Hierarchic self-organization of J-aggregates in micrometer size discotic liquid crystal ‘domes’

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Low molar mass liquid crystals formed dewetted island, or ‘dome’ structures when cast from dilute solution on substrates. Hexaalkoxytriphenylene formed hexagonal micronsiz islandes when the cast film was slowly cooled from the isotropic state. Co-casting of cyanine dyes led to hierarchic structures of fluorophores in the center of the domes, and fluorescence microscopy and microspectrometry confirmed that cyanine J-aggregates were formed.

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I. INTRODUCTION

Organic dyes and dye aggregates are widely used in various applications related to photonics, e.g. organic light emitting diodes (OLEDs), solar cells (SCs), and photographic films. For effective energy or electron transfer in these applications, the spatial ordering and arrangement of donor and acceptor units is crucial for the function of the device. Self-assembly of cyanine dyes on silver halide grains leads to sensitization of actinic light in color photographic films [1]. Ionic groups attached to metal-organic complexes facilitate the adsorption of the dye onto nanometer size TiO$_2$ particles in Graetzel-type solar cells [2]. The self-assembly of donor-acceptor compounds with sulfide headgroups into monomolecular layers on gold leads to rectifying properties [3]. These examples address the arrangement of molecules on the nanometer scale and in continuous thin films. Despite the necessity of this ordering, the problem of interfacing individual nanometer-ordered molecular arrays with the macroscopic surrounding and the built-up of more complex and hierarchic structures is rarely addressed.

On the other hand, it has been reported to form micronsiz dome patterns of both polymeric and low molar mass compounds, e.g. polystyrene, PMMA, dendrimers and non-linear optically active thienyl compounds [4, 5]. Recently we also reported that cyanine dyes form J-aggregates in mesoscopic dome patterns of polystyrene [6]. Here we report on the self-organization of photofunctional compounds on the micrometer scale to give rise to spatially separated and heterogeneous arrays, which might be useful for photonics applications.

II. EXPERIMENTAL

The cyanine dye was used as received (Aldrich). The discotic host was synthesized according to the literature by FeCl$_3$-oxidative coupling of 1,2-bis-pentioxy-benzene in CHCl$_3$ [7]. The resulting triphenylene was repeatedly recrystallized from trifluoroacetic acid until it was colorless. Glass substrates (Matsunami Neo) with a thickness of 0.15 mm were cleaned in an ozone cleaner. Images were taken with a fluorescence microscope (Olympus IX-70), equipped with a color CCD camera (SPOT RT-CL, Diagnostics Inc.). Laterally resolved fluorescence spectra were taken with a microscope spectrometer (Photon Design) with the following components: Olympus IX-50 microscope; 60× magnification lens; excitation source: Ar-ion laser (488 nm). The fluorescence light was collected, passed through appropriate filters to absorb excitation light, and relayed to the spectrometer (Jovin Yvon 320 monochromator; 150 lines/mm grating; Princeton Instruments 1340/400 EMB CCD detector) by an optical fiber (diameter 10 µm). This setup leads to a spatial resolution of 2 µm for the fluorescence spectra.

Matrix/dye mixed solutions were prepared by mixing aliquots of solutions containing the discotic matrix material and the dye. The concentration of the final casting solution was adjusted to ca. 1 mg/ml. Samples were prepared by casting ca. 100 µl onto horizontally held substrates. The samples were annealed in an oven in normal atmosphere.

III. RESULTS AND DISCUSSION

We chose 2,3,6,7,10,11-hexakis-pentioxytriphenylene (H5T), a discotic liquid crystal, because a close structural relation, the thioether, shows high electronic hole mobilities in the liquid crystalline phase [8]. Thus triphenylenes are promising materials for photoconductivity and/or electron and energy migration.

When a dilute solution of H5T is cast onto a substrate and the solvent is allowed to evaporate, H5T remains on the substrate and forms irregularly shaped aggregates. The density and the size of the aggregates depend on the concentration of H5T in the casting solution and on the kind of substrate. Good results have been achieved by using a 1 mg/ml chloroform solution and mica as a substrate. After an additional annealing step, in which the sample was placed in an oven at 130°C and allowed to cool down to room temperature over a period of 4 hours, regular hexagonal aggregates were formed (Fig. 1), similar to those observed by heating an Langmuir-Blodgett film of a discotic compound [9]. The phase transition temperatures of H5T in bulk are 69°C for the crystal to liquid-crystal transition and 122°C for the transition from the liquid crystalline D$_{no}$ phase to the isotropic phase. In situ microscopic observation showed that H5T forms

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FIG. 1: Chemical formulae of the used compounds and optical micrograph of H5T hexagonal crystals. The sample was heated to 130°C and cooled to room temperature over a period of 4 hours. The inset in the upper left corner is an amorphous dome at 130°C.

domes in the isotropic state at 130°C (Fig. 1). Since the dome is only stable at temperatures above the bulk melting point, atomic force microscopy of scanning electron microscopy cannot be used to determine the three dimensional shape of the dome. But there is evidence from previously observed samples that the domes have a spherical shape [4, 5]. Cooling down leads to a homeotropic arrangement in the liquid crystal phase and the formation of a hexagonal dome. The hexagonal shape of the dome is only stable in the liquid crystalline phase, which could not be photographed, since the hot stage did not fit under the microscope that was equipped with a camera. Finally, the crystallization of the dome starts at the edges, so that the hexagonal shape is preserved in the crystalline state at room temperature. The diameter of the hexagon does not change during crystallization and each hexagon shows a void in its center due to the thermal contraction of the liquid crystal-to-crystal phase transition upon cooling. Thus casting of a dilute solution of a discotic liquid crystalline compound can be used to form complex structures solely by dewetting, dome formation, and self-organization of molecules within each dome.

In order to evaluate the influence of this hierarchic structure – the nanometer-scale stacking of discoid molecules and the micrometer-scale dome formation with a central void – on the J-aggregation of cyanine dyes, mixed solutions of liquid crystal and cyanine dye were cast onto substrates and annealed. It became clear that high cyanine/LC ratios prevent dewetting and thus no hexagons were formed. Figure 2 shows the optical micrograph of a sample that contains 10 wt% of cyanine dye. Dendritic growth of polycrystalline aggregates can be observed, but no hexagonal domes. But a sample containing less than 6 wt% of cyanine dye did yield in the formation of hexagonal H5T crystals, as can be seen from the fluorescence micrograph of a sample that contains 5 wt% of the cyanine dye. Interestingly, the dye is concentrated in the center of the dome, as indicated by the orange fluorescence. The rim of the dome shows green fluorescence, which stems from the H5T. Fluorescence microspectroscopy, which allows the recording of fluorescence spectra of a single aggregate, clearly showed the formation of J-aggregates in the center of the dome, as can be seen in the fluorescence spectrum in Fig. 3. The sharp fluorescence peak is a clear indication for J-aggregation. Domes without added cyanine dye show a broad fluorescence peak between 500 and 700 nm with a maximum fluorescence at 580 nm, which gives rise to the above mentioned green fluorescence of the H5T part of the dome.

IV. CONCLUSIONS

We could show that a low molar mass discotic liquid crystalline compound can form micrometer-sized dome
structures upon casting from solution. Annealing led to the formation of hexagonal domes with a central void. Co-casting of a cyanine dye gave rise to hierarchic structures in which the center of the hexagonal dome contained isolated J-aggregates. Energy transfer can be expected in mixtures where donor and acceptor molecules are in close vicinity (approx. 1 to 10 nm) and the fluorescence of the energy donor overlaps with the absorbance of the energy acceptor. Furthermore, if the donor shows fast energy or electron migration, the energy transfer efficiency should increase. Our system of columnar triphenylene derivatives that show fast electron migration [8, 10] with the described fluorescence characteristics in the present paper and the hierarchic order may be useful for energy harvesting or artificial photosynthesis applications.

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