Eur. Phys. J. B **39**, 229–234 (2004)
DOI: 10.1140/epjb/e2004-00185-x

**THE EUROPEAN
PHYSICAL JOURNAL B**

Structural and optical study on a single crystal of a novel fluorinated acridine

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Received 16 January 2004

Abstract. Within a new class of anthracene-like molecules, namely tetrafluoro-acridines, a systematic study of the structural and optical properties of single crystals of a prototypical member, 1,2,3,4–tetrafluoro–7(N,N)dimethyl–amino–acridine, is illustrated. Single crystals were grown by physical vapour transport using an inert gas flow as carrier, starting from a microcrystalline powder of the pure material. The crystal structure, determined by X ray diffraction, points out that the crystals are monoclinic with molecules stacked along the *c* axis. The results of atomic force microscopy on the *ac* face of a single crystal, at both low and molecular resolution, are consistent with the X–ray diffraction data. Preliminary results of the optical properties of the single crystal, in the unique configuration accessible due to the peculiar habit of the samples, are discussed.

PACS. 61.66.-f Structure of specific crystalline solids – 68.37.Ps Atomic force microscopy (AFM) – 71.35.Cc Intrinsic properties of excitons; optical absorption spectra

1 Introduction

In the field of molecular organic materials, fluorinated molecules are receiving a large interest, due to their peculiar properties: the substitution of one or more hydrogen atoms with fluorine atoms can modify the structural and optical properties of a molecular solid [1,2]. Indeed it is well known that fluorination strongly influences the electronic properties of an organic semiconductor and, for example, it is able to convert an organic p semiconductor into a n semiconductor [3]; moreover the interaction between aromatic molecules and fluorinated aromatic molecules gives rise to peculiar supramolecular structures. Our interest was focused on a class of fluorinated molecules, namely tetrafluoroacridines, easily accessible from standard organic synthesis [4–6]. The large pool of molecules prepared has allowed us to start a systematic study of their properties and potential applications, as fluorescent dopant molecules for polymer based organic light emitting devices, as fluorescent probes in biological systems, as electron conductors in photovoltaic systems and for application in non linear optics. In this paper the growth of single crystals of 1,2,3,4–tetrafluoro–7–(N,N)dimethyl–amino–acridine, considered as a prototypical member of this class, is described; the crystal growth is aimed at obtaining single crystals suitable for the transmission measurements. The results of Atomic Force Microscopy (AFM) at both low and molecular resolution are discussed in comparison with the crystal structure. In this work the results about the (optical) transmission measurements on the grown single crystal in the UV–visible spectral region are presented and an interpretation is proposed on the basis of both the oriented gas model and solid state effects.

2 Experimental

1,2,3,4–tetrafluoro–7–(N,N)dimethyl–amino–acridine (see Fig. 1) was synthesised in accordance with a procedure reported in literature [4–6]. High structural quality single crystals were grown by physical vapour transport (PVT) with a nitrogen flow starting from a microcrystalline powder of the pure material in a glass apparatus. The phenomena involved with this process and the regimes of transport were already analysed for other organic semiconductors like 6T ([7] and references within); the apparatus we have used is similar to the systems already described in the literature by Laudise et al. [7]. Our systems is composed by an external closed glass tube and an internal glass coaxial open tube (Fig. 2); at the bottom of the external tube is located the container with the starting material. The tube used for this experiment was 20 cm high and with internal diameter of 3 cm; the internal tube has an external

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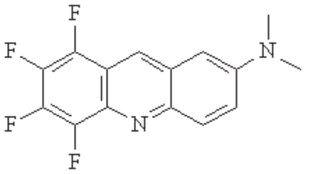

Fig. 1. 1,2,3,4–tetrafluoro–7–(N,N)dimethyl–amino–acridine.

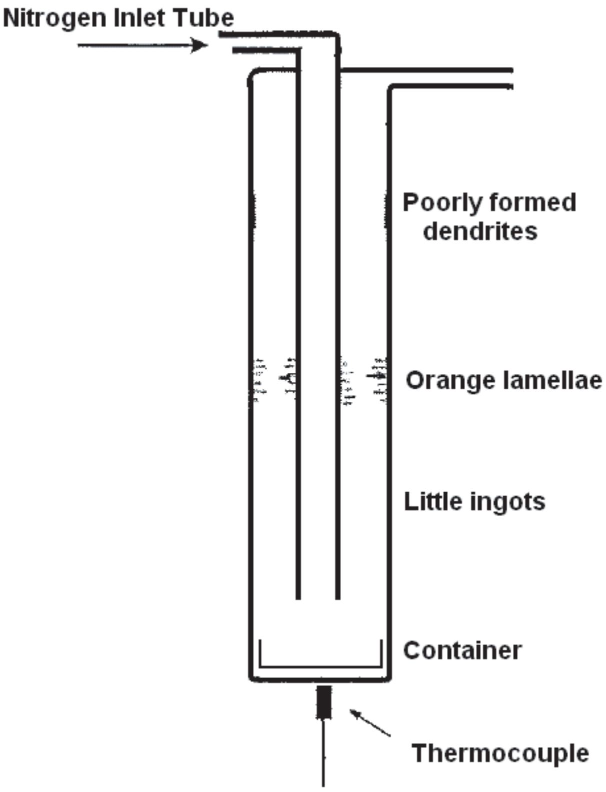

Fig. 2. Scheme of the experimental setup used for PVT growth (aluminium block is not represented).

diameter of 7 mm and an internal diameter of 5 mm. The uniform heating of the furnace is given by an aluminium cylinder with an internal hollow, where is placed the glass tube; a thermocouple is place in the lower region of the tube, to measure the temperature of the source. We found that the best single crystal for our purpose can be grown heating at the starting material at of 130 °C and with a nitrogen gas flow of 0.4/0.5 ml/s. Images of single crystals were collected with a Olympus Stereomicroscope (mod. SZX12), equipped with polarizers, and with a metallographic Leica DMLM microscope. The thickness of the crystals was measured with a stylus profiler (Dektak 8, Veeco Instruments). A Nanoscope IIIa (Digital Instruments) atomic force microscope was adopted to characterise the single crystal *ac* face topography at different resolution levels. All measurements were performed in contact mode with V-shaped silicon cantilevers with force constant of about 0.12 N/m. Absorbance measurements at normal incidence were performed in the spectral range from 1.5 eV to 5.5 eV with a resolution better than 10 meV using a Perkin Elmer Lambda 900 spectrometer; measurements were performed with linearly polarised light using Glan–Taylor calcite polarizers.

3 Results and discussion

3.1 Crystal growth

Centimetre-sized, needle shaped, orange crystals were grown by slow evaporation of a solution, but the thickness and the dimensions of these crystals make them not suitable for the optical studies. The best way found for growing single crystals of this molecule is PVT in an open glass tube held in vertical position; during growth, the starting material placed at the bottom of the tube was heated at 130 °C; since the heater is placed at the bottom of the tube, a natural temperature gradient is imposed to the system and the nitrogen flow transports the evaporated molecules through the tube towards the zone at lower temperature. Crystallisation begins in the region of the tube where the supersaturation becomes larger than unit, i.e. where the temperature is low enough to stabilize the solid phase with respect to the vapour phase. The dimensions and the shape of the crystals are influenced by different factors: the gas flow, the temperature of sublimation and the diameter of the tube, which influences the efficiency of heat dissipation. Due to the temperature gradient imposed to the system, we found crystals with different habits in different positions along the tube; at the bottom of the tube (where the supersaturation is lower but the quantity of material is higher) we found many micrometer–sized crystals with the shape of little ingots, while at the top of the tube (where the supersaturation is higher but the quantity of material is lower) we found some crystals grown with a dendritic shape. Both these kinds of crystals are not suitable for optical characterisation, but modifying the gas flow, the temperature and the diameter of the tube, we found the optimal conditions for growing in the middle part of the tube some good single crystals with the suitable dimensions for our purpose. A good crystal for optical absorption characterisation must be large enough (at least 1 mm^2) and free from cracks to minimize straight light problems; moreover it should be thin enough to avoid saturation in transmission measurements. With the above method, we were able to produce single crystals with the shape of rectangular lamellae of dimension 1×1.2 mm and 300 nm thick (see Fig. 3). We did not observe any growth hillock with the metallographic microscope and the crystal surface presents of big terraces, observed also with Atomic Force Microscope. Crystals of 1,2,3,4–tetrafluoro–7–(N,N)dimethyl–amino–acridine are monoclinic (space group $P2_1/n$ (No. 14), $a = 6.427$ Å, $b = 26.783$ Å, $c = 7.235$ Å, $\beta = 95.92°$, $V = 1239$ Å^3, $Z = 4$) [6]; crystal structure is quite similar to those observed for the other 1,2,3,4–tetrafluoroacridines already known in the literature and characterised by X–ray diffraction analysis [8]. Crystal structure was determined from samples grown from solution and X–Ray diffraction analysis pointed out that the PVT method gives the same polymorph. The $(CH_3)_2N$ nitrogen atom lies in the acridine plane, while

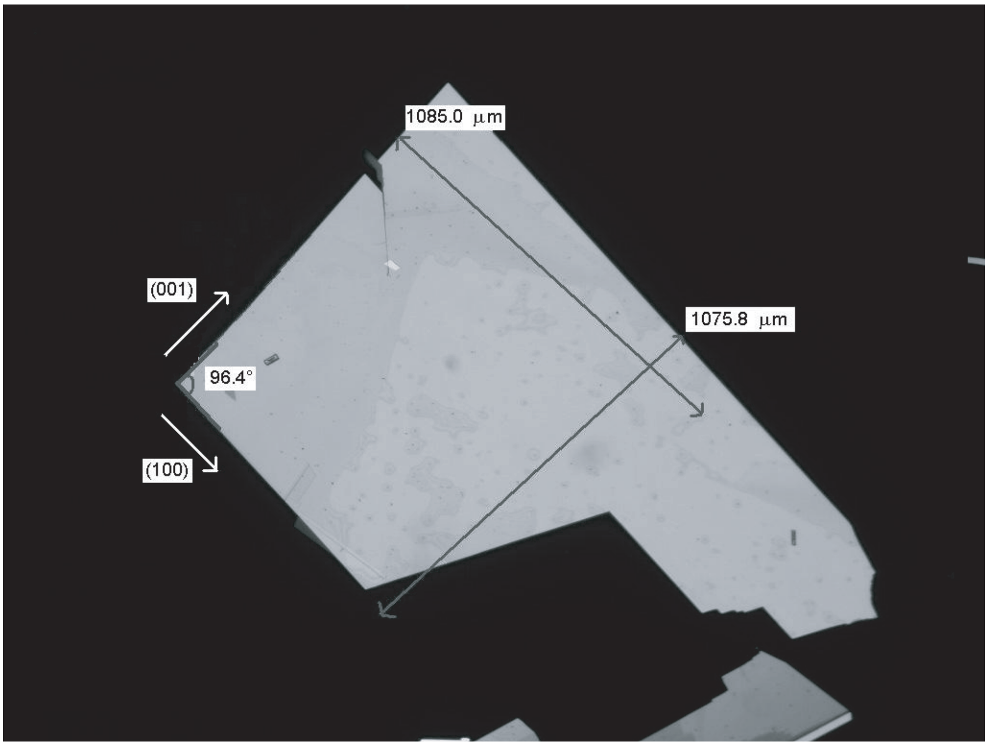

Fig. 3. Image of the single crystal used for the optical absorption measurements.

the methyl groups are slightly off plane, due to a rotation of the whole $(CH_3)_2N$ group; this behaviour suggests a significant double bond character of this N–C interaction, with the nitrogen atom close to a sp^2 configuration. The strong interaction between the nitrogen of dimethylamino moiety and the aromatic system deeply influences the electronic properties of the molecule, as reported elsewhere [6] and it originates of the charge transfer transition observed in absorption spectra both in solution and in the solid state (see below, Sect. 3.3). The crystal packing of this tetrafluoro–acridine can be described as a head–to–tail stack of molecules having the fluoroarene moiety placed above the dimethylamino group of a second molecule, with a distance between the planes of ca. 3.43 Å. This arrangement is due to the arene–perfluoroarene interaction between couple of molecules; this interaction has been reported for other related systems [9–11] and it is observed between aromatic molecules or moieties and fluorinated aromatic molecules or moieties [12]. Due to the peculiar nature of the interactions among the molecules in the crystal we can suppose that the preferred growth direction of the crystal is along the stacks (i.e. [001] direction), where we find the strongest interaction between molecules. This hypothesis was confirmed by diffraction analysis in the case of crystals grown from solution, which have the habit of long needles: the growth proceeds preferably along the [001] direction and the growth along other directions is slower. This is true also for crystals grown from PVT, with the habit of long lamellae: in this case the growth proceeds along two directions and the crystals have the habit of thin, rectangular lamellae, with only one face accessible; the measurements by optical microscope of the angles of this crystal face (Fig. 3) indicates that this is the *ac* face. This result is confirmed by AFM analysis, as discussed below.

3.2 Morphological analysis

In Figure 5a a typical AFM image collected over a $1 \times 1\ \mu m^2$ area of the *ac* face of a single crystal of 1,2,3,4–tetrafluoro–7–(N,N)dimethyl–amino–acridine is reported. The characteristic feature is the flatness of this surface showing large terraces and steps between neighbour terraces of 14 Å ca., corresponding to one half of *b* axis of the unit cell, in agreement with the previous identification of the face. No screw dislocations have been observed on the crystal surface. Molecular resolution AFM images were also collected on the large terraces to detect and measure the surface unit cell. In Figure 5b a high resolution image is shown as detected by AFM on the sample surface; the Fourier analysis of the image contrast was used to identify a unit cell for the surface lattice and the axes were measured as 6.5 Å × 7.2 Å, forming an angle of 94.5°. The height profile (Fig. 5c), measured along the white line shown in Figure 5a, shown the terraces and the steps; the trace is noisy and the value reported above was obtained averaging it out. The very good agreement with *a* and *c* axes respectively of the unit cell confirms again the previous identification of the face. The AFM analysis confirms the good structural quality of the crystal surface and a comparison with X-ray diffraction data suggests

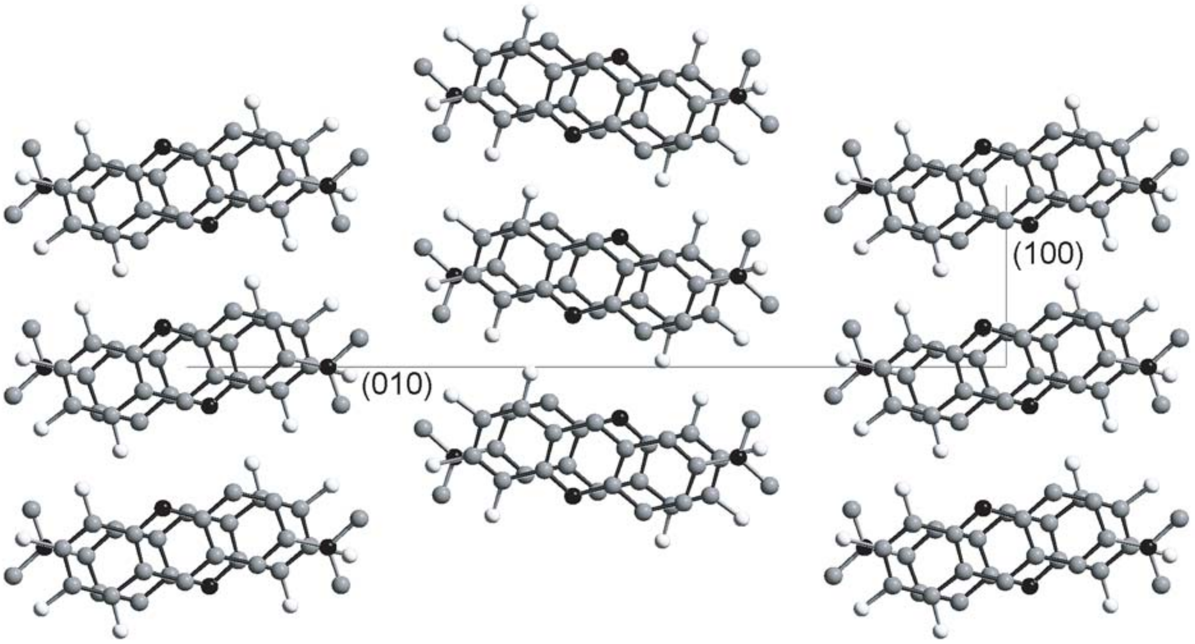

Fig. 4. Drawing of the crystal packing along the *ab* face.

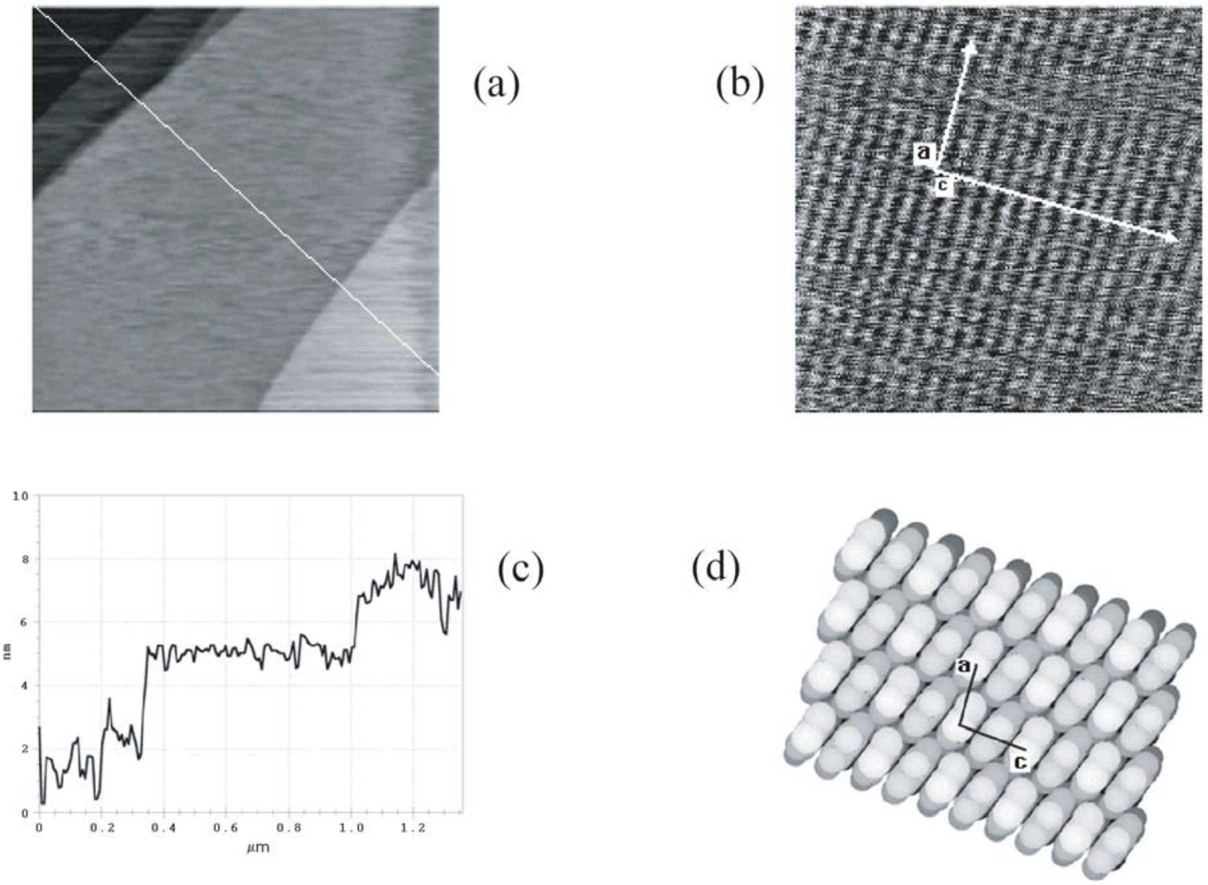

Fig. 5. a) 1 μm × 1 μm AFM image collected on the single crystal on the ac face and height profile. b) 15 nm × 15 nm AFM image (error signal) collected on one large terrace of the same sample as in a), before filtering process. c) Height profile collected on the crystal surface, showing the steps between the terraces. The profile was measured along the direction shown with a white line in Figure 5a. d) Drawing of the crystal packing along ac surface; it should be compared with Figure 5b.

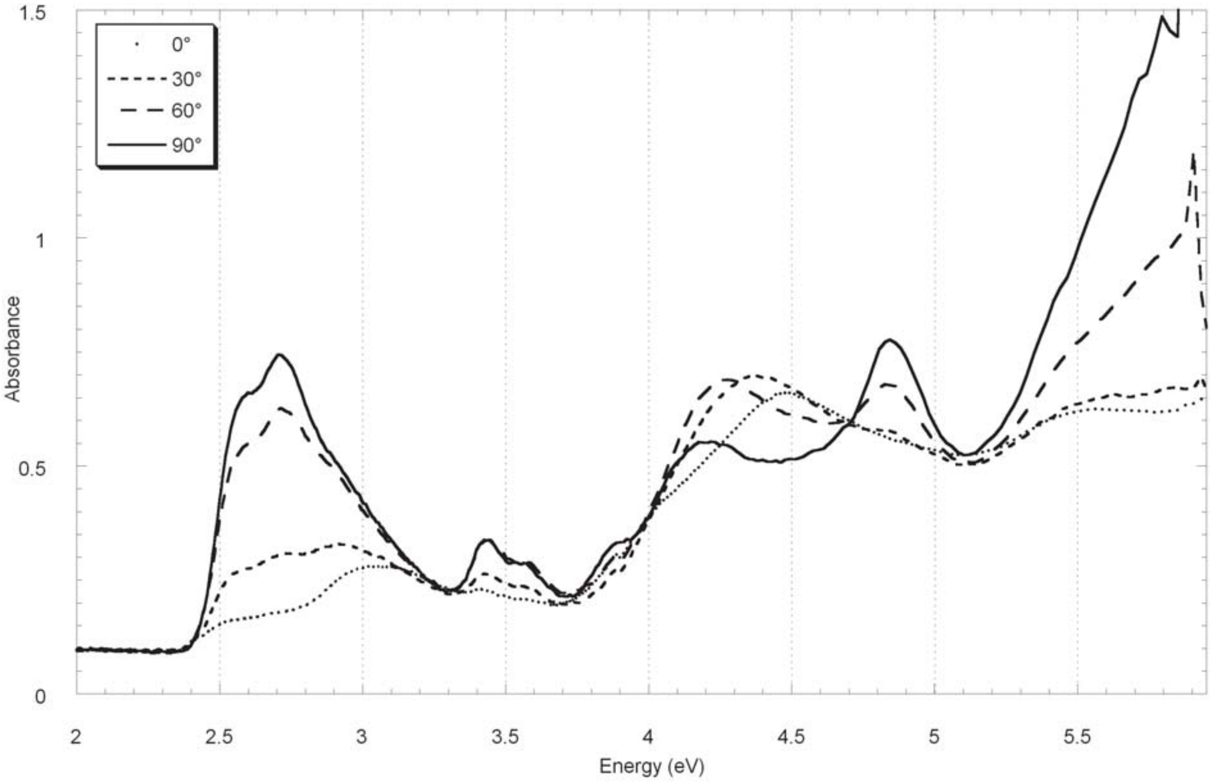

Fig. 6. Absorption spectrum of a 300 nm thick tetrafluoro-dimethyl-amino-acridine single crystal normal to the *ac* face, measured with polarised light.

that the high resolution image reflects the periodicity of the (100) and (001) planes emerging at the surface. Presumably, contrast comes from the more protruding methyl groups rising from the (010) plane are probed by the AFM tip. The high resolution AFM image should be compared with the Figure 5d where the *ac* crystal surface is shown.

3.3 Optical absorption

Optical absorption measurements were performed at normal incidence on the (010) face, the only one accessible, as identified by X–Ray diffraction, morphological and AFM analysis (Fig. 6). The main result emerging from the optical absorption measurements is that we were able to collect the absorption spectrum over until 5.5 eV avoiding saturation due to (relative) large thickness or artefacts induced by straight–light [13]; it is possible to minimize these problems only using crystalline thin films or thin single crystals of good quality (i.e. with the proper thickness and free from cracks and holes). The absorption spectrum is quite rich of bands between 2.5 eV and 5 eV, all showing a very large anisotropy, as reported in Figure 6, where are reported the absorbance spectra collected with different angles between the electric field of the polarised incident beam and the [001] direction (or *c* axis) of the crystal. The low energy bands (between 2.4 eV and 2.8 eV) are polarised along the [100] direction, i.e. polarised close to the molecular plane; for these bands the lineshape of the absorbance spectrum at 90° is quite similar to that reported for the same molecule in solution [6], where the low energy composite band (between 2.4 eV and 3.3 eV) was attributed to an intramolecular charge transfer transition between the $(CH_3)_2N$ nitrogen and the aromatic fluorinated moiety. Since in the isolated molecule the low energy transitions are polarised in the plane of the molecule (i.e. the plane formed by all the carbon atoms), we can assume that in the solid state these transitions retain the polarisation typical of the isolated molecule; this behaviour is explainable in the frame of the oriented gas model [14]. We must highlight that the high-energy part of this absorption band (between 2.8 and 3.3 eV) does not show a strong anisotropy like the low energy part of the band discussed above. Also the absorption band between 3.3 and 3.7 eV shows a strong anisotropy; this bands, as observed in solution [6], originated from the transition to the second excited state of the molecules; also this behaviour is explainable in the frame of the oriented gas model. The residual absorption observed for the 0° polarisation between 2.4 and 2.8 eV and between 3.3 and 3.7 eV maybe is due to a little misalignment of the single crystal. The high energy part (above 4 eV) of the absorption spectrum is very different from the solution spectrum and its interpretation is not straightforward; indeed the oriented gas model seems not fully applicable to the transition observed at higher energy (between 4 eV and 5 eV), probably due to the mixing between Frenkel excitons and CT states, and a deeper analysis is needed to propose a complete interpretation.

To understand the nature and the origin of such bands samples showing different faces should be grown (if possible) and analysed or transmission measurements at oblique incidence performed, to explore the optical response along different crystallographic directions.

4 Conclusions

The results about the growth of single crystals of a novel organic semiconductor were presented; we reported a useful method to grow good quality single crystals, analysing the effects of intermolecular interactions on the habit and the morphology of the crystals. Single crystals were studied by optical and atomic force microscopy, pointing out that the only face accessible is *ac* face. Optical absorption of single crystal grown by PVT was measured with different angles of polarisation, showing that we were able to growth single crystals of good quality. An interpretation of part of the absorption spectrum, in the frame of the oriented gas model, was presented; further studies are needed to understand the nature of observed transitions.

MIUR- PRIN 2001, n°2001034479006 “Composti Fluorurati: Nuovi Materiali per Applicazioni Avanzate” is gratefully acknowledged for financial support.

References

1. J.H. Williams, Acc. Chem. Res. **26**, 593 (1993)
2. Y. Sakamoto, S. Komatsu, T. Suzuki, J. Am. Chem. Soc. **123**, 4643 (2001)
3. T. Suzuki, S.B. Heidenhaim, Y. Sakamoto, A. Miura, H. Fujikawa, T. Mori, S. Tokito, Y. Taga, J. Am. Chem. Soc. **122**, 10240 (2000)
4. A.J. Adamson, R.E. Banks, A.E. Tipping, J. Fluorine Chem. **64**, 5 (1993)
5. A.J. Adamson, R.E. Banks, R. Fields, A.E. Tipping, J. Chem. Res. (M) 530 (1997); A.J. Adamson, R.E. Banks, R. Fields, A.E. Tipping, J. Chem. Res. (S) **3**, 76 (1997)
6. A. Papagni, L. Miozzo, P. Del Buttero, M. Moret, A. Sassella, G. Ridolfi, Chem. Mater. **15**, 5010 (2003)
7. C. Kloc, P.G. Simpkins, T. Siegrist, R.A. Laudise, J. Cryst. Growth, **182**, 416 (1997)
8. A.J. Adamson, Y. Archambeau, R.E. Banks, B. Beagley, M. Helliwell, R.G. Pritchard, A.E. Tipping, Acta Crystallogr. Sect. C **50**, 967 (1994)
9. C.R. Patrick, G.S. Prosser, Nature **18**, 1021 (1960)
10. J.S.W. Overell, G.S. Pawley, Acta Crystallogr. B **38**, 1966 (1982)
11. J. Potenza, D. Mastropaolo, Acta Crystallogr. B **31**, 2527 (1975)
12. A.I. Kitaigorodsky, *Molecular Crystals and Molecules* (Academic Press, New York, 1973)
13. A. Sassella, A. Borghesi, P. Spearman, S. Tavazzi, Eur. Phys. J. B **28**, 385 (2002)
14. V.L. Broude, E.I. Rashba, E.F. Sheka, *Spectroscopy of Molecular Excitons* (Springer–Verlag, Berlin, 1985)