Stereoselectivity and electrostatics in charge transfer Mn- and Cs-TCNQ4 networks on Ag(100)

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Metal intercalated Organic System on Ag(100)

$\text{TCNQ molecule} (\text{Tetracyanoquinodimethane})$

$\text{metal-TCNQ}_4 \text{ complex (chiral in 2D)}$

@ Ag(100)
Experimental facts:
Metal-TCNQ$_4$@Ag(100)

- TCNQ$_4$-Mn
- TCNQ$_4$-Cs

- Heterochiral
- Effectively less compact
- Homochiral
- More compact
- note: Cs is larger than Mn

N. Abdurakhmanova, AF, T-C Tseng, A. Comisso, S. Stepanov, A. De Vita, K. Kern
Experimental facts: Metal-TCNQ$_4$@Ag(100)

- Homochiral: Cs-TCNQ$_4$ huge domains (pink)
- Heterochiral: Effectively less compact

Note: Cs is larger than Mn

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Experimental facts: Metal-TCNQ$_4$@Ag(100)

- TCNQ$_4$-Mn
- TCNQ$_4$-Cs

**Cs-TCNQ$_4$ huge domains (pink)**
- Homochiral
- Big holes
- More compact

- Heterochiral
- Effectively less compact

*Note: Cs is larger than Mn*

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1) Rationalization of different assembly of Cs- and Mn-TCNQ4 complexes on Ag(100)

2) Electrostatic properties

3) Considerations on the role of Cs and other alkali metals in tuning substrate electrostatic properties
Single metal-TCNQ4 complex (gas phase)

- **TCNQ4-Mn**
  - Mn-N-C-C angle 180°
  - Charge isosurface shows coord. bond
  - Mn-N bond: directional, planar, difficult to deform

- **TCNQ4-Cs**
  - Cs-N-C-C angle 140°
  - Cs donates 1e to TCNQ4 (0.25e/TCNQ)
  - Cs-N: ionic, non directional, molecules free to rotate

Charge isosurface
Why Mn-TCNQ4 is heterochiral on Ag(100)?

Difference in energetics influenced by:

1) N atoms repels electrostatically
2) inter-complex H-bonds
3) formation of N-Ag bonds

Cs homochiral
- 140deg angle allows a more compact geometry
- Planar structure
- N avoid each other

Mn heterochiral
- N’s avoid each other (av dist. 4.5Ang)
- Planar structure
Why Mn-TCNQ4 is heterochiral on Ag(100)?

Hypothetical Mn homochiral structure
• “External” N repel each other (av dist. 3.3Ang)
• relaxation results in N-buckling, not compatible with surface
Mn-TCNQ$_4$ on Ag(100)

Planar structure

- N-Ag bonds
- Inter-complex H-bonds

Mn heterochiral
- 2 N-Ag bonds/TCNQ
- 1 H-bonds/TCNQ

Hypotetical homochiral
- Only 1 N-Ag bonds/TCNQ
- No H-bonds/TCNQ

Heterochiral energetically favourite on Ag(100)
(0.17eV/TCNQ more stable than homochiral)
Cs-TCNQ$_4$ homochiral on Ag(100)

- Cs lifted-up
- Non-Planar structure ("umbrella")

- Cs ionic bond allows a better steric performance and formation of 2 N-Ag and 3 H-bonds/TCNQ
- 140$^\circ$ angle and "umbrella" allows a compact geometry

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Electrostatics: charge transfer and dipoles

**TCNQ$_4$-Mn**

<table>
<thead>
<tr>
<th>CT/TCNQ</th>
<th>Dipoles/TCNQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic</td>
<td>Induced</td>
</tr>
<tr>
<td>0.33e</td>
<td></td>
</tr>
</tbody>
</table>

**TCNQ$_4$-Cs**

<table>
<thead>
<tr>
<th>DT/TCNQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic</td>
</tr>
<tr>
<td>+1.44 D</td>
</tr>
</tbody>
</table>

- Positive Cs pushed up: Strong + dipole of the neutral adlayer
- Large induced dipole, due to high N’s and CT
- Low total dipole lowers electrostatic energy
Surface-TCNQ charge transfer

Cs: $0.39 + 0.25 = 0.64e/TCNQ$

Mn: $0.33e/TCNQ$

\[
\Delta \rho_{\text{transfer}} = \rho_{\text{total}} - \left[ \rho_{\text{surface}} + \rho_{\text{TCNQ}} + \rho_{\text{M}} \right] \int_{\text{surf}}^{\text{vac}} \Delta \rho_{\text{transfer}}(z) dz
\]

- TCNQ in Cs more charged
- Huge charge hole around Cs
- C-N triple bonds break

- TCNQ absorbs charge from surface only
- Coordination bond visible
- Charge accumulates on TCNQ LUMO
Other alkali 
(comparison to Cs case)

<table>
<thead>
<tr>
<th></th>
<th>Intrinsic dipole (relative to TCNQ4-Cs) (Debye/TCNQ)</th>
<th>Induced dipole (relative to TCNQ4-Cs) (Debye/TCNQ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCNQ4-Li</td>
<td>-0.71</td>
<td>+0.18</td>
</tr>
<tr>
<td>TCNQ4-Na</td>
<td>-0.69</td>
<td>+0.23</td>
</tr>
<tr>
<td>TCNQ4-K</td>
<td>-0.45</td>
<td>+0.08</td>
</tr>
<tr>
<td>TCNQ4-Cs</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

- Intrinsic dipoles increase with size
- Induced dipole decrease
- (more negative induced dipoles)
- Possibility of fine tuning electrostatics? (e.g. deposition of a mixture of alkali)

AF, A. Comisso, A. De Vita, in preparation
Summary

• Different chirality and geometry: ultimately due to different nature of the metal-TCNQ bond

• Better steric performance of Cs-TCNQ$_4$ to form bonds: stability and much larger domains

• Cs-TCNQ$_4$: large induced dipoles, low total dipole: lower electrostatic energy

• Lifting of alkali in relaxation: possibility to tune the CT and dipole as function of alkali concentration?