

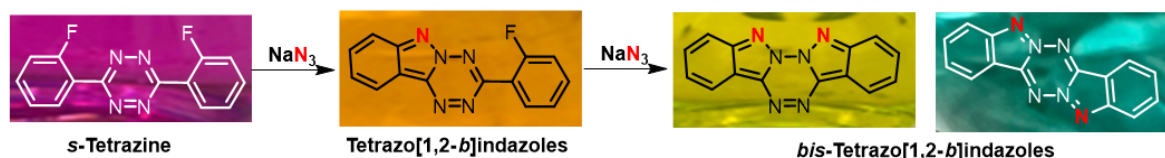
# Looking for Tetrazine-based red dyes: a theoretical insight

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Among the large world of dye development, the ones emitting in the red or infrared wavelengths are of particular interest for their biological application. Moreover, small, rigid and planar molecules without (transition) metal are one of the many requirements for practical use in the OLED large-scale industry. In that respect, it has been shown that *N*-heterocycles-based molecules<sup>1,2</sup> are good candidates to match these requirements.



We have recently developed a way to synthesize a class of *N*-rich polyaromatics from ortho-fluorinated aryl-*s*-tetrazine<sup>3,4</sup>, see the upper Figure. The UV absorption properties evolve strongly upon cyclization: *s*-Tetrazine is purple while the mono-cyclized tetrazo-[1,2-*b*]indazole is orange and the bis-cyclized tetrazo-[1,2-*b*]indazole is either yellow or dark-blue in its *cis* or *trans* forms, respectively.

In this presentation, I will present our theoretical efforts to rationalize the UV properties of this class of molecules and their derivatives. First, I will discuss the different steps needed to reproduce quantitatively the measured UV spectra by going beyond the vertical TDDFT calculation in order to understand the effects of the different substituents, for instance, amines, alcohol, and carbazole. Then, I will illustrate how the analyses of the electronic transitions, by detailing the charge transfer across the molecule<sup>5</sup> for instance, can drive the experimental design of more efficient molecules.

**Keywords:** Tetrazine, UV properties, TDDFT

<sup>1</sup>Daniel *et al.*, Chemistry–A European Journal 2020, 26(7), 1525-1529.

<sup>2</sup>Gutierrez *et al.*, J.Org.Chem. 2022, 87,13653.

<sup>3</sup>Daher and Bousfiha *et al.*, Angew. Chem. Int. Ed. 2023, 62

<sup>4</sup>Bousfiha and Abidi *et al.*, in preparation

<sup>5</sup>using the Theodore software: Plasser, J. Chem. Phys. 2020, 152, 084108.