Spin correlations in organic semiconductors
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Organic semiconductors differ from their inorganic counterparts by large exchange interactions and weak spin orbit coupling. As a result, parallel and anti-parallel spin configurations are highly non-degenerate and spectroscopically well-defined. Whereas singlet excitons are highly emissive, triplet excitons generally decay non-radiatively. Addition of heavy metal centres to the polymer backbone induces localized spin-orbit coupling, which can activate radiative triplet decay through phosphorescence [1]. By tuning the concentration of these triplet acceptors to match the diffusion length of the triplets (which exceeds that of the singlets), triplets can be harvested radiatively without significantly affecting the actual triplet formation pathway through intersystem crossing of the singlet [2]. Using this technique we can study the interconversion between spin states of exciton precursors (charge carrier pairs) as a function of time, temperature, and electric and magnetic fields [3]. We find that the probability of a spin change occurring in the exciton precursor state is extremely small, which suggests that the primary recombination pathway in organic light-emitting diodes is governed by spin statistics [3]. Phosphorescence spectroscopy of organic semiconductors has a number of immediate applications. Stimulated emission competes with intersystem crossing required for triplet generation so that a phosphorescent polymer laser acts as a highly non-degenerate all-optical excitonic switch [4]. Singlet-triplet mixing in metallorganics with strong spin-orbit coupling also provides a versatile method for ultrafast luminescence based molecular thermometry [5,6].