Bimolecular charge separation under the gaze of broadband fluorescence up-conversion

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We will present an investigation into the role of the excited states of radical ions in photoinduced bimolecular charge separation (CS). Taking diffusion into account, CS has been found to have a very weak inverted region.[1] It is hypothesised that this could be due to the involvement of radical excited states in the Marcus inverted region (MIR),[2] as has recently been deduced from transient IR measurements.[3]

Using time resolved broad-band fluorescence up-conversion[4,5] (which allows observation of the entire fluorescence spectrum with a sub-200 fs time resolution), multiple CS reactions have been studied, with the reactions in the normal and barrierless region showing emission from the pure fluorophore and those occurring in the MIR showing an additional emissive component (spectra at 100 fs for Perylene/TMPD and Perylene/TCNE shown in Figure 1). This additional emission is ascribed to the unrelaxed fluorescence from an excited state of a tight ion pair.

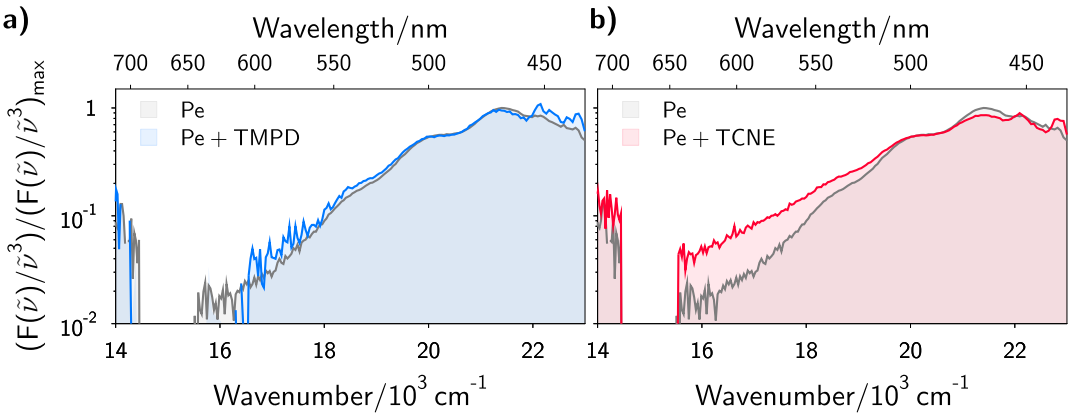

Figure 1: Spectra at 100 fs of ***a)*** *Perylene (Pe), and the Pe/TMPD (TMPD: N,N,N,N-Tetramethyl-p-phenylenediamine) pair and* ***b)*** *Pe, and the Pe/TCNE (TCNE: Tetracyanoethylene) pair. Additional components are seen with the addition of TCNE but not TMPD. The third harmonic of the gate has been excluded at 15,000 cm^{-1}.*

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