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Time resolved fluorescence measurements are presented as a function of pressure for pentacene in *para*-terphenyl at low temperature. A photosite specific pressure effect is observed at low temperature for the triclinic ($P \leqslant 5.5$ kbar) phase of *para*-terphenyl. In addition, the fluorescence lifetime of pentacene in the monoclinic (high pressure) crystal phase at low temperature is obtained. We also observe unique fluorescence decay dynamics in the pressure region (5.5–6.5 kbar) intermediate to the triclinic and the monoclinic crystal phases. The effect of pressure on the triclinic host crystal is discussed in terms of a lowering of the energy of the lowest singlet excited state (S_1) relative to the nearby triplet level (T_2) with a corresponding decrease in the intersystem crossing rate. The fluorescence dynamics also provide information on the nature of the pentacene environment in the higher pressure (i.e. > 5.5 kbar) structural phases of the *p*-terphenyl host crystal.

I. INTRODUCTION

The fluorescence lifetimes of polyacene doped polyphenyl crystals have been of interest due to the presence of multiple origins in the absorption and fluorescence spectra.[1–4] In particular, the pentacene doped *para*-terphenyl system has been well-studied due to the large transition dipole of pentacene, the narrow homogeneous linewidth, and the existence of four pentacene origin bands at low temperature.[1–17] The four photosites observed in the absorption and emission spectra of pentacene in *p*-terphenyl (labeled O_1, O_2, O_3, and O_4 in increasing energy) are attributed to the unique chromophore environments associated with the four inequivalent sites in the triclinic *p*-terphenyl crystal structure.

Crystalline *para*-terphenyl has two known solid phases. At ambient pressure, above 193 K, the solid has a monoclinic crystal structure (space group $P2_1/a$) with two equivalent molecules per unit cell.[18] At lower temperatures, the crystal is triclinic (space group $P\bar{1}$) with four molecules per unit cell.[19] Pentacene dopant molecules crystallographically substitute into the four distinct sites of the *para*-terphenyl host lattice, resulting in four different electronic origins (O_1, O_2, O_3, and O_4) in the pentacene absorption spectrum. In contrast, a pentacene doped monoclinic *p*-terphenyl crystal yields a single pentacene electronic absorption origin since there is only one unique crystallographic site in this crystal phase. The phase diagram of *para*-terphenyl is known[20–22] and the possibility of a third phase with characteristics intermediate to the two known phases has recently been discussed.[23]

In addition to their different transition energies, the four photosites exhibit unique electronic and vibronic dephasing dynamics.[1,9,12,14] For example, the characteristic fluorescence lifetimes of the photosites have been attributed to site specific intersystem crossing dynamics involving an excited triplet state (T_2) near in energy to the lowest excited singlet level (S_1). The T_2 level is believed to lie above S_1 for the lower energy photosites (O_1 and O_2) yet below the corresponding S_1 level for the higher energy photosites (O_3 and O_4).[1] Consistent with this picture is the observation that the ambient pressure intersystem crossing yield is 0.6 for O_3 and O_4 but < 0.005 for O_1 and O_2.[9,10,12] Due to the different intersystem crossing yields, the fluorescence lifetime is 24 ns for O_1 and O_2, but only 8 ns for O_3 and O_4 at ambient pressure.[8]

Previous experiments have shown that the absorption origin bands of pentacene in *p*-terphenyl red shift with increasing pressure.[22] Furthermore, the pressure induced red shift of hydrocarbon singlet states tends to be three to five times that of triplet states of the same symmetry[24,25] due to the lower polarizability of the triplet states. Such arguments suggest that as pressure is increased, the energy of the O_3 and O_4 origins can be shifted below the energy of their closest triplet states (T_2). Under such conditions, the low temperature fluorescence lifetimes of the O_3 and O_4 photosites should increase due to a reduction in intersystem crossing, as previously observed in anthracene[26] and 9-anthraldehyde.[27] In the low temperature pentacene in *p*-terphenyl system, the structural phase transition at 5.5 kbar complicates this picture. In addition, at higher temperatures, a low energy out-of-plane vibration (e.g., the "butterfly" mode at 39 cm^{-1}) has been suggested as a promoting mode for intersystem crossing,[11] in which case, pressure induced vibrational energy shifts may also be significant.

II. EXPERIMENT

Pentacene doped *para*-terphenyl ($< 10^{-5}$ mol/mol) crystals were grown from the melt at ambient pressure in a Bridgman furnace and subsequently loaded into the gasket aperture of a Merrill–Bassett diamond anvil cell (DAC)[28] utilizing modified brilliant cut diamonds with 0.8–1.0 mm culets. The hole diameter of the gasket was approximately 0.4 mm and sample thicknesses were typically 0.1–0.2 mm. Strain broadening was minimized by growing crystals from the high temperature melt (at temperatures up to 250 °C)

under nearly isobaric conditions by slow compression of the sample.[23] The major source of crystal strain is the thermal contraction and crystal phase changes associated with cooling the samples to 15 K. Pressures were measured using both the ruby luminescence method[29,30] and correlated with the frequency shift of the pentacene O_1 photosite, resulting in an estimated error of ± 0.3 kbar.[23] The sample temperature was controlled using a closed cycle helium cryostat (CTI-Cryonics 15–300 K). Retractable vacuum feed through bolt drivers permitted the pressure of the diamond anvil cell be changed at low temperature inside the cryostat.

Site specific emission spectra were obtained by exciting each photosite with the cavity dumped output of a dye laser synchronously pumped by a frequency doubled mode-locked Q-switched Nd^{3+}:YAG laser. Both the ruby-luminescence and fluorescence emission were dispersed using a 0.75 m monochromator (SPEX 1702) with an 1800 groove/mm grating. Absorption spectra were obtained by scanning the output of a 75 W xenon arc lamp with the same 0.75 m monochromator, yielding an instrumental resolution of 2 cm^{-1}. The light was directed to and from the low temperature sample by fiber optic light guides and the transmitted intensity was detected with a photomultiplier (Hamamatsu R928P).

Time resolved fluorescence lifetime measurements were obtained by selectively exciting the different pentacene photosites using the tunable output of a short pulse (35 ps) cavity dumped dye laser (1 cm^{-1} bandwidth) which was pumped by the frequency doubled output of a mode-locked Q-switched Nd^{+3}:YAG laser. The excitation pulse was spectrally filtered by detecting the emission of a strong vibronic band ~ 1400 cm^{-1} to the red of the origin. The time resolved decay of the fluorescence intensity was detected using a thermoelectrically cooled (-30 °C) photomultiplier tube with a 2.2 ns rise time (Hamamatsu R955P), a 2.0 GHz amplifier (Phillips Scientific 6954, 10X), averaged using a 400 MHz digitizing oscilloscope (Hewlett–Packard 54502A, 0.87 ns rise time), and analyzed with a computer (Macintosh SE/30). Due to the nonnegligible response times of the detector, amplifier, and the digitizing oscilloscope, the data were fit by convolving an instrumental response function with a single exponential fluorescence decay time.

III. RESULTS AND DISCUSSION

The low temperature absorption spectrum of a dilute crystal of pentacene in *para*-terphenyl at ambient pressure yields four origin peaks with frequencies 16 883 cm^{-1} (O_1), 16 887 cm^{-1} (O_2), 17 006 cm^{-1} (O_3), and 17 065 cm^{-1} (O_4).[6] Since O_1 and O_2 are only separated by 4 cm^{-1} at low pressure, they can be spectrally difficult to distinguish in the presence of sample strain at high pressure. The effect of high pressure on the absorption spectrum of pentacene in p-terphenyl is illustrated in Fig. 1. The top panel in Fig. 1 shows the pressure induced red shift for the triclinic crystal phase, while the lower two panels illustrate changes in the absorption spectrum due to structural changes of the p-terphenyl lattice. The pressure shifts for
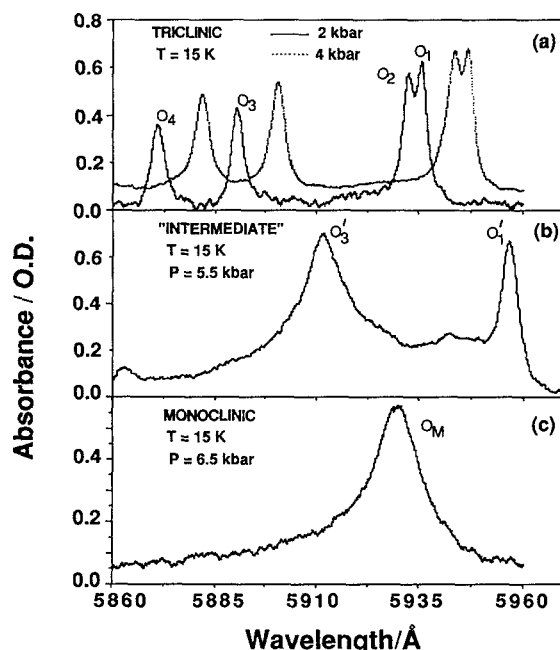

FIG. 1. (a) The low temperature (15 K) absorption spectrum of pentacene in *para*-terphenyl at pressures of 2.0 and 4.0 kbar. The pressure induced red shift in the spectrum is ~ 15 cm^{-1}/kbar and the four photosites O_1, O_2, O_3, and O_4 are attributed to pentacene in the inequivalent sites of the triclinic p-terphenyl host crystal lattice. (b) At intermediate pressure between 5.5 and 6.6 kbar, the spectrum shows two prominent absorption bands O_1' and O_3' (c) Only one photosite is observed in the low temperature absorption spectrum of pentacene in the monoclinic phase of p-terphenyl.

the four photosites of the triclinic phase are found to be 16 cm^{-1}/kbar (O_1), 15 cm^{-1}/kbar (O_2), 14 cm^{-1}/kbar (O_3), and 15 cm^{-1}/kbar (O_4), respectively.[22] Since the pressure shifts of hydrocarbon triplet state energies are typically several times less than for the corresponding singlet states of the same symmetry, we speculate a smaller red shift for the T_2 triplet state (i.e., 4 ± 0.5 cm^{-1}/kbar). Thus, a pressure of about 5 kbar may lead to a red shift of 50–60 cm^{-1} for the S_1 state relative to the corresponding T_2 states.

Figure 1(c) shows the low temperature pentacene absorption spectrum in the high pressure ($\geqslant 6.5$ kbar) monoclinic crystal phase of the p-terphenyl host lattice. In contrast to the triclinic phase, only one pentacene absorption band is observed due to the two crystallographically equivalent p-terphenyl sites per unit cell in this lattice. Figure 1(b) illustrates the pentacene absorption spectrum characteristic of a distinct local crystal structure,[23] which we observe in a relatively small pressure region (5.5–6.5 kbar) intermediate to the triclinic and monoclinic phases at low temperature. The spectrum of the intermediate phase is not an admixture of the triclinic and monoclinic spectra (including pressure shifts). In this intermediate pressure region, we observe two major absorption bands (labeled O_1' and O_3') which correlate with the extrapolated pressure shifts of the O_1 and O_3 bands of the triclinic phase. The corresponding O_2 and O_4 bands are either extremely broadened or absent. In addition, the absorption band charac-
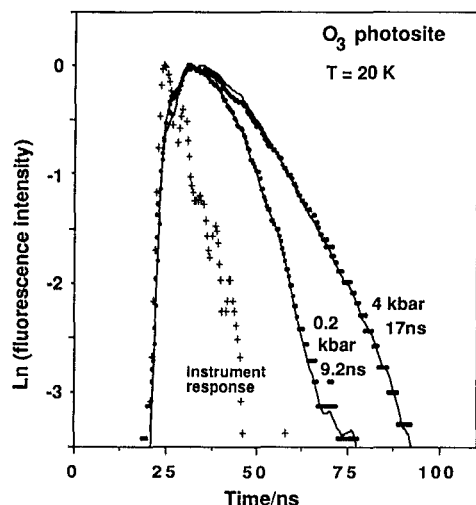
FIG. 2. A semilog plot of the low temperature (20 K) fluorescence intensity decay observed for the O_3 photosite of pentacene in p-terphenyl. The solid circles (●) are data obtained at 0.2 and 4.0±0.2 kbar. The solid curves represent the convolution of the instrument response function (+) with single exponential decay functions.
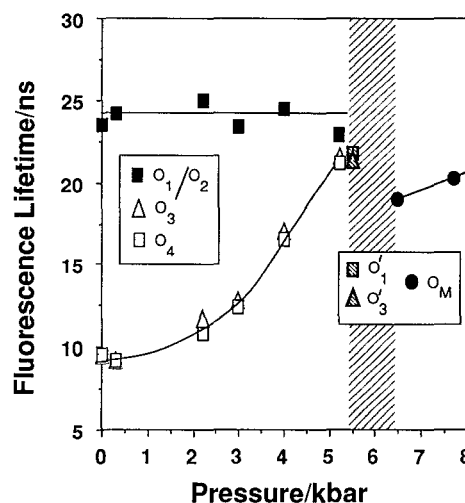

FIG. 3. The effect of pressure on the low temperature (20 K) fluorescence lifetime of the various photosites of pentacene in p-terphenyl. The lifetime of the O_1/O_2 photosite(s) showed little change with pressure, however, the fluorescence lifetimes of the higher energy, O_3 and O_4 photosites increase at higher pressures due to a decrease in intersystem crossing. The hashed portion of the figure represents the intermediate pressure region (5.5–6.5 kbar) where lifetimes were obtained for the O_1' and O_3' absorption bands. In the monoclinic crystal (>6.5 kbar), the fluorescence lifetime of the single O_M pentacene absorption band is obtained. The solid lines are guides for the eye.

teristic of the monoclinic phase is not observed in the intermediate spectrum.

The effect of pressure on the low temperature fluorescence lifetime of pentacene in p-terphenyl has been obtained at pressure over the range 0–8 kbar. As shown in Fig. 1, pentacene in triclinic p-terphenyl only exists up to a pressure of 5.5 kbar. An example of the effect of pressure on the time-resolved fluorescence intensity is illustrated for the O_3 photosite in Fig. 2. The solid curves through the data points are obtained by convolution of the instrument response with a single exponential decay function to obtain the fluorescence lifetime. Figure 2 shows a significant increase in the low temperature fluorescence lifetime of the O_3 photosite from 9.2±0.5 ns at low pressure to 17±0.5 ns at 4 kbar. Similar data were obtained for pentacene in all of the photosites and at various pressures throughout the 0–8 kbar pressure range. A single exponential decay time produced a good fit to the data except when spectral broadening gave rise to overlap of different photosite bands.

The effect of pressure on the fluorescence lifetime of pentacene in p-terphenyl is summarized in Table I and

TABLE I. Low temperature (20 K) fluorescence lifetimes of pentacene in *para*-terphenyl at high pressure.

Pressure (kbar)	Photosite fluorescence lifetimes (±0.5 ns)					
	O_1/O_2	O_3	O_4	O_1'	O_3'	O_M
0.2	24.2	9.2	9.2	···	···	···
2.2	25.0	11.7	10.8	···	···	···
3.0	23.4	12.8	12.4	···	···	···
4.0	24.5	17.0	16.5	···	···	···
5.3	22.8	21.5	21.3	···	···	···
5.5	···	···	···	21.8	21.4	···
6.5	···	···	···	···	···	19.0
7.7	···	···	···	···	···	20.3

illustrated in Fig. 3. The fluorescence decay times observed at low pressure are in good agreement with previously reported values at ambient pressure,[1,9] indicating that emission reabsorption in our samples is not a significant contributor to the observed emission decay measurements.[9] In the low temperature triclinic phase (<5.5 kbar) we observe little change in the lifetime of the O_1/O_2 photosite(s) with increasing pressure. In contrast, a significant increase is observed in the fluorescence lifetimes of the higher energy O_3 and O_4 photosites at higher pressures. At ambient pressure, the intersystem crossing yield is about 0.6 for O_3 and O_4 but <0.005 for the O_1/O_2 photosites.[9,10,12] Thus, the fluorescence lifetime of the O_1/O_2 photosite is relatively unchanged at high pressure since intersystem crossing is not a significant relaxation mechanism. In contrast, we attribute the increase in the O_3 and O_4 lifetimes to pressure induced lowering of the S_1 singlet energy level relative to the nearby T_2 triplet level, with a corresponding decrease in the intersystem crossing yield for these two photosites. At a pressure of 5.3 kbar, the lifetimes of the O_3 and O_4 photosites are close to that of the O_1/O_2 photosite, suggesting that the intersystem crossing yield for O_3 and O_4 is similar to that of O_1/O_2 at this pressure. Thus a pressure increase of 5.3 kbar red shifts the energy of the S_1 level of O_3 and O_4 photosites below that of the corresponding T_2 level.

The intermediate pressure region (i.e., 5.5–6.5 kbar) is indicated by the hashed portion of Fig. 3. The fluorescence lifetimes for the O_1' and O_3' absorption bands are observed to be very similar 21.8±0.5 and 21.4±0.5 ns, respectively. The shortening of the lifetime of O_1' relative to the O_1 site

of the triclinic phase is additional evidence for a distinct local crystal phase.

In the high pressure ($\geqslant 6.5$ kbar) monoclinic crystal phase, the low temperature fluorescence lifetime of the single O_M pentacene absorption band is 19 ± 0.5 ns at 6.5 kbar. At room temperature, the 6.5 kbar fluorescence lifetime is 15 ± 0.5 ns compared to the 9 ns lifetime reported for pentacene in monoclinic p-terphenyl at ambient pressure and temperature.[12] Since the total red shift of S_1 associated with a 6.5 kbar pressure increase is ~ 100 cm^{-1}, we attribute the relatively long lifetime of O_M at high pressure to an S_1 energy lower than the corresponding T_2 level. As shown in Fig. 3, when the pressure on the monoclinic sample is increased from 6.5 to 7.7 kbar, the low temperature fluorescence lifetime increases from 19.0 ± 0.5 to 20.3 ± 0.5 ns, due presumably to a further red shift in the O_M singlet level relative to the corresponding T_2 state. This suggests that the S_1 to T_2 splitting is small enough at 6.5 kbar such that some phonon assisted intersystem crossing may occur at 20 K. Note also that low temperature monoclinic samples (i.e., pressure$\geqslant 6.5$ kbar) do not undergo a phase transition of the p-terphenyl host lattice upon cooling from the high temperature monoclinic phase. The absence of a phase transition may give the monoclinic samples a unique strain field relative to the lower pressure triclinic and intermediate phase crystals.

The fluorescence lifetime of pentacene in the monoclinic phase at low temperature and higher pressures is approximately 21 ns. This is somewhat shorter than the lifetime of the O_1/O_2 photosites in the triclinic phase. It has been estimated that the internal conversion yield is 22% for pentacene in the triclinic phase of p-terphenyl at ambient pressure.[10,12] However, for pentacene doped into a monoclinic[31] naphthalene host crystal, the internal conversion yield is $31.5 \pm 1.5\%$.[10] Thus, the change in the p-terphenyl crystal structure from triclinic to monoclinic may result in an increase in the internal conversion rate, with a corresponding decrease in the fluorescence lifetime of O_M relative to O_1/O_2.

Previous temperature dependent fluorescence lifetime studies at ambient pressure suggest that the first excited singlet state (S_1) lies above the second excited triplet state (T_2) for the bluer photosites (O_3 and O_4), while the S_1 state of the redder photosites (O_1 and O_2) lie below their corresponding T_2 states.[1,12] This qualitative state ordering is consistent with the intersystem crossing to fluorescence ratio of about 0.6 for O_3 and O_4 and < 0.005 for O_1 and O_2 at low temperature and low pressure.[9,10,12] The interpretation of temperature dependent measurements[1,12] is complicated by spectral overlap of the photosites and the possibility of thermally induced internal conversion. In the present study, pressure dependent spectroscopic measurements have been performed under high resolution low temperature conditions, without the thermal overlap inherent to temperature dependent measurements. In has enabled us to resolve the effect of pressure on the fluorescence lifetime of the different photosites, as shown in Fig. 3. The photosite specific pressure dependent changes in fluorescence lifetimes provide more detailed information on the relative
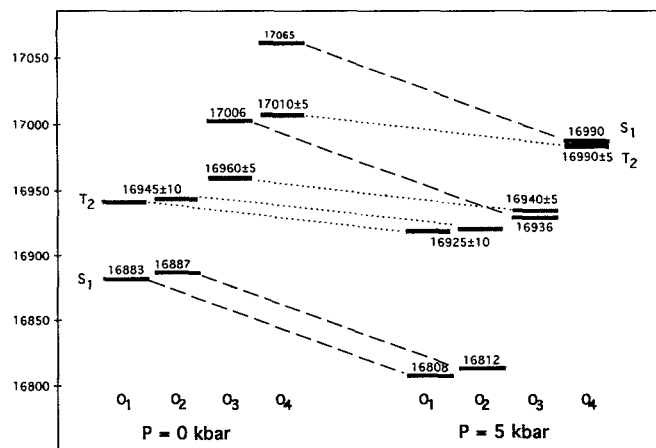

FIG. 4. An energy level diagram of the relative energies of the lowest singlet (S_1) and the nearest triplet level (T_2) for the four photosites of pentacene in the triclinic crystal phase of p-terphenyl at low temperature. The S_1 energy levels are obtained directly from observed pressure shifts in absorption energies. The T_2 levels are determined by pressure induced changes in fluorescence lifetimes and extrapolated using a 4 cm^{-1}/kbar pressure shift.

energies of the singlet and triplet states responsible for intersystem crossing in the pentacene in *para*-terphenyl system.

In Fig. 4, we present an energy level diagram of the energies and pressure shifts corresponding to the S_1 and T_2 levels of the four pentacene impurity photosites in triclinic p-terphenyl. The energy of the T_2 level associated with the O_3 and O_4 photosites has been assigned according to the observed decrease in intersystem crossing (i.e., S_1 lower in energy than T_2) at a pressure of 5.3 kbar. If the fluorescence lifetime changes are a result of changes in intersystem crossing yields, then the low temperature fluorescence lifetime should reach a maximum when the energy of S_1 drops below that of T_2. Such an analysis has been used to estimate the minimum energy of the T_2 levels of O_3 and O_4 at 5 kbar to be approximately $16\,940 \pm 5$ and $16\,990 \pm 5$ cm^{-1}, respectively. The other energy levels in Fig. 4 were placed according to the assumption that the T_2 level splittings scale with the known S_1 splittings and that the T_2 pressure shifts are 4 cm^{-1}/kbar (vs ~ 15 cm^{-1}/kbar for O_1–O_4). Within this framework, a reasonable energy for the T_2 level of O_1 is $16\,945 \pm 10$ cm^{-1}, which lies at the lower end of the range suggested by temperature dependent measurements of thermally induced intersystem crossing at low pressure.[1]

IV. CONCLUSIONS

The pressure induced increase in the low temperature fluorescence lifetime of the O_3 and O_4 photosites of pentacene in p-terphenyl is explained by a relative red shift of the S_1 energy below that of T_2 at high pressure, with a corresponding decrease in the intersystem crossing rate. A correlation of the observed absorption pressure shifts and the fluorescence lifetime changes has also been used to estimate the energies of the T_2 triplet levels for pentacene in the

four photosites of the triclinic host crystal. In addition, unique fluorescence decay dynamics have been observed for pentacene in both the higher pressure monoclinic phase (> 6.5 kbar) as well as a pressure region intermediate to the triclinic and the monoclinic crystal phases (5.5–6.5 kbar). The observed fluorescence dynamics provides additional information concerning the local structure of the pentacene impurity in these higher pressure structural phases of the *p*-terphenyl host crystal.

ACKNOWLEDGMENTS

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