

Graphene Molecules

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Synthesis of Dibenzo[*hi*,*st*]ovalene and Its Amplified Spontaneous Emission in a Polystyrene Matrix

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Abstract: A large number of graphene molecules, or large polycyclic aromatic hydrocarbons (PAHs), have been synthesized and display various optoelectronic properties. Nevertheless, their potential for application in photonics has remained largely unexplored. Herein, we describe the synthesis of a highly luminescent and stable graphene molecule, namely a substituted dibenzo[hi,st]ovalene (DBO 1), with zigzag edges and elucidate its promising optical-gain properties by means of ultrafast transient absorption spectroscopy. Upon incorporation of DBO into an inert polystyrene matrix, amplified stimulated emission can be observed with a relatively low power threshold (ca. $60 \,\mu J \, cm^{-2}$), thus highlighting its high potential for lasing applications.

Along with the development and successful commercialization of organic light-emitting diodes, extensive research has been devoted to the search for stable organic semiconductors (OSCs) that can be employed as optical-gain media in laser devices.^[1] The reasons for targeting organic lasers are 1) the excellent optical features exhibited by organic luminescent materials, 2) the tunability of their optoelectronic properties by means of structural modulation, and 3) the high solution processability^[2] that allows for the fabrication of low-cost devices. However, their considerable photodegradation upon intense laser irradiation and intrinsic instability towards air and moisture are still major obstacles.^[1b]

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Graphene materials have more recently emerged as promising alternatives for stable luminescent systems. Although graphene itself has no band gap, structural patterning into graphene nanostructures, so-called nanographenes, such as quasi-one-dimensional graphene nanoribbons (GNRs)^[3] and quasi-zero-dimensional graphene quantum dots (GQDs),^[4] allows to open a finite band gap owing to quantum confinement of the electronic wave function. Whereas top-down fabrication methods cannot precisely control the size and edge structure of the resulting nanographenes, bottom-up chemical synthesis from small molecular building blocks has been shown to provide GNRs and GQDs, or graphene molecules, with atomically defined structures.^[5] Such nanographene materials indeed exhibit intriguing luminescence features^[6] that depend strongly on the size and edge structures,^[7] making them of great interest for plasmonic^[8] and photonic applications.^[9] There have been a few reports demonstrating or implying stimulated emission (SE) signals from structurally defined GNRs^[10] and graphene molecules^[6a] by transient absorption (TA) measurements in dispersions, which suggests their possible application as optical-gain materials. However, to the best of our knowledge, there is hitherto no unambiguous proof for SE from graphene molecules, and moreover, actual amplified spontaneous emission (ASE) of such nanographene materials has never been observed in films. The exploration of ASE properties in nanographenes will provide a new class of stable materials as gain media in laser devices.

A variety of GNRs and graphene molecules featuring armchair-type edge structures have already been synthesized,^[11] but examples with extended zigzag edges are still limited despite their intriguing properties, in particular localized edge states or biradical ground-state character.^[12] Most of the graphene molecules with biradical ground states are highly unstable, hindering their in-depth characterization and application in devices.^[12b,13] On the other hand, we have recently reported a "zigzag" hexabenzocoronene (HBC) with four extra K-regions that form two zigzag edges that is highly stable and displays intriguing optoelectronic properties with a significantly smaller energy gap than the parent HBC.^[14] Nevertheless, the zigzag HBC could not be obtained without iodo groups, which quenched its photoluminescence. Examples of such stable and low-energy-gap nanographene molecules with zigzag edges are still starkly limited.

Herein, we have synthesized dibenzo[hi,st]ovalene (DBO) **1** (Scheme 1) as a novel and stable graphene molecule with both armchair and zigzag edges. DBO **1** exhibits a small optical gap (1.93 eV) based on the UV/Vis absorption

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Scheme 1. Synthesis of DBO **1.** Reaction conditions: i) $Pd(PPh_3)_4$ (0.1 equiv), Na_2CO_3 (6.0 equiv), toluene/EtOH/H₂O (4:1:1), 80°C, 6 h; ii) CuCl (1.0 equiv), DMF, 80°C, 12 h, under air; iii) PtCl₂ (0.3 equiv), toluene, 80°C, 48 h; iv) NaBH₄ (4.0 equiv), THF/MeOH (2:1), RT, 2 h; v) acetic anhydride, TEA (3.0 equiv), DMAP (0.3 equiv), DCM, RT, 2 h; vi) DDQ (4.0 equiv), DCM/CF₃SO₃H (20:1), -78°C, 2 h; vii) KOH, THF/EtOH/H₂O, 80°C, 12 h; viii) PCC (2.0 equiv), DCM, RT, 2 h; ix) MesMgBr (20.0 equiv), THF, RT, 2 h; x) BF₃·OEt₂, DCM, RT, 2 h, under air. DCM = dichloromethane, DMAP = 4-dimethylaminopyridine, DMF = dimethylformamide, PCC = pyridinium chlorochromate, TEA = triethylamine, THF = tetrahydrofuran.

spectrum and an absolute photoluminescence quantum yield (PLQY) of as high as 79%. Investigations of the excited-state dynamics, carried out by means of resonant ultrafast TA spectroscopy, clearly revealed the occurrence of SE transitions in solution. Although the prominent optical properties of DBO **1** were largely quenched in the solid state, we were able to recover the SE signal by blending the molecule with polystyrene (PS), which interestingly led to the observation of ASE action from a 1 wt % DBO **1**/PS composite film.

The synthesis of DBO 1 was carried out as shown in Scheme 1. First, Suzuki coupling of 4-dodecyl-2-(trimethylsilylethynyl)phenylboronic acid (2) and 7-bromo-2-naphthaldehyde (3) gave 7-(4-dodecyl-2-(trimethylsilylethynyl)phenyl)-2-naphthaldehyde (4) in 97% yield. Then, a CuClmediated Glaser coupling of 4 provided diaryl diacetylene 5 in 98% yield. Subsequently, the key intermediate, bis-(chrysene) dialdehyde 6 was obtained through a PtCl₂catalyzed cycloaromatization in 48% yield. Direct cyclodehydrogenation of dialdehyde 6 to 9 under various Scholl conditions failed, most probably because of the strongly electron-withdrawing properties of the two aldehyde groups. Therefore, compound 6 was reduced with NaBH₄ and then protected with acetyl groups to obtain 7 in 86% yield over two steps. Notably, the oxidative cyclodehydrogenation of 7 succeeded with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)/trifluoromethanesulfonic acid (CF₃SO₃H) at low temperature (-78°C), providing cove-edged graphene molecule 8 in 33 % yield. The low temperature was crucial for this conversion, and no product was obtained when the reaction was carried out at 0°C. The ester groups of 8 were then transformed into dialdehyde groups through a hydrolysis/ oxidation sequence in 70% yield. To convert the cove edges of 9 into zigzag edges, 9 was treated with mesitylmagnesium bromide to give a diol intermediate, which reacted with $BF_3 \cdot OEt_2$ under air to afford the target DBO 1 as a blue solid in 24% yield. The structure of DBO **1** was unambiguously confirmed by spectroscopic analysis. Figure 1 a displays the MALDI-TOF MS spectrum of **1** with an intense signal at m/z 1044.66 Da, which is consistent with the calculated molecular mass of 1044.66 Da. The experimental isotopic distribution was in good agreement with the calculated spectrum based on the chemical composition of C₈₀H₈₄. A



Figure 1. a) MALDI-TOF mass spectrum of DBO **1**. The inset shows a comparison of the calculated and experimental isotope distributions. b) Aromatic region of the ¹H NMR spectrum of DBO **1**, recorded in $[D_g]$ toluene at 100 °C (700 MHz).

well-resolved ¹H NMR spectrum of DBO **1** could be recorded in $[D_8]$ toluene at 100 °C (Figure 1b), and all of the proton resonances were assigned with the assistance of 2D NMR spectroscopy (see the Supporting Information).

The electrochemical properties of DBO **1** were studied by cyclic voltammetry (CV) in a dichloromethane solution with ferrocene as an external standard (see the Supporting Information, Figure S2). Two reversible oxidation and reduction waves were observed, indicating the stability of these redox species. The HOMO and LUMO energy levels were estimated to be -4.84 eV and -3.22 eV based on the onset oxidation and reduction potentials, respectively, which leads to an electrochemical HOMO–LUMO gap of 1.62 eV.

The UV/Vis absorption spectrum of DBO **1** in toluene solution showed a maximum at 625 nm with a large absorption coefficient of $1.83 \times 10^5 \,\text{m}^{-1} \,\text{cm}^{-1}$ (Figure 2 a). This absorption band could be assigned to a HOMO \rightarrow LUMO transition based on time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-311G(d,p) level of theory (see Figure S1 and Table S1). In comparison to the spectrum of precursor **9**, the low-energy absorption band was red-



Figure 2. a) UV/Vis absorption and fluorescence spectra of precursor **9** and DBO **1** (10^{-5} M in toluene for all measurements). b) Photographs of a toluene solution of DBO **1** with (right) and without (left) a black background, showing the red luminescence under room light.

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shifted by 88 nm owing to the formation of the zigzag edges and the extension of the aromatic core. The optical gap decreased from 2.19 eV to 1.93 eV upon conversion of 9 into **1** according to the onsets of their UV/Vis absorption spectra. The emission spectra of 9 and 1 in toluene solution displayed maxima at 561 and 637 nm, with small Stokes shifts of 23 and 12 nm, respectively, indicating the rigid structures of these two molecules. Interestingly, the emission of 1 could be observed already under room light excitation (Figure 2b), which is a clear signature of its strong emission properties. The absolute PLQY amounted to 79% (average value = 66.9% with a standard deviation of 6.6% over 35 measurements). To the best of our knowledge, this is one of the highest values reported for graphene molecules.^[15] These promising photophysical features highlight the important role of the zigzag edges in DBO 1, significantly lowering the optical gap of 9 and realizing highly efficient red light emission.

The high PLQY, the sharp absorption and emission peaks, and the small Stokes shift observed for DBO 1 prompted us to gain deeper insight into its photophysics.^[16] We carried out broadband (375-800 nm) TA measurements by using a pump pulse of 625 nm, which is in resonance with the HOMO \rightarrow LUMO transition. The transient spectrum of DBO **1** (Figure 3) displays four features, namely: 1) a negative signal centered at 450 nm that can be interpreted as photoinduced absorption (PA) from the first excited state S_1 to higher excited states S_i , 2) a positive signal at 650 nm that can be assigned to the depletion of the ground state owing to the main HOMO \rightarrow LUMO transition (photobleaching, PB), 3) another positive PB signal centered at 570 nm, corresponding to its vibronic replica, and 4) a positive signal at 695 nm. The latter is a sign of stimulated emission because 1) it is not present in the steady-state absorption and 2) it is red-shifted with respect to the main HOMO-JLUMO transition



Figure 3. a) Ultrafast transient spectra of DBO 1 in solution (0.05 mg mL⁻¹ in toluene), in a film, and as a 1 wt% blend with PS (deposited on fused silica substrates by drop-casting). b) Normalized time-decay dynamics for the SE emission signal (probe at 695 nm) for the solution, film, and 1 wt% blend with PS. The spectra and timedecay dynamics shown above were taken with a pump fluence of about 50 μ J cm⁻². c) Comparison of the luminescence of DBO 1 in solution and a 1 wt% PS composite film under UV irradiation at 365 nm.

peak.^[16a] Although the origin of the SE signal in such graphene molecules is currently under investigation, we suppose that it is related to vibronic relaxation within the higher-lying electronic excited state.

Stimulated emission signals are of great interest for acquiring direct information about possible optical-gain properties of a material. Thus this discussion focuses mainly on the SE signal while the complete transient spectra and time-dynamics (up to 1 ns) data sets are shown in the Supporting Information. From the transient spectra of DBO 1 in toluene solution (Figure 3 a, top), the degree of decay is relatively low for all of the signals (Figure S3 a, b). This is indicative of stable excited states that can sustain stimulated emission and can also explain the high PLQY.^[17] In addition, the sharp rise of all of the transient signals, along with their linear dependence on the pump fluence (see Figure S3 c, d), suggests that the photoexcitation mechanism is direct and does not involve any nonlinear processes.

For comparison, we also performed ultrafast TA studies of a soluble hexa-*peri*-hexabenzocoronene (HBC) derivative^[18] that has solely the armchair edge structure in toluene solution. The preliminary data (Figure S4) show that all of the transient features are incorporated in a large photoinduced absorption signal even at lower concentrations (down to 0.01 mg mL⁻¹). Furthermore, we did not observe any clear SE signals in the probed region (430–650 nm) for this HBC derivative, pointing to the uniqueness of the SE observed for DBO **1** and implying that the zigzag edge plays an important role in achieving the optical-gain properties in graphene molecules.

We next turned to the characterization of DBO 1 in a thin film, which is essential for device applications (Figure 3 a, middle). It appears that the transient peaks are broader than those in solution (e.g., for the PB signal: FWHM_{solution} = 19.4 ± 0.4 nm, FWHM_{film} = 34.3 ± 0.9 nm), and the intensities of all of the transient signals decrease considerably in about 200 fs (Figure S5 a, b). Thereby, the SE peak is overwhelmed by a negative PA feature in a time frame that is comparable with the instrumental resolution (Figure 3 b). The broadening of the peaks points towards the aggregation of graphene molecules in the films.^[6a] The latter effect can be indicative of ultrafast and nonradiative intermolecular charge-transfer processes in the solid state that are promoted by the effective supramolecular packing of such planar molecules,^[19] resulting in complete quenching of the PL in films.

To exploit the gain properties of the material and possibly employ these features in solid-state devices, we embedded DBO **1** into a polystyrene (PS) matrix by simply mixing solutions of these two compounds in toluene, with the amount of DBO **1** corresponding to either 10, 5, 3, or 1 wt%. Such dilution approaches have been used to inhibit intermolecular charge-transfer processes, and thus enhance SE signals^[19a,20] and ASE/laser action in luminescent conjugated polymers.^[21] Notably, this method works effectively also for graphene molecules, as blending allows one to extend the SE signal of DBO **1** for about 70 ps in the 1 wt% **1**/PS blend (Figure 3b; see Figure S6 a–h for the spectra and dynamics of all the **1**/PS films). Moreover, the PS blending leads to the recovery of the emission of DBO **1** in the solid state, and photoluminescence

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Figure 4. a) Photoluminescence spectra taken at laser power fluences below and above the ASE threshold. b) Input–output characteristics of ASE action for the 1 wt% blend in PS. c) Evolution of the ASE signal over time taken at a laser pump fluence that is five times higher than the ASE threshold (320 μ J cm⁻²).

was detected for the 1 wt % DBO 1/PS composite film upon UV light exposure at 365 nm (Figure 3 c). It is worth noting that by diluting the graphene molecule DBO 1 in the PS matrix, the transient spectral features start resembling those observed in solution, with a progressive narrowing of the PB peaks and a suppression of the PA signal (Figure 3 a and Figure S6). All of these spectroscopic findings point towards the occurrence of excitations with charge-transfer character, as it has been reported for luminescent conjugated polymers.^[16a,19a,20,22] In particular, both PA bands at 450 nm and 750 nm seem to stem from the photoinduced excitations of charges that possibly originate from intermolecular transfer, as their intensities decrease in solution and in blends with PS.

Remarkably, the 1 wt % 1/PS blend demonstrates amplified stimulated emission (ASE) action triggered above a relatively low laser fluence of $60 \,\mu J \, \text{cm}^{-2}$ (Figure 4a,b). Although PL line narrowing is observed also in the 3 wt % blend (Figure S7a,b), the laser power needed for FWHM narrowing is higher than the one required for the 1 wt % blend (ca. $150 \,\mu\text{J}\,\text{cm}^{-2}$). This suggests that the 1 wt % blend can minimize the intermolecular cross-talking (in terms of charge transfer) that is crucial for avoiding fast nonradiative deactivations and promote ASE action. Although the 10 wt % and 5 wt% blends do not show any ASE action, a PL signal was still observed (Figure S7c, d). To test the stability of DBO 1 against photodegradation, the sample was irradiated under air at a laser fluence that was five times higher than the ASE threshold $(320 \,\mu\text{J}\,\text{cm}^{-2})$, yielding only a 30% decay after 30 min of intense irradiation (2×10^6 pulses). Although 1/PS blend films were stored under air, the same ASE emission was observed for at least six months after their preparation. The remarkable stability of DBO 1 against air, moisture, and photodegradation must be ascribed to both the intrinsic robustness of its excited states and to its incorporation into the inert PS matrix.

In summary, we have synthesized DBO **1** as a novel graphene molecule with a unique combination of armchair and zigzag edges. This compound features a low energy gap and strong red emission with a remarkable PLQY of 79% as well as promising optical-gain properties with a low ASE threshold (ca. $60 \,\mu\text{J cm}^{-2}$) and high photochemical stability. With good solubility and thus enhanced processability, DBO

1 holds great potential for future applications in low-cost organic devices, such as lasers and OLEDs. Moreover, this study demonstrates the promise of graphene molecules with zigzag edges as stable and highly luminescent materials with optical-gain properties. Further variants of such graphene molecules are presently being synthesized in our laboratories and studied in view of their role as optical-gain materials.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: amplified spontaneous emission · graphene molecules · stimulated emission · transient absorption · zigzag edges

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Graphene molecules as nanoscale and structurally precise fragments of graphene have recently emerged as promising optoelectronic materials. A novel, highly luminescent, and stable graphene molecule based on dibenzo[*hi*,*st*]ovalene features remarkable optical-gain properties, thus holding great potential for applications in laser devices.

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