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RESEARCH ARTICLE

Gain and ultrafast optical switching in PMMA optical fibers and films doped with luminescent conjugated polymers and oligomers

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Abstract Conjugated luminescent polymers and oligomers, exhibiting stimulated emission (SE), are dispersed in polymethylmethacrylate (PMMA), films and optical fibers, either by blending or upon copolymerisation. With this PMMA doping, we aim to achieve gain and ultrafast optical switching. The modification of the dopant's chemical structure allows the tuning of the SE spectral region. Furthermore, we aim to achieve dopant chain isolation while maximising their concentration. In this paper, we present an overview of the research done in this area in the context of the European Union (EU)-funded research project "plastic optical fibers with embedded active polymers for data communications — POLYCOM".

Keywords plastic optical fibers, optical gain and switching, conjugated luminescent polymers dopants

1 Introduction

Conjugated luminescent polymers and oligomers have been widely explored for light-emitting diodes [1], photovoltaics [2], and field-effect transistors [3]. Stimulated emission and lasing, under photoexcitation, have been reported [4,5], though no charge injection lasing has yet been found. The chemical versatility of these molecular materials has been at the origin of the strong development of the above-mentioned applications. This has originated a new paradigm: organic (opto)electronics [6], with some products being already marketed.

A significant effort has been put in the characterisation of conjugated luminescent polymers and oligomers to unravel some of their fundamental properties and aiming at their optimisation. Among such studies, the observation of gain enlargement and ultrafast optical switching in diluted blends of a conjugated polymer (poly(9,9-dioctylfluorene), PFO) in polymethylmethacrylate (PMMA) [7,8] was particularly relevant for this work, as it prompted us to explore this route to obtain gain and switching in PMMA-based plastic optical fibers (POFs) and optical devices [9].

POFs are becoming increasingly important for local area networks, lighting and automotive applications. They combine high flexibility, low production costs and ease of optical coupling [10,11] when compared with silica/glass optical fibers (GOFs). However, POFs' attenuation is generally higher than that of GOFs, which makes them unsuitable as transmission media for long distances. PMMA and polystyrene have been widely explored as POF core materials. As carbon-hydrogen vibration overtones significantly contribute to attenuation in the usually used transmission wavelengths, a significant improvement was achieved by the development of perfluorinated materials [12]. Costs, however, limit their widely use.

To overcome the significant attenuation in POFs, lanthanides and dyes have been studied as amplification dopants [13]. This could lead to technological developments similar to the introduction of erbium amplification in GOFs and extend POFs' transmission distance. In view of previous observations [7,8] of stimulated emission (SE) spectral enlargement and ultrafast optical switching in diluted PFO/PMMA blends, we have been exploring the use of conjugated polymers and oligomers as PMMA dopants to obtain gain and ultrafast switching.

The investigation route has been focused on dopant

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search (conjugated polymers and oligomers) showing gain, and that stands PMMA polymerisation (as the dopants are mixed with the monomer, methylmethacrylate (MMA)), stands PMMA POF drawing (at temperatures around 200°C) and that can be dispersed up to high loads while preventing interchain interactions. The dopants are either chemically inert or carry reactive methacrylate (MA) groups, which allows for the dopant insertion into the PMMA chains. Ideally, the dopants should, when dispersed in PMMA, exhibit SE in spectral regions where PMMA attenuation is low.

In this paper, we describe the properties of various PMMA-doped films and POFs. In particular, we focus on the development of new dopants and present their photophysical properties and use in POFs.

2 Background and fundamentals

Figure 1 shows the attenuation spectrum of PMMA, evidencing the low attenuation spectral windows, centered at about 520, 560 and 650 nm.

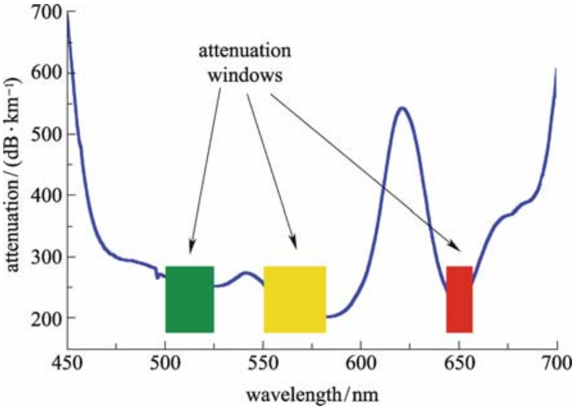

Fig. 1 PMMA attenuation spectrum

PFO (see inset of Fig. 2) is one of the most studied conjugated luminescent polymers. It is the prototype of a wide family of copolymers, which are being used in light-emitting devices, photovoltaics and field-effect transistors. PFO is a blue emitting polymer. The solid-state photoluminescence (PL) spectrum peaks at 426 and 447 nm, as shown in Fig. 2.

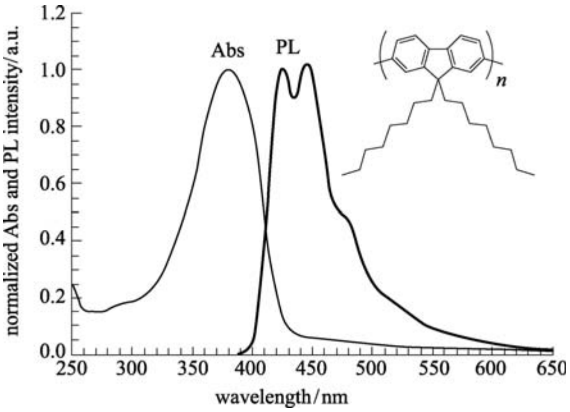

Fig. 2 Absorption (Abs) and photoluminescence (PL) spectra of PFO film (inset shows PFO molecular structure)

Blends of PFO and PMMA show very strong phase separation (see inset of Fig. 3). While in the high PFO concentration regions (darker regions in the inset of Fig. 3) the photophysics is typical of pure PFO, the diluted regions showed a distinct behaviour. As shown in Fig. 3, the transient transmission spectrum (normalized difference between excited and ground states' transmission) for pure PFO at probe delay of 2 ps after excitation at 390 nm shows SE extended up to about 490 nm. At longer wavelengths, charge absorption dominates the response. In the diluted regions, the SE extends to longer wavelengths (up to about 600 nm). This gain enlargement is attributed to a suppression of charge absorption, likely due to isolation of PFO chains that leads to a reduction of interchain interactions.

Figure 4 shows the kinetics of PFO SE at 590 nm, obtained in the diluted regions of the PMMA/PFO blend. It was further observed [7,8] that the use of a push or gate pulse at 780 nm can suppress the SE. It then recovers within 2 ps after the push pulse. This ultrafast optical switching can be used to modulate the signal.

The spectral enlargement of the SE and the optical switching with full recovery are thus associated with PFO isolated chains. Additional evidence comes from solution studies. PFO was characterised in diluted toluene solution and in mixed toluene/methanol solvent. In toluene, a good PFO solvent, we find full recovery as shown in Fig. 5. Upon addition of methanol, the absorption spectrum shows an additional peak at about 438 nm (in comparison with the typical absorption spectrum shown in Fig. 2). This additional peak is attributed to a new PFO chain conformation, named β-phase [14], with a specially extended conformation, induced by the presence of the bad methanol solvent, which is accompanied by chain aggregation [15]. In this mixed solvent, we do not find a complete SE recovery, which we attribute to the effect of interchain interactions (see Fig. 6). The mechanism proposed to account for the switching is depicted in Fig. 7 [7,8].

This switching effect has not been observed in dyes, but is observed in short conjugated luminescent oligomers[1].

These observations opened the way to explore gain and optical switching in PMMA-based POFs and films, using different conjugated polymers and oligomers as dopants.

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[1] Clark J, Lanzani G. Private communication

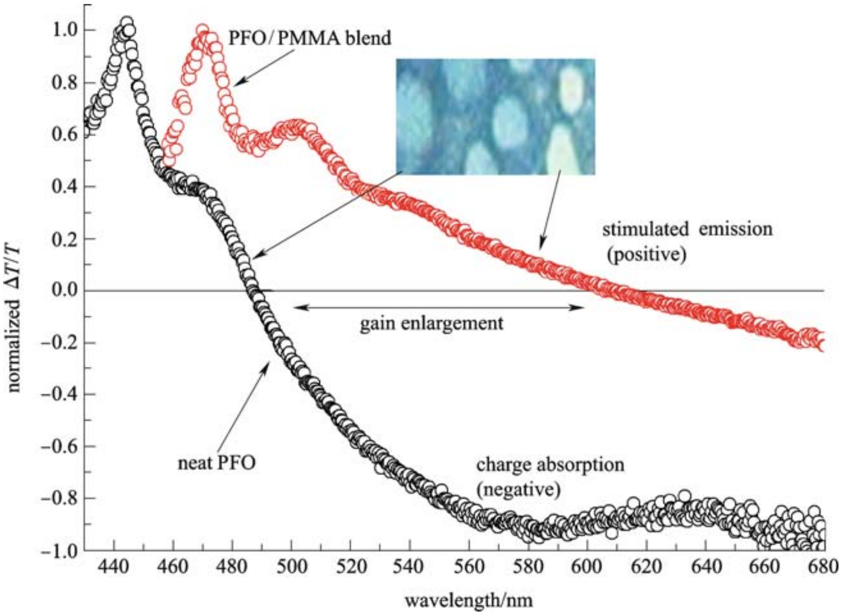

Fig. 3 Transient transmission spectra at probe delay of 2 ps for pure PFO and PFO diluted in PMMA, evidencing SE spectral range extending to longer wavelengths upon PFO dilution (inset shows a picture of a PFO/PMMA blend film)

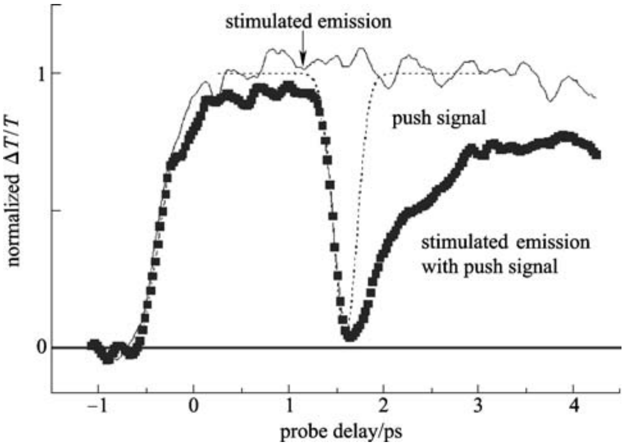

Fig. 4 Pump-probe kinetics of diluted PFO in a PFO/PMMA blend, evidencing “undisturbed” SE at 590 nm, and the effect of a 150-fs push pulse of 780 nm (SE recovers within 2 ps after push pulse)

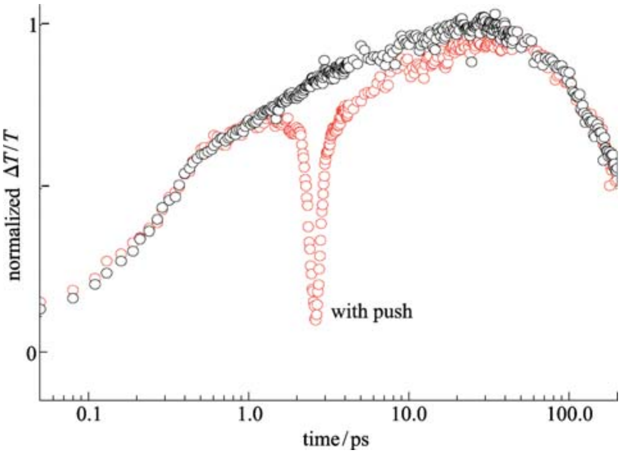

Fig. 5 Pump-probe kinetics at 480 nm for PFO in toluene with (red circles) and without push pulse, evidencing full SE signal recovery

3 Doped PMMA films and POFs

To transfer amplification and switching into PMMA POFs, there is a need to achieve a high dispersion of the dopant (conjugated polymer) and, ideally, shift the gain region into the red to match the low attenuation windows of PMMA. Two approaches were followed: 1) blending a chemically “inert” conjugated polymer or oligomer with PMMA (or MMA monomer prior to its polymerisation); and 2) mixing a reactive/functionalised conjugated polymer bearing an MA reactive group with MMA so they would be copolymerised. This last “supramolecular” approach should improve the stability of the dopant against aggregation/segregation during POF drawing. Various materials have been tested. Here, we present the results for some of such dopants, added to PMMA using both approaches.

3.1 Blue-emitting dopants

In view of the results obtained with PFO/PMMA blends, two reactive blue-emitting dopants, MA-PFO and MA-3SPF, where 3SPF stands for spirobifluorene trimer, were prepared and copolymerized with MMA. The first dopant, MA-PFO, is a conjugated polymer similar to PFO, but

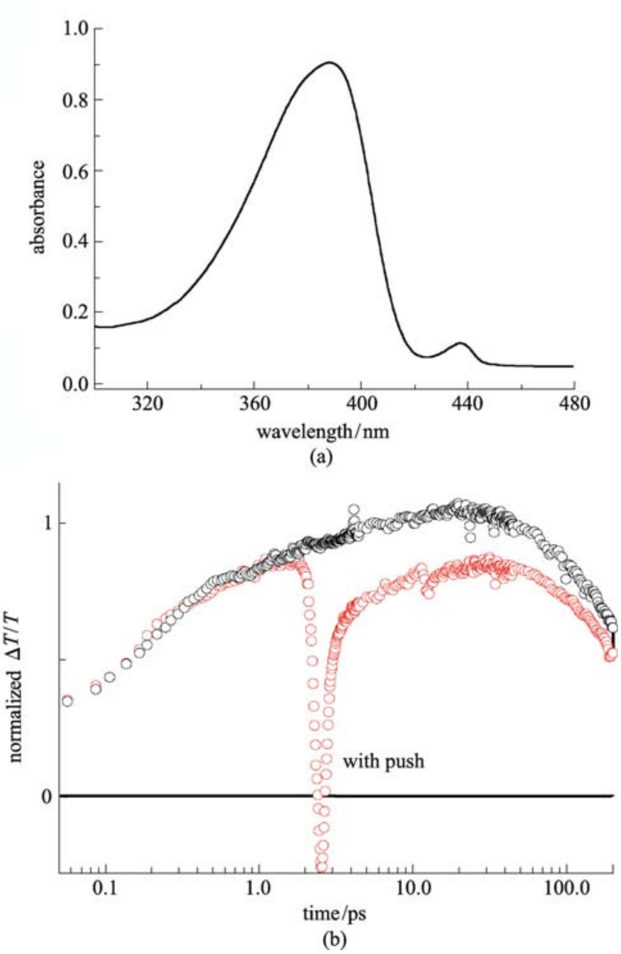

Fig. 6 (a) Absorbance of PFO in mixed toluene/methanol solvent, evidencing presence for extra peak at 438 nm; (b) pump-probe kinetics at 480 nm for PFO in toluene/methanol with (red circles) and without push pulse, evidencing absence of full SE signal recovery after push pulse

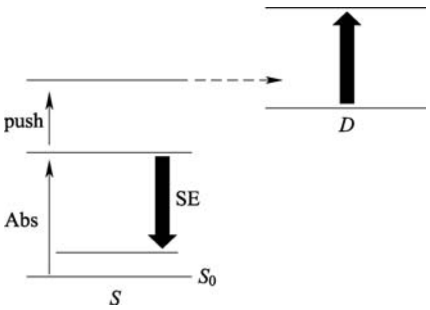

Fig. 7 Proposed switching mechanism in isolated chains of conjugated polymers (after excitation from ground state (S_0), push pulse creates upper excited states (S_n) from which charge states (D) are then created. This corresponds to the creation of separated charges (polarons), while singlet excited states S_n (excitons) are bound electron-hole pairs. The charge states D absorb the SE, leading to its quenching. At the end of the push pulse, the separated charges, which remained confined within the isolated conjugated chain, rebuild the bound excited state S, leading to SE recovery)

which contains MA side groups. Upon copolymerisation with MMA, a copolymer, PMMA-co-PFO, is obtained. The chemical structure is shown in Fig. 8. The average polymerisation degree, based on gel permeation chromatography (GPC) studies, using polystyrene standards, is $n = 26$.

The solubility of MA-PFO in MMA was found to be low (limiting value of about 0.015%, by weight), and this limited the amount of material that could be homogeneously dispersed in the PMMA matrix. The bulk copolymerisation was carried out both in test tubes (leading to the formation of glassy rods) and in an industrial environment, leading to preforms, from which POFs were drawn. The PMMA-co-PFO samples prepared in test tubes were used to carry out basic photophysical studies, both in solution and as thin films. Their properties are not much different from those of the PMMA/PFO blends. Stimulated emission up to 550 nm was observed [16], and switching was also detected, as shown in Fig. 9. However, in view of the low PFO content, the signal is very noisy. In addition, the SE does not extend up to long wavelengths as does with regular PFO doping by blending (600 nm, Fig. 3), but still to longer wavelengths than for pure PFO (490 nm).

POFs were drawn from PMMA-co-PFO, with an MA-PFO content of 0.003%, by weight. They were shown to have higher losses than the ones based on PMMA/PFO blends (with the same PFO content), as evidenced in Fig. 10. This is a quite surprising result. Scattering and absorption due to electronic transitions and vibrations are the main causes of attenuation. It appears that the use of the polymerisable dopant, when compared with PFO/PMMA blends, leads to higher scattering, which could be due to aggregate formation or imperfections. This was unexpected due to both the lower molecular weight and the presence of the polar MA reactive groups in MA-PFO, which should improve solubility and lead to more homogeneous systems.

A second blue dopant studied is a spirobifluorene derivative. Spirobifluorenes are more photoresistant than polyfluorenes, as these are prone to fluorenone formation when exposed to light in the presence of oxygen. This degradation shows up as a green emission band, leading to a whitish emission [17].

The dopant is a spirobifluorene trimer with reactive MA groups, as shown in Fig. 11. Its preparation and characterisation details will be reported elsewhere.

MMA was bulk-copolymerised with this conjugated oligomer. Glassy rods and POFs were prepared.

As shown in Fig. 12, the emission spectra of PMMA-co-PFO and PMMA-co-3SPF thin films occur in the same spectral region (in the blue). The emission maximum occurs at 413 nm for PMMA-co-PFO and at 404 nm for PMMA-co-3SPF.

Figure 13 shows the attenuation spectrum of a POF of PMMA-co-3SPF with 0.005%, by weight, content of

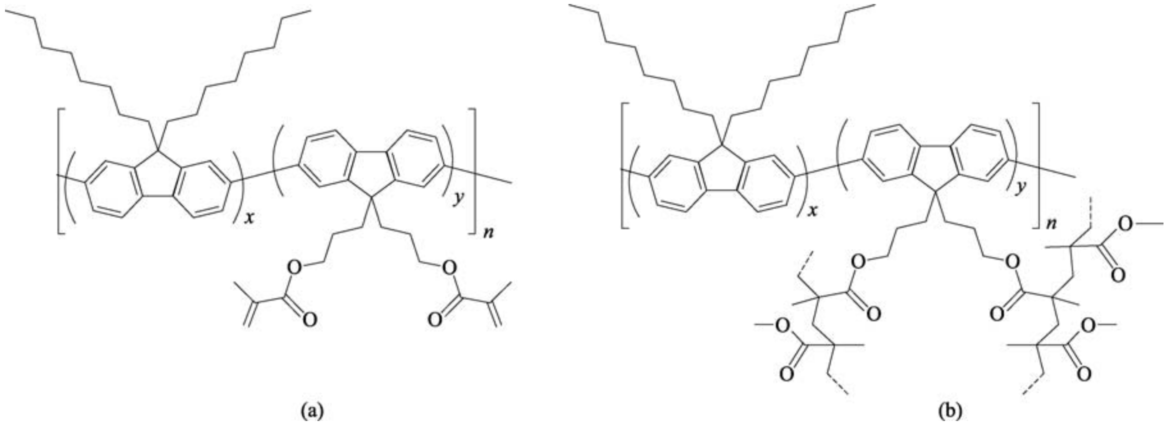

Fig. 8 Structure of (a) reactive conjugated polymer, MA-PFO, and (b) its copolymer with PMMA (PMMA-co-PFO) ($y/x = 3/100$)

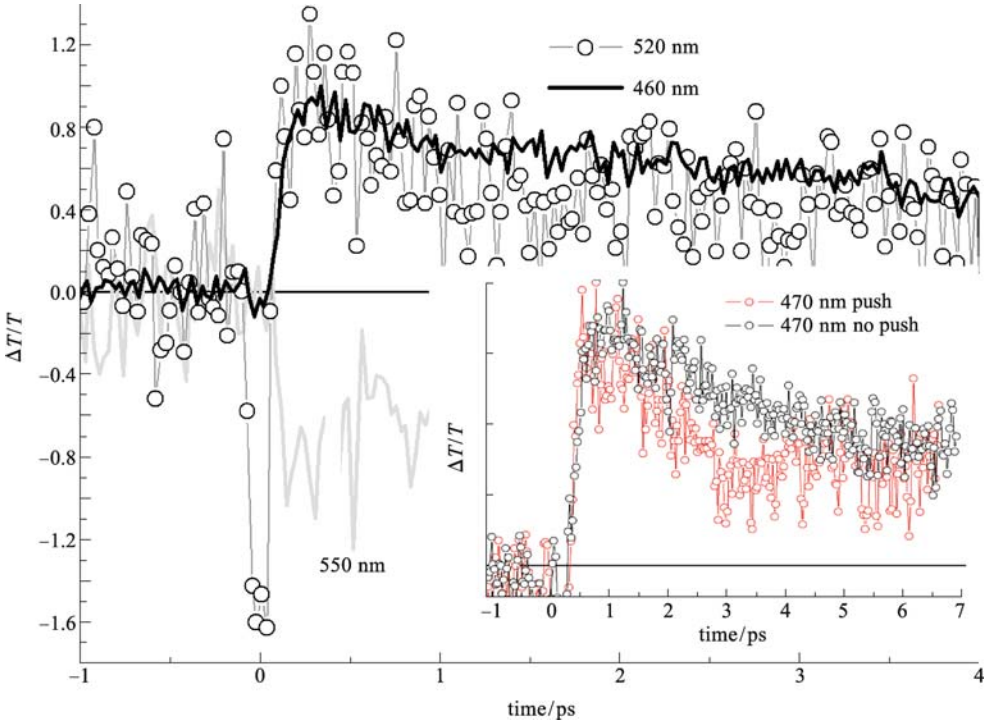

Fig. 9 Pump-probe kinetics of PMMA-co-PFO, evidencing SE at 460 and 520 nm and its absence at 550 nm, where photoinduced absorption takes over (negative value of differential transmission) (Inset shows switching at 470 nm)

dopant (MA-3SPF). The attenuation at 650 nm is 450 dB/km, which is lower than the value of 1800 dB/km found for POFs made from PMMA-co-PFO (PFO content of 0.003%), in spite of the slightly higher dopant concentration. Photophysical studies in PMMA-co-3SPF in solution and in solid state evidenced both the existence of SE and switching. In particular, SE was shown to occur in a PMMA-co-3SPF fiber, as shown in Fig. 14, up to about 490 nm. No significant differences are found in the differential transmission spectrum of the PMMA-co-3SPF POF and of PMMA-co-3SPF in solution (see Fig. 14).

In the doped systems, the maximum wavelength at which SE is still observed, 600 nm for PFO/PMMA blend, 550 nm for PMMA-co-PFO and 490 nm for PMMA-co-3SPF, is directly correlated with the emission maximum of the dopants (426, 413 and 404 nm, respectively).

To move the SE region to longer wavelengths of the spectrum, other dopants were tested, namely, green- and orange-emitting polymers and oligomers.

3.2 Green-emitting dopant

A green dopant oligomer of poly((9,9-dioctylfluorene)-alt-benzothiadiazole) (F8BT) (see Fig. 15) was tested in PMMA-based POFs. This is not a monodisperse oligomer,

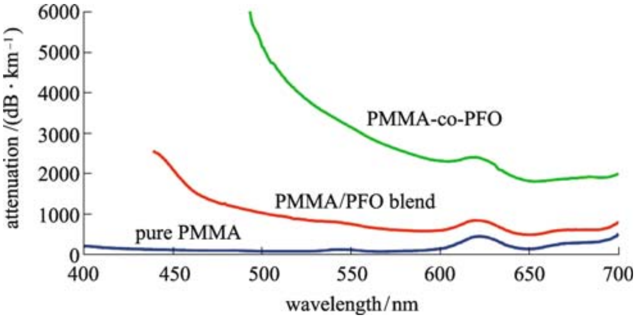

Fig. 10 Attenuation spectra of POFs made of PMMA doped with "regular" PFO and POFs based on PMMA-co-PFO copolymer having the same content of conjugated polymer (0.003%, by weight) (For comparison, the attenuation of a PMMA/POF is also shown)

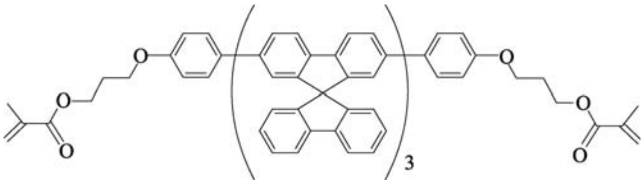

Fig. 11 Molecular structure of MA-3SPF

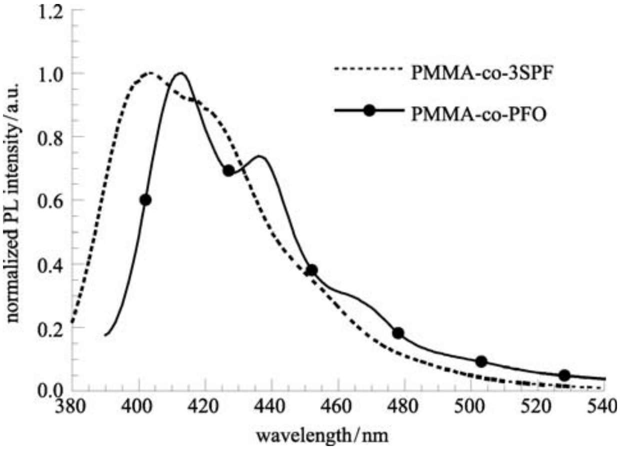

Fig. 12 Emission (PL) spectra of PMMA-co-3SPF and PMMA-co-PFO thin films, upon excitation at 358 and 380 nm, respectively

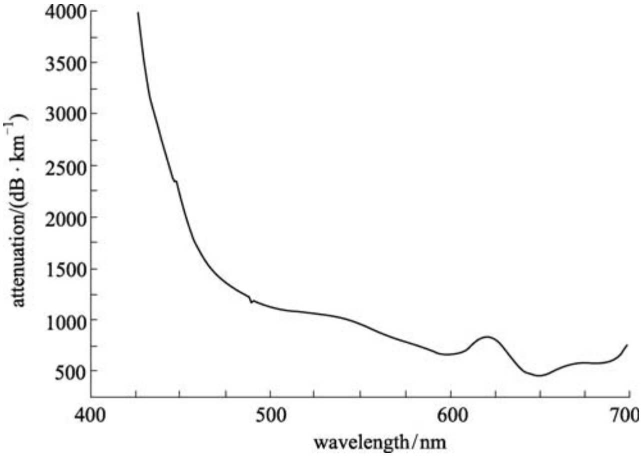

Fig. 13 Attenuation spectrum of POF made of PMMA-co-3SPF with 3SPF content of 0.005%, by weight

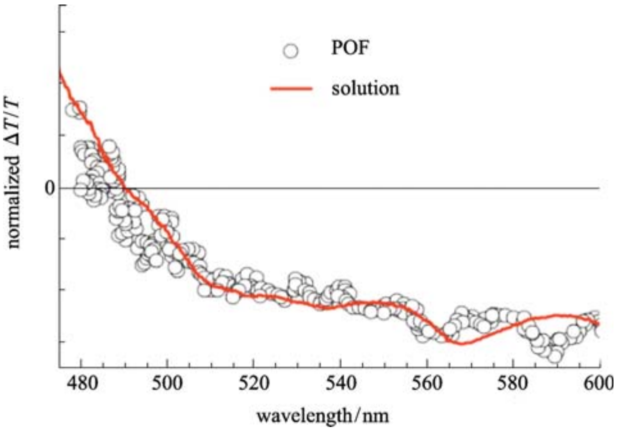

Fig. 14 Pump-probe spectra of PMMA-co-3SPF POF (open circles) and of toluene solution of PMMA-co-3SPF (red line)

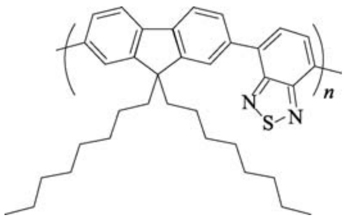

Fig. 15 Structure of green dopant F8BT (oligo(9,9-dioctylfluorene)-alt-BT) (average value of *n* is 3 (trimer))

being on average a trimer, as deduced from GPC, using polystyrene standards. Figure 16 shows F8BT trimer absorption and emission spectra in chloroform solution. We note that absorption and emission spectra of F8BT trimer are very similar to those of high molecular weight F8BT. In particular, the absorption spectrum of the trimer has two peaks at 319 and 429 nm, which are comparable to those for F8BT polymer with maximum values at about 320 and 452 nm, respectively. However, the relative intensity of the two absorption peaks is similar in the polymer, while that of the longer wavelength peak of the trimer has smaller intensity. This could point out that, on average, the number of the benzothiadiazole (BT) units is lower than that of the fluorene (F8). The PL spectrum of the trimer has a maximum at 551 nm while that of the polymer occurs at 552 nm. Figure 17 shows the attenuation spectrum measured in a POF containing 0.003% (by weight) of F8BT trimer. This was dissolved in MMA prior to its polymerisation. The attenuation at 650 nm is 1500 dB/km. Figure 18 shows the differential transmission

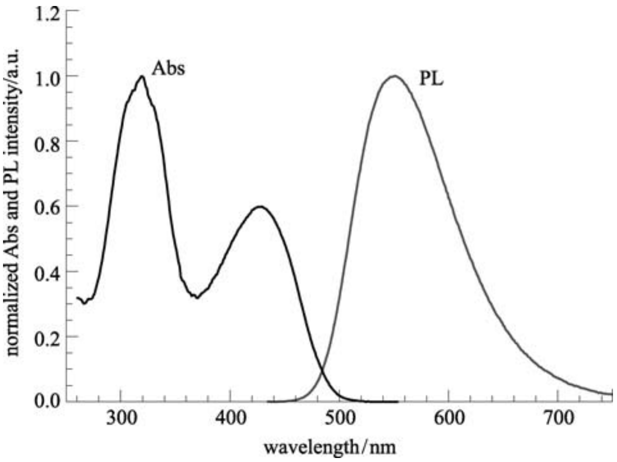

Fig. 16 Absorption and emission (PL) spectra of F8BT trimer in chloroform solution

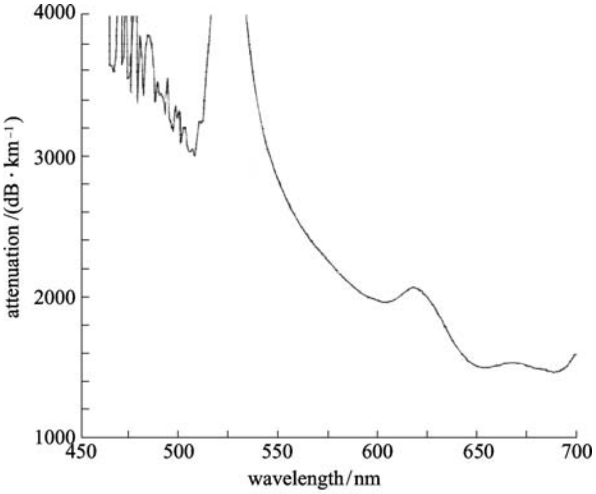

Fig. 17 Attenuation spectrum of F8BT trimer doped PMMA POF

spectrum of F8BT measured in the POF. Stimulated emission is observed up to 560 nm. Switching was also observed in the POF. The effect of the push pulse and the SE recovery after that pulse are evident in both Figs. 18 and 19.

3.3 Yellow-orange-emitting dopants

Thiophene-based conjugated polymers are being studied as PMMA dopants, as thiophene comonomers are known to lead to a red shift of the emission. The systems studied are based on fluorene-thiophene copolymers. Here, we focus on two systems, whose structures are shown in Fig. 20.

Poly(9,9-dioctylfluorene-alt-bithiophene) (F8T2) was prepared by Suzuki coupling. According to GPC results, it has a number average molecular weight $M_n = 22400$ and a weight average molecular weight $M_w = 38500$ [18]. The conjugated copolymer PF3T (see Fig. 20), which has an

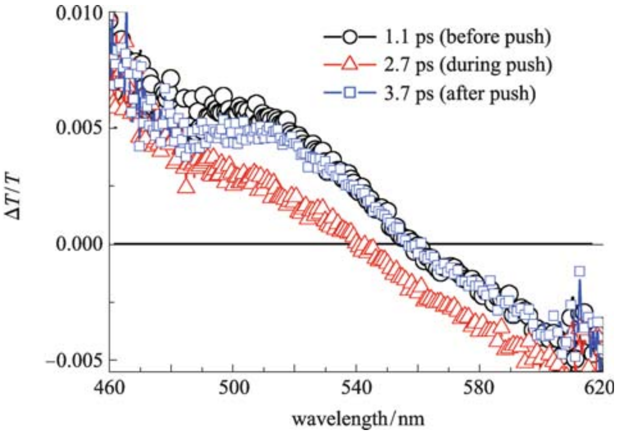

Fig. 18 Pump-probe spectra of PMMA-F8BT trimer blend POF (open circles) (effect of push (leading to switching) on SE and its recovery after push pulse are also shown)

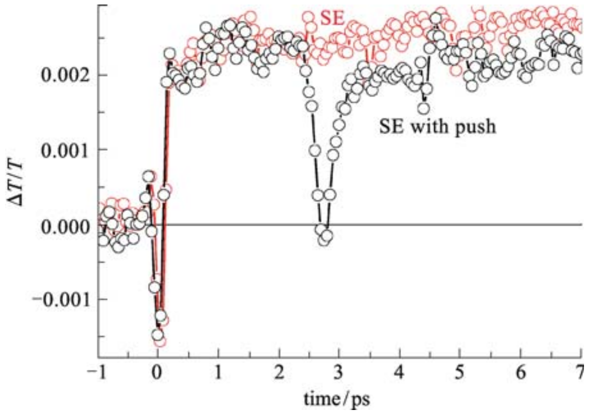

Fig. 19 Pump-probe-push kinetics of F8BT trimer-doped PMMA POF at 530 nm (switching effect is also shown, with a full recovery within about 1 ps)

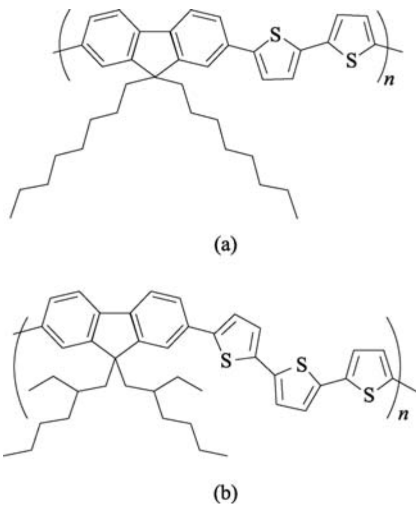

Fig. 20 Molecular structures of (a) F8T2 and (b) PF3T

extra thiophene unit, was prepared as previously reported [19]. Based on GPC results, it has M_n = 2800 and M_w = 4200. Both polymers were characterised in pure form (solution and solid state). They were also dissolved in MMA, which was then polymerised. The obtained blends were characterised in solution, and POFs were drawn.

The emission spectrum of the PF3T/PMMA blend in solution (shown in Fig. 21) has a maximum at 513 nm (green). We note, however, that films of pure PF3T emit in the orange (maximum at 567 nm [19]). Stimulated emission was measured in solution and was shown to occur up to 570 nm, which is slightly red-shifted when comparing with F8BT trimer (moving into the orange). However, no switching was observed. The attenuation of a PMMA POF doped with 0.003% PF3T is 13000 dB/km at 650 nm, which is an order-of-magnitude higher than that of the POF made with F8BT trimer-doped PMMA. We note that, in films obtained from blends of PF3T and PMMA, prepared in a common solvent, evidence for aggregation is found. This aggregation could be at the origin of the absence of switching and could also explain the higher attenuation found in the POF.

POFs drawn from the PMMA/F8T2 blend showed too high attenuation, so it was not quantified. The absorption and emission spectra of F8T2 are shown in Fig. 22.

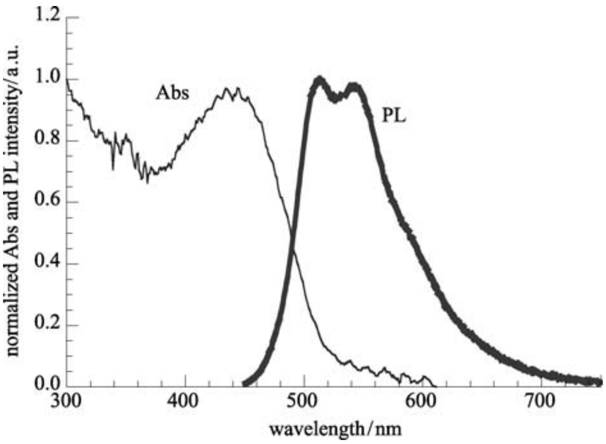

Fig. 21 Absorption and emission spectra of PF3T blended with PMMA

4 Conclusions

PMMA POFs and films can be doped with conjugated luminescent polymers to obtain gain and ultrafast optical switching. By chemical modification of the structure of the luminescent polymer, we can change the SE spectral region to match the low attenuation windows of PMMA or any other transmission medium, such as polystyrene. However, we have not yet obtained significant gain at 650 nm, which would be ideal for PMMA-based POFs (see Fig. 1). It is also observed that, upon doping with the conjugated polymer, the attenuation significantly increases, and the use of the reactive dopants so far tested does not seem to reduce that detrimental effect, though it should lead to POFs with improved stability towards aggregation/segregation. Furthermore, there is the need to increase the dopant concentrations, which requires further chemical modifications of the dopants. This work is still in progress.

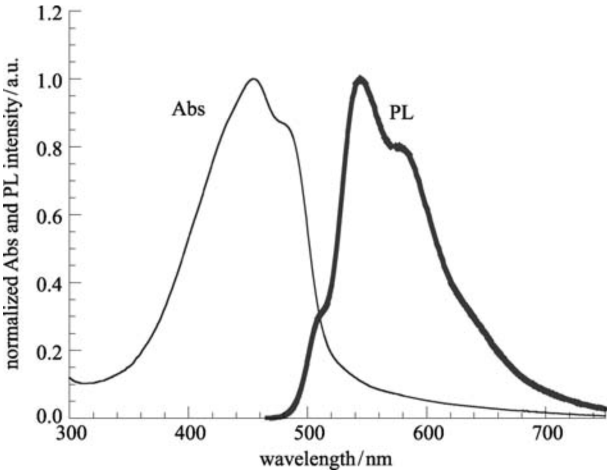

Fig. 22 Absorption and emission spectra of F8T2

Switching has been attributed [7,8] to excitation of charged states from the singlet-excited states. These charged states will then absorb all SE. The fact that SE can be recovered at the end of the push pulse has been related to chain isolation [7,8]. It should be mentioned, however, that there is a report on switching on a film of a pure conjugated polymer: a derivative of F8BT, which contains only 10% of the BT comonomer [20]. This remains a matter of debate.

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