Structural Organization of π Conjugated Highly Luminescent Molecular Material

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We report on striking evidence for a room temperature structural phase instability in *p*-hexaphenyl, inducing a nonplanar conformation of the molecules. Solid state proton NMR and single crystal x-ray diffraction allow the analysis of the organization, the individual dynamics and the involved symmetry breaking. The analysis of Raman spectra above and below room temperature reveals a singular behavior suggesting a modification of the overlap between the electronic wave function induced by the nonplanarity. These results provide a new basis to answer fundamental issues related to molecular and electronic materials and, in particular, luminescent organic devices.

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Beyond the technological issue of organic optoelectronic devices in plastic electronics [1,2], the physical properties of conjugated molecular compounds including the link between their structure and their electronic and optical characteristics are of fundamental interest in the understanding of organic and biological materials. Intensively studied for their electroluminescent properties, the so-called π conjugated compounds constitute a vast class of materials that can be used as active elements in organic light emitting diodes (OLEDs) [3]. Since Burroughes *et al.* originally demonstrated that a green-yellow light emission could be achieved in such a device [4], experimental improvements have now yielded a blue emission [5] with an outstanding quantum efficiency [6]. While the latter seems to be explained by spin dependent exciton formation [7,8], one could expect that the molecular planarity should tune the emitted wavelength by governing the band gap [9–12], thus suggesting a key role of the conformation.

Among the most promising materials are crystalline oligomers and polymers of para-polyphenylene vinylene and para-polyphenylene. Oligomers offer advantages over polymers for applications involving highly ordered structures. In particular, *p*-hexaphenyl (abbreviated below as *p*-*nP*, with $n = 6$) has the ability to self-assemble into polycrystalline samples [13], layers [14,15], nanofibers [16,17], insulated wires [18], and adsorbed single molecules [19]. Because of its considerable interest for applications from blue-light OLEDs to nanofibers, much work has been devoted to this prototypical compound, but fundamental questions remain concerning its structural organization.

In this Letter, we report on a first evidence of an important room temperature structural change in para-hexaphenyl. From a solid state proton NMR study, a quantitative description is obtained for the dynamics, the collective phenomena, and the ordering in both high and low symmetry phases. Both x-ray diffraction and Raman spectroscopy experiments performed on single crystals above and below room temperature reveal the strong coupling between structural and molecular properties.

In molecular crystals, the structural instabilities result from a delicate balance between weak forces, and so temperature, weak pressure, or atomic substitutions can drastically change the involved local potential. The oligophenyl series represents such an example. In the gaseous state, the molecules exhibit nonzero torsional angle between phenyl rings due to competing intramolecular forces: the delocalization of π electrons and the repulsion of ortho-hydrogen atoms. These forces induce a double-well intramolecular potential as a function of the dihedral angle, whereas in the crystalline state, the competing intermolecular forces favor the planar conformation. To change the resulting potential, one may modify either intramolecular forces by increasing the number n of phenyl rings or intermolecular ones with external parameters such as temperature or pressure.

The common feature of short oligophenyls is their high temperature high symmetry monoclinic phase with space group $P2_1/a$, proof of a mean planar conformation of the molecules in the crystal [20]. Upon lowering the temperature, the first three compounds of the series ($n = 2$ to 4) are known to present structural instabilities yielding a static nonplanar conformation of the molecules. In biphenyl (*p*-2*P*), the phase transition is displacive and governed by a soft mode [21]. In para-terphenyl (*p*-3*P*) and para-quaterphenyl (*p*-4*P*), a local double-well potential describes the individual dynamics and the phase transition is of the order-disorder type [22,23]. No structural or dynamical information exists concerning the most interesting, *p*-6*P*.

The polycrystalline sample of para-hexaphenyl was synthesized by electroreduction of monobromoterphenyl in the presence of a zero-valent nickel catalyst [24,25]. Purification of the powder was carried out in a four-zone oven specially designed to allow sublimation and condensation of the material in a glass tube installed in a preset

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temperature gradient. Pure hexaphenyl was isolated in the temperature range 470–540 K under a residual pressure of 10 Pa. It was characterized by UV-visible, Fourier-transform infrared spectrometer and resonance Raman scattering spectroscopies. Single crystals of *p*-6*P* were obtained by sublimation after some weeks in a sealed tube placed in an oven at a temperature around 583 K.

The nuclear spin-lattice relaxation time and resonance line spectra were studied using a Bruker SXP spectrometer. The spin-lattice relaxation time was measured by the saturation 90° pulse method at the Larmor frequency of $\omega_L = 80$ MHz.

The temperature dependence of the spin-lattice relaxation time measured over a broad temperature range is presented in Fig. 1 for *p*-6*P*, displaying the strong decrease of the spin-lattice relaxation time at room temperature. It is the NMR signature of a critical slowing down of pretransitional collective fluctuations on approaching from both sides of the transition temperature T_c [26–28]. Collective critical fluctuations are common features for group-subgroup continuous phase transitions. In the high symmetry phase, they reveal the appearance of short range ordered clusters within the disordered phase. Approaching the phase transition, these clusters grow larger [divergence of the correlation length $\xi \sim (T - T_c)^{-\nu}$] and live longer [divergence of the correlation time $\tau_c \sim (T - T_c)^{-2\nu}$ measured at a critical wave vector]. The spin-lattice relaxation rate is proportional to the spectral density $J(\omega)$, namely, the Fourier transform of an autocorrelation function. This function must integrate the contribution of these different collective modes with their relative weights [29,30]. In the fast motion regime, $1/\tau_c \gg \omega_L$, the spin-lattice relaxation rate behaves essentially like $J(0)$: $1/T_1 \sim \xi \sim (T - T_c)^{-\nu}$. $1/T_1$ is then expected to diverge on approaching the transition temperature as long as the fast motion regime is valid. In this high symmetry phase, these collective critical pretransitional fluctuations govern the spin-lattice relaxation rate in a temperature range from T_c to $T_c + 30$ K as discussed further.

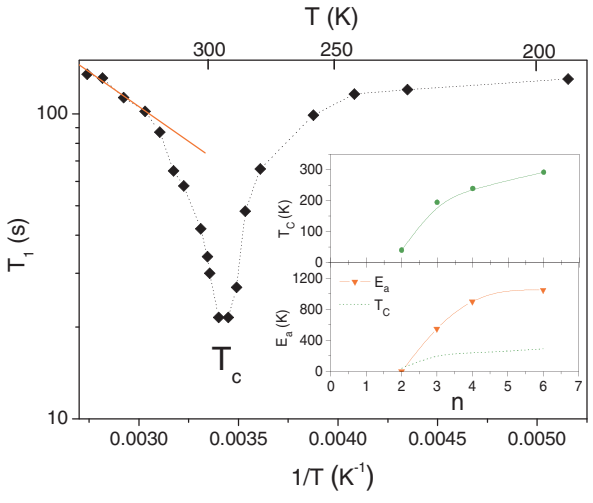


FIG. 1 (color online). Spin-lattice relaxation time as a function of the inverse of temperature for *p*-6*P*. The straight line fits the activated behavior. The inset displays the variations of the critical temperature T_c (upper panel) and the activation energy E_a (lower panel) compared to T_c (dotted line) for the *p*-*nP* as a function of the number of phenyl rings (n).

In the ordered phase equivalent arguments hold, reflecting the divergence of the static and dynamical susceptibilities on approaching the phase transition from below T_c. In this phase, the critical fluctuations are dominant in the resonance process in a narrower temperature range, defined here approximately by $T_c - 15\ \text{K} < T < T_c$.

Far above T_c, the spin-lattice relaxation time is governed by an Arrhenius law characterizing the individual reorientational jumps of the molecules in a local double-well potential. In the fast motion regime encountered here, the frequency rate τ_R^{-1} of the jumps with $\tau_R(300\ \text{K}) = 1.8 \times 10^{-10}$ s is much higher than the Larmor resonance frequency. The expression of the spin-lattice relaxation rate reads $1/T_1 = 10/3\gamma^2 \Delta M_2 \tau_R$, with γ the gyromagnetic factor and $\Delta M_2 = 1.2\ \text{G}^2$ the second moment variation of the proton NMR resonance line; $\tau_R = \tau_\infty \exp(E_a/T)$ and the activation energy $E_a = 1050\ \text{K} \pm 100\ \text{K}$ characterize the double-well potential consistent with an order-disorder mechanism for the phase transition ($E_a \gg T_c$). Concerning the series of short oliphenyls *p*-*nP*, it is worth noting that one deduces from equivalent measurements [26] a clear saturation of both activation energy and transition temperature as shown in the inset of Fig. 1. In the polymer the typical number of phenyl rings is $n = 10$–30; this saturation could infer a structural change around room temperature.

Single crystal x-ray measurements were performed on an Oxford Mar 345 diffractometer with rotating anode. Superstructure Bragg reflections appear at the critical $(1/2, 1/2, 0)$ point of the high symmetry monoclinic Brillouin zone. This means a doubling of the a and b lattice parameters when keeping a pseudomonoclinic description for the low symmetry phase. Temperature evolution of such superstructure is reported in Fig. 2 and reveals a second order phase transition with significant diffuse scattering above $T_c = 293.5$ K. According to the description of a continuous phase transition of this type, an order parameter η is defined here by the difference of occupation probability of two conformations $\eta = p_1 - p_2$. In the case of *p*-6*P*, these molecular conformations are (1) $(+, -, +, -, +, -)$ and (2) $(-, +, -, +, -, +)$, where $+$ and $-$ symbols indicate the positive and negative direction of rotation of each phenyl ring around the long axis. In the high symmetric monoclinic phase ($\eta = 0$) this potential is symmetric and the molecule is on average planar. The symmetry lowering at the phase transition reflects a preferential occupation of one of the two wells, namely, one molecular conformation. Thus, at very low tempera-

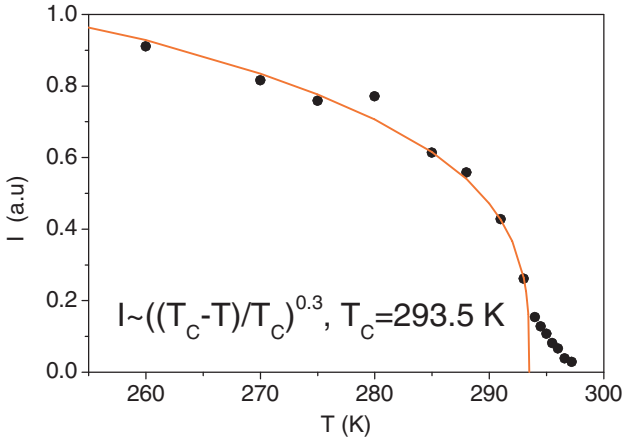


FIG. 2 (color online). Temperature dependence of averaged x-ray intensity of the superstructure reflections (1.5,1.5,1) and $(-1.5, 1.5, -1)$ measured on a single crystal of $p-6P$.

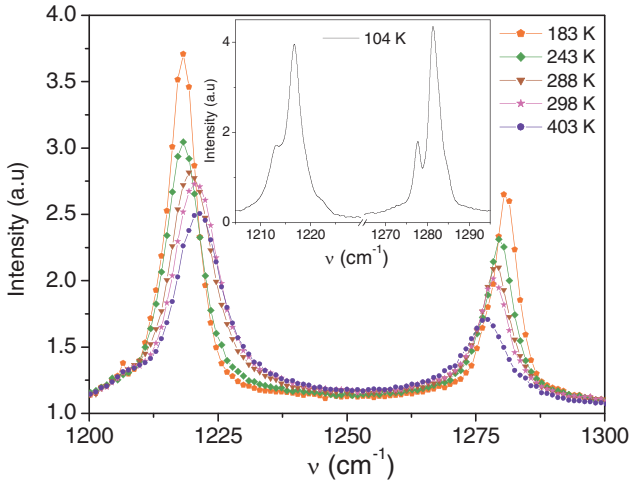


FIG. 3 (color online). Raman spectra at various temperatures obtained on single crystals of p-6P. The inset exhibits the more complex structure of these modes at low temperature.

tures when $\eta \approx 1$, the molecules show a static nonplanar conformation.

From the superlattice reflection whose intensity is proportional to the square of the order parameter $\eta \sim (T_c - T)^{\beta}$, one deduces the rather low value $\beta \approx 0.15 \pm 0.05$. This suggests the low dimensional nature of this phase transition resulting from the quasi–two-dimensional arrangement of these long oriented molecules.

The fundamental problem now concerns the reanalysis of the structural, electronic, and photonic processes in light of this phase transition. Because the last operates exactly at room temperature and most of the data were collected below that temperature, possible misinterpretations have been allowed. So, we have performed Raman measurements using a triple XY Raman spectrometer (DILOR/Jobin Yvon) and the 733.7 nm line of a Ti-Sapphire laser to improve resolution, spanning a range of temperature above and below T_c. We have focussed on two intramolecular modes displayed in Fig. 3 and identified as the inter-ring C-C stretch mode at 1278 cm^{-1} and the C-H in-plane bending mode at 1221 cm^{-1}[13,31,32]. Since these modes have been predicted to couple geometry to electronic structure most strongly [31,32], one can therefore expect an influence of this conformational transition. Indeed, one observes in Fig. 3 opposite shifts of the frequency for these modes with temperature. In order to get a more precise description, one has plotted in the upper panel of Fig. 4 the temperature dependence of these two modes. While the high frequency mode softens linearly with temperature as expected, we note that the other one displays an anomalous increase in the transition region. To avoid the regular temperature behavior, the difference $\Delta\nu = \nu_{1278} - \nu_{1221}$ is shown in the lower panel of Fig. 4, and thus reveals a singular dependence consistent with the discussed phase transition at $T_c = 293.5$ K. From our measurements, it appears that the frequency shift behaves as the x-ray intensity and thus as the square of the order parameter. While this result calls for further theoretical work to connect this frequency shift to the order parameter, we note that simulations carried out for the poly-para-phenylene displays a decrease in the frequency of the 1221 cm^{-1} mode for increasing torsional angle in qualitative agreement with Fig. 4 [31].

In the literature, previous authors [13] have interpreted the intensity ratio of these modes I_{1278}/I_{1221} to discuss planarity of these molecules up to room temperature without the knowledge of the reported phase transition. In this context, they use a Boltzmann description and extract an

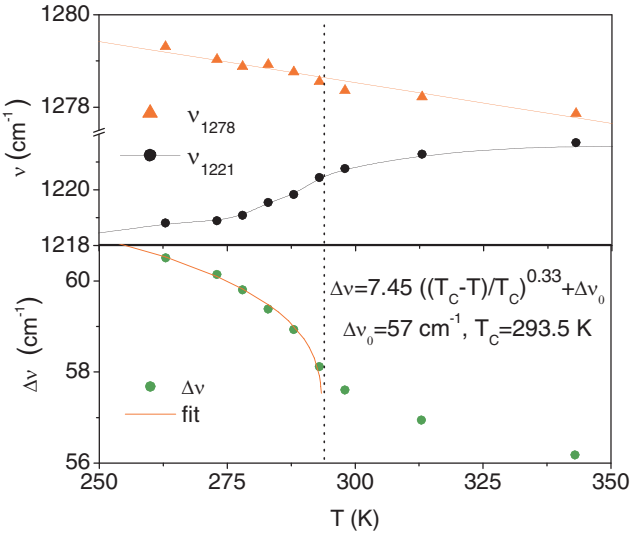


FIG. 4 (color online). Variation of the frequencies of the two main Raman modes ν_{1278} and ν_{1221} as a function of temperature (upper panel). The lower panel displays the temperature dependence of the difference $\Delta\nu = \nu_{1278} - \nu_{1221}$, where the subscripts indicate the high temperature frequencies.

activation energy for the local double-well potential of 480 K, quite different from the one reported here. Actually, since the nonplanarity evolution results from a phase transition governed by an order parameter one should thus expect a temperature dependence reflecting a singular behavior at T_c. While our experimental intensity ratio I_{1278}/I_{1221} seems to behave anomalously at the transition, it appears that it is too dependent on the fit procedure to be discussed confidently. Indeed, a lower temperature Raman spectrum as displayed in the inset of Fig. 3 reveals a complex structure of these modes, each of which consists of at least two peaks structure, while the high temperature broadening of these modes implies a sizeable overlap that prevents also any quantitative analysis of the areas.

Many other techniques are expected to probe this order-disorder phase transition since it involves both conformational and electronic states. In particular, photoluminescent data up to room temperature clearly show a redshift in both p-6P powders and films [33]. It is important to note that self-organization found in crystals is similar to the one found for powders and thin films [15] with exactly the same crystallographic parameters. As predicted by several authors in p-Polyphenyls, when the torsional angle between the phenyl ring decreases the overlap between the electronic wave functions is improved and thus the band gap is reduced [12]. So, one recovers an experimental result that could be reinterpreted considering the influence of the order parameter in light of this phase transition. Finally, it worth noting that the order of magnitude of the redshift is consistent with the previous theoretical prediction for a reasonable dihedral angle of the order of 20° [12], suggesting that numerous electronic properties should be reexamined in detail.

In this Letter, we show that hexaphenyl offers a unique opportunity to address the fundamental question of the structural organization of an organic optoelectronic material. The first evidence of a phase transition is reported and analyzed, revealing different fundamental processes around the transition temperature. The saturation of different properties such as local double-well activation energy and transition temperature arises from the comparative study of oligophenyl from $n = 2$ to $n = 6$. Regarding this tendency, an analogous phase transition from planar to nonplanar conformation may be predicted in the polymer, with a critical temperature around room temperature. The analysis of both x-ray and Raman measurements reveal a singular dependence at the transition and suggests that this conformational change could also affect electronic properties such as photoluminescence. Because of the potential of these materials in optoelectronic and photonic devices, the related properties should be reconsidered in light of these structural changes.

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