

# Energy and Charge Delocalization in J-Aggregates: Model Experiments in Monolayer Systems

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J-aggregates of cyanine and merocyanine dye are extremely interesting associates of chromophores showing particular phenomena due to intermolecular interactions. These aggregates have been discovered by Jelley and Scheibe in aqueous solution and at liquid/solid interfaces. Organized monolayers and monolayer systems provide unique possibilities for investigation of the morphology and structure of J-aggregates as well as their photophysical and photochemical behavior.<sup>1</sup>

## Formation

Water soluble cyanine dyes have been organized to J-aggregates in monolayers by using a lipid anchor electrostatically binding the chromophores. The dye molecules are either adsorbed from the aqueous subphase to a compressed lipid monolayer or co-spread with the lipid. When amphiphilic dyes are spread on the water, the formation of J-aggregates is assisted by interactions in the hydrophobic moiety of the monolayer,<sup>2</sup> and therefore, the addition of a lipid giving rise to formation of an ordered phase of the hydrocarbon chains can be beneficial. An optimization of these interactions involves the dipoles at the chain ends. When  $\omega$ -halogenated lipids are mixed with a dioctadecyl-substituted cyanine dye, the terminal dipoles contribute to the attractive interactions, and the J-aggregate is considerably stabilized as compared to lipids with methyl end groups.

## Monolayer Morphology

Two-dimensional J-aggregate crystals have been observed in monolayers at the air-water interface directly between crossed polarizers at the wavelength of the absorption maximum. The optical transition is totally polarized within a crystal. The morphology of such monolayers can now be studied by Brewster angle microscopy using light that is not absorbed by the aggregate (non-resonant) thereby avoiding photoexcitation of the dye.<sup>3</sup> The morphology of the J-aggregates depends on the nature of the dye and may be influenced by interactions with counter ions present in the aqueous subphase. Interactions with solid surfaces like quartz or gypsum have led to aggregate reorganization.

## Aggregate Structure

Several structural models have been proposed like the staircase model by Scheibe. However, only the brickstone model of Hans Kuhn seems to be adequate for the description of the optical and photophysical properties (a herringbone structure has been successfully applied to aggregates showing two bands, one shifted to longer waves and the second with an orthogonal orientation of the transition moment to shorter waves with respect to the monomer band, untypical for J-aggregates). The brickstone arrangement of the chromophores in J-aggregate monolayers of a merocyanine dye on mica has been observed directly by scanning force microscopy.<sup>4</sup> A linear arrangement of the chromophores in the J-aggregate is still widely considered, although two-dimensional systems only can account for the experimental observations.

## Energy Delocalization

The strong interchromophoric interactions in a J-aggregate give rise to a delocalization of the excited state. The model of a coherent exciton of coupled oscillators has been proposed on the basis of the temperature dependence of energy transfer from the aggregate to acceptor molecules in monolayer systems. The rate of emission depends on the number of oscillators  $N$  in the exciton, and the increasing size of the exciton with decreasing temperature causes an increasing emission rate. This phenomenon of enhanced radiative rate as compared to the dye monomer was termed "superradiance" and has gained much interest in recent years. The size of the coherent exciton is determined by the decrease of the excitation energy due to aggregation and the thermal energy acting against the association of a chromophore to the exciton. A typical number at room temperature is  $N = 10$ , and at 30 K,  $N = 100$ . The coherent exciton moves rapidly as a soliton across the two-dimensional crystal at a speed that permits to level fluctuations. The speed can be experimentally determined by incorporating energy acceptor molecules in the aggregate. For the J-aggregate of a particular dye, a single acceptor molecule placed in the aggregate quenches at room

temperature the emission of 10.000 donor molecules with 50% probability. This can be rationalized by a speed of the soliton of  $v = 10$  km/s.<sup>5</sup>

### Charge Delocalization

In an investigation of the mechanism of supersensitization of latent image formation, monolayer systems were assembled with J-aggregate monolayers in contact with a monolayer containing viologen as electron acceptor which quenches the aggregate emission. The formation of a persistent viologen radical was enhanced by doping the J-aggregate with a supersensitizer. The effect has been ratio-

nalized by a mechanism involving charge migration in the aggregate over distances as large as 4 nm.<sup>6</sup>

### References

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