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New Red Light-Emitting Conjugated Rigid-Rod Polymer: Poly(benzobisthiazole-1,4-phenylenebisvinylene)

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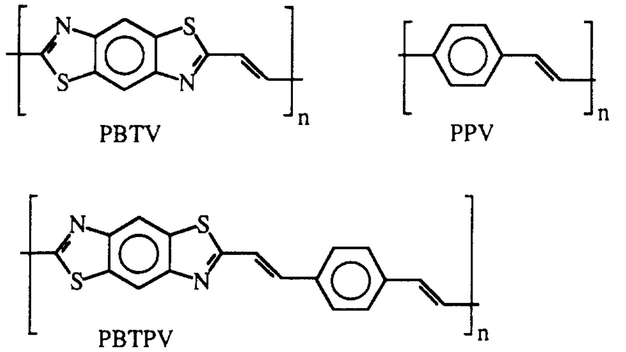
Luminescent thin films of conjugated polymers are currently of interest for light-emitting diodes (LEDs), flat panel and flexible displays, and related applications in optoelectronics in part because they can be fabricated over large areas through conventional polymer solution processing techniques.[1-8] The luminescent properties of a number of conjugated polymers have been investigated, including poly(*p*-phenylenevinylene) (PPV) and its ring-substituted derivatives,[2-6] poly(alkylthiophenes),[7] and poly(*p*-phenylene).[8] PPV has been the most widely studied conjugated polymer for LED application, and the electroluminescent quantum yield (photon/electron injected) of such devices has been significantly improved both by device engineering[3] and polymer architecture.[4,6] There is a growing need for light-emitting polymers with improved performance with respect to color of light emitted, fluorescence quantum yield, brightness, stability, and processability.

An aromatic heterocyclic derivative of PPV which can be processed by the *soluble coordination complexation*[9] approach could provide an alternative processing route to the conventional *soluble precursor*[10] route or the *bulky substituent side group*[5] approach, while preserving the luminescent, thermal, and mechanical properties of the polymer. In this paper, we report the synthesis, characterization, and photoluminescent thin films of poly(benzobisthiazole-1,4-phenylenebisvinylene) (PBTPV) which is soluble in organic solvents via complexation or in its protonated form in methanesulfonic acid. PBTPV along with the related polymers poly(benzobisthiazolevinylene) (PBTV) and PPV is shown in Chart I. PBTPV exhibits high steady-state fluorescence quantum efficiency in methanesulfonic acid ($\sim\leq 5 \times 10^{-6}$ M solutions, Φ_f = 100%) and solid-state quantum yield comparable to that of PPV.[2,11] The reasonably high fluorescence quantum yield in the solid state gives a good indication that one can successfully fabricate electroluminescent devices with this material through appropriate device engineering.[11] Also, PBTPV provides an opportunity to investigate novel features of light-emitting conjugated polymers not possible with other PPV derivatives, for example, the effects of protonation or charge transfer.

Poly(benzobisthiazole-1,4-phenylenebisvinylene) (PBTPV) was synthesized by condensation polymerization of 2,5-diamino-1,4-benzenedithiol (DABDT; Daychem Inc., Dayton, OH) with 1,4-phenylenediacrylic acid (PDAA; Aldrich). Both monomers were recrystallized[12] prior to use. A total of 1.0 g (4.08 mmol) of DABDT was dissolved in 25 g of 77% PPA (deaerated) under a nitrogen atmosphere in a glass reactor fitted with a mechanical stirrer, two gas ports, and a side arm. The reaction vessel was purged with nitrogen for 30 min, and dehydrochlorination (i.e., removal of 2HCl from the DABDT dihydrochloride) was carried out at 70 °C under vacuum. After complete dehydrochlorination, the reaction mixture was cooled down to 50 °C and 0.89 g (4.08 mmol) of PDAA was added. A total of 10.5 g of fresh P_2O_5 was added under positive pressure to compensate for the calculated theoretical water of condensation. The reaction temperature was raised to 60 °C and held at this temperature for 8 h. The temperature was further raised to 100–120 °C and maintained at this temperature for an additional 22 h. The viscous polymerization dope was poured into a beaker and precipitated with 500 mL of deionized water. The fibrous precipitate was shredded with a blender and purified by stirring in a large volume of deionized water for 3 days. The product was dried in a vacuum oven at 60 °C. The yield was ~100%.

Chart I



The intrinsic viscosity of PBTPV, measured in pure methanesulfonic acid at 30 °C by using a Cannon–Ubbelohde capillary viscometer, was 5 dL/g. Thermogravimetric analysis (TGA) obtained in flowing nitrogen at a heating rate of 10 °C/min showed that PBTPV starts to decompose at ~560 °C. The molecular structure of the new polymer was established by both FTIR and ^{1}H NMR spectra. The FTIR spectrum of a free-standing film of PBTPV showed intense bands [3033, 3000, 2923, 2852, 1622, 1558, 1516, 1489, 1418, 1403, 1312, 1265, 1180, 1054, 949, 855, 804, 656 cm^{-1}] similar to other poly(benzobisthiazoles)[12,13] and *trans*-vinylene-linked[12] benzobisthiazole polymers. Complete ring closure was inferred from the absence of any bands in the 1640–1720-cm^{-1} region that would have indicated the presence of amide or carbonyl groups. The ^{1}H NMR spectrum of PBTPV was obtained in deuterated nitromethane containing $GaCl_3$, and the resonances [δ (ppm) 9.0 (s, 2H), 8.4–8.5 (m, 4H), 8.1 (s, 2H), 8.0 (s, 2H)] were consistent with the proposed structure. Solution processing of PBTPV into films was achieved by using the previously described method of the soluble coordination complexation approach.[9,12] Thin films of good optical quality were prepared by spin coating the nitromethane/$GaCl_3$ solution of PBTPV onto glass substrates, followed by decomplexation in water to obtain the pristine polymer.

Steady-state photoluminescence studies were done by using a Spex Fluorolog-2 spectrofluorimeter under the control of a Spex DM3000f spectroscopy computer. Fluorescence measurements were made on 10^{-5}–10^{-7} M PBTPV solutions in methanesulfonic acid (MSA) and on 20–100-nm thin films. Time-resolved photoluminescence decay measurements were performed by using a time-correlated single photon counting (SPC) technique.[14] The excitation system consisted of a mode-locked frequency-doubled Nd:YAG laser (Quantronics Model 416) synchronously pumping a cavity dumped dye laser (Coherent Model 703D) circulating rhodamine 6G. The Nd:YAG laser pulses were typically 10 ps in duration at a repetition

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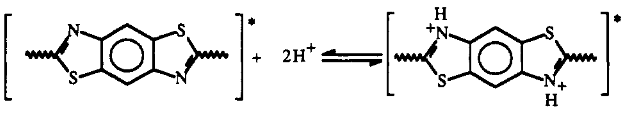
rate of 38 MHz. PBTPV samples were excited at 380 nm.

Figure 1 shows the optical absorption spectrum of PBTPV in a 10^{-6} M MSA solution. The lowest energy absorption maximum λ_{max} is at 494 nm. Also shown in Figure 1 is the photoluminescence spectrum of PBTPV in a dilute (10^{-6} M) MSA solution obtained by exciting at 450 nm. The emission spectrum shows a peak at 544 nm (yellow light) and a shoulder at ~600 nm. The small Stokes shift (~0.2 eV) indicates that the relaxation of the excited singlet state prior to radiative decay is small. The extent to which relaxation occurs after excitation but prior to fluorescence depends on both the rate of solvent orientation (a function of the viscosity of the solvent) of the solute and the rate of radiative decay. In order to shed light on the effect of solvent viscosity on the Stokes shift of PBTPV, the absorption and fluorescence spectra were taken in nitromethane and nitrobenzene containing gallium(III) chloride. The viscosities of nitromethane and nitrobenzene are respectively 0.62 and 2.0 mPa·s at 25 °C.[15] The measured Stokes shifts were 0.25 and 0.19 eV in nitromethane and nitrobenzene, respectively, showing a modest dependence on solvent viscosity. It is possible that the combined effect of the viscosity of MSA (~10.2 mPa·s at 30 °C)[9b] and the rapid radiative decay of the singlet excited state is responsible for the observed small Stokes shift of PBTPV in MSA.

The photoluminescence quantum yield Φ_f of PBTPV in MSA was determined by using a quinine sulfate (~10^{-6} M in 0.1 N H_2SO_4) fluorophore standard[16,17] with a widely accepted Φ_f value of 55%.[16,17] This fluorophore is known to be stable in solution, not quenched by oxygen, and has no significant overlap between the absorption and emission spectra. The fluorescence quantum yield of PBTPV in MSA was found to be 100% in dilute solution ($\leq 5 \times 10^{-6}$ M). However, it was observed that Φ_f depends strongly on the concentration of PBTPV in MSA. At high concentrations (10^{-5} M), the yield was as low as 15%, indicative of concentration quenching.

The origin of the high fluorescence quantum yield of PBTPV in a MSA solution is apparently due to the combined effects of a reduction of intermolecular interactions, solvent viscosity, protonation of the nitrogens in the polymer backbone, and the rigid-rod chain conformation. A reduction of intermolecular interactions combined with a viscous environment can lead to a reduction of molecular collisions and energy transfer and hence an increase in fluorescence yield. Also, nitrogen heterocycles are known to increase in basicity upon excitation (π–π^* excited state); hence, it is expected that all the nitrogens in the excited PBTPV molecule will be fully protonated:[17b]



The fluorescence quantum yield of fluorecein dye has been reported[18] to depend on pH, and it approaches 100% in 10 M H_2SO_4 in which the excited state is a fluorecein cation, whereas the neutral molecule has Φ_f = 20–25%. The occurrence of highly efficient radiative decay following excitation of protonated PBTPV in MSA suggests that population inversion, which is essential for laser action, may be achieved using this polymer. Such a mechanism is known to be operative in some laser dyes.[17b] The utility of a conjugated polymer as an efficient laser dye has been demonstrated with a xylene solution of poly[2-methoxy-5-[(2′-ethylhexyl)oxy]-*p*-phenylene] (MEH-PPV).[19] It will be interesting to demonstrate the utility of PBTPV as a lasing material, and we plan to investigate this in the future. Also, the fact that protonation of PBTPV leads to high fluorescence quantum yield suggests that with appropriate sensitization[20] the luminescent efficiency in the solid state can be significantly enhanced.[20]

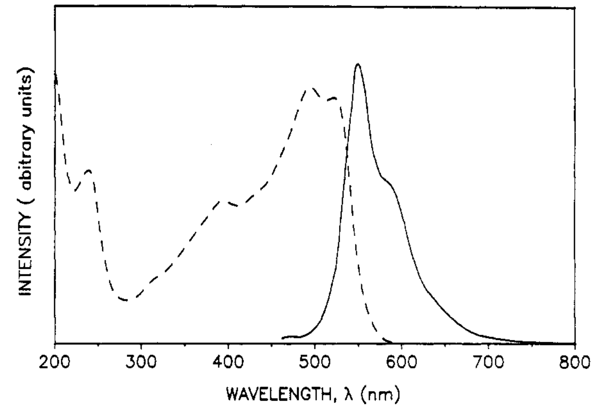


Figure 1. Absorption (dashed line) and photoluminescence (solid line) spectra of 10^{-6} M PBTPV in MSA.

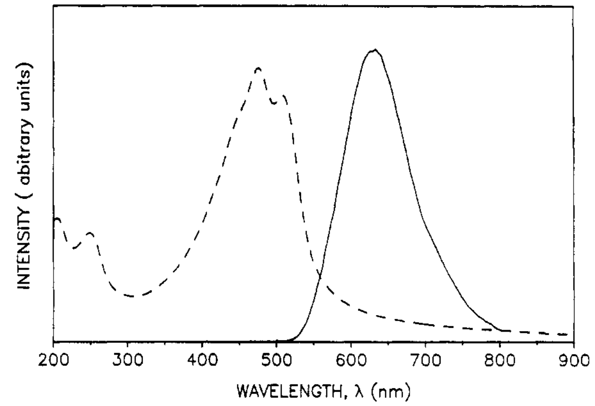


Figure 2. Absorption (dashed line) and photoluminescence (solid line) spectra of a thin PBTPV film.

The fluorescence quantum yield Φ_f of a PPV derivative, poly(4,4′-diphenylenediphenylvinylene) (PDPV), has been reported[5b] to be 1.1% in chloroform. Although the solvent used in the measurement of the quantum yield and the nature of the excited-state species play a significant role, PBTPV is in this respect a superior solution-processable, light-emitting derivative of PPV compared to PDPV.

The optical absorption spectrum of a thin film of PBTPV is shown in Figure 2. This polymer shows a strong visible absorption with a π–π^* transition (λ_{max}) at 475 nm and a shoulder at 508 nm. The corresponding band edge optical band gap of PBTPV is 2.1 eV. Although PBTPV can be viewed as an alternating copolymer of PBTV and PPV repeat units as shown in Chart I, the optical band gap as well as the λ_{max} is red shifted compared to either PPV (E_g = 2.5 eV, λ_{max} = 430 nm)[2] or PBTV (E_g = 2.2 eV, λ_{max} = 470 nm),[12] suggesting that the electronic structure of PBTPV is quite different from those of these two polymers.

Also shown in Figure 2 is the steady-state photoluminescence spectrum of a PBTPV thin film excited at 475 nm. The luminescence spectrum shows an emission maximum at 640 nm. This red emission corresponds to a Stokes shift of 0.67 eV which is considerably larger than that observed in solution spectra. An estimate of the fluorescence quantum efficiency of PBTPV thin films was obtained by using a PPV thin film having similar optical density as a standard. Fluorescence measurements were made on PPV and PBTPV samples spin coated on identical substrates (indium–tin oxide coated glass). From the

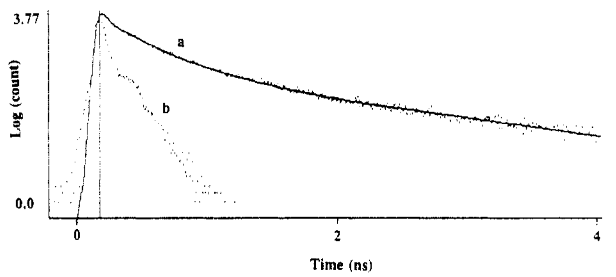


Figure 3. (a) Time-resolved photoluminescence decay dynamics of PBTPV (solid line is a fit of the experimental data). (b) Pump response.

integration of the corrected fluorescence spectra and the reported[2] efficiency of ~8% for PPV, we estimate the solid-state fluorescence quantum yield of PBTPV to be ~4–5%. No correction was made for the differences in the refractive indices of the polymers. The lower Φ_f value of PBTPV films compared to PPV may be due in part to the general trend of the effect of band gap on Φ_f.[21] However, it is interesting to note that the 2,5-dimethoxy derivative of PPV has a similar band gap as PBTPV but has a very low photoluminescence yield in the solid state.[4a] This suggests that while the band gap is an important parameter affecting the value of Φ_f[21] there are other equally important structural factors yet to be elucidated.

Time-resolved photoluminescence decay dynamics of thin films of PBTPV excited at 380 nm shows that the decay cannot be described with a single-exponential route, similar to other conjugated polymers.[22] The emission spectra of PBTPV were identical for excitation wavelengths between 380 and 480 nm, indicating that the emission is from the same electronic state. Figure 3 shows a semilog plot of photoluminescence intensity versus time. The decay dynamics was found to be independent of the intensity of the exciting laser, suggesting that the decay does not proceed by a bimolecular mechanism. Convolution and analysis of the photoluminescence decay with a nonlinear least-squares fitting show that the decay can be described with three-exponential "lifetimes" consisting of a very fast component (~38 ps) with a relative yield of 24% and two relatively long components with lifetimes of 0.28 and 1.2 ns accounting for 43% and 33%, respectively, of the excited-state decay. However, there is no physical significance of such multiexponential decay fitting of the photoluminescence decay. There are usually many possible causes for deviation from a single-exponential photoluminescence decay, including[23] heterogeneity due to kinetically distinct emitting species, relaxation processes, polymer segmental motion, electronic energy transfer, and migration. On the other hand, time-resolved photoluminescence decay dynamics of a 10^{-6} M PBTPV solution in MSA shows that the radiative decay proceeds predominantly by a single-exponential route with a lifetime of 0.35 ns and a relative yield of 80%. The long component had a lifetime of 1.28 ns, apparently arising from reabsorption of the emitted photon due to the overlap of the absorption and emission spectra.

In summary, a new red light-emitting, solution-processable, heterocyclic rigid-rod benzobisthiazole derivative of poly(*p*-phenylenevinylene), poly(benzobisthiazole-1,4-phenylenebisvinylene) (PBTPV), is reported. The protonated PBTPV in dilute methanesulfonic acid ($\leq 5 \times 10^{-6}$ M) solutions exhibits a yellow–green emission with a peak at 544 nm and fluorescence quantum yield Φ_f of 100%. PBTPV thin films, prepared from its soluble complexes in nitromethane, emit red light with an emission peak at 640 nm and an estimated quantum yield of ~4–5%, comparable to the well-known poly(*p*-phenylenevinylene). Time-resolved photoluminescence decay dynamics shows that PBTPV thin films cannot be described with a single-exponential decay. The observation of a highly efficient luminescence yield from the charge-transfer state in solution gives an indication that population inversion and hence lasing can be achieved with PBTPV. The same observation also suggests that the solid-state photoluminescence quantum yield can probably be significantly increased through sensitization.

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