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Patricia Izquierdo-Garcia, Jesus M. Fernandez-Garcia, Samara Medina Rivero, Michal Šámal, Jiří Rybáček, et al.. Helical Bilayer Nanographenes: Impact of the Helicene Length on the Structural, Electrochemical, Photophysical, and Chiroptical Properties. *Journal of the American Chemical Society*, 2023, 145 (21), pp.11599-11610. 10.1021/jacs.3c01088 . hal-04115587

HAL Id: hal-04115587

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Submitted on 25 Oct 2023

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Helical Bilayer Nanographenes: Impact of the Helicene Length on the Structural, Electrochemical, Photophysical and Chiroptical Properties

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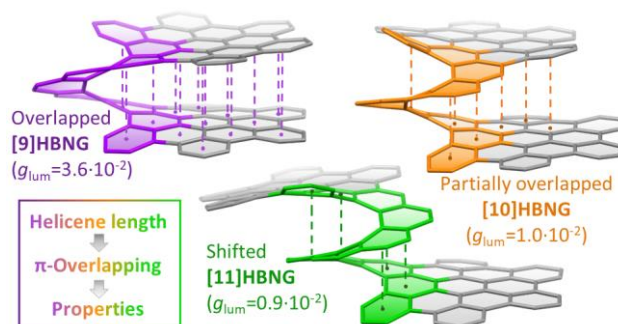
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Keywords: Helical Nanographenes, Bilayer Nanographenes, Chiroptical properties, Electrochemical properties

ABSTRACT: Helical bilayer nanographenes (HBNGs) are chiral π -extended aromatic compounds consisting in two π - π stacked hexabenzocoronenes (HBC) joined by a helicene, thus resembling van der Waals layered 2D materials. Herein, we compare [9]HBNG, [10]HBNG and [11]HBNG helical bilayers endowed with [9], [10] and [11]helicenes embedded in their structure, respectively. Interestingly, the helicene length defines the overlapping degree between the two HBCs (number of benzene rings involved in π - π interactions between the two layers), being of 26, 14 and 10 benzene rings, respectively, according to the X-ray analysis. Unexpectedly, the electrochemical study shows that the lesser π -extended system [9]HBNG shows the strongest electron donor character, in part by interlayer exchange resonance, and more red shifted values of emission. Furthermore, [9]HBNG also shows exceptional chiroptical properties with the biggest values of g_{abs} and g_{lum} (3.6×10^{-2}) when compared to [10]HBNG and [11]HBNG owing to the fine alignment in the configuration of [9]HBNG between its electric and magnetic dipole transition moments. Furthermore, spectroelectrochemical studies as well as the fluorescence spectroscopy support the aforementioned experimental findings, thus confirming the strong impact of the helicene length on the properties of this new family of bilayer nanographenes.



INTRODUCTION

The discovery of graphene by A. Geim and K. Novoselov in 2004 laid the foundations of the science of single-atom-thick layer materials or 2D materials.¹ Since this historic milestone, the development of atomically thin layer materials -with carbon and other elements of the Periodic Table- has been successfully achieved along the last recent years. The new family of mono-elemental 2D materials, namely graphyne,² borophene,³ germanene,⁴ silicene,⁵ stanene,⁶ plumbene,⁷ phosphorene,⁸ antimonene⁹ and bismuthene,¹⁰ was rapidly followed by the search for multielemental layered materials.¹¹ The main expectation is that, given their exceptional properties, 2D materials could replace conventional semiconductors to deliver a new generation

of electronics with applications in sensors,¹² low-cost organic solar cells,¹³ LEDs,¹⁴ transistors,¹⁵ piezoelectrics,¹⁶ superconductors¹⁷ or magnetism,¹⁸ among others.

Chemically, the pristine forms of these materials show strong in-plane covalent bonds and weak out-of-plane van der Waals (vdW) interactions. The stacking of several layers generates pseudocrystalline materials known as vdW layered solids.¹⁹ Remarkably, the twist angle between the layers of stacked 2D materials produces a moiré pattern forming a superlattice with a new band structure that dramatically affects the electronic properties of the material.²⁰ In this regard, Jarillo *et al.* have recently reported that a two-layered graphene having a “magic angle” of

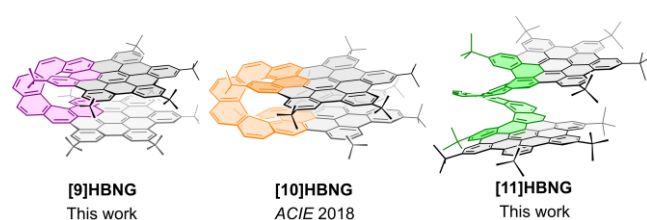
1.1° between the two honey-comb lattices shows superconductivity at 1.7 K.²¹ This finding represents an important landmark in the search for high temperature superconductivity.²²

Interestingly, the band gap properties of 2D materials can also be modified by the quantum confinement of the electrons in dimensionally reduced structures (1D, nanoribbons; 0D, quantum dots).²³ As a consequence of the edge effects in nanosized fragments of graphene, the so-called nanographenes (NGs), it is possible to open up the zero band gap of graphene, leading to semiconductor materials with potential applications in organic electronics.²⁴

Additionally, the bottom-up synthesis of monodisperse molecular NGs by using the arsenal of organic chemistry reactions allows controlling at will the size, morphology, and the ad-hoc incorporation of defects in the final structure of the molecule. This synthetic control allows, in turn, the fine-tuning of chemical, optical and electronic properties.²⁵ In the last recent years, a broad variety of molecular NGs has been synthesized by this methodology, covering a wide range of shapes, from the straightforward planar nanographenes²⁶ to curved,²⁷ twisted²⁸ or helically arranged molecular nanographenes.²⁹ The incorporation of curvature, strain or helicity in NGs may introduce asymmetry in the structures leading to the appearance of stereoisomeric forms,³⁰ that open the possibility of new applications derived from their chiroptical properties.³¹

The combination of both, stacked vdW materials and quantum confinement of electrons in nanographenes, leads to a new type of molecular bilayer NGs whose properties remain basically unexplored and scarcely reported.³² In this regard, some of the co-authors pioneered the topic³³ and our research group has recently reported a helical bilayer nanographene [10]HBNG inspired in the π -extended connection of a [6]helicene moiety and two hexabenzocoronene (HBC) units (Chart 1).³⁴ The length of the resulting [10]helicene places the HBC fragments in a AA stacking (AB for graphite) disposition.

Chart 1. Helical bilayer nanographenes (HBNGs) endowed with helicenes of different length, which results in different degrees of π -overlapping between the hexabenzocoronene layers (HBC).

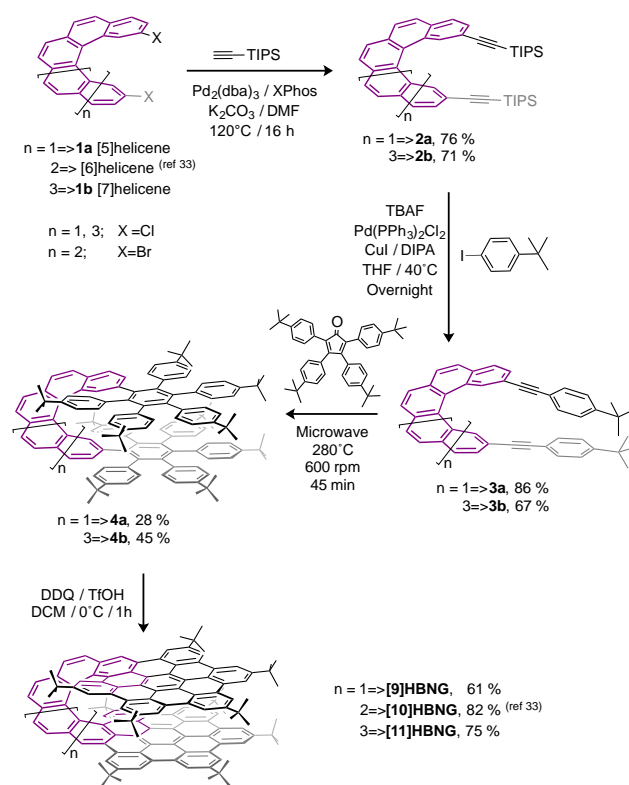


Herein, we report on the synthesis of new molecular bilayer nanographenes starting from [5]helicene and [7]helicene,³⁵ respectively. Both systems lead to the expected formation of the respective helical bilayers [9]HBNG and [11]HBNG (Chart 1). The different lengths of the helicene moiety ([9] and [11]helicenes, respectively) make the HBC layers to be disposed with a significantly different degree of overlapping between them. This allows to address electronic features arising from the co-facial coupling such as mixed valence effects in the oxidized state, excimer-like formation in the excited state and Raman vibrational properties comparable to graphene and multilayer graphene. Since the final bilayer NGs are obtained as racemates, a careful separation of their respective enantiomers has been performed by using chiral HPLC. Interestingly, the structural differences have a strong impact on their chiroptical, photophysical, electrochemical and spectroelectrochemical properties, which are discussed in the light of the previously synthesized

[10]helicene-containing bilayer [10]HBNG, whose new properties are also reported for the first time in this work. Singularly, [9]HBNG displays one of the largest chiral photoluminescence dissymmetry factors (g_{lum}) reported for pure hydrocarbons. This experimental finding arises from an alignment of the electric and magnetic transition vectors, stemming from the fine balance between vertical and layered π -conjugations.

RESULTS AND DISCUSSION

Inspired by the intriguing modification of the properties of 2D materials by twisting stacking bilayers, we decided to unveil the structural, chiroptical, photophysical, electrochemical and spectroelectrochemical properties of this family of helical bilayer nanographenes (HBNG). For that purpose, we designed a bottom-up synthetic strategy, in which starting from dihalo[n]helicenes with different lengths (dichloro[5]helicene **1a**³⁶ and dichloro[7]helicene **1b**³⁷),³⁸ it is possible to control the length of the resulting helicene in the final HBNG ([9]HBNG and [11]HBNG) and, therefore, the π -overlapping between the planar HBCs layers (Scheme 1).



Scheme 1. Synthesis of helical bilayer nanographenes [9]HBNG, and [11]HBNG from dichloro[5]helicene **1a** and dichloro[7]helicene **1b**, respectively.

I. Synthetic procedure. The preparation of [9]HBNG and [11]HBNG was achieved using our previously reported synthetic strategy employed to prepare [10]HBNG (Scheme 1). These rapid syntheses consist of only four reaction steps starting from dichloro[5]helicene **1a** and dichloro[7]helicene **1b**. Pd-catalyzed Sonogashira cross-coupling reaction with (triisopropylsilyl)acetylene led to the protected dialkynylhelicenes **2a** and **2b**, respectively. Thereafter, a new Sonogashira reaction with 4-*tert*-butyliodobenzene, with *in situ* deprotection of the TIPS groups using TBAF, added a benzene ring to each triple bond affording **3a** and **3b**. Then, Diels-Alder cycloaddition of tetra-4-*tert*-butylphenyl cyclopentadienone to the alkyne groups, followed by the retrocheletropic liberation of carbon monoxide,

led to the corresponding helicenes endowed with two penta-phenylbenzene groups **4a** and **4b**, respectively. Finally, Scholl cyclodehydrogenation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and trifluoromethanesulfonic acid (TfOH) formed 12 new C–C bonds, shaping the two HBC layers and extending the helicene backbone from [5]- and [7]- to [9]- and [11]helicene, respectively, yielding the desired **[9]HBNG** and **[11]HBNG** compounds with good yields (61 % and 75 %, respectively). The presence of ten ^tBu groups in each compound enhanced the solubility of the final new molecules allowing the

characterization by ¹H and ¹³C NMR, FTIR and mass spectrometry. The loss of 24 units in the molecular weight of **4a** (MW= 1751) and **4b** (MW= 1851) when they afford the final products **[9]HBNG** (MW=1727) and **[11]HBNG** (MW=1827), clearly indicates the formation of 12 C–C bonds in the Scholl reaction step and reveals the total graphitization of the HBC moieties. Additionally, ¹H and ¹³C NMR spectra only show the signals corresponding to a half of the molecule in both cases, revealing the presence of a C₂ rotational axis (Figures S7 and S8, see ESI).

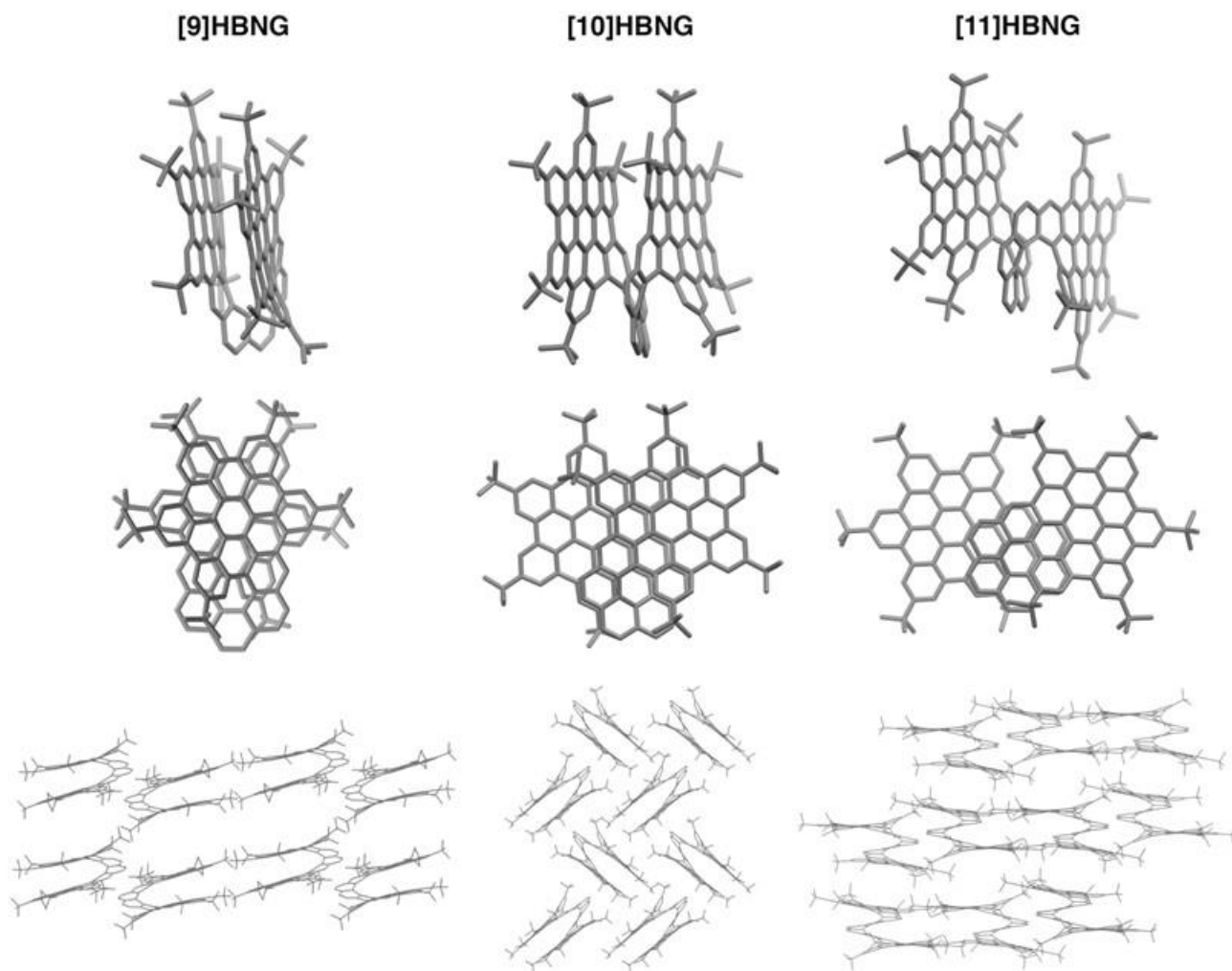


Figure 1. Molecular structures of compounds **[9]HBNG**, **[10]HBNG**³⁴ and **[11]HBNG** obtained by X-ray diffraction from single crystals (hydrogen atoms have been omitted for clarity). Lateral view (top), zenithal view (middle) and packing of the molecules where interstitial solvents have been omitted (bottom).

The structures of **[9]HBNG** and **[11]HBNG** were solved by single crystal X-ray diffraction (Figure 1). In both cases, centrosymmetric crystals containing *M* and *P* isomers were obtained from their respective racemic mixtures, unlike what happened in **[10]HBNG**, where the two isomers were spontaneously separated by crystallization, yielding enantiopure acentric crystals.³⁴

The comparison of the three crystal structures reveals some interesting facts, and explains the differences observed in their physical properties (see sections below). As expected, the length of the helicene linker was found to be crucial in achieving a convenient location of the two HBC layers of the molecules and proved to influence the overlap of the two nanographene fragments.

Thus, a total of 26 benzene rings in **[9]HBNG** are involved in intense π – π interactions resulting in a strongly overlapped bilayer when seen from a zenithal view (Figure 1 middle left, Figure S9, left). Consequently, the molecule adopts a remarkable U-shape from a side view (Figure 1, top), with a small interplanar angle of 2.37° between the layers of the HBC subunits, and a distance between the pivotal atoms of opposite ^tBu groups of 5.185 Å (C45–C127). Due to geometrical constraints, the rings of the two layers are staggered, with an average distance of 3.63 Å between the centroids of one layer and the opposite plane (Figures S9, S10, and Table S5; see ESI).

In **[10]HBNG**, the length of the helicene allows a partially overlapped AA-stacking of the two nanographene layers, with 14 rings participating in π – π interactions seen from a top view (Figure 1, middle and Figure S9, middle). The similarity with an

AA-type graphene stacking allowed the determination of an average distance of 3.54 Å between the matching centroids of opposite layers (Table S5, see ESI). The angle between the HBC planes has a value of 5.19°, giving a V-shape to [10]HBNG (Figure 1, top and Figure S9, see ESI), while the distance between the opposing ^tBu groups is 12.436 Å (C99–C127) due to the skewed structure arising from the partial overlap between HBC subunits.

In the case of [11]HBNG, the extension of the helicene linker forces the two HBC layers to separate, resulting in a shifted bilayer that presents π - π interactions between 10 benzene rings (Figure S9, right). In this HBNG, only one of the peripheral rings from each layer can participate in these bonds, and the mean distance between centroids involved in π - π interactions is 3.41 Å. The length of the molecule is the largest of the three (C45–C131=23.368 Å), and it also displays the highest angle between the two HBC layers (11.51°) generating a structure with a distorted Z-shaped lateral view.

A consequence of the diverse shapes displayed by the three HBNGs is the different packing observed for these molecular nanographenes in their crystal structures (Figure 1, bottom). [9]HBNG molecules are closely located in pairs (Figure S12, see ESI) due to the strong intermolecular π - π interactions (3.359 Å). Weak C–H \cdots π bonds join the pairs of molecules leaving huge voids, where disordered solvent molecules are lodged. Besides, columns of molecules are located at a perpendicular angle in the crystal structure of [10]HBNG, owing to C–H \cdots π interactions. Finally, the packing of [11]HBNG is achieved by C–H \cdots π supramolecular interactions between the HBNGs themselves, but also between HBNGs and the interstitial dichloroethane molecules.

II. Electrochemical and Spectroelectrochemical properties. The electrochemical properties of [9]HBNG, [10]HBNG and [11]HBNG were evaluated by cyclic voltammetry (CV, Figure 2) in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (i.e., Bu₄NPF₆) as supporting electrolyte, in a toluene/acetonitrile 4:1 mixture at room temperature. Table 1 shows the respective reduction and oxidation potentials vs Fc/Fc⁺ compared to hexa-*tert*-butylhexa-*peri*-hexabenzocoronene ^tBu-HBC as the reference.

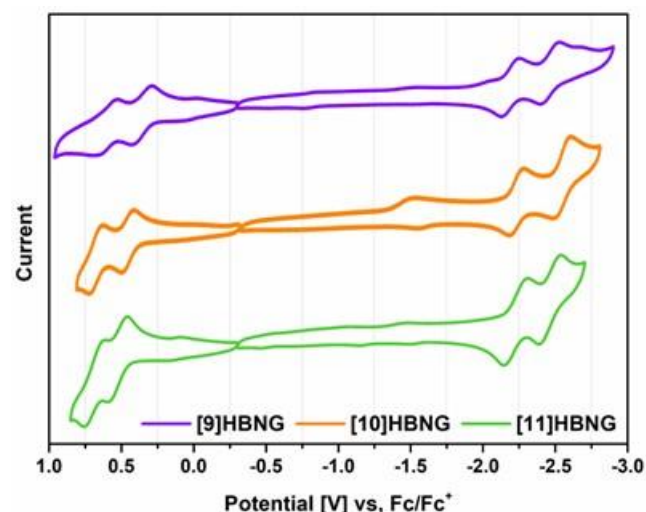


Figure 2. Cyclic voltammograms of helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG vs Fc/Fc⁺ in toluene/CH₃CN (4:1).

Table 1. First Oxidation and Reduction Potential values of ^tBu-HBC and molecular nanographenes [9]HBNG, [10]HBNG and [11]HBNG vs Fc/Fc⁺ at rt.

	E ¹ _{ox} (V)	E ² _{ox} (V)	E ¹ _{red} (V)	E ² _{red} (V)
^t Bu-HBC	0.75	-	-2.24	-2.40
[9]HBNG	0.35	0.59	-2.18	-2.46
[10]HBNG	0.46	0.67	-2.23	-2.55
[11]HBNG	0.52	0.69	-2.22	-2.46

In all three cases, two quasi-reversible oxidation waves and two quasi-reversible reduction waves are observed. The first oxidation potential follows the order [9]HBNG (0.35 V) < [10]HBNG (0.46 V) < [11]HBNG (0.52 V). Interestingly, the observed trend is the reverse to that expected according to the extension of the π -conjugation of the helicene moiety. Compared to ^tBu-HBC (0.75 V), these bilayer nanographenes are significantly better electron donors. The oxidation potentials variation seems to indicate that the larger the π - π overlapping of the two layers, the lower the oxidation potential values. This experimental finding could be accounted for by the fact that the radical-cation and the dication species (E¹_{ox} and E²_{ox}, respectively) are stabilized through the interaction between the two graphitized layers. This observation agrees with the location of the HOMO on the bilayer moieties.³⁴

Regarding the reduction potentials, previous studies on the [10]HBNG bilayer show that the reduction occurs, mainly, on the helicene region where the LUMO is located,^{29d} and reduction waves at -2.18, -2.23 and -2.22 V are observed for [9]HBNG, [10]HBNG and [11]HBNG, respectively. In this case, the smaller experimental variation might be influenced by the torsional angle as well as by the number of *ortho*-fused rings.

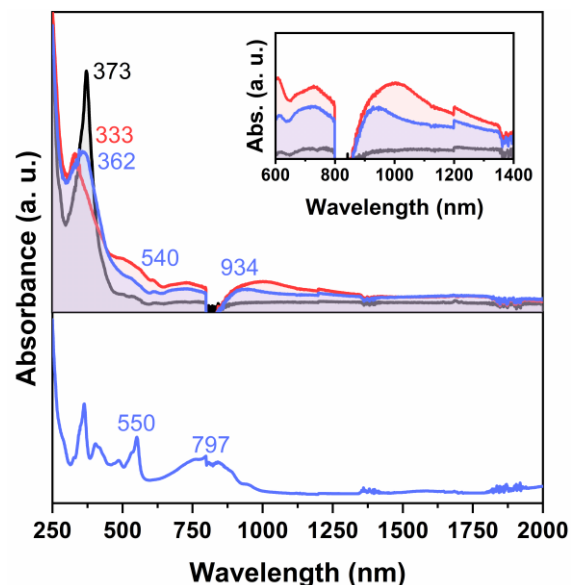


Figure 3. UV-vis-NIR electronic absorption spectra obtained upon electrochemical oxidation of [9]HBNG in a 0.1 M Bu₄NPF₆ solution in CH₂Cl₂ at room temperature by using a thin layer spectroelectrochemical cell. Black shadowed lines correspond to neutral species; blue/red shadowed lines correspond to the first/second oxidized species. UV-vis-NIR electronic absorption spectrum of ^tBu-HBC radical cation is also showed (bottom, blue line) for reference.

UV-vis-NIR spectroelectrochemical measurements of the three compounds have been carried out in a thin layer spectroelectrochemical cell (Figure 3 and Figure S17, see ESI). The first oxidation of [9]HBNG produces the appearance of two distinctive absorption bands at 934 and 540 nm that compare with those of the radical cation ^tBu-HBC at 797 and 550 nm (Figure 3 bottom; Figure S17a, see ESI). The observed 797 → 934 nm red-shift agrees with the smaller oxidation potential of [9]HBNG relative to ^tBu-HBC. The significant decrease of the oxidation potential observed for [9]HBNG might reveal a twofold effect: i) the involvement of the helicene moiety in the oxidation; and ii) based on the previous wavelength red-shift of the absorption bands, an inter-layer charge delocalization, which eventually contributes to lower the oxidation potential.

In the case of the second oxidation process, which is only observed in [9]HBNG (i.e., not in ^tBu-HBC), this further oxidation provokes a blue-shift of the main UV-Vis-NIR absorption bands, in line with the confinement of one radical cation in each HBC moiety due to charge repulsion in the dication state. The strongest absorption band of the neutral at 373 nm in [9]HBNG progressively blue-shifts on oxidation to 362 and 333 nm in the first and second oxidized species, respectively (Figure 3). Given that the strong band in the neutral state is composed of transitions emerging from the helicene and the HBC moieties, the notable affectation of this band with oxidation supports that, upon electron extraction, the charge is jointly stabilized by the two moieties.

The electronic absorption spectra of [11]HBNG in the two oxidation states display a progressive red-shift with increasing oxidation for the vis-NIR bands, in accordance with the charge being stabilized in a similar way in the two redox species of [11]HBNG.

III. Photophysical properties of the racemic mixture. The absorption spectra of the helical bilayer nanographenes [9]HBNG (overlapped bilayer), [10]HBNG (partially overlapped) and [11]HBNG (shifted bilayer) and of the monolayer nanographene, *tert*-butylated hexabenzocoronene, ^tBu-HBC, are shown in Figure 4. Their corresponding peak/shoulder wavelengths and absorption coefficients are collected in Table 2. Shoulders were determined from the second derivative of the absorption spectrum. The rigid and flat ^tBu-HBC monolayer nanographene shows a structured absorption spectrum with vibronic fine structure and a maximum at 360 nm, while the helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG display non-structured and broader absorption spectra, extended to 569, 557 and 518 nm, respectively (absorption tails with at least 1 % absorption with respect to that of the maximum), with slightly bathochromically-shifted maxima in the 373-377 nm interval. Interestingly, the helical bilayer nanographenes show allowed electronic transitions in the visible region above 400 nm, with absorption coefficients >10⁴ M⁻¹cm⁻¹. Conversely, the planar ^tBu-HBC monolayer nanographene exhibits forbidden transitions in the visible region (ε ~10³ M⁻¹cm⁻¹). Therefore, the more intense and redshifted absorption bands observed in the visible region reflect the direct involvement of both helicene and HBC moieties in the optical properties of HBNGs, in good agreement with previous literature on curved molecular nanographenes containing both subunits.^{27c}

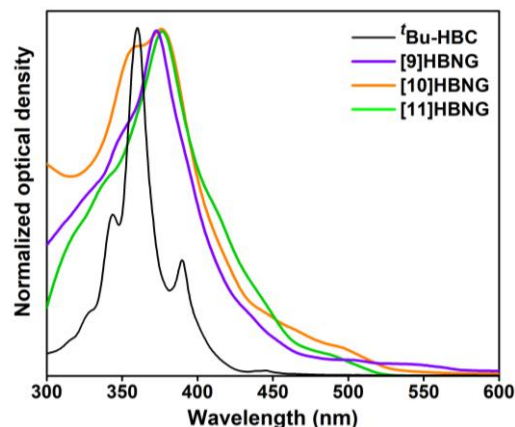


Figure 4. Absorption spectra of ^tBu-HBC and of helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG in CHCl₃.

Table 2. Data from absorption spectra of the helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG and of the monolayer nanographene ^tBu-HBC in chloroform.

	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) ^a
[9]HBNG	349 (94600); 373 (136000); 392 (86300); 435 (20600); 502 (6200); 542 (4700)
[10]HBNG	360 (98600); 377 (103900); 415 (38800); 446 (18700); 462 (14400); 494 (8700)
[11]HBNG	339 (70800); 377 (125000); 415 (58200); 444 (26100); 491 (7300)
^t Bu-HBC	344 (63750); 360 (141700); 390 (46350); 439 (1600); 441 (1650); 445 (1800)

^a $\lambda_{\text{abs}}/\text{nm}$ (± 1 nm) ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) (± 10 %)

Regarding the fluorescence of the helical bilayer nanographenes, their corresponding emission spectra are shown in Figure 5. Compared to ^tBu-HBC, they show broader, non-structured and red-shifted emission bands, with full width at half maximum (*FWHM*) values in the ~2500–3000 cm⁻¹ interval (cf. ~1600 cm⁻¹ for ^tBu-HBC). The emission spectra have two main features: i) in shape, they resemble more the emission spectra of helicenes with one molecular band disclosing vibronic resolution; and ii) the pronounced broadening is more typical of excimer-type emissions. According to (ii) the most redshifted excimer-like band is for [9]HBNG in line with the greater propensity to form interlayer interactions. According to (i), the three emissions have clear helicene contributions. Remarkably, [9]HBNG (overlapped bilayer), the bilayer helicene with the lowest number of fused benzene rings (9) and most overlapped π -structure (i.e., larger π - π interactions), displays the most bathochromically shifted fluorescence (pointing to a more stable singlet excited state as compared to [10]HBNG and [11]HBNG). It is likely that structural differences among the bilayer nanographenes considering the increasing number of benzene rings within the helicene framework, at the level of their torsional angle or their interplanar angle, resulting in different interlayer interactions, might influence the distinct fluorescence shifts and, therefore, the general photophysics of the helical bilayer nanographenes. Emission data of the monolayer nanographene ^tBu-HBC and of the helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG are collected in Table 3. The Stokes' shifts of the bilayer nanographenes are 9419 cm⁻¹ (204 nm) for [9]HBNG, 8109 cm⁻¹ (187 nm) for [10]HBNG, and 7585 cm⁻¹ (154 nm) for [11]HBNG, while the planar and more rigid monolayer nanographene ^tBu-HBC

shows the lowest Stokes' shift (7117 cm^{-1} , 124 nm). This result agrees with the lower molecular stiffness of the bilayer nanographenes studied and, notably, points to the higher singlet excited state reorganization energy of [9]HBNG compared to

Table 3. Data from the excitation and fluorescence spectra of the helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG and of the monolayer nanographene ^tBu-HBC in chloroform.

	λ_{em}^{max}/nm (shoulder)	$FWHM/cm^{-1}$ (eV)	Stokes' shift/ cm^{-1} (eV)	E_{0-0}/eV	Φ_{em}
[9]HBNG	575 (611)	2547 (0.32)	9419 (1.17)	2.35 ± 0.09	0.22 ± 0.02
[10]HBNG	543 (567)	2943 (0.36)	8109 (1.00)	2.49 ± 0.09	0.10 ± 0.01
[11]HBNG	528 (551)	3012 (0.37)	7585 (0.94)	2.58 ± 0.09	0.11 ± 0.01
^t Bu-HBC	445, 454, 464, 475, 484, 493, 518, 528, (537), 556, 567	1613 (0.20) ^{27c}	7117 (0.88)	2.65 ± 0.13 ^{27c, 39}	0.02 ± 0.01

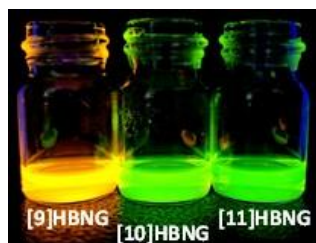
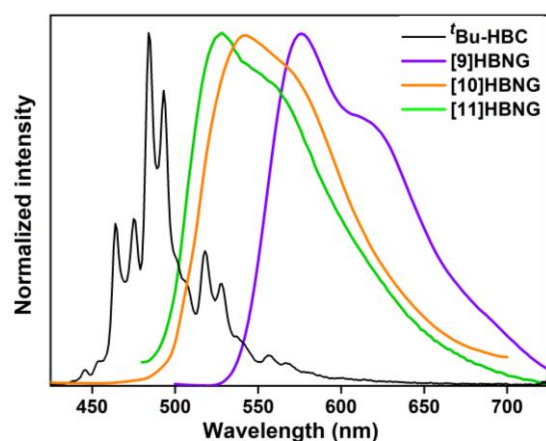


Figure 5. Fluorescence spectra of ^tBu-HBC and of helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG in CH₃Cl. Samples of [9]HBNG, [10]HBNG and [11]HBNG in CH₃Cl under 365 nm lamp irradiation (bottom).

The estimated optical energy gaps were obtained from the intersections between the normalized excitation and emission spectra of the helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG, as shown in Table 3. The found values are between 2.3 and 2.6 eV. The fluorescence quantum yields (Φ_{em}) of [9]HBNG, [10]HBNG and [11]HBNG (0.22, 0.10 and 0.11 respectively) were determined at room temperature using N₂-purged solutions with optical densities < 0.1 at 395 nm, by comparison with the emission spectra of riboflavin in ethanol ($\Phi_{em} = 0.30 \pm 0.03$). Φ_{em} variation of the three HBNGs does not follow the energy gap law, however, they can be accounted for, in part, by the increasing contribution of the excimer-like emission which enlarges the FLQY in [9]HBNG despite having the smallest optical gap.

[10]HBNG and, in particular, [11]HBNG (the one with the lowest degree of overlap).

Regarding the time-resolved emission of helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG, fluorescence decay profiles in chloroform at 300 K are shown in (Figure S18, see ESI). While [9]HBNG and [10]HBNG, the HBNGs with strongly and partially overlapped bilayers, required multiexponential fittings of the decay function, [11]HBNG, the one with a shifted bilayer, exhibited a monoexponential behaviour. The discrete lifetime components (τ_i), preexponential factors (B_i), zero-time intensities (I_i) and averaged lifetimes (intensity weighted, τ_{Int} , or amplitude weighted, τ_{Amp}) are collected in (Table S6, see ESI). The intensity-weighted average lifetimes of [9]HBNG (13.4 ns) and [10]HBNG (12.2 ns) determined at the wavelength of the emission intensity maximum display longer lifetimes than [11]HBNG (8.7 ns), which exhibits the most blue-shifted emission among the helical bilayer nanographenes, according to the less stable nature of its singlet excited state of higher energy.

From the amplitude-weighted fluorescence average lifetimes and fluorescence quantum yields, the radiative (k_r) and non-radiative (k_{nr}) deactivation rate constants of the respective singlet excited states were calculated (Table S7, see ESI).⁴⁰ Interestingly, while all the k_r values are rather similar among the studied helical bilayer nanographenes (ca $1-2 \times 10^7\text{ s}^{-1}$), [10]HBNG and [11]HBNG, the molecular nanographenes with less bilayer overlaps, show the largest k_{nr} values ($1-1.5 \times 10^8\text{ s}^{-1}$), which could be due to their higher structural mobility because of their less overlapped nature compared to their more π -stacked and constrained counterpart [9]HBNG. As a result, it could be concluded that the greater the structural overlap between nanographene layers, the more the relative radiative deactivation is favored, leading to higher emission quantum yields and longer fluorescence lifetimes.

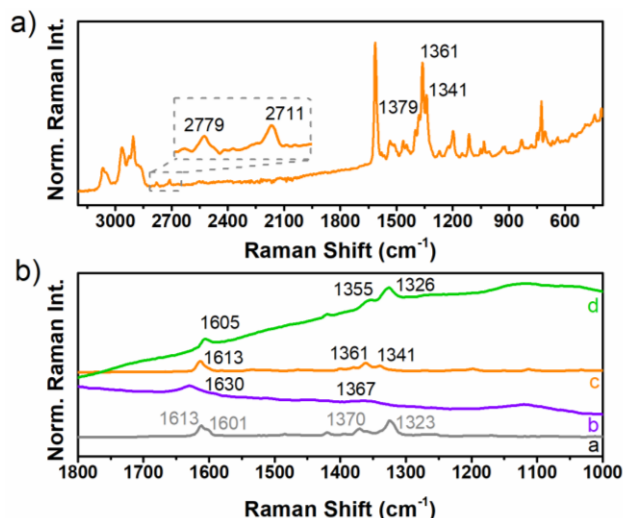


Figure 6. a) Solid-state Raman spectrum at room temperature of [10]HBNG (λ_{exc} = 1064 nm). b) Raman spectra of a) **Bu-HBC** (λ_{exc} = 1064 nm), b) [9]HBNG (λ_{exc} = 325 nm) c) [10]HBNG (λ_{exc} = 1064 nm) and d) [11]HBNG in solid state at room temperature.

The Raman spectra of the three bilayer compounds (Figure 6), have been measured and obtained in solid state by using different excitation laser wavelength to avoid the adverse effect of fluorescence. Indeed, for [10]HBNG and [11]HBNG, the 1064 nm-Raman spectra were obtained whereas for [9]HBNG large fluorescence and reabsorption in the NIR region precludes to obtain Raman spectra of quality. Contrarily, however, these were obtained in [9]HBNG by excitation in the UV region with the 325 nm laser Raman line. The Raman spectra are all characterized by the presence of two main groups of bands at 1600 and 1350-1300 cm^{-1} which are the typical G and D Raman bands which feature the vibrational Raman spectra of graphene and graphitic-like systems (Figures S20 for the assignment of the most representative Raman bands in terms of vibrational normal modes according to the theoretical spectra (Figure S19, see ESI). In particular, the 1064 nm Raman spectrum of [10]HBNG represents the molecular version of the complete Raman spectrum of graphene and multilayer graphene. The packing of graphene layers, one on the top of the other, produces the activation and appearance in the Raman spectra of new bands associated with the double and triple wavenumbers of the fundamental phonon Raman vibrations. The occurrence of such multiphonon bands is an intrinsic characteristic of the piling of graphene layers. In the Raman spectrum of [10]HBNG, it is clearly observed the presence of overtones and combination bands, which are the molecular equivalent of the multiphonon Raman bands in multilayered graphene.

Among the Raman spectra of the three bilayer compounds, that of [10]HBNG shows the largest similarity with that of **Bu-HBC** in the wavenumber region of the G Raman band at 1613 cm^{-1} whereas the G band of [9]HBNG at 1630 cm^{-1} is that with the largest difference relative to **Bu-HBC**. The variation 1613 (**Bu-HBC**) \rightarrow 1630 ([9]HBNG) cm^{-1} can result by the vibrational mixing of these C-C bond stretching of the HBC moiety with that of the helicene (Figure S20), an effect that might account for the wavenumber upshift of these Raman bands.

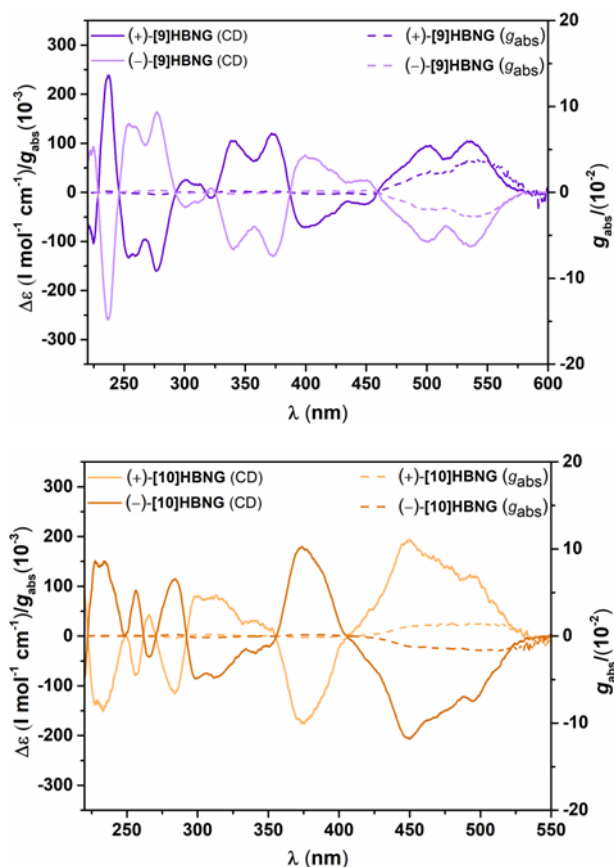
IV. Chiroptical properties of enantioenriched HBNGs. Racemic helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG were resolved by means of semi-preparative CSP HPLC using Chiralpak IE column and a mixture of heptane and 1% isopropyl alcohol in toluene. The purity and optical rotation of the separated enantiomers of [9]HBNG,

[10]HBNG and [11]HBNG are shown in Table 4. All enantioenriched samples show excellent enantiomeric excess (*ee*) except for the case of (+)-[10]HBNG that shows 73 % *ee*. Additionally, the chiroptical circular dichroism for the six enantioenriched samples were measured in THF (2.5×10^{-5} M).

Table 4. Data from the separation of the racemic HBNGs by HPLC.

	OR ^a [α] _D ²⁰	10 ² × <i>g</i> _{abs}	HPLC <i>ee</i> (%)
(+)-[9]HBNG	+6706	+3.6	98
(-)-[9]HBNG	-7120	-2.8	99
(+)-[10]HBNG	+2447	+1.4 ^b	73
(-)-[10]HBNG	-4480	-1.6	99
(+)-[11]HBNG	+4033	+1.0	99
(-)-[11]HBNG	-4270	-1.0	99

^aOptical rotation in THF. In addition to the loss of material during chromatography (especially in the case of [10]HBNG, there were residual solvents present in the resolved samples, mainly toluene and/or dichloromethane. Section 9, see ESI). The larger discrepancy in the absolute values of the optical rotations of the opposite enantiomers is due to the presence of residual solvents after HPLC separation, see ESI for details. ^bCorrected to optical purity (i.e. scaled by a factor of ~1.4).



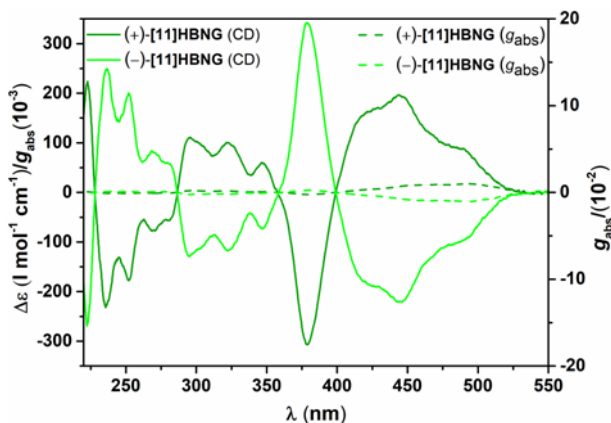


Figure 7. Circular dichroism spectra of (+)-[9]HBNG and (-)-[9]HBNG (above), (+)-[10]HBNG and (-)-[10]HBNG (middle), and (+)-[11]HBNG and (-)-[11]HBNG (below). The CD spectrum of (+)-[10]HBNG (including g_{abs} factor) is corrected to optical purity (i.e. scaled by a factor of ~ 1.4).

The CD spectra of [10]HBNG and [11]HBNG show mainly two critical points in the visible region at 380 nm and 450 nm, arising from the helicene linker and the HBC layers, respectively (Figure 7). However, CD spectra of [9]HBNG show three maxima or minima in the same region at 380, 400 and 530 nm, in this case the contribution of the helicene linker and the HBC are mixed indicating that the total overlap of the HBC layers can play an important role in the chiroptical properties (see below). Comparing the CD spectra of [10]HBNG with the previously described spectrum of *M*-[10]HBNG,³⁴ the absolute configuration of both enantiomers of [10]HBNG can be assigned as (*P*) for the dextrorotatory enantiomer and (*M*) for the levorotatory enantiomer.

Note that the absorption dissymmetry factors (g_{abs}) are quite high ($1\text{--}3.6 \times 10^{-2}$) and of the same order as the g_{lum} values (see below), reflecting small structural and electronic reorganization of the excited state prior to the emission process. In addition to the optical rotation and circular dichroism of chiral molecules, a particular focus has recently been put on their circularly polarized emission (CPL).⁴¹ Helicenes have shown to display rather strong CPL activity with emission dissymmetry factors (i.e., g_{lum}) values as high as 10^{-2} .⁴² Recently, the possibility to incorporate heteroatoms (Si, S, B, N, P) into helicene frameworks by using different synthetic strategies has attracted a special attention with the aim of creating structural diversity and tuning the photophysical properties of such systems.⁴³ However,

Table 5. TD-DFT/B3LYP/6-31G quantum chemical calculations of the relevant quantities defining the g_{abs} for the three compounds.**

	Wavelength ^a	Oscillator strength (f) ^b	ETDM (μ) module ^c	MTDM (m) module ^d	ETDM/MTDM angle (θ) ^e	Rotational strength (R) ^f	$10^2 \times$ dissymmetry factor (g_{lum}) ^g
[9]HBNG	406.6	0.0771	1.0160	2.6270	3.4	$2.664 \cdot 10^{-39}$	1.03
[10]HBNG	404.4	0.0671	0.9453	1.4014	17.78	$1.261 \cdot 10^{-39}$	0.56
[11]HBNG	389.5	0.0548	0.8385	1.7485	63.51	$0.654 \cdot 10^{-39}$	0.37

^a In nanometers, ^b In atomic units, ^c Electric transition dipole moments in 10^{-18} esu·cm, ^d Magnetic transition dipole moments in 10^{-21} erg/Gauss, ^e In degrees, ^f In erg.esu.cm/Gauss, ^g Dimensionless values.

CPL-active all-carbon PAHs are still scarce and the preparation of PAHs with strong CPL activity is still challenging.⁴⁴

Interestingly, [10]HBNG and [11]HBNG exhibit intense CPL spectra, positive for the (*P*) enantiomers and negative for the (*M*) ones. Remarkable g_{lum} values (i.e., $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$, I_L and I_R being the left- and right-handed luminescent emissions, respectively) were obtained. Indeed, g_{lum} values of $+1.1 \times 10^{-2} / -1 \times 10^{-2}$ at 540 nm for (*P*)-[10]HBNG and (*M*)-[10]HBNG, and of $+8.4 \times 10^{-3} / -8.9 \times 10^{-3}$ at 535 nm for (*P*)-[11]HBNG and (*M*)-[11]HBNG, were measured, respectively. Note that higher absolute values were found for the (*M*) enantiomers as compared to the (*P*) ones, probably due to higher chemical and enantiomeric purities. Remarkably, much higher g_{lum} values were obtained for (*P*)-[9]HBNG and (*M*)-[9]HBNG, i.e. $+3.6 \times 10^{-2} / -3.6 \times 10^{-2}$ at 580 nm, respectively (Figure 8).

The experimental values of g_{lum} agree very well with the theoretical values in Table 5 calculated from the quantum chemical quantities, such as the electric transition dipole moment (ETDM, μ) and the magnetic transition dipole moments (MTDM, m) according to the equations:

$$R = |\mu| |m| \cos \theta$$

$$g_{\text{lum}} = (4|m|/|\mu|) \cos \theta$$

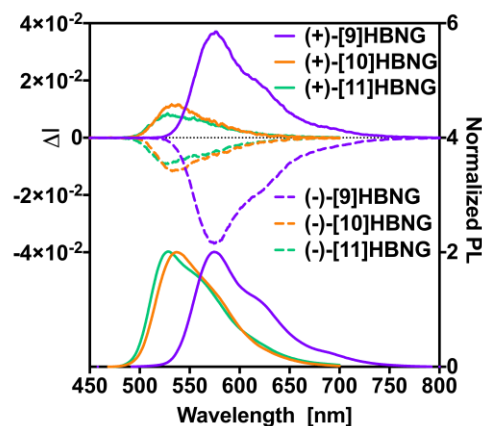


Figure 8. CPL/PL spectra of (*P*) and (*M*) enantiomers of [9]HBNG, [10]HBNG and [11]HBNG in THF at room temperature and at concentrations around 10^{-5} M.

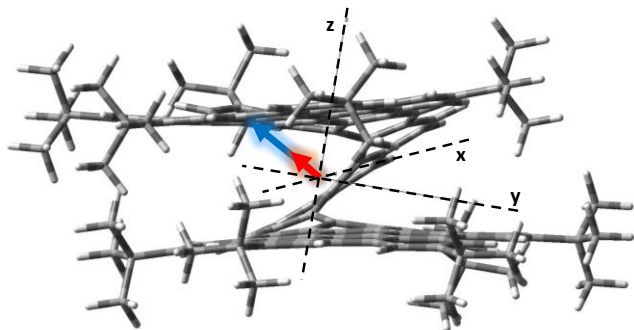


Figure 9. Direction and moduli of the ETDM (blue arrow) and MTDM (red arrows) in [9]HBNG.

Table 5 summarizes the main values obtained with TD-DFT quantum chemical calculations for the three compounds. We adopt the accepted approximation of discussing the experimental g_{lum} compared with the computationally available g_{abs} when emission and absorption corresponds to the same lowest energy electronic transition. The dissection of the g_{abs} values in term of the microscopic quantum chemical quantities allows us to provide guidelines to account for the different chiroptical performance of the three compounds. First, TD-DFT calculations nicely predict the experimental variation of the g_{lum} in the three compounds as well as their order of magnitude. The largest value is found out in [9]HBNG with a value above 10^{-2} which is very remarkable for organic pure hydrocarbon dyes. On the other hand, the values for [10]HBNG and [11]HBNG are smaller by a factor close to 4 in good agreement with experiments. We have found out that the moduli of the ETDM and MTDM transition vectors are the largest in [9]HBNG whereas displaying the smallest/largest angle/cosine between them, thus the three factors add to produce the largest g_{abs} for [9]HBNG (Figure 9 and Figure S25, see ESI, show the direction and moduli of the ETDM and MTDM for the three systems). This fact points out to the design in [9]HBNG to be optimal for g_{abs} . The largest value for ETDM in [9]HBNG comes from a significant extension of the optical HOMO-to-LUMO one-electron excitation over the more planar HBC moiety, a situation that is more favorable in [9]HBNG because of the smallest helicene segment. On the other hand, the largest MTDM module, conversely, arises because there is a significant extension, among the three compounds, of the HOMO-LUMO excitation over the helicene curvature, thus promoting a pseudo-local rotation of the electron density during HOMO-LUMO excitation at the origin of the MTDM. This interpretation is supported by the electrochemical data: i) the smallest oxidation potential of the three compounds in [9]HBNG indicates an important extension of the HOMO, among the three compounds, in the HBC units further helped by the inter-layer interaction. And ii) the smallest potential for the first reduction in [9]HBNG supports that the LUMO is greatly extended over the helicene but also with participation of the HBC unit. This synergistic combination of the frontier HOMO and LUMO orbitals between the helicene and the HBC produces the optimal situation for the increment of g_{lum} .

As proposed by Zinna and coworkers,⁴⁵ one may consider the brightness, defined as $B_{CPL} = \epsilon \times \Phi \times g_{lum} / 2$. By this way, we take into account the overall process through absorption, quantum yield and dissymmetry factors efficiencies. Average values of 81, 20 and 27 for [9]HBNG, [10]HBNG and [11]HBNG, respectively, are obtained (Table 6). These values are signifi-

cantly higher than the average B_{CPL} values of helicene derivatives (B_{CPL} 14.10 for [9]helicenes and 1.35 for [11]helicenes)⁴⁵ and highlight the fact that a balanced π -extension of the chromophore between the planar HBC (promoting large ETDM) and the pro-chiral helicene (promoting large MTDM) is an appealing alternative to obtain good emission and chiroptical properties.

Table 6. Data from the circular polarized luminescence of the enantioenriched helical bilayer nanographenes [9]HBNG, [10]HBNG and [11]HBNG.

	ϵ (λ_{exc}) ^{a, b}	Φ_{Fluo} ^a	$10^2 \times g_{lum}$	B_{CPL} ^b
(+)-[9]HBNG	20600(440)	22	+3.60	81
(-)-[9]HBNG			-3.60	81
(+)-[10]HBNG	38800(420)	10	+1.10 ^c	21 ^c
(-)-[10]HBNG			-1.00	19
(+)-[11]HBNG	58200(420)	11	+0.84	27
(-)-[11]HBNG			-0.89	28

^a ϵ and Φ_{Fluo} were obtained from the racemic mixture, ^b $M^{-1} cm^{-1}$, ^c g_{lum} and B_{CPL} of (+)-[10]HBNG is corrected to optical purity (i.e. scaled by a factor of ~ 1.4).

CONCLUSIONS

In summary, we have carried out the bottom-up synthesis of two new helical bilayer nanographenes, namely [9]HBNG and [11]HBNG, following a similar methodology to that used for previously synthesized [10]HBNG. A full comparative spectroscopic (electronic, vibrational Raman and chiroptical), electrochemical and solid-state study of the three compounds is carried out. Interestingly, comparison of [9]HBNG, [10]HBNG and [11]HBNG helical bilayers endowed with [9], [10] and [11]helicenes embedded in their structure, respectively, afford distinctive and unexpected properties, depending upon the overlapping degree between the two HBCs, determined from the X-ray data obtained for the three NGs.

The cyclic voltammetry reveals, unexpectedly, the strongest electron donor character for the lesser π -extended system [9]HBNG, which is also supported by the spectroelectrochemical studies. The significant decrease of the oxidation potential observed for [9]HBNG and the red-shift observed in the absorption bands of the radical cation of [9]HBNG, have been accounted for by a charge delocalization between the two HBC layers, which eventually contributes to a lower oxidation potential. Actually, this inter-layer communication could also underpin the differences found in the fluorescence spectrum measured for [9]HBNG when compared to compounds [10]HBNG and [11]HBNG.

The differences observed for [9]HBNG, due to its strong overlapping between the two layers, is also found in the exceptional chiroptical properties that it exhibits, with values of g_{lum} as high as 3.6×10^{-2} .

Thus, the experimental findings show that this type of helical bilayer nanographenes (HBNGs), formed by two π - π stacked hexabenzocoronenes (HBC) covalently connected through a (chiral) helicene, resemble van der Waals layered 2D materials, where the overlapping between the layers defines the properties of the materials. These findings pave the way to new NGs whose properties can be controlled by the length of the embedded helicene and the inter-layer interactions.

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website.

Data for [9]HBNG and [11]HBNG (CIF)

Synthetic procedures, additional figures/schemes of physical properties and characterization data (PDF)

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Notes

The authors declare no competing financial interest. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

Financial support from the Spanish MICINN (Project PID2020-114653RB-I00) is acknowledged. NM and JMF-G. thank the financial support by the ERC (SyG TOMATTO ERC-2020-951224). SMR thanks the UMA for her Margarita Salas postdoctoral fellowship under the “Plan de Recuperación, Transformación y Resiliencia” funded by European Union-Next Generation EU and the Spanish Ministry of Universities. SMR, FJR and JC also thank the Research Central Services (SCAI) of the University of Málaga. J.C. acknowledges the Ministère de l'Éducation Nationale, de la Recherche et de la Technologie, the Centre National de la Recherche Scientifique (CNRS). IGS thanks for the financial support to the Czech Science Foundation (Reg. No. 20-23566S) and the Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences (RVO: 61388963). RR thanks Xunta de Galicia for a postdoctoral fellowship.

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