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A core copolymer approach to improve the gain properties of a red-emitting molecule[†]

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We report a new approach to improve the gain characteristics of a red-emitting based molecule. The insertion of the active dye between two polymeric arms prevents the inter-molecular interactions deleterious for the gain. By means of the ultra-fast pumpprobe technique we found an efficient energy transfer between the polymer and dye. High gain in the nanosecond timescale regime has been proved.

Since their discovery, conjugated polymers have been a growing area of interest for optoelectronic research and applications such as transistors and photovoltaic.^{1,2} Their high optical gain, as well as their low cost processability and easily tunable optical properties, make them suitable to be used as lasing materials or amplifying media.^{3,4} In particular organic materials have been recently used for signal regeneration in polymeric optical fibers (POF).⁵ For these photonic applications it is very important to control the inter-chain charge photo-generation yield, which is often detrimental, as the charge absorption band overlaps spectrally with the stimulated emission. Therefore, charge generation acts to quench the stimulated emission, gain and lasing action. Different approaches have been tried so far⁶⁻⁸ to control this mechanism. An attractive approach could be the "core polymer" strategy, wherein a molecular dye is inserted as a core between two arms of a semiconducting polymer.^{9,10} This powerful strategy has been applied successfully in polymeric OLED materials but never focused to enhance the optical gain for advanced applications.

In this communication we synthesize a new molecule (F-BT-T-)₂ (see inset Fig. 1 bold, in the text called R48A) *via* Suzuki Coupling (SC) between 2,2'-bithiophene-5,5'-diboronic acid bis(pinacol) ester (T2diBor) and 4-bromo-2,1,3-benzothiadiazole-7-(9,9-dioctylfluorene)¹⁰ and the new corresponding core copolymer (R1A see inset Fig. 1) obtained by SC between two arms of



Fig. 1 Absorption (on the left) and emission spectra (on the right) of the R48A core (symbols, $\lambda_{exc} = 500$ nm) and the R1A (solid line $\lambda_{exc} = 400$ nm). In the inset the chemical structure is shown, with the core in bold.

poly(9,9'-dioctylfluorene-*co*-benzothiadiazole)-Br terminated (PF8BT-Br)¹¹ and T2diBor. The simple coupling of a T2 unit, instead of a preformed dye, represents a strong chemical simplification with respect to the core and end polymer previously reported;^{9,11} moreover the use of the high energy T2 unit ensures that the only contribution to the red part of the spectra is due to a completely core formed polymer solving the problem of residual unreacted dye. With this straightforward approach the two PF8BT polymeric chains are expected to play a double role: shields to avoid inter-molecular interactions and indirect pump excitation for the red-emitting molecule through an efficient Förster energy transfer mechanism.

In the following we will first describe the photophysical properties of the R48A molecule with respect to the R1A copolymer by means of the ultrafast pump-probe technique, then we will describe the characterization of the R1A optical gain by studying its amplified spontaneous emission (ASE).

A spin coated film of R48A from a toluene solution (15 mg ml^{-1}) on a fused silica substrate has been prepared.

Fig. 1 shows the absorption and the emission spectra of R48A (symbols) and R1A (lines). The absorption spectrum of the R48A (solid circles) shows a broad band with a peak at

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525 nm, while the photoluminescence (PL) spectrum (open circles) shows a peak at 670 nm. In order to study the photophysical characteristics of this molecule, we perform a classical pump-probe measurement with ≈ 150 fs time resolution,¹² upon excitation at 530 nm with 280 μ J cm⁻² (see the ESI⁺ for details). Fig. 2a shows the chirp-free differential transmission $(\Delta T/T)$ spectra of R48A for different time delays between the pump and the probe. The spectrum at 0 fs time delay (solid line in Fig. 2a) shows the excited states present instantaneously after the pump excitation: a stimulated emission (SE) band at around 650 nm and a photoinduced absorption (PIA) band over 700 nm both due to singlet excitons population (see dynamics in the ESI[†]). The contribution of the ground state bleaching (GSB) is visible at wavelength shorter than 530 nm. At longer probe delays (see open squares Fig. 2a) the positive signal becomes negative indicating the formation of a new PIA band which we attribute to the generation of interchain charges. These charges are probably created by exciton-exciton annihilation as also reported in ref. 13; additional measurement studies are in progress to prove it. Anyway in this communication we focus on the fact that this band spectrally overlaps with the SE one, "quenching" the gain of the molecule after few ps.

The R1A copolymer (see chemical structure in the inset of Fig. 1) is proposed to be an alternative to solve the problem of the "Gain Quenching". A drop-cast film of around 250 nm is prepared. The absorption and the emission spectra are shown in Fig. 1. In the R1A absorption (solid line) spectrum the core contribution is still visible (broad band at 560 nm) but the predominant contribution is the one due to PF8BT at 470 nm.¹⁴ The core absorption spectrum overlaps with the emission of the PF8BT centred at 550 nm (not shown in Fig. 1) as reported in the literature,¹⁴ satisfying the necessary conditions for the Förster Resonant Energy Transfer (FRET),¹⁵ where the core is the acceptor and PF8BT is the donor. The PL spectrum of the copolymer (broken line) is therefore determined by the core, with a main peak at 660 nm (Fig. 1).

Pump probe measurements are also performed on the R1A film pumped at 390 nm with 100 μ J cm⁻² (see Fig. 2b).⁶ This excitation energy has been chosen in order to not have any spectral narrowing due to amplified spontaneous emission from the film. Even if the core absorbance is non-zero at 390 nm,



Fig. 3 (a) Dynamics of the copolymer R1A (closed symbols) and the core R48A (open symbols) at 660 nm. (b) Experimental data (symbols) and fitting (solid line) of the R1A dynamics at two wavelengths.

in the pump-probe spectrum at zero probe delay we can see only the PF8BT contribution (solid line Fig. 2b), with ground state bleaching (GSB_d) below 470 nm, stimulated emission (SE_d) at 560 nm and photoinduced absorption (PIAd) at 760 nm, in agreement with previous studies.¹⁶ Therefore, by pumping at 390 nm, we can distinguish between contributions due to PF8BT (instantaneous) and contributions due to the core (delayed). At increasing time delays we have two growing bands at 560 nm and at 675 nm which, as shown in Fig. 1 and 2a, we can attribute, respectively, to the GSB_a and to SE_a of the core. Interestingly, the SE_a band due to the core is still present at 400 ps probe delay. In this way, we can clearly see that, upon addition of the side chains to the core, the formation of charges is inhibited. Fig. 3a compares the dynamics at 660 nm for the R48A (open symbols) and the R1A (solid symbols). It is evident how in the copolymer the core gain is still present even at very long probe delays. In this new structure the molecule is shielded by two long polymeric arms, which do not just prevent the generation of intermolecular charges but also allow an indirect pump excitation of the core through an energy transfer mechanism, reducing, in this way, also the probability of formation of charges normally induced by an excess of energy after direct excitation.17

In order to study more in depth the energy transfer mechanism, it is possible to set the balance equation of the populations of the excited states, taking into account all the possible excitation/decay routes (see ESI[†] for details). By fitting the solutions of these equations to the experimental data (Fig. 3b), we can obtain the physical quantities that characterize our system: the radiative lifetime of the core $\tau_a \sim 500$ ps and the value of the Förster radius $R_0 \sim 2.6$ nm, which is comparable with that of a similar organic blend.^{16,18,19} The stimulated emission signal from R1A is quite long-living, making this polymer a good candidate for amplification in the ns time-scale regime, excitation not possible for a R48A film due to the shorter gain lifetime. This is verified experimentally by obtaining amplified spontaneous emission (ASE) with ns excitation pulses.

ASE is obtained by pumping the film at 355 nm (3 ns pulse duration) with a rectangular stripe spot excitation (1500 \times 100 μ m²) and the spectrum is collected at the edge of the film using a spectrograph (see ESI† for details). The spectra as a function of the excitation energy density are shown in Fig. 4. No degradation of the sample is found, as can be seen from the spectrum taken after the set of measurements (see the dark grey curve in Fig. 4). We can clearly notice a peak centered at



Fig. 4 Spectral evolution of the PL from the R1A film as a function of the excitation energy density. Inset: evolution of the FWHM (open triangles) and of the PL intensity at 660 nm (closed circles: experimental data, line: numerical fit) as a function of the stripe length.

660 nm arising for an excitation energy density threshold of around 1.2 mJ cm⁻².

To calculate the gain value g(660 nm), we consider the spectral evolution as a function of the stripe length. Fig. 4 shows the evolution of the emission intensity at the ASE peak (660 nm) and of the Full Width at Half Maximum (FWHM) as a function of the stripe length, for an excitation energy density of $\sim 1.4 \text{ mJ cm}^{-2}$. The narrowing occurs only when the pumped region is long enough to provide a sufficient gain in the medium to overcome the loss mechanisms. The output intensity of the excited stripe follows the relation:²⁰

$$I(\lambda) \propto \frac{1}{g(\lambda)} \left(\mathrm{e}^{g(\lambda)l} - 1 \right)$$

where $I(\lambda)$ is the output intensity, $g(\lambda)$ is the wavelength-dependent gain and l is the length of the excited stripe. We have to point out that $g(\lambda)$ is the net gain of the material, given by a positive contribution (ASE) and a negative contribution due to all the loss mechanisms of the waveguide.²¹ The ASE peak shows a distinctly large gain (~30 cm⁻¹) for an excitation energy density just above the ASE threshold (1.4 mJ cm⁻²). This value is high enough to consider this copolymer as a good candidate for photonic applications.²¹⁻²⁴

We have reported a new approach to avoid intermolecular interactions such as exciton–exciton annihilation and consequently formation of charges in a red-emitting molecule, suitable for photonic applications. The molecule has been "isolated" between two long polymeric chains, creating a new copolymer. Those chains not only act as shields for the molecule but also allow an indirect pump-excitation through an efficient Förster energy transfer mechanism. Photophysical characterization shows the presence of a long-living gain in the core molecule "encapsulated" in the copolymer with respect to the shorter gain lifetime of the core molecule on its own. We measured a net gain of ~ 30 cm⁻¹, making this material suitable for photonic applications.

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