Correlative microscopy of morphology and luminescence of Cu porphyrin aggregates

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Abstract

The transfer of energy and information through molecular aggregates requires as one important building block: anisotropic, cable-like structures. Knowledge on the spatial correlation of luminescence and morphology represents a prerequisite in the understanding of internal processes and will be important for architecting suitable landscapes. In this context we study the morphology, fluorescence and phosphorescence of nanoaggregates on surfaces in a spatially correlative way. We consider lengthy strands and isotropic islands as two morphologies. It turns out that phosphorescence is quite strong compared to fluorescence and the spatial variation of the observed intensities is largely in line with the amount of dye. However, in proportion, the strands exhibit more fluorescence than the isotropic islands, suggesting weaker non-radiative channels. The ratio of fluorescence to phosphorescence appears to be correlated with the degree of aggregation or internal order. The height at which luminescence apparently saturates is explained in the context of the multireflection of incident and emitted light inside the dye. This is supported by correlative photoemission electron microscopy which is more sensitive to the surface region. The lengthy structures exhibit a pronounced polarization dependence of the luminescence with a relative dichroism of up to about 60%, revealing the substantial perpendicular orientation preference of the molecules with respect to the substrate and parallel with respect to the strands.

Keywords: molecule aggregate, atomic force microscopy, fluorescence, phosphorescence, exciton, porphyrin, correlative microscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Organic crystals are attractive materials for opto-electronics and as light harvesting systems [1, 2]. They show high flexibility in preparation so that they can allow one to arrange for landscapes which are beneficial for processes such as field enhancement, energy transport, and charge separation. Upon illumination, Frenkel excitons are generated in molecule crystals. Compared to Wannier excitons in conventional semiconductors, Frenkel excitons exhibit higher binding energies and accordingly smaller spatial extents.

For enabling long energy transfer paths, the aim is to transport excitons over large distances through the aggregate. Basically, two mechanisms are considered: in Forster transfer, excitons hop through the crystal mediated by dipole–dipole interaction, while in Dexter transfer the direct exchange of electrons occurs. Though in Dexter type transfer diffusivity is substantially smaller, longer lifetimes may overcompensate for this drawback [3]. Note that Forster energy transfer suffers from shorter radiative lifetimes as a result of a larger transition dipole moment. In [3] it is put forward that Dexter transfer may be surprisingly robust against disorder; however, it requires intermolecular wave functions to overlap, usually implying finite electric conductivity. In organic dyes, singlet excitons typically come along with the Forster transfer mechanism and fluorescence, while for triplet excitons, Dexter transfer and phosphorescence are the dominating mechanisms. Triplet excitons can be the result of ordinary
inter-system crossing, e.g. involving spin–orbit interaction or charge transfer states [4], but may also occur due to singlet exciton fission [5].

In specific configurations, lengthy molecule aggregates could be locally illuminated, e.g. via plasmonic nanoparticles, and the paths of excitations could be tracked through the structure landscape by means of spatio-temporal mapping. Such a scenario requires the solid characterization of dye aggregates in terms of how morphology and molecular aggregation affect the distribution of excitations, either observed as luminescence or as electron emission. Traditionally, predominantly spectroscopic studies have been employed to assess dynamic characteristics of excitons; recently, the number of microscopy studies addressing spatial properties of excitons has been evolving. Fluorescence microscopy has been used in the past to study the spatially dependent properties of dye molecules. In a tetraene/anthracene-based dye blend, aggregates form fibers exhibiting white luminescence with anisotropic polarized emission [6]. In porphyrin nanotubes, time-resolved photoluminescence has been used to determine singlet and triplet exciton diffusion speeds and coherence effects [7, 8]. An opposite transport anisotropy for singlet and triplet excitons has been observed in tetracene crystals [9]. Enhanced optical near fields have been found in diindenoperylene (DIP) especially at the domain boundaries of the crystal, which is interpreted as strong coupling of the tip plasmon with the exciton polariton [10]. Apart from ensemble spectroscopy spatially resolved polarization and lifetime maps can reveal information on the degree of order, the orientation of the molecules, and the competition of luminescence versus non-radiative de-excitation pathways of individual aggregates or assemblies. In [11], a polarization dichroism of 80% was determined for two distinct morphologies of thiophene derivatives. This was attributed to different levels of energetic disorder in the assemblies. A difference of molecular alignment in micrometer long string- and rod-type J aggregates of thiacyanine-based molecules has been revealed by means of fluorescence microscopy under polarized light excitation [12]. In the case of thiacyanine aggregates, the excitation polarization was varied and a stronger emission with polarization along the fiber axes was observed. It was concluded that the long axis of the molecule is aligned along the fiber axes [13]. Just slightly different exciton lifetimes were reported for rod- and sphere shaped porphyrin aggregates [14]. Here we are interested in the related properties of copper porphyrin, (5, 10, 15, 20-tetra-undecylporphyrinato)copper(II), hereafter CuTUP, with a special focus on the interplay between morphology and luminescence properties. Porphyrins are interesting because of their strong absorption in the region around 400 nm (Soret band). Respectively, they can be locally excited via plasmonic near fields of Ag nanoparticles which might allow the tracing of the path of energy transfer through the aggregates. CuTUP has a few particularly remarkable characteristics. The Cu center is expected to promote intersystem crossing, so that long-lived, triplet-like excitonic states may also get populated. The choice for the alkyl-type side groups is motivated by their chemical innocence and high flexibility, the latter allowing for versatile conformations. Spatial flexibility can assist monolayer adsorption on inert substrate surfaces via interfacial adjustment or entanglement of the alkyl chains and the formation of three-dimensional lengthy aggregates via their flexible bending or curling. As a first step to answer the question of which types of excitations are present in nanaggregates of the molecules and how they depend on structural features and on the environment, we investigate morphology, fluorescence, and phosphorescence of porphyrin aggregate structures via correlative microscopy methods.

The outline of this work is as follows: in order to correlate exciton properties to the morphology of the aggregates, we investigate spatially resolved fluorescence and phosphorescence using luminescence microscopy as well as the height and shape of the same objects by atomic force microscopy (AFM) in a correlative way. As an extension we present polarization-dependent data which is used to additionally address the internal structure of the aggregates. In order to corroborate the interpretation of the observed effects, we finally compare the optical data to the results obtained by photoemission electron microscopy, which offers a higher sensitivity to the aggregates’ surface area and hence a more pronounced intensity dependence on the local height of the objects.

2. Experiment

We prepared different structures of CuTUP aggregates on substrate surfaces and studied their morphology, fluorescence, and phosphorescence by correlative AFM and optical microscopy. The copper-based porphyrin was functionalized with undecyl tails at the four meso-positions; the synthesis has been described earlier [15]. Side groups are very flexible and therefore enhance solubility, including non-aromatic solvents. Alkyl chains are known to facilitate the binding of molecules on graphite surfaces, as has been shown in STM studies of monolayers [16]. If not otherwise stated, we prepared 3D stands via drop casting of a 1 to 2 × 10−4 molar CuTUP-heptane solution without any post-rinsing. As substrates we use silicon, highly oriented pyrolytic graphite (HOPG), or glass. In the course of the evaporation of the solvent, characteristic tree-like structures grow on the surface; occasionally shorter, straight structures or largely isotropic islands occur.

Photoluminescence images are taken with an inverted microscope (Olympus IX73). The fluorescence images are acquired using bandpass filters with transmission in the range 540 nm–580 nm for excitation and 595 nm–665 nm for emission, respectively, which corresponds to the Q band fluorescence region of CuTUP. Likewise a bandpass filter in the range 400 nm–700 nm and a long pass filter (>750 nm) are used for phosphorescence excitation and detection, respectively. The resolution as estimated from line profiles of small dot-like structures is ~450 nm and ~500 nm for fluorescence and phosphorescence, respectively, both in good agreement with theoretical values defined by Rayleigh criterion.

Photoluminescence spectra are recorded in confocal mode (’NT-MDT NTEGRA spectra’ with spectroscopy module). The 532 nm excitation wavelength is filtered out from emission by a corresponding Raman edge filter. The fluorescence lifetimes of the aggregates are measured and analyzed with a fluorescence lifetime imaging microscope and corresponding software.
Then, tree-like aggregates form. Occasionally the dewetting front relocated wobbles and already-grown tree aggregates can be detached and surface, by dust particles or other contaminations wed down, e.g. by approaching topographic irregularities on the surface, by dust particles or other contaminations wed down, e.g. by approaching topographic irregularities on the surface. When the dewetting front is transiently pinned or otherwise slowed, the shrinkage of the droplet, the aggregation rate is enhanced. Region with the fast, uninterrupted retraction of the dewetting front, isotropically shaped aggregates form for all chosen substrates. Molecular aggregates. In our case, larger dendritic and smaller rod-like objects are observed as roughly perpendicular to the strand axis. This is a first sign of molecular order in the strands. Below, we show on the basis of polarization dichroism that the lengthy structures are substantially ordered. The isotropic islands show heights between 70 nm and 120 nm, and diameters in the range of 0.6 μm to 1.5 μm, (see figures 3(a), (b)). Isotropic structures dominate if the substrate is glass. On HOPG, we can obtain a well ordered monolayer of flat-lying molecules exhibiting two characteristic lattices covering the whole surface [15] upon rinsing. We did not test this for the other two substrates because surface structure is not crystalline. An AFM topography and a phase image of a molecular strand and the domain structure of the monolayer is shown in figures 2(f) and (g), respectively.

3.2. Morphology, adhesion, and structure

Three-dimensional aggregates are observed on silicon as well as on glass and HOPG. In the following, we describe the morphology of the elongated tree-like and the more isotropic structures. Tree structures are several 10 nm, up to 200 nm high (figure 2(a)) and show fluorescence as well as phosphorescence (figures 2(b), (c), see also section 3.4). The strands have belt-shaped profiles (figure 2(d)) exhibiting a wide spectrum of widths from ~100 nm to ~1000 nm. In contrast to longer strands, the small structures are quite straight, suggesting a fully relaxed conformation on the substrate. The larger tree-like aggregates bend on length scales of ~10 μm. For the flatter structures (below ~30 nm) luminescence is below the detection limit of our microscope. A very striking feature is a rather uniform splitting angle of around 26°–29° at bifurcations, as obtained from a large number of tree-like objects. This points to a structural motif contained this intermolecular angle. The value of the angle is quite robust in that it does not depend on substrate material or detailed parameters during preparation, e.g. vapor pressure. In certain regions, the structures appear to be agglomerates of smaller rod-like objects (figure 2(e)). If curved fibers are cleaved by means of the AFM tip, the two ends jump into a straight configuration, revealing that the strands are subject to tension as a consequence of the attachment to the surface (not shown). At the same time, this points to rather weak adhesion which is in line with the observation that whole aggregates are dislocated during preparation via forces due to the moving dewetting front (see figure 1(c)). Cutting strands by means of an AFM tip results in quite flat surfaces at the cleft perpendicular to the strand axis; apparently cleavage occurs along a crystallographic plane, which is observed as roughly perpendicular to the strand axis. This is a first sign of molecular order in the strands. Below, we show on the basis of polarization dichroism that the lengthy structures are substantially ordered. The isotropic islands show heights between 70 nm and 120 nm, and diameters in the range of 0.6 μm to 1.5 μm, (see figures 3(a), (b)). Isotropic structures dominate if the substrate is glass.

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3.3. Deposition at modified evaporation rate

Spray deposition is an option to enhance solvent evaporation and may reveal whether crystallites already had precipitated.
prior to drop casting in the solution or not. Inspection by optical microscopy and AFM shows that the aggregates are much smaller and hardly exceed 40 nm heights; no tree-like aggregates have formed and predominantly isotropic, almost circular structures are found (figure 3(c)). So we conclude that the tree-like strands do not pre-form in solution before contact with the surface, but rather in the course of the shrinkage of the droplet due to the evaporation of the solvent. For spray deposition, we used the same concentration as in drop casting. The spray diffuser is made of brown glass and a nozzle and

Figure 2. Geometry and luminescence of tree-like aggregates. (a) Survey AFM morphology, (b) correlative fluorescence image (exposure 20 s), and (c) correlative phosphorescence image (exposure 3 s). (d) Line sections along the path indicated in (a). (e) AFM example of a tree-like structure which seems to be composed of smaller, rod-shaped aggregates. (f) AFM topography and (g) phase of a sample after rinsing. Apart from a remaining thin strand (diagonal bright line, see inset for a line profile) domains of different polymorphs of monolayer aggregates are visible, most notably in the phase image (dark versus bright patches in (g)). The substrate is silicon for images (a)–(d) and HOPG for (e)–(g), respectively.
tube of polyethylene, respectively. We applied one shot by a typical finger press from a large distance of about 75 cm. Smaller distances such as a few cm lead again to tree-like aggregates, probably because the deposited aerosol droplet diameter has already become macroscopic or due to droplet coalescence. Another approach in structure variation – this time with lowered evaporation rate – is aggregation under higher solvent vapor pressure, which is achieved by placing the samples inside a small box during evaporation which is not tightly closed. This yields lengthy, curly, thin structures (figure 3(d)).

3.4. Luminescence intensity versus height

We observe fluorescence in the region of the Q bands around 600 nm using a filter cube designed for the fluorescence marker ‘Texas Red’. The emission window covers a substantial part of the Q-band fluorescence regime of CuTUP. For this filter cube, the excitation window does not include the Soret band (~400 nm); consequently, relatively weak fluorescence may be expected. However, a modified filter cube optimized for Soret excitation did not result in significantly higher fluorescence signal. This might be explainable in the context of the efficient transition to triplet-like states like described in [4, 18] which may be selective with regard to the initially excited state. Due to the resulting low intensity, the minimum height of objects with detectable emission beyond the noise floor is around 30 nm. Another consequence is that Raman lines become comparable in intensity, such that the fluorescence regime may be ‘contaminated’ by Raman emission lines, e.g. C-H stretch modes [21–23] to a relevant extent as the comparison of spectra with excitation at different wavelengths (632.8 nm, 532 nm, and 405 nm) confirmed that the sharp features in figure 4(a) correspond to Raman lines. We observe strong phosphorescence in the transition energy regime of triplet states (800 nm–1000 nm, see figure 4(a)). Here, a long pass filter cube (>750 nm) is used to account for the spectral width of the signal. Due to the different widths of excitation and emission windows used in the two filter cubes, the value for the ratios of fluorescence intensity divided by phosphorescence are difficult to estimate on the basis of the microscopy data. Optical spectroscopy at 532 nm laser excitation reveals that phosphorescence is considerably stronger than fluorescence, particularly taking into account

![Figure 3](image_url)

Figure 3. (a) AFM topography of almost isotropic aggregates on silicon. (b) Normalized line profiles from correlative AFM (black), fluorescence (green), and phosphorescence (red) micrographs along the path indicated in (a). (c) Optical dark field image of structures formed by spray deposition on glass. (d) Dark field image of branched aggregates grown at increased vapor pressure on glass.
possible Raman emission (figure 4(a)). In the case of the monomer, fluorescence is essentially absent and phosphorescence completely dominates the emission (not shown). When comparing the luminescence of the different morphologies discussed above, subtle differences in the intensity distribution of structures of similar height are observed which we address in the following. For the intercomparison of different structures we use a double quotient of intensity slopes fluorescence phosphorescence ratios

\[
\text{slope}_{\text{fluor,strands}} / \text{slope}_{\text{phos,strands}} \text{slope}_{\text{fluor,isol}} / \text{slope}_{\text{phos,isol}}
\]

From correlated luminescence and AFM measurements, we obtained the luminescence intensity as a function of structure height for a large number of CuTUP nanostructures. In figure 4(b), we show the behavior for the tree-like objects; the behavior of isotropic structures is qualitatively similar. In the height regime of flat structures (below ∼50 nm) the fluorescence intensity tends to rise parabolically with structure height; at intermediate heights, the intensity rises about linearly with structure height; beyond a certain threshold height which is ∼100 nm in the case of fluorescence and ∼130 nm in the case of phosphorescence, the intensity appears to saturate, or even start to decrease again as suggested by the fluorescence data (green data points in figure 4(b)). In the linear regime, we evaluate the slopes of the behavior of intensity with respect to height. To eliminate the effects from the different illumination conditions and exposure times, the comparison is applied to intensity slope ratios fluorescence/phosphorescence for the tree and isotropic structures respectively. This reveals higher ratios of the lengthy structures than for the isotropic ones. Hence, fewer non-radiative channels appear to be available for the lengthy structures, or the dipole transition probability for fluorescence is enhanced there. Possibly, upon the assembly of the isotropic structures, a higher degree of disorder is retained. This is in agreement with observation that the dewetting line moves substantially faster during the aggregation of these structures and molecule transport is then less directional compared to the assembly of the lengthy, tree-like structures. A lower degree of order in the isotropic structures is further supported via roughness inspection. The lengthy structures exhibit AFM corrugations below 1 nm, while the isotropic structures appear ten times rougher and thereby may contain more quenching sites. Additionally, the ragged morphology at the border of the isotropic aggregates suggests a lower degree of order or smaller domain sizes compared to the strands. These observations corroborate the notion that the molecular ordering in the strands is better. This means that the lower fluorescence to phosphorescence ratio of the isotropic islands is related to their lower structural order.

Sets of correlated microscopy images can be further inspected in order to address lateral effects. In particular, cross sections can elucidate how far luminescence depends on morphological features. For the strands as well as the isotropic structures, we observe that cross sections taken in AFM topographies are narrower than respective cross sections in luminescence images (figures 2(c) and 3(c)). This can be attributed to the lower spatial resolution of optical imaging versus AFM. In AFM, the ‘resolution’ is roughly proportional to the height; in optical microscopy, the resolution is a fixed
an oscillatory behavior of the...direction along the direction parallel to the strands. Silicon is used as a substrate here.

value (at one wavelength). Luminescence appears to be rather homogeneously distributed over the structure and the borders of the aggregates neither show higher nor particularly lowered intensity. This means that quenching at the sides is not obvious.

3.5. Internal molecular ordering

To learn about the orientation of the transition dipole moments in the strands, polarization microscopy is employed. We illuminated the sample by unpolarized light and acquired fluorescence images under unpolarized excitation. The color-scale is given with respect to an arbitrary reference angle. Emission is predominantly polarized along the direction parallel to the strands. Silicon is used as a substrate here.

Figure 5. Map of directions with maximum luminescence intensity reflecting the dichroism of tree-like structures. This is extracted from polarization-filtered fluorescence images under unpolarized excitation. The color-scale is given with respect to an arbitrary reference angle. Emission is predominantly polarized along the direction parallel to the strands. Silicon is used as a substrate here.

4. Discussion

4.1. Optical density of states effects on excitation and emission

When discussing lateral variations and differences between structures, it is necessary to consider various phenomena involved in the experiment. Luminescence intensities can become altered at the stage of absorption, at internal processes, and at emission. One may discriminate the effects of the variation of the optical local density of states: vertically, i.e. due to mirroring at opaque substrates, or laterally, i.e. due to light landscapes. The molecular structures may guide light, depending on their shape and size [29] which could lead to better or worse matching of electric field directions to transition dipole moments. Lengthy structures are obviously more likely acting as optical fibers and Poynting vector directions then lie preferably along the fiber axis. This could change absorption if the transition dipole moments of the aggregate are also oriented predominantly in transversal direction with respect to the fiber axis. With the isotropic shapes, this would rather not result in modulated absorption. As will be shown in 4.3, the aggregates themselves give rise to a modulated optical density of states. We first address possible molecule-aggregate effects and neglect influences of morphology. A selection of possibilities is depicted in figure 6; this includes pathways associated with monomers [30] as well as options specific for oligomers and aggregates.

4.2. Aggregation effects on luminescence

Most luminophores show weaker luminescence if aggregated compared to monomers. This is referred to as aggregation-caused quenching and is due to additional non-radiative...
de-excitation possibilities in the solid state. However, a number of species show the reverse phenomenon, i.e. aggregation-induced emission enhancement (AIE) [31]. Compared to a monomer, in an extended aggregate there is a frustration of vibrational motion, rotation of subunits (e.g. methyl groups), and of configurational relaxation possibilities, affecting internal conversion. A different extent of order in an aggregate may already modulate the degree of freedom and thereby shift the relative ratio of non-radiative versus emissive de-excitation pathways. The observation of higher ratio fluorescence to phosphorescence of the structures with lengthy morphology versus isotropic as described above might originate from a kind of AIE. In particular, the alkyl side groups with their methyl ends attached to the meso-positions of the porphyrin could get locked in the dense aggregate and no longer be available for non-radiative energy transfer. Another option for the elevated fluorescence/phosphorescence ratio of strands would be superradiance [32] which should come along with increased decay rates. Fluorescence lifetime imaging on the tree-like structures reveals lifetimes in the regime of some nanoseconds (∼9 ns on average) with two main contributions at ∼3.5 ns and ∼9 ns. This value is compatible to that of the monomer as measured in heptane (∼7 ns, see [17]). The spatial lifetime distribution of these structures is largely homogeneous. Additionally, triplet states of the same molecule showed quite little lifetime heterogeneity in a photoemission study [18]. These results indicate that superradiance is not the dominant mechanism in this case. On the other hand, they are compatible with small superradiating subunits within partially ordered aggregates, giving rise to a slight lifetime reduction with respect to monomer.

4.3. Effect of multiple reflections on intensity behavior

Which effect is responsible for the observed plateau in intensity, in both fluorescence and phosphorescence? Internal reflection will give rise to multireflection at the dye-air and at the dye-silicon interfaces. We thus invoke the multireflection approach which includes interference. In addition, the penetration depth of radiation is finite and so is the volume of the aggregate to be illuminated by the radiation, which is included by a finite absorption coefficient. Both the incident wavelengths and the emissive wavelengths are taken into account. The variation of refraction indices should be moderate for fluorescence in the relevant optical wavelength regime. For CuTUP aggregates we assume refractive index n to be near 2 [33] as silicon n is near 4. According to the Fresnel equations, a node is expected at the interface between substrate and dye, while an antinode is expected at the interface between dye and air. To elucidate the effect of internal reflection of luminescence, we performed simulations similar to those in [34] for a thin film of molecules on the substrate using optical properties of related molecules [33]. The vertical variation of excitation intensity is also affected by the finite attenuation length inside the structure which is of the order of a few 100 nm. Luminescence light is treated to be monochromatic with a wavelength of 630 nm for fluorescence. The simulation is done for fluorescence, since for the phosphorescence, the optical properties of the molecule and substrate vary dramatically within the wavelength range of excitation and emission. The observed emission intensities are calculated from an integral over the aggregate thickness where both absorption within the material and reflections at the interfaces are taken into account. No fitting parameters are involved. The resulting curve is shown in figure 4(c) and agrees well with the experimental data (figure 4(b), green data points). The simulations also reveal that the apparent plateau in the experiment is due to the first oscillation of the fluorescence intensity.

In order to verify the participation of internal multi-reflections and absorption giving rise to the observed curve shape of correlation plots such as shown in figure 4(b), we employ a similar analysis based on photoemission electron microscopy (PEEM). In contrast to earlier PEEM experiments where interference effects have been utilized for obtaining object heights either using Lloyd’s mirror geometry [35] or x-ray standing waves [36], here we evaluate optical interferences within the dye structure. The sample is illuminated by a pulsed laser (λ = 269 nm, see [18] and [17] for details) and the intensity of photo-emitted electrons is analyzed as a function of the local structure height. The advantage of PEEM is that it is only sensitive to a thin layer (< 30 nm) close to the surface such that the integration over the entire aggregate thickness hardly smears out interference effects. Figure 7 shows the experimental data together with a fit to a simple model similar to the one described above. In contrast to optical microscopy, only the incident light is relevant (which is monochromatic here) because second-order effects due to the reabsorption of luminescence light do not play a considerable role. Pronounced oscillations are clearly visible and good agreement with the model confirms the occurrence of optical internal reflections within the strands. The presence of a negative slope for a certain height range also implies that there is anticorrelation between PEEM and AFM images which we indeed observe (figure 7(b)). Due to its high surface sensitivity, the PEEM data corroborate the interpretation and confirms the applicability of the multireflection model although the molecular structures are of sub-micrometer lateral dimensions.

4.4. Fluorescence properties in view of internal molecule arrangement

We now briefly address the question of whether the luminescence data shown in this work may provide hints on the dominating internal configuration, i.e., H-type as opposed to J-type aggregates. In contrast to the more commonly studied 1D aggregation in liquids, a 3D nanocrystal implies the coexistence of different internal coupling regimes such that both configurations are expected to be present, depending on the crystallographic axes considered. In case the Davydov splitting is strong, a clear distinction of J- and H-aggregates is not straightforward. For 1D crystallites, red-shifted narrow absorption band and fluorescence with small Stokes shift is
expected with J-type molecule stacking, and blue-shifted absorption with a weak or no fluorescence compared to the monomer for H-aggregates \[37, 38\]. Luminescence microscopy as conducted here is not sensitive to such shifts due to the relatively large spectral excitation and emission ranges (see above). In addition, spectrally resolved data are not entirely conclusive: first, the relatively broad fluorescence peaks impede the accurate determination of peak positions, particularly in view of the very weak emission of the monomer. Second, one would have to account for the role of the solvent, necessary for the reference spectrum, implying different dielectric environments for monomer and aggregate. Another approach would be to directly determine the internal structure and conclude on the dominating arrangement based on high-symmetry directions. This is, however, not straightforward because conventional diffraction methods require larger crystallites and more material. Another option would be high-resolution scanning probe microscopy such as in-liquid monitoring by AFM during the dissolution or formation of the aggregates, which may shine light on the detailed growth process and therefore on the internal structure. Solvent composition is then delicate because adhesion of the 3D structures on the surface must be sustained in the course of the process and during measuring.

5. Conclusion

CuTUP aggregates have been prepared on surfaces such as silicon, glass, and HOPG and studied with respect to...
luminescence and morphology. The residence time of the dewetting front determines the aggregate morphology. Two types of morphologies have been observed: (i) anisotropic, lengthy, tree-like shapes and (ii) almost isotropic structures. Phosphorescence is generally favored over fluorescence and the local structure volume appears to be the main parameter governing luminescence intensity. Lengthy tree-like structures exhibit maximal fluorescence in proportion to phosphorescence compared to other morphologies such as flat or isotropic aggregates, and to monomers which exhibit an increasingly large phosphorescence fraction. This is compatible with the effect of aggregation-induced fluorescence enhancement and/or phosphorescence quenching. Fluorescence dichroism up to 60% is observed for the lengthy structure, being in accordance with substantial molecular order. Correlations of height determined by AFM with the luminescence intensity for the same sample area reveal a rather complex dependence. A simple model taking into account multi-reflections within the aggregates along the vertical direction can explain the observed behavior, as well as the pronounced height-dependent oscillations observed in photoemission maps. The observed variations of the fluorescence versus phosphorescence intensity behavior appear to reflect the degree of order in the aggregates, see figure 8 for an illustration. Hyperspectral mapping could give further insight into the energetics of the involved transitions. The work presented here also serves as a basis to investigate in a next step metal-assisted luminescence enhancement [39] and migration effects in configurations where the molecule strands are coupled to plasmonic nanostructures.

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