Intramolecular photoinduced electron transfer in low temperature glasses. Charge transfer and local triplet states dynamics in bichromophoric systems.

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Recent advances in the use of thermally activated delayed fluorescence (TADF) for enhancing the efficiency of organic light emitting diodes (OLED) have attracted considerable attention to the triplet state dynamics involving local and charge transfer (CT) triplet states in donor-acceptor (D–A) molecules [1-2]. In spite of great progress in improving device efficiencies, the mechanism of reverse intersystem crossing (RISC) based TADF is still not fully understood. One of the major unresolved issues is the effect of D–A relative orientation on RISC, and consequently on TADF efficiency and kinetics in structures allowing for strong intramolecular CT character. A deeper understanding of the triplet state dynamics is hindered, i.a., by the scarcity of suitable systems showing coexistence of CT and local (LE) triplets.

The two types of triplet states can be simultaneously observed by dual phosphorescence of D–A structured tri- (LTAM) and diarylmethane lactones (LDAM) [3-4], and their dynamics is followed with ns- to ms-time resolved luminescence spectroscopy. In LDAM, ~100 fs photoinduced electron transfer (ET) populates a charge-separated $^1[D^{\bullet+}–A^{\bullet-}]$ state, which subsequently decays radiatively and via ISC to a CT ($^3[D^{\bullet+}–A^{\bullet-}]$) and donor-centered ($[^3D^*–A]$) triplet states [5]. In spite of very close energies and small energy gap, ΔE_{ST}, between the $^1[D^{\bullet+}–A^{\bullet-}]$ and $^3[D^{\bullet+}–A^{\bullet-}]$ states, the delayed fluorescence in LDAM is negligible or not observed at all, indicating that other factors are important for TADF to be operative. In a 77 K glass, the recombination of $^1[D^{\bullet+}–A^{\bullet-}]$ and $^3[D^{\bullet+}–A^{\bullet-}]$ states is non-exponential with multirelaxation time behavior (on ns and ms time scales, respectively), and is strongly dependent on glass polarity. The results are interpreted in terms of a polar glass model [6]. The photophysics of a series of differently substituted LDAM and LTAM will be presented to show consistency and generality of the structure-property relationship for the D–A structures.

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