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Optical Properties of a Supramolecular Assembly Containing Polydiacetylene

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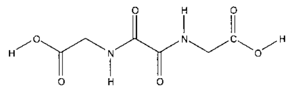
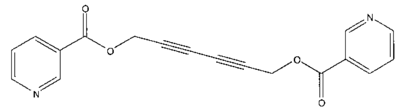
We report polarized optical measurements of a new type of single-crystal supramolecular assembly containing isolated chains of polydiacetylene (PDA): poly(1,6-bis(nictonyloxy)-2,4-hexadiyne). Room-temperature spectra reveal a large anisotropy, confirming the low-dimensional nature of the material. In particular, the characteristic optical signature of PDA correlates well with the chain orientation from the X-ray crystal structure. A near-infrared charge-transfer band is also observed, which we attribute to low-energy charge transfer from the polymer backbone to the pyridine rings. Temperature-dependent spectra reveal a weak doublet splitting of the optical bands, indicating a slight distortion of the side chains which contain the pyridine ring at low temperature.

I. Introduction

Supramolecular assemblies are multifunctional materials, which have the potential to be engineered for a specific purpose and/or multifunctionality. According to the structure of the functional groups, the constituent molecules automatically and preferentially arrange themselves into large supramolecular structures with long-range order in which the building block molecules are bound together by forces such as intermolecular hydrogen bonding or metal complexing. For instance, oxalamides, pyridones, and pyrimidones are functional groups that are well-known to assemble in one dimension via hydrogen bonding.[1−4] Donors and acceptors have also been incorporated in an organized way to control lattice size.[5] Mesoporous silica materials have been produced which contain functionalized monolayers.[6,7] Some examples of well-known supramolecular complexes assembled with metal−ligand interactions include porphyrins complexed with palladium ions, guanidinium−sulfonate hydrogen-bonded arrays, and gallium arsenide films.[8] Supramolecular assemblies and nanostructure materials have generated a great deal of attention lately due to the tunable nature of various physical properties such as photophysical response, electronic characteristics, and second-harmonic generation.[9]



1,6-bis-nictonyloxy-2,4-hexadiayne



N,N′-oxalyldiglycine

Figure 1. Chemical structure of 1,6-bis(nictonyloxy)-2,4-hexadiyne and *N,N′*-oxalyldiglycine, the two molecular building blocks of the cocrystal.

Recently, a polydiacetylene-containing cocrystal was synthesized using supramolecular chemistry to achieve a highly orientated structure. Here, the building blocks of the new cocrystal are 1,6-bis(nictonyloxy)-2,4-hexadiyne and *N,N′*-oxalyldiglycine (Figure 1). Incorporating a diacetylene with a pyridine functional group and a carboxyl polymer allows the building block molecules to organize via hydrogen bonding into a cohesive network. A thermal polymerization then creates the polymer chains. The result is well-ordered stack of self-assembled polymers in the *ac* plane with the PDA chains along the *a* direction, as shown in Figure 2. Essentially, the unit cell is composed of chromophoric PDA groups plus various space-filling groups (carboxyl polymer), which orientate the other components. That PDA can be readily incorporated into supramolecular assemblies provides microscopic control over molecular placement and spacing and, therefore, may ultimately lead to new strategies and improved control of both linear and nonlinear optical properties.

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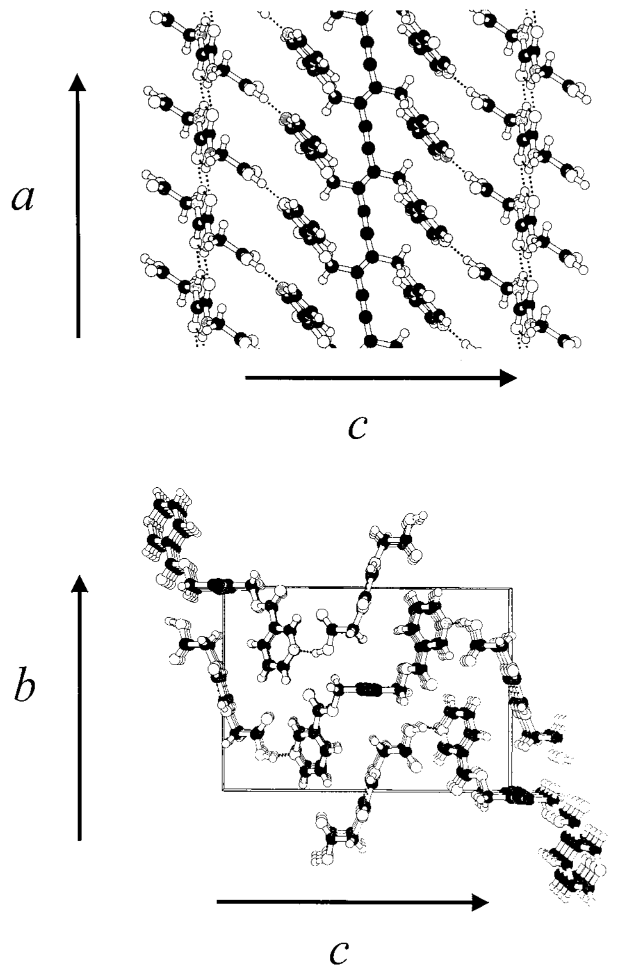

Figure 2. (Upper panel) crystal structure of poly(1,6-bis-(nictonyloxy)-2,4-hexadiyne) cocrystal in the *ac* plane and (lower panel) crystal structure of poly(1,6-bis(nictonyloxy)-2,4-hexadiyne) cocrystal in the *bc* plane. Note that the PDA chains run along the *a* direction.

Previous optical studies of more traditional PDA-based single crystals, such as polydiacetylene-bis(toluene sulfonate) (PTS),[10−12] 1,6-di-*N*-carbazolyl-2,4-hexadiyne (DCHD),[13,14] and poly-5,7-dodecadiyne-1,12-diol-bis(phenylurethane) (TCDU-A),[15,16] demonstrate a strong optical response in the visible regime. Room-temperature data has the lowest energy electronic transition (excitonic in nature) in the 15000−16000 cm^{-1} range, with vibronic structure at higher energy (17000−21000 cm^{-1}). These features correlate to the electronic and coupled vibrational transitions in the PDA polymer backbone. The temperature-dependent spectra for PTS show a pronounced splitting of the electronic and vibronic bands at 5 K attributed to a second-order phase transition (∼190 K) with a doubling of the unit cell along the parallel chain direction.[9] PDA has also been of sustained interest as a nonlinear optical material.[17,18] More recently, PDA has been incorporated into a variety of multilayed materials using self-assembly techniques.[19−21]

To ascertain the optical constants of poly(1,6-bis-(nictonyloxy)-2,4-hexadiyne), we have measured the polarized optical reflectance of the cocrystal sample as a function of temperature. Our goal is to understand the electronic nature of the material and correlate the optical response with the overall molecular orientation in the crystal.

II. Experimental Section

Single crystals of poly(1,6-bis(nictonyloxy)-2,4-hexadiyne) were prepared from 1,6-bis(nictonyloxy)-2,4-hexadiyne and *N*,*N*′-oxalyldiglycine (Figure 1) in the presence of methanol to construct the supramolecular assembly (Figure 2).[22,23] A thermally allowed topochemical reaction occurs, whereby the diacetylene units rotate slightly to convert to polydiacetylene. The "derived name" of the polymer might be the PDA of the bis-nicoinate of 2,4-hexadiyn-1,6-diol, although our cocrystal was actually made by a coupling process. The crystal has an average sample width of ∼0.15 mm, and a mosaic was prepared for the reflectance measurements. The sample has a metallic gold luster, which reflects red in the *c* direction. The space group is $P2_1/n$ with the following cell constants for a monoclinic lattice: a −4.884 ±4 Å, b −13.015 ±14 Å, c −18.585 ±27 Å, and β −91.03 ± 10°. The large face is defined by the *ac* (010) plane, as shown in Figure 2. The closest approach of the pyridine ring to the polymer backbone is ∼4.65 Å.

Near-normal polarized optical reflectance spectra of the cocrystals were measured in the *ac* plane with a modified Perkin-Elmer λ-900 spectrometer in the 4800−33000 cm^{-1} energy range. An aluminum mirror was used as the reference. The optical axes of the crystal were determined as those displaying the greatest anisotropy at 300 K, and analysis of the structure shows good correspondence with the *a* and *c* directions. For each polarization, reflectance measurements were made at several temperatures between 300 and 10 K. Temperature control was achieved using an open-flow cryostat. After completion of these measurements, an aluminum overcoat (∼200 nm Al) was used to correct for the mosaic nature of the sample as well as the surface scattering to obtain the absolute reflectance spectra.

A Kramers−Kronig analysis of the reflectance spectra was used to obtain the optical constants of the cocrystal. This analysis calculates the complex dielectric function

$$\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) = \epsilon_1(\omega) + \left\{\frac{4\pi i}{\omega}\right\}\sigma_1(\omega) \qquad (1)$$

from the measured reflectance and the phase shift integral. Here, $\epsilon_1(\omega)$ is the real part of the dielectric function, and $\sigma_1(\omega)$ is the optical conductivity. Thus, $\epsilon_1(\omega)$ tells us how a material disperses energy, whereas $\sigma_1(\omega)$ provides information on the lossy response. $\sigma_1(\omega)$ is related to the absorption as $\alpha(\omega) = [4\pi\sigma_1(\omega)]/[n(\omega)c]$ where $n(\omega)$ is the refractive index.[24] Therefore, it measures frequency-dependent dissipation. Our high-fre-

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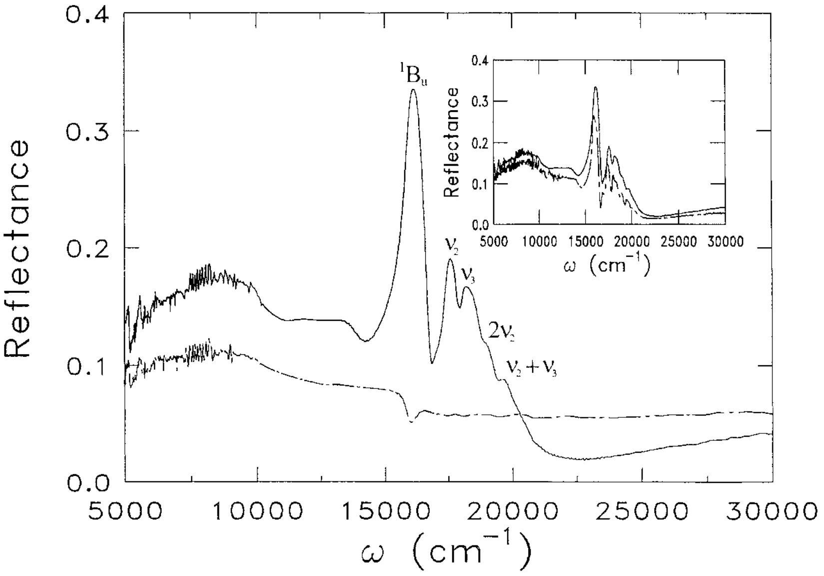

Figure 3. Room-temperature reflectance spectra of the poly(1,6-bis(nictonyloxy)- 2,4,hexadiyne) as a function of frequency: solid line, *a* direction; dashed line, *c* polarization. Inset: Power reflectance of the poly(1,6-bis(nictonyloxy)-2,4-hexadiyne) as a function of frequency at 300 (solid line) and 10 K (dashed line) in the *a* polarization.

quency data were extrapolated as $\omega^{-1.50}$, and the low-frequency data extrapolated to zero frequency as a constant, appropriate for a semiconductor.[24] Advantages of measuring both the optical conductivity and dielectric constant is that it can provides useful information for potential device applications.

III. Results and Discussion

A. Room-Temperature Spectra. The 300 K power reflectance of poly(1,6-bis(nictonyloxy)-2,4,hexadiyne) is shown in Figure 3 for the two principal polarization directions. This cocrystal is highly anisotropic, with signature PDA bands in the optical regime present only along *a*. These bands are fairly narrow and well-defined, indicating a well-oriented sample, which is expected for a cocrystal with an organized network of polymer chains and space filling/directing groups. In other highly orientated PDA crystals, similar anisotropy has been observed.[14,15]

The electronic excitation centered near 16000 cm^{-1} (Figure 3) corresponds to a $\pi \rightarrow \pi^*$ excitation for the conjugated backbone in the diacetylene portion of the cocrystal. This feature is assigned as a ^1B_u exciton, consistent with previous investigations of other PDA crystals.[16,25] Vibronic features are observed on the higher energy side of the ^1B_u exciton, and these features are separated by vibrational quanta. For instance, higher energy peaks are due to the vibronic structure associated with ν_2, ν_3, and their combination modes, such as $2\nu_2$ and $\nu_2 + \nu_3$. Here, ν_2 and ν_3 are characteristic vibrational frequencies in the system due to the carbon double-bond and triple-bond stretching vibrations, respectively. These vibrational features are common to the polymer backbone and are observed in other PDA crystals.[15,25,26] For instance, the high-energy vibronic structures in PTS and DCHD are almost identical to those in our sample.

The spectra in Figure 3 also display a broad electronic band in the near-infrared (NIR) region (5000−10000 cm^{-1}) for both *a* and *c* polarizations. The intensity of the band is slightly stronger along *a*. We assign this feature as a charge-transfer excitation, and several molecular-level origins are possible. The NIR structure may be related to a charge transfer from the PDA backbone to the electron-deficient pyridine rings in the cocrystal. X-ray studies show that the proton is located on an oxygen of the carboxylic acid which is hydrogen-bonded to the nitrogen of the pyridine ring, so the cocrystal is not a salt.[27] Despite this fact, the electron affinity of the ring should be reasonable. The 4.65 Å distance from the pyridine ring to the polymer backbone also makes this scenario attractive. However, the pyridine rings have an 80° dihedral angle with respect to the diacetylene plane, meaning they are nearly orthogonal; this makes charge transfer more difficult. A second less likely possibility is that following a local charge disproportion (separation) on the diacetylene and pyridine groups (perhaps involving the nearby carboxyl group), low-energy hopping takes place between rings. Ring-to-ring spacing of ~4.9 Å (essentially, the length of the *a* axis) supports this supposition, and such local charge-transfer mechanisms are well-known in a variety of molecular systems.[28] That the broad NIR electronic feature is unique to the cocrystal indicates the likely involvement of the pyridine rings in the charge transfer. Indeed, observation of this structure extends the number of potential photophysical and electronic processes that can be encountered in PDA-based materials.

B. Temperature Dependence. The inset in Figure 3 displays the full power reflectance spectra of poly(1,6-bis(nictonyloxy)-2,4-hexadiyne) at 300 and 10 K along

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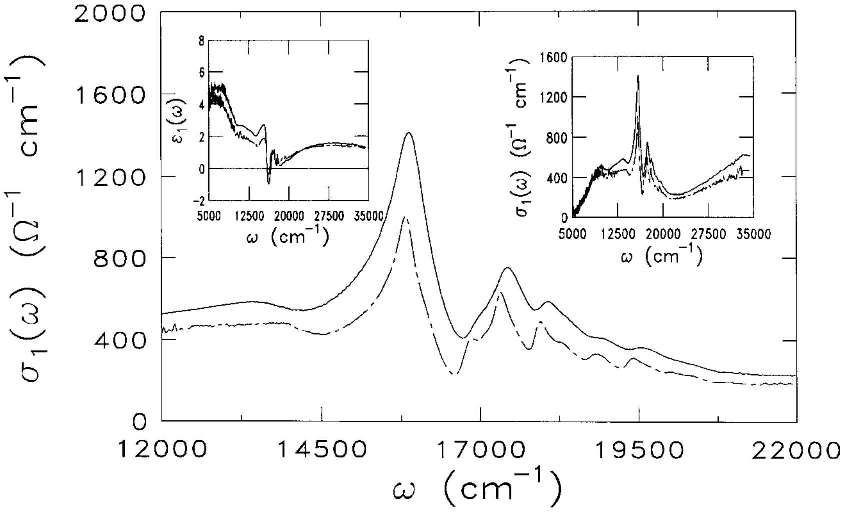

Figure 4. Frequency-dependent optical conductivity of poly(1,6-bis(nictonyloxy)-2,4-hexadiyne) along the *a* direction as a function of temperature: right inset, full view of the optical conductivity as a function of frequency; and left inset, dielectric constant as a function of frequency for poly(1,6-bis(nictonyloxy)-2,4-hexadiyne); solid line, 300 K; dashed line,10 K.

the chain direction. There is an overall decrease in the reflectance at low temperature, which translates into lower residual conductivity in Figure 4. A weak doublet structure on the bands between 17000 and 20000 cm^{-1} is observed as well. The doublet structure develops gradually, becoming more pronounced with decreasing temperature. The charge-transfer feature displays reduced oscillator strength at low temperature, likely the result of slight twists of the pyridine ring.

Figure 4 displays the optical conductivity of poly(1,6-bis(nictonyloxy)-2,4,hexadiyne) along the *a* axis at 300 and 10 K. A characteristic doublet structure is observed in the PDA-related bands at low temperature, indicative of additional charge localization or structural distortion in the material. Similar behavior has been observed in other forms of PDA and was attributed to a second-order phase transition with a doubling of the unit cell along *a*, and/or a slight modification of the side-group orientation.[9] For instance, in PTS the occurrence of the unit cell doubling produces splitting in the reflectance spectrum below 190 K.[29] However, the doublet character of these modes in our cocrystal appears progressively over the full temperature range of investigation, suggesting that the sample reaches low temperature without a well-defined structural transition. This indicates that the side-chain distortion, the likely origin of the doublet structure in our cocrystal, is not dramatic. Finally, it is notable that the PDA signature bands between 15000 and 20000 cm^{-1} are red-shifted at low temperature relative to the 300 K positions. This slight red-shift may be due to electron−phonon coupling, where the degree of red-shift corresponds to the strength of the coupling constant.[30,31]

The right-hand inset of Figure 4 shows the full range of the optical conductivity. Note that $\sigma_1(\omega) \rightarrow 0$ at low frequency, as expected for a semiconductor. We estimate the optical gap, 2Δ, as $\sim$5000 cm^{-1}; it is fairly independent of temperature. The left-hand inset of Figure 4 displays the real part of the dielectric constant as a function of frequency at 300 and 10 K. The value of the dielectric constant as $\omega \rightarrow 0$ is $\sim$4.5, which is a low value consistent with the semiconducting nature of the material. The value of the dielectric constant as $\omega \rightarrow 0$ is $\sim$1.5, indicating that most of the oscillation strength is accounted for in the Kramers−Kronig calculation.

IV. Conclusion

We report the polarized optical reflectance spectra of poly(1,6-bis(nictonyloxy)-2,4,hexadiyne) as a function of temperature, and calculated the optical constants of the material using a Kramers−Kronig analysis allowing us to extract both real and imaginary dielectric response. Major spectral features include characteristic PDA bands in the optical regime (which are strongly polarized along the chain direction), a NIR charge-transfer band related to electron-deficient pyridine rings structures, and doublet structure in the PDA bands at low temperature which we attribute to a slight distortion of the ring-containing side groups of the PDA. Overall, the cocrystal does not seem to display any sudden structural modification with temperature. It is an important attribute of engineered materials with multifunctionality that the molecular placement should be maintained over a wide temperature range. Thus, it is likely that the extension to incorporate other elements (such as polytriacetylene) or dopants into the system will be profitable.

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