

TAT X-Mers – A strategy towards precise star-shaped π -conjugated multi-TATs

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Planarized polycyclic triarylaminines constitute an increasingly important subfamily within the compound class of triarylaminines. The rigidity of their molecular scaffold imparts superior π -conjugation when compared to their propeller-shaped open congeners. Therefore, they often have completely delocalized frontier molecular orbitals. Due to their low oxidation potentials, they are promising candidates for dopant-free and cost-effective hole-conductors. Moreover, they are often strongly emissive. Pivotal representatives of this compound class are triaxatruxenes (TATs; Figure 1, structure shown in blue).^[1] TATs consist of three indoles that are fused to a common benzene ring and possess a planar, π -extended, C_3 symmetric skeleton. They can be readily deposited on substrates by vapor deposition or solution film processing.

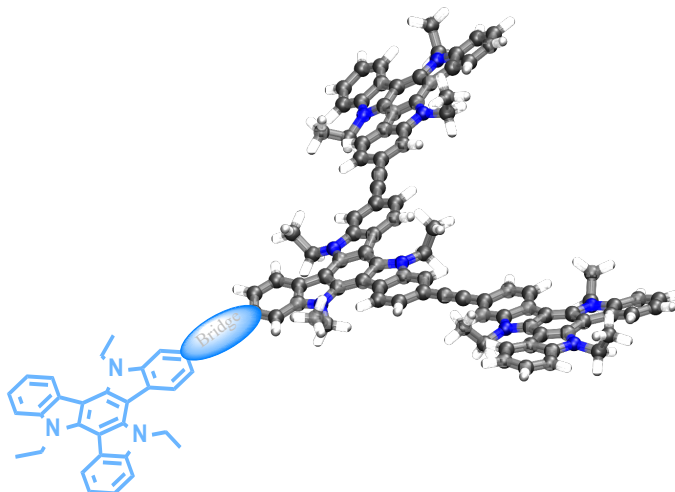


Fig. 1: Schematic depiction of a TAT tetramer with one central TAT bridging three peripheral ones.

We have recently shown that triethyl-substituted triaxatruxenes (Et^3TATs) may serve as a programmable molecular switches when deposited on Ag(111) by electron spray deposition.^[2] Owing to a mismatch between the positions of the Ag atoms in the substrate and of the N atoms of the TAT skeleton, the molecules can adopt several distinct binding states, which differ with respect to tilting and the orientation of the ethyl substituents. Scanning tunneling microscopy (STM) was used both to measure the actual state of a molecule and to switch this state. In dense layers, n neighboring TAT molecules ($n = 2-4$) combine to coupled ensembles with 3^n several different, hypothetical states, several of which could be identified.

We now address the question, whether a direct, covalent linking of individual TAT subunits improves this coupling. To these ends, we set out to prepare linear TAT dimers, V-shaped TAT trimers and star-shaped TAT tetramers and examined their electronic and optical properties by electrochemical and spectroelectrochemical methods as well as quantum chemical calculations. We also probed their emissive properties by spectroscopy and their behavior on the Ag(111) substrate.

TAT X-mers show at least one oxidation per TAT unit and, in their corresponding oxidized states, intervalence charge-transfer transitions in the near infrared, indicating extensive electronic delocalization. The TAT X-mers are also strongly fluorescent. These properties make them promising candidates for hole-conductors and as optically active materials in OLEDs.

References:

- [1] V. Bocchi, G. Palla, *Tetrahedron* **42**, 18 (1986).
- [2] A. Bauer, M. Maier, M. Fonin, R. F. Winter, *Adv. Mat.*, **32**, 12 (2020).