Fluorescence hysteresis based on programmable photo-switching overcoming conventional limitations

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Oral contribution

We report the design and synthesis of a dendritic molecular architecture that combines two distinct photoswitchable units: a diarylethene (DAE, switchable between open and closed forms) and a dicyanomethylene-4*H*pyran (DCM, E/Z-isomerizable) fluorophore. The system was constructed using a predictable molecular dynamics approach and a click chemistry strategy [1–3]. This molecular construct exhibits a fluorescence hysteresis effect driven by intramolecular Förster Resonance Energy Transfer (FRET). The hysteresis arises from a kinetic mismatch between the switching speeds of the DAE and DCM units, leading to non-linear and light-dependent fluorescence responses. Our design enables programmable, FRET-mediated fluorescence switching, where sequences of UV and visible light produce distinct emission states. Notably, these emission states can be generated under identical illumination conditions, bypassing the limitations imposed by traditional photo-stationary equilibria. This fluorescence hysteresis allows the system to act as an optical memory, encoding multiple fluorescence states. Moreover, it is capable of establishing fluorescence–absorption correlation cycles under various wavelength combinations, a property that holds promise for multiplexed bioimaging, programmable drug delivery, and monitoring dynamic cellular processes.



Fig. 1 (a) Conception of the chemical building block combining two different isomerization mechanisms and its extensible structures; (b) Fluorescence hysteresis mechanism illustration; (c) Potential biological applications of integrating the building block.

References

[1] Y. Zhou, S. Maisonneuve, F. Maurel, J. Xie and R. Métivier, "Competitive Photoisomerization and Energy Transfer Processes in Fluorescent Multichromophoric Systems", Chem. Eur. J. e202202071 (2022).

[2] N. Baggi, A. Léaustic, Y. Zhou, R. Metivier, F. Maurel and Pei Yu, "Tuning the photochemical ring-closing reaction efficiency in diarylethene-based photoswitches through engineering of internal charge transfer", Phys. Chem. Chem. Phys. 25, 7741-7749 (2023).
[2] Y. Zhou, S. Maisonneuve, L. Casimiro, P. Retailleau, J. Xie, F. Maurel and R. Métivier, "Photoisomerization of a 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4*H*-pyran analog dye: a combined photophysical and theoretical investigation", Phys. Chem. Chem. Phys. 24, 6282-6289 (2022).