

Ultrafast optical gain switch in organic photonic devices

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We have developed novel organic photonic devices which are capable of all-optical ultrafast gain switching for use in data communication networks and lab on chip type applications. We have exploited different kinds of devices such as a solid state film, a doped plastic optical fibre and an optofluidic microchannel. We have achieved ultrafast switching (<150 fs) over a broad wavelength range (~100 nm) with a switch on/off ratio of at least 70%.

Introduction

The coming years will see an huge increase in network-based services. Such services are seen as fundamental for the successful development of an information-based society. The introduction of supplier chain management by the production industry will require local area networks (LANs), bridging different production centres which are kilometres apart. Furthermore, household-based services will increasingly become more integrated, which will also require high intra-LAN cross-connection density. For all these reasons, the development of faster, all optical communications is seen as a critical enabling technology. In this paper we show novel organic devices to be employed for the achievement of ultrafast all-optical gain switches. Fig. 1 shows the working principle in three of the most commonly reported photonic amplifier geometries (slab waveguide,¹⁻⁴ doped plastic optical fibre,^{5,6} optofluidic channels^{7,8}). The optical signal (input) travels along one of the devices, a pump pulse amplifies the input signal while a gate pulse “kills” the amplification. In this way we have achieved a gain switch controlled by a gate pulse.

This paper is divided into two main sections. The first section is dedicated to explaining the physical principle behind the switch

behaviour, and the spectroscopic techniques utilized. The second section presents the results obtained from three different photonic devices: a solid state film, a doped plastic optical fibre (POF) and an optofluidic channel. The first device is realised using a solid state organic film. The film is made doping an inert matrix (PMMA) with poly-dioctylfluorene. We find an almost complete gain recovery and a possible gain switch rate of 300 GHz.^{9,10} The second photonic device consists of doped plastic optical fibres. POFs are¹² nowadays the best candidates to substitute the inorganic fibres for local area networks data communication. The last device is an optofluidic microchannel, where we use the properties of a diluted polyfluorene solution to obtain a gain switch¹¹ with a maximum on/off switch rate in the THz region.

Section I: physical principle behind the ultrafast gain switch behaviour

Conjugated polymers are highly fluorescent with large stimulated emission cross-sections, and are easy to ‘tune’ by changing their chemical structure.^{13,14} These unique properties have opened up a rapidly expanding world of optoelectronic devices that combine the electrical properties of traditional inorganic semiconductors with the flexibility, manageability and ease of production of plastics.^{15,16} It is well known that photoconductivity in conjugated polymers is mainly based on two mechanisms: on-site dissociation of non thermalized higher-lying excitons states^{17,18} (shown by process (3) in Fig. 2), and disorder assisted exciton dissociation in an inhomogeneously broadened DOS.^{19,20} Increased charge photo-generation yield, is often detrimental for many photonic applications such as lasers and amplifiers, as the charge absorption band overlaps spectrally with the stimulated emission, shown by (4) in Fig. 2. Therefore, charge generation acts to quench the stimulated emission, gain and lasing action. It is therefore critical to be able to control the charge generation (3) and recombination dynamics (5) in conjugated polymers for optical amplification applications. A step towards this control is to fully understand charge photo-generation. To that end, we study the effect of interchain interactions on charge photogeneration by isolating conjugated polymers in an inert matrix as PMMA (in the first device), by doping a plastic optical fibre and by using a diluted polyfluorene

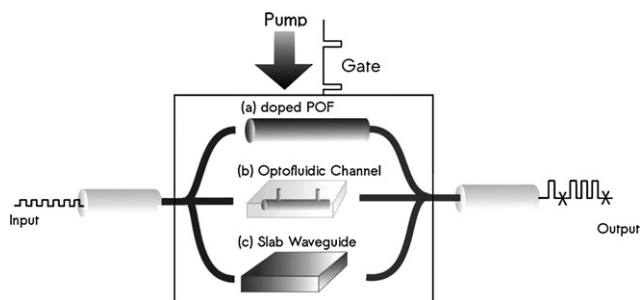


Fig. 1 A schematic of the working principle for three different all optical gain switches organic devices.

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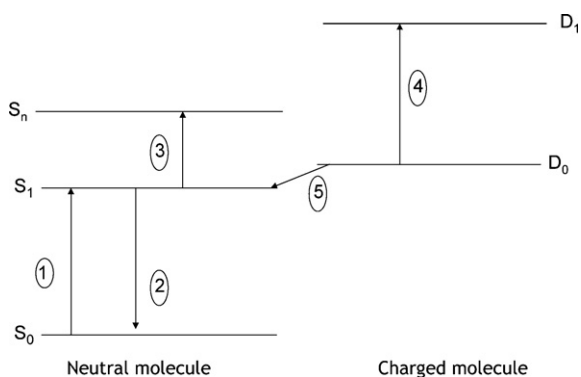


Fig. 2 A schematic energetic diagram showing light-matter interactions in conjugated polymers. (1) Absorption of light (S_1-S_0) and formation of exciton, (2) stimulated emission (SE), (3) re-excitation to S_n , to form charges (D_0) (4) absorption by the charges D_0-D_n (which overlaps spectrally with SE) and (5) recombination of the charges to form an exciton (S_1) and recovery of the stimulated emission.

solution (in the last device). In this way we have achieved an almost complete suppression of interchain charges.

Experimental technique: P&P and PPP experiments

We performed conventional pump-probe experiments (P&P) and three beam experiments (PPP). In the conventional P&P, the pump (390) is the second harmonic of the 780 nm mode of a Ti:sapphire laser (150 fs, 4 μ J, 1 kHz repetition). The beam is focused to a 230 μ m diameter spot giving an excitation energy density between 1 mJ cm^{-2} and 0.1 mJ cm^{-2} . The probe beam is a white light continuum (450–750 nm) created by focusing the 780 nm pump laser on a sapphire plate. The two beams are spatially overlapped on the sample and the probe beam is kept very weak during the experiment.

In PPP spectroscopy,²¹ three beams are spatially overlapped in a small-angle configuration. The temporal delay of the *push* (780 nm) with respect to the *pump* (390 nm) is kept fixed during the experiment. The probe is delayed with respect to the pump and push using a computer-controlled delay stage. The different delays of the push respect to the pump used for the different samples are just due to a different alignment of the experimental apparatus. The three beams are in a non-collinear (small angle) geometry to ensure reduction in detection of the pump scattering. They are placed orthogonally to the solid state film and to the microchannel while for the experiment with the doped POF, the three beams were overlapped at the front of it.

CW-photoinduced absorption measurements at 90 K were performed with a 10 mW 375 nm Omicron diode laser chopped at a repetition rate of 80 Hz. Probe light was provided by a tungsten lamp filtered by a spectral products monochromator. Phase sensitive detection was carried out with a Stanford Instruments lockin amplifier and a Si photodiode. Samples were cooled down in an Oxford Instruments closed circuit He cryostat.

Section 2: novel photonic devices

Ultrafast optical switch based on a solid state film

The sample consists of a film drop cast from a toluene solution of either pure poly-fluorene (PFO) at a concentration of 10 mg ml^{-1} ,

(pristine sample) or of 10% PFO doped in a PMMA matrix (50 mg ml^{-1}) (doped sample). The doped samples appear very inhomogeneous, indicating a possible phase separation between the two components.²²

Fig. 3 shows the absorption (Δ) and emission spectra (\blacktriangle) from the pristine sample. Fig. 4 shows the pump-probe spectra for the pristine (aggregated PFO, \square) sample and the doped one (dispersed PFO, \circ) at 1 ps delay. We found that, for the pristine sample, there are three different spectral regions: stimulated emission (SE) (until 480 nm), a first photo-induced absorption band (PA) due to photogenerated interchain charges

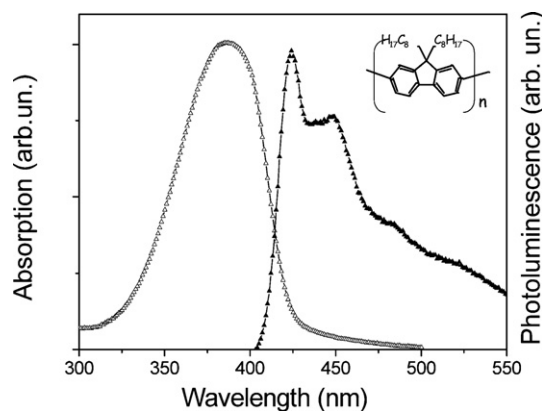


Fig. 3 Absorption (Δ) and photoluminescence (\blacktriangle) spectra for a film of polyfluorene. The inset shows the chemical structure of the polymer.

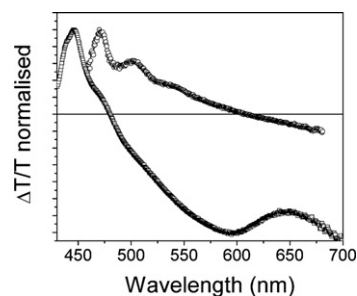


Fig. 4 Pump-probe spectra for a drop cast film of polyfluorene (\square), and for a drop cast film of polyfluorene doped PMMA (\circ).

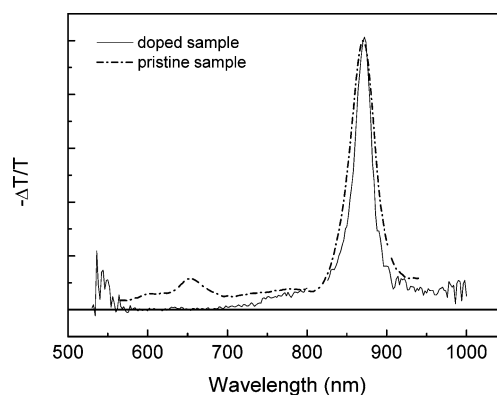


Fig. 5 CW photoinduced absorption spectra for the drop cast film of polyfluorene ($---$), for a drop cast film of polyfluorene doped PMMA ($—$).

(480 nm– 650 nm) and a second photoinduced absorption band due to S_1 – S_n transition (starting from 650 nm).^{23,24} Dispersed PFO shows a complete different transient transmission spectrum: the stimulated emission region is enlarged from 480 nm to 600 nm pointing towards reduction in the first photoinduced absorption band assigned to inter-chain charges. Further insights regarding the nature of long-lived excited states in PFO aggregated and dispersed are provided by CW photoinduced absorption measurements displayed in Fig. 5. Based on previous measurements in fluorene-based compounds we assign the narrow absorption peak located at low energy to triplet T_1 – T_n transitions.^{25,26} In aggregated PFO (---) we observe in addition an absorption band with peak at 650 nm and vibronic replica at 600 nm assigned to long-lived charges.²⁵ Interestingly, such absorption band is completely absent in dispersed PFO (—). This observation can be explained as due to the inter-chain nature of long-lived charges and the lesser inter-chain interaction present in the dispersed PFO sample. Therefore, by dispersing conjugated polymers in PMMA we have isolated the polymeric chains avoiding the creation of long-lived interchain charges. Recently a different way to hinder interchain interactions has also been shown.²⁷

We have exploited these interesting properties for the development of an ultrafast photonic switch. Fig. 6 shows the pump–push-probe experiment for different wavelengths. The push pulse arrives at 1.5 ps after the pump pulse. In all dynamics we observe an evident reduction of SE due to push re-excitation and consequent depletion of S_1 states, responsible for gain.

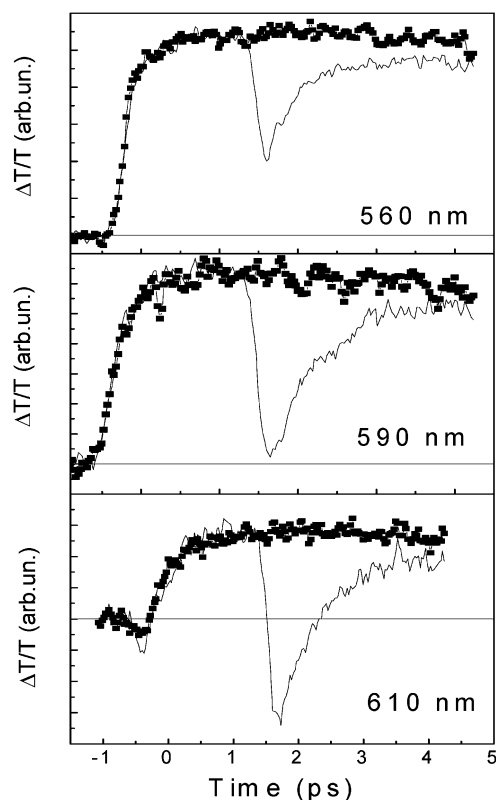


Fig. 6 Dynamics at different wavelengths with push (—) and without (■) for a drop cast film of polyfluorene doped PMMA.

Re-excitation to an upper lying S_n state increases the probability for excitons to dissociate into charge-pairs, as demonstrated by photocurrent cross-correlation experiments performed by Muller *et al.* in m-LPPP²⁸ and Frankevich *et al.* in PPV.²⁹ The overall result is an increase in charge PA. Remarkably, the recovery time of SE proceeds in about 1 ps, beyond the timescales for internal conversion from S_n (50 fs³⁰) and within the typical lifetime of intra-chain charges.⁹ Charge pairs can coexist on the same chain owing to the long polymer conjugation length which support the geminate e–h as separated quasi-particles, (an intrachain charge transfer state). Langevin recombination of intra-chain charges back into S_1 states results in a recovery of the SE signal.

Another interesting observation is the non-uniform push-induced change in SE across the 560–610 nm range which reflects the interplay between: SE reduction and increase in intra-chain charge PA which spectrally overlaps with the tail of SE. Thereby, at 560 nm the overall push effect is a 50% reduction in SE whereas at 610 nm a gain–loss regime is achieved due to dominance of PA respect to SE. The relative loss value respect to initial gain is as high as 60%. Such strong push-induced PA derives from larger associated cross-section from charge absorption transitions exceeding those of associated neutral states. Other explanations such as multiple fission into charge quartets cannot be strictly ruled out and constitute matter for further investigations. We find however that not all charges recombine into singlets, some of them go directly to the ground state or get trapped. From our measurements we estimate a return of $\approx 90\%$ of singlets states with a possible maximum gain on/off rate of 300 GHz.

Ultrafast optical gain switch in doped POF

Although POFs have been a niche technology for decades, they offer extremely easy handling and the use of low cost components, despite their limitations in terms of distance and speed.^{31,32} The increasing demand for high speed, low cost connections in short distance transmission systems open new application areas for POFs. The possibility to dope POFs with functional materials opens a wide range of new applications such as all-optical amplifiers, switches, sensors, scintillators and so on. In this work, we demonstrate ultrafast gain POF switches which operate in the blue spectral region (440–490 nm). These are produced by doping the PMMA POF with the fluorine heptamer (PF7). The sample used consists of a 2mm doped-POF polished at both ends. Doped polymer optical fibers (POFs) were produced using an adapted preform-drawing technique by LUCEAT s.p.a.³³ The dopant oligofluorenes were added to liquid methylmethacrylate monomer (MMA) at a concentration of 0.02% by weight to produce preforms (~ 4 cm in diameter) which were then drawn into fibers using a standard technique.³² The resultant doped POFs are step-index fibres with diameters of 1 mm and are clad with 25 μ m fluorinated polymer.

Fig. 7 shows the pump–probe spectrum on the doped POF at 1 ps probe delay. The spectrum is similar to those measured elsewhere for similar materials^{34,35} and so we assign the positive signal (440–490 nm) to stimulated emission and the negative signal in the near infra-red to absorption from the first excited singlet state (S_1) to a higher-lying singlet state (S_n).

Fig. 8 shows the gain switch at 480 nm. In this case the push beam is delayed respect to the pump of 1.5 ps. The recovery in

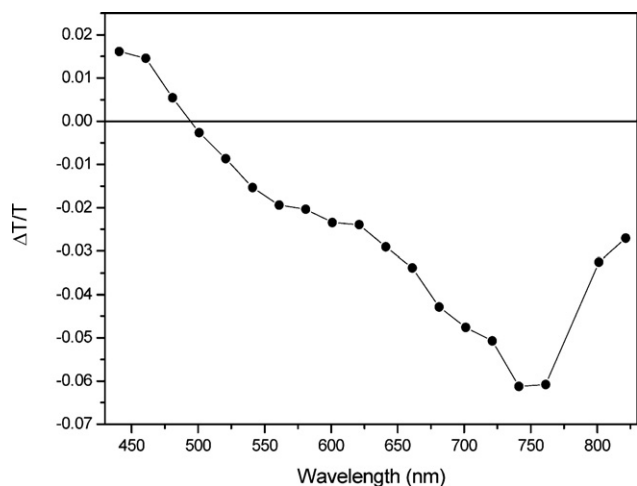


Fig. 7 Pump probe spectrum for the POF doped with PF7 at 1 ps probe time delay.

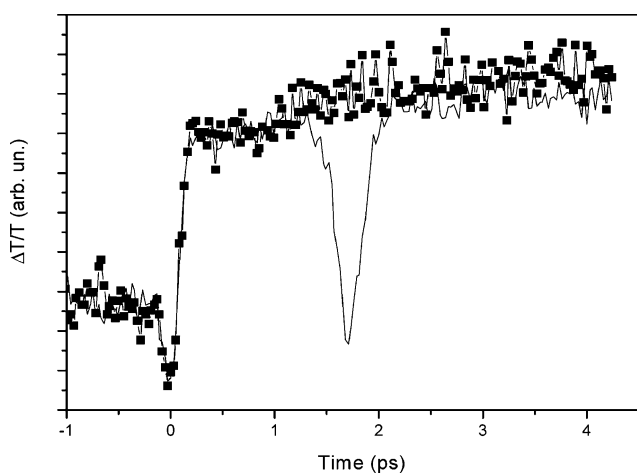


Fig. 8 Dynamics at 480 nm with push (—) and without (■) for the doped POF.

this case is total and very fast (around 500 fs) indicating the real possibility of utilising this device in short range data communication networks.

Ultrafast optical gain switch based on a microfluidic microchannel

The blend of the polymer with an inert matrix has allowed to study the photophysics of isolated chains bringing to the achievement of a fast gain switch. Further improvement has been achieved in the performance of a doped POF. We then tried to achieve a an optofluidic gain switch using a dilute PFO solution (3 mg ml^{-1}) placed in a femtosecond laser fabricated microchannel.¹¹

Optofluidics is a very active and rapidly expanding field.^{7,8} This is due to the many advantages optofluidic devices have over other photonic structures. They are easy to integrate with other optical and microfluidic functions, enabling signal processing for data communication or optical sensing in lab-on-a-chip. Simple replacement of the fluid can dramatically change the

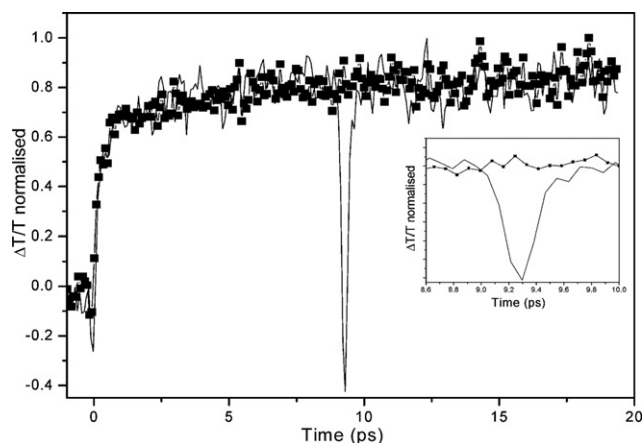


Fig. 9 Dynamics at 480 nm with push (—) and without (■) for the optofluidic microchannel. The inset shows an enlargement of the switch behaviour.

properties of the device allowing quick and easy tailoring of its characteristics.

According to the femtosecond laser irradiation followed by chemical etching (FLICE) technique, the microchannel (diameter $\sim 100 \mu\text{m}$) is fabricated in two steps:³⁶ irradiation with a Ti:sapphire laser at 780 nm (150 fs, 4 μJ , 1 kHz repetition rate, $10 \mu\text{m s}^{-1}$ writing speed); etching of the modified region in 20% aqueous solution of hydrofluoric acid for 3 h in an ultrasonic bath. The circular cross section of the channel is obtained by astigmatic shaping of the writing beam.³⁷ In order to have practical access to the microchannel we also fabricated two access holes on the top surface with the same technique. The two access holes on the top surface greatly simplify the filling of the channels and avoid the dripping of the solution out of it.

Fig. 9 shows the dynamics at 480 nm with (—) and without push (■). In this case the delay between the pump and the push beams is 9 ps. The full recovery of the stimulated emission after the push is found to be an instrument-limited recovery ($<150 \text{ fs}$) providing potential switching rates well into the THz region. These results demonstrate the huge potential of optofluidics; the combination of the femtosecond laser microfabrication flexibility and three-dimensional capability with the remarkable optical properties of conjugated polymers opens the way to further integration of optical switches and offers exciting opportunities for developing amplifiers and lasers in optical communications and lab-on-a-chip type applications.

Conclusion and feasibility

In this paper we have demonstrated the possibility of achieving ultrafast gain switch over a broad wavelength region ($\sim 100 \text{ nm}$) with potential on/off switch rates up to the THz range. We have exploited three different photonic devices: a solid state film, a doped plastic optical fibre and an optofluidic microchannel. The work outlined here is a breakthrough in all-optical switching for organic photonics. In general, optical switching can either have high on/off ratios but slow response times (resonant processes) or have fast response times but low on/off ratios (non-resonant processes). The switching mechanism described here is not only resonant, with high on/off ratios, but is also ultrafast

owing to the one-dimensional nature of conjugated polymers. However, problems with resonant processes can occur due to the large amount of energy absorbed, resulting in possible thermal or photo-damage of the photonic device. This in turn may limit the actual achievable switching rates, which we estimate to be 100 MHz for current devices. To increase the damage threshold of conjugated polymers the use of them in solution can be a good answer. Photo-degradation of polymers in inert atmosphere is likely to be due to thermal effects. In solution, local heating by the pump laser will cause convection and thus the photo-excited conjugated polymers will be able to lose their excess thermal energy before being re-excited. In this way, we expect the damage threshold of solutions to be much higher than the one in solid state. An opto-fluidic switching device can be the right choice to reach a very fast gain switching rate over a broad wavelength region.

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