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DFT STUDY OF ABSORPTION AND EMISSION SPECTRA OF FORMYL-SUBSTITUTED AZULENYL DITHIENYLCYCLOPENTENE

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Abstract. Rational control of the optical properties of azulene-based photoswitches requires a detailed understanding of how molecular functionalization influences their electronic structure. DFT calculations have been used to investigate azulenyl dithienylcyclopentenes bearing CHO substituents in comparison to experimental spectra. The calculated absorption and emission spectra agree with experimental ones and reveal that extension of the π-conjugated framework is the primary origin of the bathochromic shifts, whereas substituents progressively tune molecular polarization. Frontier molecular orbital and natural transition orbital analyses show that the electronic excitations remain predominantly π→π* with increased locally excited/intramolecular charge-transfer character, rather than evolving into fully separated charge-transfer states. These findings establish substituent engineering as an effective strategy for tailoring the photophysical response of azulene-based molecular photoswitches while preserving their characteristic anti-Kasha fluorescence.

Keywords: azulenyl-functionalized dithienylcyclopentenes, TD-DFT, MEP, FMO, NTO, absorption, emission, fluorescence;