

Laser action from a sugar-threaded polyrotaxane

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We present gain and lasing results from a polyrotaxane consisting of a conjugated polymer (polyfluorene-*alt*-biphenylene) threaded through sugar macrocycles (β -cyclodextrin). Encapsulation suppresses interchain charge separation, leading to lasing emission not observed in the unthreaded polymer, and enlargement of the stimulated emission in threaded polymer is observed. We demonstrate all-optical switching distributed feedback laser. © 2009 American Institute of Physics. [DOI: 10.1063/1.3179689]

Conjugated polymers (CPs) are promising materials in photonics.^{1–3} Optical gain in CPs has been observed in a number of experiments.^{4,5} The distributed feedback (DFB) grating is the most widely used for testing and demonstrating lasing properties, due to the simple manufacturing technology, the possible industrial scaling and the easy solid state integration.^{6–8} Recently, applying the pump-probe (PP) technique to investigate laser devices, the detrimental role of interchain interactions has been demonstrated.⁹ At the rather high excitation density needed for population inversion, the photogeneration of charges cannot be avoided. This leads to a loss mechanism which increases the laser threshold and degrades the emitting properties.

In this paper a study on CPs threaded through sugar macrocycles is presented. These “insulated molecular wires,” known as *polyrotaxanes*,¹⁰ have the characteristics to preserve all the single chain properties of the threaded CPs, while strongly inhibiting the interchain interactions. We study the excited state dynamics in films, comparing threaded and unthreaded polymers, demonstrating the possibility of all-optical signal control. We show that threaded CP chains better qualify for photonic application than unthreaded materials.

The active material is polyfluorene-*alt*-biphenylene (PFBP·Li) with a cyclodextrin (β -CD) ring around the core. PFBP·Li is an example of the larger fluorene-based family of CPs, which is attractive for photonic applications.¹¹ Polyfluorenes (PF) show strong stimulated emission (SE) in the blue spectral region¹² and can be used as active layers in DFB lasers.^{7,13,14} The chemical structure of the polymers under investigation is shown in Fig. 2. The synthesis of PFBP·Li polyrotaxane threaded with β -CD (PFBP·Li $\subset\beta$ -CD) is described elsewhere.¹⁵ The PFBP·Li and PFBP·Li $\subset\beta$ -CD have an average degree of polymerization of $n=10$, and the polyrotaxane has an average threading ratio of 1.1 β -CD per unsubstituted biphenylene unit. Both are dissolved in water (20 mg/ml) and spin-coated onto a patterned glass substrate to obtain a film thickness

~250 nm. The fabrication of DFB structure is described elsewhere.⁷ The final grating pattern was ~60 nm and period of $\Lambda=290$ nm.

To study the gain and switching properties of both polymers we employed pump probe (PP), pump-push-probe (PPP)¹⁶ spectroscopy and the amplified spontaneous emission (ASE) technique. The pump (390 nm, 180 fs) is resonant with the absorption band of both polymers.¹⁵ The push (780 nm) is resonant with an excited singlet state absorption of PFBP·Li was delayed with respect to the pump by 3 ps. Detection of the temporal evolution of the differential transition dynamics is recorded at selected wavelength (10 nm bandwidth filters) with a standard lock-in technique. For ASE measurement the samples were optically pumped (390 nm) using an excitation focus on rectangular excitation ($\sim 0.14 \times 1.03$ mm²).⁹ The emitted light was collected with a fiber bundle placed close to the sample edge and fed to a grating spectrometer (Oriel Instaspec IV) with a resolution of 0.5 nm equipped with a charge-coupled device (CCD). In DFB laser measurements the collection fiber bundle was placed normal to the sample surface. PP and PPP measurements were performed in the air while ASE/lasing under N₂ atmosphere (sample encapsulation). This allowed longer exposure times with no degradation after hours of operation.

Figure 1 shows both the spectra at a fixed pump intensity and fixed time delay together with the kinetics at two different pump intensities. The chirp-free differential transmission spectra $\Delta T/T$ of the naked and threaded polymers at 2 ps time delay are displayed in Fig. 1(a). The spectrum of the neat polymer shows a positive band, which matches with the photoluminescence (PL)¹⁵ assigned to SE, and a large negative structure due to photoinduced absorption (PA). PA consists of two different bands PA_D peaking at 560 nm (2.22 eV) and PA_S peaking around 700 nm (1.76 eV). PA_D has a different dynamics from SE and is attributed to transitions of charged states.¹⁷ PA_S has similar deactivation dynamics as SE and is assigned to optical transitions within the singlet manifold.⁹ The spectrum of PFBP·Li $\subset\beta$ -CD shows two differences (i) PA_D is absent and (ii) there is an enlargement of the SE band by ~30 nm (0.15 eV) which indicate that charges do not form in the threaded polymer. This is under-

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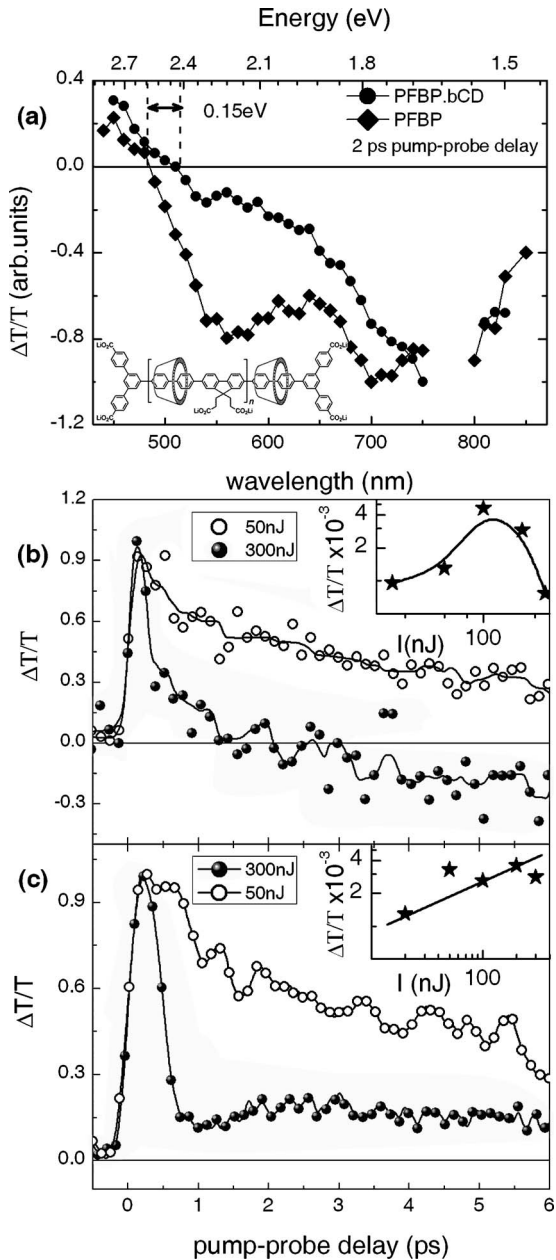


FIG. 1. (a) $\Delta T/T$ at 2 ps probe delay for the PFBP·Li (full rectangular) and PFBP·Li \subset β -CD (full circle). $\Delta T/T$ dynamics (460 nm) at different pump energy 50 nJ/pulse (open circle) and 300 nJ/pulse (full circle) for (b) PFBP·Li and (c) PFBP·Li \subset β -CD. Inset: $\Delta T/T$ vs pump energy.

stood as a consequence of the *suppression of interchain interactions*.

PP measurements with the probe set at 460 nm and with a vary pump energy are shown in Figs. 1(b) and 1(c). At the low pump fluence, the polymers present similar decay kinetics. At high excitation fluence, SE turns negative after less than 2 ps only in the naked polymer. The process responsible for this behavior is the photogeneration of charge-separated states whose absorption overcomes SE. In the threaded chains SE survives even at high fluence, when a fast decay component becomes dominant in the relaxation dynamics. This can be explained in terms of excited state population depletion induced by ASE.¹⁸

Threading leads to important effects on the excited state dynamics, which are highlighted in PPP experiments.¹⁶ Figure 2 shows the normalized SE kinetics at 460 nm. In the naked chain the push pulse (spectrally located within the

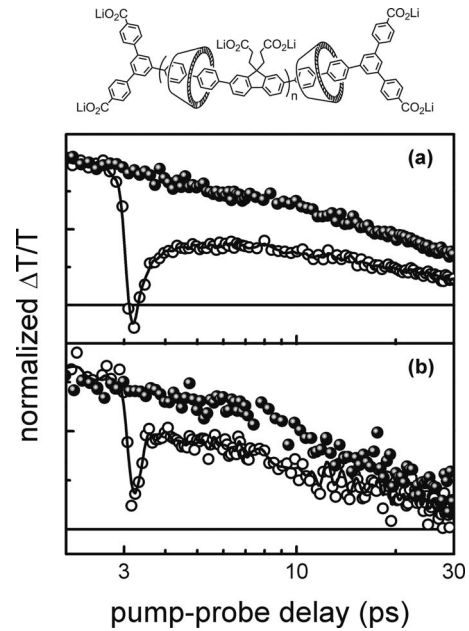


FIG. 2. Chemical structure of PFBP·Li \subset β -CD is shown. The cone represents the β -CD; PFBP·Li has an identical structure except without β -CD units. $\Delta T/T$ kinetics for (a) PFBP·Li and (b) PFBP·Li \subset β -CD at 460 nm. PP kinetics (black spheres); PPP kinetics with re-excitation 3 ps after pump (open circle).

PA_S) causes a gain switch-off, and makes the signal become negative. Recovery take place on two different time scales: <400 fs and over \sim 80 ps. In contrast SE of the threaded chain [Fig. 2(b)] is instantaneously reduced by \sim 80% but does not turn into negative. Its recovery is fast (<400 fs) with a small tail in the picosecond time domain. After 20 ps the SE is fully recovered. The fast recovery is due to the internal conversion and intrachain charge-generation, while the slow tail is caused by longer-lived interchain charges.⁹ Again our results demonstrate the improved performance of the threaded chain, and show that threading with the sugar macrocycles prevents charge hopping to other chains and thus results in a faster intrachain dynamics. Note, in contrast to previous work in matrices,¹² here a bulk sample with densely packed chains is used.

The obtained results foster the use of PFBP·Li \subset β -CD as an active medium in an all-optically controlled DFB device. From PP the gain cross-section (at 450 nm) is $\sigma_{SE} = 5.13 \times 10^{-17} \text{ cm}^2$ and the gain $g = \sigma_{SE} N_{ex} = 398 \text{ cm}^{-1}$. ASE and lasing are reported in Fig. 3 on flat and corrugated surfaces, respectively. For the naked chain [Fig. 3(a), dotted line] the ASE narrow spike (FWHM=14 nm) (FWHM denotes full width at half maximum) is observed at 450 nm on top of a broad PL band for excitation densities $>100 \mu\text{J}/\text{cm}^2$. For the threaded chain [Fig. 3(a), dashed line] ASE line-narrowing at 435 nm (FWHM=8 nm) for excitation density around $30 \mu\text{J}/\text{cm}^2$ (factor of three smaller) is observed. When pumping the DFB the emission line becomes almost one order of magnitude narrower (FWHM < 1 nm) [Fig. 3(a), black line], as a characteristic of the feedback action. The threshold for laser action is $45 \mu\text{J}/\text{cm}^2$. The contradictory finding of a laser threshold higher than ASE can be rationalized by taking into account that ASE and lasing are probed on different areas, probably the ASE threshold at the DFB spot is higher than the laser threshold. Alternatively this finding could be attributed to the

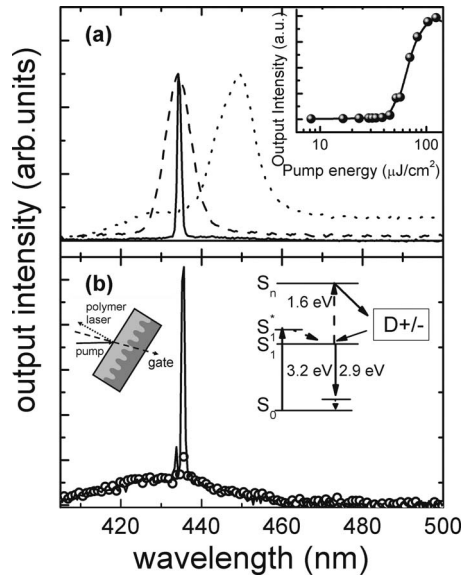


FIG. 3. (a) Normalized laser emission (line) and ASE (dashed line) spectra for the PFBP-LiC- β -CD. ASE for a PFBP-Li (dotted line). Inset: Output intensity for a laser emission as a function of the absorbed pump fluence. (b) Laser emission spectrum (line) and emission when the laser is completely shut off (empty circles) by the gate. Inset (left side): the experimental set-up. Energy level diagram for optical gain media in the presence of the gate (right side).

losses due to the length L of the grating.⁷ Anyway, the very narrow line (<1 nm) observed for emission from the DFB is a clear indication of lasing. Note that laser action using the neat polymer chain *could not be achieved* even at high pumping rates. We believe that the lack of the laser action could be explained by the charge absorption which plays crucial role at high pump intensities [see Figs. 1(b) and 1(c)]. In keeping with the other results presented here, this indicates that threading is highly advantageous for lasing, even if in absolute terms we did not yet achieve the top limit performance (Table I). The better chain isolation is highlighted by the blueshift of ASE peak of rotaxane, indicating lack of spectral migration.¹⁰

Figure 3(b) shows that the lasing emission (black line) is almost completely switched off when the gating beam reaches the laser area (open circle). The remaining broad emission spectrum corresponds to PL of PFBP-LiC- β -CD. The laser switching mechanism is a combination of gate induced depletion and charge photogeneration following S_n population.⁸ There are three effects which are detrimental for emission: S_1 depletion, charge absorption, and S_1-D_0 nonra-

TABLE I. Excitation conditions and threshold values for lasing for different CPs in DFB structure. Note, it is difficult to compare the values due to the different laser pulse duration used in the experiments.

Material	Threshold ($\mu\text{J}/\text{cm}^2$)	Excitation	Ref.
PFBP-LiC- β -CD	45	$\lambda_{\text{exc}}=390$ nm, $\tau=180$ fs	Our result
F8BT	85	$\lambda_{\text{exc}}=400$ nm, $\tau=200$ fs	7
MEH-PPV	25	$\lambda_{\text{exc}}=355$ nm, $\tau=3$ ns	19
PPV	40	$\lambda_{\text{exc}}=337$ nm, $\tau=4$ ns	20
PFO	64	$\lambda_{\text{exc}}=355$ nm, $\tau=10$ ns	13

diative quenching.¹⁶ The theoretical modulation rate of 200 GHz is suggested from PPP (see Fig. 2).

In conclusion, the effect of supramolecular encapsulation on the photophysics and on the consequent photonic properties of a CP was investigated. We found evidence for improved optical gain in solid samples. We envisage an ultrafast all-optical gain switching molecular device, which could be used for all-optical signal control and logic gates where the active medium contains threaded CPs. In addition, the characteristic of these materials can eventually open new routes toward electrically or hybrid driven lasers, due to possible separation between transport and emission within the supramolecular architecture.²¹

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