

Effect of temperature and pressure on the optical properties of polyfluorene

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June 19, 2002

Abstract

We present photoluminescence (PL) and Raman scattering studies from polyfluorene as a function of hydrostatic pressure and temperature. The PL backbone emission blue shifts and changes dramatically around 20 kbar becoming primarily a single peak. This is related to the emission from keto defects in the sample. The Raman modes shift to higher energies and exhibit unexpected antiresonance lineshapes at higher pressures, indicating a strong electron-phonon interaction.

Keywords: Photoluminescence; Raman scattering; Hydrostatic pressure; Other conjugated polymers

1. Introduction

Polyfluorenes (PF) have emerged as attractive alternatives to other conjugated polymers for display applications due to their efficient blue emission and high hole mobility at room temperature [1]. An understanding of the influence of intermolecular interactions is crucial since the luminescence efficiencies of polymers are known to decrease in the solid state. Hydrostatic pressure is a valuable tool to tune such intermolecular interactions and the molecular geometry in these systems.

In this work we probe the optical properties of poly[2,7-(9,9'-bis(2-ethylhexyl))fluorene (PF2/6) via photoluminescence (PL) and Raman scattering as a function of hydrostatic pressure. PF2/6 forms planar monomer units but has a torsional degree of freedom between adjacent monomer units; its synthesis is described in Ref. [1]. Upon further processing some PF films are known to display a β phase, which has a more extended intrachain π -conjugation, in addition to the regular glassy (α) phase [2]. This phase is completely absent in PFs with branched side groups [3]; hence we would not expect the β phase at ambient pressure in our sample.

2. Experimental Details

The photoluminescence (PL) and Raman spectra were measured from powder samples of PF2/6. The PL spectra were recorded with an Ocean Optics spectrometer using the 351 nm line from an Ar⁺ laser. Raman measurements were carried out in a backscattering geometry using the 647 nm line of a Kr⁺ laser. The scattered light was detected using a SPEX triple equipped with a CCD array. Pressure studies were conducted in a Merrill-Bassett type diamond anvil

cell (DAC) with cryogenically loaded argon as the pressure medium. Pressure was measured via the luminescence of a ruby chip placed in the sample chamber.

3. PL Results

Figure 1 (a) shows the PL spectrum of PF2/6 at selected values of pressure. The 0-0 transition (2.9 eV) at ambient pressure is barely visible due to self-absorption effects. The PL line shape changes dramatically at about 20 kbar: the backbone emission becomes very weak and a strong orange emission at 2.4 eV emerges. Beyond 20 kbar the 2.4 eV emission becomes dominant and completely overwhelms the backbone emission. The vertical dashed line in Fig. 1 (a) clearly shows that the 0-1 emission blue shifts with increasing pressure. A careful fitting of the PL spectra with Gaussian line shape shows that all the backbone PL vibronics including the 0-0 and the 0-2 transitions blue shift with increasing pressures at the rate of 0.27 meV/kbar and the 2.4 eV emission red shifts with increasing pressure at the rate of 0.70 meV/kbar. This is in contrast to the other conjugated polymers and molecules where the PL emission from the backbone red shifts with increasing pressures [4]. This may be related to the helical conformation of PF2/6 which prevents a higher overlap of wavefunction between neighboring chains.

Recent work shows that the 2.3-2.4 eV emission in PF is related to the emission from keto defects sites (9-fluorenone sites) [5]. These defect sites act as guest emitters which can efficiently trap singlet excitons created on the conjugated polyfluorene backbone by a dipole-dipole induced Förster-type energy transfer. The keto defect sites can be accidentally incorporated into the π -conjugated PF backbone due to the presence of non-

alkylated or monosubstituted fluorene sites during synthesis or as a result of a photo-oxidative degradation.

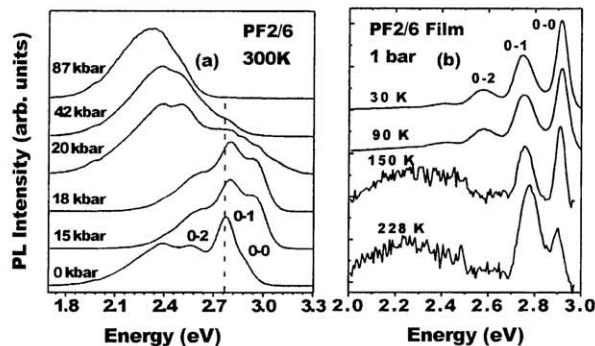


Fig. 1. (a) PL spectra of PF2/6 powder for selected pressures. (b) PL spectra of a PF2/6 film at 1 bar and for selected temperatures.

Our PL data as a function of pressure suggests that beyond 20 kbar the emission from keto defects is greatly enhanced indicating an efficient energy transfer to the defect sites due to enhanced intermolecular interaction. The emission from the defect sites is also thermally activated: the PL emission from a PF2/6 film (of thickness ~ 4000 nm) at 1 bar shows a broad peak at 2.3 eV above 150 K as shown in Fig. 1 (b). A thinner film (~ 100 nm) of PF2/6 at 1 bar does not show this trend at higher temperatures indicating that the keto defect concentration in our sample is quite low.

We found that the overall PL intensity (the keto emission) goes up noticeably at 42 kbar. A temperature dependence of the PL at this pressure shows that the relative intensity of the backbone transitions change. This may be related to a liquid crystal phase transition.

4. Raman Results

The inset of Fig. 2 shows the Raman spectrum of PF2/6 powder at ambient pressure and room temperature. Since PF2/6 has a torsional degree of freedom between the monomer units, at lower temperatures the molecule should be more non-planar compared to that at room temperature where the average conformation is planar. Raman intensities show subtle changes when conjugated molecules change from a planar to non-planar conformation [6]. Our temperature dependent Raman studies on PF2/6 indicate that the 1417 cm^{-1} mode is from the C-C stretch within the monomer whereas the 1342 cm^{-1} and the 1290 cm^{-1} modes are from phenyl rings connecting the monomer units. This agrees well with the Raman mode assignment of PFO [7]. The Raman peaks in the 1600 cm^{-1} and the 1100 cm^{-1} region are from the intra-ring C-C stretch mode and the side groups, respectively.

The break in the x-axis (Fig. 2) at $\sim 1300\text{ cm}^{-1}$ denotes the region where the diamond peak from the DAC has been removed for clarity. The Raman frequencies increase linearly with pressure. Beyond 20 kbar all the Raman peaks are not clearly observed due to the strong PL emission. The asymmetry of the Raman peaks is greatly enhanced with

increasing pressure, indicating an antiresonance effect which is most likely due a high electron-phonon interaction between the Raman phonons and the (real) PL transitions. Such effects have been observed in doped inorganic semiconductors [8].

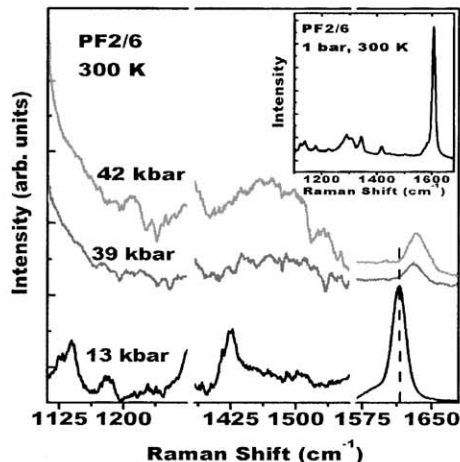


Fig. 2. Raman spectra of PF2/6 at selected pressures. Each region of the graph has been scaled individually to highlight the key features of each spectrum. The inset shows the Raman spectrum of PF2/6 at 1 bar.

5. Conclusion

Hydrostatic pressure induces a very efficient energy transfer of the singlet excitons to the keto defect sites; beyond 20 kbar the PL emission from these sites overwhelms the backbone emission. The Raman modes shift to higher energies exhibiting a strong electron-phonon interaction under pressure.

S.G. acknowledges the support by the Petroleum Research Fund #35735-GB5 and the Research Corporation #CC5332. U.S. thanks SONY International Europe, Stuttgart, and the DFG for financial support.

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