Endothermic charge-transfer mediates shallow distance-dependent triplet energy migration

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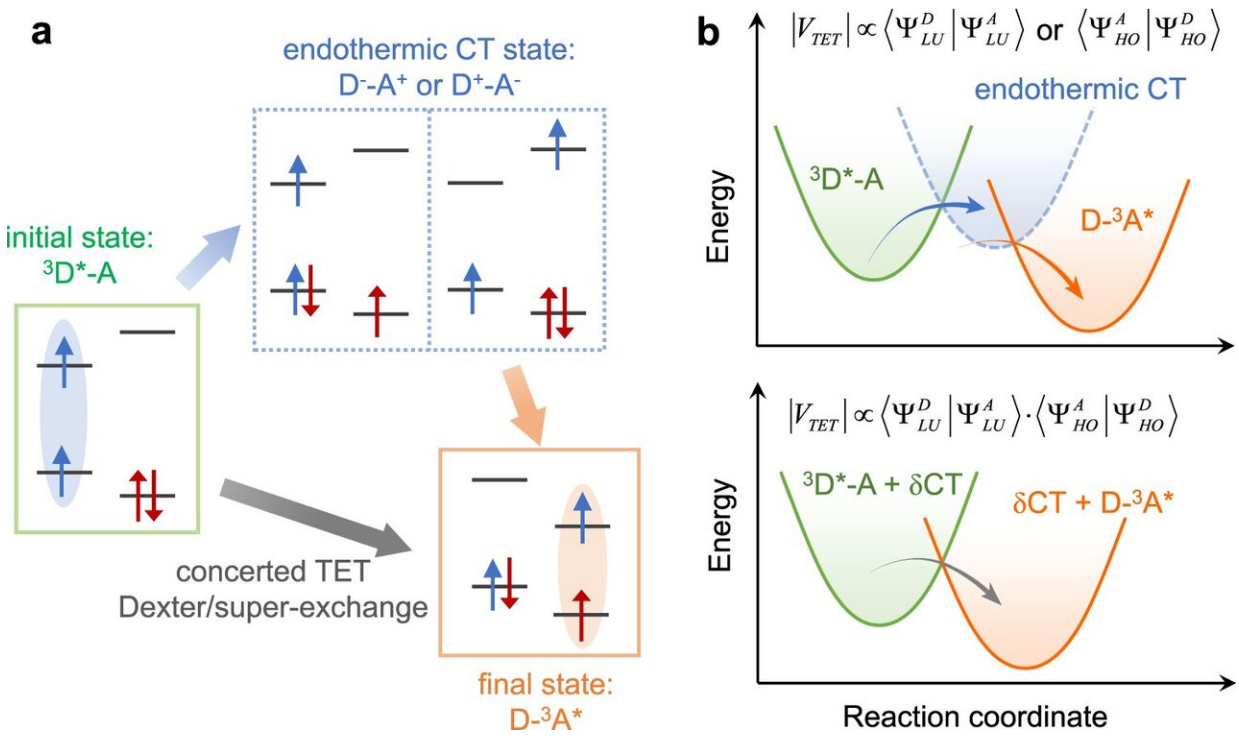

a Schematic depiction of the initial and final states and intermediate endothermic CT states. 3D*-A and D-3A* are the initial and final states, respectively, whereas D−-A+ and D+-A− are the possible endothermic charge-transfer (CT) states. The red and blue arrows indicate the spins of the electrons in the donor and acceptor, respectively. b Concerted (lower) versus endothermic CT-mediated (upper) TET mechanisms drawn in reaction coordinate diagrams. Note that, although not considered in Dexter's original formula, the initial and final states in concerted TET could be mixed with virtual CT states (super-

exchange). The electronic coupling matrix elements (|VTET|) for concerted and endothermic CT-mediated TET are expressed in terms of donor and acceptor wavefunctions, where D and A stand for donor and acceptor and LU and HO stand for lowest unoccupied and highest occupied molecular orbitals, respectively. Credit: *Nature Communications* (2021). DOI: 10.1038/s41467-021-21561-1

Recently, a research group led by Prof. Wu Kaifeng from the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences (CAS) found that endothermic charge-transfer-mediated triplet energy transfer (TET) is a new mechanism featuring shallow distance-dependence.

This study was published in *Nature Communications* on March 9.

The researchers investigated TET from colloidal CdSe quantum dots (QDs), featuring systematically varied ZnS shell thicknesses, to surface-anchored anthracene molecules.

Time-resolved spectroscopy measurements showed no evidence for anthracene cation and/or anion formation, excluding exothermic charge transfer (CT)-mediated triplet migration.

The TET rate decreased with increasing ZnS shell thickness, with rate attenuation clearly following the trend of hole probability density on QD surfaces rather than the product of electron and hole probability densities. This observation evidenced an endothermic hole-transfer-mediated mechanism.

Temperature dependence of the transfer rate further confirmed the endothermic hole transfer process. The shallow distance dependence of

endothermic CT-mediated TET enabled efficient triplet migration over donor-acceptor separation beyond Dexter or super-exchange paradigms.

More information: Runchen Lai et al. Shallow distance-dependent triplet energy migration mediated by endothermic charge-transfer, *Nature Communications* (2021). DOI: 10.1038/s41467-021-21561-1

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