

Features of the exciton self-trapping in molecular aggregates

A.V. Sorokin, I.I. Grankina, I.Yu. Ropakova, S.L. Yefimova

*Institute for Scintillation Materials of NAS of Ukraine,
60 Nauky Ave., Kharkiv, 61072, Ukraine
e-mail: sorokin@isma.kharkov.ua*

Supramolecular high-ordered assemblies, called J-aggregates, possess a number of unique spectral properties, which distinctly differ from those of the individual molecules: a narrow absorption band, near-resonant fluorescence, high oscillator strength, giant third-order susceptibility, effective resonant energy migration, etc. Specificity of J-aggregates optical properties is governed by the electronic excitations delocalized over molecular chains and molecular (Frenkel) excitons formation due to translational symmetry and strong dipole-dipole interaction between molecules in the J-aggregate chain. One of the J-aggregate characteristic features is the narrow red-shifted exciton band, called J-band, which width is determined by the exciton coherence (or delocalization) length. Thus, J-aggregates are examples of molecular nanocrystals formed by cyanines, porphyrins, merocyanines, perylenes and other dyes. However, the exciton properties of J-aggregates often differ from those of typical molecular crystals. First of all, it is associated with the predominant one-dimensional J-aggregate geometry in solutions or two-dimensional geometry in films and on surfaces, while molecular crystals typically exhibit three-dimensional ordering. Another feature is a strong influence of significant configurational randomness of the J-aggregate environment leading to the exciton localization, which plays a very important role in the optical dynamics.

Unique spectral properties make J-aggregates excellent candidates for novel photonic materials especially in the form of thin films, particularly, polymer films. Indeed, while in solutions J-aggregates often possess low photostability, in polymer films their stability becomes much higher. However, J-aggregate formation in polymer films reveals also some drawbacks, such as low fluorescence quantum yield of formed J-aggregates. One of the possible reasons is exciton self-trapping in a more rigid environment. The exciton self-trapping appears when the excitons localize themselves in the self-induced potential well caused by the large lattice distortion under the condition of strong exciton-phonon coupling.

The feature of J-aggregates is a strong dependence of exciton-phonon coupling, and hence the self-trapping efficiency, on the exciton coherence length [1-3]. Indeed, it was demonstrated that the exciton-phonon coupling is less for the J-aggregates with larger the exciton coherence length [1]. Thus, if one will increase the exciton coherence length for J-aggregates it will lead to exciton-phonon coupling weakening and, hence, to the exciton self-trapping suppression, resulting to the J-aggregate fluorescence enhancement [4,5].

The present report is devoted to reviewing the features of the exciton self-trapping in J-aggregates depending on their formation conditions. Also the ways to control the self-trapping efficiency, and, hence, the fluorescence quantum yield, are shown.

- [1] Yu.V. Malyukin, A.V. Sorokin, V.P. Semynozhenko, *Low Temp. Phys.* 42, 429 (2016).
- [2] A.V. Sorokin, N.V. Pereverzev, I.I. Grankina, S.L. Yefimova, Yu.V. Malyukin, *J. Phys. Chem. C*, 119, 27865 (2015).
- [3] A.V. Sorokin, I.Yu. Ropakova, S. Wolter, R. Lange, I. Barke, S. Speller, S.L. Yefimova, Yu.V. Malyukin, S. Lochbrunner, *J. Phys. Chem. C*, 123, 9428 (2019).
- [4] G.Ya. Guralchuk, I.K. Katrunov, R.S. Grynyov, A.V. Sorokin, S.L. Yefimova, I.A. Borovoy, Yu.V. Malyukin, *J. Phys. Chem. C*, 112, 14762 (2008).
- [5] A.V. Sorokin, I.I. Grankina, I.I. Bepalova, A.V. Aslanov, S.L. Yefimova, Yu.V. Malyukin, *J. Phys. Chem. C*, 124, 10167 (2020).