

Controlling Intermolecular H-atom Abstraction with Ultrafast Pump-Push-Probe Spectroscopy †

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† Presented at Materials Chemistry and Physics (Materials Chemistry 2020) - International e-Conference

Received: 16.09.2020; Revised: 20.09.2020; Accepted: 24.09.2020; Published: 27.09.2020

Abstract: We utilize ultrafast multi-pulse pump-push-probe transient absorption spectroscopy and time-resolved photoluminescence to monitor excited-state H-atom transfer from hydroxylic compounds to the heptazine derivative 2,5,8-tris(4-methoxyphenyl)-1,3,5,6,7,9,9b-heptaazaphenylene (TAHz). The heptazine moiety is structurally related to the monomer unit of the ubiquitous organic polymeric photocatalyst, carbon nitride. We show that TAHz can photochemically abstract an H-atom from water, in addition to generating H₂ in aqueous suspensions with photocatalytic activity matching that of carbon nitride. In our multi-pulse experiment, we use resonant pump pulse to photoexcite TAHz to a bright high-lying excited state, and after a relaxation period of roughly 6 ps, we use a NIR (1150 nm) pulse to “push” the chromophore to a higher-lying excited state. When phenol is present, the push induces a persistent decrease ($\Delta\Delta OD$) in the initial excited-state absorption, indicating the push pulse engenders a divergence in the photochemical branching ratios. In the presence of electron-donating substituted phenols, the magnitude of $\Delta\Delta OD$ diminishes markedly due to the increased excited-state reactivity of the complex accompanied by the cathodic shift in the phenol oxidation potential. Thus, the H-atom abstraction appears to proceed without aid from the additional energy of the push pulse. These results reveal new insight into the branching ratio among unreactive localized heptazine excited states and reactive intermolecular charge transfer states of H-bonded heptazine chromophores. More generally, this work provides new insight into molecular design strategies to control the excited-state photochemistry of aza-aromatic materials toward important reactions such as H-atom abstraction from water.

Keywords: Ultrafast spectroscopy; photochemistry; solar energy; photocatalysis

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Funding

This research was supported by the U.S. National Science Foundation (NSF) under Grant No. CHE-1846480.

Acknowledgments

This research has no acknowledgment.

Conflicts of Interest

The authors declare no conflict of interest.