

# Spectroscopic Investigation and Theoretical Modelling of Benzothiadiazole-based Charge-Transfer Chromophores: From Solution to Nanoaggregates

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Thanks to its electronic properties, high molar extinction coefficient and photoluminescence quantum yield, chemical and photochemical stability, 2,1,3-benzothiadiazole (BDT) has recently attracted interest as a building block for small-molecule fluorescent probes. So far, many BDT derivatives have been successfully tested for the imaging of cells and tissues, and in perspective, the exploration of the properties of this new class of fluorophores is promising for bioimaging applications [1].

In this joint experimental and theoretical work we focus on a family of multipolar V-shaped chromophores bearing an A'-D-A-D-A' structure, where BDT, acting as the central electron acceptor (A), is linked to two thiophene-based electron donating moieties (D) end-capped with alkyl-cyanoacetate substituents (A') [2].

A full spectroscopic characterization in solution reveals intense fluorescence emission and high absorption in the visible region, which can be tuned via the D groups, of potential interest for imaging purposes. In order to circumvent the poor solubility of these dyes in water and to increase their biocompatibility, stable aqueous suspensions of organic nanoparticles (ONPs) were prepared via the reprecipitation method, and fully characterized. Spectroscopic analysis revealed the partial formation of J-aggregates for some of the ONPs.

In order to thoroughly understand and rationalize the experimental properties of these aggregates, a theoretical modelling was performed through an essential-state approach, where the isolated molecule is described in terms of few basis states coinciding with its main resonating structure. Starting from the molecules in solution, a three-state model for quadrupolar D-A-D chromophores, including electron-vibration coupling and polar solvation [3], was validated against experimental data. Then, in a bottom-up approach, the model has been extended to include interchromophore interactions and has been applied for the description of simple prototypical aggregates of quadrupolar V-shaped dyes, making thus sense of the main experimental results.

[1] B. A. D. Neto, P. H. P. L. Carvalho, J. R. Correa, *Acc. Chem. Res.* **48**, 1560 (2015).

[2] B. Bardi, C. Dall’Agnese, K. I. Moineau-Chane Ching, A. Painelli, F. Terenziani, *J. Phys. Chem. C*, **121**, 17466 (2017).

[3] F. Terenziani, A. Painelli, C. Katan, M. Charlot, M. Blanchard-Desce, *J. Am. Chem. Soc.* **128**, 15742 (2006).