Modulation of Waveguide Behaviour of an ICT 2*H*- Benzo[*d*][1,2,3]Triazole Derivative with Graphene

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ABSTRACT

Needle-like supramolecular structures prepared by the organized aggregation of a 2*H*-benzo[*d*][1,2,3]triazole derivative with few-layer graphene using the slow diffusion technique are described. The as-prepared aggregate shows, by using scanning electron microscopy (SEM), the formation of needles with graphene attached on the surface, which was corroborated by Raman spectroscopy and optical microscopy. The graphene-modified aggregate acts as a selective optical waveguide for green light, in contrast to the pristine aggregate which emits green and red light. These new materials may be of crucial importance for the development of high-performance optoelectronic devices.

Keywords

Waveguide. Self-Assembly

Few layers graphene

2*H*-benzo[*d*][1,2,3]triazole. Optoelectronic devices

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1. Introduction

Among the most promising materials which are currently under investigation, well-defined nano- and micro-structured materials have received increasing attention due to their potential applications in the electronic and photonic fields.¹⁻³ Their individual molecular structures make them excellent building blocks to obtain supramolecular aggregates with potential applications as device elements and inter-connects.⁴

Within this framework, intramolecular charge transfer (ICT) molecules which exhibit multifunctional properties, such as multiple electroactivity or photoactivity, offer a wide range of applications in organic electronic devices⁵ due to their semiconductor character and high charge carrier mobilities.⁶

Supramolecular self-assembling⁷ processes offer wonderful synthetic advantages for tuning the size, shape and distribution of the formed aggregates, hence exploiting the supramolecular interaction for controlling the growth of ICT compounds as microtubes, microrods and cubic structures in large quantities and with high morphological and chemical purity.

In particular, in the area of organic nanophotonics, the confinement of optical waves in shape-shifting organic nanostructures is really interesting because of their potential use in “smart” nano-optical devices, such as optical waveguides,⁸ photonic detectors and optical sensors.⁹ Currently, a new technology named optical networks-on-chips (ONoCs) has emerged in the last years,¹⁰ to be placed at the forefront with the objective of providing higher bandwidths and shorter latencies with reduced energy consumption. The most important component is the waveguide, which is the photonic equivalent of a wire. Although optical networks have already proved themselves to be useful for long distances and chip-to-chip communication, their establishment as on-chip networks still requires an intensive research effort, both in designing new required mechanisms and devices, and in successfully proving their superiority against their electronic counterparts in compensating for the migration cost towards the new technology.

Nowadays, an increasing focus of attention has been placed on optical waveguides fabricated from low-molecular-weight organic compounds.¹¹ This kind of waveguides contain different

types of light-active materials which can be excited by an external light source that guides the emitted light instead of the incident light. Furthermore, the waveguides are made of transparent media with higher refractive indexes than their environment, hence they can keep light transmitting internally by total reflection at the interface.

In these days, attractive modifications have been described in the aggregates with waveguide behaviour. It is noteworthy that among them is the epitaxial self-assembly of binary molecular components into branched nanowire heterostructures with potential applications as high-speed data highways in optical communication,¹² or the hybridization of organic semiconducting microrods with functionalized gold nanoparticles.¹³

Graphene has emerged as a promising alternative material for novel photonic and optoelectronic devices due to its interesting properties, especially its high carrier mobility and zero bandgap.¹⁴

In comparison with the conventional metal film, the conductivity of graphene can be modified by means of chemical doping, electric or magnetic fields, and/or gate bias voltage.¹⁵

Systems based on graphene embedded into an optical waveguide have been an object of great interest in the last years, motivated by the fact that highly localized photons of the waveguide can interact very efficiently with graphene.¹⁶ This stronger confinement of plasmons in graphene can create strong light-matter interactions and it can potentially be used to build different types of optical devices. For these reasons, optical waveguides incorporating graphene as the electro-optical element are a promising platform for future electro-optical modulators. Their operational principle is based on tuning the optical conductivity $\sigma(\omega)$ of graphene by the application of a gate voltage, thus changing the modal propagation constants K_y .

Finally, it is noteworthy that one of the most intriguing optical properties of graphene is its universal linear absorption coefficient of 2.3% for normal incident light, but within a short interaction length.¹⁷ In a recent study, it is described that complete absorption can be achieved by integrating graphene on a waveguide.¹⁸

To our knowledge, studies in the body of literature to date on the modulation of waveguides with graphene, use polymer¹⁹ or inorganic²⁰ waveguides with graphite formed by vapour phase

deposition, or there are purely theoretical articles.^{16a-21} However, no waveguide studies based on discrete graphene-doped molecules have been reported.

In this context, and based on our ongoing research line in small organic molecules with waveguiding behaviour,²² in this paper we describe the doping of 4,7-bis(benzo[*b*]thiophen-2-ylethynyl)-2-(3,5-bis(trifluoromethyl)phenyl)-2*H*-benzo[*d*][1,2,3]triazole (**1**) with graphene.

In this sense, our objective was to design new optical waveguide structures in order to eventually apply them in the recent optical technology.

2. Results and Discussion

Recently, we have described the self-assembling properties of several ICT derivatives based on the 2*H*-benzo[*d*][1,2,3]triazole (BTz) moiety (Figure 1), exhibiting potential application as waveguide with emissions at different wavelengths and tunable colours.²³ Among all of them, aggregates formed by 4,7-bis(benzo[*b*]thiophen-2-ylethynyl)-2-(3,5-bis(trifluoromethyl)phenyl)-2*H*-benzo[*d*][1,2,3]triazole (**1**) showed one of the most promising behaviours as waveguide with green and red emission at the ends of the thick filaments which are generated by self-assembly.

Figure 1. ICT derivatives based on the 2*H*-benzo[*d*][1,2,3]triazole (BTz) moiety

Taking advantage of the excellent properties of this aggregate, the aim of this work is to modulate or improve its behaviour as a waveguide using graphene in the process of self-assembly, due to the excellent properties described of graphene in the waveguiding behaviour.

Our research group has developed an easy and inexpensive ball milling process to exfoliate graphite into few-layer graphene (FLG) (≤ 4 layers) using melamine as exfoliating agent in solvent-free conditions.²⁴ By virtue of recent optimizations in the graphene preparation process,^{24c} we have been able to obtain FLG in the form of a fine powder. The redispersion of this powder can be easily achieved by mild sonication in polar solvents, including aqueous media. This advantage was crucial for the subsequent interaction of FLG with the organic compound.

The as-prepared graphene was employed in the self-assembly process of compound **1**. In order to achieve the aggregate, the slow diffusion technique was employed. Thus, 1 mg of compound **1** was dissolved in 2 mL of tetrahydrofuran (THF), acting as a good solvent, and was gently placed in a larger and sealed vessel containing CH₃CN as a poor solvent. After several days of slow diffusion, a precipitate was observed in the vial. By visual inspection, the aggregate of compound **1** presented a nucleation point with yellow ribbons emerging from it (Figure 2a). The same procedure was employed to generate the aggregate with graphene. In this case, 0.05 mg of FLG was added to the THF solution, obtaining a final black aggregate as an agglomerate of black needles (Figure 2b). In both cases, the formation of well-defined needles was observed.

Figure 2. Aggregates of compound **1** (a) and compound **1** + FLG (b) formed by the slow diffusion technique.

The formation of organized aggregates was visualized by using scanning electron microscopy (SEM) in samples deposited onto a glass substrate (Figure 3). As we have previously reported,²² in the SEM image compound **1** formed well-defined needles with a length of 700 μm and a

width of 5-14 μm (Figures 3a and 3b). Similarly, the inspection of the image of the hybrid aggregate, formed by compound **1** and FLG, showed similar morphology. Although, in the latter case, bright spots attached to the walls of needles are observed. This fact could be an indication of the presence of graphene.

Figure 3. SEM images (298 K, 1×10^{-4} M, glass substrate) of the needles formed by the self-assembly of **1** (a), (b) and **1** + FLG (c), (d)).

Images with an optical microscope were also obtained (Figure 4)

Figure 4. Optical microscopy images of: a) pristine needles showing the transparency; b) and c) pristine needles excited with a 350 nm lamp. d) needles in the presence of graphene. Scale bars are 200 μm in all cases. Measurements were carried out on a drop-casted glass plate.

In order to establish if graphene was attached to the aggregate surface of **1** or within it, we performed Raman and X-Ray diffraction experiments.

Raman spectra with point-based laser allowed us to observe the overall spectroscopic profile of both components: aggregate of compound **1** and with FLG. Figure 5 displays the characteristic spectra of the three main situations: aggregate **1**, FLG, and the hybrid aggregate.

Figure 5. Representative Raman spectra for aggregate **1** (bottom), FLG (centre), and the hybrid aggregate (top). Each spectrum is the average of at least 15 different spectra, taken at random locations across the samples.

Raman spectroscopy provides essential structural information for graphene, which is contained in its most visible bands: the G-band (here at 1581 cm^{-1}), related to the stretching vibrations of the sp^2 network; the disordered vibration mode in carbon materials, D-band (here at 1333 cm^{-1});

and the second-order vibration mode, 2D-band (here at 2675 cm^{-1}). The appearance of a shoulder at $\sim 1600\text{ cm}^{-1}$, together with the shape and width of the 2D-band, denotes the few-layer nature of graphene.^{24c}

Analogously, in organic compounds, Raman spectroscopy provides useful insights into the vibrational modes involved in the existing chemical bonds. In this particular case, the profile of aggregate **1** exhibits peaks corresponding to stretching (ν) vibrations of aliphatic C-C bonds (1293 cm^{-1}), trifluoromethyl groups (1379 cm^{-1}), aromatic N=N bonds (1424 cm^{-1}), aromatic C=C bonds (1471 cm^{-1} , 1513 cm^{-1} , 1582 cm^{-1}), and C=N double bonds (1621 cm^{-1}). A very prominent band was found at 2193 cm^{-1} which corresponds to the stretching of C $\equiv$ C triple bonds. The alkyne Raman feature is very useful for identification purposes, since it does not usually overlap with any other peak in organic samples, hence it has been used by other authors for the Raman tracking of small organic molecules in complex media.²⁵

Figure 6. a) Optical microscopy image (100x) of crystallized aggregate of compound **1**. Scale bar = 20 μm ; b) optical microscopy image of the crystallized aggregate of **1**/ FLG mixture (100x). Scale bar = 20 μm ; c) two-dimensional Raman mapping in a selected region from of a 2D band from graphene (in green) and alkyne band (in red) from compound **1**. Scale bar = 10 μm ; d) superposition of b) and c); e) additional

optical microscopy image of the crystallized aggregate **1**/ FLG mixture (100x). Scale bar = 10 μm ; f) two-dimensional Raman mapping of e). Scale bar = 10 μm

As seen using the optical microscope (Figure 6a), aggregates of compound **1** show a crystalline morphology, consisting of thick bundles made of small needles (around 5-15 μm diameter), consistent with SEM observations, and this morphology is conserved when mixing compound **1** with FLG (Figures 6b, e). The presence of graphene is spotted through the two-dimensional Raman mappings (Figures 6c, d and f), and corresponds to the small black clouds observed in Figures 6c, d, f, and again this is consistent with the bright spots observed in SEM. In general terms, it is clearly distinguishable how organic aggregate still crystallizes as needles in the presence of FLG but, in the latter case, graphene ends up being deposited on the surface and surroundings of those aggregates. FLG is physically contacting aggregate of **1** in some points, and even the wrapping of needles by FLG is noted (Figure 6c, bottom right corner). A co-crystallization of both components, or the appearance of new phases or structures, does not seem to occur.

In order to clarify the way in which both components interact, we also performed a depth profile analysis at different points of the mixed sample (Figure 7), and the conclusion is that FLG is only deposited on the surface of the aggregate, since FLG could not be detected beyond 4 μm across the width of a needle.

Figure 7. a) Optical image of the aggregate **1** + FLG mixture. Scale bar = 10 μm ; b) and c) depth Raman analysis in the spots indicated as “2” and “1”, respectively, in a); c) and e) overhead projection of spectra displayed in b) and d) respectively.

The structure of the aggregates was studied using crystal X-ray diffraction but, unfortunately, only compound **1** gave suitable crystals for this technique, but the aggregate with graphene did not give suitable crystals. As shown in Figure 8a, the crystal structure revealed that compound **1** is packed in a herringbone-type pattern. Two molecules have a face-to-face slipped stacking motif and pairs of molecules are arranged in the herringbone pattern.

Figure 8. X-ray diffractometric analysis of compound **1**. Panel (a) shows the general packing view. Panel (b) shows the unit cell composed of two molecules. Panels (c), (d) and (e) show the non-covalent interactions between the molecules of **1** in the crystal in the a, b and c axes, respectively.

There are two molecules per unit cell, which are twisted 146° (Figure 8b). In the a-axis the interactions that cause the zig-zag aggregation are observed, which are mainly due to the triple bonds. The main interactions are: CH ... π interaction between the H₅ of the BTz and an acetylene carbon, interaction between the H₆ of the BTz and the C-6 of another BTz, CH ... π interaction between the H₃ of a benzothiophene and an acetylenic carbon, and interaction between the H₄ of a benzothiophene ring and an S atom of another benzothiophene ring.

In the b-axis, slipped π stacking of the aggregate is observed, the cause of this stacking being the trifluoromethyl groups and the nitrogens of the BTz. The interactions that control this type of stacking are: hydrogen bonds between the fluorine atom of one CF₃ and the *ortho* protons of N-Ph, hydrogen bonds between N₁ and N₃ of one BTz and H₆ and H₇ of another BTz; interactions between the H₃ and H₄ of a benzothiophene with the S and the C₇ of another benzothiophene, respectively.

Finally, interactions between S and C₅, and between H₇ and C_{3a} of two contiguous benzothiophenes, caused a CH- π slipped-type packing on the c-axis.

Published studies on the solid-state order of organic semiconductors revealed the importance of intermolecular close contacts and stacking in the fabrication of efficient devices,²⁶ highlighting the importance of slipped π stacking with herringbone packing.

Figure 9. PL microscopy images of the needles-like aggregates of BTz derivative **1** (a), (b) and (c) and BTz derivative **1** + FLG (d), (e) and (f)

In order to analyze the role played by graphene in the behaviour of the aggregates as waveguide, we investigated the propagation of light in the aggregates formed by BTz derivative **1** and in the hybrid aggregate with FLG. The aggregates were irradiated with a mercury lamp capable of excitation at any wavelength and the fluorescence images were recorded using a fluorescence microscope coupled to a camera. The obtained images are depicted in Figure 9.

A closer inspection of the PL images shows that both samples are able to absorb blue, green and red light upon excitation at 340–360, 430–480 and 540–560 nm, respectively.

Interestingly, the aggregate of compound **1** is able to transmit green and red light at the end of the needle upon excitation. Hence, the irradiation of the thick filament generated upon self-assembly induces the longitudinal propagation of the light and highly brilliant spots are visible at the opposite ends of the needles (Figures 8b and 8c), demonstrating the behaviour as an optical waveguide. In contrast, images 8d-e indicate that graphene attached to the surface of the aggregates acts as a cut-off filter, enabling a selective behaviour of the waveguide, but only for the transmission of the green colour. Note that the colours blue and red are not transmitted (Figures 8d and f).

A similar effect has been described in the body of literature, whereby organic aggregates which can act as a waveguide that guides green-blue light, but emits only green light when the guide distance increases.²⁷ This observation is attributed to the self-absorption of the blue light during the light propagation process, hence, only the unabsorbed green light is transmitted. Based on these results, in our case, a tentative explanation could be indicated that graphene induces a different energetic overlap between light and the aggregate. The hybrid aggregate would absorb

the lower energy (red colour), which is perhaps prompted by different intermolecular interactions and thus only the unabsorbed green light would be emit.

By a slight change in chemical structure, we have obtained a more selective organic waveguide, a phenomenon that is scarce, and that would be of great interest for real application in miniaturized complex photonic devices. The results described in this work will allow a deeper understanding of the role played by graphene in the behaviour of waveguides.

2. Experimental

All Reagents were used as purchased. All air-sensitive reactions were carried out under an argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230–240 mesh or Scharlau 60, 230–240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Varian Unity 500 (^1H : 500 MHz; ^{13}C : 125 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

MALDI-TOF mass spectra were obtained on a Bruker Autoflex II TOF/TOF spectrometer (Bremen, Germany) using dithranol as the matrix. Samples, co-crystallized with the matrix on the probe, were ionized with a nitrogen laser pulse (337 nm) and accelerated under 20 kV with time-delayed extraction before entering the time-of-flight mass spectrometer. Matrix (10 mg/mL) and sample (1 mg/mL) were separately dissolved in methanol and mixed in a matrix/sample ratio ranging from 100:1 to 50:1. Typically, a 5 μL mixture of matrix and sample was applied to a MALDI-TOF MS probe and air-dried. MALDI-TOF MS in positive reflector mode was used for all samples. External calibration was performed by using Peptide Calibration Standard II (covered mass range: 700–3200 Da) from Care (Bruker). The applied peak (m/z

determination) detection method was the threshold centroid at 50% height of the peak maximum.

SEM images were obtained on a JEOL JSM 6335F microscope working at 10 kV. The samples for SEM imaging were prepared by a controlled precipitation using the appropriate solvent or by slow diffusion by using mixtures of solvents, depending on their solubility properties (see the corresponding Figure Caption for a detailed description). The corresponding solid was deposited onto a glass substrate and the remaining solvent was slowly evaporated.

Optical microscopy images were obtained with a Nikon ECLIPSE LV100Pol microscope equipped with a DS-Vi1 camera. Fluorescence images were recorded on a Leica TCE SP2 confocal microscope with a mercury lamp that is capable of excitation at any wavelength. However, a series of filters was used to select the excitation wavelength and absorption. These correspond to wavelengths in the colours blue ($\lambda_{\text{exc}} = 320\text{--}380\text{ nm}$, $\lambda_{\text{em}} = 410\text{--}510\text{ nm}$), green ($\lambda_{\text{exc}} = 4500\text{--}490\text{ nm}$, $\lambda_{\text{em}} = 515\text{--}565\text{ nm}$) or red ($\lambda_{\text{exc}} = 475\text{--}495\text{ nm}$, $\lambda_{\text{em}} = 520\text{--}570\text{ nm}$).

Raman spectroscopy was carried out in a Renishaw inViaTM microspectrophotometer, by using a 633 nm wavelength laser. Point-based spectra were collected by using the 100x objective (N.A. = 0.85), 5% of the maximum laser power, and 10 s of exposition time at each pulse, in order to avoid thermal damage to the sample. Every spectrum was baseline-corrected and normalized (to its own highest intensity band) using the Renishaw Wire 4.4 software tool. As regards to two-dimensional mappings, a line-based laser option was used (streamline) under the same conditions, except for the laser power (100% in this case). The probed areas were approximately $100\text{ }\mu\text{m}^2$. The identification of each component was made on the basis of the intensity of a specific peak. For the aggregate **1**, the peak at 2193 cm^{-1} was chosen for being the most intense peak and for having no overlapping peaks in the FLG profile. As for FLG, even if the most intense peak is the G-band (1581 cm^{-1}), the presence of similar peaks in the organic aggregate's profile led us to choose the 2D-band (2675 cm^{-1}) as a representative feature. Specific colours were assigned to each peak (red for 2193 cm^{-1} and green for 2675 cm^{-1}) which were plotted simultaneously, by using the Wire 4.4 software, according to the intensity of the respective peaks. The regions where the aggregate **1** was the most abundant are depicted in red, the regions

where FLG was dominant appear in green, and for those minor intersections where both components are in similar ratio, the mapping shows a light-yellow colour. For the depth profile analysis, the Raman equipment was set to work in confocal mode, collecting single spectra at every 1 μm step from the surface of the sample inwards, up to 10 μm depth.

The sample preparation for Raman measurements was performed by drop casting a THF solution onto a clean piece of SiO_2/Si wafer (WRS Materials) and leaving the solvent to evaporate in the open air.

3. Synthetic procedure

*4,7-bis(benzo[*b*]thiophen-2-ylethynyl)-2-(3,5-bis(trifluoromethyl)phenyl)-2H-benzo[*d*][1,2,3]triazole (1):*

A mixture of 2-(3,5-bis(trifluoromethyl)phenyl)-4,7-dibromo-2H-benzo[*d*][1,2,3]triazole (0.100 g, 0.2 mmol), 2-ethynylbenzo[*b*]thiophene (0.064 g, 0.40 mmol), DBU (0.061 g, 0.40 mmol), CuI (0.002 g, 0.01 mmol) and Pd-EncatTM TPP30 (0.018 g, 0.007 mmol) was charged under argon to a dried microwave vessel. CH_3CN (1 mL) was added. The vessel was closed and irradiated at 130 $^\circ\text{C}$ for 20 min. The crude reaction product was purified by chromatography, eluting with hexane/ethyl acetate (9/1) to give 0.122 g (yield 94%) of an orange solid. M. p.: 273–274 $^\circ\text{C}$. $^1\text{H-NMR}$ (CDCl_3 , ppm) δ : 9.18 (s, 2H, *o*-N-Ph), 8.14 (s, 1H, *p*-N-Ph), 7.81–7.86 (m, 4H, *o*-H-benzothiophene), 7.73 (s, 2H, H-benzotriazole), 7.72 (s, 2H, H-thiophene), 7.39–7.42 (m, 4H, *m*-H-benzothiophene). $^{13}\text{C-NMR}$ (CDCl_3 , ppm) δ : 145.2, 140.8, 131.9, 130.1, 125.9, 125.8, 124.9, 124.2, 122.3, 122.0, 121.0, 114.2, 91.1, 90.2, 82.5. MS calcd for ($\text{C}_{34}\text{H}_{15}\text{F}_6\text{N}_3\text{S}_2$) M^+ 643.061, found 643.328.

Few-layer graphene preparation:

Few-layer graphene (FLG) was prepared by an established method in our laboratories, based on the mechanochemical exfoliation of graphite. Characterization of this FLG is described in the

Supporting Information. The process is fully detailed elsewhere.²⁴ Briefly, in a typical experiment, 22.5 mg of melamine (Sigma-Aldrich, CAS no. 108-78-1) and 7.5 mg of graphite powder (Bay Carbon, SP-1 grade) were introduced into a sealed stainless steel jar provided with 10 stainless steel balls (1 cm diameter each), and the solids were ball-milled in a planetary ball mill (Retsch, model no. PM100) for 30 min at 100 rpm. The solid mixture was suspended in 20 mL of deionized water and inserted into a regenerated cellulose dialysis sack (Spectrum Labs, Spectra/Por MWCO = 6-8 kDa). The aqueous suspension was dialyzed against deionized water at 70 °C, with frequent water replacements and mild sonication pulses, until no melamine was detected in the washing waters. Finally, the resulting aqueous suspension of FLG was rapidly frozen in liquid nitrogen and lyophilized for a few days until reaching a fine powder, which was used in further experiments. According to a complete set of characterization techniques, our FLG powder is composed by flakes of 3-4 layers on average, being around 500 nm diameter, and a residual content of melamine and oxygen lower than 0.8 and 8 wt%, respectively.^{24c}

4. Conclusions

In summary, the self-assembly of 4,7-bis(benzo[*b*]thiophen-2-ylethynyl)-2-(3,5-bis(trifluoromethyl)phenyl)-2*H* benzo[*d*][1,2,3]triazole (**1**) in the presence of graphene is reported. These aggregates are obtained by a slow diffusion technique using THF/CH₃CN as soluble and insoluble solvents, respectively. The as-prepared aggregates appear in the form of needles with graphene attached to the surface, which was corroborated by Raman spectroscopy and optical microscopy.

The graphene-modified aggregates exhibit waveguiding properties that allow the propagating of the incident light along the length of the supramolecular structures. The most important aspect to note is that the presence of graphene causes the aggregate to emit only green light, in contrast to the pristine aggregate which emits green and red light. Therefore, graphene provides a novel performance to the aggregates by making them more selective in their waveguide behaviour. Moreover, X-ray analyses indicated a slipped π -stacking with herringbone packing within the

aggregate, which is very relevant for the organic semiconductor properties. These outcomes will allow a deeper understanding of the role played by graphene in the behaviour of waveguides.

Hence, the construction of new organic aggregates with waveguide behaviour is of paramount relevance for the development of high-performance optoelectronic materials. These findings will have important repercussions in the development of high-performance nanotechnological devices with tailored optoelectronic properties.

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