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Title: Self-Assembled Oligothiophenes for Photocatalytic Hydrogen Production and Simultaneous

Organic Transformation

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Abstract:

Herein, we have fabricated self-assembled semiconducting organic nanomaterials with various morphologies (1D-fiber, 2D-flakes, and 2D-nanosheets) made of small conjugated oligomer 2,2':5',2":5",2"-quaterthiophene (α-QTH) by a simple solution-based coprecipitation method. By simply varying the good-solvent-to-bad-solvent ratio, we can critically tune the self-assembly process and eventually can control the intermolecular interactions of the constituent molecules in these self-assembled nanostructures. Different types of self-assembled nanostructures have been utilized for photocatalytic solar H2 production. The H2 production efficiencies directly depend on the morphology of self-assembledselfassembled nanomaterials as well as intermolecular interactions of QTH molecules. The overall photocatalytic properties are further correlated with the ongoing photophysical properties by means of detailed steady-state and time-resolved fluorescence spectroscopy and dimer-based time dependent-density functional theory (TD-DFT) calculations. Furthermore, femtosecond transient absorption spectroscopy has been utilized to explore the detailed photoinduced exciton dynamics by global analysis of spectrally resolved pump-probe traces. In addition to that, the overall photocatalytic activities are further supported by an in-depth electrochemical study. Finally, a boost in photocatalytic H2 production has been observed by using 4-methylbenzyl alcohol (4-MBA) as a specific hole scavenger for the completion of the redox cycle. Therefore, the present system can be utilized for simultaneous solar H2 production and the specific organic transformation through a green and cost-efficient

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