

Tomáš Baše,¹ Zdeněk Bastl,² Vladimír Havránek,³ Jens Langecker,¹ Jan Macháček¹
¹ Institute of Inorganic Chemistry, AS CR, v.v.i. 250 68 Husinec-Řež 1001, Czech Republic
² J. Heyrovský Institute of Physical Chemistry, AS CR, v.v.i. Dolejškova 3, 182 23 Prague 8, Czech Republic
³ Nuclear Physics Institute, AS CR, v.v.i., 250 68 Husinec-Řež, Czech Republic
 E-mail: tbase@iic.cas.cz (T.B.)

Preamble

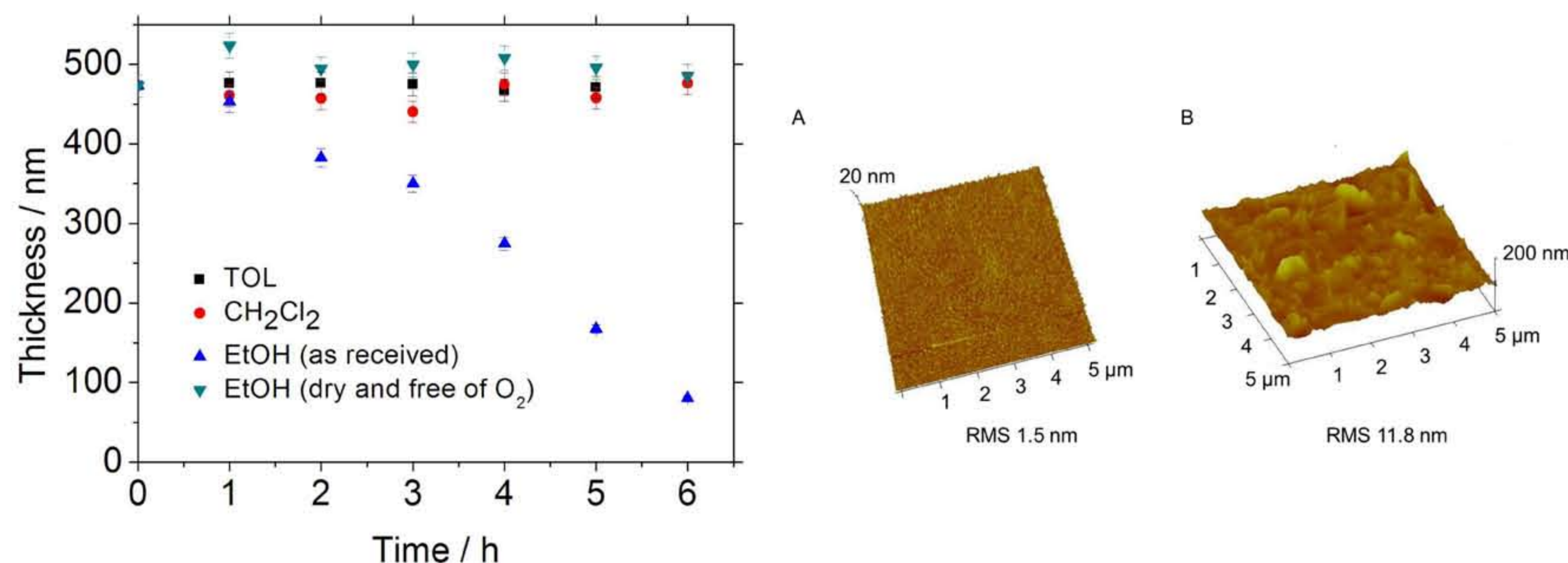
In this contribution, we report on the interactions between dicarba-*closo*-dodecarborane-dithiol isomers (also called carboranedithiols) and polycrystalline copper films as a part of our systematic exploration of carborane-based SAMs on metal surfaces.¹⁻⁶

Motivation

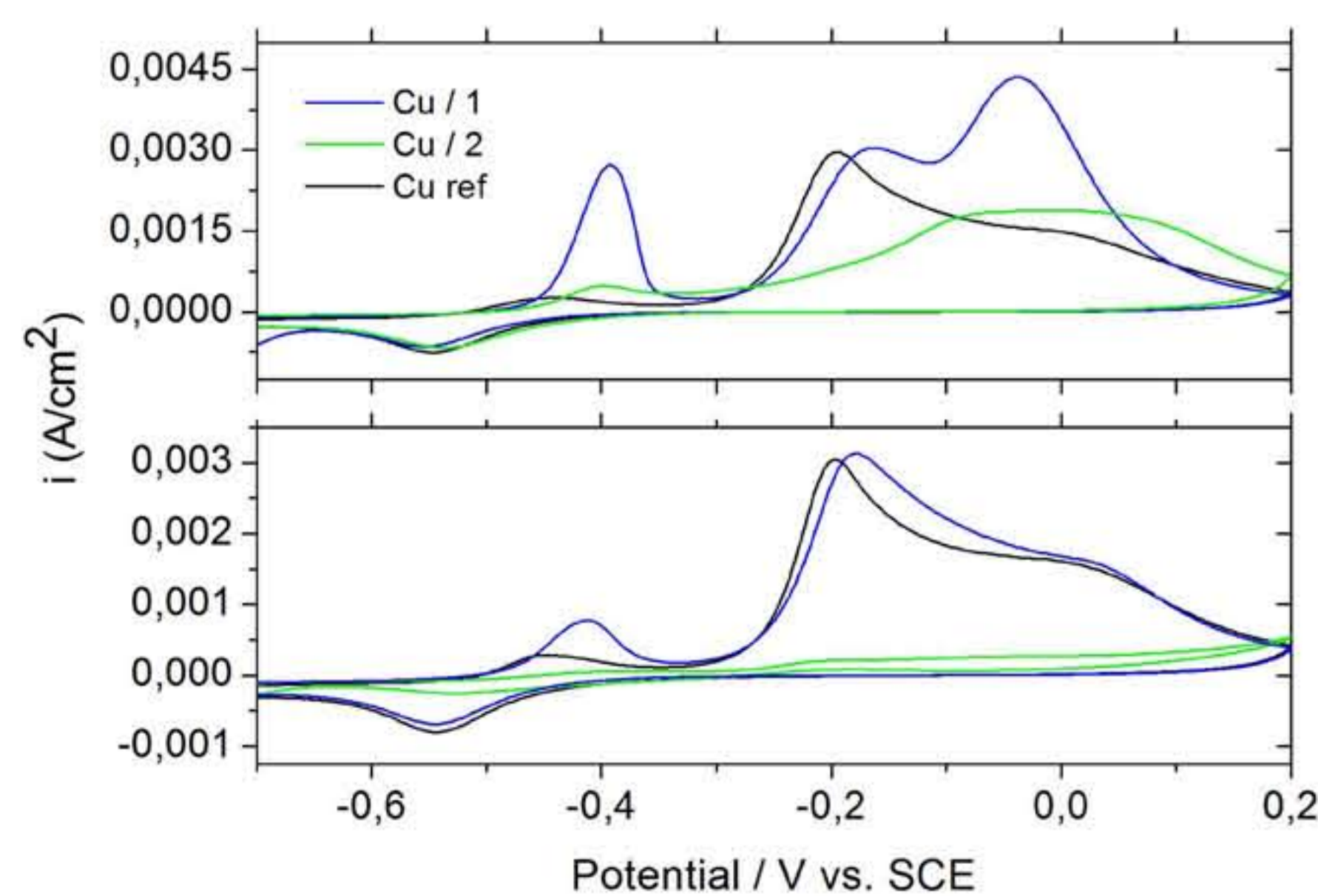
Carboranedithiols have several features that distinguish them from commonly studied hydrocarbons. Their *quasi*-aromatic 3-D structures are derived from a twelve-vertex icosahedral geometry, they are thermally robust, and stable toward oxidation and exposure to high-energy radiation. It is these features that make them potential candidates for stable molecular devices and related technologies.

Copper film etching (aerobic vs. anaerobic conditions)

Polycrystalline copper film exposed to an EtOH solution of 1,2-(SH)₂-1,2-C₂B₁₀H₁₀ displayed etching.



Electrochemistry

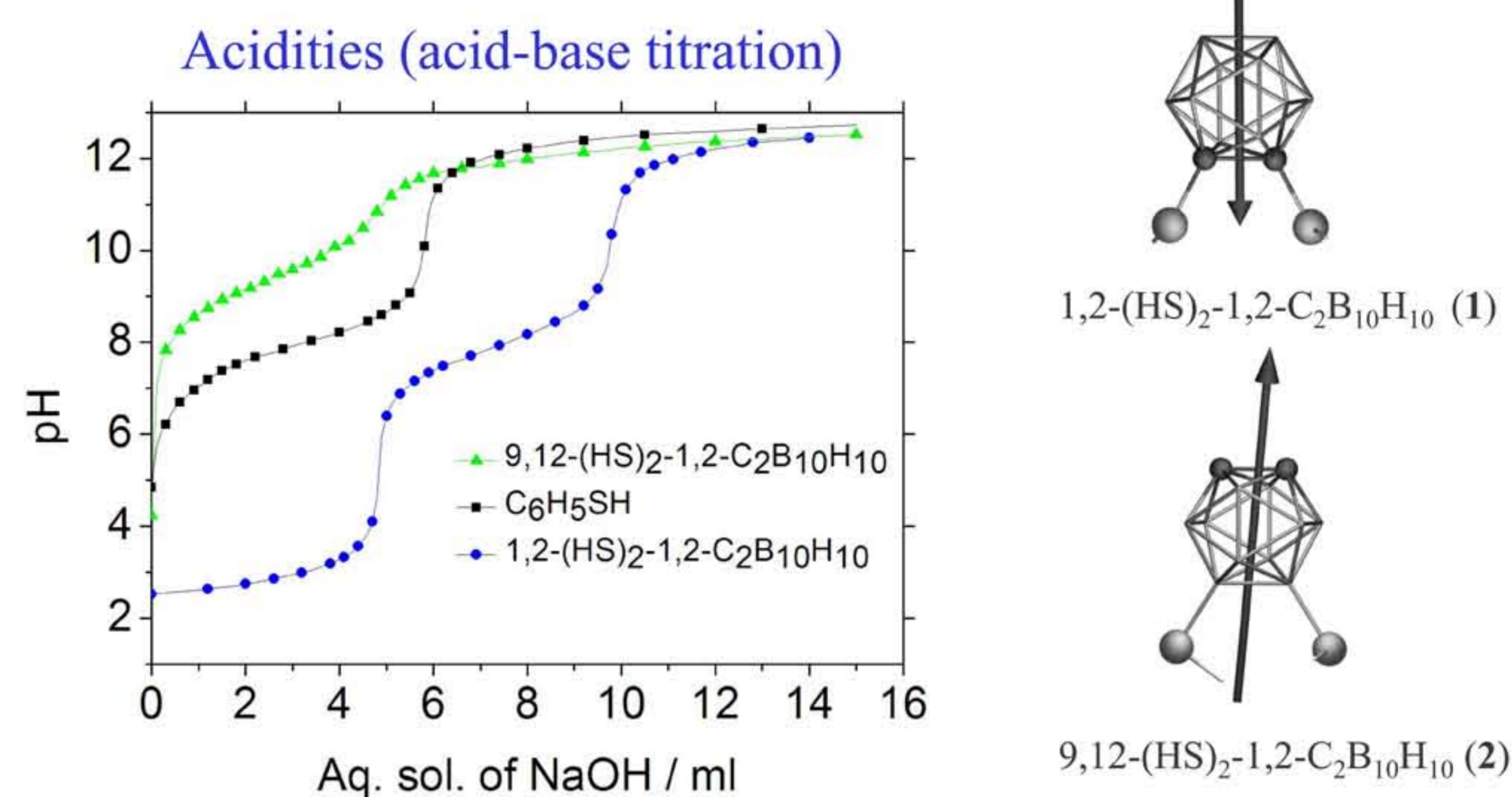


While isomer 1,2-(SH)₂-1,2-C₂B₁₀H₁₀ showed etching of polycrystalline copper film in an ethanol solution in the presence of oxygen isomer 9,12-(SH)₂-1,2-C₂B₁₀H₁₀ showed suppression of copper substrate oxidation. Figure on the left shows cyclic voltammetric current response vs. applied potential for copper film as prepared (black lines), modified with 1,2-(SH)₂-1,2-C₂B₁₀H₁₀ (blue lines, Cu / 1), and modified with 9,12-(SH)₂-1,2-C₂B₁₀H₁₀ isomer (green lines, Cu / 2). Scanning was performed in an aqueous solution of KOH bubbled with O₂. Potential range for scanning was set up from -1.2 to 0.2 V (upper graph) and from -0.7 to 0.2 V (lower graph).

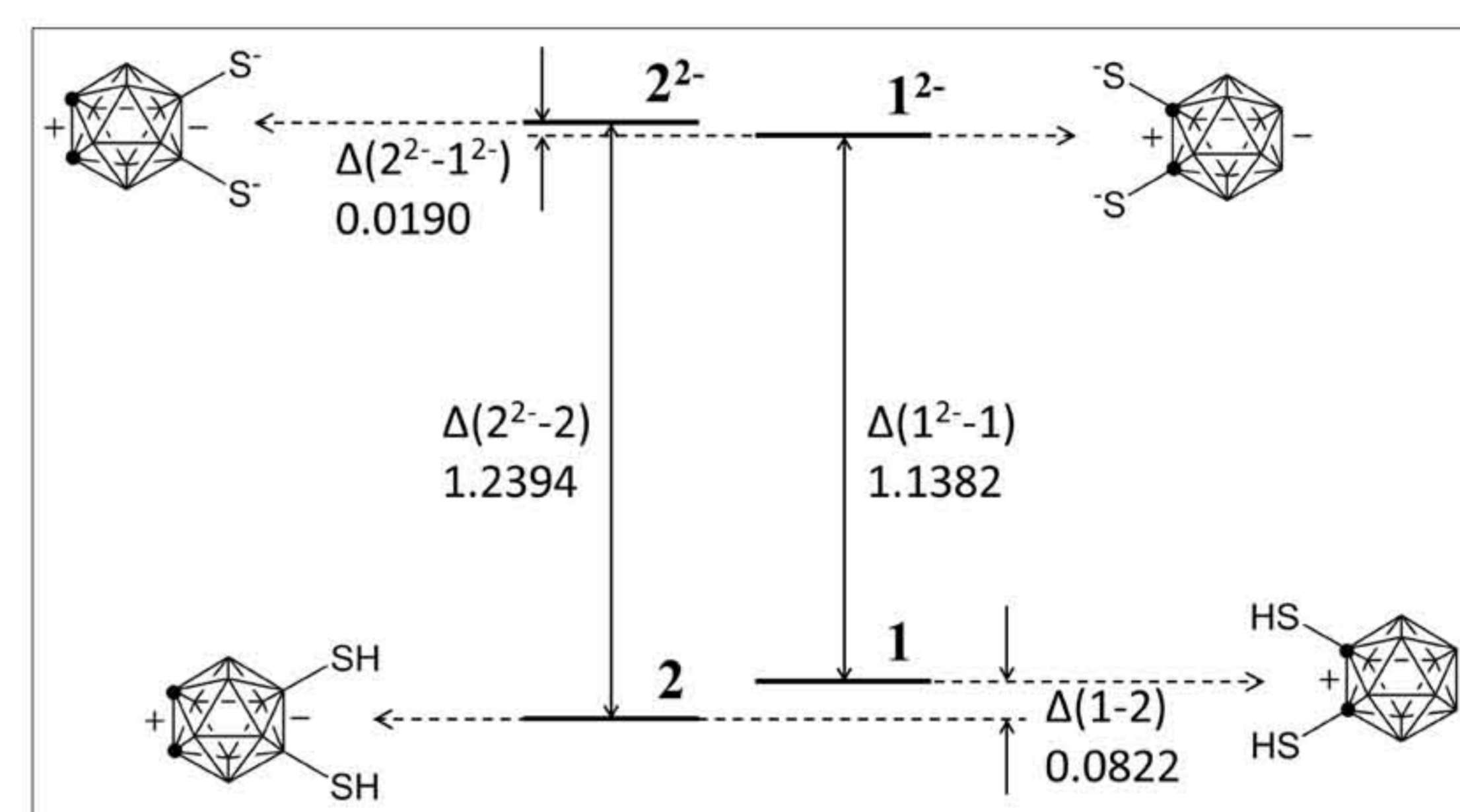
References

- 1) Baše, T.; Bastl, Z.; Plzák, Z.; Grygar, T.; Plešek, J.; Carr, M. J.; Malina, V.; Šubrt, J.; Boháček, J.; Večerníková, E.; Kříž, O. *Langmuir* **2005**, *21*, 7776.
- 2) Baše, T.; Bastl, Z.; Šlouf, M.; Klementová, M.; Šubrt, J.; Vetushka, A.; Ledinski, M.; Fejfar, A.; Macháček, J.; Carr, M. J.; Londesborough, M. G. S. *J. Phys. Chem. C* **2008**, *112*, 14446.
- 3) Baše, T.; Bastl, Z.; Londesborough, M. G. S.; Macháček, J. *NSTI-Nanotech* **2008**, ISBN 978-1-4200-8503-7, Vol. 1, 312-315.
- 4) Lübber, J. F.; Baše, T.; Rupper, P.; Künniger, T.; Macháček, J.; Guimond, S. *J. Colloid Interf. Sci.* **2011**, *354*, 168.
- 5) Baše, T.; Bastl, Z.; Havranek, V.; Lang, K.; Bould, J.; Londesborough, M. G. S.; Macháček, J.; Plešek, J. *Surf. Coat. Tech.* **2010**, *204*, 2639.
- 6) Bould, J.; Macháček, J.; Londesborough, M. G. S.; Macías, R.; Kennedy, J. D.; Bastl, Z.; Rupper, P.; Baše, T. *Inorg. Chem.* **2012**, *51*, 1685.

Isomers 1,2-(SH)₂-1,2-C₂B₁₀H₁₀ and 9,12-(SH)₂-1,2-C₂B₁₀H₁₀



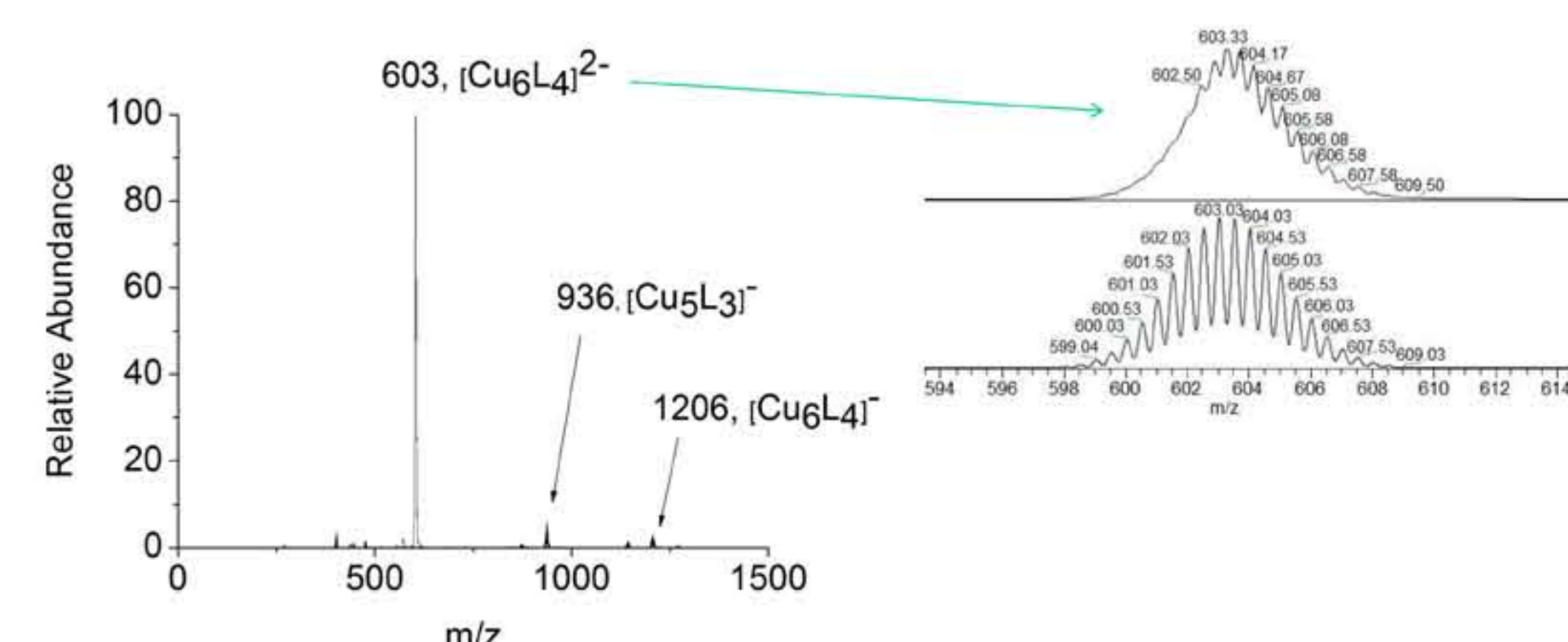
Relative stabilities



Relative stabilities of 1 and 2, and of their deprotonated forms, 1²⁻ and 2²⁻. All values are in Hartree. Hydrogen atoms in vertices of the icosahedra are omitted for clarity and the 1 and 2 positions of carbon atoms in the skeleton are marked with larger black dots.

[Cu₆(L)₄]²⁻, L: 1,2-(S⁻)₂-1,2-C₂B₁₀H₁₀

Cu cluster prepared in a reaction between bulk Cu₂O and isomer 1,2-(SH)₂-1,2-C₂B₁₀H₁₀. ESI MS analysis with experimental and theoretical isotopic distribution patterns are shown below.



Conclusions

1. Isomer 1,2-(SH)₂-1,2-C₂B₁₀H₁₀ showed etching of polycrystalline copper film in an ethanol solution in the presence of oxygen.
2. SAM of isomer 9,12-(SH)₂-1,2-C₂B₁₀H₁₀ showed suppression of copper surface oxidation.
3. Both isomers required different anaerobic experimental conditions for the preparation of their SAMs.

Acknowledgement

This study has been supported within the project nos. AVOZ40320502, P205100348 (GAČR), and KAN100400702 (AS CR).