Polarization anisotropy of photoluminescence from triphenylamine-based molecular single crystal

Abstract

We present an experimental study of the polarization of the photoluminescence (PL) emission from a (Z)-3-(4-(diphenylamino)phenyl)-2-(pyridin-2-yl)-acrylonitrile (DPPyACN) single organic crystal. Our measurements show that the photoluminescence (PL) emission spectrum of the crystal consists of three highly polarized PL bands with different polarization ratios. The spectral position of one of these bands is the same as that of the PL emission of the molecule in dilute solutions in different "poor" solvents. Thus, we relate the different polarization ratios of the PL bands to different physical origin of the PL emission.

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1 Introduction

Organic crystals have recently become an important object of study because of their excellent optical properties and the possibilities of designing better molecular materials for different applications. It has been found that organic crystals with strong π-π intermolecular interactions frequently exhibit a high photoluminescence emission [1]. Among these crystals there are those formed by aromatic amines that are now increasingly finding application in optoelectronics as hole-transport materials in nano-devices. In particular, triphenylamine and its derivatives are well-known as hole-transport solid-state electroluminescent materials for photovoltaic applications that have been shown to have a high luminescent efficiency [2, 3].

Despite a considerable amount of theoretical work in this field, the lack of detailed understanding of the changes in the molecular electronic configuration due to the intermolecular interactions within the crystal still remains. It is known that organic molecules conserve their identity within an organic crystal because intermolecular interactions are weaker than intramolecular interactions. Nevertheless, the interactions between molecules can modify the molecular electronic configuration and, consequently, the optical properties of the organic crystal may differ from those of the isolated molecule. It has been observed that the stacking of the molecules within the crystal can lead to both, photoluminescence (PL) emission quenching [4], or PL intensity increase [5]. The importance of considering the intermolecular bonds in the study of PL spectra and PL efficiency has been shown for some particular crystal structures

[6]. However, the changes in the electronic energy spectra caused by the intermolecular bonds within a certain crystal depend on crystal symmetry and have to be analyzed on a case-by-case basis.

The study of the PL emission provides insight into the microscopic basis of the crystal structure, such as the arrangement and interaction of the molecules within the crystal. The analysis of the PL polarization brings additional information about the spatial organization and symmetry of the crystal, allowing the determination of the crystallographic orientation of the molecules. Moreover, by analyzing the differences of the polarization patterns of different PL features, the contributions of the molecules and of the interconnections between them to the PL emission spectrum can be identified.

On the other hand, Raman scattering is frequently used to characterize the molecular structure by determining the modes of molecular motion, such as vibrations and rotations, and comparing their frequencies with the "fingerprints" of known materials. Furthermore, Raman spectroscopy with polarized incident light is also used to determine the orientation of the molecules within the crystal [7].

Here we study the experimental polarization angular dependence of the PL of organic single crystals consisting of DPPyACN molecules. The PL spectrum of the crystal contains three highly polarized PL bands with different polarization ratios. To identify some of the PL bands of the crystal, the PL emission spectra of the molecule in different dilute solutions were independently measured. These spectra show a maximum at the same wavelength as one of the PL bands of the crystal. We also compare the PL emission polarization with the polarization of the Raman spectrum.

2 Growth and experimental setup

(Z)-3-(4-(diphenylamino)phenyl)-2-(pyridin-2-yl)-acrylonitrile (DPPyACN) single crystals were grown by slow solvent evaporation using the following procedure: 0.020 g of DPPyACN, synthesized according to the procedure reported in Ref. [8], was dissolved in 10 ml of an ethyl acetate-hexane (3:1) mixture and stored at 4°C; then, after 5 days, the crystals were obtained.

The angular dependencies of the PL polarization was measured at room temperature using a conventional experimental setup, which includes a close-cycle He cryostat, a TRIAX550 monochromator, and a liquid-nitrogen-cooled charge-coupled-device (CCD) detector. The optical excitation for PL was provided by an Ar+ laser (having an excitation wavelength of 514.5 nm). To

analyze the polarization of the PL emission, a quartz depolarizer and a linear polarizer were installed before the sample: thus, the exciting laser beam was first depolarized and then linearly polarized before being focused on the sample surface with an objective. The PL emission was collected by the same objective and went through the same polarizer and depolarizer. Therefore, we detected the PL emission having the same polarization as the exciting beam. To eliminate the polarization due to the grating, another depolarizer was installed at the entrance slit of the monochromator. To obtain the integrated PL intensity, the area under the PL peak was calculated by integration of the PL curve.

Raman spectra were measured in the backscattering geometry using a Renishaw InVia micro-Raman system equipped with a Leica microscope and an infrared semiconductor laser with an excitation wavelength of 785 nm. Laser light was focused on the sample through the 50 magnification microscope objective providing a laser spot size in the range 1–3 μm. The scattered light from the sample was collected through the same microscope, directed then through a spectrometer, and finally detected with a CCD detector. The laser power was kept at approximately 3 mW to prevent sample heating. In the Raman measurements the exciting laser beam was linearly polarized, whereas the scattered light was detected without distinguishing its polarization.

3 Experiment and discussion

The DPPyACN crystal is a long yellowish crystal, with approximate dimensions of 0.1 × 0.1 × 1 mm, and transparent in the visible spectral range. The polarization directions are defined using the long axis of the crystal as a reference.

The spectrum of the PL emission from the crystal under a 514.5 nm excitation wavelength consists of three bands with maxima at approximately 533, 569, and 607 nm (see figure 1). Moreover, the PL emission is highly polarized along the direction perpendicular to the crystal long axis, with different polarization ratio for each PL band. (The polarization ratio, ρ, is defined as it is shown in the figure 1b)

Figure 1.

a) PL emission spectra for two orthogonal polarizations. Each peak in the spectra is fitted with a Gaussian curve. b) Polarization angular dependence for different spectral PL bands. Dotted line corresponds to the function $\cos4(\theta)$.
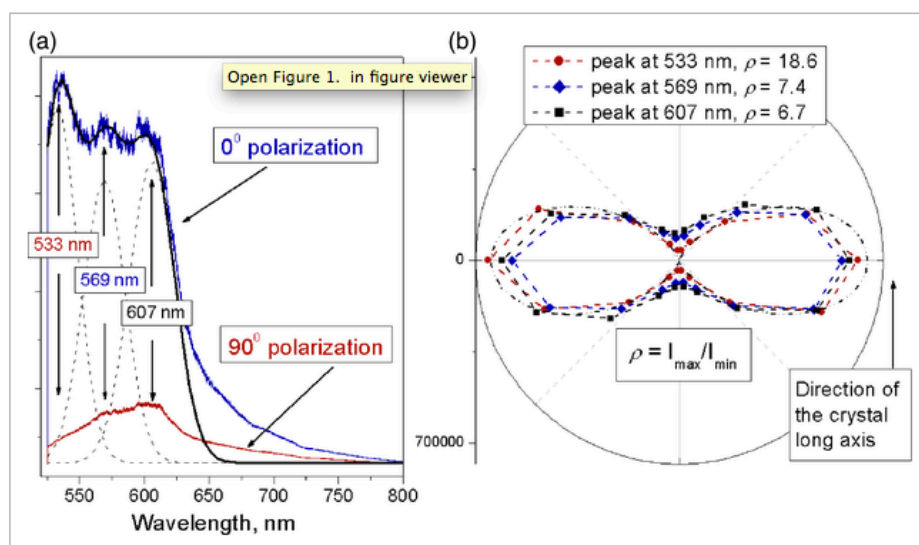
To get information about the optical properties of the isolated molecule, the PL spectra were measured for dilute solutions (3·10−4 M) in three different solvents: methanol, acetone, and acetonitrile. It is well known that all specific interactions influence the electronic spectrum of the molecule. These organic solvents were chosen since they are known to be a poor solvents, which means that the interaction between the solute molecules is stronger than that between a solute molecule and the solvent. Therefore, the PL emission from these solutions is not influenced by the interaction between the solute molecules and the solvent. To prepare these solutions, solvents of spectroscopic grade of purity were used, and preliminary checked for the absence of absorbing or fluorescent impurities within the scanned spectral range.

Figure 2 displays the PL spectra of the solutions of DPPyACN in these solvents. The inset shows the molecular structure. One can see that the spectral positions of the PL maxima for all these solutions are close to each other and close to 607 nm: thus, the 607 nm peak in the crystal PL spectrum can be attributed to the simple molecule emission.

Figure 2.

PL spectra from different dilute solutions. The structure of the DPPyACN molecule is shown in the inset
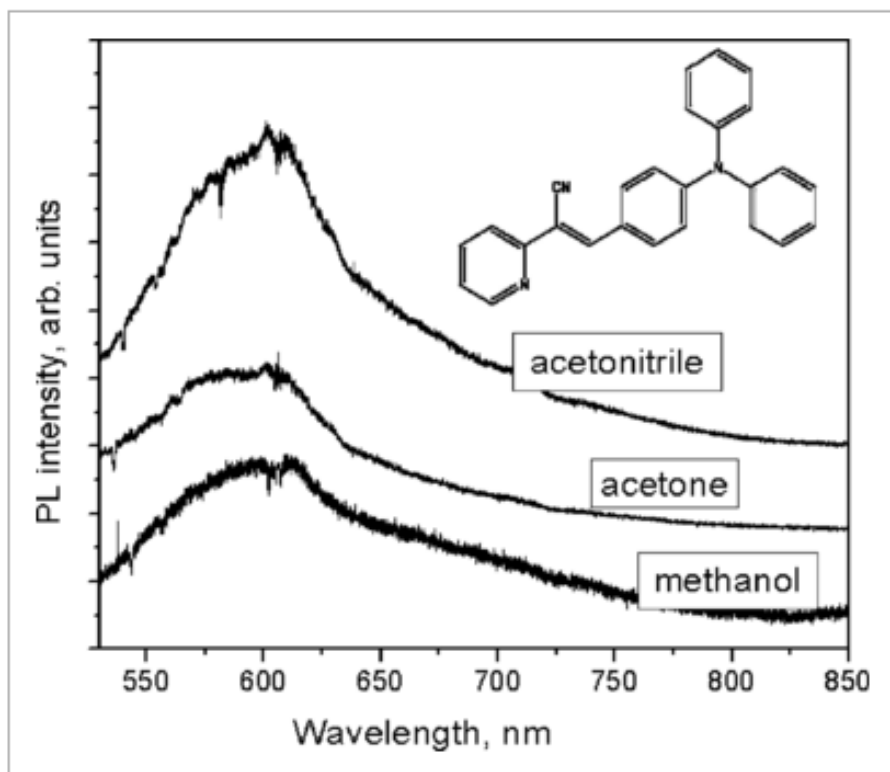
We also studied the Raman spectra of the DPPyACN crystal. PL emission and Raman scattering occur due to different effects: The former depends on the electric dipole vibrations, while the later depends on changes in the polarizability tensor. Therefore, using Raman data one can analyze the characteristic vibrations of the functional groups of the molecule. The polarized Raman scattering from the crystal contains information about the orientation of the molecules within the crystal. The intermolecular or external vibrations, or lattice modes, which involve movements of the molecule as a whole, are usually located in the low frequency region (<300 cm-1), therefore we suppose that the Raman spectra mostly contain the intramolecular modes.

Figure 3 shows the polarized Raman spectra of the crystal. The Raman spectrum of the DPPyACN crystal is complicated, and therefore it is not easy to identify all the observed lines. However, several lines can be associated with the characteristic vibrational modes of interatomic bonding of functional groups, namely the line at 1580 nm is related to the aromatic C=C stretching, and the line at 1177 nm is related to the C-H bending of the benzenoid rings [9]. Besides, for each frequency found for the individual molecule, series of vibrations, or progression modes, close to this frequency are found in the Raman spectra of the crystal because of the vibrational coupling between the molecules [10].

Figure 3.

Raman spectra for two orthogonal polarizations.
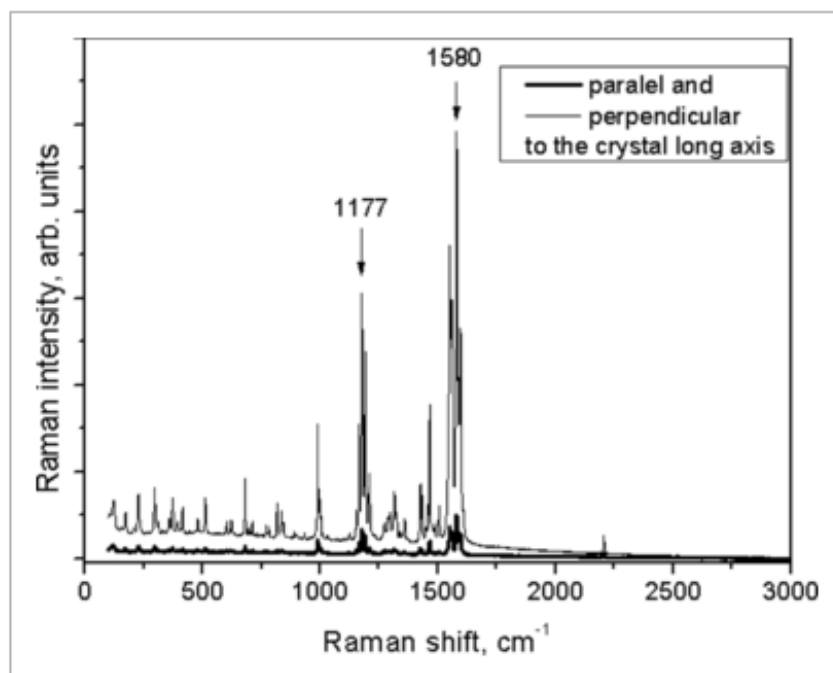
The Raman spectrum, when excited by light polarized perpendicular to the long crystal axis, mostly contains the same lines as that excited by the parallel polarization, however its intensity is several times greater. Raman intensity is maximized when the electrical field vector of the incident light is parallel to the long axis of the molecule, which has the largest polarizability. Thus, we can assume that the orientation of the long axis of the molecule is perpendicular to the crystal long axis, consequently the Raman scattering polarization is consistent with the PL polarization.

The solid or liquid (solvent) environment influences the conformation of the molecule. Within a dilute solution, where molecules are separated from each other, they can be twisted, and this non-planarity can reduce the radiative processes, as it was suggested in Refs. [11] and [12]. Inside the crystal the molecules have more planar conformation and this helps to increase the rate of radiative transitions and as a result the light emission.

The simplest model describes a molecule under optical excitation as an electric dipole. When linearly polarized light interacts with the dipole transition moment of the molecule, the absorption rate of the molecule is orientation dependent, and the emission rate has also a similar dependence. Thus the light emitted by the molecule is frequently highly polarized. We measured the emission polarized in the same direction as the exciting beam, so the excitation light was first absorbed by the crystal and then reemitted. One can see in figure 1 that the

polarization pattern can be fit by a cosine function raised to the fourth power. The intensity dependence described by the function $\cos2(\theta)$ is characteristic of linearly polarized light, thus the absorption occurs on a linearly polarized oscillator and then the emission takes place from the oscillator polarized along the same direction.

Moreover, all three PL bands are polarized along the direction parallel to the long molecular axis. The maximum of the PL emission spectrum of the solution is located at 607 nm, and therefore the band of the crystal PL emission spectrum with the maximum at the same wavelength corresponds to the emission of the molecule within the crystal. Further, this PL band at 607 nm is the less polarized band, probably because of slight differences in the orientation of the molecules within the crystal. The fact that the polarization of different spectral bands is different points to their possible different origin. If we suppose that the emission spectra of the molecule emission is altered as a whole by the interactions with another bonded molecules, and that all the peaks are related to emission of the molecule, all the spectrum bands would be equally polarized. This is in contradiction with the observed values.

Two additional, almost equidistant, bands in the crystal PL emission spectrum can be due to the interactions with internal molecule vibrations corresponding to the phonon replicas. If this is the case, the energy of these two bands must be smaller and their intensity lower than these of the main band, which is not observed in our experiments. Thus, we can also reject this hypothesis. Another possible reason for modification of the PL emission spectrum of the organic crystal could be a change in the molecules geometry. As was mentioned above, a molecule can be twisted in solution, whereas in a crystal close packing it becomes rigid due to the strong intermolecular interactions that inhibit intramolecular motions. It is also possible that the additional bands, observed in the PL spectrum of the crystal, are also present in the emission spectrum of molecule in the solution, but they are absorbed by a solvent.

However, we believe that the best model that explains the presence of the additional blue-shifted bands within the crystal PL spectra is a model of coupled resonators. The molecules excited by electromagnetic radiation can be seen as induced dipoles with the fundamental frequency corresponding to the energy of the emission peak, coupled with one another by their electric and magnetic fields. This coupling can make the spectrum of two coupled resonators with the same resonant frequency split in two bands, whereas the value of the splitting depends on the coupling constant. In fact, this effect is used in the design of the bandpass filters. Therefore, the bands at 533 and 569 nm could result from the emission processes, involving intermolecular interactions, and their polarization rates would characterize the alignment of the molecules and the orientation of the intermolecular bonds within the crystal.

4 Conclusions

Single organic crystals have a long-range structural ordering and frequently exhibit optical anisotropy. The analysis of the PL emission polarization helps to understand the role of intermolecular interactions, establishing a correlation between molecular packing and optical properties and clarifying the nature of electronic transitions within the crystalline structure.

We measured and analyzed the PL emission from organic crystals consisting of (Z)-3-(4-(diphenylamino)phenyl)-2-(pyridin-2-yl)-acrylonitrile molecules and grown as long crystals with a thickness of approximately 100 μm. The PL emission was studied both in solutions and in solid crystals. The PL emission of the crystal excited at 514.5 nm has three PL bands with different angular polarization dependence, and polarized perpendicular to the crystal long axis. Assuming that each peak of the emission spectrum corresponds to a certain inter- or intra-molecular bond, the different angular dependences point out to differences in the physical origin of the PL emission processes inside the crystal.

Acknowledgments

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