Pump–Push–Probe for Ultrafast All-Optical Switching: The Case of a Nanographene Molecule

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In the last two decades, the three-beam pump–push–probe (PPP) technique has become a well-established tool for investigating the multidimensional configurational space of a molecule, as it permits disclosure of precious information about the multiple and often complex deactivation pathways of the excited molecule. From the spectroscopic point of view, such a tool has revealed details about the efficiency of charge pair generation and conformational relaxation in π-conjugated molecules and macromolecules. In addition, PPP is effectively utilized for modulating the gain signal in conjugated materials by taking advantage of the spectral overlap between stimulated emission and charge absorption in those systems. However, the relatively low stability of conjugated polymers under intense photoexcitation is a crucial limitation for their real employment in plastic optical fibers (POFs) and for signal control applications. Herein, the role of PPP for achieving ultrafast all-optical switching in π-conjugated systems is highlighted. Furthermore, new experimental data on optical switching of a newly synthesized nanographene molecule, namely dibenzo[hi,st]ovalene (DBOV), is reported. The superior environmental and photostability of DBOV and, in general, of graphene nanostructures can represent a great advantage for their effective applications in POFs and information and communications technology.

1. Introduction

Back in 1990 the scientific community working on organic semiconductors was engaged in a large research effort aimed at identifying new nonlinear optical materials for all-optical communication.[1] The basic notion was the observation that large π-electron delocalization, typical in conjugated polymers and large molecules, should be associated with large susceptibility values.[2] In turn, nonlinear terms of susceptibility, typically third order, could be implemented in a number of photonic devices expected to be efficient and fast. In a decade, excellent results were obtained in fundamental knowledge, essentially dealing with the synthesis of new compounds,[3] the understanding of structure–property relationship,[4] and the realization of advanced spectroscopy experiments,[5] yet practical achievements suitable for further development into real applications did not arrive. Organic semiconductors in different shapes indeed demonstrated very large nonlinear optical coefficients,[6] but their stability under optical pumping, optical guiding properties (e.g., optical losses), and spectral range of operation (often limited to the UV–vis) were not appropriate for information and communications technology (ICT). Slowly, the interest toward this thematic turned down while electroluminescence for organic light-emitting diodes,[7] and later photovoltaics,[8] emerged as new frontiers for material development. More recently, ultrafast all-optical switching was reported in solid-state amplifiers, plastic optical fibers, optofluidic channels, and lasers based on resonant excited state effects.[9] Essentially, the detrimental photoinduced absorption (PA) associated with charge carriers that spectrally overlap with stimulated emission (SE) hampering electrically pumped lasing in most organic semiconductors was exploited for modulating gain.[10] Because charge carrier lifetime can be modulated by controlling intermolecular interactions, such induced quenching could be made extremely fast, resulting in a transient switching of the gain signal. Such all-optical control is fast (sub-picosecond) and large (easily modulating 100% of the gain signal) in spite of being resonant. This breaks the common knowledge fast-small-nonresonant versus slow-large-resonant.[1,10] However, it does not circumvent the problem of energy management since in a resonant process a lot of energy is deposited in the materials and requires efficient dissipation. As a matter of fact, this limits the modulation rate several orders of magnitude below the theoretical limit. In this context, new 2D materials, in particular nanographene molecules,[11] appear as interesting candidates for...
readdressing the challenge, as those materials present well-defined excited state dynamics and usually rather high environmental stability.

In this article, we provide a summary of recent advances in the pump–push–probe technique and its application to ultrafast all-optical switching in \( \pi \)-conjugated systems. Moreover, we report new interesting results on ultrafast switching of stimulated emission signal in a newly synthesized stable nanographene molecule, which holds great promise for possible future applications of these novel advanced functional materials in photonics and ICT.

2. The Pump–Push–Probe Experiment

In terms of a wave interaction picture, the pump–push–probe (PPP) experiment is a nonlinear fifth-order process. However, in the well-separated pulses regime this experiment is simply accounted for by a double modulation picture. First, the pump pulse places population into the excited state. Second, the push pulse displaces part of this population to a higher lying excited state. From this higher lying state the molecule can either simply return to the initial excited state or it can take a different path, reaching another excited state. In this case, deactivation back to the initial excited state might become longer than by direct internal conversion. In a system with inversion symmetry, a one-photon transition with energy equal to the sum of pump and push photons energies reaches an excited state that is different from that reached by the consecutive absorption of pump and push pulses (two-step transition). This difference comes from the dipole selection rule that couples opposite symmetry states. Therefore, deactivation can occur along very different paths in the two situations because it involves states of different symmetries, albeit almost equienergetic. This demonstrates that the PPP technique allows exploring the multidimensional configurational space of a molecule. In particular, it can identify branching routes in the deactivation path of excited states (Figure 1). Often such branching points lead to charged states that require a minimum excess energy to be accessible. The opening of different decay paths above a certain energy causes

![Figure 1. Schematic (not in absolute energy scale) showing the possible branching routes from excited states occurring upon sequential pump → push excitation. These can include autoionizing states\(^{12,13}\) and ultrafast conformational relaxations.\(^{13}\)](image)

the breakdown of the Vavilov rule. In conjugated polymers such as poly(p-phenylene vinylene) (PPV)\(^{12}\) or ladder-type methyl-substituted poly(paraphenyl (m-LPPP)\(^{13}\) and poly(9,9-dioctylfluorene) (PFO),\(^{14}\) the PPP technique has been used to identify autoionizing states. In fluorene oligomers, the PPP technique allowed to observe ultrafast nonadiabatic planarization following the push re-excitation.\(^{13}\) In photonics, the PPP technique is the natural tool for investigating optical switching since the push pulse acts as a modulation on the probe transmission.\(^{16}\) An alternative to a push-induced electronic transition is the push-induced vibrational transition, when the push photon energy is in the vibrational range, typically mid-IR.\(^{17}\) In this configuration, the push effect is like a local heating, bringing excess vibrational energy to the initial excited state.

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3. Pump–Push–Probe for All-Optical Switching

A number of experimental studies have shown the role of charge carriers as intrinsic loss in the optical gain process of conjugated materials.\cite{18} Such a competition arises from the fact that in general charged polaron states have optical transitions (electroabsorption) just below the neutral absorption edge (Figure 2), as a result of the local lattice relaxation around the charge (polaronic relaxation).\cite{19} This in turns leads to a strong overlap with SE whose spectrum also lies below ground state absorption, and which becomes eventually overtaken by PA in the solid state where charge generation due to intermolecular effects becomes significant (Figure 3a). Therefore, this phenomenon hampers the occurrence of electrically pumped lasing action for organic conjugated systems, as in this case charge absorption is massive and unavoidable and overwhelms optical gain dramatically.

On the other hand, selective excitation of the charged states can be effectively utilized for optically switching on/off the SE signal. However, to achieve charge recombination and hence recovery of SE in the picosecond time regime, it is necessary to exploit the intrinsic 1D character of conjugated chains as isolated and electronically confined elements, in which photogeneration of long-lived interchain charge pairs is suppressed. For instance, previous studies on isolated conjugated polymer chains have shown evidence of early events (<300 fs) of intrachain charge dynamics.\cite{20}

In this case, charge pairs decay geminately on the ultrafast time scale (~500 fs) to the lowest singlet state due to the strong confinement of such excitations within a single polymer chain. This interesting property of isolated conjugated polymer chains can be thus exploited for the development of an ultrafast photonic switch based on a three-pulse sequence.\cite{21} Here, the pump pulse populates the singlet excited state $S_1$, while the time-delayed push pulse depletes $S_1$, thus reducing the optical gain experienced by the probe pulse. In addition, as anticipated in the previous paragraph, the push-induced re-excitation to $S_n$ promotes excitons dissociation into charge pairs.\cite{13,22} This eventually results in an increase of the PA associated with intramolecular charge pairs and hence quenching of the SE signal, as reported in Figure 3b.\cite{21} Interestingly, recovery occurs within 1 ps, a time scale that is considerably longer than internal conversion from higher lying excited states on (~50 fs)\cite{23} and can be connected to intrachain charge recombination.\cite{24} Therefore, the exploitation of PA generated by the resonant push pulse enhances the modulation depth in the SE signal at the cost of a longer recovery time, yet the process is fast enough to allow sub-ps responses. This in fact demonstrates the possibility of achieving resonant ultrafast optical switching in conjugated polymers, with potential operational frequencies in the THz regime. Furthermore, the switching process exhibits a relatively high on/off ratio that is typical for resonant processes, coupled with an ultrafast response that conversely is unusual for such events. However, some stability problems may arise due to the large amount of energy absorbed and quickly dissipated when the radiation is in resonance, thus limiting the actual operational switching rate. This critical issue justifies the search for new stable $\pi$-conjugated materials capable to undergo ultrafast resonant optical switching, which ideally show a higher resilience toward environmental stimuli and photoexcitation than conjugated polymers.\cite{25}

4. Ultrafast Resonant Switching in a Graphene Molecule

The geometric confinement of graphene down to the molecular level into quasi-1D (graphene nanoribbons, GNRs)\cite{11,26} and...
quasi-0D (graphene quantum dots, GQDs)\cite{11,27} structures via bottom-up and top-down methods can open a finite bandgap in its electronic structure. In this regard, bottom-up chemical synthesis offers the possibility to produce defect-free GNRs and GQDs with atomically precise structures and defined optical properties, permitting to establish a reliable structure–property relationship. For these reasons, chemical synthesis allows full exploitation of nanographene features, thus making possible the use of such structurally defined graphene fragments in the fields of optoelectronics and photonics.\cite{28} Within the context of photonic applications, these extended π-conjugated systems have attracted a growing interest very recently due to their relatively high environmental stability and optical properties that can easily be tuned by modifying both size and edge configurations.\cite{29} These are ideal properties for possible employment of nanographene molecules in laser and signal control applications.

We have recently characterized a novel nanographene molecule, dibenzo[\(\pi\)]stilbenevalene (DBOV) (Figure 4), with low HOMO–LUMO gap, high photoluminescence quantum yield (79% in solution), and small Stokes shift (\(\approx 30\) meV).\cite{30,31} Furthermore, DBOV shows stable SE and amplified spontaneous emission (ASE; Figure 4c) with remarkable environmental and operational stability, yielding only a 30% decay after 30 min of intense excitation in air with a pump fluence 5 times higher than ASE threshold (320 \(\mu\)J cm\(^{-2}\), 2 \(\times\) 10\(^6\) pulses; Figure 4d).\cite{30} Photostability under intense light irradiation with successive laser pulses is an important aspect to take into account for actual application of organic materials in photonics (i.e., lasing and optical switching). For comparison, nonencapsulated conjugated polymers exhibit typically a 50% PL decay after \(\approx 10^6\) pulses.\cite{30} Therefore, our nanographene permits to achieve a photostability that is more than 1 order of magnitude higher than conjugated polymers, an advantage that can play an important role for future applications of nanographenes in THz optical switching (vide infra).

The differential transmission (\(\Delta T/T\)) spectrum of DBOV in solution (Figure 5a, top graph) displays four main features, namely: i) a negative signal centered at 450 nm that can be attributed to PA from \(S_1\) to \(S_\infty\); ii) two positive peaks at 625 and 570 nm that can be connected to photobleaching (PB) of the ground state and its vibronic replica; iii) a positive signal at 695 nm that can be ascribed to SE. However, if we move from solution to solid film the SE signal at 695 nm is overwhelmed dramatically by a negative PA feature in the near-infrared region within 200 fs (Figure 5, central graph). On the other hand, dilution of DBOV in a polystyrene (PS) matrix (1 wt%) permits to recover the SE and suppress such PA signal that, therefore, has to be related to the intermolecular distance experienced by the nanographene molecules (Figure 5a, bottom graph). Interestingly, long-delay pump–probe experiments carried out on DBOV solution (Figure 5b,c for spectra and dynamics) highlight the delayed building-up of the PA signal appearing after decay of the PB and SE bands, suggesting that such signal is also present in solution, although it appears at very long delay times. Based on these results, and on new experimental evidence acquired for DBOV derivatives very recently,\cite{13} we attributed the PA signal in the near-infrared to charge induced absorption due to the occurrence of ultrafast intermolecular charge separation in the solid state, promoted by the effective supramolecular packing of such planar molecules.\cite{34} In this scenario, the presence of this signal in solution can be linked to charge pairs delocalized in DBOV π-aggregates. This effect can be exploited to suppress the SE signal, especially in quantum confined systems like nanographene, in which ultrafast charge recombination can allow the effective recovery of the emission (the on-state) in a sub-picosecond time regime, as it has been observed in isolated polyfluorene chains\cite{20b} (see above). To achieve this in analogy with the aforementioned studies, we set up a PPP experiment,\cite{13} in which a delayed push beam at 800 nm (i.e., 1 ps after the pump excitation) causes the re-excitation from the \(S_1\) to the \(S_\infty\) level promoting charge generation (see Figure 6 for the experimental scheme).

To investigate the impact of the intermolecular distance on the SE switching dynamic of DBOV, we performed conventional ultrafast pump–probe and three-beam PPP spectroscopy in two solutions in toluene with different concentrations (0.1 and 0.01 mg mL\(^{-1}\)), and in a DBOV:PS blend at 1 wt% (Figure 7). In our experiment, we pumped in resonance with the main π → π\(^*\) transition at 625 nm, pushed at 800 nm, and
Figure 4. a) Molecular structure of DBOV. b) Normalized visible absorption and photoluminescence of DBOV in toluene solution (0.05 mg mL\(^{-1}\)). c) ASE action of the DBOV:PS blend at 1 wt% d) Time evolution of the ASE signal under irradiation with an excitation fluence 5 times higher the ASE threshold (320 \(\mu\)J cm\(^{-2}\)) in air without any encapsulation. Adapted with permission.\^[30] Copyright 2017, Wiley-VCH.

Figure 5. a) Ultrafast \(\Delta T/T\) spectra at three pump–probe delays of DBOV toluene solution, film, and DBOV:PS blend at 1 wt%. b) Long-delay \(\Delta T/T\) spectra for DBOV in toluene solution showing the building-up of a long-lived PA signal after depopulation in the gain region (x-axis in the logarithmic scale). We attribute this feature to charge pairs delocalized in DBOV aggregates. c) Long-delay (till 1 \(\mu\)s) transient dynamics at probe wavelengths corresponding to the gain region of DBOV: a) Adapted with permission.\^[30] Copyright 2017, Wiley-VCH.
Figure 6. Scheme of a pump–push–probe experimental setup. In our experiment, we excited at 625 nm (pump, orange beam), re-excited at 800 nm (push, dark red beam), and probed with a white-light continuum (probe, green beam). We run the experiment by acquiring separately the pump–probe and the pump–push–probe signals.

Figure 7. a,c,e) $\Delta T/T$ spectra for the conventional pump–probe (gray spheres) and three-beam PPP (orange line) technique for DBOV in toluene solution at 0.1 and 0.01 mg mL$^{-1}$ and DBOV:PS blend at 1 wt%. We pumped at 625 nm, pushed at 800 nm (Ti:Sapphire laser fundamental), and probed with a white-light continuum. The PP and PPP spectra are taken at a pump–probe delay of 1 ps and no push–probe delay. b,d,f) Dynamic of the SE signal (695 nm, orange line) and at 645 nm (blue line) after re-excitation with the push beam (excitation energy = 7 $\mu$J) for the three samples.
probed with a white-light continuum (430–770 nm). The ΔT/T spectra for the three samples (Figure 7a,c,d) clearly show a dramatic quenching of the SE upon re-excitation with the pump beam for all samples (pump-push delay at 1 ps; push excitation energy 7 µJ). The effect of the push beam is in fact twofold: i) depletion of the S1 population and ii) creation of a large photo-induced absorption band due to charge absorption. Note that the spectral shape of the push-induced negative band is different from solution (both 0.1 and 0.01 mg mL−1; Figure 7a,e) to the DBOV:PS blend (Figure 7c), with the former peaking at 645 nm and the latter featuring a broad band shape covering almost the whole transient spectrum (500–750 nm). This might be related to different geometrical reorganization of the molecule upon push excitation when passing from solution to the rigid polymer matrix, although this has not been fully investigated yet and constitutes matter for further studies. Dynamics of the SE signal at 700 nm upon push modulation at ≈1 ps is shown in Figure 7b,d,f for the three samples. At this push excitation energy (7 µJ), in particular, we not only switched off by 100% the SE signal, but we also achieved a gain–loss regime due to the transient dominance of the PA with the respect to SE. On the other hand, the recombination dynamic shows significant differences among the samples: whereas in the DBOV:PS blend and 0.01 mg mL−1 solution (Figure 7b) the recombination process is incomplete and occurs in ≈500 fs (rise time 400 fs); in the DBOV:PS blend and the 0.01 mg mL−1 solution (Figure 7d,f) the signal recovers totally within a time frame comparable to our pulse width (150 fs). We attribute the incomplete recovery of the SE signal to charge pairs delocalization in DBOV aggregates, as a consequence of the strong tendency of such systems to form π-stacks,[35] thus corroborating the long-delay pump–probe results. In this scenario, the increased PA signal outside the SE region (645 nm, blue curve in Figure 2b) after push arrival is related to the absorption of charge delocalized within the aggregates. On the other hand, both in the PS:DBOV blend and diluted solution we probe mostly isolated molecules, in which it is unlikely to find stabilized charge pairs. Here, we speculate that the push beam probably permits to access a state with charge-transfer (CT) character (i.e., Sπ) whose absorption overlaps with the SE region, and that can be a precursor to free charges[36] similarly to what has been demonstrated in oligofluorenes.[15] The CT state absorption spectrum resembles that of the charge pair, explaining the similar spectral competition with SE, albeit on a very short time scale associated with the intramolecular CT lifetime.

In Figure 8, we show the SE dynamics of DBOV:PS blend films as a function of push energy (Figure 8a) and pump-push delay time (Figure 8b). As it has been anticipated in the previous paragraph, we observe a crossover from gain to loss at the highest push energies that amplifies the switching magnitude, whereas by pushing with an energy of 1 µJ we could not access that regime but still achieved a relatively strong SE quenching (86%). In addition, interestingly, we note a similar switching off/on behavior up to 10 ps pump-push delay (Figure 8b) that is due to the relatively long SE signal lifetime in such a molecule (≈400 ps)[13]. These films are of practical interest for possible future applications of nanographene systems in POFs and logic circuits.

Note that although the switching process is particularly efficient and rapid for DBOV thanks to excitation confinement, this is still a resonant process that deposits a considerable amount of energy onto the material (see above). Therefore, despite our system can in principle operate at repetition rates up to the terahertz regime, stability and energy dissipation issues have to be taken into account seriously when exciting at those frequencies. In our case at 1 THz, assuming one will use the minimum switching energy for achieving 10% SE modulation (0.1 µJ) that can be already sufficient for applications,[21] the power to be dissipated is ≈100 kW. Our data on ASE photostability under 2 kHz laser irradiation indicate that DBOV can easily dissipate more than 1 kW in air. Thus, we can achieve 10 GHz at these conditions. Interestingly, this improved photostability represents a clear advantage over conjugated polymers, and further suggests that encapsulation and refinement in sample preparation/ manipulation might open the way for possible operation in the THz regime.

5. Conclusions

Herein, we have highlighted the contribution of PPP to investigate the complex photodynamics of conjugated molecules and to achieve efficient ultrafast all-optical switching. As a spectroscopic tool, PPP has allowed to gain insights into the charge
generation process in conjugated molecules, identifying a strong spectral overlap between optical gain and charge absorption. Such an effect that can be detrimental for most photonic applications (i.e., lasers) can be exploited for modulating the gain signal. In this case, the push beam permits to access charged states whose absorption quenches stimulated emission and gain. If the conjugated system is adequately isolated, intramolecular geminate recombination of charges allows ultrafast (sub-picosecond) and effective on/off resonant switching. However, the resonant process requires an efficient energy dissipation, thus posing critical stability issues in the view to employ conjugated molecules in real devices. In this regard, nanographene molecules can represent a valid alternative to conjugated poly[oligo]mers owing to their higher photostability and to the possibility to easily control the optoelectronic properties by selectively modifying their edge configurations. Interestingly, we showed that a newly synthesized nanographene molecule, namely DBOV, can sustain efficient and ultrafast resonant gain switching. The relatively high photostability displayed by DBOV, and more in general by nanographenes, can be a key asset for future applications of these novel functional materials in POFs and photonics.

6. Experimental Section

Sample Preparation: The synthesis of DBOV was carried out through the method that we reported previously. For the pump–probe and pump–push–probe measurements in solution, the molecule was dissolved in toluene with a concentration of 0.1 and 0.01 mg mL\(^{-1}\). For DBOV: polystyrene solid blends (1% weight ratio), we dissolved the proper amount of material in a 40 mg mL\(^{-1}\) polystyrene solution in toluene (PS, Aldrich, \(M_\text{w} = 200\,000\)). Then, the blends were spin-cast onto a glass substrate with a spin speed of 1000 rotations min\(^{-1}\) yielding a thickness of \(\approx 400\) nm, as measured by profilometry.

Pump–Probe and Pump–Push–Probe Measurements: We employed an amplified Ti:Sapphire laser with 2 mJ output energy, 1 kHz repetition rate, a pulse width of \(\approx 100\) fs, with a central energy of 1.59 eV (800 nm). We used a pump wavelength of 625 nm, in resonant with the main \(\pi \rightarrow \pi^*\) transition, with a spot diameter of 200 \(\mu\)m, a pump energy of 20 nJ, and a fluence of 60 \(\mu\)J cm\(^{-2}\). Such pump pulses were generated by using optical parameter amplification (OPA) in the visible range. As push pulse we used the Ti:Sapphire laser fundamental (800 nm), with a spot diameter of 500 \(\mu\)m, energies of 1, 2, 4, and 7 \(\mu\)J, and fluence of 0.5, 1, 2, and 3.5 \(\mu\)J cm\(^{-2}\). As a probe pulse, we used a broadband white-light supercontinuum generated in a sapphire plate, extending from 450 to 780 nm. The pump–probe and pump–push–delay were set by means of two mechanical delay stages. The experiment was run by acquiring separately the pump–probe and the pump–push–probe signals. The pump–push–probe setup is depicted in Figure 6.

Long-Delay Pump Probe: For the long-delay pump–probe spectroscopy, the pump light is obtained from a Q-switched Nd:YVO\(_4\) laser (fundamental wavelength 1064 nm). This laser is electronically triggered and synchronized to the Ti:Sapphire laser (which continues to provide the probe light pulses) via an electronic delay. The Q-switched pulses have a width of \(\approx700\) ps FWHM, and the system has a combined time resolution and jitter of \(\approx200\) ps. We pumped at 532 nm by employing a frequency doubling crystal.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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