

Transfer of Organic Networks from Metal to Dielectric Surfaces



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Motivation

1- and 2-dimensional covalent organic networks are widely studied for possible applications as electronic materials and graphene analogues [1-3]. Radical covalent coupling typically requires specific substrates to catalyze the on-surface reaction. Metallic surfaces are commonly chosen to act as catalysts for schemes that require dehalogenation of the molecules as a route to the formation of covalent bonds.

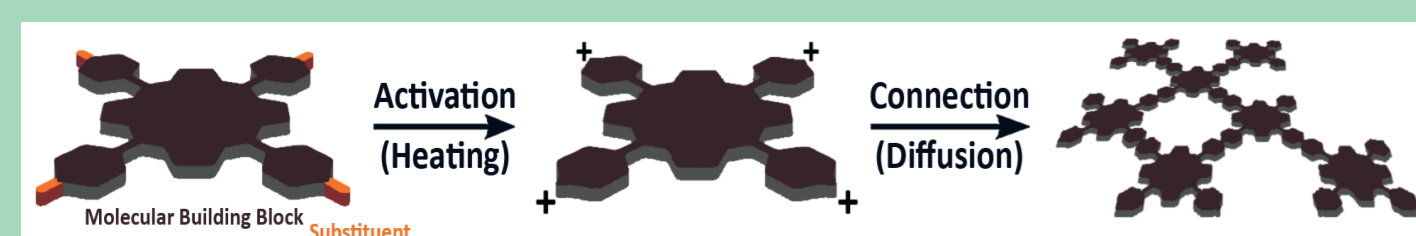


Figure 1: Concept of the formation of covalently bound networks by connecting activated molecular building blocks.

The resulting networks with interesting optical and / or electrical properties cannot be investigated while the structures remain on a metal substrate. To overcome this problem we have developed a method to transfer covalent frameworks to a separate substrate.

This poster shows the transfer process on the example of a 2-dimensional tetra (bromo phenyl) porphyrin (TBPP) network, that was formed on gold and subsequently transferred to SiO₂. TBPP forms continuous random networks on gold. It also exhibits good optical properties: thin layers down to one monolayer can still be detected with fluorescence spectroscopy.

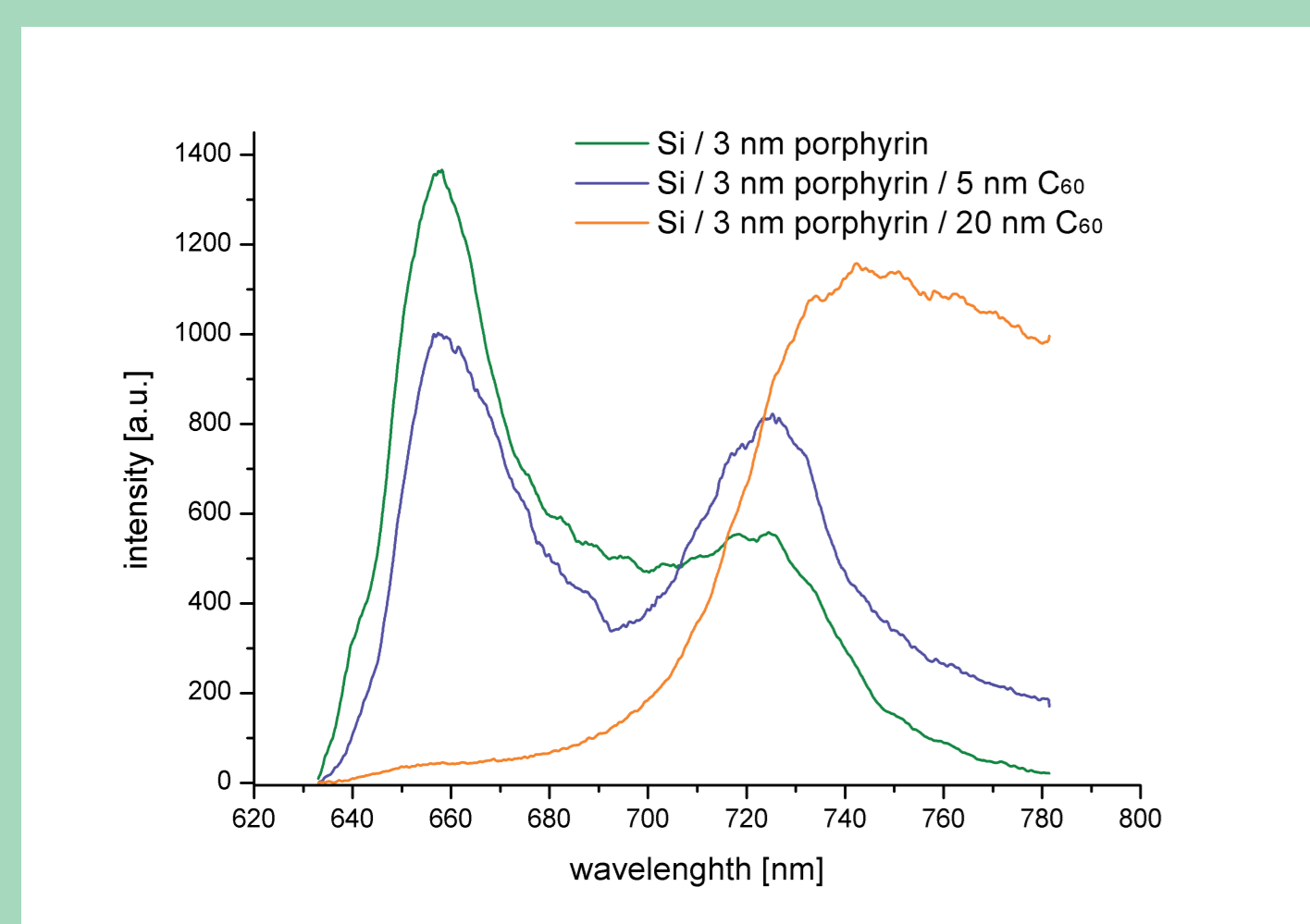


Figure 2: Fluorescence spectra of thin TBPP layers on SiO₂ without and with a C₆₀ cover layer. TBPP shows a characteristic double peak @ 658 nm and 727 nm, C₆₀ shows a very broad peak @ ~750 nm.

Step 9: Removal of the C₆₀

The C₆₀ can be removed either using specific solvents such as toluene or carbon-disulfide or by annealing the sample. While solvents tend to be the quicker process, annealing in vacuum is cleaner, as it avoids further contact to any chemicals.

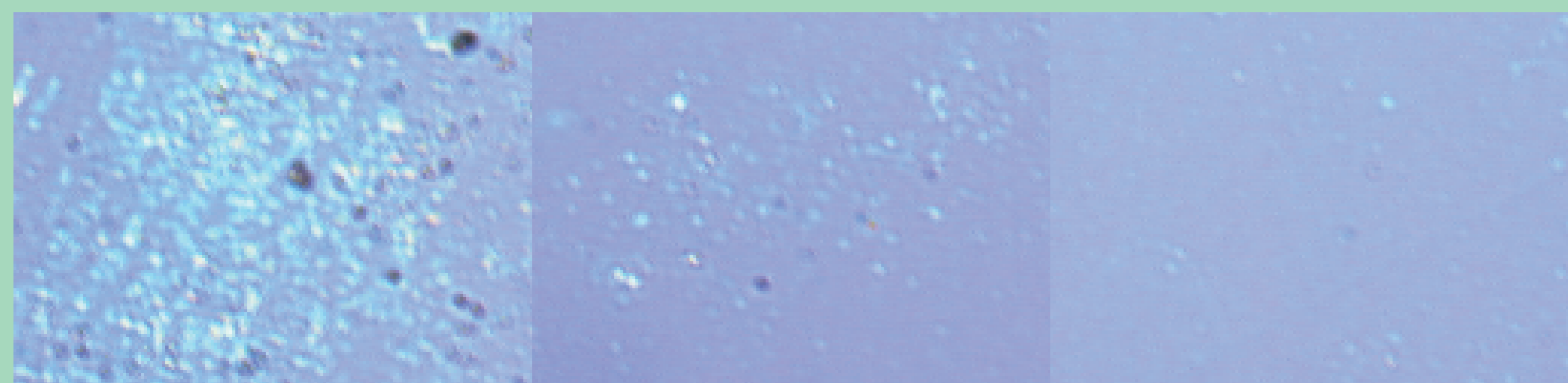


Figure 6: Optical microscopy images (150 μm x 100 μm) of a transferred sample before any treatment (left), after dipping in toluene for 30 sec (middle), and after annealing in HV @300°C for 120 min (right). The light blue patches are C₆₀, TBPP cannot be resolved.

Conclusions and Outlook

C₆₀ works as a 'glue' between gold and PDMS, a different approach to template stripping. Covalent organic frameworks, as well as thin layers of organic molecules, can be transferred from gold to any other substrate.

This opens up a whole range of possibilities to investigate electrical and optical properties of promising 2-dimensional covalent organic networks.

The immediate subsequent steps for this are to put contacts onto the transferred networks and measure conductivity, as well as produce and transfer networks made of different molecular building blocks.

Step 1: Deposition of Tetra (bromo phenyl) porphyrin in UHV

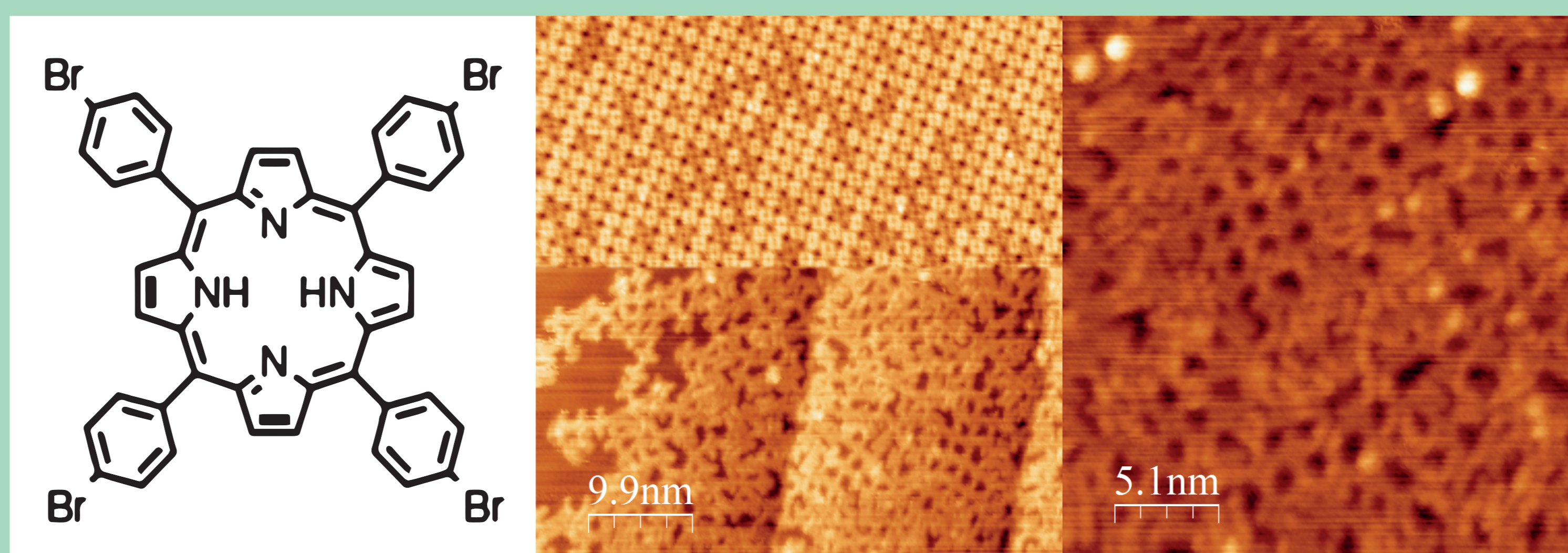
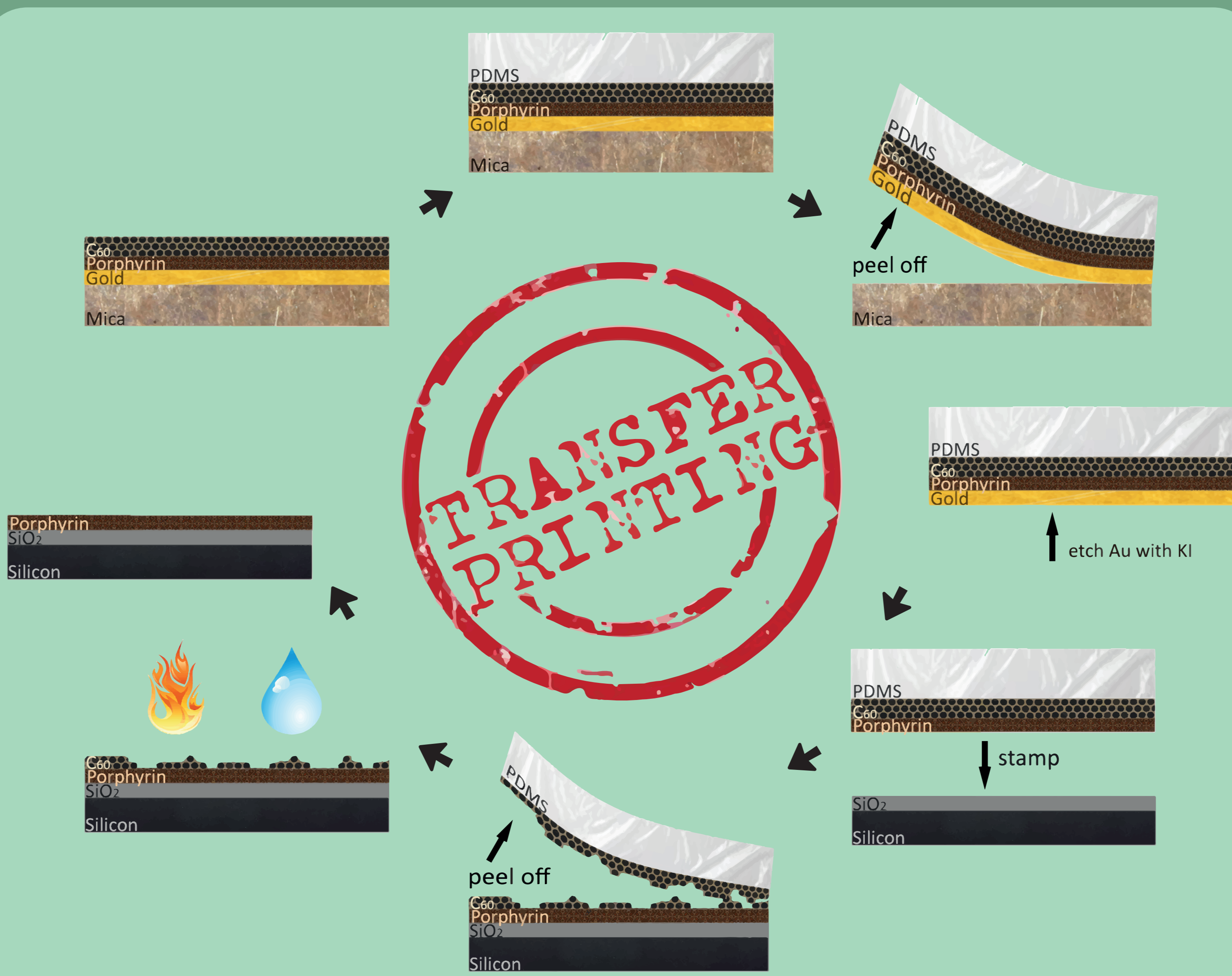


Figure 3 a: Structure of tetra (bromo phenyl) porphyrin molecule; b top: STM image of the self assembled structure of TBPP; b down & c: STM images of continuous random networks of TBPP

Tetra (bromo phenyl) porphyrin molecules are deposited onto a clean gold(111) on mica substrate and the resulting self-assembled close-packed structure is imaged with STM. Deposition of the same molecule onto gold(111) on mica annealed to 200°C leads to covalently bonded extended networks.



Step 2: Deposition of C₆₀

An approximately 15 nm thick layer of C₆₀ is then deposited onto the TBPP / gold / mica sandwich in UHV. The C₆₀ has adhesive properties and thus facilitates the removal of a gold film from the mica substrate. Additionally it serves as a buffer layer to preserve the network when it is stamped onto the target substrate.



Figure 4: Peeling of PDMS off a gold / mica sample without and with a layer of C₆₀. The adhesive properties of C₆₀ enable clean removal of the gold off the mica.

Step 3: Coat with PDMS

After removing the sample from the UHV chamber, the sample is coated with a thick layer of PDMS, an elastomer, as support to facilitate handling of the sample during the transfer.

Step 4: Peel the sandwich off

The PDMS / C₆₀ / porphyrin / gold sandwich can now easily be peeled off the mica, leaving the gold exposed.

Step 5: Remove the gold layer

The exposed thin gold layer is subsequently etched in gold etchant (aqueous potassium iodide) for a few minutes to leave the porphyrin network exposed.

Step 6: Transfer the network

The network is stamped onto silicon. This is done by pressing the porphyrin / C₆₀ / PDMS sandwich onto a clean piece of SiO₂ / Si wafer.

Step 7: Peel the PDMS off

When removing the elastomer, some of the C₆₀ sticks to the silicon substrate, the rest remains on the PDMS.

Step 8: Fluorescence spectroscopy of the transferred molecules

The success of the transfer of the porphyrin can be verified by fluorescence spectroscopy. To investigate the distribution of the transferred porphyrin network and the overlaying C₆₀, a map covering a 500 μm x 500 μm area in the centre of the silicon substrate is taken. The porphyrin has been transferred covering most of the sample. The thickness of the C₆₀ layer varies across the sample.

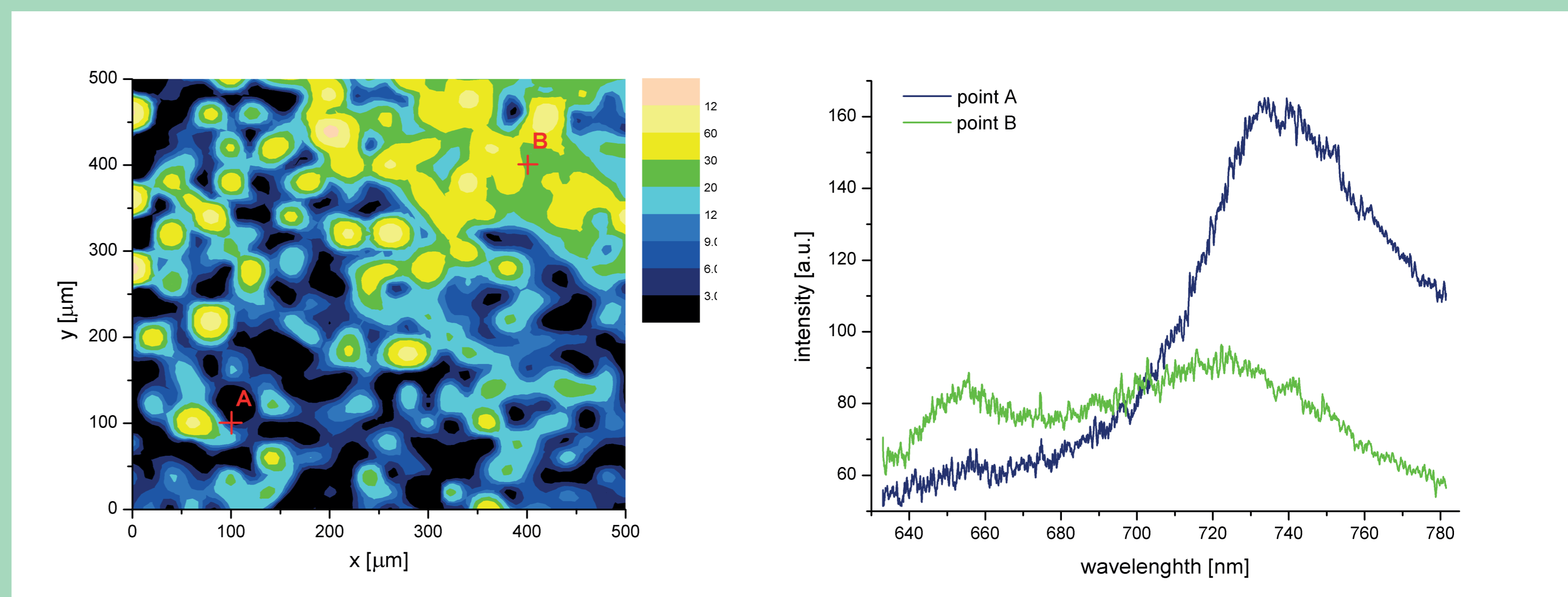


Figure 5 left: Fluorescence spectroscopy map of the porphyrin peak @ 658 nm with subtracted background @ 630 nm. Bright regions show exposed porphyrin on the silicon substrate, while dark regions can either be porphyrin covered by thick layers of C₆₀ or regions where the transfer failed. right: sample spectra at two different points on the map - point A shows the spectrum of porphyrin covered by C₆₀ where the porphyrin peak @ 658 nm is just visible. The second porphyrin peak is covered by the more dominant C₆₀ peak @ ~750 nm. Point B shows the characteristic double peak of porphyrin @ 658 nm and 727 nm.

References and Acknowledgement

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- [3] Blunt *et. al.*: Templating molecular adsorption using a covalent organic framework, Chemical Communications 2010

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