

# Stereoselectivity and electrostatics in charge-transfer Mn- and Cs-TCNQ<sub>4</sub> networks on Ag(100)

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Self-assembly provides a very promising bottom-up fabrication strategy that has been employed in many different fields like organic electronics, crystal engineering and design of hybrid nanocomposite materials. The most impressive display of the self-assembly potential for both reproducibility and scalability is found in biological systems where long-range interactions typically drive very complex stereoselective assembly processes. Stereoselective assembly also occurs in much simpler molecular systems at surfaces, where it is readily accessible to direct experimental observation. For instance, the crystallization of a mixture of chiral molecules typically results either in the formation of crystals having a unit cell containing two different enantiomers (racemates), or in the separation of enantiomers forming crystals of a single handedness (racemic conglomerates). However, the specific behaviour of a particular chiral molecule is generally difficult to predict and must be experimentally determined. In this context, the investigation of the assembly behaviour of charged organic molecules and different metal linkage atoms on metal substrates can help in clarifying and tuning some functional properties of metal-organic interfaces.

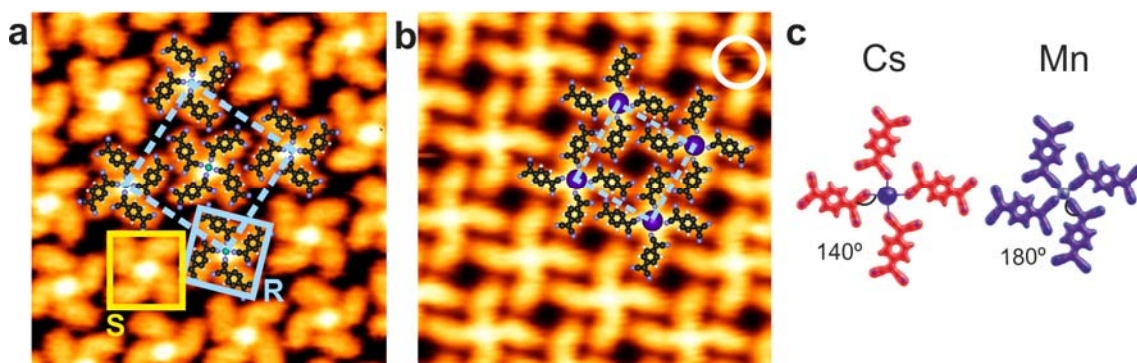


Figure 1: (a) STM image ( $8 \times 8 \text{ nm}^2$ ) of Mn-TCNQ<sub>4</sub> achiral superstructure. Yellow and blue squares symbolize clockwise R- and anti-clockwise S-enantiomers, respectively. (b) STM image ( $8 \times 8 \text{ nm}^2$ ) of Cs-TCNQ<sub>4</sub> chiral superstructure. The white circle indicates a Cs vacancy. (c) Cs- and Mn-TCNQ<sub>4</sub> electron density isosurface of isolated complexes. Mn forms directional coordination bonds, whereas Cs fully transfers its valence electron to the molecules establishing an ionic bond.

The chiral and electrostatic properties of metal-organic superstructures obtained from achiral TCNQ molecules co-deposited with Cs and Mn metal atoms on the Ag(100) surface were investigated by means of scanning tunnelling microscopy (STM) and density functional theory (DFT) calculations. We find that both Mn and Cs adatoms form intermediate chiral metal-TCNQ<sub>4</sub> windmill complexes (R and S enantiomers in Fig. 1). The complexes consist of a central protrusion representing the metal atom that binds to one cyano group of each of the four TCNQ molecules. The complexes assemble into superstructures that are equally packed, however, while Mn-TCNQ<sub>4</sub> assemble into achiral domains (Fig. 1a), Cs-TCNQ<sub>4</sub> induce strictly chiral domains which are also much more extended (Fig. 1b).

We performed DFT calculations in order to rationalize the structural differences of the two metal complexes and the emergence of the distinctive chiral ordering. The charge density isosurfaces of individual gas-phase units (Fig. 1c) show that Cs donates its valence electron to TCNQ<sub>4</sub>, and the resulting ionic bond allows free rotations of the molecules around the Cs<sup>+</sup> ion, whereas Mn forms a rigid, directional coordination bond with the molecules. Both metals yield a stable complex but with different metal-N-C bonding angles of  $\sim 180^\circ$  and  $\sim 140^\circ$  for Mn and Cs, respectively.

Gas-phase calculations of chiral Cs-TCNQ<sub>4</sub> and achiral Mn-TCNQ<sub>4</sub> superstructures indicate that they are planar and stable at the experimental distance (cf. Fig. 2a,b). In comparison, the Mn-TCNQ<sub>4</sub> hypothetical chiral superstructure with equal density (Fig. 2c) shows that the outer, negatively

charged nitrogen atoms of the single complexes (red circle in Fig. 2c) get too close to each other, where their mutual repulsion is decreased by an out-of-plane buckling of  $\sim 1$  Å. This buckling would be highly unlikely on the metal surface, since the cyano groups are expected to form a relatively strong bond with the Ag substrate [1]. Similar calculations performed for the chiral Cs–TCNQ<sub>4</sub> network reveal that the  $\sim 140^\circ$  Cs–N–C bond angle allows an arrangement where the nitrogen atoms are sufficiently separated (Fig. 2b) yielding a completely planar structure.

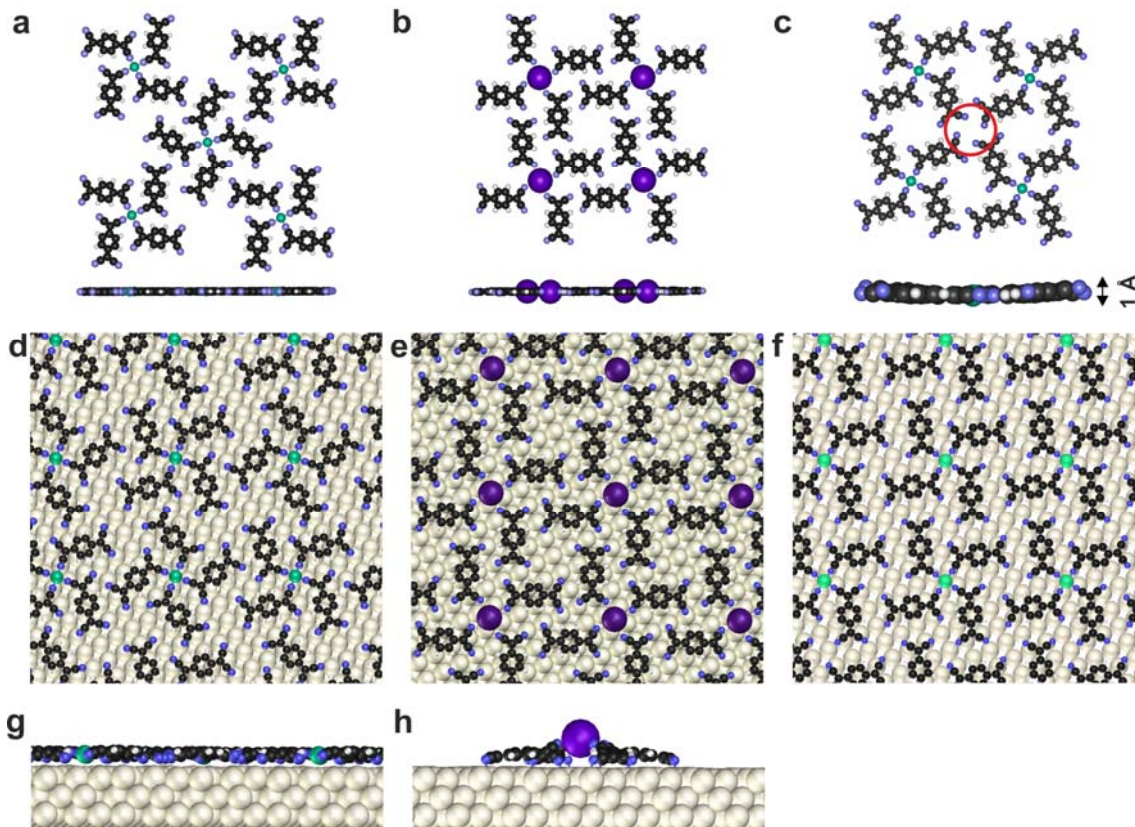


Figure 2: DFT simulations of periodically repeated complexes in the (a-c) absence and (d-h) presence of the surface. (a,d) Achiral Mn–TCNQ<sub>4</sub> structure observed in the experiment. The fully relaxed structure remains planar. (b,e) Planar Cs–TCNQ<sub>4</sub> structure. (c) Hypothetical chiral Mn–TCNQ<sub>4</sub> structure. The outer nitrogen atoms repelling each other (red circle) are buckled. (e,h) Highly non-planar Cs structure. (f) Hypothetical chiral Mn–TCNQ<sub>4</sub> structure.

DFT calculations of Mn– (Fig. 2d,g) and Cs–TCNQ<sub>4</sub> (Fig. 2e,h) networks including the Ag(100) substrate rule out the possibility of N-buckling for both complexes since the outer nitrogen atoms form covalent bonds with the surface. For Mn– TCNQ<sub>4</sub> (Fig. 2d) we obtain two N–Ag bonds/TCNQ by the outer nitrogen atoms of the complex and one inter-complex hydrogen bond per TCNQ is formed. The Mn–N–C bond alignment remains straight. On Ag(100), the experimentally observed achiral arrangement more stable than the hypothetical chiral organisation (Fig. 2f) since in the latter structure only one N–Ag bond/TCNQ is formed and no inter-complex hydrogen bond would be realized. The straight Mn–N–C bonds lead to a repulsion of the negatively charged external nitrogen resulting in a slightly rotated configuration.

The large, stable and chiral domains formed by the Cs–complexes are ultimately made possible by the Cs–TCNQ bond flexibility. The non-straight Cs–N–C bond angle allows the formation of two N–Ag bonds/TCNQ and, at the same time, of three inter-complex hydrogen bonds/TCNQ. We note that the Cs–N–C bond angle allows the same packing density of the Mn–TCNQ<sub>4</sub> domains, despite the individual unit being substantially larger (Fig. 1c).

The significant differences in the relaxation pattern of the two metal–organic layers indicate that the Cs bonded adlayer is electrostatically more stable. We find that while Mn–TCNQ<sub>4</sub> remains

essentially flat (Fig. 2g), the Cs–TCNQ<sub>4</sub> complexes become highly non-planar on the surface, with the Cs atoms together with their bonding N atoms significantly lifted up from the surface (Fig. 2h). The structure has relevant effects on the surface electric dipole. The relation between the different bonding patterns and the relative electrostatic stability of the adlayers is revealed by the analysis of their electron density displacement field  $DF(x,y)$ , defined as

$$DF(x,y) = \int_{z_{sub}}^{vacuum} \Delta\rho(x,y,z)dz, \text{ where: } \Delta\rho \equiv \rho - (\rho_{TCNQ} + \rho_{metal} + \rho_{Ag})$$

where  $z_{sub}$  defines a plane dividing substrate and adlayer. This quantity represents the electron density of the interacting system minus the densities of its three separated constituents in their electrically neutral state. In Fig. 3a the Mn coordination bonding displacement pattern is clearly visible, while the black depletion zones at the Cs positions reveal the complete ionization of the alkali atoms.

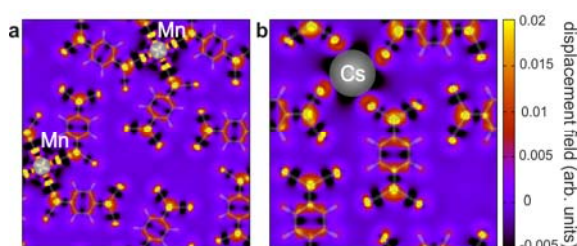


Figure 3: Charge density displacement field of (a) Mn–TCNQ<sub>4</sub> and (b) Cs–TCNQ<sub>4</sub>. The plots account for the difference of electron charge density between the fully interacting system and its non-interacting components. The structure model is superposed to the plots.

The strong electron acceptor TCNQ undergoes electron transfer from the surface for both adlayer structures resulting in an overall negative surface electric dipole. Interestingly, the calculations show that the electron transfer for the Cs complexes is significantly larger than for Mn, whereas the electric dipole is somewhat smaller for the Cs– compared to the Mn–bonded adlayer. A large cancellation occurs in the Cs–adlayer by the positive dipole of the “lifted up” Cs cations. Therefore a higher charge transfer on TCNQ and a smaller electric dipole can be achieved at the same time further stabilizing the Cs–TCNQ<sub>4</sub> supramolecular assembly.

In this special case the racemate formation or chirality segregation are a consequence of the dissimilar nature of the Cs– and Mn–ligand bonding: switching from directional coordination (Mn–TCNQ<sub>4</sub>) to flexible ionic bonding (Cs–TCNQ<sub>4</sub>) results in the switch from achiral to chiral domains. Thus, the control of the intracomplex stiffness offers a route to steer long-range organizational chirality, possibly providing a tool for the chiral design of organic crystals. Furthermore, our results suggest that alkali atom bridging can be useful to control the stability of self-assembled structures of electronegative organic molecules on metal surfaces due to the flexibility of the ionic bond and the enhanced stability by electrostatic effects. The latter can be also used to tune the overall electronic level alignment of the metal–organic system, which is of great interest in organic electronics [2].

#### References:

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