Enhancing the Electronic-Coupling and Band Gap Tunability of Ferrocenyl Molecular Ultra-Thin Film with Pd and Cu Doping

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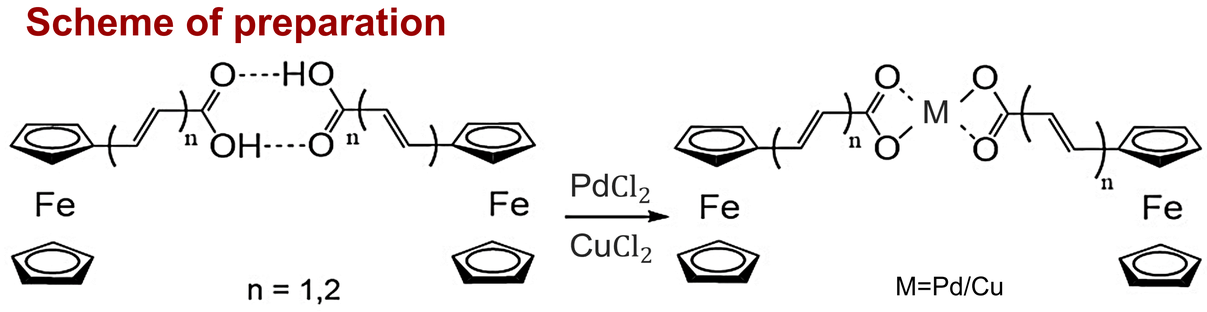
Introduction

- To improve charge transport in molecular film, metal dopants are introduced at specific ligand sites. This enhances the electronic coupling between the molecules, leading to better charge transport.

- Carboxyl functional group (–COOH) is suitable for metal doping, as it offers a four-fold coordination site. It has been effectively used in the formation of Surface confined Metal- Organic Network (SMON) on surfaces.

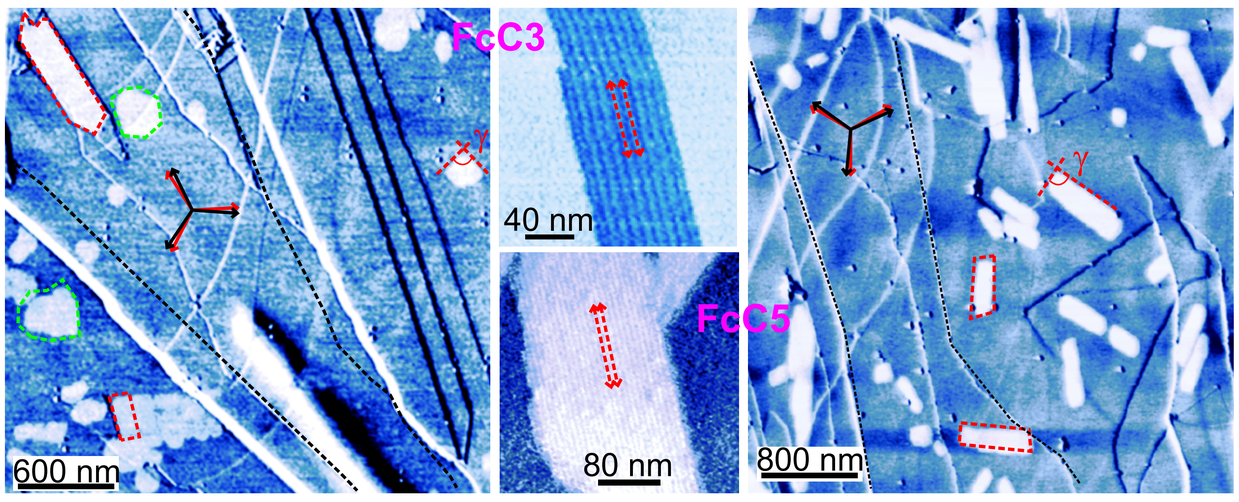
- Two ferrocenyl molecules, 3-ferrocenyl propanoic acid (FcC3) and 5-ferrocenyl penttadienoic acid (FcC5) are used for creating Pd and Cu SMON.

Scheme of preparation



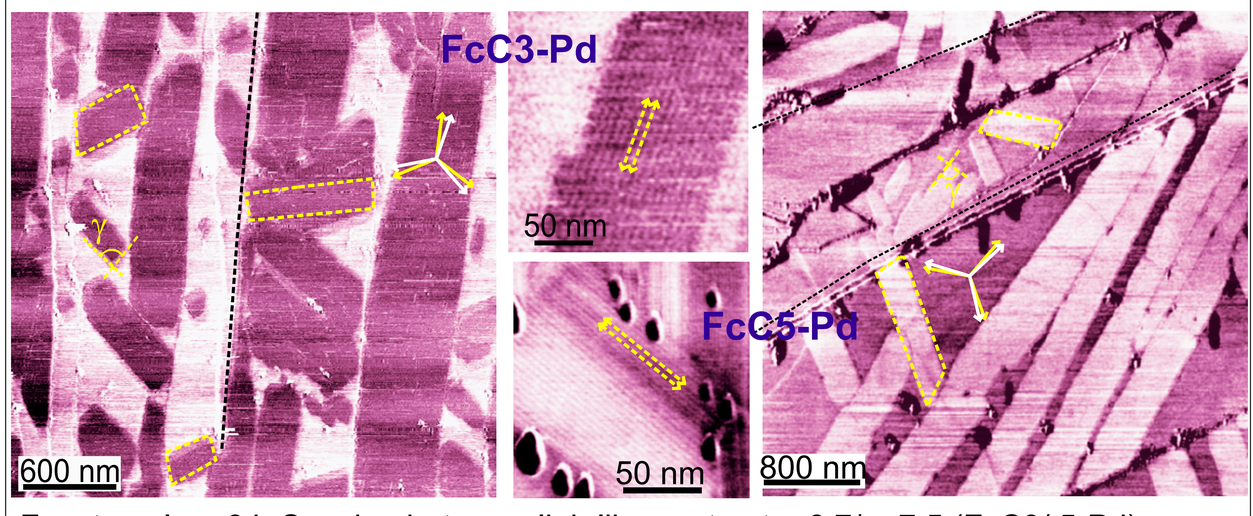
3-ferrocenyl propanoic acid (FcC3) and 5-ferrocenyl pentadienoic acid (FcC5)

AFM phase images of adlayer of FcC3 and FcC5



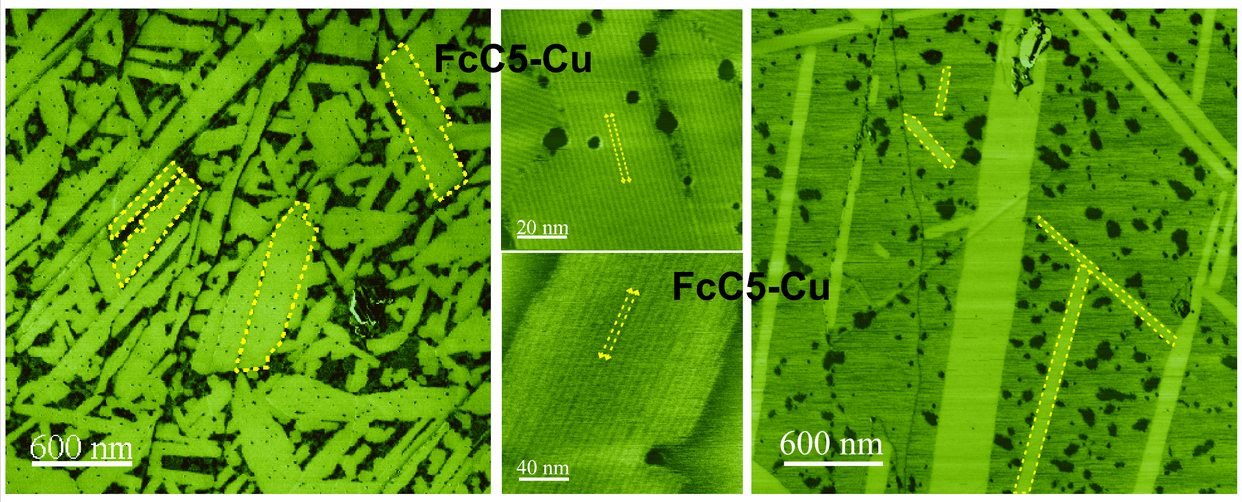
Facet angle ~ 83°; Spacing between link-like contrast ~ 6.7 (FcC3), ~ 7.4 (FcC5) nm

AFM phase images of SMONs of FcC3-Pd and FcC5-Pd



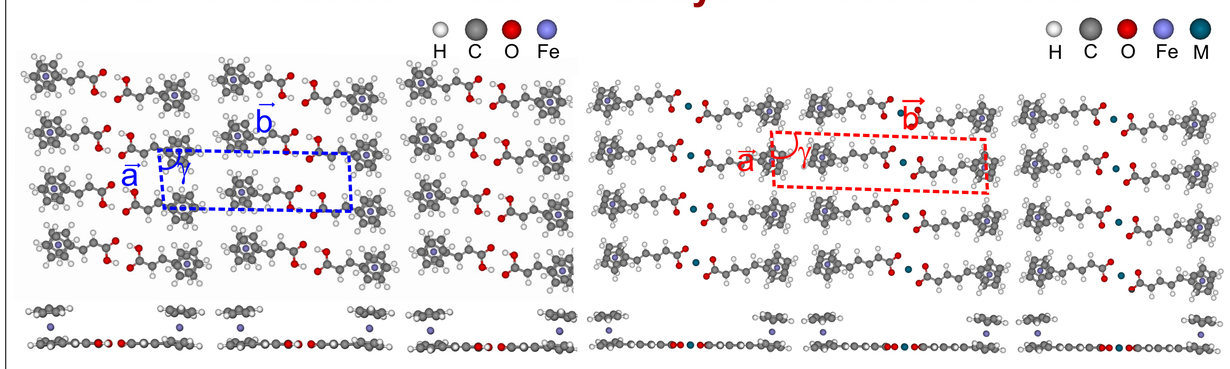
Facet angle ~ 84; Spacing between link-like contrast ~ 6.7/ ~ 7.5 (FcC3/ 5-Pd) nm

AFM phase images of SMONs of FcC3-Cu and FcC5-Cu



Facet angle ~ 85.5°; Spacing between link-like contrast ~ 6.8/ ~ 7.5 (FcC3/ 5-Cu) nm

Tentative molecular model for adlayer of FcC3 and FcC5-M

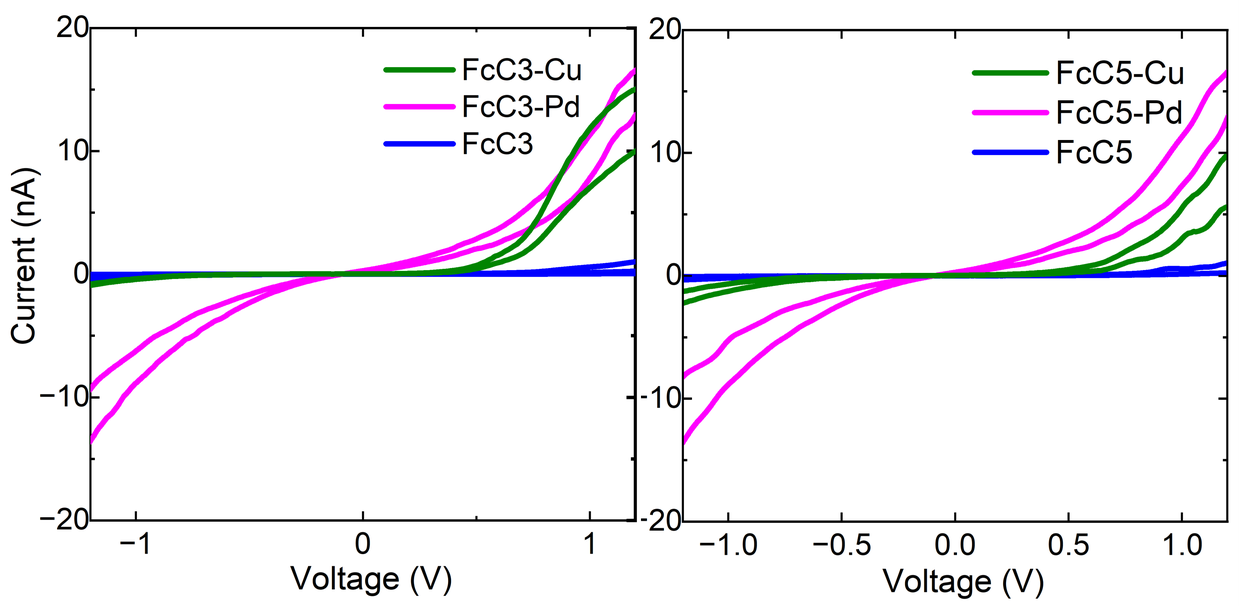


M = Pd / Cu

Lattice Parameters: a = 0.6 nm, b = 2.1 nm, γ = 86°

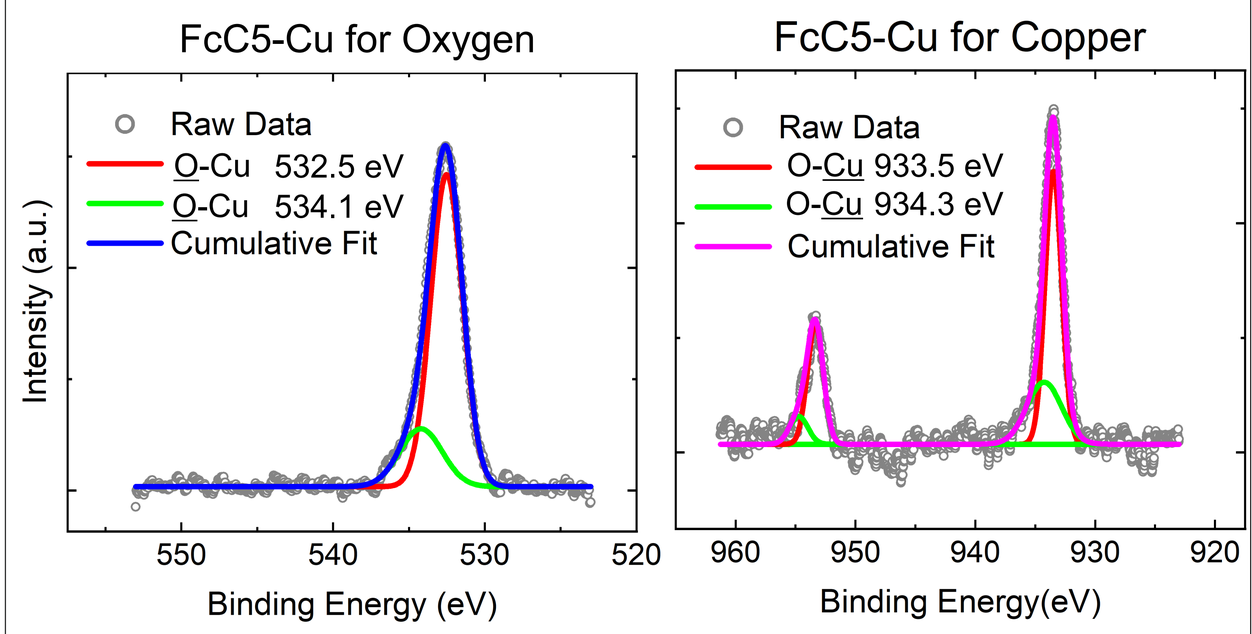
Lattice Parameters: a = 0.65 nm, b = 2.58 nm, γ = 85.3°

I-V measurements of adlayer and SMON of FcC3/FcC5



An enhancement in current of about 10 to 20 times upon doping; while Pd doping shows a symmetric I-V, Cu shows asymmetric I-V

XPS Analysis of FcC5-Cu



X-Ray Photoelectron Spectroscopy showing the binding with Oxygen and Copper

Summary

- Using AFM and STM, we have investigated the growth patterns of adlayer of FcC3 and FcC5 with and without Pd/Cu metal on HOPG at ambient conditions.

- Conductivity of adlayer and SMONs are measured using conductive AFM in contact mode. Results show that Pd/Cu-doped SMONs exhibit significantly higher conductivity compared to undoped adlayer.

- Using XPS we show the coordination of Pd/Cu in the SMON.

- We attribute a reduction in the HOMO-LUMO gap for the increased conductivity in SMON.

References

1) Mishra, V.; Gopakumar, T. G. Comparing interactions in three-fold symmetric molecules at solid-air interface. *Surf. Sci*. **2019**, 680, 11–17.

2) Mishra, V.; Mir, S. H.; Singh, J. K.; Gopakumar, T. G. Rationally Designed Semiconducting 2D Surface-Confined Metal-Organic Network. *ACS Appl. Mater. Interfaces* **. 2020**, *12*, 51122–32.

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