Fast identification of rubrene polymorphs by lattice phonon Raman microscopy

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A B S T R A C T

Confocal Raman microscopy in the lattice phonon region has been used to study the polymorphism of the organic semiconductor 5,6,11,12-tetraphenyl-tetracene (rubrene). Following literature guidelines, crystals of rubrene have been prepared using a number of solution growth and vapour deposition methods, obtaining samples of different morphologies which could be related to the various polymorphs of this compound. The technique has enabled us an easy and non invasive identification of the three known polymorphs and of their phase homogeneity with a lateral spatial resolution below 1 μm.

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1. Introduction

Rubrene (5,6,11,12-tetraphenyl-tetracene) is one of the most studied organic semiconductors, due to its high carrier mobility and interesting optoelectronic properties [1—8]. The molecule consists of a tetracene backbone with two phenyl groups as substituents on both central rings (Fig. 1). Each of these bulky groups has a certain degree of flexibility, with their orientation influencing the optimal crystal packing and hence the polymorphs which can be formed.

Besides the need of high purity compounds for device fabrication, the crystal structure is a key factor in governing the carrier mobility in these systems, as the intermolecular electronic overlap is a function of the molecular arrangement in the unit cell. Therefore, each structure of a certain compound possesses its own transport characteristics, which may drastically change from one crystalline modification to the other [9], becoming one of the major factors in the semiconductor device's performance [4—8]. Rubrene is a remarkable example of this phenomenon. Of its three known polymorphs, only the orthorhombic one displays outstanding field-effect transistor properties as single crystals or in films [10,11], possessing an ideal matching of molecular structure, electronic structure and crystal structure to drive its unique characteristics. The less characterized monoclinic form, however, has been shown by DFT calculations to be the most promising for singlet fission, thus resulting the most appealing for photovoltaic efficiency [12].

The coexistence of more solid phases in a sample (phase mixing) is also a widespread phenomenon, especially when dealing with systems such as films, whose growth is more under kinetic than thermodynamic control, or when nucleation takes place at a substrate, with the formation of surface induced polymorphs (SIPs) [13]. In these cases, the lack of phase homogeneity constitutes a disrupting source of disorder with hindering effects on the charge carrier mobility [14,15].

In view of this situation, a technique allowing for the fast identification of polymorphs and phase inhomogenities is of great importance. Since their early applications, X-ray diffraction (XRD) methods were recognized as the technique of choice for the characterization of the crystal structure of a material. In recent years, however, much effort has been put in the search of both experimental techniques to identify and computational tools to predict new crystal phases, with the aim of understanding the solid state landscape and the kinetics [16]. Following previous investigations [17—19] we apply to rubrene the method of lattice phonon Raman

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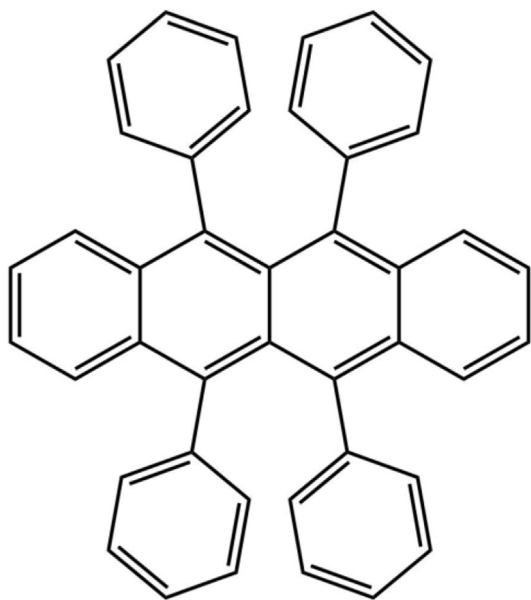
Fig. 1. Chemical structure of rubrene (5,6,11,12-tetraphenyltetracene).

spectroscopy as a successful procedure of crystal phase recognition. Working in confocal microscopy, the different polymorphs and their phase homogeneity were easily identified with a lateral spatial resolution below 1 μm.

2. Polymorphism of rubrene

Polymorphism in rubrene has only recently been highlighted, with three polymorphs currently identified in the literature and having orthorhombic, triclinic and monoclinic structures. The orthorhombic form very likely possesses the lowest free energy over a wide temperature range as it is the one commonly grown by physical vapour transport and sublimation methods. It belongs to the space group Cmca and has been recently re-investigated by Jurchescu [20] and Matsukawa [21], and it is coincident with those observed in earlier reports [22,23]. The triclinic structure, initially reported by Akopjan [24], was not reproduced until eventually found to crystallize from aniline or from 2-propanol together with the orthorhombic one, from which it can be easily distinguished because of a different morphology [21]. Very early and incomplete results by Taylor [25] concerned a monoclinic polymorph which likely is the one finally isolated from solution by Huang [26]. In the latter paper, a re-precipitation method was employed, which gave 1D ribbons and 2D plates that were identified as the triclinic and the monoclinic phases, respectively, in the absence of the most commonly reported orthorhombic form. The crystal packing of the three polymorphs is remarkably different and is shown in Fig. 2. Orthorhombic rubrene (Cmca, Z = 4) displays an effective π-stacking in the crystal b direction (green in the Figure) and a herringbone molecular arrangement. The large charge-carrier mobility measured in orthorhombic rubrene has been attributed to the herringbone packing motif which produces a large overlap of the π-conjugated tetracene backbones. The triclinic (P$\bar{1}$, Z = 1) form displays the π-stacking in the crystal a direction (red in the Figure), with some slippage in the molecular stack, which affects the π-π interactions, and no herringbone structure. Thus, a decreased overall orbital overlap accounts for a much poorer charge mobility compared to that of the orthorhombic polymorph [21]. Finally, π-stacking is not present in the packing of the monoclinic polymorph (P2$_1$/c, Z = 2), which shows no relevant charge transport properties.

High quality rubrene films of the orthorhombic form [6] can be grown by hot wall deposition or by abrupt heating of the amorphous layer [27]. Owing to its molecular conformation, it is difficult to grow good quality crystalline films of rubrene by solution methods. Various techniques have been employed, obtaining either the triclinic [28] or the orthorhombic [29,30] form.

The two lesser known rubrene polymorphs have not been experimentally characterized as the orthorhombic structure to allow for their identification by spectroscopic methods [31]. In view of this situation it appears useful to employ the above mentioned spectroscopic technique capable to readily discriminate among rubrene crystal phases, to check their physical purity, their crystallinity and their coexistence in different growth methods.

3. Experimental

The commercial product from Aldrich (purity > 98%) was purified by repeated sublimations. Large crystals of the orthorhombic form can be grown by vapour methods such as physical vapour transport (PVT) [32] or sublimation. In the pursuit of good quality crystals with few surface defects, in our experiments the PVT vessel was vacuumed and repeatedly flushed with argon. The hot end of the furnace was kept at 300 °C and the system was maintained at a gradient of ≈ 14 °C/cm. Rubrene deposition took place in the range 200–225 °C and the crystals were left to grow for seven days. After this time, as seen in Fig. 3, large flat platelets, with a maximum larger dimension of 50 mm, had accumulated in the middle part of the ampoule. Various morphologies and thicknesses were in fact observed along the vessel, with the flat orange crystals having very smooth surfaces and the red needle-like crystals appearing rougher. At lower furnace temperatures a polycrystalline powder was usually obtained.

The triclinic and monoclinic rubrene polymorphs can be grown from solution in a number of solvents. We have adopted the re-precipitation and the solvent diffusion methods reported by Huang [26], which proved to be reliable giving reproducible results.

The re-precipitation method consists in introducing a saturated solution of the compound in a non-solvent. The procedure is very effective when metastable forms are sought and has been used, for instance, to obtain one of the three polymorphs of diphenylanthracene [33]. A 3.0 ×10^{-2} mol/l stock solution of rubrene in CHCl$_3$ was subjected to sonication for 20'. Thus, volumes of 50 μl of it were injected into different volumes (1.50, 1.00, 0.25 and 0.125 ml) of the non-solvent methanol and maintained at room temperature till the formation of a crystalline precipitate. For larger quantities of the non-solvent (and therefore in higher super-saturation conditions), the triclinic form can be selected, with the shape of 2D hexagonal or rhombic plates. With methanol volumes lower than 0.5 ml only the 1D ribbon of the monoclinic should be obtained instead.

In the solvent diffusion method [26], rubrene crystals were grown at the liquid interphase between a saturated CH$_2$Cl$_2$ solution of the compound and methanol. As in Ref. [26], crystals with platelets and block-like morphologies were obtained, which were found to belong to the triclinic and to the monoclinic structures, respectively.

Phonon spectra were obtained with a Jobin Yvon T64000 Raman spectrometer coupled to an optical microscope (Olympus BX40) with 50x or 100x objectives, which allowed for a lateral resolution of about 1 μm with a *nominal* field depth from about 7 to 25 μm. Spectra were recorded spanning the low frequency region of the lattice phonons (10–150 cm^{-1}). The excitation was from a Krypton ion laser (647.1 nm) with an incoming power below 1 mW focused on the sample. Spectra were simultaneously detected also in the higher wavenumber range (150-2000 cm^{-1}), where intramolecular vibrations of the rubrene tetracene backbone and of the phenyl