J. Phys. Chem. A **2001,** *105,* 7759−7764

Two-Photon Spectroscopy of π-Conjugated Polymers: The Case of Poly[1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne] (PolyDCHD-HS)

Laura Moroni, Pier Remigio Salvi, and Cristina Gellini*

Laboratorio di Spettroscopia Molecolare, Dipartimento di Chimica, Universita' degli Studi di Firenze,
Via Gino Capponi 9, I-50121 Firenze, Italy

Giovanna Dellepiane,[†,‡] Davide Comoretto,[†,‡] and Carla Cuniberti[‡]

Istituto Nazionale di Fisica della Materia (INFM), Dipartimento di Chimica e Chimica Industriale,
Universita' degli Studi di Genova, Via Dodecaneso 31, I-16146 Genova, Italy

Received: February 21, 2001; In Final Form: May 30, 2001

The two-photon fluorescence excitation and optoacoustic spectra of red polyDCHD-HS in benzene solution at room temperature have been investigated in the 1600−750 nm exciting wavelength region (effective two-photon energy ∼1.55−3.31 eV). The spectra obtained by the two detection techniques are of comparable accuracy, and the observed band profiles are in good agreement. Two electronic band systems have been observed and assigned to two-photon allowed $A_g \rightarrow A_g$ transitions. Both A_g states are at energies higher than that of the strongly one-photon allowed $1B_u$ state. An estimate of the absolute two-photon absorptivity of polyDCHD-HS at 406.0 nm (∼3.05 eV) is given by means of the optoacoustic method. Our results are discussed on the basis of the current theories on electronic states of π-conjugated polymers and compared with reported data on these systems.

I. Introduction

Organic π-conjugated polymers have received considerable attention in the past years, and several studies have been reported on linear and nonlinear optical properties of these systems and on theoretical models for their interpretation.[1−9] Recent interest has grown for application in material science as potential candidates for photonic devices since the optical response may be varied through the insertion of appropriate substituents along the polymer units.[10−14] This opens attractive perspectives for controlling material properties by molecular engineering.

Assuming a C_{2h} symmetry for the polymer backbone, the energy ordering of the two lowest $\pi\pi^*$ excited states has been shown to be $2A_g/1B_u$ or, alternatively, $1B_u/2A_g$ as a function of several factors, including the bond alternation parameter and on-site and nearest-neighbors Coulomb interaction terms.[3,6−8,15,16] From a chemical point of view these quantities may be tuned acting on the polymer chemical nature, chain length and conformation, and sample morphology.[3,4] In polydiacetylenes (PDAs) for which two forms, blue and red, occur, the relative location of the two states depends, among other things, on the effective conjugation length, larger for the blue than for the red form. For instance, blue poly[1,6-bis(*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD) shows a two-photon resonance below the onset of the strong one-photon absorption.[17] Similarly, the lowest $\pi\pi^*$ state of blue poly 5,7-dodecadiyne-1,12-diyl-bis-ethyluretane (PDA-4U2) as a thin film on a glass substrate has been observed at 1.9 eV and assigned to the $2A_g$ state.[18] On the other hand, the situation is less definite for red polymers, probably due to the reduced conjugation length. While in poly-(4-BCMU) the $2A_g$ state is still found at energies lower than $1B_u$,[19,20] in red PDA-4U2 $1B_u$ and $2A_g$ are almost degenerate, around 2.33 eV.[18]

Gerade excited states have been probed by means of several spectroscopic techniques including two-photon,[2,21−26] transient absorption,[15,16,27] third harmonic generation,[17,18] and *z*-scan spectroscopy.[28] Two-photon absorption has the advantage with respect to other techniques of a direct detection of upper A_g states since the purely electronic transition from the ground state to $2A_g$ (and to all other A_g states, as well) is two-photon active.[29,30] In fact, two-photon spectroscopy has been instrumental in giving evidence of an A_g state below the strongly one-photon allowed $1B_u$ in linear polyenes[31−37] and in related systems such as retinal[38] and iso-tachysterol.[39]

Recently, poly[1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD-HS, see Figure 1), a polymer with high solubility in common organic solvents due to the insertion of long alkyl chains on the carbazolyl substituents, was obtained. The solid-state structure of this polymer is of the columnar type, with the columns formed by the polycarbazolyldiacetylene chains assembled in a hexagonal bidimensional lattice.[40] Previous reports on this polymer were concerned with photoinduced absorptions,[41−44] luminescence,[45] time-resolved studies,[46] guided propagation of light,[47,48] UV−vis absorption, fluorescence, and FT-Raman solution studies.[49]

In the present paper we will report the results of a two-photon spectroscopic investigation on the red form of polyDCHD-HS in benzene solution at room temperature in the spectral range 375−800 nm (∼3.31−1.55 eV) using both fluorescence and optoacoustic detection. The first detection system has been used because of the sizable fluorescence emission of the polymer in benzene[49] ($\eta \simeq 10^{-2}$). The second method relies instead on the shock wave generated in the sample by non radiative relaxation processes following light absorption.[50,51]

---

* To whom correspondence should be addressed. E-mail: cris@chim.unifi.it.

[†] INFM.

[‡] Dipartimento di Chimica e Chimica Industriale.

10.1021/jp010677o CCC: $20.00

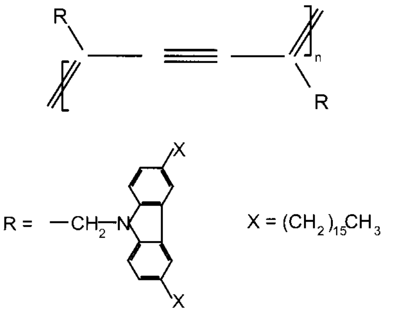

Figure 1. The molecular structure of poly[1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD-HS).

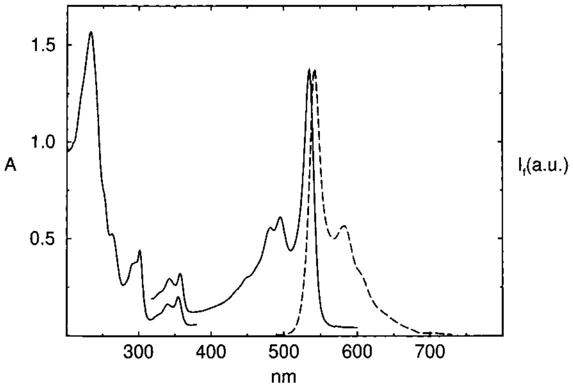

Figure 2. Absorption (solid line, absorbance units on the left) and fluorescence (dashed line; $\lambda_{exc} = 476$ nm; I_f, arbitrary units) spectra of a $\sim 10^{-5}$ M polyDCHD-HS solution in benzene. The intensity of the origin band in the fluorescence spectrum is normalized to that of the corresponding absorption band. The absorption spectrum below 300 nm has been measured using cyclohexane as solvent.

II. Experimental Section

PolyDCHD-HS has been synthesized according to the procedure described in ref 40 and stored in a small flask at room temperature in the dark. Solutions of polyDCHD-HS in the concentration range $10^{-3}-10^{-5}$ M were prepared using benzene-h_6 and -d_6 (both spectroscopic grade) as solvents, following considerations on improved quality and resolution of the one-photon spectrum with respect to other solvents.[49]

The exciting radiation for two-photon measurements comes from the idler beam of an optical parametric oscillator (OPO) pumped by the third harmonic (355 nm) of a ~10 ns pulsed Nd:YAG laser with 10 Hz repetition rate. Two different experimental arrangements were used according to the method chosen to probe the two-photon process. In the first, the incident beam, with a constant energy of ~280 μJ through all the spectral range of interest, is focused by means of a $f = 150$ mm lens on a 10 mm thick cell. The fluorescence induced by the two-photon transition is collected at 90° with respect to the incidence direction onto a photomultiplier placed behind an optical filter with a transmittance window between 500 and 600 nm, the region of the fluorescence emission (see Figure 2). A second filter, an infrared cutoff blocking the radiation in the range 730–2000 nm while transmitting in the visible, ensures a high straylight rejection. Despite these precautions it was not possible to prevent completely the detection of excitation light at wavelength below 800 nm. The upper scan limit of our fluorescence excitation spectrum was ~830 nm, while the lower 1600 nm.

In the second type of experiment (optoacoustic detection), the incident energy is smaller, ~160 μJ, and the focusing lens tighter than before ($f = 50$ mm) in order to match typical values of two-photon optoacoustic experiments.[51] An ultrasonic transducer (Panametrics V103–RM), in contact with the sample cell through a thin grease film, detects the pressure wave due to volume expansion of the small absorption region. An acoustic wave with amplitude P is generated because of heat conversion of the non radiatively relaxed part of the absorbed energy. In the linear absorption regime, P depends on several factors according to the expression[50]

$$P \propto \frac{\beta v_a}{C_p} \alpha E_0$$

where E_0 is the laser energy, β the thermal expansion coefficient, C_p the specific heat at constant pressure, v_a the acoustic velocity, and α the linear absorption coefficient of the medium. If the laser beam is tightly focused as in our case, the power density in the focal region increases and may give rise to nonlinear processes such as two-photon absorption.[50] The experimental conditions were optimized detecting first the two-photon optoacoustic signal of pure benzene-h_6[51] exciting at 497.4 nm (~2.49 eV). Being the method free from straylight detection, it was possible to study the polyDCHD-HS spectrum up to 750 nm. In addition, the linear optoacoustic spectra of the pure solvents (benzene-h_6 and -d_6) were measured between 750 and 1300 nm and used as reference to identify vibrational overtone bands of the solvent[52] in the solution spectra.

The one-photon absorption spectrum of polyDCHD-HS $\sim 10^{-5}$ M measured with a Cary 5 spectrophotometer at room temperature in the range 280–700 nm in benzene-h_6 and up to 200 nm in cyclohexane of spectroscopic grade is shown in Figure 2. In the same Figure is reported the fluorescence spectrum of the benzene solution taken exciting at 476 nm with a conventional spectrofluorimeter (JASCO FP-750, $\Delta\lambda_{exc} = 10$ nm, $\Delta\lambda_{em} = 10$ nm). The spectrum was found to be substantially similar to that obtained by exciting with laser radiation at 476 nm ($\Delta\lambda_{exc} = 0.2$ nm, $\Delta\lambda_{em} = 0.3$ nm) apart from a better spectral resolution in the last case. The fluorescence spectrum of polyDCHD-HS in cyclohexane has lower intensity and higher diffuseness than in benzene.

Finally, an attempt was made to estimate the contribution of the carbazolyl residue to the one- and two-photon absorption of polyDCHD-HS. To this purpose carbazole (from Aldrich) was purified several times by recrystallization from ethanol and benzene. The one-photon spectrum of carbazole $\sim 10^{-4}$ M in benzene and cyclohexane was taken on the Cary 5 spectrophotometer. Comparing these results with those from Figure 2, it is evident that the high energy parts of the polyDCHD-HS spectrum, from 360 to 200 nm, with the strongest bands at 354, 301, and 233 nm, have to be assigned to electronic transitions of the carbazolyl substituent. The fluorescence excitation spectrum of carbazole $\sim 10^{-3}$ M in benzene solution was measured in the 830–1300 nm range with the same optical arrangement used for polyDCHD-HS.

The two-photon spectra of polyDCHD-HS and carbazole were acquired point by point, i.e., measuring at each wavelength the sample and incident signal and then switching to the next wavelength, 2.5 nm away, for a new measurement. Given the large number of points, the actual profile has been easily interpolated and replaced by continuous lines.

III. Results

The fluorescence excitation spectrum of polyDCHD-HS $\sim 10^{-3}$ M in benzene solution at room temperature in the range 830–1300 nm (~1.49–0.95 eV) is shown in Figure 3. No

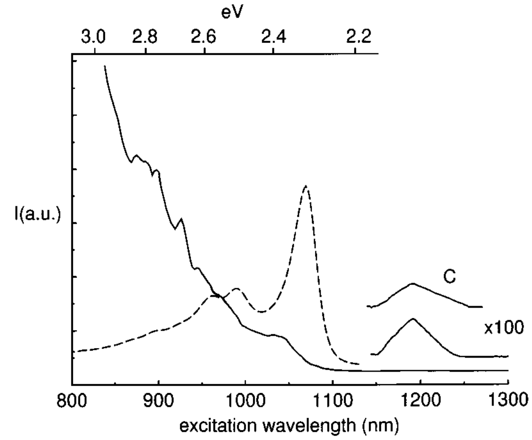

Figure 3. The two-photon fluorescence excitation spectrum of polyDCHD-HS ~10^{-3} M in benzene. Lower abscissa scale: exciting wavelength. Upper abscissa scale: effective two-photon energy (eV). On the right: fluorescence excitation spectra of pure carbazole (C) and of polyDCHD-HS (both ~10^{-3} M in benzene; equal incident intensities; 1150−1300 nm spectral range; ×100 scaled) due to five-photon processes (see text for details). The one-photon spectrum of polyDCHD-HS ~ 10^{-5} M in benzene is reported as a dashed line in the figure for the sake of comparison.

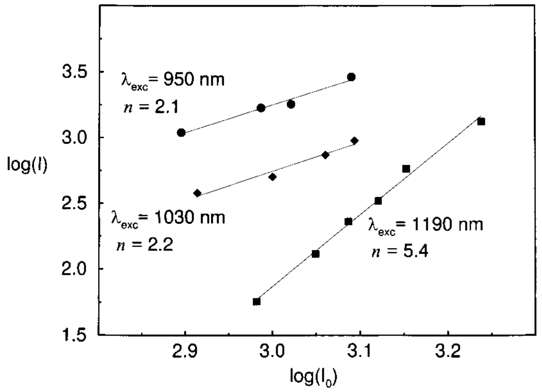

Figure 4. Dependence of the fluorescence signal on the incident intensity (expressed as $\log I \propto n \log I_0$) by exciting at 950, 1030, and 1190 nm. The slope n of the linear relation defines the number of photons involved in the absorption process at the indicated wavelength.

substantial difference is found in the spectral profile varying the concentration between 10^{-3} and 10^{-5} M. The spectrum shows two absorption regions: a first band, very weak and with maximum around 1190 nm (~ 1.04 eV, with reference to the exciting wavelength), and a structured absorption extending from ~1070 nm (~1.16 eV) to ~830 nm (~1.49 eV) with a first band around 1030 nm (~1.20 eV) and increasing intensity toward lower wavelengths. No absorption is observed above 1300 until 1600 nm (~0.95−0.77 eV).

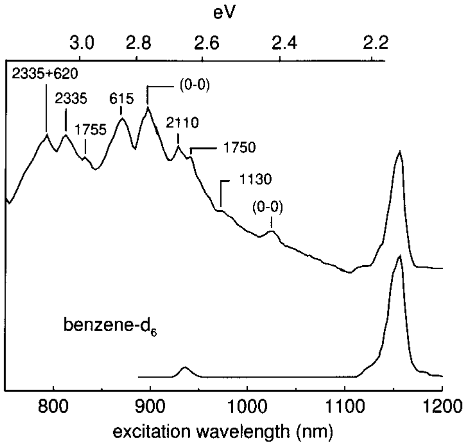

Figure 5. Upper: the optoacoustic spectrum of polyDCHD-HS ~ 10^{-3} M in benzene-d_6 by exciting in the spectral range 750−1200 nm. The upper abscissa scale (eV) indicates the effective two-photon energy. Origin bands and main vibronic intervals (cm^{-1}) are also indicated in the figure. Lower: the optoacoustic spectrum of pure benzene-d_6 between 900 and 1200 nm showing the third and fourth C−D overtone.

The order of the absorption process is different in the two regions. Accurate measurements were carried out about the dependence of the induced fluorescence signal I on the incident intensity I_0 to establish the number of photons n involved in the nonlinear process. The results are shown in Figure 4, where it may be seen that by exciting at both 1030 and 950 nm wavelengths, the fluorescence signal follows a quadratic dependence on the incident intensity. This result means that a two-photon transition occurs at these wavelengths. The same dependence is found for other excitation wavelengths included in the second region so that all the observed absorption below 1070 nm up to 830 nm is attributed to two-photon processes. On the contrary, the 1190 nm band depends on a number of photons higher than 2. An average value of ~5.4 is estimated from Figure 4, and therefore, the band has been assigned to a five-photon process. Since the same band with equal dependence on incident intensity is observed in pure carbazole (~10^{-3} M in benzene, room temperature; see Figure 3) while no signal is detected from the solvent alone, it was concluded that the 1190 nm band corresponds to an excitation localized on the carbazolyl residue.

The 1070−830 nm two-photon absorption region is due to $\pi\pi^*$ transitions of the polymer chain given that the lowest absorption of the carbazolyl residues occurs around 350 nm. The comparison with one-photon data on polyDCHD-HS in the appropriate energy range (see Figure 3) shows the pronounced difference between the two spectra, as expected for a centrosymmetric system. The origins fall at 534.0 nm (~2.32 eV, one-photon) and at 515.0 nm (~2.41 eV, two-photon). The one-photon vibronic structure, observed at 1512, 2072, 3595, ~4280 cm^{-1} from (0−0) and reasonably assigned to double and triple C−C stretching modes and their combinations,[45] has no two-photon counterpart. In addition, the two spectra show intensity profiles opposite one to the other as a function of decreasing wavelength. These points may be taken as evidence of two-photon activity for states, electronic and/or vibronic, one-photon silent.

The optoacoustic spectra of polyDCHD-HS have been measured both in benzene-h_6 and -d_6 solutions ($c \simeq 10^{-3}$ M) between 1200 and 750 nm (~1.03−1.70 eV) at room temperature. Two contributions to the optoacoustic signal are considered in this work, one linear as a function of the incident intensity and due to solvent C−H (or C−D) overtones and a second quadratic, related to two-photon processes of the solute. In the spectral region under investigation the second and third C−H overtone are found at 1190 and 880 nm, in agreement with reported data,[52] while the third and fourth C−D overtones are at 1150 and 930 nm. Being, however, the overtone intensities of benzene-d_6 weaker than those of -h_6, the two-photon spectrum of polyDCHD-HS in benzene-d_6 results in being less distorted because there are less overlapping linear signals in its spectrum than there are in that of benzene-h_6. The two-photon spectrum of polyDCHD-HS in benzene-d_6 is presented in Figure 5. There is consistency between fluorescence excitation and optoacoustic sets of data because radiative and nonradiative relaxation processes of comparable yield are probes for detection of the two-photon transitions. Band maxima are, however, better appreciated from the optoacoustic spectrum as it shows on the whole higher resolution. The spectrum may be split into two regions of quite different intensity, below and above 900 nm (~1.38 eV), according to the proposed assignment of the next section.

IV. Discussion

The lowest $\pi\pi^*$ states of polyDCHD-HS have been classified as belonging to A_g and B_u symmetry species on the basis of an *all-trans* (C_{2h}) geometry of the polymer backbone.[4,53,54] As a result, in the dipole moment approximation, one- and two-photon selection rules concerning electronic transitions starting from the ground state ($1A_g$) are mutually exclusive: $1A_g \rightarrow nA_g$ ($n \geq 2$) are two-photon allowed though one-photon forbidden, while the opposite is valid for $1A_g \rightarrow nB_u$ ($n \geq 1$) transitions. However, B_u states may be two-photon active when vibronic coupling with A_g or B_g states is considered. In the first case this leads to a vibronic $B_u \times b_u = A_g$ excitation and in the second to a $B_u \times a_u = B_g$ excitation. In a first approximation, the second route, i.e., $1A_g \rightarrow B_u \times a_u$, may be excluded from our analysis as B_g states are expected to have predominant $\pi\sigma^*$ (or $\sigma\pi^*$) character and therefore energy much higher than that of $\pi\pi^*$ A_g states, thus not favoring the vibronic mixing.

Our experimental results indicate that the origin of the two-photon absorption spectrum occurs at 514.0 nm (~2.41 eV, average between optoacoustic and fluorescence excitation values), ~730 cm^{-1} above the origin of the $1B_u$ state. Following previous considerations the two alternatives for band assignment, i.e., (i) as a $A_g \rightarrow B_u \times b_u$ vibronically induced transition due to a b_u mode (730 cm^{-1}, excited-state frequency) or (ii) as an allowed transition, either to the origin, $A_g \rightarrow A_g$, or to a higher lying vibronic state, $A_g \rightarrow A_g \times a_g$, should be discussed.

In aromatic molecules two-photon activity of the lowest $\pi\pi^*$ excited states, generally of u symmetry, has vibronic character, mostly due to false origins built on u vibrational modes ("Kekule modes") coupling efficiently the ground with the final $\pi\pi^*$ state.[29,30,55-57] This does not occur in the two-photon spectra of linear polyenes.[1] While there is a strong evidence about the $2A_g$ origin being at an energy lower than that of $1B_u$ and much information concerning the associated Franck–Condon $2A_g \times a_g$ structure, no experimental observation has been reported nor suggestion advanced on two-photon active $1B_u \times b_u$ transitions in these systems.[1,58] On this basis, the second choice should be preferred and accordingly the 514.0 nm band is assigned as an allowed transition. We note also that the fluorescence quantum yield of polyDCHD-HS is relatively high,[49] $\eta \simeq 10^{-2}$, and that the fluorescence and one-photon absorption spectra have clear mirror symmetry and a small energy gap, ~ 0.03 eV, between origin bands (see Figure 2). Since these spectral properties depend sensibly on the $2A_g/1B_u$ relative location,[15,18,27] these data suggest that the origin of the $1B_u$ state lies below that of the $2A_g$ state in polyDCHD-HS. As a consequence, the observed origin of the two-photon spectrum at 514.0 nm should correspond to the (0–0) $1A_g \rightarrow 2A_g$ transition. The Franck–Condon structure built on this band is weakly visible: three bands, ~1130, 1750, and 2110 cm^{-1} from the spectral origin, are sufficiently defined. The first and the third have been assigned to C–C single and triple bond stretchings, respectively, in agreement with ground-state results.[45] The second is in good agreement with the frequencies of C–C double bond stretching of linear polyenes in the $2A_g$ state,[37] which increase to 1740–1800 cm^{-1} from ground-state frequencies in the range 1550–1610 cm^{-1}.

It has been already noted the strong intensity increase of the optoacoustic spectrum exciting below 900 nm. It is unlikely that the well-developed band structure could be interpreted as a progression on the lower lying $A_g \times a_g$ vibronic bands. On the contrary, a second excited A_g state with origin at 448.5 nm (~2.76 eV) and vibronic additions 615, 1755, 2335, 2335 + 620 cm^{-1} is a more plausible attribution. Our assignment matches closely that recently proposed for a sequence of two A_g bands observed by second harmonic generation spectroscopy in PDA-4U2.[18] The reported energy gap between the two A_g states, 0.33 eV, is compatible with the 0.35 eV gap found in the present paper. Further, two or more A_g states were already identified by two-photon spectroscopy in other PDAs.[19,24,28]

High third-order nonlinearities have been measured for π-conjugated polymers.[3] As an example, the cubic susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ responsible for third harmonic generation is up to 4 orders of magnitude larger in polyDCHD than in silica and its spectral behavior has given evidence of the $2A_g$ state below the strong one-photon allowed $1B_u$.[17] These systems may be also characterized by the two-photon absorptivity δ[59] or by the two-photon absorption coefficient β. The absolute two-photon absorptivity in GM units (1 GM = 10^{-50} cm^4 sec molecule^{-1} photon^{-1}) of polyDCHD-HS $\simeq 10^{-3}$ M in benzene has been evaluated with optoacoustic detection by exciting around 812 nm (~ 1.53 eV). As a reference value, δ of the $A_g \rightarrow B_{2u} \times b_{2u}$ vibronic transition of pure benzene at $2\tilde{\nu} = 40\,212$ cm^{-1} was used. This value, equal to 0.1 GM, is usually taken as prototype value of vibronically induced two-photon intensity.[51] The average result of several measurements using in the two cases equal incident intensities and the same optical arrangement and, in addition, checking each time the quadratic dependence of the signal on I_0 is $\delta \simeq 10^4$ GM ($2\tilde{\nu} = 24\,630$ cm^{-1}, ~ 3.05 eV). This value corresponds to a two-photon absorption coefficient $\beta \simeq 0.2$ cm/GW, considering the relation[25,59] $\beta(2\tilde{\nu}) = \delta(2\tilde{\nu}) \cdot n^2 N/(\pi c h \tilde{\nu})$, where n is the refractive index, N the number density of absorbing species (molecules cm^{-3}), and $\tilde{\nu}$ the exciting frequency (cm^{-1}). Two-photon coefficients β have been already reported for crystalline systems, such as a film of poly(3-BCMU)[24] and a single crystal of PDA paratoluenesulfonate,[28] and are found to be 170 and 700 cm/GW, respectively, at their band maxima. Our result compares well with these data, considering that β depends on N and for our ~ 10^{-3} M solution N is approximately 3–4 orders of magnitude smaller than for crystalline systems.

Experimentally, no evidence of A_g bands below the origin of $1B_u$ comes from our study. The result should be related in our opinion to the short average conjugation length of red PDAs and to substituents whose overall effect is to shift $2A_g$ to energies higher than $1B_u$.[5] As to this point, however, particular attention was paid to the weak 1190 nm band of the fluorescence excitation spectrum (see Figure 3), naïvely attributed in a first moment to a two-photon band of polyDCHD-HS and then, by comparison with the spectrum of pure carbazole in the same experimental conditions, more properly to an electronic excitation of the carbazolyl residue. It is worth noting that in pure carbazole the band is part of a weakly structured five-photon absorption up to ~830 nm (~1.49 eV), not reported in this work, with an intensity ~10^{-2}–10^{-3} times that of polyDCHD-HS. The analysis of the carbazole spectrum is not object of the present work. Here we only advance two experimental considerations which favor the observation of a transition otherwise too weak to be detected. First, a strong absorption band with maximum around 230 nm (~0.39 eV) is observed in the one-photon spectrum of pure carbazole indicating the occurrence of an excited state at an energy approximatively 5 times that of the 1190 nm excitation photons. Second, virtual intermediate

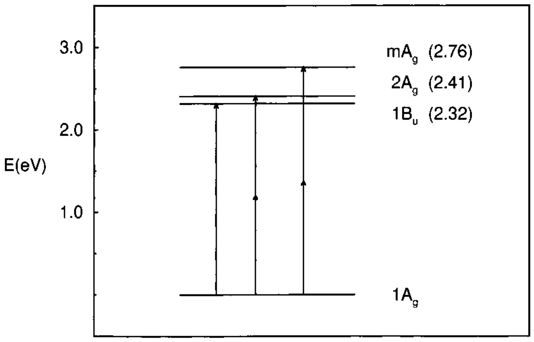

Figure 6. Energy level diagram of the first few excited $\pi\pi^*$ states of polyDCHD-HS resulting from this work and refs 40 and 49. The single arrow stands for one-photon, and double arrows for two-photon transitions.

levels of the five-photon process closely approach the real S_1 and S_2 levels of carbazole[60,61,62] so that the whole transition should be better viewed as a three-step, 3+1+1, process.

Finally, it is helpful to discuss briefly our results in the context of current theories on nonlinear optical effects in π-conjugated polymers considered as one-dimensional periodic systems.[5,6,8] In this approach a limited number of exciton $\pi\pi^*$ states is taken into account: (i) the lowest one-photon active $1B_u$; (ii) a unique charge-transfer A_g state, usually denoted as mA_g, having an extremely large dipolar coupling with $1B_u$; and (iii) a second B_u state, nB_u, which marks the conduction band onset and is strongly coupled to mA_g.[6,8] Within this theoretical framework three- and four-state models were assumed to calculate third-order susceptibilities and two-photon absorption.[9,19,63] In addition, it was found that for medium/large bond alternation values a more localized excitonic state, $2A_g$, has a high transition dipole with $1B_u$.[8] Despite this, the contribution to the two-photon spectrum of $2A_g$ was estimated much smaller than that of mA_g, due to cancellation effects between dipole products involving close lying B_u states, i.e., $\langle 1A_g|\mu|1B_u\rangle\ \langle 1B_u|\mu|2A_g\rangle$ and $\langle 1A_g|\mu|2B_u\rangle\ \langle 2B_u|\mu|2A_g\rangle$.[9] Qualitatively, our data fit satisfactorily the model once the second A_g band system starting at 448.5 nm (~2.76 eV) is assigned to the mA_g state.

V. Conclusions

In this work two-photon absorption spectroscopy has been employed to reveal electronic states of gerade symmetry in polyDCHD-HS in solution. Both fluorescence excitation and optoacoustic detection methods give two-photon results of comparable accuracy which have been discussed in terms of two allowed $A_g \rightarrow A_g$ $\pi\pi^*$ transitions. A schematic representation of the various energy levels of red polyDCHD-HS resulting from this and previous work[40,49] is summarized in Figure 6. As it may be seen in this figure, a major result of our study is the location of the lowest excited A_g state at about 90 meV above the strongly one-photon allowed $1B_u$ state in red polyDCHD-HS. This clearly shows the wide range of opportunities offered by molecular engineering to chemically modulate the electronic properties of PDAs. Moreover, the different location of the $2A_g$ with respect to the $1B_u$ state found in red PDAs provides evidence of the important role played by the nature of the substituents and by the conjugation length on the electronic properties of these polymers. Further two-photon studies on the polymer as a function of solvent and temperature are in progress to investigate on this point.

Acknowledgment. This work was supported by the Italian Consiglio Nazionale delle Ricerche (CNR) and by the Ministero dell'Universita' e della Ricerca Scientifica e Tecnologica (MURST). The authors are grateful to the referees for their suggestions and corrections.

References and Notes

(1) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; Vol. 6, p 1.

(2) Soos, Z. G.; Ramasesha, S.; Galvao, D. A.; Kepler, R. G.; Etemad, S. *Synth. Met.* **1992**, *54*, 35.

(3) Etemad, S.; Soos, Z. G. In *Spectroscopy of Advanced Materials*; John Wiley and Sons: New York, 1991; p 87.

(4) Soos, Z. G.; Galvao, D. S.; Etemad, S. *Adv. Mater.* **1994**, *6*, 280.

(5) McWilliams, P. C. M.; Hayden, G. W.; Soos, Z. G. *Phys. Rev. B* **1991**, *43*, 9777.

(6) Guo, D.; Mazumdar, S.; Dixit, S. N.; Kajzar, F.; Jarka, F.; Kawabe, Y.; Peyghambarian, N. *Phys. Rev. B* **1993**, *48*, 1433.

(7) Beljonne, D.; Cornil, J.; Shuai, Z.; Bredas, J. L.; Rohlfing, F.; Bradley, D. D. C.; Torruellas, W. E.; Ricci, V.; Stegeman, G. I. *Phys. Rev. B* **1977**, *55*, 1505.

(8) Chandross, M.; Shimoi, Y.; Mazumdar, S. *Phys. Rev. B* **1999**, *59*, 4822.

(9) Mazumdar, S.; Guo, F. *J. Chem. Phys.* **1994**, *100*, 1665.

(10) Sutherland, R. L. *Handbook of Nonlinear Optics*; Dekker: New York, **1996**.

(11) Pope, M.; Swenberg, C. E. In *Electronic Processes in Organic Crystals and Polymers*, 2nd ed.; Oxford Science Publishers: Oxford, 1999; p 1182.

(12) Schön, J. H.; Dodabapur, A.; Kloc, C. H.; Batlogg, M. B. *Science* **2000**, *289*, 599.

(13) Schön, J. H.; Dodabapur, A.; Kloc, C. H.; Batlogg, M. B. *Science* **2000**, *290*, 963.

(14) *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: New York, 1997; Vols. 1−4.

(15) Bourdin, E.; Davey, A.; Blau, W.; Delysse, S.; Nunzi, J. M. *Chem. Phys. Lett.* **1997**, *275*, 103.

(16) Frolov, S. V.; Bao, Z.; Wohlgenannt, M.; Vardeny, Z. V. *Phys. Rev. Lett.* **2000**, *85*, 2196.

(17) LeMoigne, J.; Thierry, A.; Chollet, P. A.; Kajzar, F.; Messier, J. *J. Chem. Phys.* **1988**, *88*, 6647.

(18) Manaka, T.; Yamada, T.; Hoshi, H.; Ishikawa, K.; Takezoe, H. *Synth. Met.* **1998**, *95*, 155.

(19) Torruellas, W. E.; Rochford, K. B.; Zanoni, R.; Aramaki, S.; Stegeman, G. I. *Opt. Commun.* **1991**, *82*, 94.

(20) Guo, D.; Mazumdar, S.; Dixit, S. N. *Nonlinear Opt.* **1994**, *6*, 337.

(21) Baker, C. J.; Gelsen, O. M.; Bradley, D. D. C. *Chem. Phys. Lett.* **1993**, *201*, 127.

(22) Periasamy, N.; Danieli, R.; Ruani, G.; Zamboni, R.; Taliani, C. *Phys. Rev. Lett.* **1992**, *68*, 919.

(23) Harrison, M. G.; Urbasch, G.; Mahrt, R. F.; Giessen, H.; Bässler, H.; Scherf, U. *Chem. Phys. Lett.* **1999**, *313*, 755.

(24) Banfi, G. P.; Fortusini, D.; Dainesi, P.; Grando, D.; Sottini, S. *J. Chem. Phys.* **1998**, *108*, 4319.

(25) Zhao, M.; Cui, Y.; Samoc, M.; Prasad, P. N.; Unroe, M. R.; Reinhardt, B. A. *J. Chem. Phys.* **1991**, *95*, 3991.

(26) Samoc, M.; Samoc, A.; Luther-Davies, B. *Synth. Met.* **2000**, *109*, 79.

(27) Haacke, S.; Berrehar, J.; Lapersonne-Meyer, C.; Schott, M. *Chem. Phys. Lett.* **1999**, *308*, 363.

(28) Lawrence, B.; Torruellas, W. E.; Cha, M.; Sundheimer, M. L.; Stegeman, G. I.; Meth, J.; Etemad, S.; Baker, G. *Phys. Rev. Lett.* **1994**, *73*, 597.

(29) Goodman, L.; Rava, R. P. *Acc. Chem. Res.* **1984**, *17*, 250.

(30) Callis, P. R. *Annu. Rev. Phys. Chem.* **1997**, *48*, 271.

(31) Hudson, B. S.; Kohler, B. E. *Chem. Phys. Lett.* **1972**, *14*, 299.

(32) Hudson, B. S.; Kohler, B. E. *J. Chem. Phys.* **1973**, *59*, 4984.

(33) Granville, M. F.; Holtom, G. R.; Kohler, B. E. *J. Chem. Phys.* **1980**, *72*, 4671.

(34) Fang, H. L. B.; Thrash, R. J.; Leroi, G. E. *J. Chem. Phys.* **1977**, *67*, 3389.

(35) Fang, H. L. B.; Thrash, R. J.; Leroi, G. E. *Chem. Phys. Lett.* **1978**, *57*, 59.

(36) Holtom, G. R.; McClain, W. M. *Chem. Phys. Lett.* **1976**, *44*, 436.

(37) Kohler, B. E.; Spangler, C.; Westerfield, C. *J. Chem. Phys.* **1988**, *89*, 5422.

(38) Birge, R. R.; Bennet, J. A.; Hubbard, L. M.; Pierce, H. F.; Kliger, D. S.; Leroi, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 2519.

(39) Pierce, B. M.; Bennet, J. A.; Birge, R. R. *J. Chem. Phys.* **1982**, *77*, 6343.

(40) Gallot, B.; Cravino, A.; Moggio, I.; Comoretto, D.; Cuniberti, C.; Dell'Erba, C.; Dellepiane, G. *Liquid Crystals* **1999**, *26*, 1437.

(41) Comoretto, D.; Moggio, I.; Dell'Erba, C.; Cuniberti, C.; Musso, G. F.; Dellepiane, G.; Rossi, L.; Giardini, M. E.; Borghesi, A. *Phys. Rev. B* **1996**, *54*, 16357.

(42) Comoretto, D.; Moggio, I.; Cuniberti, C.; Musso, G. F.; Dellepiane, G.; Borghesi, A.; Kajzar, F.; Lorin, A. *Phys. Rev. B* **1998**, *57*, 7071.

(43) Comoretto, D.; Moggio, I.; Cuniberti, C.; Dellepiane, G.; Giardini, M. E.; Borghesi, A. *Phys. Rev. B* **1997**, *56*, 10264.

(44) Comoretto, D.; Dellepiane, G.; Cuniberti, C.; Rossi, L.; Borghesi, A.; LeMoigne, J. *Phys. Rev. B* **1996**, *53*, 15653.

(45) Luzzati, S.; Moggio, I.; Comoretto, D.; Cuniberti, C.; Dellepiane, G. *Synth. Met.* **1998**, *95*, 47.

(46) Lanzani, G.; Stagira, S.; Cerullo, G.; DeSilvestri, S.; Comoretto, D.; Moggio, I.; Cuniberti, C.; Musso, G. F.; Dellepiane, G. *Chem. Phys. Lett.* **1999**, *313*, 525.

(47) Giorgetti, E.; Magheri, G.; Sottini, S.; Chen, X.; Cravino, A.; Comoretto, D.; Cuniberti, C.; Dell'Erba, C.; Dellepiane, G. *Synth. Met.* **2000**, *115*, 257.

(48) Giorgetti, E.; Magheri, G.; Gelli, F.; Sottini, S.; Comoretto, D.; Cravino, A.; Cuniberti, C.; Dell'Erba, C.; Moggio, I.; Dellepiane, G. *Synth. Met.* **2001**, *116*, 129.

(49) Alloisio, M.; Cravino, A.; Moggio, I.; Comoretto, D.; Bernocco, S.; Cuniberti, C.; Dell'Erba, C.; Dellepiane, G. *J. Chem. Soc., Perkin Trans. 2* **2001**, page 146.

(50) Patel, C. K. N.; Tam, A. C. *Rev. Mod. Phys.* **1981**, *53*, 517.

(51) Tam, A. C.; Patel, C. K. N. *Nature* **1979**, *280*, 304.

(52) Patel, C. K. N.; Tam, A. C.; Kerl, R. J. *J. Chem. Phys.* **1979**, *71*, 1470.

(53) Shuai, Z.; Beljonne, D.; Bredas, J. L. *J. Chem. Phys.* **1992**, *97*, 1132.

(54) Kohler, B. E.; Schilke, D. E. *J. Chem. Phys.* **1987**, *86*, 5214.

(55) Friedrich, D. M.; McClain, W. M. *Chem. Phys. Lett.* **1975**, *32*, 541.

(56) Salvi, P. R.; Marconi, G. *J. Chem. Phys.* **1986**, *84*, 2542.

(57) Salvi, P. R.; Foggi, P.; Castellucci, E. *Chem. Phys. Lett.* **1983**, *98*, 206.

(58) Bennet, J. A.; Birge, R. R. *J. Chem. Phys.* **1980**, *73*, 4234.

(59) Anderson, R. J. M.; Holtom, G. R.; McClain, W. M. *J. Chem. Phys.* **1979**, *70*, 4310.

(60) Bree, A.; Zwarich, R. *J. Chem. Phys.* **1968**, *49*, 3344.

(61) Chakravorty, S.; Ganguly, S. *J. Chem. Phys.* **1970**, *52*, 2760.

(62) Bree, A.; Taliani, C. *Chem. Phys. Lett.* **1983**, *98*, 62.

(63) Dixit, S. N.; Guo, D.; Mazumdar, S. *Phys. Rev. B* **1991**, *43*, 6781.