

Abstract

Ultrafast Excited-State Dynamics and Aggregation Behavior of 2,5-Bis(2,2':6',2''-Terpyridine-4'-yl)-Thieno[3,2-b]Thiophene: Experimental and DFT Study [†]

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The aggregation behavior of π -conjugated molecules critically influences their excited-state dynamics and thus their performance in optoelectronic applications. In this work, we deal with the title substance (hereafter referred to as **Tt**), used as a unimer for metallo-supramolecular polymers, and study the dynamics of its photophysical properties in various solvents using femtosecond transient absorption spectroscopy (fs-TA) (Helios-fs, Ultrafast Systems, Sarasota, FL, USA), steady-state absorption (Shimadzu UV-2401PC instrument, Kyoto, Japan) and emission spectroscopy (Jobin Yvon Instruments S.A., Inc., Edison, NJ, USA), and dynamic light scattering (DLS) (Zetasizer Nano, Malvern Instruments, Malvern, Worcestershire, UK). Experimental studies are completed with DFT and time-dependent DFT calculations, providing more detailed insight into the electronic structure of **Tt** and excited-state processes in it.

In aprotic solvents such as toluene and DMSO, **Tt** predominantly exists as free solvated molecules, exhibiting long-lived excited states with lifetimes extending up to hundreds of picoseconds. In contrast, different types of aggregation behavior have been observed in proton-donating solvents. In pure and aqueous hexafluoropropan-2-ol, HFIP and HFIP (aq), the formation of nanoaggregates ranging from 12 to over 1000 nm in size has been observed by DLS. These aggregates exhibit blue-shifted absorption bands characteristic of H-type aggregation and show significantly accelerated excited-state decay due to enhanced nonradiative relaxation pathways. Interestingly, in the more acidic solvent mixture of pH 1 (HFIP/0.01 M HClO₄ in H₂O (4:1)), a red-shifted absorption band characteristic of J-type aggregation has been observed.

Solvent polarity and hydrogen bonding strongly modulate excited-state lifetimes, with the fastest internal conversion observed in acidic HFIP/water mixtures. Solvation dynamics in HFIP/0.01 M HClO₄-H₂O mixtures were complete within 1.2 ps, further influencing relaxation processes. In the most acidic environment tested (HFIP/0.01 M HClO₄ in H₂O (4:1); pH = 1), relaxation is considerably faster than in other solvent systems due to hydrogen bonding.



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The combination of experimental and theoretical analyses reveals how hydrogen bonding and aggregation govern the photodynamics of **Tt**, providing valuable insights for designing polymeric materials with tailored optoelectronic properties.

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