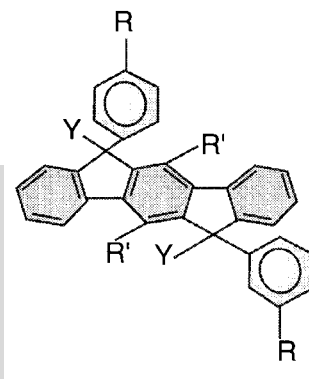


Squeezing Organic Conjugated Molecules— What Does One Learn?***

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The effects of hydrostatic pressure on conjugated polymers, in particular polyphenyls (see Figure for monomer unit) have been studied using photoluminescence, absorption, photo-induced absorption, and Raman spectroscopy. The effect of pressure on the singlet and triplet excitons and polarons allows an understanding of localized and delocalized electronic states. Changes in the intensity ratios of Raman bands that correspond to vibrations of a perpendicular and a coplanar array of phenyl rings in the chain, and comparison with calculated intensities, demonstrate the influence of pressure on the polymer's conformation.



1. Introduction

When hydrostatic pressure is applied to a solid or liquid, the interatomic spacings are decreased, thus squeezing the electron clouds together and simulating a closer packed system. Geometric changes can take place in the arrangement of the molecules or phase transitions can be induced in the case where an alternate crystalline arrangement is energetically preferred. Even in situations where the geometric arrangement remains unchanged, dramatic changes can occur in the electronic energy levels of the materials, since the overlap of the electronic wavefunctions is strongly affected by changes of even a few percent in the interatomic spacing. For example, GaAs changes from a grey solid of bandgap 1.4 eV to a deep red solid with a bandgap of 2.0 eV by the application of a mere 60 kbar (60 000 atm) of hydrostatic pressure.^[1] It is the power to affect the energy levels in a solid that makes hydrostatic pressure a unique tool in the study of new optical materials such as organic conjugated molecules.

Conjugated molecules are characterized by highly delocalized electron wavefunctions along the molecule backbone. Undoped conjugated molecules behave as semiconductors with bandgaps of 1.4–3 eV. In recent years considerable interest has been directed towards undoped conjugated molecules as replacements for conventional inorganic semiconductors in optical devices. The emission of light by molecules in an electric field (electroluminescence) was first demonstrated in poly(*p*-phenylenevinylene) (PPV) in 1990.^[2] Two other materials that are attractive because of their high photoluminescence (PL) quantum yield are ladder poly(*p*-phenylene) (LPPP) for blue light emitting diodes (LEDs),^[3–5] and the oligophenyl *para*-hexaphenyl (PHP), which has been successfully used to create elements for a red–green–blue color display.^[6]

Although the photophysical properties of conjugated molecules have been investigated since the discovery of conducting polyacetylene,^[7] fundamental properties of the electronic states, such as the nature of the ground and excited states, are not fully understood. Since high PL yield is the primary consideration in optical devices such as LEDs, mechanisms that decrease PL yield such as competing non-radiative processes, transitions that depopulate the ground state due to reabsorption of singlet photons, or situations that involve intermolecular interactions are crucial to the understanding and design of these devices.

The technique heretofore used to tune intermolecular interactions was chemical substitution. While this method allows some variation in tuning interchain distances, it necessarily changes the nature of the chemical bonds. The application of hydrostatic pressure, in contrast, increases intermolecular interaction and changes the molecular geometry without any chemical changes in the materials. Furthermore, hydrostatic pressure allows a study of the materials in a region of phase space not

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accessible by chemical techniques. Hence, pressure is a “clean” way to investigate the influence of molecular geometry. The nature of the geometry changes can be deduced from their influence on electronic and vibrational transitions by comparing experimental results with calculations. Pressure also allows us to see which transitions/states are connected to each other, e.g., via a population/depopulation mechanism, and also to determine which states are of different origin, i.e., show different rates of change in the spectral features under pressure.

We have conducted optical studies to investigate the vibrational and electronic properties of chosen organic molecules, using PHP (an oligophenyl) and m-LPPP (a polyphenyl) as models of chain and ladder molecules. Both materials have been synthesized with high chemical purity and then purified to reach low defect density.

PHP forms monoclinic crystallites,^[8] and is characterized by a torsional degree of freedom between the neighboring phenyl rings. In the crystalline state the molecules are arranged in layers, forming a herringbone type of arrangement as shown in Figure 1a. The ladder type LPPP, called m-LPPP due to the methyl group in the Y-position in Figure 1b does not form crystallites owing to the bulky side groups, and shows no torsional degree of freedom between the neighboring phenyl rings due to the methyl bridge between the rings. m-LPPP has high intrachain order due to its planar phenyl rings, and has excellent solubility owing to the large side groups. It has proved to be the best material within the LPPP family from the point of view of stability and PL quantum yields. Up to 100 phenyl rings can be polymerized with an average conjugation length of more than ten phenyl rings. Both PHP and m-LPPP are known to show stimulated emission.^[9–11]

2. Applying Pressure: The Diamond Anvil Cell

Diamond anvil cells^[12] are built or can be purchased in a variety of configurations dictated by the range of pressure required for the experiment and by any special circumstances such as low temperatures, wide scattering angle for X-ray work, etc. The cell we use is of a Merrill–Bassett design,^[13] and consists of two triangular plates of Be–Cu each with a central removable seat that holds a diamond anvil. The diamonds are specially selected to have a low intrinsic fluorescence so that they are suitable for low intensity Raman signals. They are about 1/3 carat each in weight, have their ends polished into culets of 0.6 to 0.9 mm in diameter and are of a modified brilliant design with a sixteen-sided culet. The stainless steel gasket that sits between the diamonds is pre-indentated by the diamond culets to a thickness of about 70 μm; a 250 to 300 μm hole drilled in the center of the indentation forms the sample chamber. For Raman or luminescence mea-

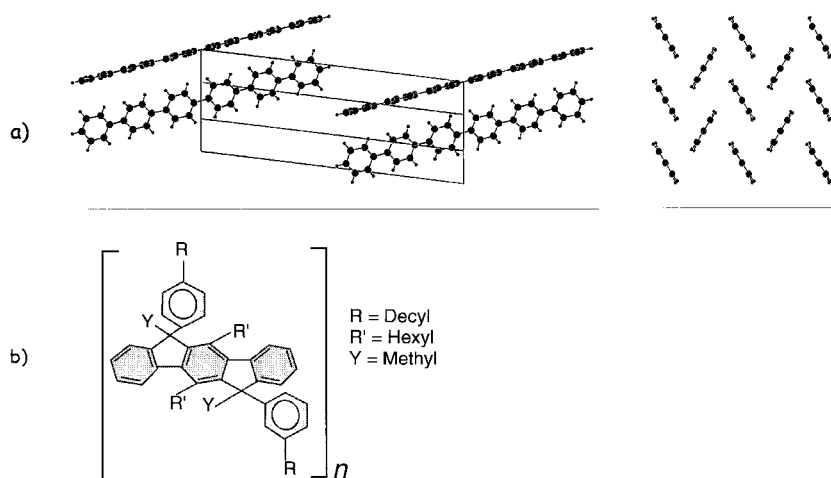


Fig. 1. a) Crystal structure of PHP. b) Molecular formula of m-LPPP.

surements a small $100 \times 150 \times 30 \mu\text{m}^3$ piece of the sample is placed in the hole. For absorption measurements we dissolve a small amount of the sample in a solvent such as toluene and drop cast it on the face of one of diamonds to form a film. The edges of the film are then scraped off, leaving a film only in the center of the diamond. A small chip of ruby is also placed in the hole in order to measure the pressure in-situ via the energy shift of the fluorescence of ruby.^[14]

The success of a diamond anvil cell lies in the care of alignment. The diamond culets should be aligned so that they are optically parallel to each other, and are exactly lined one above the other. Hydrostatic pressure requires a pressure-transmitting medium. Ethanol–methanol mixtures are frequently used in pressure studies. For cryogenic studies, however, liquefied noble gases are frequently used, notably argon^[15] and helium.^[16] In our studies we use argon, which is loaded by forming a sealed area around the diamonds, but leaving a small gap between the diamond and the gasket. Argon is liquefied in situ, and its liquefaction is assured by viewing the sample chamber through a microscope. When liquid has filled the sample hole, the bolts on the cell are tightened, sealing the sample hole with the diamonds. Once sealed, a cell will maintain pressure for several months; it can also be cycled up and down in pressure a few times before the gasket fatigues.

3. The Electronic States in Organic Conjugated Molecules

Figure 2 is a schematic diagram of various electronic levels describing the transitions that produce emission and absorption in m-LPPP. Absorption of light occurs via the creation of a singlet excited state S_1 , as well as phonons. After photoexcitation, de-excitation occurs via several mechanisms including: non-radiative recombination which leads to a depopulation of S_1 via the creation of phonons; radiative recombination of S_1 , which leads to PL; population of the lowest lying triplet state T_1 via intersystem crossing from S_1 , which can be probed by

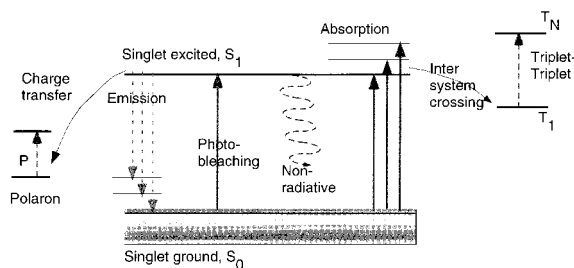


Fig. 2. A schematic diagram of energy levels in conjugated molecules, showing the ground and excited states involved in absorption, PL and PB, and the polaron and triplet states populated from the excited state.

$T_1 \rightarrow T_N$ triplet-triplet absorption (TT); dissociation of the bound electron-hole-pair into a free electron-hole-pair, which then creates one positive and one negative polaron, giving rise to intra-polaron absorption (P). The population of triplet and polaron states leads to a small depopulation of the ground state, causing photobleaching (PB) of the absorption. Vibronic excitations are associated with most of these energy levels, and can be observed in the transitions (not all vibronics are shown in Fig. 2). Involvement of no phonons is expressed as 0-0 transition, one phonon as 0-1 transition and so forth.

The presence of polarons and triplet excitons might be a fundamental problem for laser diodes made from *para*-phenylene type molecules since the processes represent absorption of the emitted light of singlet excitons. Polarons, which can be described as charges with a surrounding elastic deformation, are only observed in transient experiments in pure m-LPPP films since most of them decay in a few milliseconds. Their lifetimes can be increased via external stabilization due to defects produced by photooxidation. Our photooxidized sample was prepared by illuminating the m-LPPP film for 8 min with 50 mW of ultraviolet (UV) radiation from the 351.1 nm Ar^+ line.

In order to observe all the states listed above, we perform three distinct experiments on the same sample: photoluminescence (excited using the 351.1 nm UV line), absorption to observe the singlet excitons, and photomodulated absorption^[17,18] to observe the polaron, triplet-triplet absorption and PB (which is 180° out of phase with respect to the triplet absorption).

4. Electronic States under Pressure

The spectra observed for the electronic states in m-LPPP are shown in Figure 3 and Figure 4. All spectra are observed to shift to lower energies with increasing pressure, and to broaden as well, although at different rates. PL and absorption are shown at 300 K, while the TT, P, and PB spectra were taken at 80 K. We also note that photooxidation does not dramatically change the electronic properties of the material, except for the polaron lifetime. Peak positions and linewidths were obtained by fitting the spectral lineshapes to Gaussians. The energies of various transitions under pressure are shown in Figure 5. The red shift of the energies is described by $E(P)$

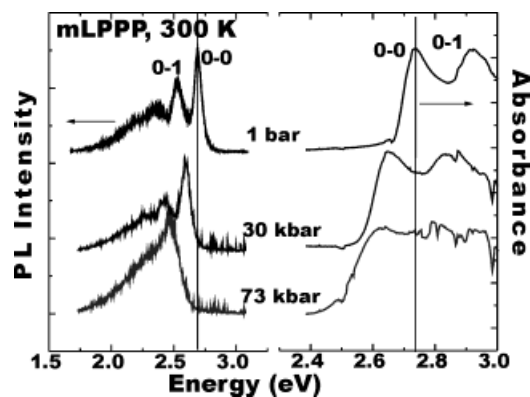


Fig. 3. PL (left) and absorption (right) spectra of m-LPPP at room temperature, showing the vibronics in the spectra. All spectra red shift and broaden with pressure.

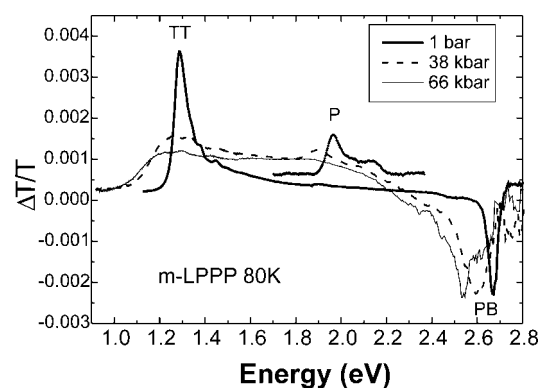


Fig. 4. Photoinduced absorption of m-LPPP at 80 K under pressure, showing the TT, P, and PB spectra. Note the broadening and red shift of all spectra [18].

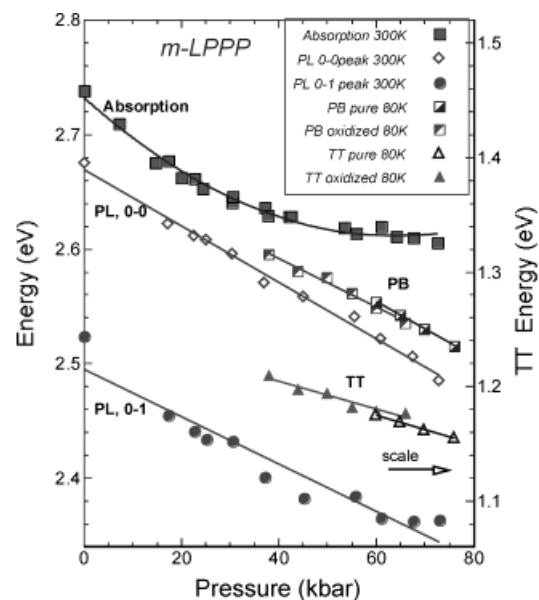


Fig. 5. Energies of the electronic levels under pressure in m-LPPP as observed in PL, absorption, and photo-induced absorption experiments. In addition to the fundamental transitions between ground and excited states, intra-polaron and triplet-triplet transitions are shown.

$= E(0) + \alpha P$, where $E(0)$ the energy at $P = 0$ kbar, and α is the pressure coefficient in units of meV/kbar. A nonlinear term is

observed only for the 0–0 absorption peak. The coefficients obtained are listed in Table 1.

The pressure coefficients for PB and 0–1 PL are practically identical to each other, implying that these two transitions are not influenced by any competing ones. In contrast, the 0–0 PL

Table 1. Transition energies and pressure coefficients for as prepared m-LPPP film (with the exception of the polaron transition, which is for the oxidized film).

Transition	$E(0)$ [eV]	α [meV/kbar]
PL, 0-0	2.67	-2.47 ± 0.07
PL, 0-1	2.50	-2.08 ± 0.21
Absorption, 0-0	2.73	-3.78 ± 0.2 [a]
Photobleaching (PB)	2.68	-2.10 ± 0.1
Triplet-triplet	1.28	-1.20 ± 0.1
Polaron	1.97	-2.10 ± 0.2

[a] Nonlinear term $+0.29 \pm 0.003$ meV/kbar².

is influenced by the absorption spectrum since the Stokes shift in m-LPPP is <0.1 eV. The different α s for the 0–0 and 0–1 PL reflect the fact that the PL emission peaks move closer to each other and broaden with increased pressure. Broadening is also observed in the PB and TT-absorption spectra.

One effect that results in a red shift of all electronic spectra^[19] is an increase in the degree of conjugation. One way of increasing the degree of conjugation in short conjugated molecules is simply to increase their length, i.e., add more conjugated bonds, which clearly cannot happen without chemical intervention. However, the effective conjugation depends on the degree of overlap of the π -electron wavefunctions.^[20] Our observed experimental red shifts under pressure can be explained as due to a higher degree of conjugation arising from the stronger overlap of π -electrons, either due to a higher degree of planarity or shorter inter-ring bonds.^[21]

We find, however, that all transitions do not red shift in a parallel fashion. The 0–0 absorption peak shift is larger than that of the PL and also contains a nonlinear component in pressure. We note that the absorption edge appears to shift at a slightly different rate as compared with the 0–0 peak, owing to the increased broadening. The PL, along with the TT, PB, and P signals all originate from the chains with the longest effective conjugation, i.e., only the sites lowest in transition energy, to which excited states migrate. Absorption, in contrast, reflects all the different chain segments. It is therefore also much broader and shows how all the different sites evolve under pressure. If the relative shift in transition energies under the influence of pressure is greater for smaller segments, this will lead to the observed stronger shift for absorption.

Computations by Puschnig et al.^[22] in the formulation of three-dimensional (3D) band structure density functional theory of the dielectric constant allow an understanding of the absorption via the imaginary part of the dielectric constant, $\text{Im}(\epsilon)$. These calculations show that when the inter-ring single bond between two phenyl rings is shortened, a red shift of the bandgap occurs, but with no broadening of the bands. The

shift is due to an increase in the bandwidth of the delocalized valence and conduction bands along the molecule axis, which is equivalent to a stronger π -electron overlap. In contrast, when the a - and b -axis (interchain) distances are decreased, $\text{Im}(\epsilon)$ blue shifts and broadens strongly due to the increased bandwidth of the localized bands perpendicular to the molecule axis. A combination of these two effects, which one would expect for hydrostatic pressure, results in a net red shift and broadening. From the calculated bulk modulus, this shift was calculated to be 2 meV/kbar, in agreement with experiment.

Upon increasing the conjugation length the shift of the TT-transition was calculated to be smaller than the shift of the singlet–singlet transition because the triplet states are localized at one phenyl ring.^[23] This localization is not due to extrinsic disorder but is an intrinsic property of the triplet wavefunction induced by the exchange term.^[24] Therefore, our result of a small TT-absorption shift of -1.2 meV/kbar is consistent with the theoretical prediction: as pressure varies the degree of conjugation, the triplet transitions are less affected than the singlet transitions (absorption, PL, PB). Polarons, however, are three to four times more extended^[25] than the triplet. Therefore their pressure behavior resembles that of the singlet states—their respective α is close to the singlet values, which is in excellent agreement with the behavior observed for oligophenyls.^[26]

5. Vibrational States under Pressure

There have been numerous studies of the crystal structure of the oligophenyls of poly(*para*-phenylene) (PPP), starting with the determination of the biphenyl structure in the late 1920s. A closer look at X-ray data reveals that PPP and its oligophenyls adopt conformations such that the phenyl rings within each molecule are on the average coplanar, but undergo librational motion. The repulsion between the ortho hydrogens leads to a torsion of neighboring phenyl rings with respect to the single bond connecting them. In the crystalline environment, however, the intermolecular forces tend to planarize the molecules. A torsional angle of 27° is predicted in single isolated PPP chains and 17° in the crystalline environment. Under pressure the molecules are brought closer together and forced to become more planar. This geometric change to planarity is monitored via the vibrational modes using Raman scattering, thus probing the vibrations from individual phenyl rings.

The Raman spectrum of the oligophenyls is mainly characterized by four intense modes of A_g symmetry. It has been observed that the Raman intensity ratio of the inter-ring C–C stretch mode (1280 cm^{-1}) to the C–H in plane bending mode (1220 cm^{-1}) (I_{1280}/I_{1220}) is a good indication for the number of conjugated phenyl rings in the molecule chain.^[27] This is also a test for planarity, since simulations show that a higher number of conjugated phenyl rings result in a lower torsional angle between the phenyl rings. For biphenyl I_{1280}/I_{1220} is

about 25 and beyond hexaphenyl the ratio of the intensities is close to unity. Raman scattering of the anions of oligophenyls (going from *p*-terphenyl up to PHP) also shows that I_{1280}/I_{1220} decreases as the oligophenyl length is increased.

Figure 6 shows a typical Raman spectrum of PHP at 1 bar. The high-energy mode at 1600 cm^{-1} is the ring C–C stretch

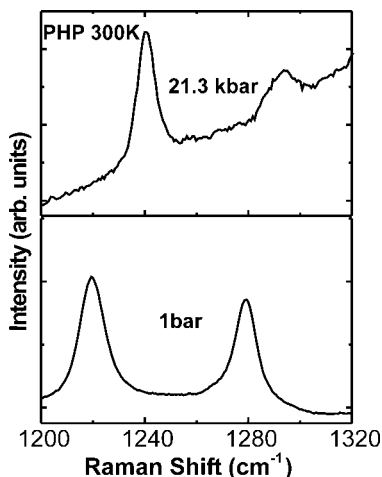


Fig. 6. Raman spectra of PHP with and without pressure at room temperature.

mode. We have measured the three Raman modes as a function of pressure. The frequencies of all three modes increase with pressure and can be fit to $\omega(P) = \omega(0) + (d\omega/dP)P$, where P is in kbar.

The most striking feature of the Raman spectrum of PHP under high pressure is a sharp decrease in the ratio of the intensities of the 1280 cm^{-1} peak to the 1220 cm^{-1} peak, (I_{1280}/I_{1220}) as seen in a 21.3 kbar spectrum in Figure 7. The ratio of I_{1280}/I_{1220} decreases from 0.8 to 0.3 between 0 and 15 kbar, beyond which it remains almost a constant. Unusual effects are also observed in the frequencies and linewidths of the modes, to be discussed in a future publication.^[28]

From Raman studies on oligophenyls of different length it is known that I_{1280}/I_{1220} decreases with increasing chain length. At the same time the oligophenyls become more pla-

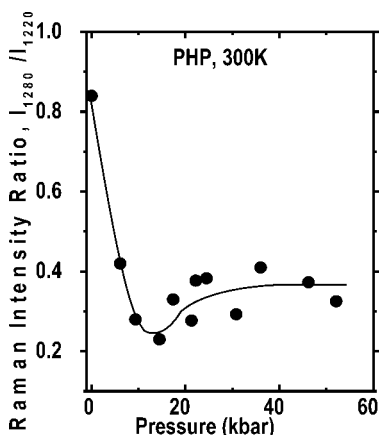


Fig. 7. The ratio of the Raman intensities of modes associated with the inter-ring C–C stretch and the C–H in-plane bending modes in PHP, I_{1280}/I_{1220} , under pressure. Note the sharp drop near 15 kbar, indicating planarization of the molecule.

nar with increasing chain length, which is deduced from X-ray studies and theoretical calculations. Therefore I_{1280}/I_{1220} is an indicator of planarity in these materials, where a larger I_{1280}/I_{1220} ratio corresponds to a larger torsional angle (lower planarity). The decrease in I_{1280}/I_{1220} under pressure that we observe in PHP is an indication that the molecule becomes more planar, i.e., the torsional angle between neighboring phenyl rings decreases between 0–15 kbar. Moreover, I_{1280}/I_{1220} does not change between 15 and 70 kbar showing that maximum planarity is reached.

This result is in excellent agreement with our calculations for the intensities of these modes in a simpler biphenyl molecule for the planar and non-planar geometries. Our calculation yields a decrease in the intensity ratio of a factor of 4.5 upon planarization. Experimentally we find a decrease of a factor of 2.8 in I_{1280}/I_{1220} upon planarization in the larger PHP molecule, which is reasonable in the light of the calculated value in biphenyl.

6. Conclusion

By using two model molecules, one a non-planar system that planarizes under pressure, thereby exhibiting changes in the molecular geometry, and the other a planar system where geometric changes do not occur, but there is a distinct increase in intermolecular interaction, we are able to expand our understanding of several different optical transitions via a series of three different experiments on the same sample that probe localized and delocalized states. Theoretical calculations on these systems are currently in progress, and we expect that this will allow further development of the design of new molecules that can be simulated by using the thermodynamic parameter of pressure.

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