Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Revealing the switching mechanisms of an OFF-ON-OFF fluorescent logic gate system

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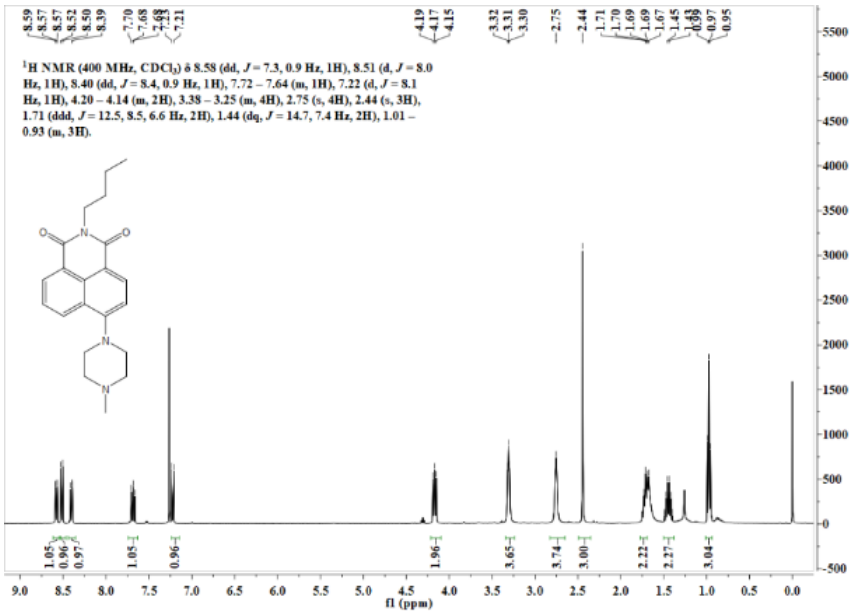

Figure S1. ^{1}H-NMR spectrum of **M3**.

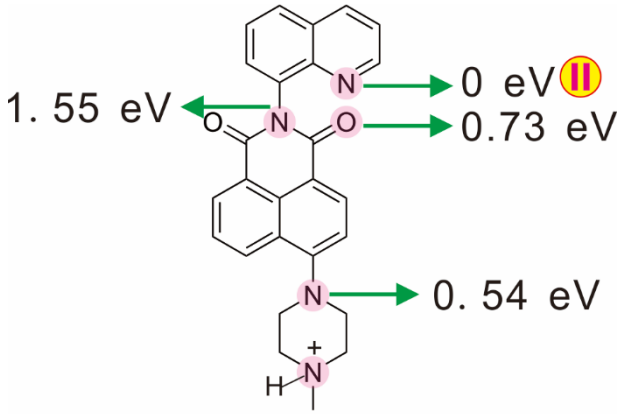

Figure S2. Possible four protonated positions of **M1-1H** and relative Gibbs free energy of the corresponding protonated products (with two protons). Site **II** shows the highest reactive activation towards protonation (forming **M1-2H**).

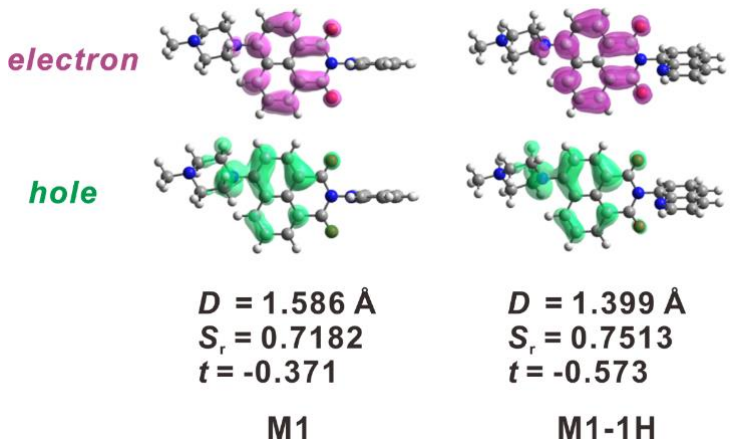

Figure S3. Distribution of hole and electron in **M1** and **M1-1H**. Green donates hole and pink for electron; D is the centroid distance of hole and electron; S_r is overlap between hole and electron; *t* index is designed to measure the degree of hole and electron separation in the charge transfer direction. If $t < 0$, hole and electron is not complete separated, and a more negative value of *t* indicates a smaller degree of charge transfer.[1]

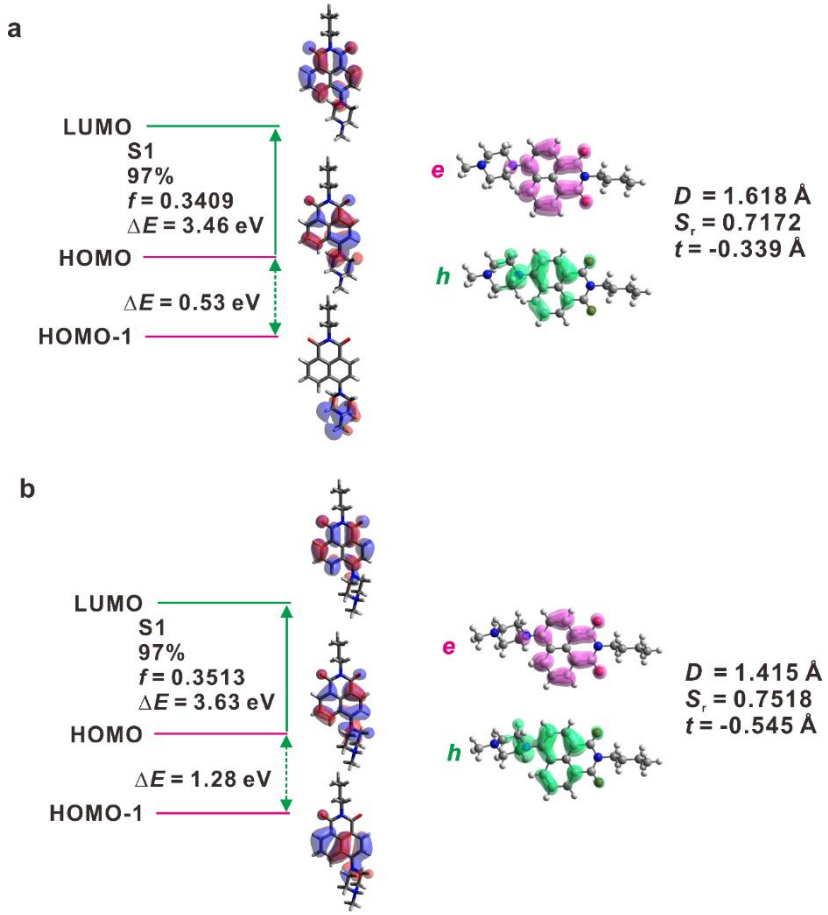

Figure S4. Distribution of molecular frontier orbitals, electronic transitions, and hole-electron analysis (a) before the protonation of **M3** and (b) after the protonation of **M3**. Green donates hole and pink for electron; D is the centroid distance of hole and electron; S_r is overlap between hole and electron; *t* index

is designed to measure the degree of hole and electron separation in the charge transfer direction.

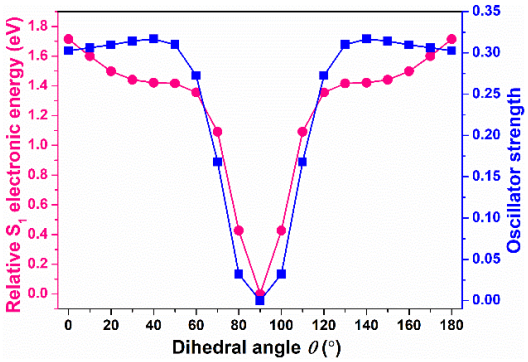

Figure S5. Potential energy surface (pink) of **M3** in the S_1 state and corresponding oscillator strength (blue) in acetonitrile, calculated using M062X.

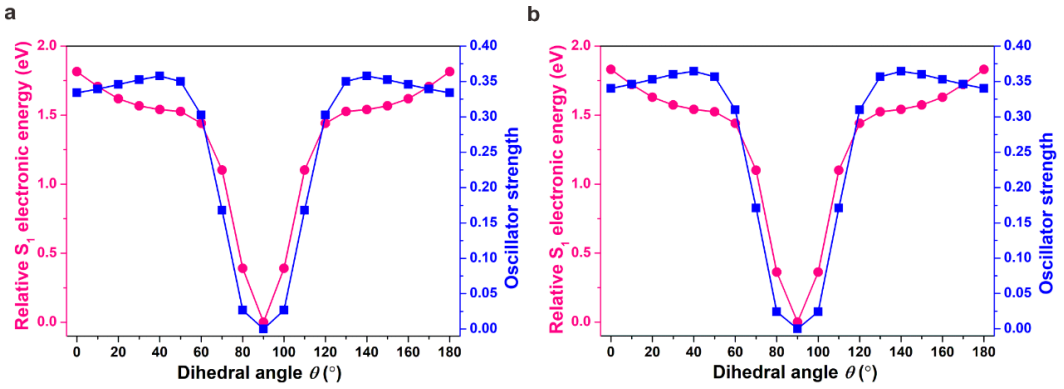

Figure S6. Potential energy surface (pink) and corresponding oscillator strength (blue) of **M1** in the S_1 state in acetonitrile, calculated using CAM-B3LYP (**a**) and ωB97XD (**b**) functionals.

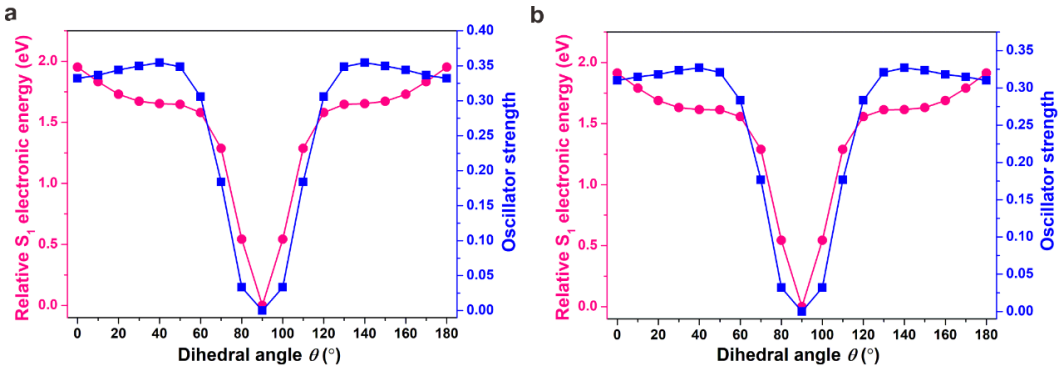

Figure S7. Potential energy surface (pink) and corresponding oscillator strength (blue) of **M1** (a) and **M3** (b) in the S_1 state in water, calculated using M062X functional.

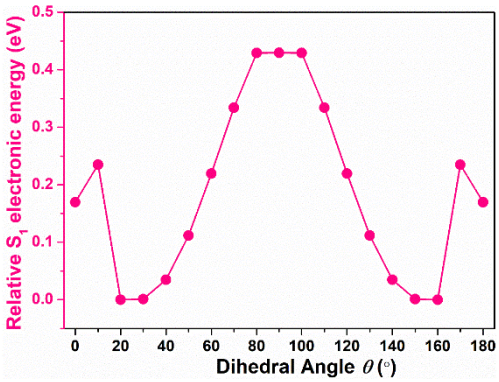

Figure S8. Relative potential energy surface (pink) of **M1-1H** in the S_1 state in acetonitrile, calculated using M062X in combination with liner solvation model.

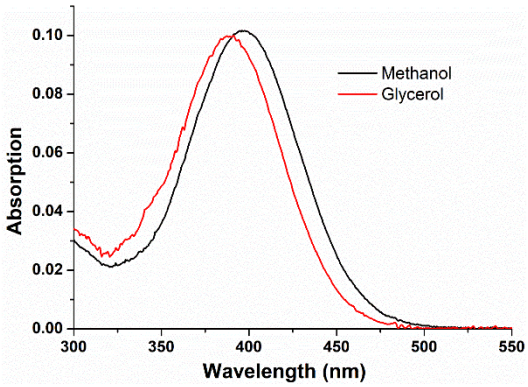

Figure S9. UV—vis absorption spectra of **M3** in methanol and glycerol ([**M3**] = 10 μM).

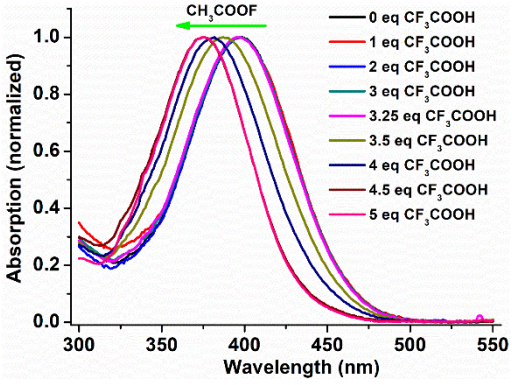

Figure S10. Normalized UV-vis absorption spectra of **M3** upon titration with 0 – 5 eq. of CF_3COOH in methanol.

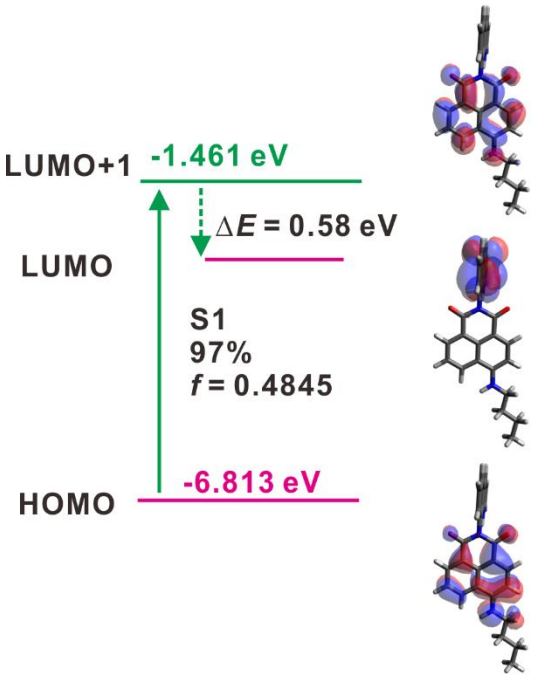

Figure S11. Molecular frontier orbitals and electronic transitions of **M2** in acetonitrile.

Reference

1. T. Le Bahers, C. Adamo and I. Ciofini, *J. Chem. Theory Comput.,* 2011, **7**, 2498-2506.