

Ferrocenyl-TATs – Model systems to probe modification of a molecular switch

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The molecular scaffold of planarized polycyclic triaryl amines provides enhanced π -conjugation when compared to their open propeller-shaped counterparts with ensuing superior delocalization of the frontier orbitals HOMO and LUMO. Pivotal representatives of this compound class are triazatruxenes (TATs, see the left panel of Figure 1).^[1] TATs consist of three carbazole units that are annulated to a common, central phenyl ring. *N*-Alkyl-substituted TATs can be deposited on substrates by vapor deposition or solution film processing techniques.

We have recently shown that *N,N',N''*-triethyl-triazatruxene (^{Et3}TAT), when deposited on Ag(111), can serve as a molecular switch.^[2] A mismatch between the positions of the TAT N atoms and the Ag atoms of the substrate imposes a tilted arrangement of TAT molecules with shorter and longer Ag-N interactions. Application of a suitable potential to a STM tip triggers directional switching between the three degenerate binding states in clockwise or counterclockwise directions with the directionality of over 90 %.

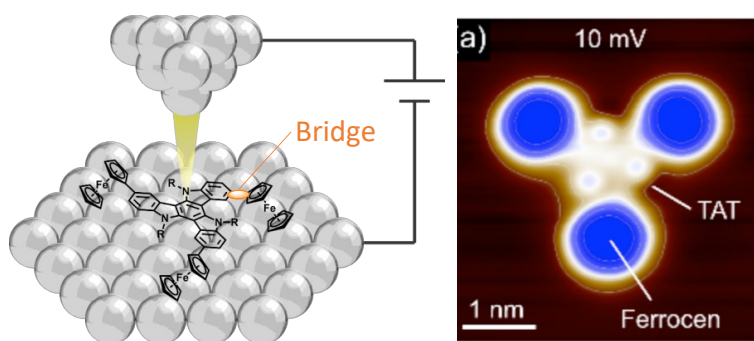


Fig. 1: Cartoon of the investigation of a *Ferrocenyl*-substituted TAT in the STM (left) and depiction of the respective measurement (right).

In order to being able to couple the mechanical degrees of freedom to the magnetic ones and investigate their behavior under current excitation, we aim at introducing substituents with a magnetic anisotropy to the TAT scaffold. Primary candidates are metallocenes like nickelocene or manganocene. As it is unclear how such substituents impact on the observed switching behavior of TATs, we prepared a small library of mono-, di- and triferrocenyl-substituted TATs, making use of the robust derivative chemistry of ferrocenes. These modified TATs show one reversible oxidation per ferrocenyl unit and one for the TAT core. Spectroelectrochemical studies reveal charge transfer transitions from the TAT core to the oxidized ferrocenium entities in the respective cationic forms. STM studies showed that the switching behavior of ^{Et3}TAT is retained with, however, a slightly decreased switching rate compared to ^{Et3}TAT itself, thus proving the viability of our concept.

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).