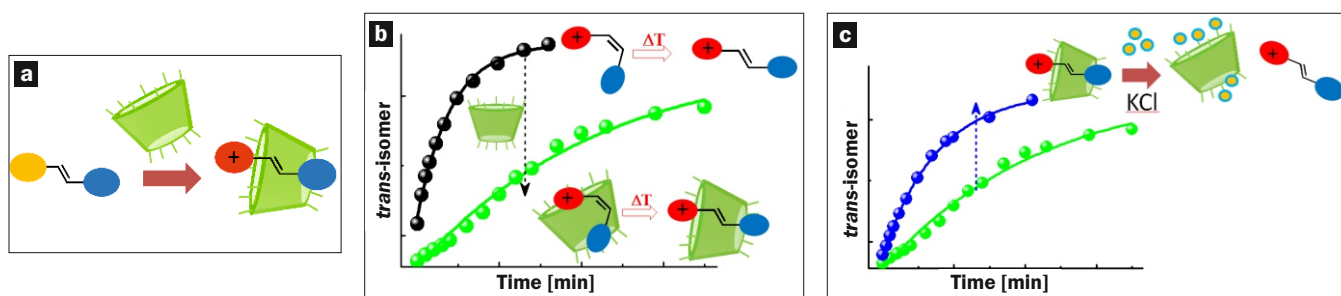


Photoisomerism in Confinement

Multiple Effects of a Nanocavity on Photoactive Guest Dynamics



Schematics of host (SCD) induced guest (DSP) protonation (a), retardation in the kinetics of cis-trans isomerization of DSP upon complexation by SCD (b) and stimuli responsive disruption of host-guest complexation accompanied by reversal in the kinetics of cis-trans isomerization by addition of KCl.

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Macrocylic confinement unlocks the photoisomerization potential of a guest dye, stabilizes the *cis* isomer and also imparts stimuli response, all of which are important for design of novel photo functional materials.

Photoactive molecules that undergo reversible changes in their geometry, structure or colour upon exposure to light are integral to many biological processes including vision, phototaxis and generation of proton-motive force. Moreover, photoisomerization and photochromism are important phenomena that find useful applications in areas like optical storage; light operated molecular machines and photo-pharmacology. Nature has achieved remarkable efficiency and control over its light-driven biological functions by spatial confinement of photoactive species within special pockets created in active sites of proteins. Learning from nature, chemists also seek to manipulate light induced phenomena and obtain the desired optical response by encapsulation inside different kinds of synthetic nanocavities.

In a recent study (S. Dutta Choudhury, *Langmuir* 38, 2022, 14819), it has been shown that confinement of the photoactive hemicyanine dye, *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (DSP) within an anionic β -cyclodextrin macrocycle, sulfated- β CD (SCD), produces multiple interesting effects on its reversible *trans-cis* isomerization process. Interestingly, under normal conditions DSP is inactive toward photoisomerization due to a fast alternate pathway of nonradiative relaxation via formation of twisted intramolecular charge transfer state. However, on protonation of DSP, the intramolecular charge transfer pathway is blocked and its photoisomerization potential can be revived. It is found that the SCD macrocycle plays an important role in this regard by influencing the protonation equilibrium of DSP. The greater affinity of the anionic SCD host for protonated DSP compared to the unprotonated form, leads to "host assisted guest protonation", which provides the desired impetus for unlocking the photoactivity of DSP.

Importantly, the encapsulation of DSP by SCD not only activates the *trans-cis* isomerization of the dye but also significantly retards the thermal back conversion of the *cis* isomer to the *trans* isomer. This is brought about due to stabilization of the *cis* isomer inside the macrocyclic host by geometrical confinement as well as favourable electrostatic interactions. Furthermore, the contribution of electrostatic effects on the host-guest interaction also makes it possible to tune the kinetics of reverse *cis-trans* isomerization of DSP with the help of external stimulants. A simple additive like KCl is found to disrupt the host-guest complexation and consequently influence the recovery of the *trans* isomer of DSP. The SCD induced stimuli responsive, reversible isomerization of DSP is certainly an interesting case from the perspective of chemical sensing or light operated functional materials with host-guest systems.