

Interpreting Long-Lived Triplet Radical Ion Pairs with Constrained Density Functional Theory

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Calculations using constrained density functional theory (CDFT) offer clues to explaining the dramatically different kinetics of ion recombination for cations of 9,9'-dihexylfluorene, $F_1^{+\bullet}$, in pairs with radical anions of 1,4-benzoquinone, ($F_1^{+\bullet}, BQ^{\bullet-}$) and tetracyanoethene, ($F_1^{+\bullet}, TCNE^{\bullet-}$). The positive and negative ions were created by ionization of *o*-xylene using pulse radiolysis. Their fast recombination led to coulombically-bound triplet ion pairs (CBIPs), whose lifetimes were measured spectroscopically. ${}^3(F_1^{+\bullet}, BQ^{\bullet-})$ has an energy above that of a local triplet ${}^3BQ^*$, while ${}^3(F_1^{+\bullet}, TCNE^{\bullet-})$ lies below local triplets, which results in a large yield of long-lived triplet CBIPs in the latter, in contrast to the former.

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