

Competitive Photoisomerization and Energy Transfer Processes in Fluorescent Multichromophoric Systems

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A series of dicyanomethylene-4*H*-pyran (DCM)-based multichromophoric (multi-DCMs) were synthesized and their photophysical characteristics were measured. Based on the already known DCM $E \leftrightarrow Z$ photoisomerization and photoswitchable fluorescence properties,^[1-3] the multi-DCM molecules exhibit multiple possibilities of intramolecular Förster resonance energy transfer (FRET) processes.

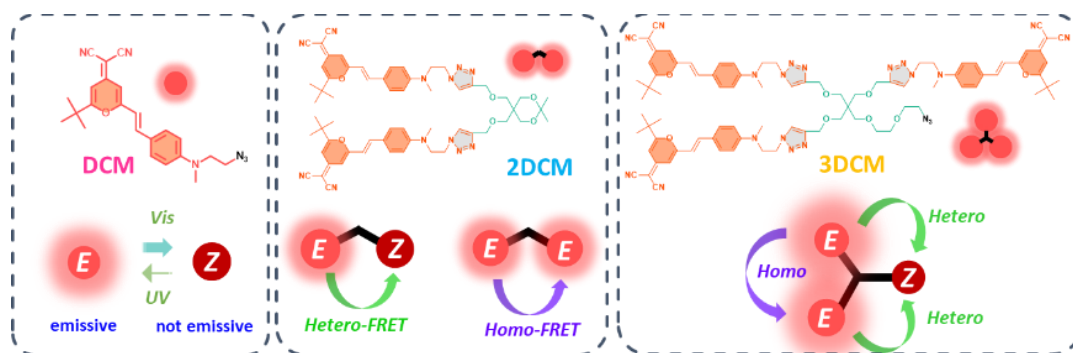


Figure 1. Structure of multi-DCMs and their corresponding isomerization, proposed FRET models.

The homo-FRET property was validated by the steady-state fluorescence anisotropy. The proposed homo-FRET and hetero-FRET models were set up and run in the molecular dynamics (MD) simulations. The simulation results were analyzed by the trajectory-based techniques, and derived Markov state models, revealing the high FRET efficiencies and the conformational transition patterns between the DCM units.

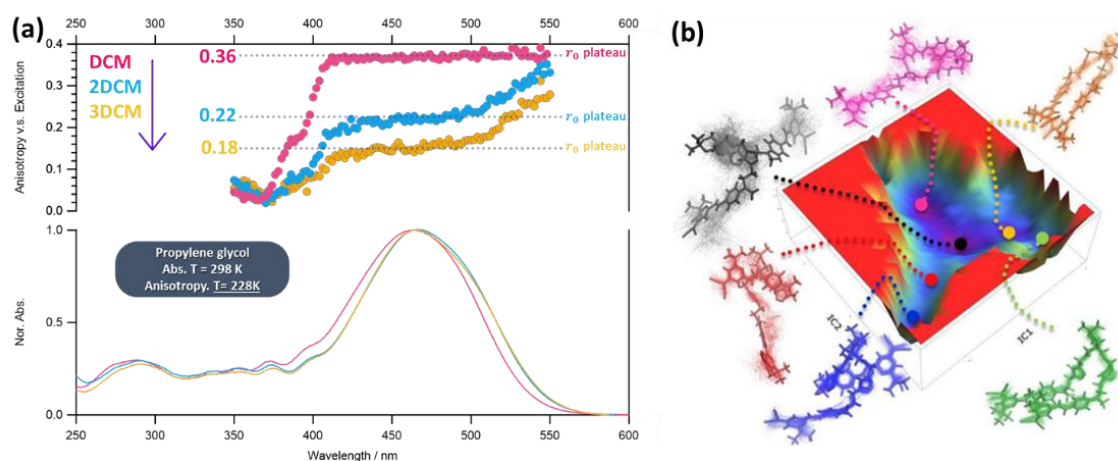


Figure 2. (a) Fluorescence anisotropy of DCM (pink), 2DCM (blue) and 3DCM (orange) in propylene glycol at -45°C , collected as a function of excitation wavelength. (Bottom) Absorption lines of DCM (pink), 2DCM (blue) and 3DCM (orange) in propylene glycol at -45°C . (b) 200 ns MD trajectories of (EE)-2DCM visualized on time-lagged independent component analysis free energy landscape and the corresponding clustered conformations.

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