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One-dimensional substructure of cyanine dye J-aggregate monolayers resulting from non-classical multistage crystallization

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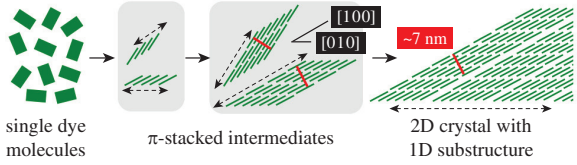
The irregular one-dimensional substructure of cyanine dye J-aggregate monolayers resolved by high-resolution atomic force microscopy is inherited from the first stages of multi-stage monolayer crystallization.



Molecular self-assembly due to the noncovalent π-stacking interaction of large conjugated π-electron systems is the origin of the unusual photophysical and electron-transport properties of so-called J-aggregates and other organic monolayers, which are currently used in optoelectronic applications.[1–4] In J-aggregate monolayers with planar molecular conformations, three types of the arrangement of adjacent stacked dye molecules (staircase, ladder and brickwork ones) are considered, which induce a characteristic red shift of J-aggregate optical spectra with respect to the monomer peak observed in highly diluted solutions.[1,5] Another prominent optical feature, the narrowness and strength of the red-shifted peak, is determined by the exciton coherence length, which is a structure-dependent parameter. Recently, crystallographic analysis of two-dimensional shapes has been conducted for monolayer J-aggregates of the monomethine cyanine dye 3,3′-di(γ-sulfopropyl)-5,5-dichloromonomethinecyanine [Dye-1, Figure 1(*a*)], which were observed in atomic force microscopy (AFM) and optical fluorescence images.[6,7] The results self-consistently indicate the staircase molecular arrangement in the J-aggregate monolayer skew strips with the staircases directed along the strips, as shown schematically in Figure 2(*a*). Moreover, the J-aggregates with an alternative (tubular) morphology were shown to be formed by the mechanism of helical winding of strips.[6,7] An unexpected feature revealed by the AFM visualization of Dye-1 J-aggregate monolayers with extreme spatial resolution is the fine irregular linear substructure formed by close-packed parallel nanostrips separated by a characteristic distance of 6–10 nm [Figure 2(*b*)].[6,7] Very similar substructures have been observed in J-aggregates of other cyanine dyes.[8,9] In this study, we concluded that the observed inhomogeneity at a nanometer scale is the intrinsic feature of J-aggregate monolayers indicating a nonclassical multi-step crystallization mechanism.

Figures 2 and 3 show the large- and small-scale AFM topography images of the monolayer J-aggregates of Dye-1 and

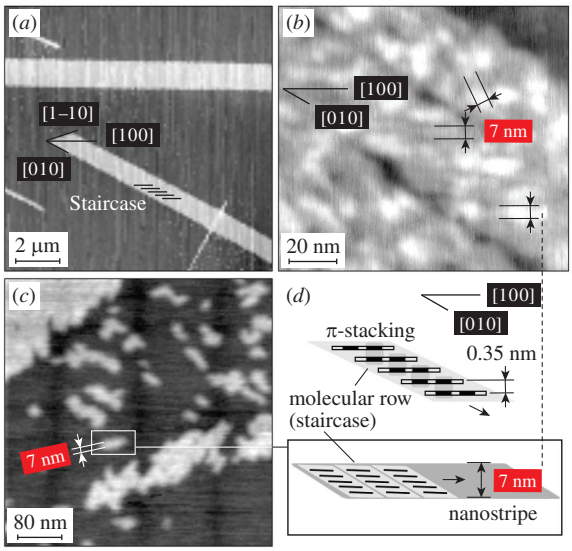


Figure 2 AFM images of Dye-1 J-aggregate skewed strips taken at (*a*) large and (*b*) small scales. (*c*) AFM image of linear precursors formed 1 min after the start of aggregation in a 0.15 mM Dye-1 solution in 5 mM ammonium acetate. (*d*) Structural model of linear precursors (nanostrips) as lateral aggregates of π-stacked molecular rows (staircases).

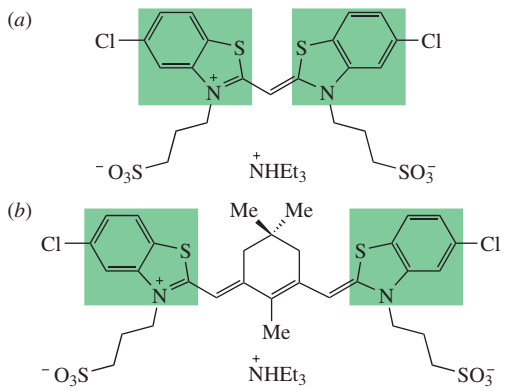


Figure 1 Studied cyanine dyes with highlighted heterocycles: (*a*) Dye-1 and (*b*) Dye-2.

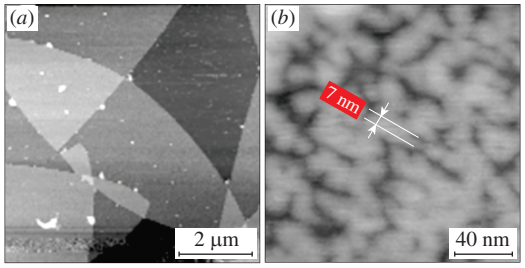


Figure 3 AFM images of Dye-2 leaf-like J-aggregates taken at (*a*) large and (*b*) small scales.

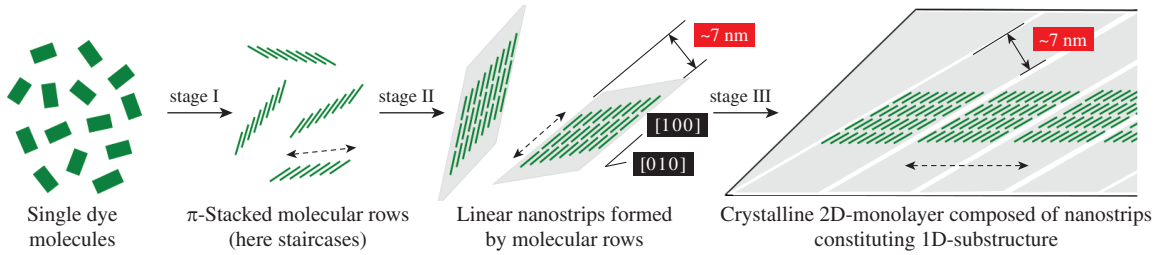


Figure 4 Three-step crystallization of J-aggregate monolayers. At each stage, constituent units grow in directions shown by dashed arrows.

3,3′-di(γ-sulfopropyl)-5,5′-dichlorobenzothiazolemonomethine-cyanine [Dye-2, Figure 1(*b*)]. The large-scale morphologies of J-aggregates are different: skewed strips in Dye-1 and leafs in Dye-2 [*cf.* Figures 2(*a*) and 3(*a*)]. Despite the large-scale morphological difference, the high-resolution small-scale images reveal similar quasi-one-dimensional linear substructures with a distance of ~7 nm between constituting nanostrips [*cf.* Figures 2(*b*) and 3(*b*)]. Moreover, the AFM measurements of early growth stages of Dye-1 J-aggregates [Figure 2(*c*)] revealed multiple isolated narrow fibrillar nanoobjects with widths close to the width of nanostrips in Figure 2(*b*) (the measured width of ~10–15 nm is larger due to the AFM broadening). Our explanation of the imperfectness of J-aggregate monolayers observed at a nanometer scale for different cyanine dyes[6–9] invokes a nonclassical two-stage or multistage crystallization mechanism, which was developed over the past two decades for the crystallization of inorganic and organic compounds and proteins.[10–18] In this approach, the crystallization is considered as a multistage process with small precursor units (multimolecular transient intermediates) formed at first stages, which (rather than single molecules in a classical nucleation mechanism) participate at later stages in the formation of large two-dimensional or three-dimensional crystal shapes. The nanoscopic precursors can be directly observed by cryogenic electron microscopy or AFM.[19–23]

Figure 4 illustrates the proposed three-step mechanism of the formation of intrinsically rough J-aggregate monolayers. At the stage I, the molecular rows of stacked dye molecules (staircases or ladders depending on the type of molecular arrangement in J-aggregates) are rapidly formed *via* strong intermolecular π-stacking interaction [Figure 2(*d*)]. As soon as the row length reached a critical value, their side-by-side aggregation started to result in the formation of linear nanostrips (stage II) as observed using AFM [Figure 2(*c*)]. At the stage III, the nanostrip aggregates formed (again in a side-by-side manner) crystallographically well-defined two-dimensional crystal shapes; the monolayer thus inherited the one-dimensional structure of nanostrips as building units. For a quasi-periodicity of ~7 nm measured by AFM, the expected number of dye molecules constituting the molecular rows is about 20 [7 nm/0.35 nm, Figure 2(*d*)]. Figure 2(*c*),(*d*) indicates that the model shown in Figure 4 is consistent with the data of combined AFM and optical fluorescence polarization measurements of the orientation of nanostrips and molecular dipoles in Dye-1 J-aggregates.[7]

In conclusion, the irregular linear substructure in J-aggregate monolayers can be explained by multistep crystallization. Note that the three-step crystallization mechanism (Figure 4) has a distinctive feature of the changeover in the growth direction not considered, to the best of our knowledge, in other crystallizing systems. Particularly, in the formation of the Dye-1 oblique monolayer strips, the growth directions are [010] at the stage I, [100] at the stage II and again [010] at the stage III. Moreover, due to the presence of intrinsic irregularities at a nanometer scale, J-aggregate monolayers should be considered as imperfect mesocrystals[24,25] despite the fact that they have the well-defined crystallographic habits of perfect two-dimensional crystals. The observed characteristic spatial inhomogeneity imposes an upper limit of about ~10 nm on the exciton coherence length; thus, it can strongly influence exciton transport in the J-aggregate monolayers.

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