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Researchers discover new charge transfer and separation process

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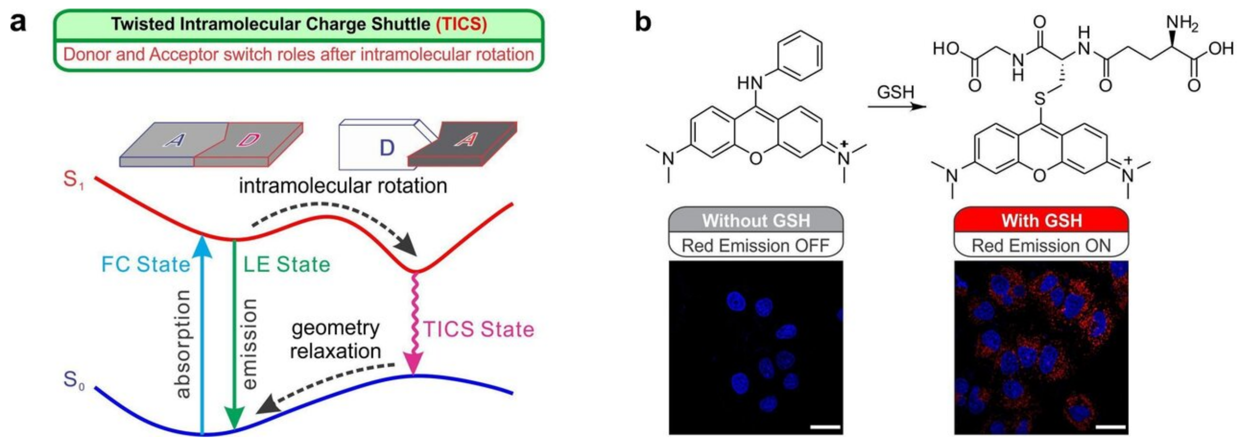

(a) Schematic illustration of the twisted intramolecular charge shuttle (TICS) mechanisms; 'D' and 'A' denote electron-donating and electron-accepting fragments, respectively. (b) Reaction mechanism of a TICS based GSH fluorescent probe, and confocal microscope images of HeLa cells stained with the probe and Hoechst 33342 (a nucleus stain with blue emissions). No red emissions were observed in cells that were pre-treated with 1 mM NMM to remove GSH, while intense red fluorescence was present in cells with GSH. Scale bar = 20 μm. Credit: SUTD

Charge transfer and separation is a fundamental process in the energy conversion that powers life on Earth. Besides deployment in solar cells and photocatalysts, this process is found in photosynthesis, as it enables energy conversion by harvesting light and then transferring and converting it into chemical energy.

However, deeper understanding of charge transfer and separation at the molecular level continues to be a challenge, as this process is very quick—light absorption-induced charge transfer and separation takes place over a few femtoseconds to a few picoseconds.

An international team of researchers from the Singapore University of Technology and Design (SUTD), Chinese Academy of Science, Pohang University of Science and Technology and Vanderbilt University, overcame this challenge by using fluorescence in their model systems and studying the change in fluorescence output—intensity, lifetime and wavelength, etc.—and discovered a new charge transfer and separation process called twisted intramolecular charge shuttle (TICS). In TICS molecules, the charge donor and acceptor fragments dynamically switch roles after absorbing light and experiencing a structural twisting, thus exhibiting a 'charge shuttle' phenomenon.

The unique bidirectional, role switching TICS process differentiates it from a similar process of unidirectional charge transfer called twisted intramolecular charge transfer (TICT). While TICT has facilitated the development of many functional materials and devices such as bright and photostable fluorophores, dark quenchers, viscosity sensors and polarity sensors, TICS paves a new avenue for chemists to construct unique and useful fluorescent probes in a wide range of chemical families of fluorophores.

For instance, the research team constructed TICS fluorescent probes that can be used to detect glutathione, an antioxidant found in plants and animals that is essential in removing many toxic chemicals in biological cells. Similarly, another type of specifically constructed TICS-based probe would be able to detect phosgene, a colourless and highly toxic gas that was used as a chemical weapon agent during World War I, which could potentially be used in terrorist attacks.

SUTD's Assistant Professor Liu Xiaogang explained how the research team developed TICS-based glutathione fluorescent probes and their efforts to transform the dye chemistry from trial and error into molecular engineering.

"Research in this area of study has often been based on trial and error. At SUTD, where design is a key component in our research strategy, we made sure to take on a design-centric approach in our research process. We first analysed chemical big data and spotted a pattern between molecular structures and fluorescent properties. After understanding this TICS process, we then designed a probe to prove this concept," said Assistant Professor Liu.

More information: Weijie Chi et al, A Photoexcitation-Induced Twisted Intramolecular Charge Shuttle, *Angewandte Chemie International Edition* (2019). DOI: 10.1002/anie.201902766

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