

EC-STM-Investigations of Molecular Squares

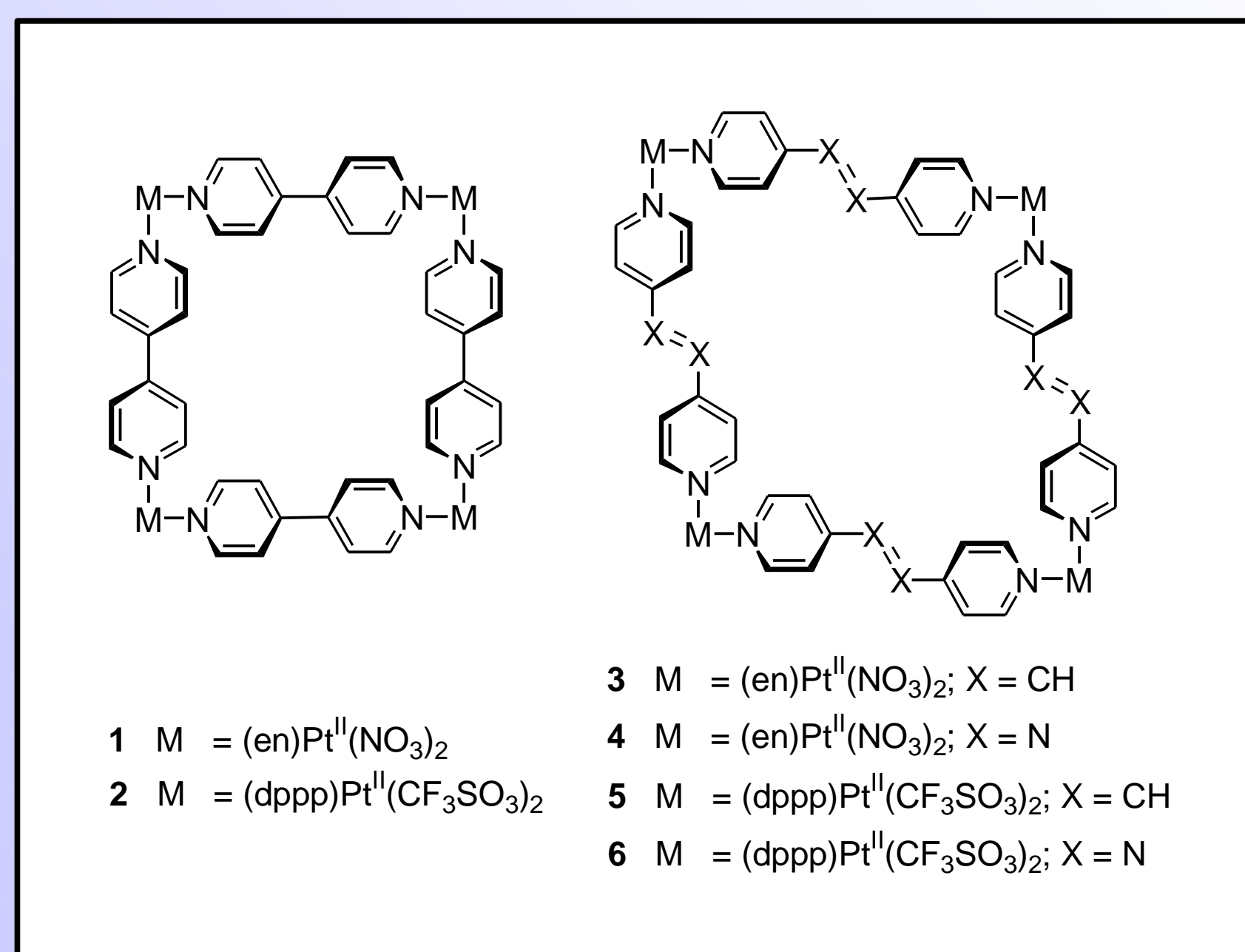
Alexander Rang^a, Caroline Safarowsky^b, Peter Broekmann^b, Christoph A. Schalley^a

^aKekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, D-53121 Bonn, email: c.schalley@uni-bonn.de

^bInstitut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, 53115 Bonn, email: broekmann@thch.uni-bonn.de

I. Introduction

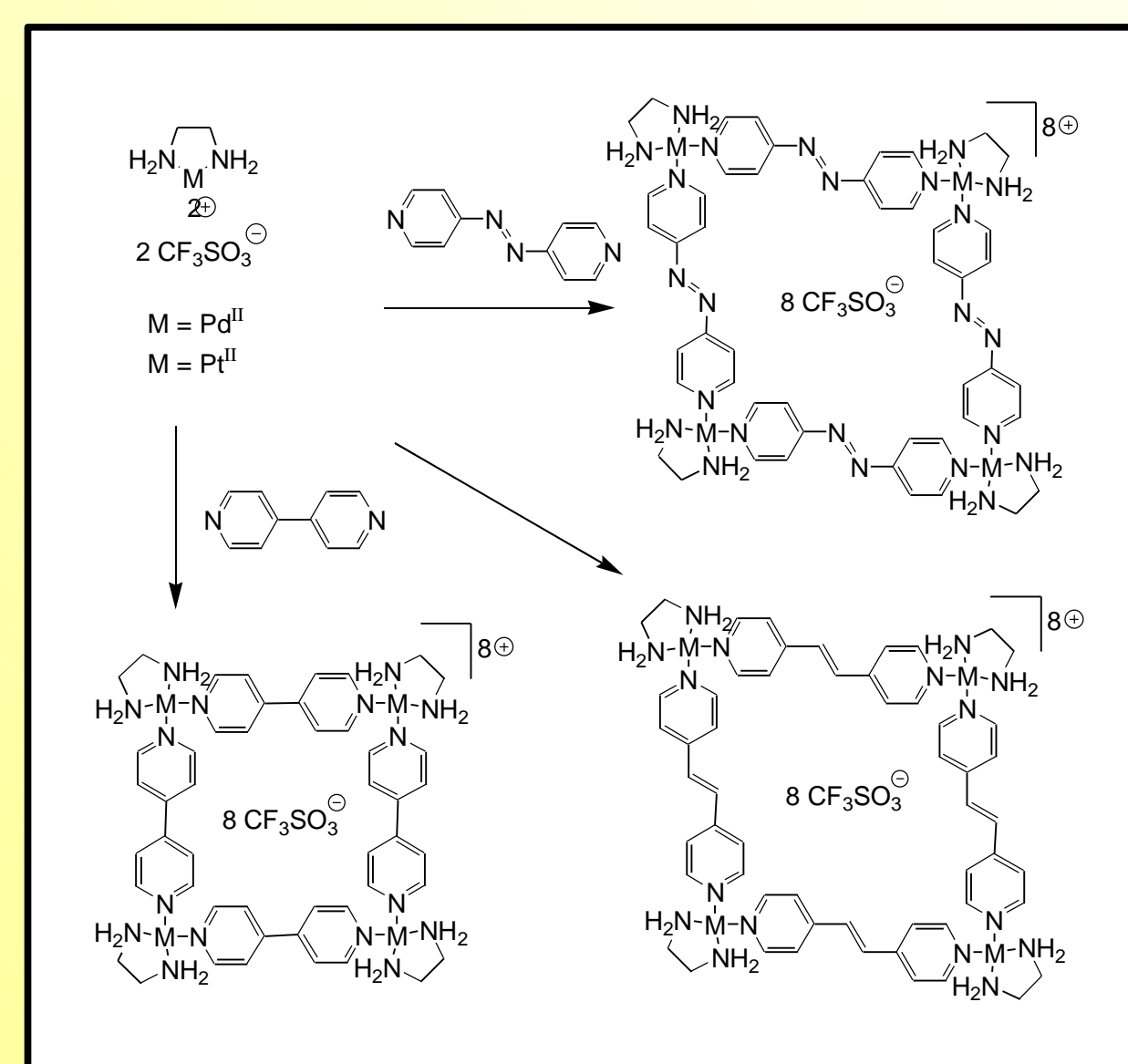
Molecular Squares are known since the beginning of the 1990's. Fujita, Stang, Lees and their colleagues introduced the very first examples of these interesting species; first applications were developed by the groups of Würthner (electro- and photo-chemistry), Hupp (transport and molecular recognition).



II. Synthesis through Self-Assembly

Mixing equimolar amounts of metal complexes (corners) and organic ligands (edges) results in the desired metallacycles in excellent yields, driven by thermodynamically controlled self-assembling processes.

Self-assembly of the components has the advantage that syntheses of the resulting compounds is kept as simple as possible.

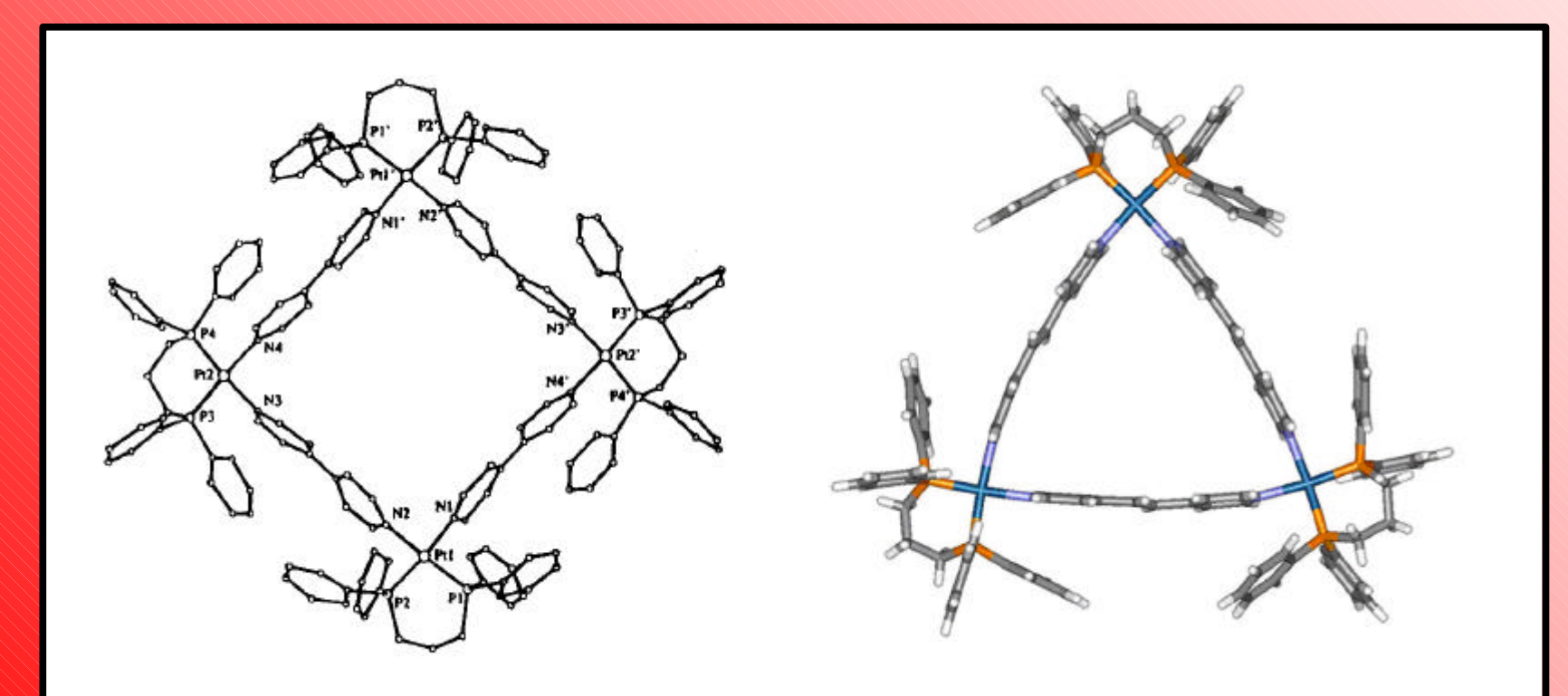


III. Squares or triangles?

In solution, the squares are in equilibrium with triangles. If the organic ligand is rigid, the equilibrium is shifted towards the squares. With a flexible ligand, triangles are entropically favored.

Differentiation of the resulting species is possible by standard NMR-techniques (¹H, ¹³C, ³¹P-NMR, and DOSY-Spectra (Diffusion Ordered Spectroscopy)) as well as mass-spectrometric analysis (ESI) and crystal-structure analysis.

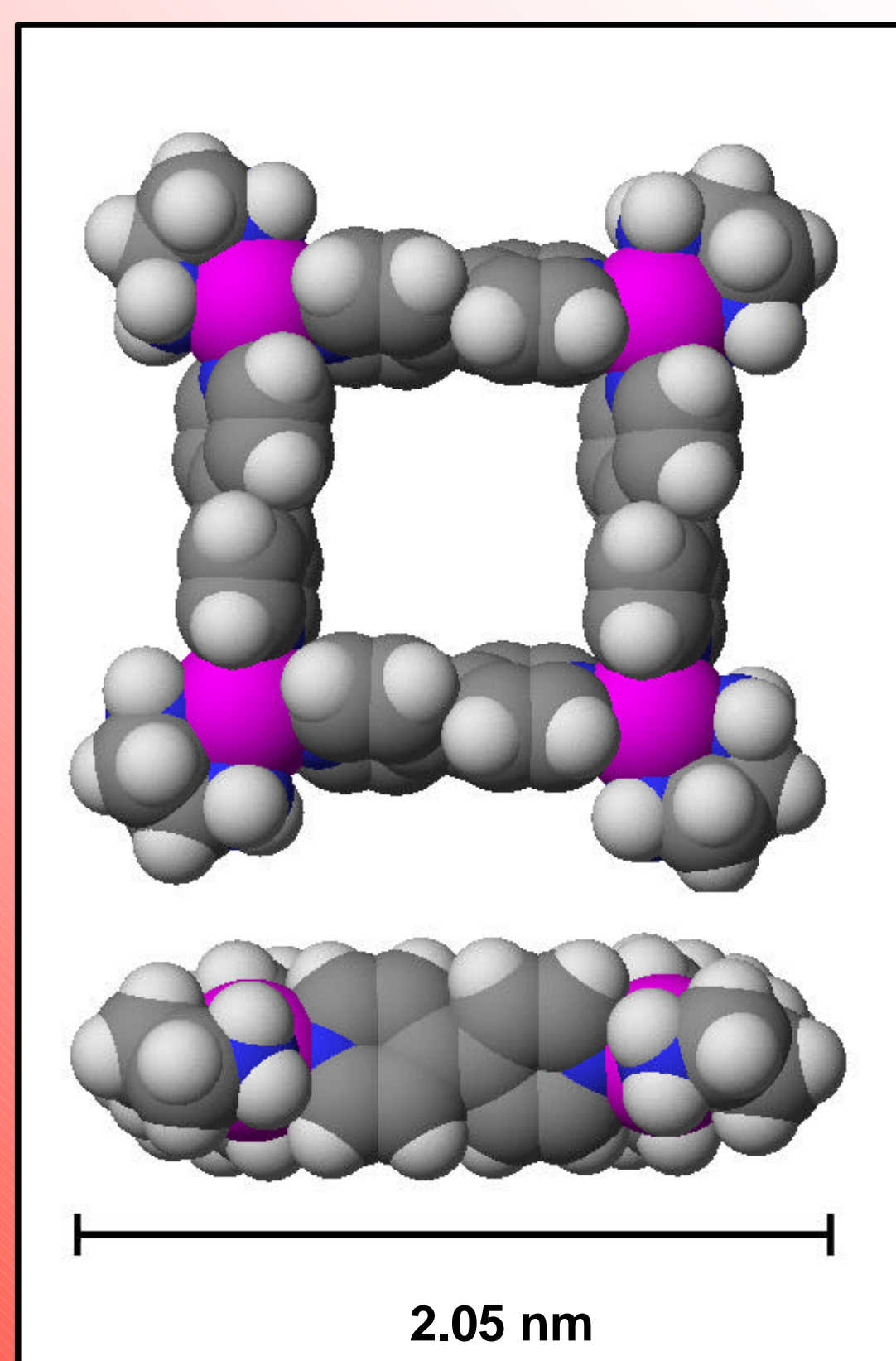
ESI-MS-spectra clearly show that the equilibrium depends on the solvent system, concentration, and temperature, while the crystal structure of compound 5 shows the expected square and compound x crystallizes as a triangle.



IV. Square Dimensions as Obtained by Molecular Modeling

The space filling molecular model of square 1 was minimized with the MM2 force field, as implemented in the CACHE 5.0 program package for Windows (Fujitsu Ltd. 2001, Krakow, Poland).

The dimensions along the edge as total width including van-der-Waals radii of the peripheral hydrogen atoms amounts to 2.05 nm.

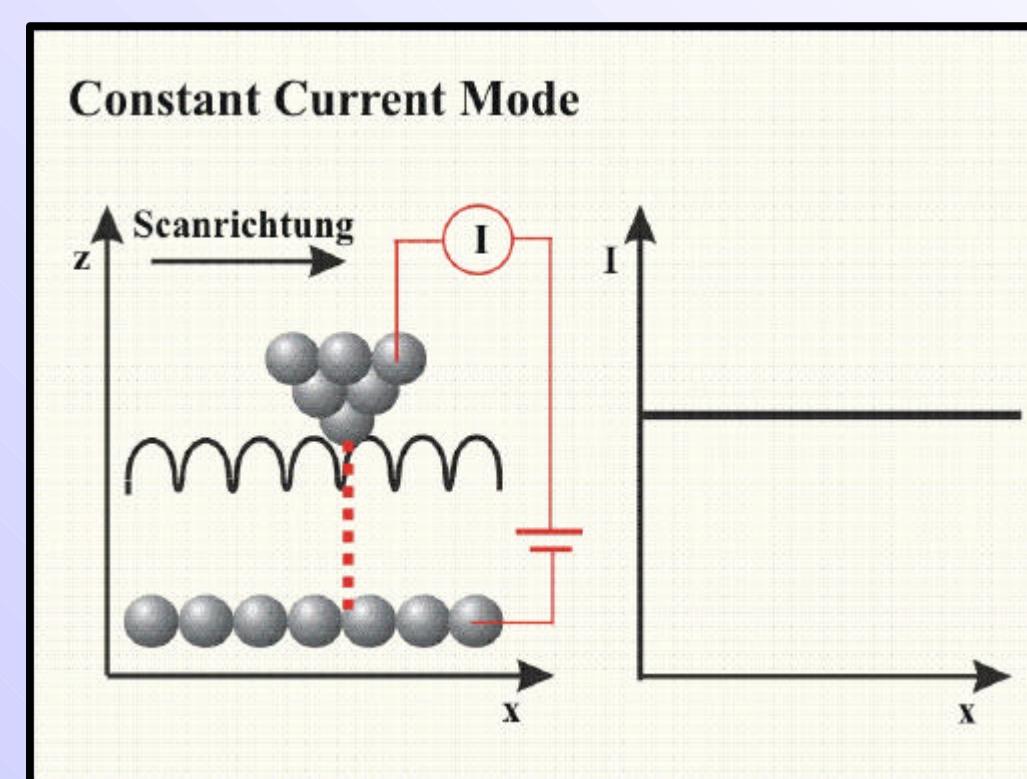
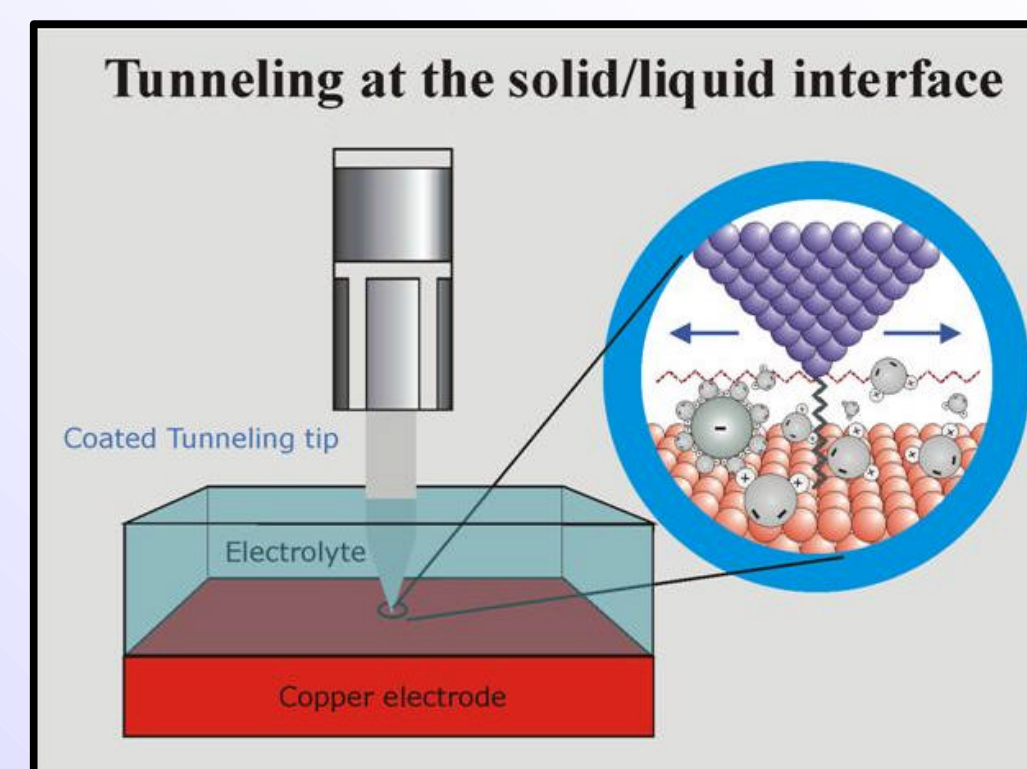


V. Basic Principles of Electrochemical STM

The measuring principle of scanning tunneling microscopy is based on the quantum mechanical tunneling effect. If the tip is in close proximity to the surface (0.2–1nm), tunneling contact is realized.

By applying a voltage between the metal electrode and the tunneling tip, it is possible to achieve a directional current.

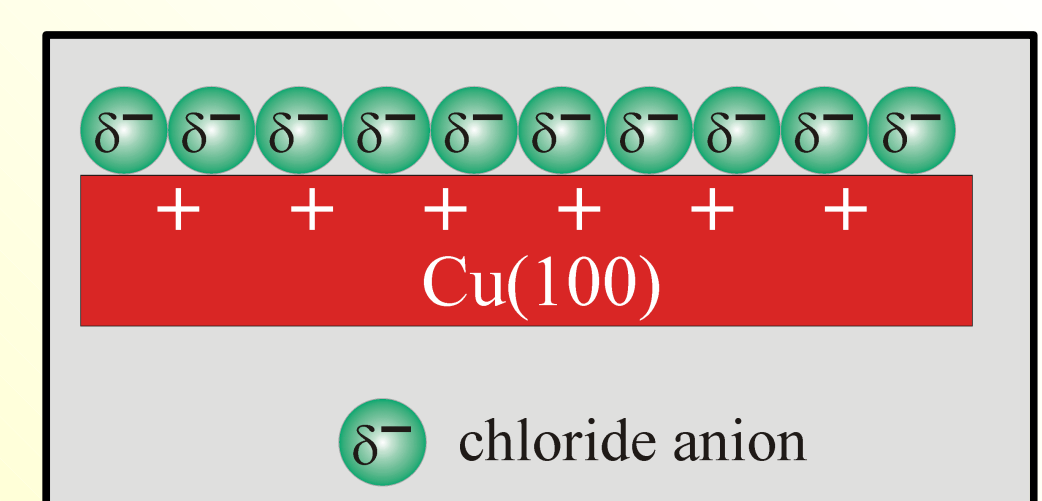
If we use an atomically sharp tip, the line by line scanned sample mirrors the atomic surface morphology. The tunneling process occurs at a solid/liquid interface as well and offers the opportunity to adsorb ions from an aqueous electrolyte by applying a voltage to the metal surface.



VI. First-Order Templation: Chloride on Cu(100) Electrode

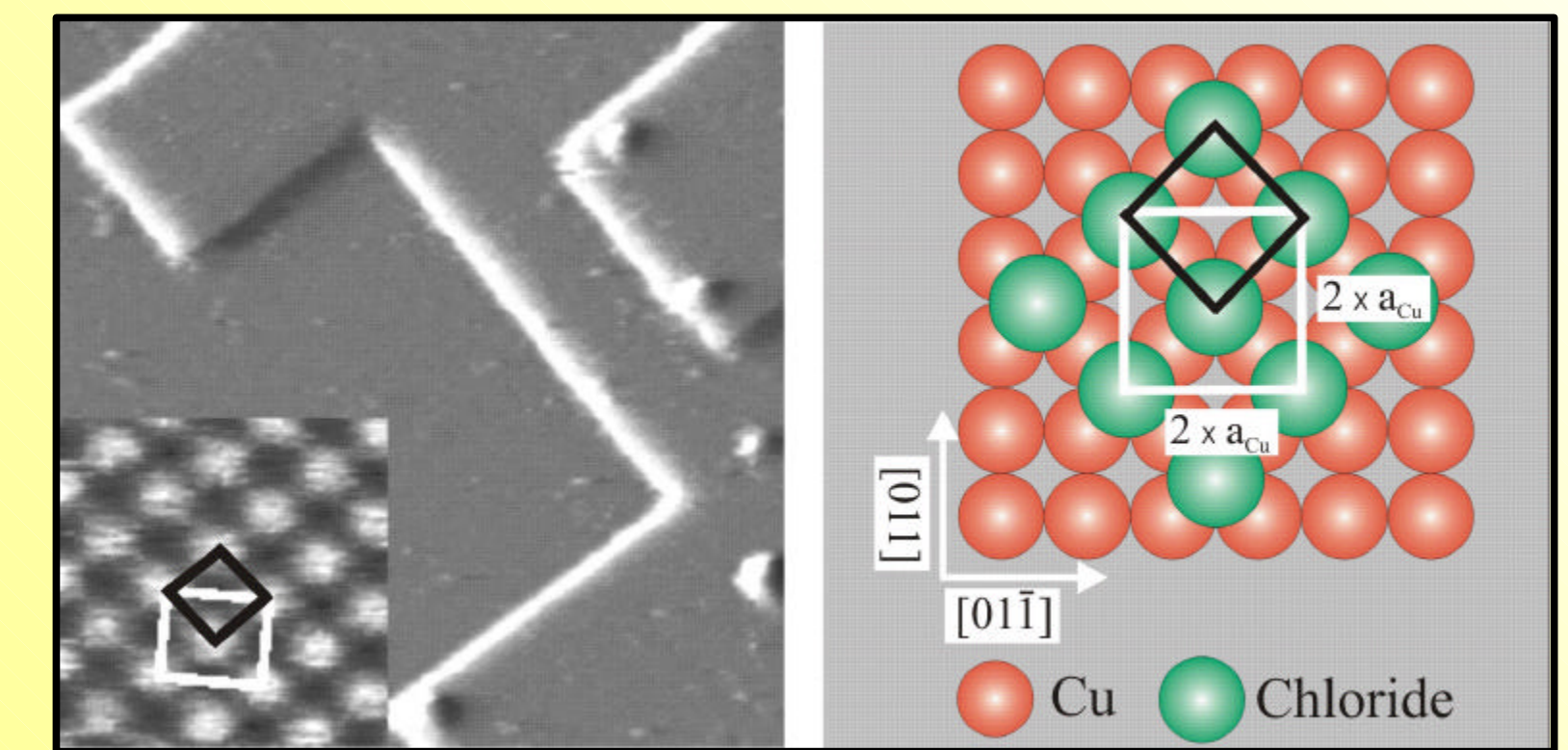
Specifically adsorbed chloride anions almost fully retain their negative charge upon adsorption.

Chloride anions adsorb on the copper surface and form a c(2 x 2)-adlayer.



The step edges of the copper sample are preferentially aligned along the <001> directions corresponding to the close packed chloride rows.

Every single dot is assigned to a chloride anion.



VII. Second-Order Templation: Flat-Lying Squares

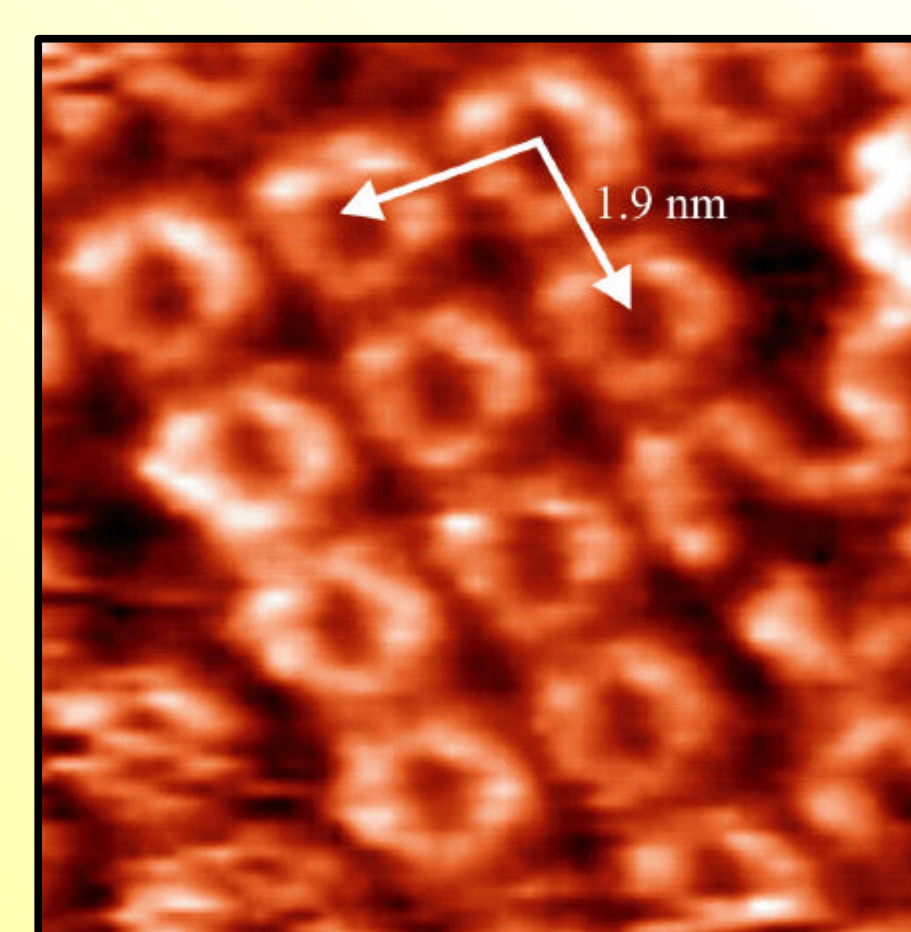
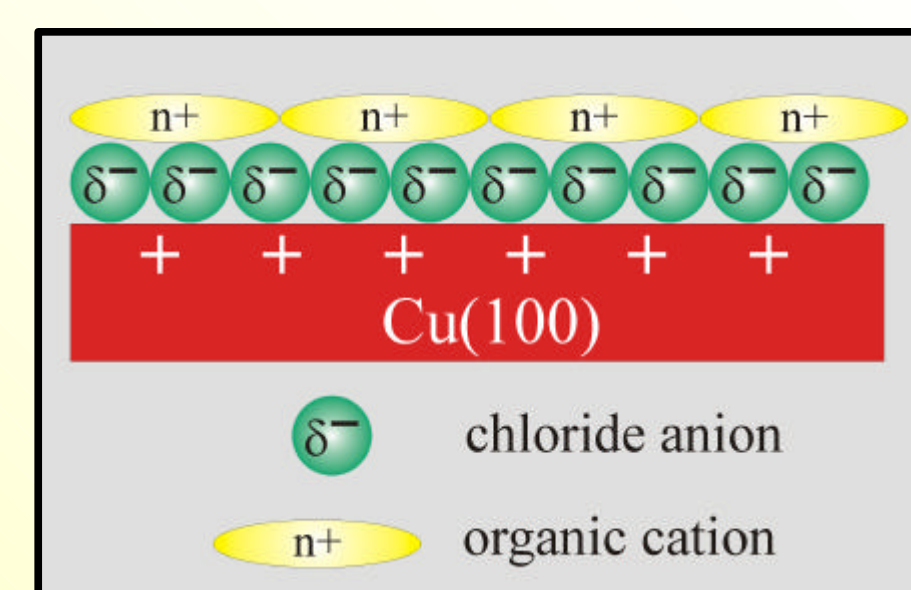
Replacing the pure supporting electrolyte by a mixture of 0.1 mM Fujita square, 10 mM HCl and 5 mM KCl causes the deposition of squares on the chloride-covered surface.

The resulting STM images reveal a highly ordered structure with fourfold symmetry.

The ring-shaped features are assigned to single supramolecular squares.

The stronger adsorbate-substrate interaction forces the squares to adsorb parallel to the surface.

The distance of 1.95 nm from cavity to cavity corresponds to the length along one of the edges of the molecule including van-der-Waals-radii.



VIII. Avoiding Oligomerization: Optimized Sample Preparation

A side effect of the preparation in an acidic electrolyte is an oligomerization of the squares 1.

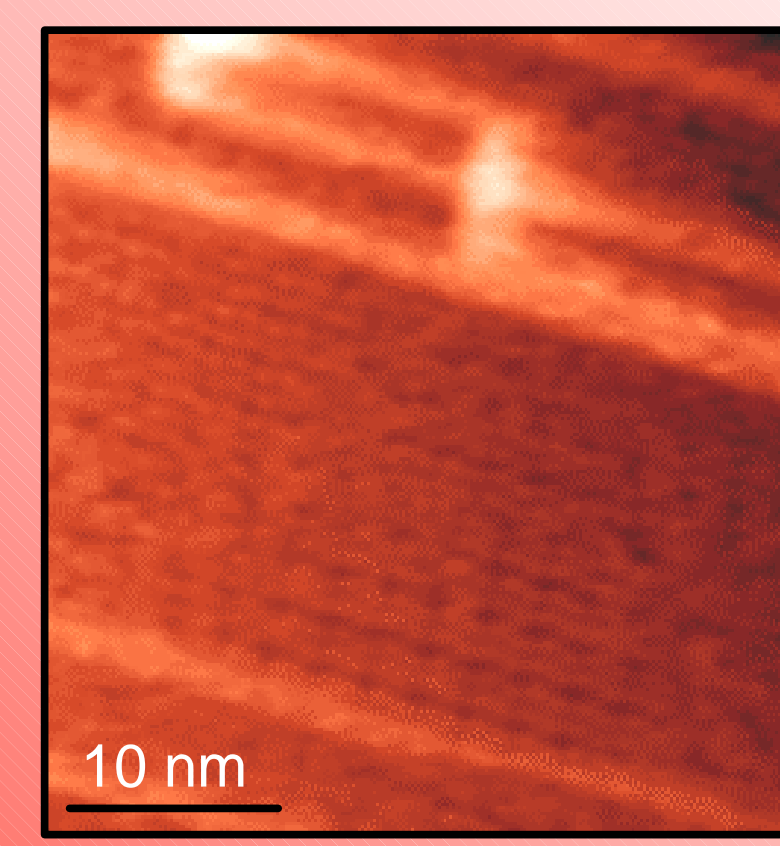
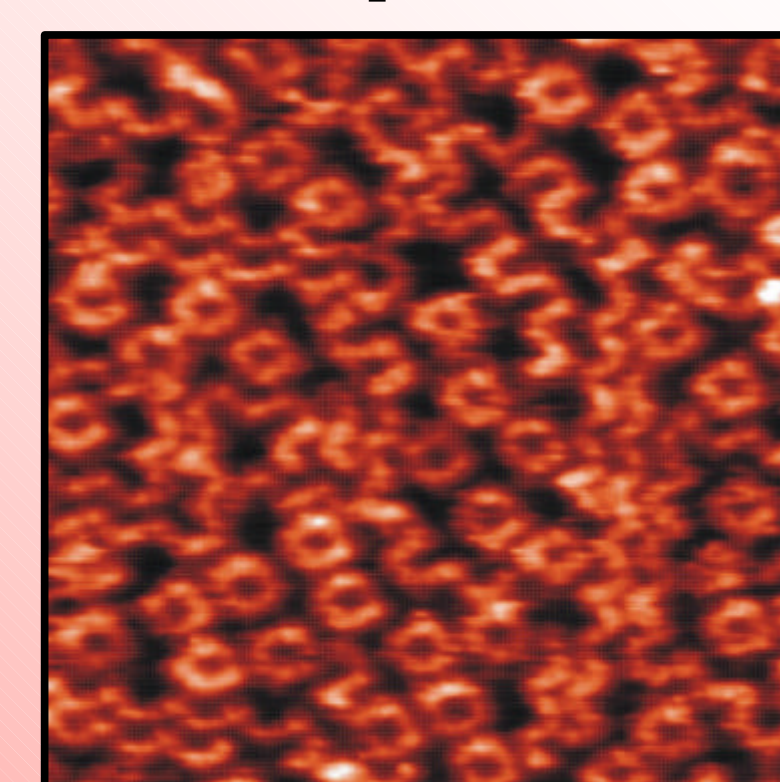
The STM images show string- and chain-like fragments

Reducing the contact time with the hydrochloric acid and dissolving the square in pure water helps to avoid oligomerization and optimizes the sample preparation.

Long range order of the molecular square 1 can then be achieved:

Adsorbate covered terraces with step edges aligned parallel to the <001> directions are found.

The squares are arranged along the step edges and therefore parallel to the close packed chloride rows in large domains.



IX. Conclusions

In conclusion, the supramolecular squares are lying flat on the electrode surface. The nearest neighbour distance of 1.95 nm agrees well with the calculated van-der-Waals diameter of 2.05 nm.

Most likely, the adsorbate-substrate interactions are mainly governed by attractive electrostatic interactions between the negatively charged chloride layer and the positively charged Pt^{II} cations, while the lateral ordering is apparently dominated by short-range van-der-Waals interactions.

Since the copper surface determines the structure of the well-ordered chloride adlayer and because the chloride layer determines the arrangement of the squares on the surface, one might describe this as a second-order template effect.

X. Outlook

In view of the square/triangle equilibria observed for larger analogs of 1, several interesting questions arise, which should be answered in the near future:

- Is it also possible to adsorb triangles?
- Is it possible to adsorb squares and triangles simultaneously?
- What is the role of the surface in these processes?
- Will different geometries result, if different surfaces are chosen?

Acknowledgement

We would like to thank Prof. Dr. Klaus Wandelt for helpful discussion and are grateful to Heidi Mansikamäki for solving the crystal structure of 5. C. A. S. acknowledges a Liebig fellowship from the Fonds der Chemischen Industrie and financial support from the Deutsche Forschungsgemeinschaft. A. R. thanks the German National Merit Foundation for support with a scholarship.