

Morphology and optical properties of tetracyano-*p*-xylene single crystals

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We report on a class of organic single-crystal semiconductors (tetracyano-*p*-xylene) with tunable blue-green emission. The crystalline structure, the shape and orientation of the constituent molecules, and the bond length have been determined by atomic force microscopy and compared with the results of x-ray diffraction. The obtained structural parameters were used to evaluate the electronic states and to calculate the optical absorption spectra of the crystal. Due to the nonplanar geometry of the tetracyano-*P*-xylene molecules and to the closely packed arrangement, the individual character of the molecule is not preserved in the crystalline phase, and a precise description of the optical spectra is obtained by considering molecular clusters consisting of at least three molecules with bond length and symmetry identical to that obtained by the structural experiments. [S0163-1829(98)52316-8]

The increasing interest in organic materials has pushed up the research on organic semiconductor crystals of easy processability and low cost for optoelectronic applications.^{1,2} The main advantage of these systems is the relatively simple way of engineering their optical and electronic properties by chemical addition of suitable groups or by electrochemical doping.

In this Rapid Communication we report on a class of highly pure, single-crystal organic semiconductors, the tetracyano-*p*-xylene (TCNX) ($C_{12}N_4H_6$), which exhibit a very efficient blue-green tunable emission. The data presented in this paper were obtained by using an electron acceptor molecule, the tetracyano-*p*-quinodimethane (TCNQ) both as starting reagent and dopant in different solutions, resulting in an organic semiconductor compound based on a TCNQ hydrogenated form. The TCNX crystals crystallize from saturated solutions of TCNQ containing small amounts of 1,8 octanedithiol. We show that closely packed molecular crystals form with typical intermolecular bonding length of 3.8 Å and chain length of 5.85 Å. The crystal structure obtained by the simulation of the x-ray diffraction patterns is fully consistent with that measured directly by high-resolution atomic force microscopy (AFM). The high-quality crystals exhibit semiconductorlike optical properties, namely strong blue-green luminescence and sharp Frenkel-like excitation resonances in the absorption spectra. Our calculations, based on the complete neglect of differential overlap (CNDO) method, reveal that the absorption spectrum of the crystal is affected primarily by the intermolecular interaction, and can be described quite accurately only if the measured molecular deformation and bonding length in the crystalline phase are taken into account.

The crystal growth was catalyzed by the formation of self-assembled dithiol monolayers that spontaneously form in ethanol solution and act as substrates for the TCNX crystals. The shape and color of the single crystals were found to depend crucially on the growth temperature and on the solvent used. White transparent platelets were grown at room

temperature (RT) from solutions of TCNQ in acetonitrile. Pale yellow needle-shaped crystals were instead obtained at RT using saturated ethanol solutions of TCNQ, due to the presence of unreacted TCNQ as a substitutional impurity in the TCNX lattice. Higher growth temperatures ($\leq 70^\circ C$) in the presence of excess TCNQ, result in a dark-green mixture characterized by the coexistence of neutral and ionized TCNQ molecules and TCNX. In other words a proper control of the growth conditions yields a family of materials: spanning from highly pure TCNX crystals emitting in the blue to a compound containing TCNX and excess of TCNQ emitting in the green. Furthermore, the band gap of TCNX was found to reduce with increasing the TCNQ content, together with a concomitant enhancement of the emission efficiency.

The structural analysis of the crystals was carried out by means of x-ray diffraction (XRD) and confirmed by atomic force microscopy with atomic resolution of the (100) surface. Diffraction data have been collected, at room temperature with the Siemens automated four-circle single-crystal diffractometer R3m/V. The structure was determined by a standard procedure using the commercial SHELXL93 software package. The experiments reveal the excellent crystalline ordering of the grown structures and provide the bonding length and the unit cell structure. The XRD measurements show that the highly pure and the slightly doped TCNX crystals have the same structure with space group $C2/c$. The unit cell of the crystal [Fig. 1(a)] has a monoclinic structure and contains four molecules, where shape is described in detail in Fig. 1(b).

The crystal may be viewed as a stack of (001) planes, separated by about 3.8 Å, containing chains of molecules with aromatic rings parallel to each other in the stacking direction. Such a packed structure ensures a strong overlap between the aromatic π electrons orbitals, so that a high degree of electron delocalization is expected along the stacking axis. In the following we will show that, unlike the most common organic materials, such electron interaction between

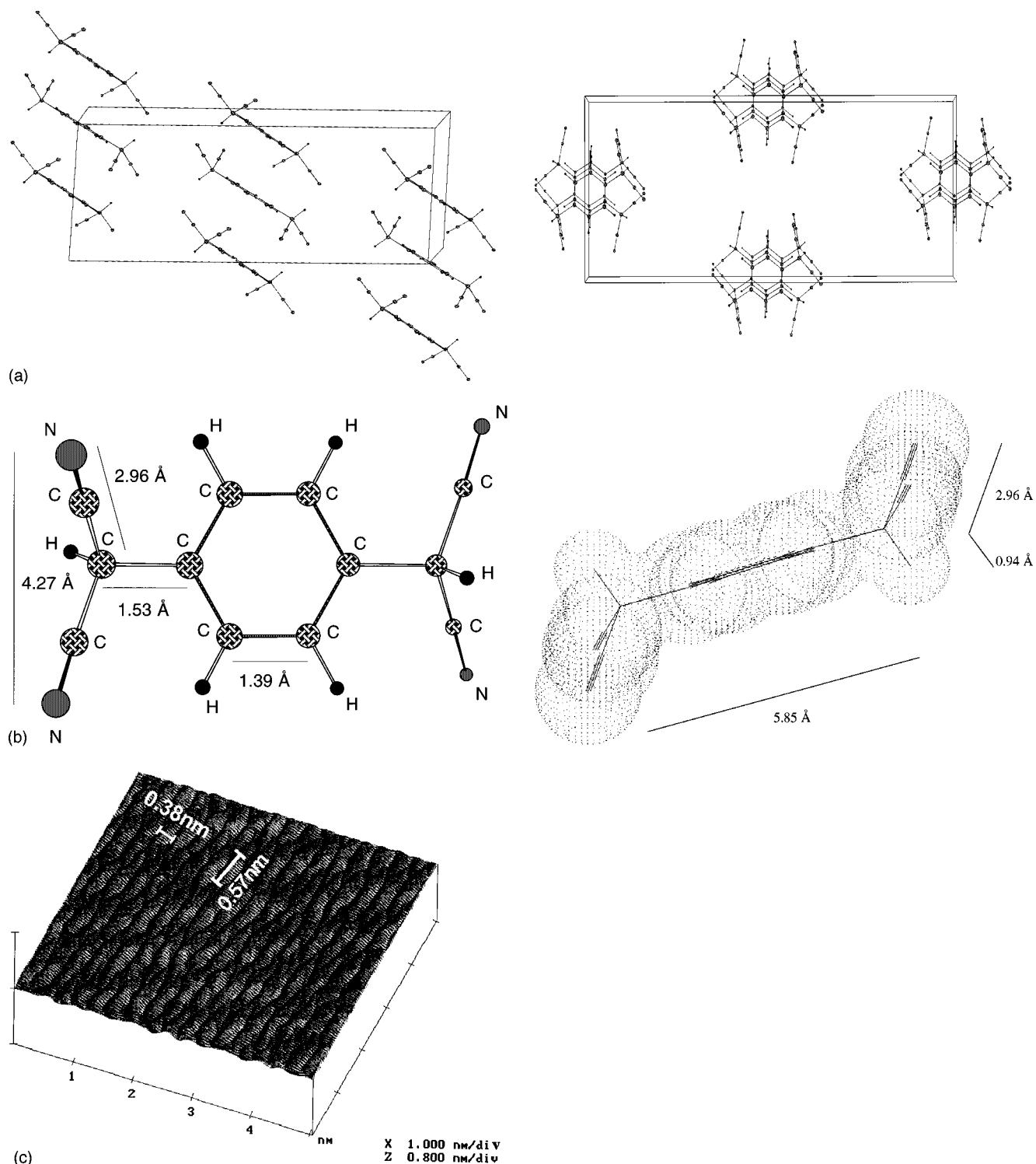


FIG. 1. (a) TCNX unit cell obtained from the XRD measurements (left: top view, right: front view). The size of the unit cell and the characteristic angles of the monoclinic symmetry are: $a=18.432 \text{ \AA}$, $b=7.240 \text{ \AA}$, $c=7.648 \text{ \AA}$, $\alpha=90^\circ$, $\beta=101.15^\circ$, and $\gamma=90^\circ$. The x-ray line is the molybdenum line at $\lambda=0.71073 \text{ \AA}$. (b) Detailed shape of the TCNX molecule obtained from the XRD measurements. (c) AFM image of the surface of the crystal.

molecular layers results in optical spectra of the crystalline phase of TCNX substantially different from that of the constituting individual molecule.

Figure 1(c), shows an atomic resolution AFM picture of the TCNX crystal on the 100 plane after a fast Fourier transform filtering. Though less accurate, the high-resolution AFM image provides a clear visualization of the molecular

shape and packaging predicted by the XRD analysis. The bonding length of 0.38 nm and the length of the molecules 0.57 nm extracted by the AFM nanograph are in excellent agreement with the XRD results of Figs. 1(a) and 1(b).

By virtue of the good crystalline quality, these materials exhibit extremely efficient room-temperature luminescence and strong excitonic features. In Fig. 2(a) we display the

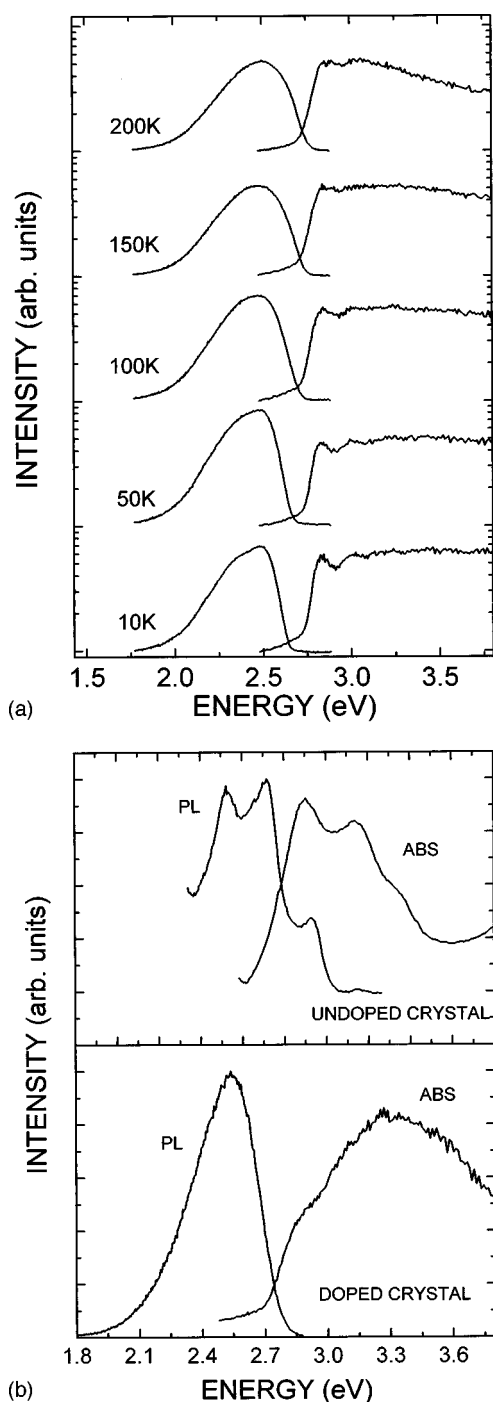


FIG. 2. (a) Temperature-dependent absorption and luminescence spectra of the doped TCNX crystal. (b) Absorption and luminescence spectra recorded at 10 K for the pure and the doped TCNX crystals.

temperature-dependent absorption and luminescence spectra taken from the lightly doped TCNX crystal. At low temperature, the absorption edge exhibits a sharp tail with a distinct exciton resonance splitted by about 200 meV from the continuum. The luminescence is Stokes shifted by about 200 meV and shows a strongly asymmetric low-energy tail. With increasing temperature, the exciton resonance smears out and exhibits a typical thermal dissociation behavior. Unlike the case of inorganic semiconductors, we do not observe any thermal-induced red shift of the absorption edge. Such a be-

havior indicates that thermal expansion and vibration of the lattice do not affect the ground-level energy of the crystal. The lack of interaction between phonons and single particles suggests that the absorption resonance is primarily due to Frenkel-like excitons localized within one or a few molecular planes of the crystal, thus being quite insensitive to lattice coupling. From the continuum-resonance splitting observed in the absorption spectra of Fig. 2(a) we can infer a localization energy of about 200 meV for the Frenkel exciton of the TCNX crystal. This value corresponds to a localization length of the order of the interlayer spacings and is quite interesting in view of the optical nonlinearities expected for strongly localized excitons in organic media.

A rather sensitive temperature-dependent behavior is conversely observed in the luminescence spectra, whose high-energy tail is enhanced at high temperature. This suggests the occurrence of delayed fluorescence, where the radiatively deactivated singlet levels are thermally populated by the low-lying triplet states. The possibility that triplet levels are involved in the radiative deactivation is indeed supported by the observation of an excited-state lifetime of the order of 10^{-6} s.

In Fig. 2(b) we compare the room-temperature absorption and luminescence spectra of the pure and doped TCNX crystals. These spectra show how the gap of the crystal can be tuned in the blue-green spectral region, with a higher energy absorption onset for the pure TCNX structure.

In order to provide a quantitative description of the electronic and optical spectra of these crystals we have performed a theoretical calculation based on the complete neglect of differential overlap (CNDO) based on the different CNDO parametrizations developed to calculate the valence band width,³ or the bond lengths.⁴ In addition, our theoretical method includes configurations interactions (CI) (Ref. 5) for a better description of the optical and electronic properties. The parametrization adopted here follows the Sichel and Whitehead scheme.⁶ The Mataga expression has been used for γ_{AB} integrals⁷ and the off-diagonal one-electron core Hamiltonian matrix is

$$H_{\mu\nu} = \frac{1}{2} \alpha (\beta_A^0 + \beta_B^0) S_{\mu\nu},$$

where $S_{\mu\nu}$ is the overlap matrix and β_A^0 and β_B^0 are bonding parameters. The parameter α is the same used for other organic crystals.⁸

The first important result of our calculation is that any attempt to describe the single-molecule spectrum by using the measured structure of the TCNX molecules in the crystal (see Fig. 1) fails. The total energy and heat formation indicate that the experimental geometry does not represent an equilibrium configuration for the isolated molecule. This suggests that the TCNX molecules undergo structural distortions upon crystallization, in order to reach a configuration where the high-electron density nitrile peripheral groups occupy opposite sites with respect to the aromatic ring plane, thus minimizing the electrostatic repulsion. As a consequence, the neutral excited electronic state of the crystal cannot be reproduced by considering an isolated TCNX molecule. In order to take into account the molecular arrangement and the intermolecular interactions we extended

our analysis to the case of a cluster of molecules formed along the crystallographic directions. The obtained results show that the more relevant intermolecular interactions take place along the direction normal to the aromatic rings. Calculations performed on different clusters of molecules along the [001] direction show that a minimum of three molecular units are needed to describe the optical behavior of the crystal. The atom positions in the molecules are chosen according to the corresponding experimental crystal structure. The optical spectra are reproduced by the CI method, by expanding the wave function of the molecular electronic states in a set of functions corresponding to distinct orbital excitations. The use of 80 monoexcited configurations is a good choice to describe the observed absorption spectrum: calculations performed using a higher number of monoexcited configurations show relevant modifications only in the energy region above 4 eV (not covered by the experiment). In Fig. 3 we present the theoretical results obtained for a TCNX single molecule (dashed-dotted line) and for a cluster of three molecules (dashed line) compared with the experimental absorption spectra of the pure TCNX in solution (dotted line) and in the crystalline phase (solid line). The theoretical curves are obtained as a sum of Gaussians whose center and height correspond to the transition energy and oscillator strength, respectively, with a half width of 0.2 eV. The calculated transition spectrum of the single TCNX molecule compares with neither the experimental spectrum of the TCNX in solution, characterized by a unique peak at about 3.8 eV, nor with the crystalline absorption. The mismatch between theory and experiment obviously comes from the use of the atomic coordinates deduced from the experimental structure of the molecules in the crystal, which is distorted by the environmental interaction and is quite different from that of the isolated molecule. The main features of the experimental absorption spectrum of the TCNX crystals (continuous line in the range between 3.0 and 3.5 eV) are instead well-represented by the theoretical calculation obtained using a cluster of three molecules (apart from the exciton resonance around 2.5 eV). The striking differences between the electronic transitions spectrum predicted for the single-molecule and for the three-molecules cluster in the [001] direction, originate from the relevant superposition between the aromatic carbon atoms electronic orbitals. This is clearly evidenced in the inset of Fig. 3 where we show the electron orbitals contour map of the fundamental state in a plane per-

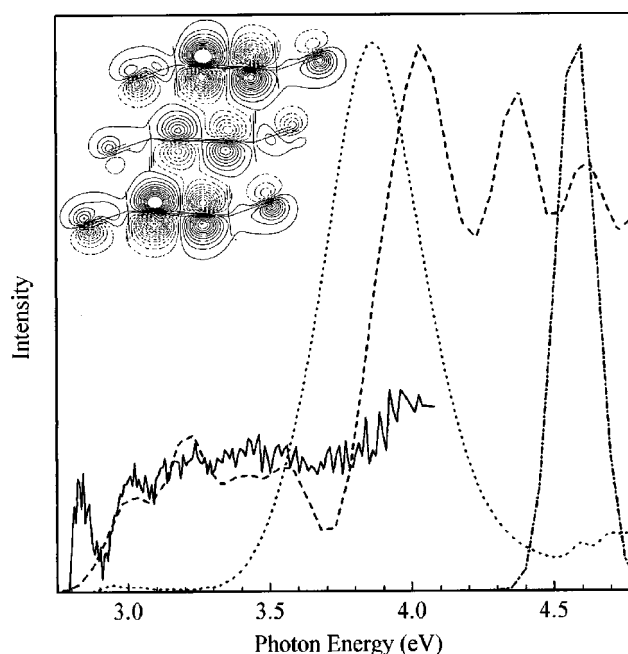


FIG. 3. Experimental absorption spectra (at 10 K) of the crystal (solid line), of a solution of TCNX (dotted line), and theoretically evaluated absorption spectra for a single molecule (dashed-dotted) and for three molecules (dashed). Inset: Contour map of the electron orbitals of the three-molecules cluster in the [001], on a plane perpendicular to the aromatic rings.

pendicular to the aromatic rings, showing the overlap of the wave functions along the stacking direction of the crystalline planes.

In conclusion, the optical properties of the highly ordered TCNX crystals, characterized by an intense green-blue luminescence, have been presented and discussed on the basis of semiempirical molecular orbital calculations. Owing to the nonplanar geometry of the TCNX molecules and to the highly packaged arrangement, the individual isolated molecule character is not preserved in the crystalline phase absorption, although it is possible to define a finite-size cluster of molecules, accounting for the intermolecular interaction, which permits a reasonable description of the optical properties of the crystal.

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