Investigating Bimolecular Symmetry Breaking Charge Separation in Highly Concentrated Perylene Solutions

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Symmetry breaking charge separation (SB-CS) enables the conversion of solar energy into charge carriers by photoinduced electron transfer between identical molecules (M).[1] Generally, SB-CS is studied in systems in which the two chromophoric moieties undergoing SB are covalently linked, M*-M → M^+-M^-.[2] Examples of bimolecular SB-CS, M* + M → M^+ + M^-, of organic chromophores yielding free ions, on the other hand, remain scarce due to solubility or aggregation issues of the dyes at high concentrations.

Here, we explore the excited state dynamics of Perylene (Pe) and its alkyl substituted derivatives[3] in highly concentrated solutions using transient absorption spectroscopy. By mapping out the excited state dynamics from subpicosecond to microsecond timescales, we demonstrate that the locally excited (LE) state undergoes quenching through excimer formation[4] in concentrated solutions. Moreover, we observe the characteristic bands of the perylene ions[5] in polar solvents next to the excimer decay, highlighting the possibility of bimolecular SB-CS in these systems (see Figure 1).

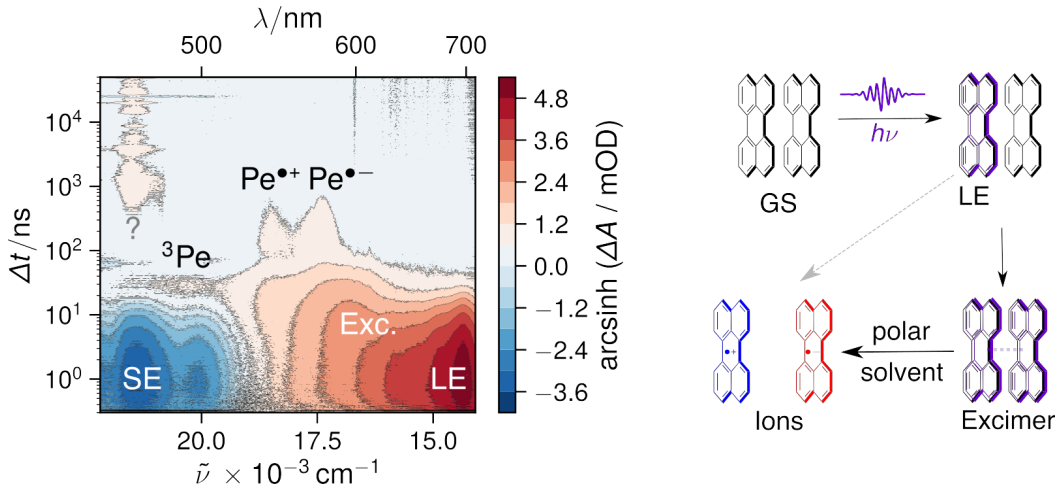

Figure 1: Nanosecond-microsecond visible transient absorption spectrum of Pe (1 mM) in acetonitrile showcasing bimolecular SBCS as well as excimer formation.

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