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Blue superradiance from neat semiconducting alternating copolymer films

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higher oligomers, on dielectric investigations in films, and on the correlation of polarization stabilities with the non-linear properties.^[13] This work will also include results from an AB-type polymerization leading to polymers structurally analogous to **5**, **14**, **15**, and **16**.

In conclusion we have introduced a new synthetic method based on a simple cation-anion reaction leading to donor/acceptor-substituted phenylenevinyls and have characterized the materials using spectroscopic and electrochemical methods. The strength of this approach is in particular the combination of extended π -conjugation with strong dipole moments in each repeat unit and the availability of well-defined and readily processable materials that allow the investigation of cooperative dipole-dipole interactions in solution.

Experimental

General procedure for the cation-anion coupling reaction: NaH (2 mmol) was added to a solution of benzylium (1 mmol) in 3 ml of dry DMF at -60°C in an argon atmosphere. After stirring for 1 h, the cation **4** (1 mmol) was added in 2 ml dry DMF. The resulting mixture was stirred for 8 h at -50°C and was then allowed to reach room temperature overnight. Filtration of the reaction mixture over SiO_2 followed by removal of the solvent under vacuum yielded the donor/acceptor stilbene **5**. For further purification **5** was reprecipitated from a THF solution into petrol ether (60/40).

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Blue Superradiance from Neat Semiconducting Alternating Copolymer Films

By Hendrik Jan Brouwer, Victor V. Krasnikov, Alain Hilberer, and Georges Hadziioannou*

The introduction of light emitting diodes (LEDs) based on poly[*p*-phenylene vinylene] (PPV) in 1990^[1,2] triggered intensive research in the field of semiconducting conjugated polymers. This led to the elaboration of various other polymer LEDs with high efficiencies^[3] and covering the whole visible spectrum.^[4-7] Complementary, optoelectronic devices, such as photodetectors^[8] and photovoltaic cells,^[9] with conjugated polymers as the active medium have also been demonstrated with high efficiencies and are becoming competitive with their inorganic counterparts. It was realized that the high photoluminescence (PL) quantum yield and appreciable Stokes shift of conjugated polymers made them promising candidates as laser media in diluted solutions and solid blends, the ultimate target being the elaboration of electrically pumped polymer lasers operating in the visible wavelength regime. Despite the fast sub-nanosecond decay, the substantially decreased PL quantum efficiency and the photo-induced absorption, stimulated emission was observed in optically pumped neat semiconducting polymer films in several ultrafast spectroscopy studies,^[10,11] indicating the possible development of solid-state polymer lasers.

Soon after the introduction of polymer LEDs, efficient laser action of the semiconducting polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) in the liquid state,^[12] operating in the yellow/red wavelength region, was reported. Recently, laser emission from dilute blends and blends containing titanium-dioxide nanocrystals^[13,14] has been demonstrated. Finally, lasing from neat conjugated polymers has been achieved under pulsed optical excitation in a microcavity^[15] and in a thin film configuration.^[16]

In conjugated organic molecules, light emission is established by radiative decay of mobile π - π^* singlet excitons.^[17] The bandgap in semiconducting polymers is roughly determined by the extent of π -delocalization along the backbone, the so-called effective conjugation length. A way to control the conjugation length, and thus the color of emission, is to prepare partially conjugated, alternating copoly-

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mers.^[4-7] Such copolymers differ from their fully conjugated counterparts, due to the higher intrachain resistivity induced by the non-conjugated repeating units. These copolymers can be seen as long chains of separated small dye molecules connected by small spacer units. It has been shown that optically-excited copolymers of this kind (with distyrylbenzene units as the active chromophore) can generate blue laser light in the liquid state, with high energy conversion efficiencies.^[18]

In this communication we report the observation of superradiant emission in neat films of the blue-light emitting alternating copolymer poly[dimethylsilylene-*p*-phenylene-vinylene-(2,5-di-*n*-octyl-*p*-phenylene)-vinylene-*p*-phenylene] (abbreviated as Si-PPV in the following).

The Si-PPV copolymer ($M_n = 60\,000$, $M_w = 25\,000$, $M_w/M_n = 2.4$) has a well-defined backbone consisting of regularly alternating distyrylbenzene and fully saturated dimethylsilylene units. In Figure 1 (inset), the structure of

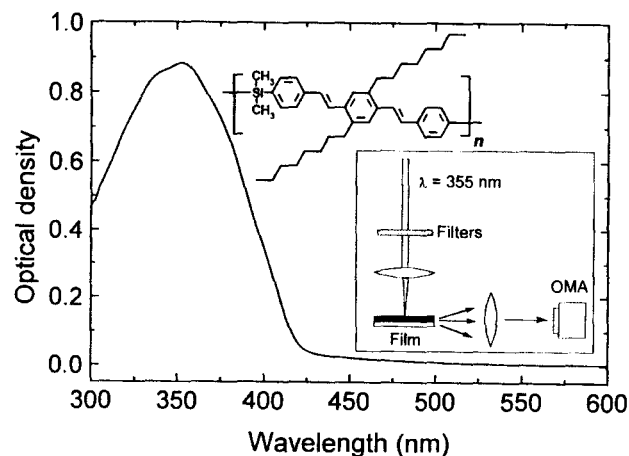


Fig. 1. Absorbance spectrum of a Si-PPV copolymer film with a thickness of 150 nm. Insets show the chemical structure of the Si-PPV repeat unit and the scheme of the experimental setup.

the repeat unit is given. The presence of the two octyl side-chains on the distyrylbenzene unit provides solubility of the polymer in common organic solvents such as tetrahydrofuran (THF), chloroform, and toluene. The synthesis and characterization of the Si-PPV copolymer was described in a previous publication.^[7] Figure 1 shows the absorbance spectrum ($\lambda_{\max} = 352$ nm) of a spin-coated Si-PPV film, with a thickness of 150 nm. The copolymer exhibits a large absorption coefficient ($\alpha_{352\text{ nm}} = 1.3 \times 10^5 \text{ cm}^{-1}$) due to the high density of chromophores. The sharp absorption edge indicates that the formation of aggregates is minimal. PL-quantum yields as high as $\Phi_{\text{PL}} \approx 0.6$ have been measured in solution.^[7]

We have measured light emission spectra from a series of Si-PPV copolymer films, with different film thickness, the experimental setup of which is depicted in Figure 1. The typical spectral evolution as a function of excitation energy is shown in Figure 2 (spectra 1, 2, and 3) for a 150 nm thick

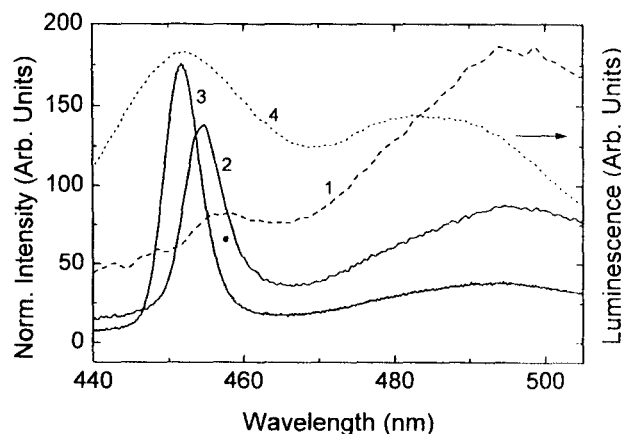


Fig. 2. Fluorescence spectrum (4) and emission spectra normalized to the excitation energy of a Si-PPV copolymer film (thickness 150 nm, spin-coated on glass): 1) emission spectrum below lasing threshold, $E_{\text{exc}} = 7.5 \times 10^{-2}$ mJ and emission spectra above threshold; 2) $E_{\text{exc}} = 0.25$ mJ; 3) $E_{\text{exc}} = 1$ mJ.

sample. The emission spectra are normalized on excitation energy. For comparison, a fluorescence spectrum (4), collected at an angle of 30° with respect to the film, is also incorporated. An increase in pump energy resulted in spectral narrowing and the appearance of a sharp peak surrounded by a broad luminescence tail. The superlinear increase in amplitude of the sharp peak, as well as the sublinear growth of the broad tail, are also evident in Figure 2. As a result of such behavior, the higher the excitation energy the more dominant the spectrally narrow emission becomes, while the broad luminescence background is relatively suppressed. This becomes even more evident in Figure 3, where the normalized intensity ratio of superradi-

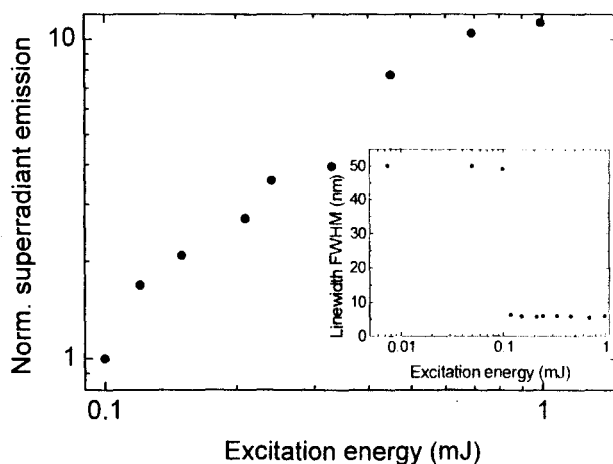


Fig. 3. Normalized intensity ratio of superradiant emission and fluorescence as a function of excitation energy. Inset shows emission line-width as a function of excitation energy.

ant emission and fluorescence as a function of excitation energy is shown. The ratio increases at higher excitation energies. Above an energy threshold of approximately

0.1 mJ, narrow blue emission with a full width at half maximum (FWHM) of 6 nm emerged from the edge of the film (see inset, Fig. 3). The main features of the spectral behavior of our system remained the same for any light collection angle. Only the relative amplitude of the sharp maximum with respect to the amplitude of the broad tails, and the shape of the emission spectrum below threshold depended on the angle of observation. It should be mentioned that the threshold of breakdown lies at approximately 1.5–2 mJ, depending on the film quality, allowing measurements at pump energy levels well above the threshold of spectral narrowing.

The observed appearance of a spectrally narrow peak above a well-defined energy threshold, and the relative suppression of the broad luminescence tails indicating the spectral energy redistribution within the emitted light, is a clear signature of light induced net gain in the neat copolymer films and is common for laser generation in the superradiant regime.

Lasing in the superradiant regime requires an induced net gain with a sufficient length of interaction for the generated light. In our case, we believe that the superradiant emission propagates through a waveguide formed by the thin polymer film, based on the following four observations. 1) The spectral shape of emission below the threshold of lasing differs from the luminescence spectrum collected under an angle of 30° (Fig. 2, spectra 1 and 4). This difference can be explained as being due to the waveguiding of light collected at the edge of the film and is caused by the dispersions of both the absorption tail and waveguiding. 2) We observed a dramatic increase in lasing threshold with decreasing excitation spot size, while keeping the light intensity the same. 3) The spectral behavior revealed no dependence on the thickness of the glass slide. 4) A decrease of film thickness from 150 to 50 nm resulted in the absence of laser generation at any pump energy up to the damage threshold, which indicates the existence of a cutoff thickness.

The wavelength of the superradiant peak ($\lambda_{\max} = 452$ nm) at high pump energies coincides with the maximum of the fluorescence emission spectrum (Fig. 2). The exact reason for the recorded blue-shift (of approximately 5 nm) of the laser emission with increasing excitation energy is not quite clear. Most likely it is caused by light-induced depopulation of the ground state of the photoactive chromophores and/or light-induced excited state absorption, which is usually red-shifted. The possible role of light-induced absorption due to interchain interaction and the influence of singlet-triplet intersystem crossing also cannot be excluded.

In conclusion, we have observed lasing in the superradiant regime in optically pumped, neat Si-PPV copolymer films. This lasing occurred as a result of the combination of optically-induced net gain and waveguiding in the thin film above a threshold energy of approximately 0.1 mJ, when pumped with the third harmonic radiation of a Nd:YAG la-

ser. Above the threshold, coherent light emission with a narrow spectral bandwidth (FWHM = 6 nm, $\lambda_{\max} = 452$ nm) emerged from the edge of the film, while the broad fluorescence was suppressed. The observation of superradiant emission in thin polymer films with a low energy threshold offers hope for the possible development of solid-state electrically-pumped polymer lasers.

Experimental

Thin films were fabricated by spin-coating the copolymer from a toluene solution (5% w/w) onto square glass slides. The solution was filtered (0.2 mm filters, Spartan 13/30) prior to spin-coating to ensure good optical quality films. After spin-coating, the films were dried under vacuum at 50 °C to remove all residual toluene and stored in nitrogen to prevent oxidation. A Dektak 3030 ST surface profiler was used to determine the layer thickness. The absorbance spectra of the films were measured with a SLM-Aminco 3000 array spectrophotometer. The third harmonic of a Nd:YAG laser (Quanta-Ray GRC 130-50, $\lambda = 355$ nm, pulse width = 15 ns), operating at a repetition rate of 1 Hz, was used for photoexcitation of the films. The beam was focused to an elliptical spot size of 5.0×2.5 mm² with a cylindrical lens. Neutral density filters were used to attenuate the excitation energy. The copolymer films were excited under normal incidence. The emitted light emerging from the edge of the films along the long-axis of the beam spot was collected with a lens and focused into a multimode optical fiber input of an optical multichannel analyzer (Chromex 250 SI polychromator with Chromcam I CCD detector). The acceptance cone (full angle) was approximately 10°. All photoexcitation experiments were performed under ambient conditions.

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