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J-Aggregation in α-Sexithiophene Submonolayer Films on Silicon Dioxide

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Abstract: We report on the observation of J-aggregates in submonolayer films of α-sexithiophene grown on silicon dioxide. Photoluminescence spectroscopy reveals that submonolayers are formed by molecules lying flat on the substrate with a head to tail configuration. Excitation energy dependence of photoluminescence shows a red-shifted absorption with respect to isolated molecules and a negligible Stokes shift between absorption and emission. The pronounced structural order of J-aggregates is reflected in the fwhm of the emission bands. From time-resolved and low-temperature photoluminescence experiments, we infer a quantum yield of the J-aggregate between 0.6 and 1. The demonstration of spontaneous formation of J-aggregates of π-conjugated systems on amorphous silicon-based substrates can be relevant for the development of organic−inorganic hybrid photonic devices.

Introduction

J-Aggregates have attracted great attention because they are the only molecular systems where electronic excitation is delocalized over several molecular units. Many cooperative and coherent phenomena, such as giant oscillator strength and superradiance, arise from this delocalization and make these systems strongly emissive.[1] These phenomena together with other nonlinear optical properties are important for applications in different optoelectronic devices such as OLED,[2] organic optical microcavities,[3] and ultrafast optical switches.[4] J-Aggregates of cyanine dyes and porphyrins are well known and have been studied for many years[1,5] both in solution and in the solid state.

Particularly appealing would be to obtain these aggregates with π-conjugated oligomers,[6−8] trying to combine the unique optical characteristics of J-aggregates with the electrical properties of organic semiconductors.[9,10] The crystalline structure of conjugated oligomers such as oligothiophenes, oligophenylenes, and oligophenilene-vinylenes in thin films and crystals is based on stacked layers in which the long molecular axes are parallel

to each other with a herringbone configuration.[11−13] This configuration is highly favorable for charge transport,[10,14] because it favors the overlap between π orbitals. However, because the transition dipoles are oriented along the molecular axis, the herringbone structure naturally leads to H-aggregates,[14−19] which are characterized by poor photoluminescence efficiency. Although a few observations of J-aggregation of conjugated oligomers with the concomitant presence of other species such as H-aggregates and excimers have been reported,[6] it remains to be demonstrated that these aggregates can be obtained in thin films on amorphous substrates such as silicon dioxide (SiO_2), which is ubiquitous in electronics. Moreover, the increasing interest for silicon-based structures in photonics[20] makes J-aggregates of π-conjugated systems on SiO_2 relevant for hybrid organic−inorganic photonic devices.

In a recent paper,[21] we studied the supramolecular organization in thin films of α-sexithiophene (T6) on silicon dioxide. For films of nominal thickness below 2 nm, we demonstrated the coexistence of regions where molecules lie with the long molecular axis parallel to the substrate and islands in which

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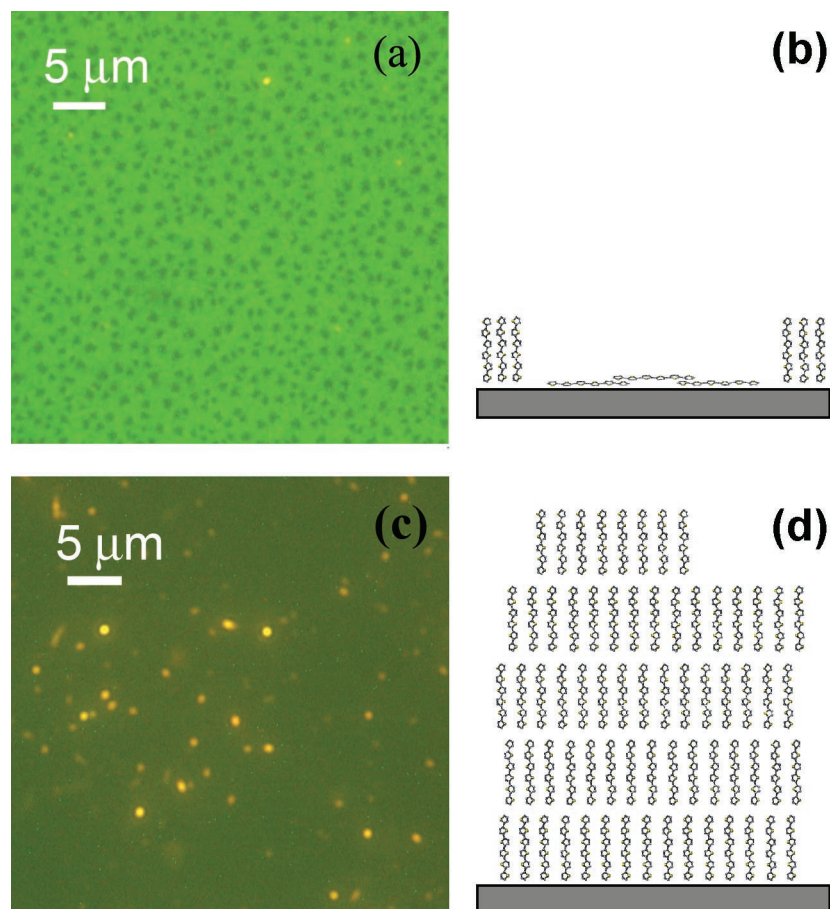
Figure 1. PL wide-field images of T6 submonolayer (a) and multilayer films (c). Scheme of the molecular orientation in submonolayer (b) and multilayer films (d). Excitation/detection conditions are the same.

molecules are perpendicular. Once the nominal thickness of the film is increased over the submonolayer regime (>2 nm), T6 molecules are perpendicular to the substrate and have spectroscopical properties similar to those of the single crystal.

Here, we focus on the photoluminescence (PL) characteristics of the submonolayer film that is dominated by aggregates of molecules parallel to the substrate. By means of a detailed analysis of the PL properties of T6 on silicon dioxide, we demonstrate the presence of head to tail interactions in submonolayer films. Low-temperature experiments evidence the presence of a well-ordered J-like structure. PL time-resolved measurements indicate that in the submonolayer film exciton relaxation is mainly radiative.

Experimental

T6 ultrathin films were grown by sublimation in an organic molecular beam apparatus at a base pressure of 10^{-8} Pa. The thermally grown silicon dioxide substrates were sonicated in acetone and 2-propanol for 30 min and transferred to the vacuum chamber. The deposition was performed at a rate of 0.12 nm/min, keeping the substrates at 120 °C. The film nominal thickness was monitored via a quartz oscillator placed near the substrate. The samples studied in this paper have a nominal thickness of 0.3 nm (submonolayer film) and 10 nm (multilayer film).

Films of T6 dispersed in polymethylmetacrilate matrix (T6/PMMA) were prepared by drop casting a dioxane solution (T6 concentration < 10^{-5} M) on a quartz plate. Single-crystal PL was obtained by excitation with unpolarized light perpendicularly to the herringbone (**bc**) plane.

PL images and PL spectra of the films were performed with a Nikon Eclipse 2000-E laser scanning confocal microscope adapted to perform

spatially and time-resolved spectroscopy. The entire setup has been described in detail elsewhere.[22] All PL images were obtained exciting with a high-pressure Hg lamp in the range 2.43−2.76 eV and detecting below 2.39 eV with a CCD camera, keeping the same excitation/ detection parameters. PL spectra were obtained in a backscattering configuration exciting with the second harmonic of a femtosecond Ti: Sapphire laser or with cw lasers (Ar+ 2.54 eV and HeNe 2.28 eV). Detection was performed with a monochromator (spectral resolution at 500 nm ∼2 meV) coupled to a streak camera (time resolution ∼2 ps) for wavelength-resolved PL decays.

Low-temperature spatially resolved PL spectra were measured with a coldfinger liquid helium cryostat designed for optical microscopy. Room-temperature PL decays were measured with the sample in air or under inert atmosphere without appreciable differences.

All of the spectra were corrected for the detector spectral sensitivity. PL time decays were fitted with monoexponential or biexponential functions according to the best-fit results.

Results and Discussion

Figure 1a,c shows the PL images of the submonolayer and multilayer films, respectively. A detailed analysis of the film morphologies is reported in ref 21. In the submonolayer film, the dark regions are islands of molecules standing on the substrate and the emission is due to molecules lying flat on silicon dioxide. A schematic representation is displayed in Figure 1b. The bright spots in the PL image of multilayer film correspond to emission from islands of molecules that start to

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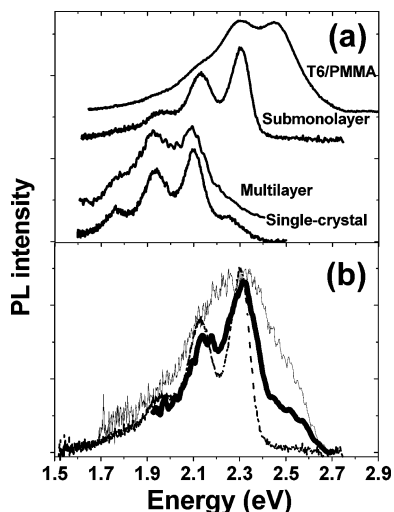
Figure 2. (a) Room-temperature PL spectra of T6/PMMA, submonolayer film, multilayer film, and single crystal. Excitation energy is at 3.1 eV for T6/PMMA, 2.8 eV for submonolayer film, and 2.54 eV for the other samples. Spectra are vertically displaced for the sake of clarity. (b) PL spectrum of submonolayer film at 295 K (dashed line) during annealing at 425 K (thin line) and at 295 K after the heating cycle (thick line). Excitation was performed at 2.82 eV.

grow over the fourth molecular layer (Figure 1d).[21] Thus, only regions with a high accumulation of material are visible, whereas the rest of the film is almost dark. It is important to note the relatively high PL intensity of the submonolayer film with respect to the multilayer film. This is particularly striking when considering that the film nominal thickness in the submonolayer is almost an order of magnitude less than that in the multilayer.

Figure 2a shows the room-temperature PL spectra of T6 in different aggregation forms: T6/PMMA, submonolayer film, multilayer film, and single crystal. In PMMA matrix, T6 molecules are isolated with frozen conformations and the PL spectrum overlaps with those already reported in the literature for T6 noninteracting molecules.[12,23]

The multilayer PL is similar to that of the single crystal, although the spectrum is inhomogeneously broadened. Submonolayer film PL is characterized by a well-resolved vibronic progression with fwhm of the purely electronic 0−0 band of 92 meV (for comparison, the fwhm of the 0−0 line of the single crystal is 78 meV) and is dominated by this peak. The 0−0 is located at 2.3 eV, significantly red-shifted with respect to the spectrum of T6/PMMA and slightly blue-shifted with respect to the 0−0 of the single crystal (∼2.26 eV).

We can rule out that the red shift of submonolayer PL with respect to T6/PMMA is purely due either to a planarization of thiophene rings or to molecule/substrate interactions. The hypothesis of planarization is unlikely because red shifts of the order of 100 and 60 meV are observed for the planarization of quaterthiophene,[24,25] while in our case the shift is 155 meV. Moreover, because silicon dioxide is a chemically inert surface, the formation of chemical bonds or interactions capable of

modifying T6 energy levels as in the case of metal substrates is to be excluded.[26]

These arguments prompted us to consider the presence of effective intermolecular interactions between molecules that lead to the formation of ordered aggregates. Furthermore, this is supported by the fact that the submonolayer PL shows a well-resolved vibronic progression with fwhm comparable to that of the single crystal. Spectral line narrowing is directly correlated with the presence of intermolecular interactions, as has been pointed out in several studies on molecular aggregates.[27,28]

To confirm the hypothesis of the existence of well-ordered aggregates in submonolayer films, we have annealed the samples under argon atmosphere up to 425 K for 30 min. In Figure 2b are reported the PL spectra of the submonolayer film measured at 425 K, and at 295 K before and after the annealing process. The spectrum at 425 K is unstructured and compares well with that of T6/PMMA and with that obtained by drop casting a dilute solution (concentration < 10^{-6} M) of T6 on SiO_2. After the annealing process, the spectrum at room temperature has broader peaks slightly shifted toward high energy and a shoulder appears in correspondence with the PL emission of T6/PMMA. If the molecules would be randomly adsorbed on the surface and not orderly aggregated, the annealing process would not change the structured PL spectrum once the film is slowly brought back to room temperature. The broadening of peaks and the appearance of the PL band corresponding to isolated molecules are evidence of partial destruction of the supramolecular order in the aggregates and the presence of noninteracting molecules on SiO_2.

As mentioned above, one of the most striking differences between the spectra of the two vacuum sublimed films is the distribution of intensity among the vibronic bands. In the multilayer film, the 0−0 transition is weakly photoluminescent and the spectrum is dominated by the 0−1 vibronic transition as is in the single crystal. This is a specific fingerprint of H-type aggregates of π-conjugated oligomers with a herringbone molecular packing.[15,17,18,29] On the contrary, the spectrum of the submonolayer film presents a vibronic progression dominated by the 0−0 transition. Because the distribution of intensity among vibronic bands of the PL is highly sensitive to molecular packing and intermolecular interactions, it is clear that the spectra correspond to two different types of aggregation.

In the simple case of a physical dimer, side by side or head to tail interactions can lead to H- or J-aggregates, respectively.[30,31] In pure H-aggregates, the optical-allowed transition concentrates on the top of the exciton band, and thus these systems are excited at higher energy with respect to the monomer. Excitons relax quickly to the bottom of the exciton band with a nonradiative process. The subsequent transition to the ground state is forbidden by optical selection rules. As a consequence, exciton relaxation to the fundamental state mainly occurs through nonradiative channels, which explains the low PL quantum yield.[30]

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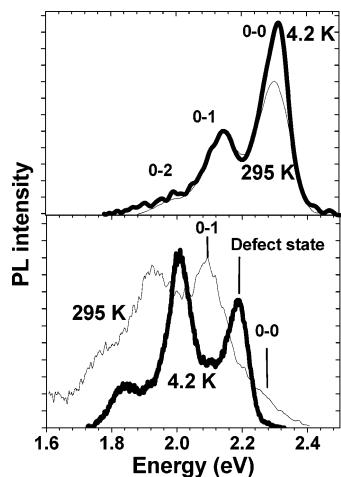
Figure 3. PL spectra of submonolayer (top) and multilayer (bottom) films at room temperature (thin line) and 4.2 K (thick line). Spectra are normalized with respect to the 0−1 vibronic transition. Excitation at 2.54 eV.

In J-aggregates, the oscillator strength of the electronic transition is concentrated at the bottom of the exciton band. As a consequence, they show red-shifted absorption with respect to the isolated molecule, null Stokes shift, and allowed optical transition in emission.[32] The pronounced exciton delocalization of these systems even at room temperature (~10 molecules for dyes) causes the appearance of only a narrow 0−0 line in the absorption and PL spectra.[32]

PL of the multilayer film is easily explained considering the single-crystal properties. The PL spectrum of the single crystal is dominated by the 0−v ($v \geq 1$) vibronic progression that is mainly polarized perpendicularly to the herringbone plane. The 0−0 transition is partially forbidden due to dipole orientation and molecular packing in the H-aggregate configuration[33,34] and is thus strongly suppressed in the PL spectrum. The weak 0−0 emission is entirely polarized in the herringbone plane along the *b* crystal axis.[17,34]

In the submonolayer film, the Franck−Condon progression and the PL intensity higher with respect to that of the multilayer film (Figure 1a,b) are fingerprints of the allowed transition of J-aggregates. A limited exciton delocalization and the strong exciton−phonon coupling typical of π-conjugated oligomers preclude the possibility to observe only the 0−0 line and prompt the intensity of the 0−1 and 0−2 bands.

It is known that at low temperature the exciton delocalization in J-aggregates increases due to the reduced exciton−phonon coupling. Thus, we expect that at 4.2 K the relative intensity of the 0−0 transition in the submonolayer PL spectrum would further increase. Figure 3 shows the PL spectra of the sub-monolayer and multilayer films at room temperature and at 4.2 K. The spectra are normalized with respect to the 0−1 vibronic transition. At low temperature, the energy positions of the PL peaks of the submonolayer film are unchanged with an increase of intensity of the 0−0 transition. On the contrary, new bands appear in the 4.2 K spectrum of the multilayer film. As has
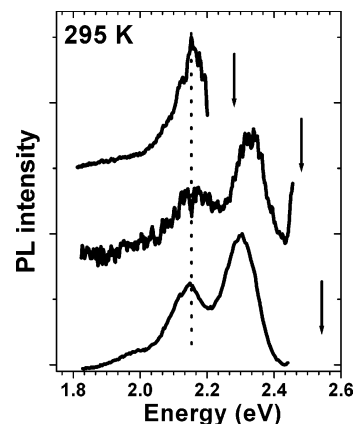

Figure 4. Excitation energy dependence PL spectra at room temperature. The arrows indicate the excitation energy. Spectra are vertically displaced for clarity. The dashed line is at 2.15 eV corresponding to the energy of the 0−1 peaks.

been reported extensively in the literature,[35] the origin of this emission at lower energy is due to energy transfer to defect states. The lack of emission from low-energy defect states in submonolayer film confirms the high degree of structural order in the J-aggregates. The increased relative intensity of the 0−0 emission is in agreement with the previous arguments related to exciton delocalization.

The vibronic progression in the submonolayer PL is due to a vibrational mode with frequency ~1260 cm^{-1}, whereas in the multilayer film and in the single crystal the mode frequency is 1460 cm^{-1}. The 1460 cm^{-1} vibrational mode is due to the C=C double bond stretching, and it is intense in the Raman spectrum of T6.[36] On the contrary, modes with frequency near 1260 cm^{-1} have a weak Raman intensity[36] and are ascribed to CCH bending.[37] The mode of the submonolayer PL could then be due to either a combination of low-frequency modes or an enhanced coupling of the electronic transition with bending modes.

The first case can be excluded because intense progressions are usually observed for modes that modify the π-conjugated backbone and not for a combination of low-frequency modes.[34] The second hypothesis can be reasonable considering that flat lying molecules are in direct contact with the surface. The surface can represent a physical constraint for C=C stretching, enhancing the coupling of the exciton with modes that involves the periphery of the molecule such as CCH bendings.

Figure 4 shows room-temperature PL spectra of the sub-monolayer film for different excitation energies, from the bottom: 2.54, 2.48, and 2.28 eV (arrows in the figure). It is important to note that it is possible to excite efficiently the submonolayer film at 2.28 eV, whereas under the same excitation conditions no PL is detected for T6 in PMMA. Although the excitation at 2.28 eV is below the 0−0 emission peak, the 0−1 peak is not appreciably red-shifted. This result confirms the absence of defect states below the exciton band, as is also shown by the low-temperature measurements, and

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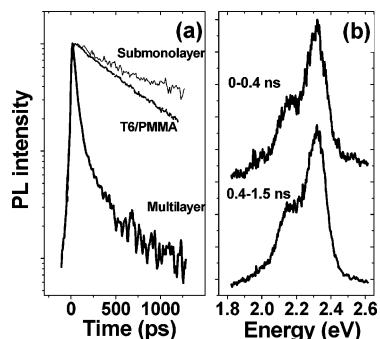
Figure 5. (a) Room-temperature PL decays of T6/PMMA, submonolayer, and multilayer films. (b) Room-temperature PL spectrum of the submonolayer film at different times. Spectra are vertically displaced for clarity.

points to the fact that the Stokes shift between absorption and emission is practically zero.

Exciton dynamics of T6 in the different aggregation forms has been studied with time-resolved PL measurements. Figure 5a shows spectrally integrated PL decays of the T6/PMMA, the submonolayer, and the multilayer films. The dynamics of the PMMA film is monoexponential with a decay time of 800 ps, comparable to that of molecules in solution (900 ps).[23] The PL decay of the 10 nm film is biexponential with lifetimes τ_1 100 ps and τ_2 400 ps. The low fluorescence quantum yield of the T6 multilayer film (10^{-4}) (ref 38) indicates that the fast PL decay is dominated by nonradiative processes such as internal conversion and charge transfer.[29,39]

The PL dynamics of the submonolayer film is slower with respect to that of the multilayer film and can be fitted with a biexponential decay with a first component of 700 ps (weight coefficient 0.48) and a second one of about 2 ns (weight coefficient 0.52). The biexponential decay is a further indication of molecular aggregation in contrast to the monoexponential that is typical of isolated molecules. Figure 5b shows the PL transients recorded in two different time windows after excitation (0−0.4 and 0.4−1.5 ns). The absence of spectral dynamics allows us to exclude that defect states or other species (e.g., excimers) are at the origin of the long-living component.

Typically in J-aggregates the radiative decay rate (k_{agg}^r) is higher than that of the isolated molecule (k^r). This effect is due to the coherent coupling of transition dipole moments that give rise to a single dipole with an oscillator strength N times bigger than that of the single chromophore, where N is the number of coherently coupled dipoles.[32]

$$k_{agg}^r = N \times k^r \qquad (1)$$

This phenomenon is called superradiance, and, if the quantum yields of the aggregate and isolated molecules are comparable, it manifests as a shortened lifetime by a factor $1/N$ with respect to the isolated molecule. k_{agg}^r can be obtained from the equation:

$$\Phi = \tau/\tau_{agg}^r \qquad (2)$$

where Φ is the quantum yield and τ is the measured lifetime. Because the PL of the submonolayer film has no spectral dynamics (Figure 5b), we can calculate a weighted mean PL

lifetime $\langle\tau\rangle$, ref 40:

$$\langle\tau\rangle = (A \times \tau_1) + (B \times \tau_2) = 1.38 \text{ ns} \qquad (3)$$

where A and B are the weight coefficients. An accurate measurement of the PL quantum yield for this sample is not possible due to the difficulties in determining the absorption cross section of a monomolecular layer. As a consequence, determination of N is quite difficult. Considering $N = 1$, $k^r = k_{agg}^r$ according to eq 1. Because the k^r for T6 is equal to 0.44 $\times 10^9$ s^{-1} (ref 23), we can estimate Φ (eq 2) as being ∼0.6.

The experimental observation that at low temperature (4.2 K) the integrated PL intensity does not appreciably increase and PL decay times are the same suggests that the quantum yield is about 1 as expected for a J-aggregate. In this case, we can calculate τ_{agg}^r from eq 2 and make an estimation of N equal to 1.7. In principle, N should be an integer value that represents the number of molecular transition dipole moments coherently coupled. It has been recently observed in single dimer experiments[41] that N could also be ∼1.5 in a regime of intermediate coupling where excitation is not fully delocalized over two molecules. It must be also considered that only in a purely head to tail arrangement do the entire molecular dipoles sum coherently. In practical cases, only favorably oriented components of the molecular dipole do sum. Considering this hypothesis, 1.7 should be considered as a lower limit value for the number of molecules over which the exciton is delocalized in the J-aggregate.

Conclusions

We have observed experimental evidence of J-aggregation in submonolayer films of T6 sublimed on a technologically relevant substrate such as silicon dioxide.

A detailed analysis of the PL spectra at room temperature shows that the submonolayer PL arises from head to tail interactions between the adsorbed chromophores. The J-aggregate is characterized by a high degree of structural order as shown by the limited spectral narrowing of PL vibronic bands. This order supports exciton delocalization, which is enhanced at low temperature. Time-resolved PL measurements underline the presence of highly emissive aggregates in which the quantum yield has a value between 0.6 and 1.

The J-aggregation is promoted by the orientation of molecules in the film. In thicker films, the reorientation of molecules perpendicular to the substrate precludes the formation of J-aggregates of T6 and leads to H-type aggregates.[21]

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