Supporting Information

Comparative photophysical investigation of doubly-emissive photochromic-fluorescent diarylethenes

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1. Supporting data on spectroscopy

1.1 Steady-state spectroscopy, solvatochromism

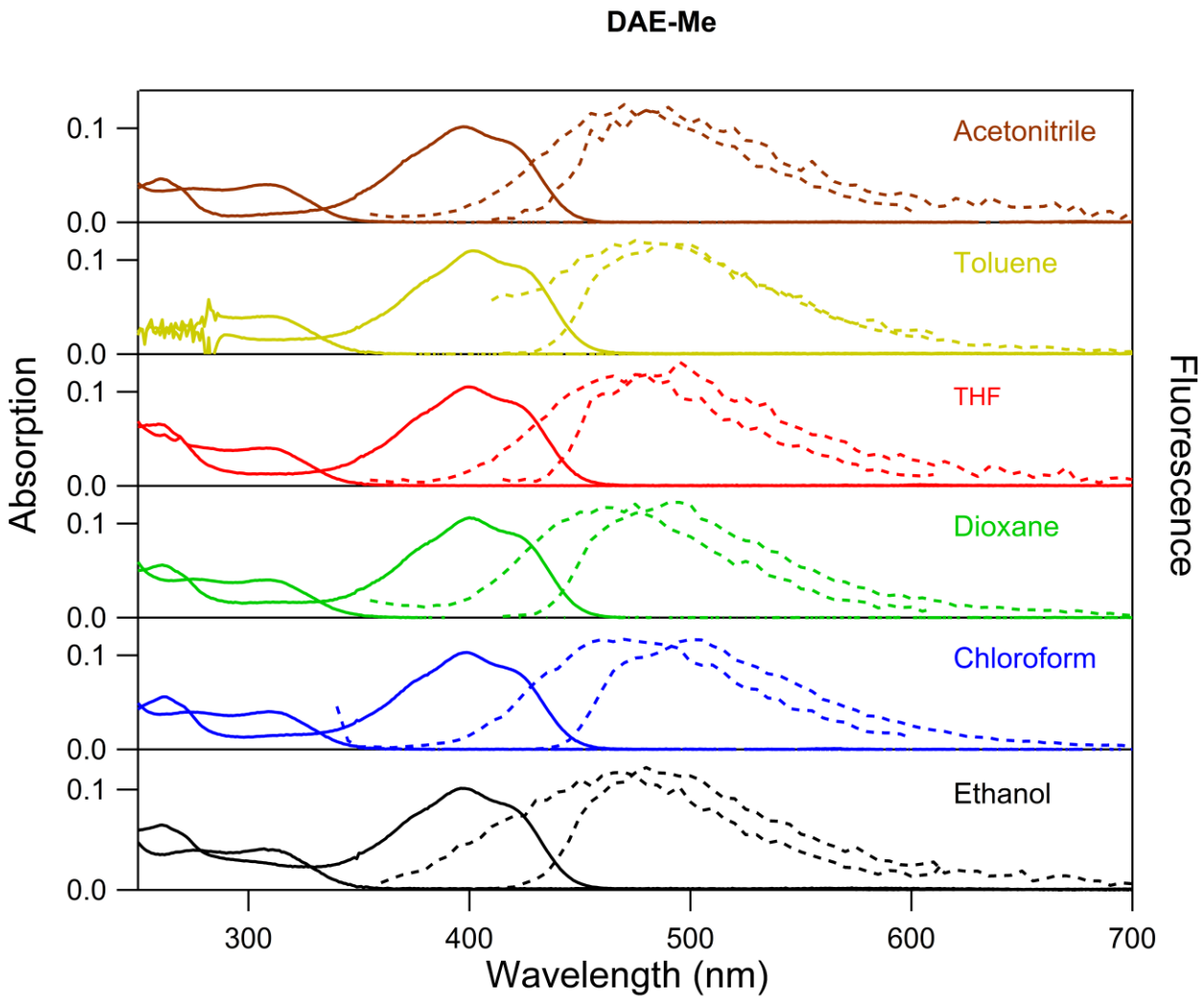

Figure S1. Absorption (bold lines) and fluorescence (dashed lines) spectra of **DAE-Me** in OF and CF in different solvents.

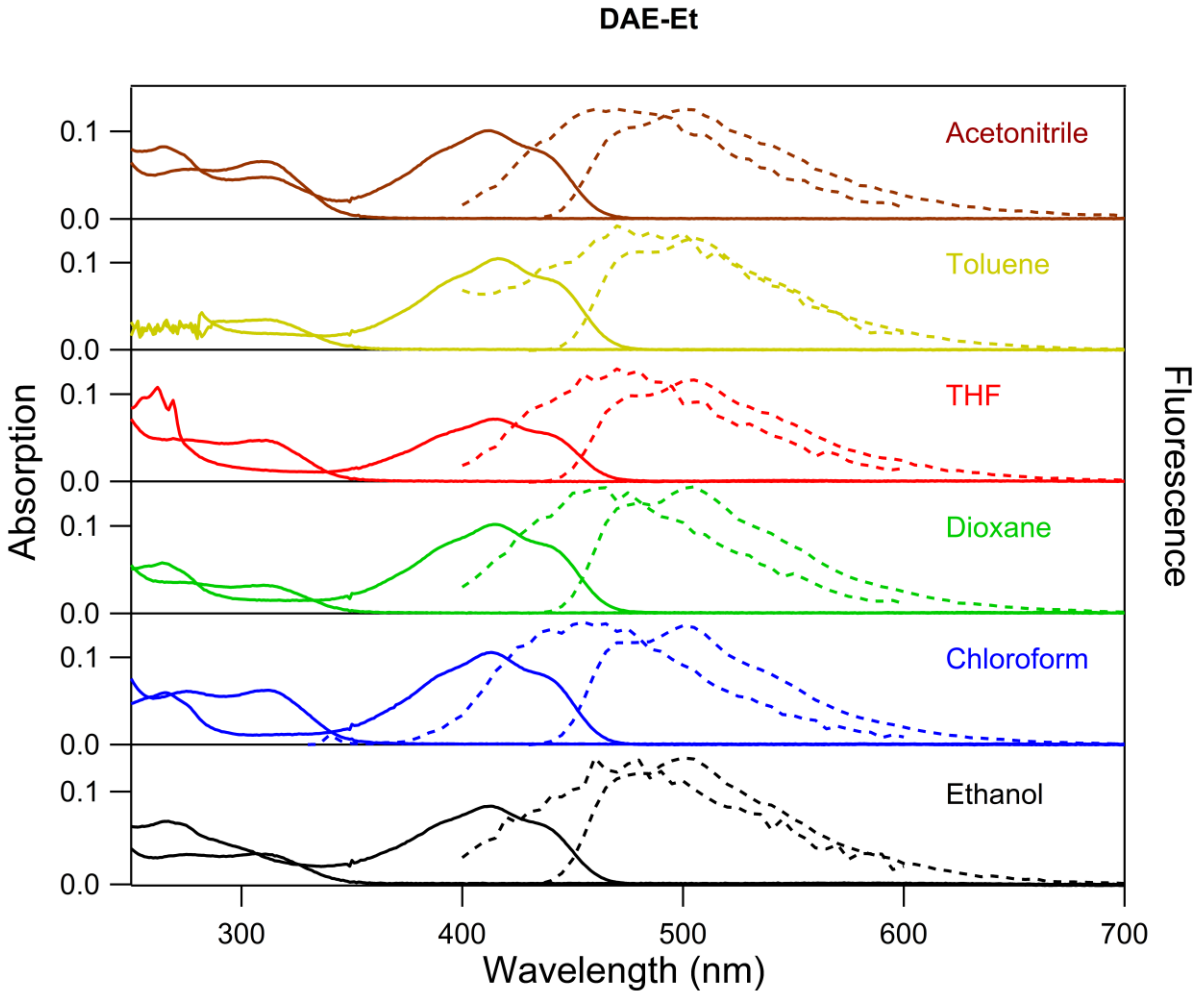

Figure S2. Absorption (bold lines) and fluorescence (dashed lines) spectra of **DAE-Et** in OF and CF in different solvents.

1.2 CF absorption spectra obtained by the Fischer's method and HPLC

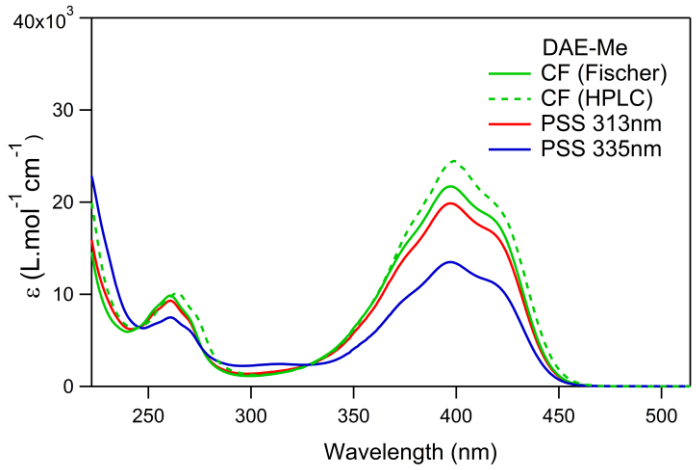

Figure S3. Absorption spectra of **DAE-Me** in the CF, obtained by the Fischer's method and by HPLC. Photostationary states (PSS) under irradiation at 313 nm (PSS 313 nm) and 335 nm (PSS 335 nm) are also represented.

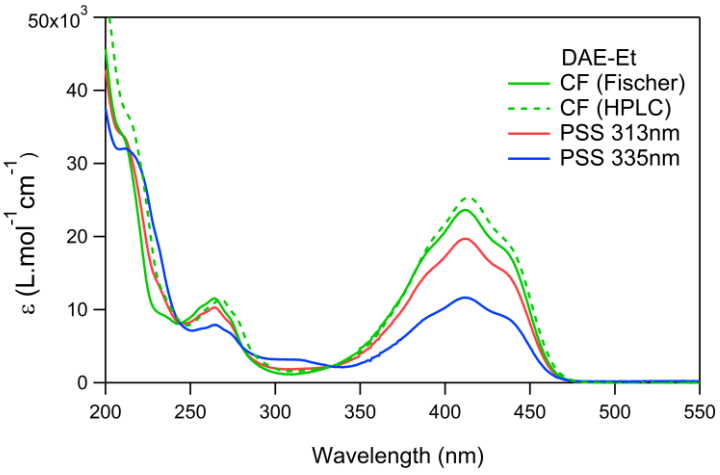

Figure S4. Absorption spectra of **DAE-Et** in the CF, obtained by the Fischer's method and by HPLC. Photostationary states (PSS) under irradiation at 313 nm (PSS 313 nm) and 335 nm (PSS 335 nm) are also represented.

1.3 Femtosecond transient absorption spectroscopy

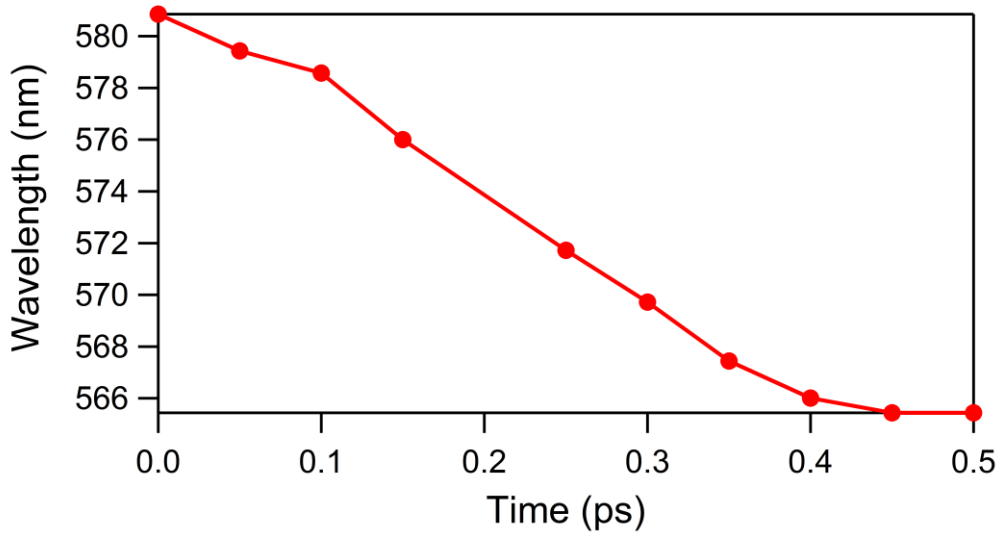

Figure S5. Evolution of the maximum wavelength corresponding to the ΔAbs positive band of the excited state of **DAE-Me** during the time-interval 0 – 0.5 ps (vibrational relaxation process).

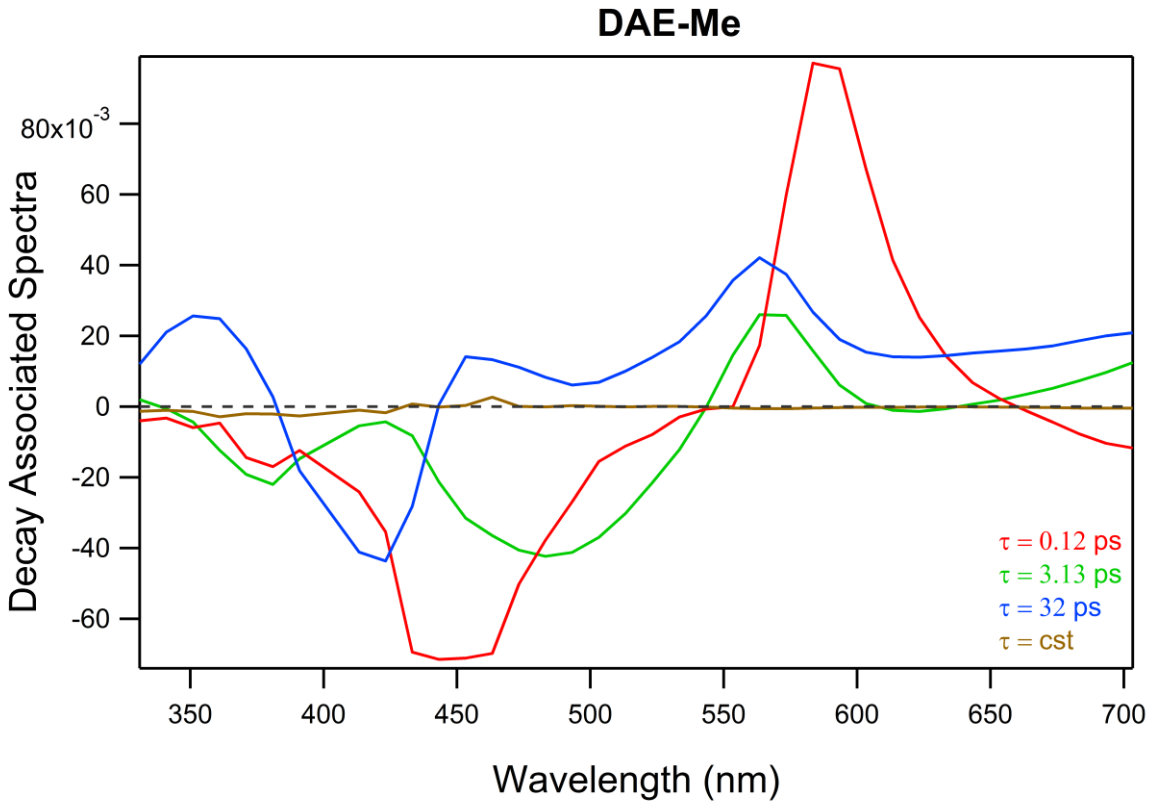

Figure S6. Decay Associated Spectra (DAS) obtained by global fitting with three exponential functions and one constant, convoluted with a Gaussian shaped pulse of 110 fs (FWMH), of kinetics traces every 5 nm obtained from transient absorption experiments on **DAE-Me**.

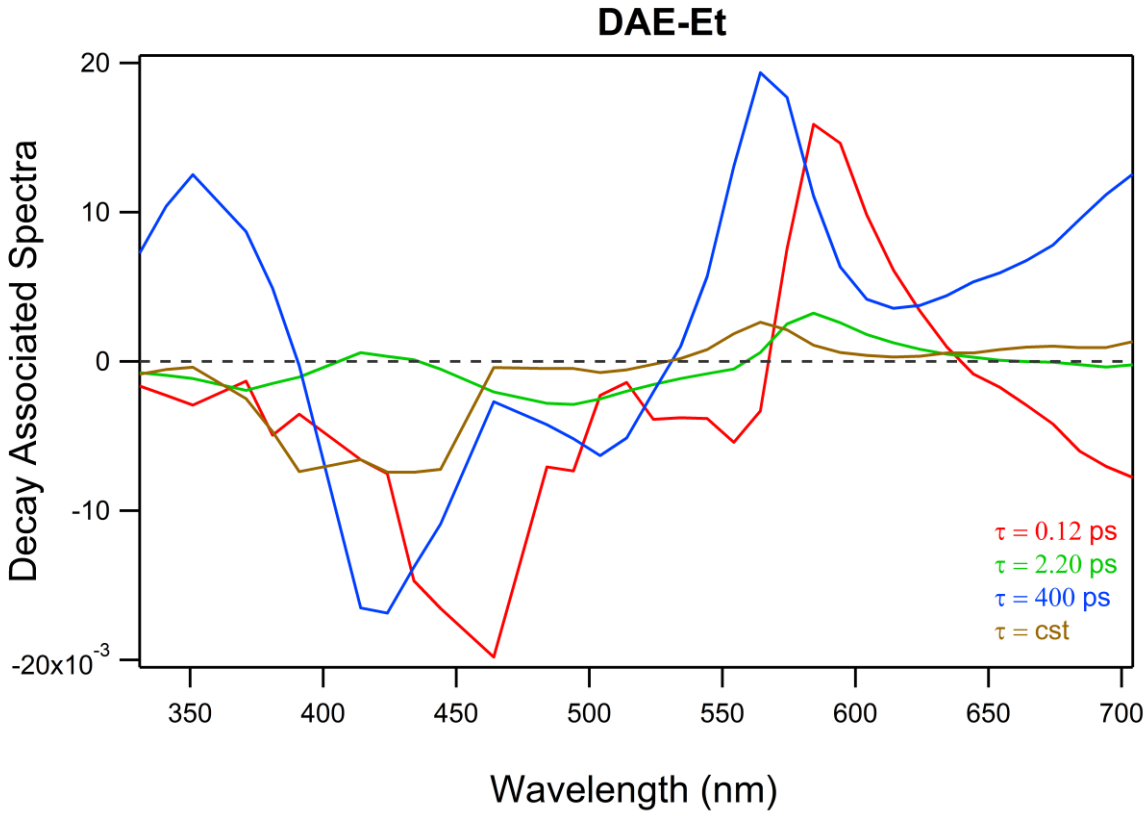

Figure S7. Decay Associated Spectra (DAS) obtained by global fitting with three exponential functions and one constant, convoluted with a Gaussian shaped pulse of 110 fs (FWMH), of kinetics traces every 5 nm obtained from transient absorption experiments on **DAE-Et**.

2. Supporting data on theoretical calculations

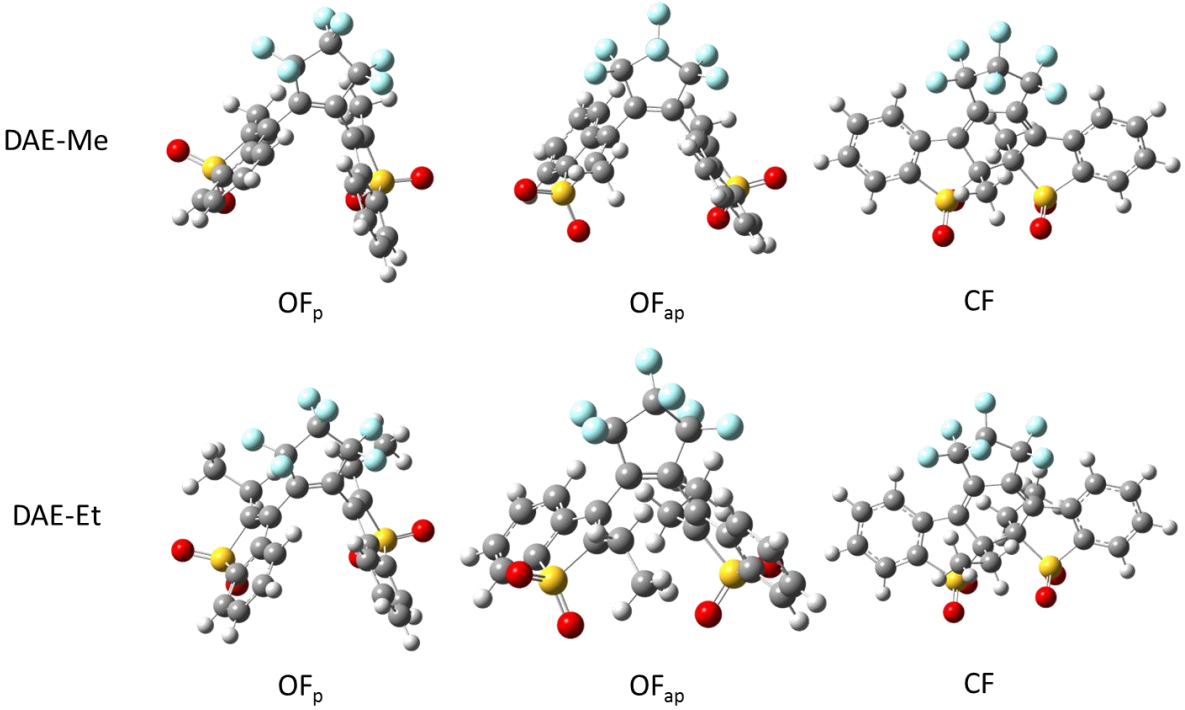

Figure S8. Geometry optimizations for **DAE-Me** and **DAE-Et** in the OF(ap), OF(p) and CF.

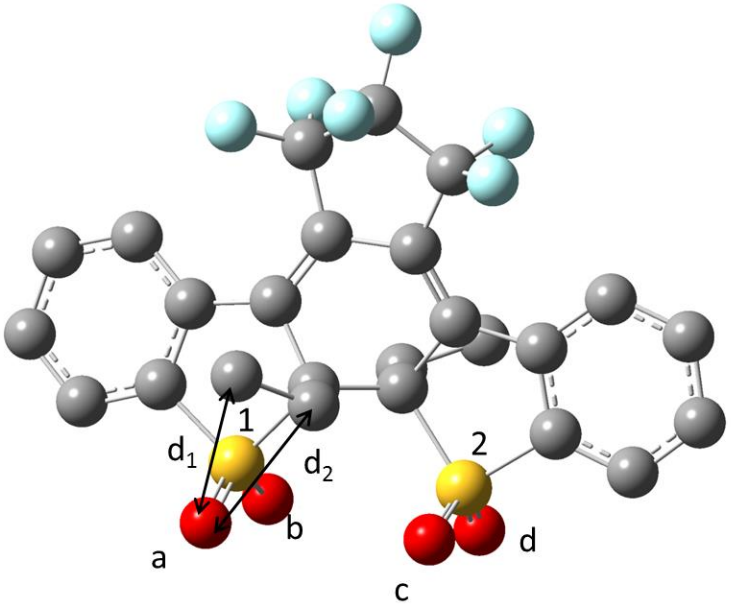

Figure S9. Visualization of distances d_1 and d_2 between O and C atoms for **DAE-Et** (CF).

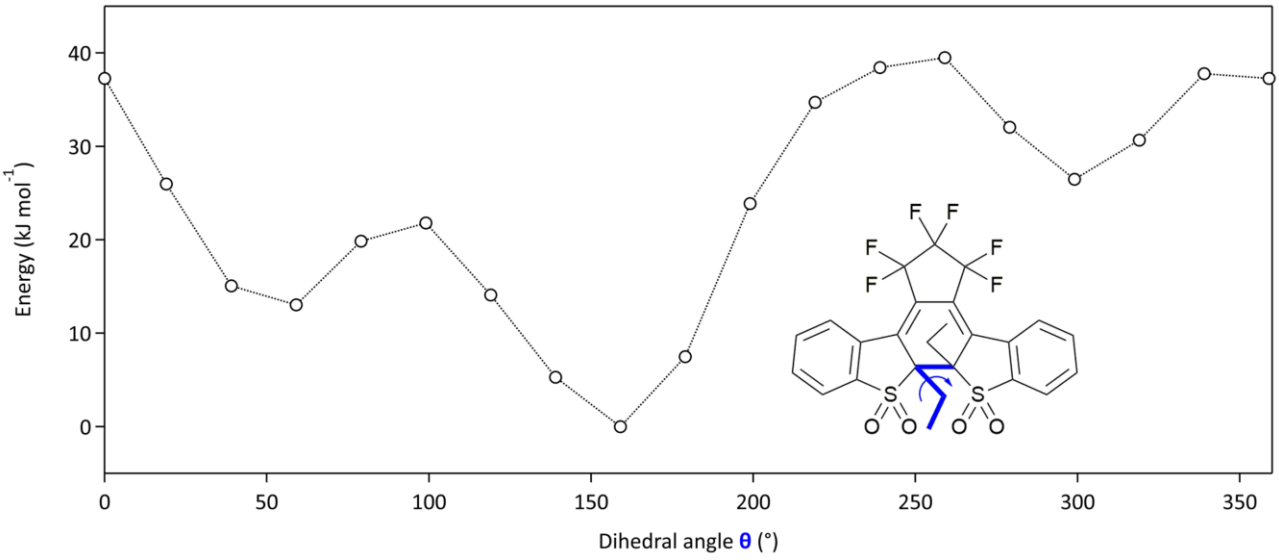

Figure S10. Energy profile of the **DAE-Et** (CF) molecule in the ground state, as a function of the dihedral angle θ (corresponding to the ethyl rotation), showing one sharply defined global minimum, and two additional local minima. DFT calculations were performed at the B3LYP/6-311+G(d,p) level with the IEFPCM model for acetonitrile.