

Supporting Information:

Donor-Acceptor Properties of a Single-Molecule Altered by On-Surface Complex Formation

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Distribution of different adsorption types

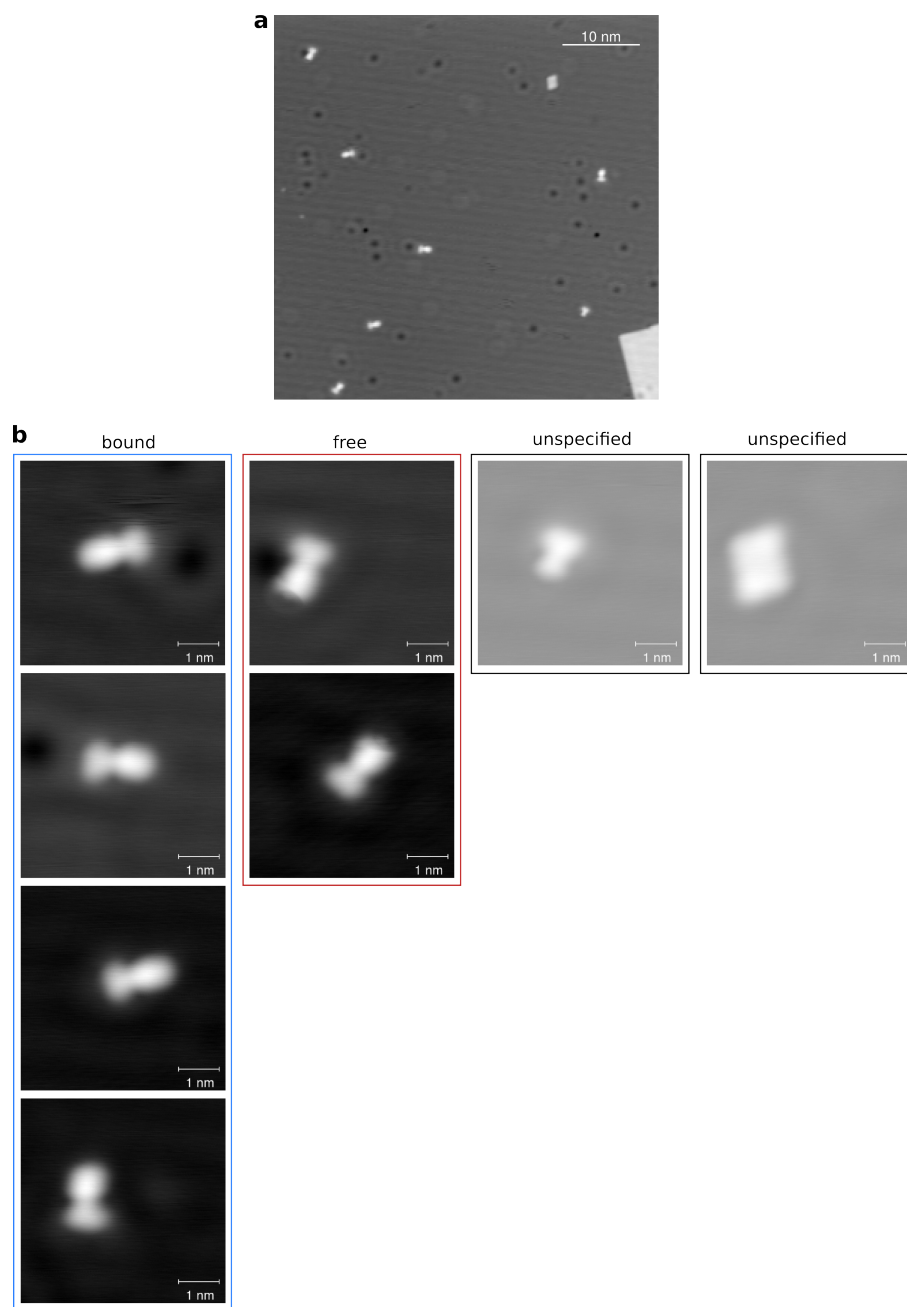


Figure S 1: Distribution of *bound* and *free* molecules of TTF-dppz adsorbed on 2 ML NaCl/Cu(111). **a**, The overview STM image shows a ratio of 2:1 between *bound* and *free* molecules which is representative to the observed distribution in general. **b**, STM images of *bound* and *free* adsorption types together with some rare unspecified adsorbates.

Adsorption sites of TTF-dppz on NaCl (2ML) on Cu(111)

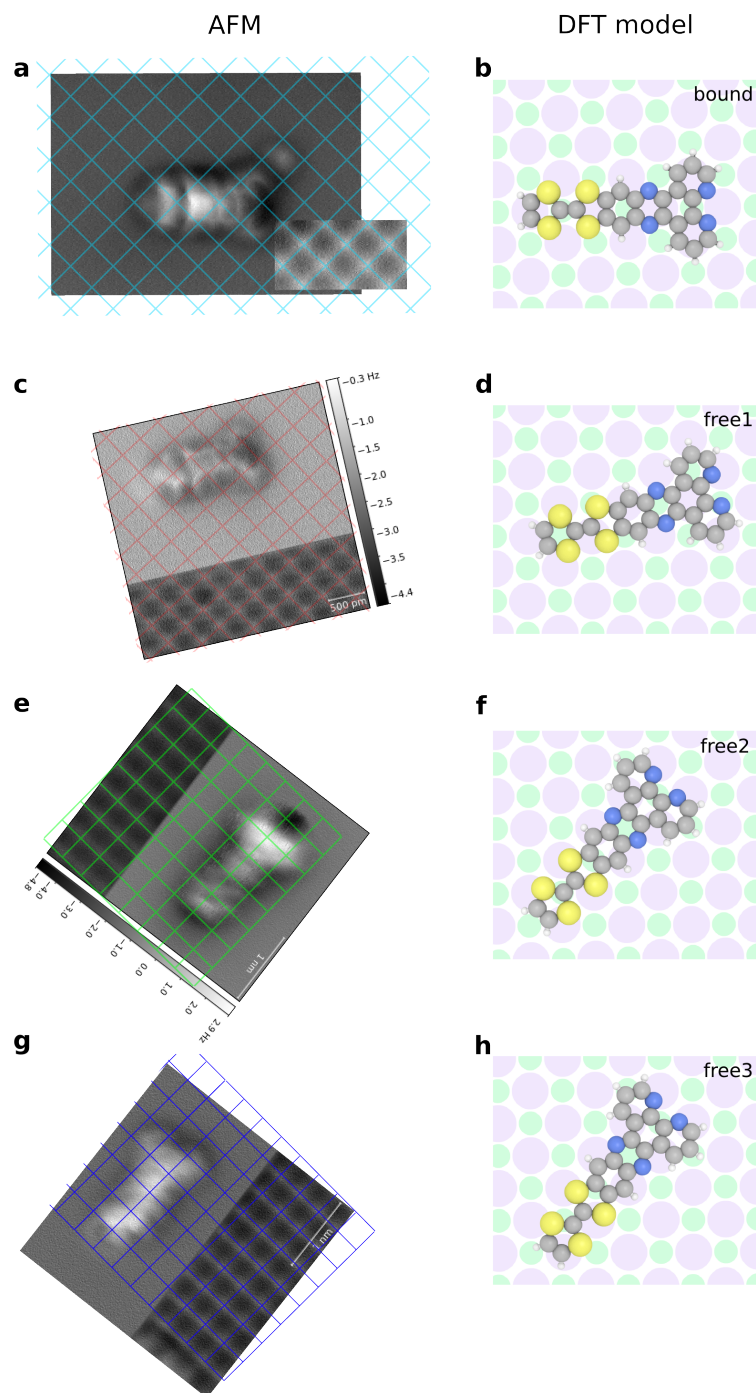


Figure S 2: **Adsorption sites of TTF-dppz.** Left: AFM images of single molecules together with NaCl lattices obtained from images of the substrate. Right: Corresponding models derived from DFT calculations.

Calculated electronic properties of TTF-dppz

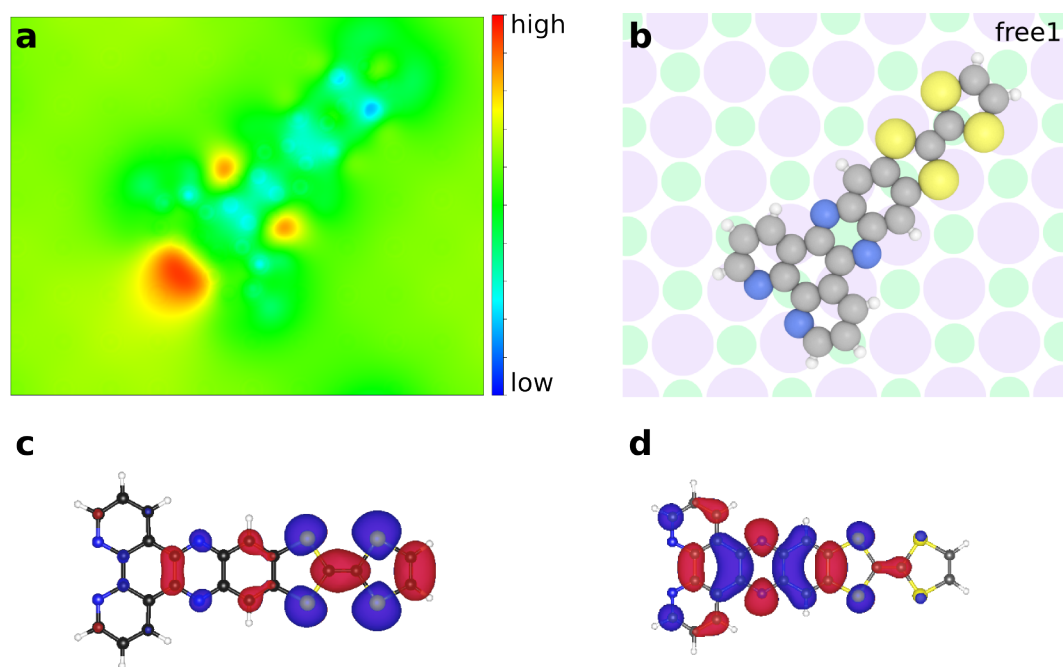


Figure S 3: **Electronic properties of TTF-dppz.** **a**, electrostatic potential and **b**, adsorption site of a *free* molecule. **c,d**, HOMO and LUMO of TTF-dppz in the gas phase. The molecular orbitals of TTF-dppz are spatially separated which is characteristic for an electron donor-acceptor molecule.

Further details on the synthesis of TTF-dppz

General Air and/or water-sensitive reactions were conducted under Ar in dry, freshly distilled solvents. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz for ^1H and 75.5 MHz for ^{13}C . Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak (DMSO- d_6 , ^1H = 2.5 ppm; THF- d_8 , ^{13}C = 67.57 ppm). Coupling constants (J) are given in hertz (Hz) and peak multiplicities are described in the following way: s, singlet; d, doublet. High-resolution Mass Spectra (HRMS) were recorded with ESI (electrospray ionization) on a Thermo Scientific LTQ Orbitrap XL in the positive mode.

Materials 6-(1,3-dithiol-2-ylidene)-[1,3]dithiolo[4,5-*f*]-2,1,3-benzothiadiazole was synthesized according to the literature procedure¹. Tetrahydrofuran (THF) was stirred over sodium/benzophenone and then distilled immediately prior to use for anhydrous reactions. Unless stated, all other reagents were purchased from commercial sources and used without additional purification.

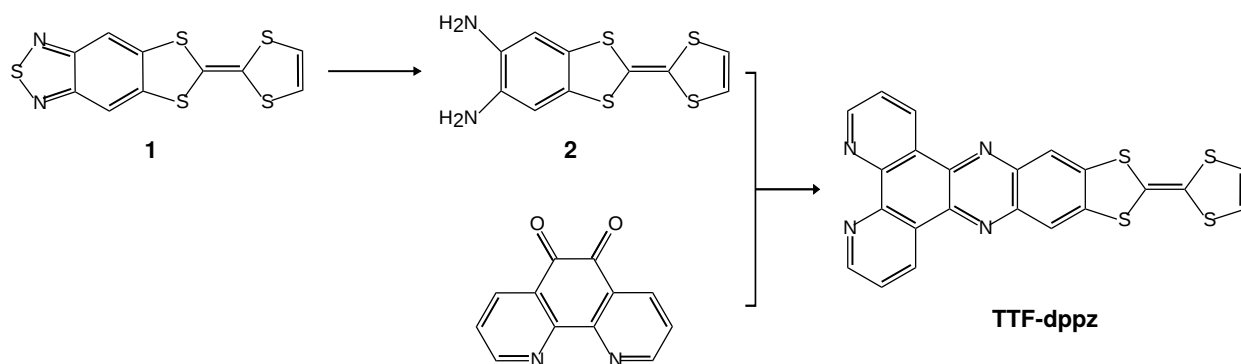


Figure S 4: **Synthesis of TTF-dppz.**

REFERENCES

- (1) Geng, Y.; Pfattner, R.; Campos, A.; Hauser, J.; Laukhin, V.; Puigdollers, J.; Veciana, J.; Mas-Torrent, M.; Rovira, C.; Decurtins, S.; Liu, S.-X. A Compact Tetrathiafulvalene-Benzothiadiazole Dyad and Its Highly Symmetrical Charge-Transfer Salt: Ordered Donor π -Stacks Closely Bound to Their Acceptors. *Chem. - Eur. J.* **2014**, *20*, 7136-7143.