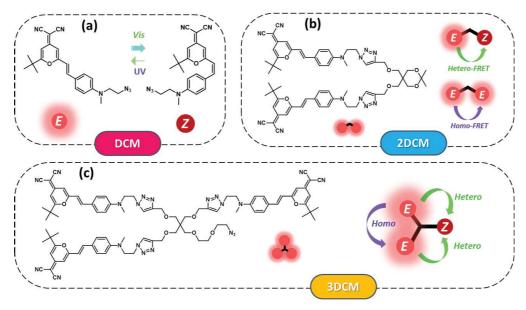
## Competitive photoisomerization and energy transfer processes in fluorescent multichromophoric systems

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Multichromophoric systems showing both fluorescence and photoisomerization are fascinating, with complex interchromophoric interactions. The experimental and theoretical studies of a series of compounds, bearing two and three 4-dicyanomethylene-2-tert-butyl-6-(p-(N-(2-azidoethyl)-N-methyl) aminostyryl)-4H-pyran (DCM) units are reported. The photochemical properties of multi-DCM derivatives, namely **2DCM** and **3DCM**, were compared to the single model azido-functionalized **DCM**, which exists in two forms (*E* and *Z* isomers, **Figure 1a**). Steady-state spectroscopy and photokinetics experiments under UV or visible irradiation indicated that intramolecular energy transfer processes take place among the DCM units. Homo- as well as hetero-energy transfer processes between adjacent chromophores were further confirmed by anisotropy and time-resolved fluorescence experiments (**Figure 1b, 1c**). Molecular dynamics (MD) simulations for **2DCM** were carried out and analyzed using a Markov state model, providing geometrical parameters (mutual orientation and distance between chromophores) and energy transfer efficiency. This work contributes to a better understanding and rationalization of multiple energy transfer processes occurring within multichromophoric systems.



**Figure 1.** (a)  $E \leftrightarrow Z$  photoisomerization illustration of the model azido DCM molecule. (b) Structure of (*EE*)-2DCM and intramolecular energy transfer processes (homo-FRET and homo-FRET) illustration. (c) Structure of (*EEE*)-3DCM and intramolecular energy transfer processes illustration.