Photophysics of Self-Assembled Monolayers of a π-Conjugated Quinquethiophene Derivative

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ABSTRACT: The photophysics of fully and partially covered self-assembled monolayers (SAMs) of a quinquethiophene (5T) derivative have been investigated. The monolayers behave as H-aggregates. The fluorescence of fully covered SAMs is weak and red-shifted, and the extinction is blue-shifted as compared to that of single molecules. The fluorescence of partially covered SAMs is dominated by that of single molecules on the surface. The extinction spectra are similar for fully and partially covered monolayers, which show that even the smallest islands are H-aggregates. The extinction spectra furthermore closely resemble those for 5T single crystals, which demonstrates that in oligothiophene crystals the intermolecular interactions within one layer molecules are stronger than the interlayer electronic coupling.

INTRODUCTION

Conjugated organic molecules are applied in a wide array of opto-electronic devices such as solar cells, field-effect transistors, and light emitting diodes.1 Their photophysics has been widely investigated.2−4 Emphasis has been on oligothiophenes as they are soluble in common organic solvents, environmentally stable, and synthetically accessible. Comprehensive investigations of the photophysics of oligothiophenes in solution up to 7 thiophene units have been reported.5−8 The photophysics of single crystals is more complicated. Optical excitation in single crystals yields a bound electron hole pair or exciton, first introduced by Frenkel in 1931.9 In organic molecular crystals, the dielectric constant is small. The Coulomb interaction between the electron and hole leads to a large binding energy on the order of 0.1−1 eV. Frenkel excitons thus tend to be small, of the same order as the size of the unit cell.

Oligothiophenes usually crystallize in structures with two or four molecules in the unit cell. Optical properties of oligothiophene crystals have been studied in considerable detail, both experimentally10,11 and theoretically.12−17 Complete understanding is complicated by the three-dimensional molecular packing with more than one molecular in the unit cell and the electronic coupling between molecules being different in all three directions. The exciton can couple to both intermolecular vibrations and photon states, yielding polaritons. Furthermore, the optical response of the crystals could be affected by the presence of surface states, defects, and disorder.18−21 The problem may be simplified by studying two-dimensional layers of oligothiophene molecules rather than the three-dimensional crystals; however, the optical properties of oligothiophene SAMs have so far not been reported.

Closely packed, two-dimensional, self-assembled monolayers (SAM) of a quinquethiophene (5T) derivative have recently been reported.22 The observation of Bragg rods in grazing incidence X-ray diffraction measurements indicates a high degree of in-plane order. Not surprisingly, corresponding self-assembled monolayer field-effect transistors exhibit a bulk-like carrier mobility, large current modulation, and high reproducibility.23,24 The oligothiophene moieties are oriented with their long axis perpendicular to the surface.25

Intermolecular interactions in a monolayer of chromophoric molecules give rise to formation of an exciton band.26−29 In a first-order approximation, the electronic structure of the exciton band can be understood by treating the excited-state intermolecular interactions as a coupling between transition dipole moments of the individual constituent molecules. For oligothiophenes, the transition dipole moment for the allowed transition from ground state to the first excited singlet state S1 is oriented along the long axis of the oligothiophenes. For arrays of oscillating transition dipoles oriented perpendicular to the surface, all dipole–dipole interaction energies are positive. For this arrangement, there will be only one allowed transition that is blue-shifted (i.e., occurring at higher frequency) with
respect to the transition in the single molecule. The two-dimensional array of perpendicularly oriented molecules is thus expected to behave as an H-aggregate; see Figure 1. In an H-aggregate, the lowest optical transition is forbidden. Nevertheless, fluorescent emission is possible due to perturbation by molecular vibrations and disorder. The residual fluorescence from H-aggregates with an extremely low quantum yield is red-shifted in comparison with the single molecules.

In contrast for a two-dimensional lattice of transition dipoles oriented in plane and arranged in a brickwork pattern (see Figure 1), a red-shifted absorption is predicted provided that the head-to-tail in-plane interaction is stronger than the cofacial lateral coupling. This is typical for J-aggregates. In a J-aggregate, only the optical transition to the lowest energy state is allowed. Consequently, J-aggregates show a small Stokes shift and fluorescence with a high quantum yield. Although for dense SAMs, J-aggregation may not be expected, we note that J-type aggregation on a surface has been reported for sexithiophene and is a common type of two-dimensional molecular arrangement for cyanine dyes.

Here, we investigate the photophysics of partially and fully covered monolayers. By comparing optical properties as a function of aggregate size, we investigate the length scale of in-plane interactions. From a comparison of the measured spectra with those reported for single crystals, we estimate the importance of out-of-plane interlayer interactions.

**EXPERIMENTAL METHODS**

Self-assembled monolayers (SAM) were prepared on silicon monitor wafers covered with a 200 nm layer of thermally grown SiO₂ to study the morphology and on quartz to measure the extinction spectra. Quartz was chosen as an optically silent substrate. The chemical structure of the self-assembling molecule, chloro [11-(5′′-ethyl-2,2′,5′′,2′′′,5′′′′-quinqueithien-5-yl)undecyl]-dimethylsilane (1), is shown in Figure 2a. The molecule consists of a conjugated quinquethiophene core. To bind the molecules to the SiO₂ surface, a monochlorosilane anchoring group was attached via an undecane spacer. The compound contains an inactive impurity (2) that cannot bind to the SiO₂ surface. The chemical structure is presented in Figure 2a as well. Co-crystallization is reported to be unlikely but could not be excluded. As a model compound to study the behavior of single molecules in solution with no possibility to dimerize, 5-ethyl-5′-(undec-10-eyl)-2,2′,5′,2′′,5′′,2′′′,5′′′-quinqueithiophene (3) was used. This molecule is an isomer of 2 with the double bond between the primary and secondary carbon atoms of the alkenyl substituent.

To grow the SAM, the surface was activated by an oxygen plasma treatment followed by acid hydrolysis. The SAM was formed by submerging the activated substrate into a 1 mM solution of the molecule in dry toluene. The coverage was varied by changing the incubation time from 5 min to 2 weeks. After monolayer formation, the substrates were rinsed with dry toluene and dried with N₂.

The morphology was investigated by atomic force microscopy (AFM) measurements using a Veeco Dimension 3100 atomic force microscope equipped with a Nanoscope IV control unit. The profile measurements were performed in noncontact tapping mode. Typical topography images (20 μm × 20 μm) of partially covered SAMs on SiO₂ are presented in Figure 2a–d, and that of a fully covered SAM is shown in Figure 2e. The AFM images show that the SAM grows in the form of islands.

The height differences in the topography are 3.5 nm, in perfect agreement with the calculated length of the molecule. A small fraction of the islands shows a bilayer, most likely due to the presence of dimers in the solution.

Fluorescence spectra were recorded on an Edinburgh F900 fluorescence spectrometer. The sample compartment was flushed with nitrogen. Fluorescence spectra were corrected for the wavelength dependence of the sensitivity of the detection channel and for a small dark count rate of the thermoelectrically cooled photomultiplier tube. Extinction spectra were recorded on a Perkin-Elmer lambda 900 spectrophotometer. Fluorescence decay times were obtained using a time correlated single photon counter using a Edinburgh FS 920 spectrophotometer.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Quantaer XM from Ulvac-PHI, employing monochromatic Al Kα radiation with a spot of 100 μm, scanning across an area of 1200 μm × 500 μm. The chemical state and the atomic concentrations of the elements present on the surface were determined from narrow-scan measurements. Measurements were done at a takeoff angle of 60°. The information depth is then approximately 6 nm.

**RESULTS AND DISCUSSION**

To analyze the photophysics of the monolayers, we first measured the optical properties of the single molecule as a function of temperature. The active molecule is not stable in solution; the compound is prone to dimerization. Hence, we...
used a nonactive model compound that has the same π-conjugated quinquethiophene (5T) core. Figure 3 shows the normalized fluorescence (red), fluorescence excitation (blue), and extinction (black) spectra of compound 3. The solid lines represent spectra measured of toluene solutions at 293 K. The dashed lines were measured in a glassy 2-MeTHF matrix at 80 K. The fluorescence is due to the optically allowed S₁→S₀ transition and exhibits a maximum at about 2.3 eV. The vibronic fine structure is based on a 1400 cm⁻¹ fully symmetric vibrational mode, which is typical for the 5T-moiety and which is associated with changes in the bond length alternation upon optical excitation. The vibronic fine structure gets more pronounced at low temperature. Previous studies have shown that the loss of resolution at room temperature is due to the torsional flexibility around the single bonds joining the thiophene units that leads to a significant thermal population of nonplanar conformers of the 5T moiety.31 In the excitation spectrum, a vibronic progression similar to that in emission is observed. The frequencies of the active mode are the same and associated Huang–Rhys factors similar. A small change in Huang–Rhys factor is often observed for π-conjugated oligomers.31,32 From the extinction spectra, a Stokes shift of 0.5 eV is determined. The maximum extinction coefficient amounts to 4 \times 10⁴ M⁻¹ cm⁻¹.

From integration of the molar extinction coefficient for the molecule in toluene solution over the photon energy range corresponding to the S₀→S₁ transition and correcting for the local Lorentz-field in the solvent, we determine a transition dipole moment μ for the S₀→S₁ transition with a magnitude of 8.1 D. The transition dipole moment is oriented along the long axis of the molecule.33

Extinction spectra of self-assembled monolayers on quartz are presented in Figure 4a. The normalized spectra are identical. The spectra were measured with the incident beam under an angle of 57° with the substrate normal. The extinction...
increases with incubation time due to changes in the monolayer coverage. XPS measurements were performed to derive the coverage. The sulfur 2p peak with binding energy of 163.7 eV was used as a marker for the thiophene units. The peak intensity is presented in Figure 5 together with the maximum extinction at 3.45 eV as a function of incubation time.

Figure 5. Monolayer coverage from XPS and extinction measurements. The sulfur 2p peak intensity at 163.7 eV binding energy (black circles) and optical density at 3.45 eV (red circle) as a function of incubation time. The line is a guide to the eye.

coverage increases with incubation time. A full monolayer is obtained after about 4 h. A quantitative analysis of the XPS data showed that the layer thickness of the SAM is 4.2 nm assuming a densely packed monolayer, which is in agreement with the calculated length of the molecule and the AFM data. The good agreement between XPS and extinction measurements shows that self-assembly growth ends upon formation of a fully covered monolayer.

The extinction spectra for a fully covered SAM as a function of angle of incidence are presented in Figure 4b. Two extinction bands with maxima at 3.5 and 4.5 eV are observed. The dependence of extinction on the orientation is clearly different for the two bands: the band at 4.5 remains almost constant when changing the angle of incidence, while the band at 3.5 eV increases in intensity for large angles of incidence. Assuming a dipole model and including a correction for the local electric field at the quartz–air interface based on the Fresnel coefficients, one predicts that transitions with transition dipole moment in the plane of the monolayer (so perpendicular to the surface normal) do not depend strongly on angle of incidence. In contrast, transition dipole moments parallel to the surface normal are predicted to give zero extinction at normal incidence with the extinction rising steeply for angles of incidence going away from normal. We therefore assign the 4.5 eV band to a transition polarized in the plane of the layer. This assignment is compatible with the large b-polarized component of the corresponding transition for the 5T single crystal and is compatible with substantial charge-transfer character for this transition.

The rise of the extinction of the 3.5 eV band with angle of incidence shows that this transition is polarized primarily along the surface normal. This is in agreement with an almost upright orientation of the molecules as derived from grazing incidence X-ray diffraction measurements. The substantial extinction near normal incidence indicates a considerable component of the transition dipole moment in the plane of the film, which most likely arises from a charge-transfer contribution to the transition.

In comparison to the single molecules, the maximum of the first optical extinction band at 3.5 eV of the monolayer has shifted to higher frequency. The blue shift of about 0.5 eV matches very closely to optical data reported for a thin layer (95 nm) of quinquethiophene molecules deposited by vacuum sublimation and is indicative of an H-aggregate as elucidated in Figure 1. An H-aggregate is formed when the transition dipole moments are parallel aligned. Here, the transition dipole moment is along the molecular backbone, and analysis of the extinction measurements as a function of angle has shown that the molecules themselves are indeed aligned almost perpendicular to the substrate. The extinction spectra for the monolayer feature a low energy, low intensity absorption wing extending down to 2.5 eV. A similar wing is observed for oligothiophene crystals. Theoretical analysis indicates that the wing arises from transitions to the lower exciton levels of the H-aggregate with vibronic coupling inducing a small, but nonzero transition probability. The energy difference between the onset of extinction (2.5 eV) and the extinction maximum (3.5 eV) is, in first approximation, a measure for the exciton bandwidth. In a simplified description including only nearest neighbor interactions between the ST molecules, the exciton bandwidth equals $4V$, with $V$ the excited-state interaction energy between neighbors. In the dipole approximation, $V$ equals $\mu^2/(4\pi\epsilon_0\epsilon_r\lambda_0^3) = 0.4$ eV. To calculate $V$, we have used the...
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experimentally determined value for the transition dipole moment (μ = 8.2 D, see above). a₀ = 0.45 nm is obtained from the geometric mean \(\sqrt{(ab)/2}\) of the lattice constants a and b determined from X-ray scattering on the monolayers, taking into account that the unit cell contains two molecules.

We note that the radiative lifetime of an H-aggregate is larger than that of a single molecule. However, the measured lifetime of the fluorescence from a complete monolayer (0.8 ns) is shorter than the lifetime for the fluorescence from the single molecules in solution (1.0 ns) and from the lifetime for substrates with only partial coverage (1.0 ns). From this, we conclude that additional intermolecular interactions between 5T molecules in the complete monolayer reduce the probability for photon emission and lead to a change in the band shape of the fluorescence as expected for an H-aggregate. Analysis of the full fluorescence decay trace of the complete monolayer (see the Supporting Information) indicates contributions from species with lifetime exceeding 1 ns, indicating heterogeneity in the population of emitting species.

The extinction spectrum of the fully covered SAM is almost identical to that of a quinquethiophene single crystal.\(^{35,38}\) Apparently, the two-dimensional polycrystalline monolayers have an optical transition similar to that of three-dimensional single crystals, which demonstrates that in oligothiophene crystals the intermolecular interactions within one layer molecules are stronger than the interlayer electronic coupling.

Interestingly, the band shape of the extinction shows no significant variation with coverage, a fact that becomes apparent after normalizing the spectra to unit intensity at 3.45 eV as shown on the right side of the Figure 4a. Even the extinction of substrates after 5 min incubation time is similar to that of a fully covered SAM. The size of the islands is then in the order of 1 μm, which gives an upper limit for the length scale needed to form an H-aggregate.

The fluorescence spectra of the monolayers on quartz are presented on a semilogarithmic scale in Figure 4c. Similar spectra have been obtained for monolayers on Si-monitor wafers. Despite the fact that analysis of extinction spectra has shown that all monolayers are H-aggregates, the fluorescence spectra are a strong function of coverage. Fully covered SAMs obtained upon many hours incubation time (the red and orange lines) show a typical H-aggregate fluorescence. The peak is red-shifted with respect to that of the single molecule, and the intensity is low because the optical transition is forbidden as elucidated in Figure 1. The onset of fluorescence from the full monolayer (2.6 eV) matches with the absorption tail (2.5 eV); the 0.1 eV difference may be related to thermal excitation. In contrast, the partially covered SAMs show, apart from the H-aggregate emission at 1.9 eV, a strong fluorescence at higher photon energies. The peak positions correspond to that of the isolated molecule. Hence, the luminescence at higher photon energy originates from single molecules, either isolated on the substrates or physisorbed at the edges of the assembled islands. Contrary to H-aggregates, the optical transition in single molecules is allowed. Hence, their contribution swamps the contribution of the aggregated species because of their much higher fluorescence quantum yield. Hence, in an almost complete monolayer, a small number of single chromophores can still overwhelm the contribution of the aggregated 5T molecules, and so fluorescence is a sensitive method to monitor the final stages of closed monolayer formation.

■ CONCLUSION

The photophysics of self-assembled monolayers of a quinquethiophene (ST) derivative on Si monitor wafers and quartz substrates has been investigated. The coverage has been varied by varying the incubation time in the solution. The coverage has been determined from XPS measurements. The good agreement between XPS and extinction measurements shows that the self-assembly ends upon formation of a fully covered monolayer. The monolayers behave as H-aggregates. The fluorescence of fully covered monolayers is weak and red-shifted compared to that of single molecules. At the same time, the extinction is blue-shifted. The parallel packing of the molecules is confirmed by analysis of the extinction as a function of angle of incidence. The molecules are oriented almost perpendicular to the substrate. The extinction spectra are similar for fully and partially covered monolayers that contain only self-assembled islands. Even the smallest islands are H-aggregates. To accurately determine the length scale for H-aggregate formation, smaller islands than investigated here are required. The extinction spectra are furthermore similar to that of a ST single crystal, which demonstrates that in oligothiophene crystals the intermolecular interactions within one layer molecules are stronger than the interlayer electronic coupling.

■ ASSOCIATED CONTENT

Supporting Information
Synthesis of oligothiophene derivative 3, and fluorescence decay analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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