

Aligned terrylene molecules in a spin-coated ultrathin crystalline film of *p*-terphenyl

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Abstract

We report on the use of a simple spin casting procedure to fabricate very thin crystalline films of *p*-terphenyl doped with fluorescent terrylene molecules. By performing single molecule studies, we show that the guest molecules are oriented normal to the plane of the film. We find that despite the very low thickness of the *p*-terphenyl matrix, as thin as only 20 molecular layers, about half of the embedded emitters withstand photobleaching for illumination times of at least a day.

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1. Introduction

Emitter-doped thin films are of great interest for fundamental studies and for devices. Compared to bulk media, thin films increase the ratio between the fluorescent and matrix molecules in the illuminated area, therefore optimizing the signal-to-noise ratio in single molecule detection. Thin coatings also provide chemical protection for emitters and can be easily stacked to form multilayered systems. In addition, the vicinity of the dopant fluorophores to the upper surface of a thin film makes them suitable for scanning near-field optical microscopy. From a fundamental point of view thin films offer an elementary form of a confined geometry in which all molecules ‘see’ the surfaces, making them suitable for studying the role of interfaces in various phenomena such as modification of the spontaneous emission rate, change of the phonon density of states, and the influence of surface defects on spectral lines.

In an ideal fabrication process one would like to control the lateral and axial coordinates of each atom in the film. In particular, for many optical applications it is desirable to implant emitters of well-defined orientations

at predetermined locations. The most commonly produced thin layers, however, are amorphous and are realized by evaporative deposition or by spin casting. These methods are inexpensive and straightforward, but they do not offer atomic scale control. To obtain crystalline thin films with lateral and axial order scientists usually resort to more sophisticated techniques such as self-organization or molecular beam epitaxy in ultrahigh vacuum. Recently ten Grotenhuis et al. [1] demonstrated that one may produce thin microcrystals and crystalline films [2] of organic molecules also by spin casting. Beside its simplicity, this approach is particularly interesting because spin coating usually yields amorphous layers of material under conditions far from thermodynamic equilibrium. In this work we have extended this method to fabricate ultrathin films of *p*-terphenyl doped with fluorescent terrylene molecules. We show that the film has a crystalline nature and that the guest molecules are aligned perpendicular to its plane.

The crystal structure of *p*-terphenyl has been well studied [3]. It forms platy crystals with (001) faces, and at room temperature it has a monoclinic unit cell of dimensions $a = 8.1 \text{ \AA}$, $b = 5.6 \text{ \AA}$, $c = 13.6 \text{ \AA}$ with the angle β between a and c being 92.1° . Ten years ago Kummer et al. doped *p*-terphenyl crystals with a very low concentration of terrylene, introducing a system that has become an important work horse for single molecule spectroscopy [4,5]. These crystals are com-

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monly produced in a co-sublimation process whereby the size, shape and quality of the samples depend on parameters such as temperature and its gradients in the sublimation chamber, pressure of the buffer gas, as well as timing of the heating and cooling processes. In our laboratory we have been interested in fabricating crystals of nanometer thickness [6,7]. We have found that although it is possible to obtain microcrystals via sublimation, it is not easy to control all the parameters to reach the nanometer scale. This prompted us to turn to spin casting.

2. Experimental

2.1. Film preparation and characterisation

To produce the desired films we spin coated 20 μl of a solution of *p*-terphenyl in toluene (3 mg/ml), containing a small quantity of terrylene (10^{-7} M) onto a glass cover-slip. This was done in a two-step process (30 s at 1000 RPM followed by 2 s at 3000 RPM) on a commercial spin coater (PWM32, Headway Research, Inc.), yielding areas of film that covered several mm^2 on the substrate. Fig. 1a shows an optical microscope image of a typical sample area, containing both film and bare glass regions. In order to examine the crystalline nature of the film, the sample was placed between two nearly crossed polarizers. Fig. 1b displays the image when the sample was rotated by 90° . The intensity transmitted through the glass regions was found to be independent of the sample orientation whereas the intensity from the film regions strongly depended on the orientation of the sample. The entire film region shown in the figure, covering several hundreds of squared microns, behaved indistinguishably when rotating the sample. This birefringence suggests that the *p*-terphenyl film is crystalline with the same optical axes over several hundreds of squared microns.

To characterize the topography of the film we have performed atomic force microscopy (AFM) on various samples. In Fig. 1c we show an AFM image of an area that again contains a mixture of film and glass. Fig. 1d displays the profile of the film across a glass stripe, illustrating that the thickness of our samples varied typically between 20 and 30 nm. Although the film is generally very flat, the cross section shows that over length scales of microns the film thickness might undergo modulations of a few nanometers. On the other hand, we have also found regions that showed plateaus and terraces with height differences of about 1 nm, which within our measurement error, are consistent with molecular steps. The mechanism of film formation is complex and dependent on a large number of parameters [2]. Its full understanding requires extensive studies that go beyond the scope of our current work. Here we

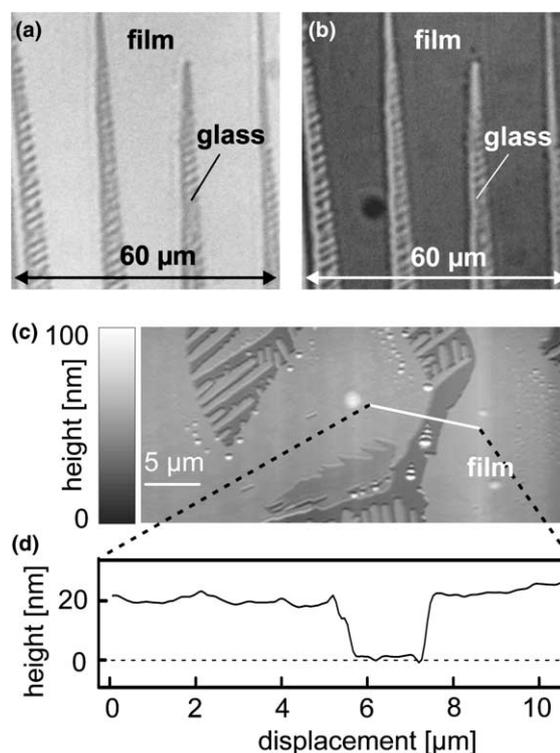


Fig. 1. (a,b) Polarization microscopy images of a sample region containing both *p*-terphenyl film and bare glass. The sample is rotated relative to the crossed polarizers by 90° between the two images. The birefringent crystalline film rotates the polarization, resulting in a contrast inversion between the two images. (c) AFM topography image of a sample. (d) The topography profile corresponding to the cross section marked in (c). The film is typically flat to a few nanometers over several hundreds of squared microns.

mention that we have also obtained micro- and nano-crystals with thickness of a few hundred nanometers by annealing our samples [7–9].

The growth of *p*-terphenyl is known to favor the (001) crystal plane as the extended surface [5]. Furthermore, the insertion geometry of terrylene in *p*-terphenyl causes its transition dipole moment to orient approximately parallel to the *c* axis of the host crystal [10]. Therefore, given the observed birefringence in Fig. 1a,b, we might also expect that, as shown in Fig. 2a, the *a* and *b* axes of our films lie in the substrate plane and that the dopant dye molecules are highly aligned. To elucidate this feature and other optical properties of terrylene in these films, we have performed single molecule experiments.

2.2. Single molecule fluorescence studies

In the past decade a number of groups have exploited various near- and far-field techniques to determine the locations and orientations of single fluorescent molecules [9,11–18]. Our studies were carried out on a wide-field fluorescence microscope shown in Fig. 2b. A frequency doubled Nd:YAG laser (Crystalaser,

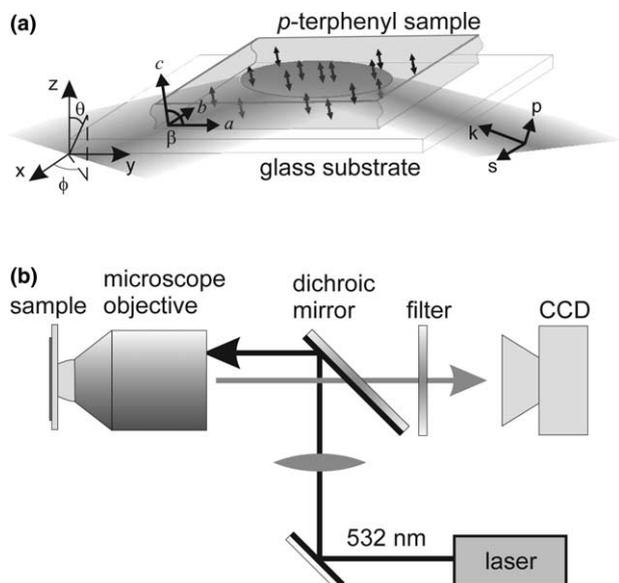


Fig. 2. (a) Schematics of the *p*-terphenyl film lying on a glass substrate. The axes *a*, *b*, *c* denote the crystal axes. Dopant terrylene molecules are oriented with their transition dipole moments approximately perpendicular to the substrate. The diagram also shows the total internal reflection illumination scheme for achieving a large electric field component of the laser beam along the transition dipole. (b) Experimental fluorescence microscopy setup. See text for details.

GCL-025-L, $\lambda = 532$ nm) provided a linearly polarized excitation beam which was reflected by a dichroic mirror (540DRLP, Omega Optical) into an oil immersion microscope objective (Nikon 100 \times , N.A. 1.3). A lens before the dichroic mirror focused the excitation light onto the back-focal plane of the objective, so that an area of around 15 μm in diameter on the sample was illuminated with a parallel beam. By shifting the excitation beam laterally off-axis, we chose the direction of the incident beam so that it was totally internally reflected by the *p*-terphenyl-air interface, as illustrated in Fig. 2a. This ensures that in the illuminated area the electric field of the excitation beam has a considerable component along the transition dipole moment of terrylene molecules. Fluorescence from the sample was collected by the microscope objective and transmitted through the dichroic mirror. Two long-pass cut-off filters (538 ALP, Omega Filters) were used to remove the remaining excitation light. The fluorescence was then imaged onto a CCD camera (PCO Sensicam qe, pixel size 6.5 μm) by a 400 mm camera objective, producing an effective magnification of 200. We estimate the fluorescence detection efficiency of the setup to be about 3%.

In order to distinguish the areas of the sample covered by *p*-terphenyl from the rest, we implemented a weak diffuse white light illumination in transmission. Fig. 3a shows a simultaneous white-light and fluorescence image of a film containing a glass island. The excitation laser beam only illuminates the central region.

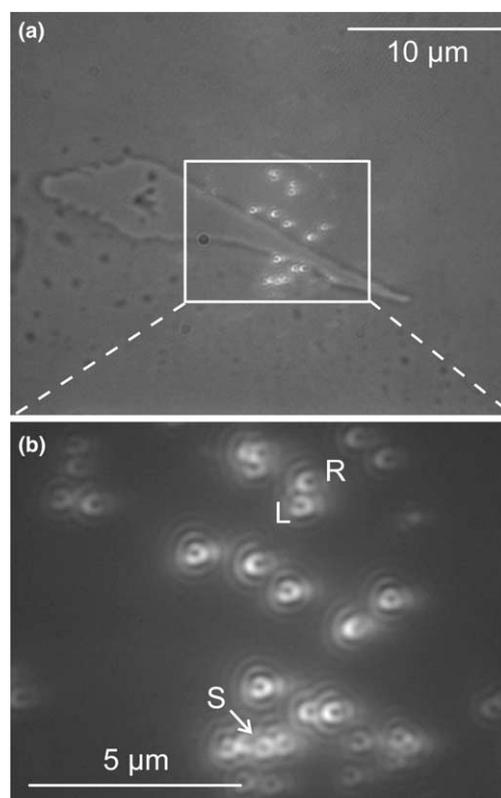


Fig. 3. (a) Simultaneous fluorescence and white-light image shows that molecules are only found in film regions. (b) The enlarged fluorescence image shows that all molecules exhibit a nearly ring-like emission pattern, characteristic of vertically oriented dipoles. Two molecules labelled L and R exemplify asymmetries of the emission pattern to the left and to the right, while the molecule labelled S shows an example of a molecule with perfect doughnut-like symmetry.

The bright spots display single fluorescent terrylene molecules, only observed in the *p*-terphenyl film. In Fig. 3b we display an expanded fluorescence image of the area marked by the white rectangle in Fig. 3a. We note that strikingly, all the molecules produce nearly ring-shaped images.

Doughnut patterns have been previously observed by Dickson et al. [13] in single molecule experiments and have been attributed to molecules with emission dipoles along the optical axis [18]. Let us consider a dipole oriented along the *z* direction (see Fig. 2a). In a homogeneous bulk medium the maximum intensity of its emission occurs for $\theta = 90^\circ$. Introduction of an interface in the *x*-*y* plane close to the dipole rearranges this distribution along θ [19], but leaves the radiation isotropic with respect to ϕ . When this emission is collected and collimated by a microscope objective along the *z* direction it forms a doughnut mode with radial polarization [20]. In order to investigate the polarization of the fluorescence light in our experiment, we placed a linear polarizer in the detection arm. In Fig. 4a we first display the intensity distribution for three molecules recorded without any polarization element. Figs. 4c–f then show

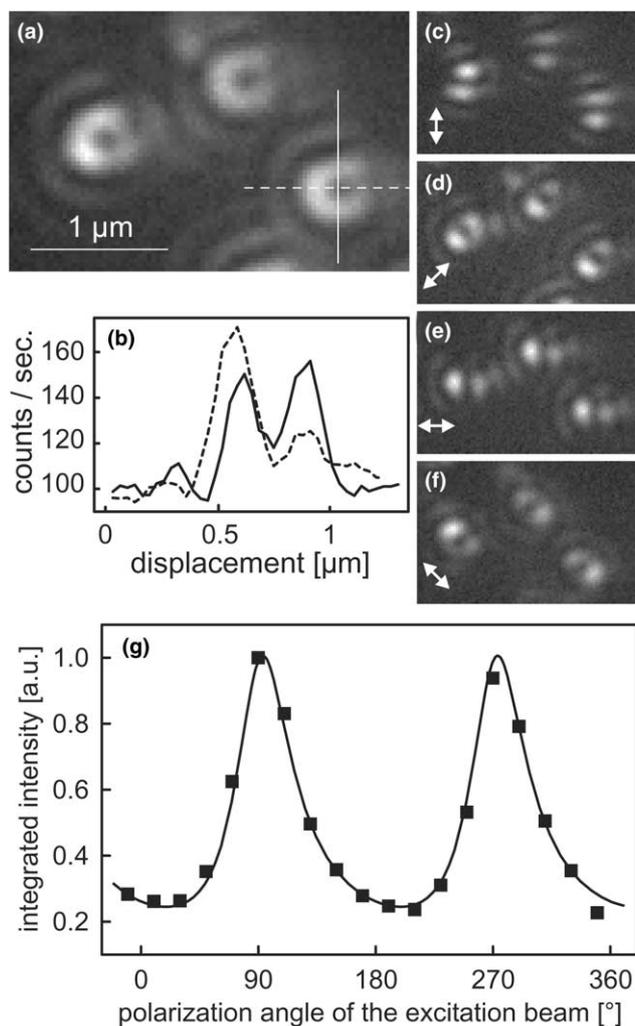


Fig. 4. (a) Fluorescence images of three terrylene molecules in film, displaying characteristic ring-shaped patterns. (b) The indicated cross sections show a clear minimum in the center of the pattern and quantify its deviation from a perfectly symmetric doughnut shape. (c–f) By rotating a polarizer in the detection path, we show that the emission pattern is radially polarized. The arrows indicate the polarization in each image. (g) The symbols plot the fluorescence intensity of a single molecule as a function of the incident laser polarization. The solid line shows a fit, considering a dipole model and taking into account the polarization dependence of the reflectivity from the dichroic mirror.

the emission patterns of the same molecules for different orientations of the polarizer, as indicated by the arrows. The fact that the fluorescence images rotate with the polarization clearly illustrates that the emission is radially polarized.

A closer look at individual rings in Fig. 3b reveals that indeed, often the images do not have a perfect circular symmetry. The two neighboring patterns labelled L and R represent examples of rings that are open to the left and to the right, respectively. This effect is shown more clearly in Fig. 4a and in the two cross sections plotted in Fig. 4b. The observed asymmetry is attributed to the slight tilt of the emission dipole with respect to the

optical axis. This intensity distribution can be used to extract the inclination angle if one carefully characterizes the optical system and uses electromagnetic calculations to fit the experimental images [18,21]. In our case the strong refraction anisotropy of *p*-terphenyl ($n_1 \sim 1.6$, $n_2 \sim 1.7$, $n_3 \sim 2$) makes such calculations quite complex so that here we do not attempt a quantitative comparison with theory.

Before we continue we comment on two aspects of the observed images. First, we point out that although in the earlier work the origin of the ring-shaped image was associated to an out-of-focus aberration in the optical system [13], we find that the doughnut-like images do not change when we defocus the microscope objective. Indeed, more recent theoretical [18] and experimental [22] reports support our observation that for axially oriented dipoles one always expects a doughnut-shaped image on the camera. Next, we remark that the images are accompanied by weaker concentric rings (e.g., see Figs. 3b and 4a), which we assign to Airy fringes caused by the finite aperture of the collection system.

As a final check that terrylene molecules are oriented nearly perpendicular to the film, we studied the dependence of the fluorescence signal for various excitation polarizations (see Fig. 2a). In order to do this, we rotated the polarization of the laser beam before the dichroic mirror, characterized the reflectivity of the mirror as a function of incident polarization, and recorded the total fluorescence intensity. The symbols in Fig. 4g plot the raw data for a single molecule as a function of incident polarization. The solid curve shows a fit to the experimental results based on a \cos^2 dependence, after correcting for the polarization response of the dichroic mirror. We observe the highest excitation efficiency at a polarization angle of about 7° relative to the plane of incidence (i.e., polarization angle of 97° in 4g). Within the experimental error, and considering that the plane of incidence is randomly chosen with respect to the crystal axes, our results are consistent with the findings of Bordat and Brown [10] that terrylene molecules are incorporated into the *p*-terphenyl crystal at an angle between 99.3° and 106.1° , relative to the crystal *a* axis. A quantitative study of the molecular orientation requires more thorough tomographic measurements at different planes of incidence. Nevertheless, our investigations clearly demonstrate that the transition dipole moments of all embedded terrylene molecules are nearly perpendicular to the film. Moreover, the knowledge of the insertion geometry of terrylene in *p*-terphenyl [10] lets us infer that the *a* and *b* *p*-terphenyl crystal axes lie in the plane of the glass substrate.

2.3. Photostability of terrylene molecules

In addition to the uniform orientation of terrylene molecules in the *p*-terphenyl film, a remarkable feature

of our samples is the unusually high resistance of the fluorophores to photobleaching. Limited photostability has been reported for almost all molecular emitters [23] and poses a serious challenge to the widespread application of single molecule techniques. As an exception to this seemingly universal rule, only a small fraction of terrylene molecules has been reported to be stable up to hours when embedded in *p*-terphenyl crystals thicker than 10 μm [24,25]. The explanation for this photostability has been that these isolated molecules are well protected in crystalline matrix against diffusing quencher agents such as oxygen. Considering that our films are merely 20 molecular layers thick, a high degree of photostability is quite surprising.

Fig. 5a shows a fluorescence image of a sample shortly after it was illuminated for the first time. About half of the molecules photobleached within a few minutes after exposure to laser radiation, but the remaining molecules were exceptionally photostable for very long times. Fig. 5b displays an image of the same sample area after 3 h of constant radiation, showing that as many as half of the molecules have survived. We mention that all these measurements were performed on samples that were exposed to air at all times. Taking into account the collection efficiency of the setup and a count rate of about 25000 s^{-1} for a single molecule, we estimate that surviving molecules emitted more than 10^{10} photons over the period of 3 h. It would be interesting to determine a ‘half-life’ for the photostability of these molecules, but we could not observe any change even after a constant overnight illumination.

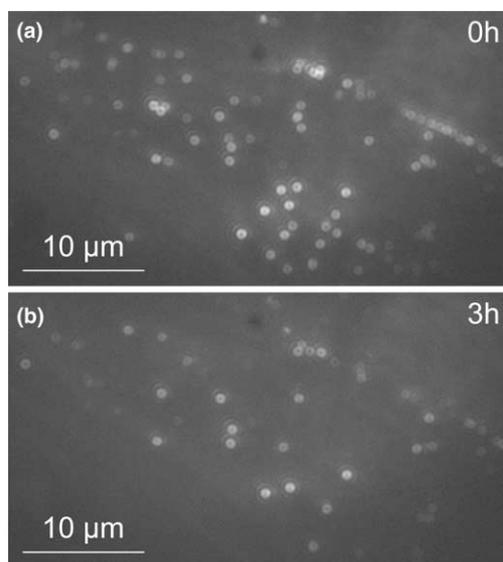


Fig. 5. Wide-field fluorescence images before (a) and after (b) 3 h of constant illumination. As many as half of the molecules demonstrate a very high degree of photostability. We also note that as opposed to the emission patterns of Fig. 3b, the images in this figure are perfectly doughnut-shaped.

3. Summary

In conclusion, we have fabricated ultrathin films of *p*-terphenyl doped with terrylene by using a simple spin coating procedure, a method that is usually associated with the production of amorphous films. By applying polarization microscopy, AFM and wide-field fluorescence microscopy, we demonstrated that the films are crystalline and that the dopant molecules are highly oriented in them. The fluorescent molecules were found to be spectacularly photostable, despite a surrounding matrix as thin as 20 molecular layers. Further experiments are required to fully understand the film formation during spin casting. It is also very interesting to investigate the spectral properties of terrylene in these *p*-terphenyl films at low temperature and with very high spatial resolution [9]. The well-defined orientation of the emitters, their photostability, and their vicinity to the film-air interface make them ideal for a number of experiments, ranging from near-field optical microscopy [6,11] to quantum optics [9,25].

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