spectra of each compound (see the Supporting Information, section 7).

The absorption spectra of molecular nanographenes 1a–c show similar shapes and energies with three sharp absorptions in the UV region (1a: 317, 356, and 378 nm; 1b: 320, 357, and 380 nm; 1c: 318, 354, and 377 nm) and three weak bands in the vis region (1a: 395, 419, and 444 nm; 1b: 397, 419, and 445 nm; 1c: 395, 419, and 444 nm). In comparison, the spectrum of 'Bu-HBC shows a similar shape, with three sharp absorptions in the UV region (344, 360, and 390 nm) and weak bands in the vis region (439, 441, and 443 nm). The bands of the spectra of 'Bu-HBC are red-shifted in comparison to nanographenes 1a–c because of the more conjugated structure of 'Bu-HBC, which is in agreement with that observed in the electrochemical analysis.

Time-dependent (TD) DFT calculations were carried out on the model 1a' to determine the nature of the vertical transitions associated with the observed UV/vis absorptions. Our TD-DFT calculations nicely reproduce the occurrence of the two bands at 419 and 444 nm (λ_{calc} = 418 and 420 nm, respectively), having a rather low oscillator strength (f = 0.028 and 0.020, respectively), which agrees with rather low ε observed experimentally (see Figure 6). These transitions are the result of the one-electron transition from the nearly degenerate HOMO and HOMO-1 (π-molecular orbitals delocalized in both DBPP moieties with no measurable coefficient in the central C₆F₄ fragment, see Figure 7) to the LUMO, respectively. Interestingly, the LUMO is a π*-molecular orbital delocalized along the entire molecule because of the presence of twisted π-orbitals connecting the central aryl ring with the DBPP fragments. The more intense band at ca. 395 nm (λ_{calc} = 410 nm, f = 0.18) is assigned to the HOMO–2 → LUMO transition. In this occasion, the HOMO–2 does exhibit coefficients in the central C₆F₄ fragment (Figure 7), thus confirming that the electronic communication in this compound by π-conjugation is not entirely suppressed despite the lack of coplanarity of the DBPP–C₆F₄–DBPP fragments.

Emission spectra of nanographenes 1a–c are also very similar. The spectra show three bands (1a: 446, 474, and 505 nm; 1b: 448, 476, and 507 nm; 1c: 446, 473, and 504 nm) in the vis region. Once again, in comparison to the emission spectra of 'Bu-HBC, the bands are red-shifted in the case of 'Bu-HBC. In addition, the optical energy gap of nanographenes 1a–c was calculated by the intersection of the absorption and the emission spectra (1a, 2.79; 1b, 2.78; and 1c, 2.79 eV). These energy gaps are higher than that of 'Bu-HBC (2.69 eV) because of the lower extension of the π-conjugation between the DBPP–C₆F₄–DBPP. The noncoplanarity of these fragments leads to a HOMO and LUMO spatial separation that has special interest in delayed fluorescence applications.

## CONCLUSIONS

The synthesis of a new family of molecular nanographenes (1a–c) constituted by two orthogonal DBPP units covalently connected through a tetrafluorobenzene ring is reported. Interestingly, the new nanographenes have a chiral nature stemming from the chiral axis existing along the whole molecule. As expected, X-ray crystal analysis of 1a reveals the existence of both enantiomers cocystalizing in a single monocrystal because of the disposition of the two DBPP moieties around the central tetrafluorobenzene ring.

The absolute configuration of the obtained enantiomers can be described by the helical arrangement of the fragments around the chiral axis DBPP–C₆F₄–DBPP. Furthermore, both enantiomers were resolved by chiral HPLC. Notably, replacement of a t-butyl group in each DBPP unit leads to a new pair of diastereoisomers (syn–anti) which are nearly degenerate and whose rotational barrier has been determined experimentally by 1H NMR from the Eyring equation to be ΔG° = 24.6 kcal/mol at 40 °C with a half-life of t_{1/2} = 107 min. The new series of compounds 1a–c shows interesting electrochemical and photophysical properties. Density functional theory (DFT) calculations nicely predict the occurrence of the two bands at 444 and 419 nm in the UV–vis spectra stemming from the HOMO and HOMO–1 to the LUMO transitions, respectively. Interestingly, the LUMO orbital is delocalized along the entire molecule because of the presence of twisted π-orbitals connecting the central aryl ring with the DBPP fragments, which allows the electronic communication along the entire molecule.

By performing the Scholl reaction of 5c at −78 °C, the free synthesis of the three DBPP–C₆F₄–DBPP fragments in the readily formed compound 6 is possible because of the lack of the C–C bond in the unsubstituted phenyl group. In agreement with the aforementioned results, the most stable conformation calculated by DFT for 6 shows a nonchiral...
orthogonal arrangement, which is in sharp contrast to the helical arrangement observed for chiral compound 1c.

These so-far unknown molecular nanographenes represent one step further in the family of chiral nanographenes and pave the way to an alternative methodology to obtain molecular nanographenes with control on their chemical structure and, therefore, on their chiral and optoelectronic properties.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c05977.

Synthetic procedures, additional figures and schemes of physical properties and characterization data, computational details, and Cartesian coordinates of all species described in the text (PDF)

Accession Codes
CCDC 2070237 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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