Exploring Photogenerated Radicals in Self-assembled Urea-Tethered Triphenylamines

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Triphenylamine (TPA) radical cations stabilized by substitution on the *para*-position hold promise as spin-containing building blocks for polymer magnets. Self-assembly potentially affords an alternative strategy for stabilizing organic radicals, which might relax constraints on TPA substituents. Herein, we examine the effect of assembly on the stability of photogenerated radicals of urea tethered triphenylamines. Triphenylamine containing *bis*-urea macrocycles and urea tethered linear analogues were synthesized and their crystal structures determined.[1-3] These crystalline materials control the distinct microenvironments around the photoactive groups. Upon excitation in solution, triphenylamines with unsubstituted *para*-positions form radical cations that rapidly degrade. Upon UV-irradiation of the supramolecular assemblies, both linear and macrocyclic systems display remarkably persistent and regenerable radicals as monitored by EPR. The line shape of the EPR spectra and quantity of radicals can be modulated by polarity and by presence of heavy atoms, either covalently connected and or within supramolecular complexes. Transient absorption spectroscopy, cyclic voltammetry and time-dependent density function theory were also used to probe formation of these radicals and follow photoinduced electron transfer from host to guest.[4]

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