Persistent and Regenerable Photogenerated Radical Formation from Self-assembled Triphenylamine Urea Dimers

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Abstract: Materials that contain delocalized radicals have applications in photovoltaics and magnetic materials. Typically, these materials are made from compounds that have inherent radicals within them, i.e. the building blocks already have free radicals. However, it is of interest to design materials that could generate stable free radicals without this prerequisite. Indeed, triphenylamine dimers assembled through urea hydrogen bonding give such a material. Simple UV-irradiation of these dimers after self-assembly results in persistent and regenerable radicals.[1] Approximately 1 in 150 molecules generate a radical after irradiation with no change in the assembled crystal lattice. Moreover, after radical decay, radical concentrations can be restored with additional UV-irradiation. This presentation will highlight how the radicals are formed, how persistence and generation can be modulated, and the effects radical formation has on the subsequent photophysical properties. These changes will be examined by discerning the difference in these properties between both linear and cyclic dimers of triphenylamines; the latter of which forms porous 1D channels after assembly and can act as a host to undergo single-crystal-to-single-crystal transformations with different guests allowing for the visualization of how different guests impact radical formation. Overall, this research gives insight on the photogeneration of radicals and how it can modulated through solid-state assembly.

(1) A. J. Sindt, B. A. DeHaven, D. F. McEachern, D. M. M. M. Dissanayake, M. D. Smith, A. K. Vannucci, and L. S. Shimizu, *Chem. Sci.*, 2019, **10**, 2670.