

Photoinduced Charge Transport in Films of Tricarboyanine Dye Assisted by Nanoscale Disorder of Dye Aggregates

Oleg Dimitriev¹, Petro Smertenko¹, Yuri Slominskii²

¹ V.Lashkaryov Institute of Semiconductor Physics NAS of Ukraine, pr. Nauki 41, Kyiv 03028, Ukraine

² Institute of Organic Chemistry NAS of Ukraine, 5 Murmanska Str., Kyiv 02660, Ukraine

Mechanism of photoinduced charge generation in disordered organic films has been a subject of discussions during last decades. Usually this process is assigned to either extrinsic or intrinsic mechanism, which requires or does not require driven force, respectively, and which is dependent on such factors as film crystallinity and packing motifs, static and dynamic disorder, excess energy, entropy, local electrostatic environment, the presence and dynamics of competing relaxation channels, external conditions (electric field or temperature), etc. Although it is recognized that disorder often promotes ultrafast generation of polaron pairs, more studies are needed to quantify how exactly the molecular packing drives charge separation. Here we investigate charge generation and transport in films of tricarboyanine dye which has relatively long conjugated backbone and absorbs in the near-infrared (NIR), implying that its relatively large Frenkel exciton can dissociate easily. Molecules of these dye couple to each other in the condensed state yielding the formation of either J-aggregates or mixed J- and H-aggregates, depending on the applied conditions. We compare three kinds of films, i.e., a submonolayer film composed of dye microcrystals, an amorphous thick film, and a composite film of dye in the PVA polymer matrix. Whereas the first two films demonstrated the presence of both J- and H-aggregates (or JH structure), the last one was composed of pure J-aggregates, which were identified by characteristic spectral features (Fig. 1). The first two films demonstrated also charge photogeneration independent of whether J- or H-aggregates were selectively excited, while the film composed of J-aggregates showed no apparent charge photogeneration and its photocurrent was equal to the dark current (Fig. 2). In addition, current-voltage characteristics revealed a diode-like behavior for the films containing mixture of J- and H-aggregates, while the film composed of J-aggregates showed an ohmic-like behavior (Fig. 2). At the same time, our previous ultrafast spectroscopy studies (Dimitriev et al, *J. Phys. Chem. C* (2021), 125, 9855–9865) proved that the dye J-aggregates are able to photogenerate polarons. Based on the obtained data, we conclude that while a single dye aggregate here is able for charge photogeneration, there should be a certain driven force for the nanoscale charge separation. Such a driven force is provided here by disorder in the aggregate arrangement, i.e., the coexistence of J- and H- aggregates. Overcoming the barrier between J- and H-aggregates leads to further contribution of the photogenerated charge to the photocurrent and the diode-like behavior of I-V characteristics, while photogenerated charge in the J-aggregate system does not experience any driving force. We conclude that the charge photogeneration in films of tricarboyanine dye has the extrinsic mechanism with prevailing monomolecular injection.

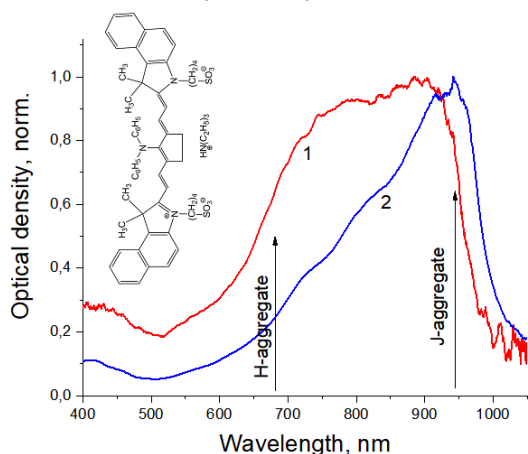


Fig. 1. Electronic absorption spectra of (1) amorphous film composed of mixed J- and H-aggregate and (2) J-aggregate in PVA matrix. Insert shows dye structure.

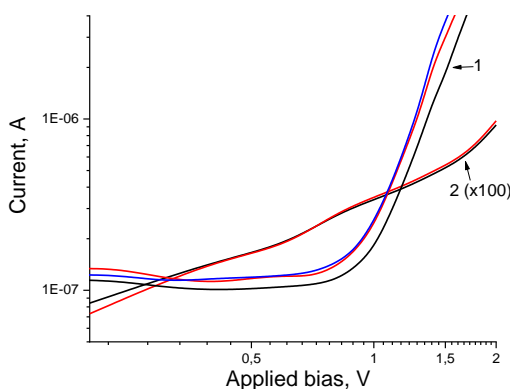


Fig. 2. I-V curves of (1) amorphous film composed of mixed J- and H-aggregates and (2) J-aggregates in PVA matrix. Black lines indicate dark current, blue and red the photocurrent under illumination at 660 and 950 nm, respectively.