

A two-photon pumped polyfluorene laser

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A tunable two-photon pumped solid-state laser based on polyfluorene is reported. A detailed investigation of the two-photon absorption in polyfluorene for both nanosecond and femtosecond time regimes in solution, and solid-state allows the determination of the most favorable conditions for lasing. Tunable distributed feedback lasers are made by spin coating from a polyfluorene solution on corrugated silica substrates and lasing is achieved under two-photon excitation at 640 nm with an absorbed energy density at lasing threshold of 1.3 mJ/cm². These results highlight an alternative pumping scheme for blue organic semiconductor lasers. © 2009 American Institute of Physics. [DOI: 10.1063/1.3149827]

Semiconducting polymers are a family of organic semiconductors displaying a variety of very attractive photophysical properties such as broad emission that can span the entire visible spectrum, high photoluminescence quantum yield, and large optical gain.^{1,2} The combination of low concentration quenching with solution-processability allows simple fabrication of solid-state devices for a wide range of optoelectronics applications including light-emitting diodes,^{3,4} optical amplifiers,^{5,6} and lasers.^{7,8}

Among these polymers, polyfluorene (PFO) (see inset of Fig. 1 for chemical structure) is considered to be a benchmark blue-emitting material and extensive research has been performed on its electrical, photophysical and structural properties.^{9,10} Studies have also shown its very attractive properties as a laser gain medium, including low lasing threshold and excellent tunability, highlighting PFO's importance for lasing.¹¹ However, as is the case with all organic blue emitters, the absorption of PFO lies in the ultraviolet part of the spectrum where the choice of compact optical pump sources is somewhat limited. One alternative approach is using two-photon pumping, whereby two photons of longer wavelength (lower energy) are absorbed simultaneously to bridge the energy gap of the material and thus the pump wavelength can be shifted from the UV toward the red part of the spectrum where powerful red laser diodes might ultimately be used for optical pumping. Past studies of two-photon absorption in PFO have described some aspects of its nonlinear absorption properties using either nanosecond or femtosecond excitation,^{12,13} but a study across the two time domains has not been produced and two-photon pumped lasing in PFO has not been demonstrated.

In this letter we report on a tunable two-photon pumped solid-state PFO laser pumped at 640 nm. We perform a complete characterization of two-photon absorption and fluorescence under both nanosecond and femtosecond excitations and study the pump wavelength and energy dependence of the nonlinear optical properties of PFO in solution and in film. Two-photon pumped distributed feedback PFO lasers are made by spin coating from solution onto corrugated silica substrates that are tunable across 16 nm in the blue part of

the spectrum, demonstrating an alternative route for optically pumped lasers using commercially available conjugated polymers.

To evaluate the potential for two-photon pumped lasing in PFO, we initially mapped the two-photon absorption and corresponding photoluminescence as a function of pumping wavelength. This allows the magnitude of the two-photon absorption as well as the most efficient pump wavelength for two-photon induced fluorescence to be determined. To that end two excitation sources were used, a nanosecond optical parametric oscillator with a pump pulse duration of 4 ns and a femtosecond optical parametric amplifier system that produced 100 fs pulses, allowing for a wide range of pump wavelengths as well as a comparison between the effects of long and short pump pulses. In both cases the pump beam illuminated a cuvette containing a 10 mg/ml solution of PFO in toluene and both the transmission of the pump beam

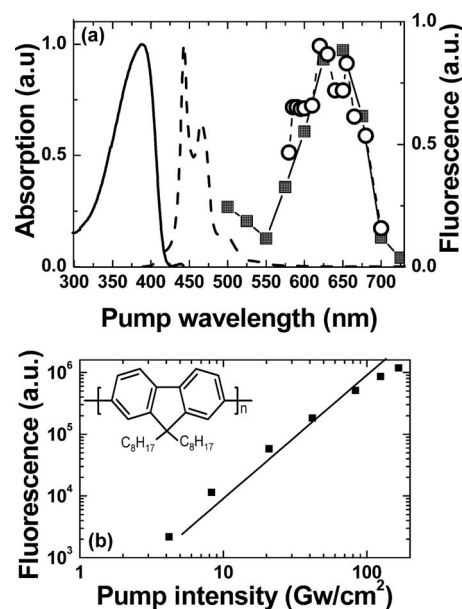


FIG. 1. (a) Linear absorption (solid line) and fluorescence (dashed line) of PFO along with two-photon fluorescence excitation spectra for both nanosecond (solid squares, solid line) and femtosecond (open circles, dashed line) pump pulses. (b) Energy dependence of PFO fluorescence in solution for 640 nm, 100 fs excitation. The solid line corresponds to a square dependence. The inset shows the chemical structure of PFO.

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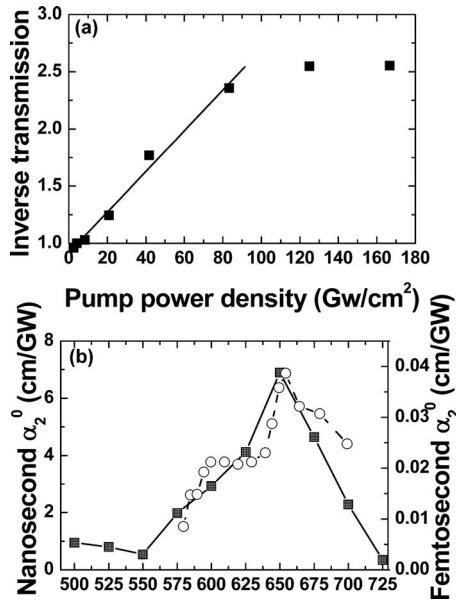


FIG. 2. (a) Inverse transmission as a function of pump power density for a PFO solution under two-photon femtosecond illumination. The straight line is a linear fit based on Eq. (1). (b) Two-photon absorption coefficients across different pump wavelengths for both nanosecond (filled squares, solid line) and femtosecond (open circles, dashed line) pumpings of PFO solution.

through the cuvette and the resulting material fluorescence were recorded for different pump wavelengths and energies.

Figure 1(a) shows the collected fluorescence intensity as a function of pump wavelength for both nanosecond (solid squares) and femtosecond (open circles) pulses, along with the linear absorption of PFO (solid line) in the UV part of the spectrum for comparison, and the fluorescence spectrum (dashed line). A broad peak can be seen at 650 nm for the two-photon induced fluorescence for both nanosecond and femtosecond pump pulses, indicating the most efficient pump wavelength region. The induced fluorescence has a square dependence on the pump intensity, as seen in Fig. 1(b), indicating that it is indeed the result of two-photon excitation.

To evaluate the magnitude of the nonlinear absorption in the material, we used the dependence of the pump beam transmission on the pump intensity to extract the nonlinear absorption coefficient of PFO across different wavelengths. Assuming that the absorption coefficient is independent of the pump energy, the transmission of the pump beam through the material can be described by

$$1/T = \alpha_2^0 z I_0 + 1, \quad (1)$$

where T is the transmission of the pump beam through the material and I_0 is the incident pump beam intensity.¹² The transmission data for a PFO solution can be seen in Fig. 2(a) and can be used to extract the nonlinear absorption coefficient of PFO across different pump wavelengths, as seen in Fig. 2(b) where we plot the calculated two-photon absorption coefficient as a function of the pump wavelength for both nanosecond (solid squares) and femtosecond (open circles) pump pulses. This graph shows a peak at 650 nm for both time domains that closely matches the fluorescence behavior described previously. The maximum values of the absorption coefficients were 6.9 cm/GW for nanosecond pulses and 0.04 cm/GW for femtosecond pump pulses, values that can be translated to two-photon absorption cross-sections δ assum-

ing that each chromophore consists of approximately seven fluorene units.¹⁴ The resulting two-photon absorption cross-section values are 9.6×10^{-46} cm⁴ s photon for nanosecond excitation and 5.6×10^{-48} cm⁴ s photon for femtosecond pulses. The difference of approximately 100 times between nanosecond and femtosecond results could be attributed to stronger excited-state absorption (ESA) when pumped with long pump pulses.¹⁵

The femtosecond two-photon absorption coefficient was also measured for a thin film (600 nm film thickness) of PFO on a glass substrate using the same technique in order to evaluate the behavior of the material in the solid-state under similar conditions to the actual laser device. The pump wavelength was chosen to be 640 nm and the resulting absorption coefficient was calculated to be 2.3 cm/GW under these conditions, a factor of 100 times higher than the corresponding solution value of 0.023 cm/GW that is consistent with the increase in the chromophore concentration from solution to film. It is also encouraging to see that the closer packing of the polymer chains does not seem to introduce any additional loss mechanisms in comparison to the solution.

In order to examine the potential for lasing based on two-photon pumping, a solid-state laser was fabricated by spin-coating a thin film of PFO from a 30 mg/ml toluene solution at speeds between 1000 to 1600 rpm on top of two-dimensional distributed feedback gratings. The period of the gratings was $\Lambda = 260\text{--}280$ nm and this range was chosen to match the feedback provided by the Bragg condition to the peak wavelength of the material's amplified spontaneous emission spectrum for the different film thicknesses according to

$$\lambda_{\text{Bragg}} = 2n_{\text{eff}}\Lambda/m, \quad (2)$$

where n_{eff} is the effective refractive index of the laser gain medium, m is the Bragg order, and Λ is the period of the grating. In our experiments we chose a grating for $m=2$ so that the radiation would be emitted perpendicularly to the surface of the film. The pump beam was incident at a small angle on the sample to separate it from the emitted beam and the output lasing spectrum was collected normal to the surface of the film by a spectrograph. The pump intensity was then varied and the corresponding device optical output was recorded across different pump wavelengths and intensities. We used a femtosecond laser system for pumping the polymer laser as the available pump power density was higher than the nanosecond system. The pump wavelength was chosen to be 640 nm, close to the maximum of the two-photon fluorescence excitation spectrum, allowing for efficient harvesting of the excitation light.

When increasing the pump energy above a certain threshold value, a narrow peak of full width half maximum less than 0.6 nm appears in the emission spectrum, and a coherent beam is emitted normal to the film, indicating that laser action has begun. The lowest recorded threshold was 1 $\mu\text{J}/\text{pulse}$, corresponding to 42 mJ/cm². Since two-photon absorption is much weaker than linear absorption, only 3% of the pump intensity is absorbed through the film, meaning that the absorbed energy density lasing threshold is 1.3 mJ/cm². This is much higher than the one-photon pumped lasing threshold in PFO,¹⁶ a difference we attribute to additional losses due to ESA. Despite these losses, it is still possible to induce population inversion in the gain me-

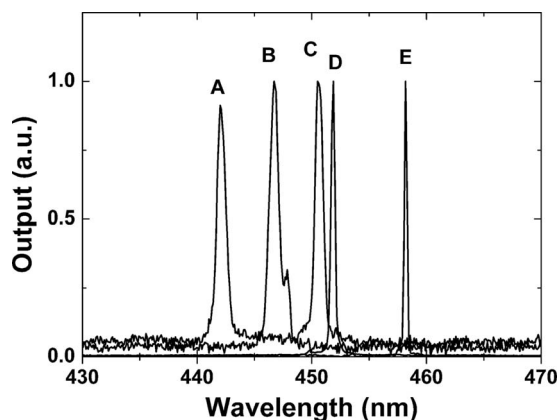


FIG. 3. Emission spectra of two-photon pumped PFO lasers (A: 442 nm, B: 447 nm, C: 450 nm, D: 452 nm, and E: 458 nm). Spectra D and E were measured using a higher resolution spectrometer.

dium, assisted to a great extent by a high solid-state photoluminescence quantum yield of 73% in our material.

By using different combinations of film thickness (675–850 nm) and grating periods (260–280 nm), it was possible to tune the output wavelength of the laser devices we fabricated across more than 15 nm (Fig. 3). This is a consequence of the broad available optical gain in organic semiconductors, demonstrating the versatility of these materials as laser gain media. The large thickness also allowed for multiple lasing modes to achieve lasing, as seen for peak B in Fig. 3. The lowest threshold was achieved for a lasing wavelength of 443 nm, which very closely matches the peak wavelength of the PFO's amplified spontaneous emission spectrum. Previous reports of two-photon pumped organic semiconductor lasers have been restricted either to a green-emitting polymer¹⁷ or bisfluorene dendrimers,¹⁸ neither of which are widely available materials.

In conclusion, we have demonstrated a blue tunable two-photon pumped solid-state PFO laser based on distributed-feedback gratings, with a lasing threshold value of 42 mJ/cm² corresponding to an absorbed energy density threshold of 1.3 mJ/cm². Photophysical studies of the nonlinear absorption properties of PFO have been performed under both nanosecond and femtosecond illuminations to investigate the material's nonlinear properties in solution and in thin films to determine the most favorable conditions for

lasing. These results demonstrate the potential for exploiting nonlinear optical properties to implement alternative optical pumping schemes toward compact and practical polymer solid-state lasers based on widely available materials, and demonstrate the considerable potential of fluorene polymers in this domain.

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