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Novel self-assembled supramolecular dyads on graphene

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INTRODUCTION



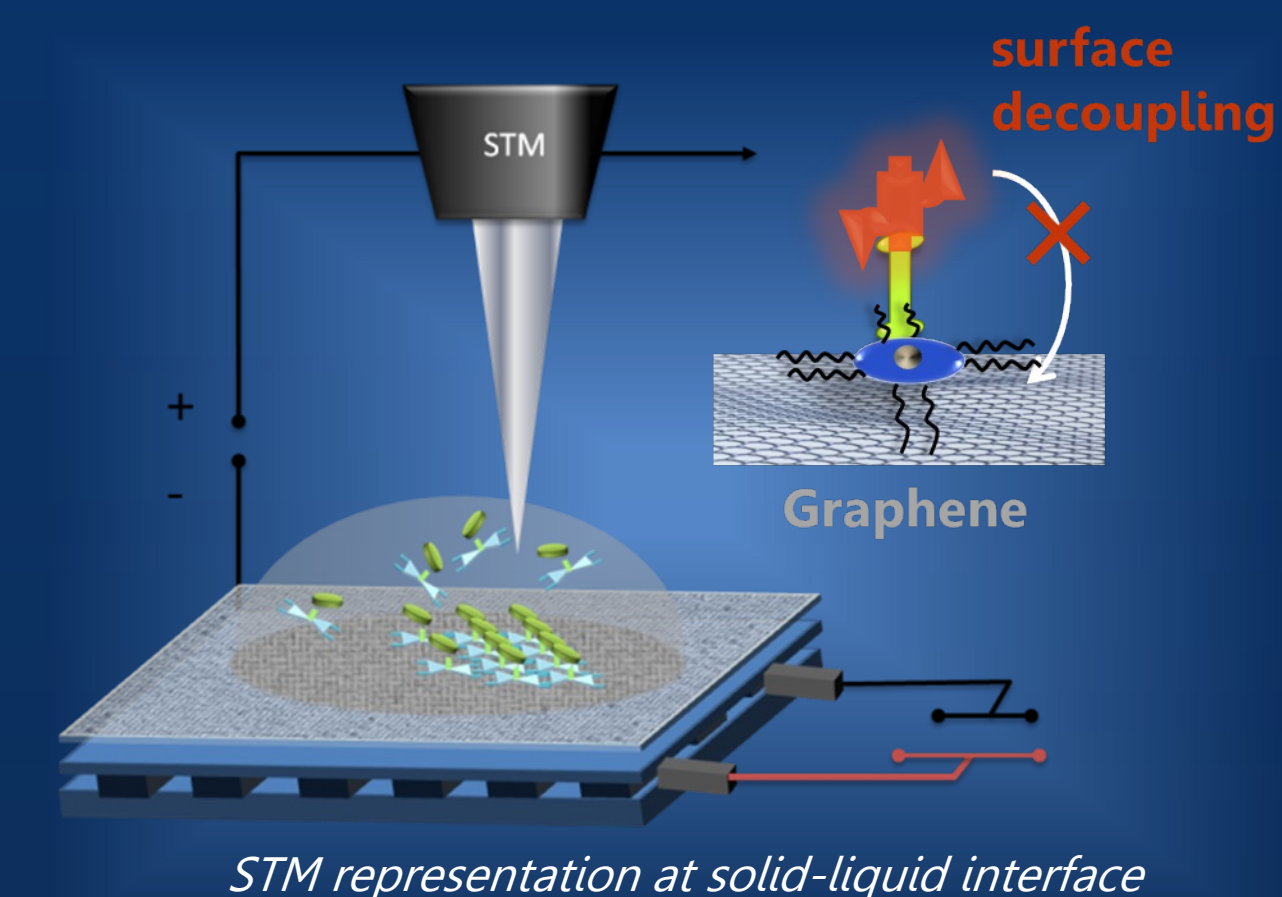
To develop new functional materials, nanoscopic scale architecture control is necessary¹. As a bottom-up synthesis strategy, molecular self-assemblies on surface have been explored, and have demonstrated good control of patterning on various surfaces². From these surfaces; graphene is of interest due to its versatility and potential in future semiconductive devices³. The work presented here describes the functionalization of a graphenoid surface via a supramolecular approach.

Chem. Sci. 2018, 9 (8), 2028–2041.

PROJECT GOALS

We aim to synthesis of **versatile** and **functionalized building-blocks** which **self-organize** on **graphenoid surfaces**. We are mainly interested in :

- **Tuning the surface** self-assembly via the functionalisation of the molecular building blocks
- **Grafting a fluorescent functionality** decoupled from the surface
- **Studying by Scanning Tunnelling Microscopy (STM)** the topology of the molecular 2D-assemblies



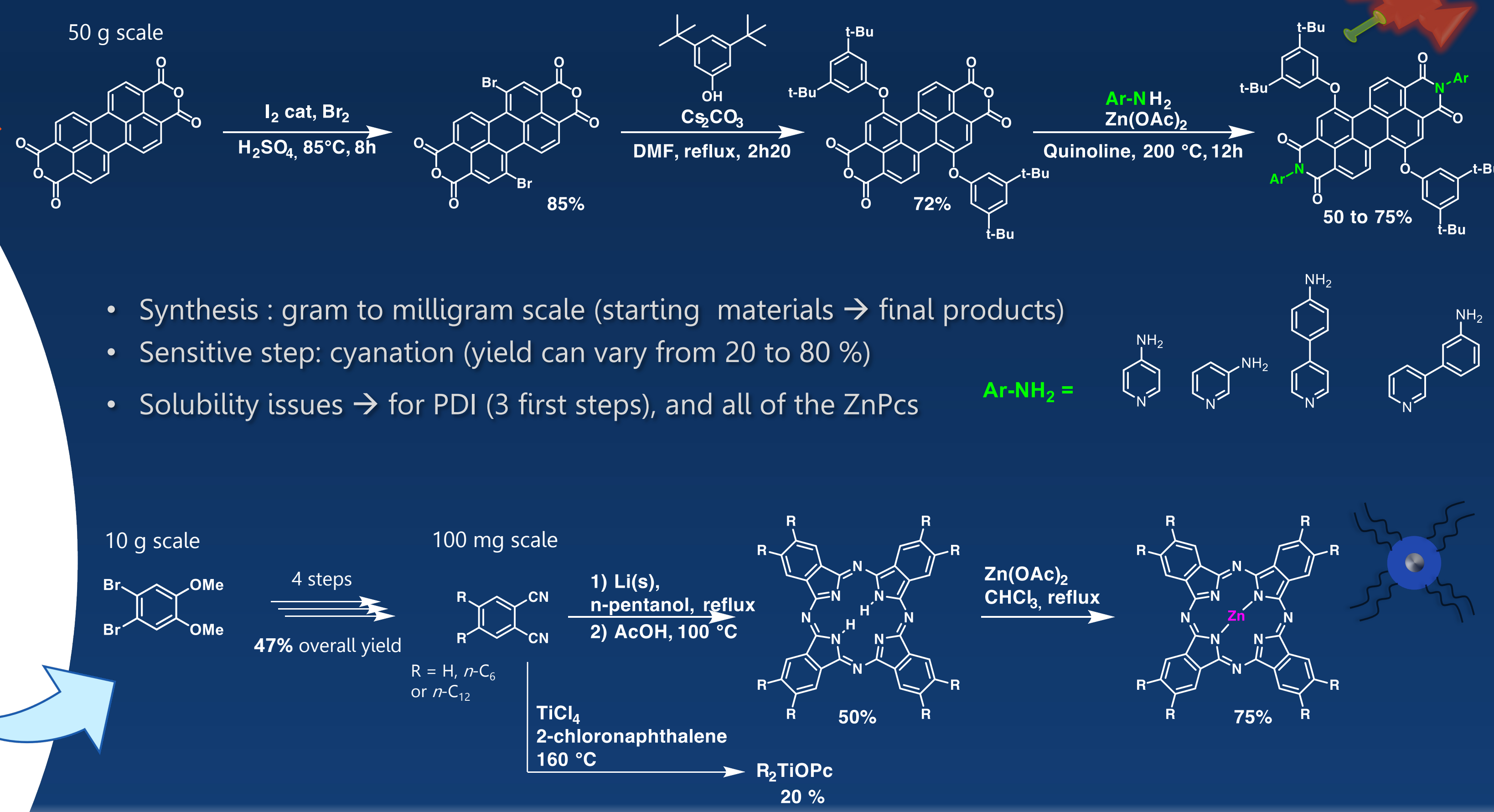
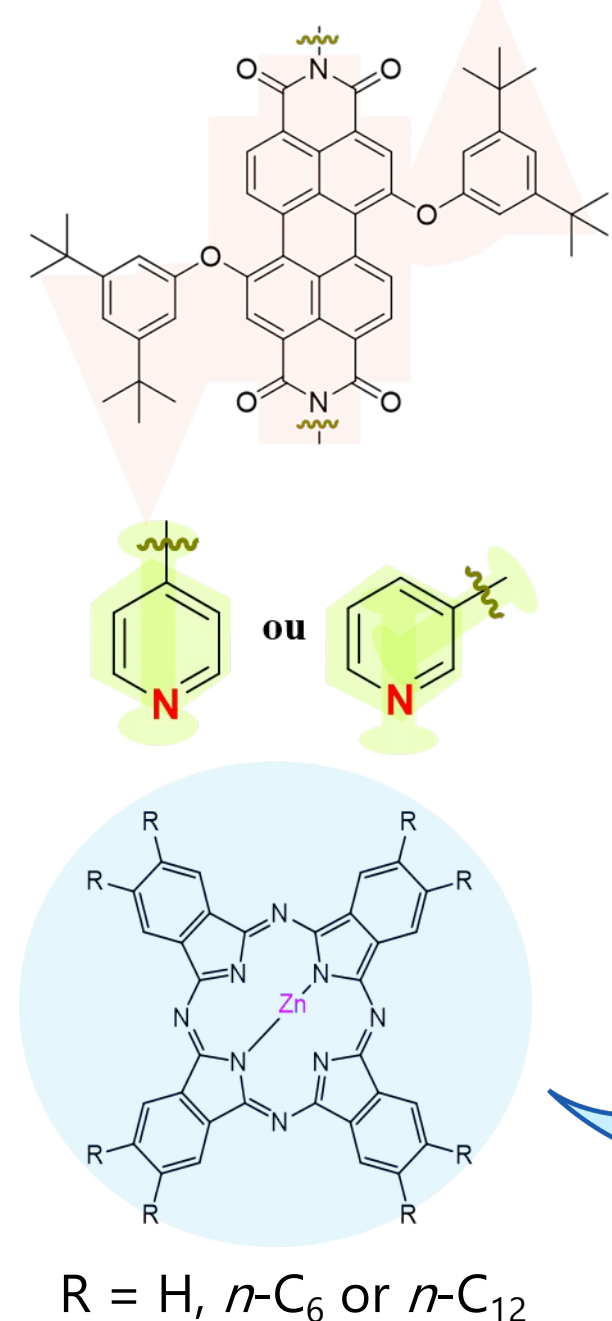
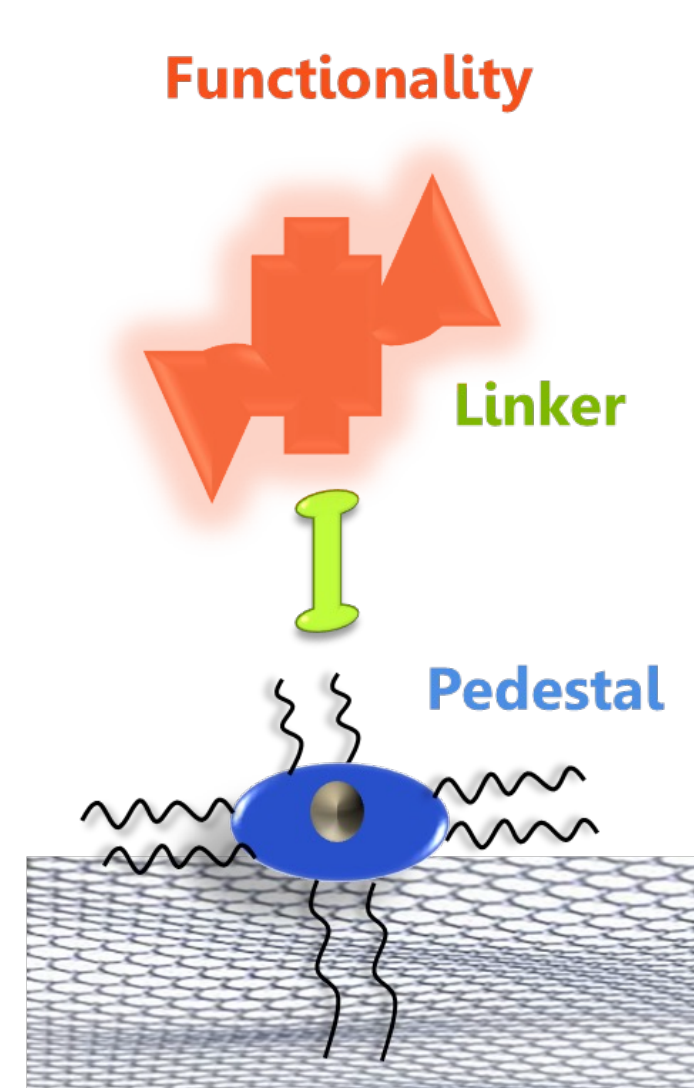
Design strategy and syntheses

These 'smart' **building-blocks** were designed with the aim to develop a **homogeneous, functional, integrated self-assembly** on a graphenoid surface. With this molecular design strategy we are able to **fine-tune** the self-assembly, **orientation** and **functionality** via modification of:

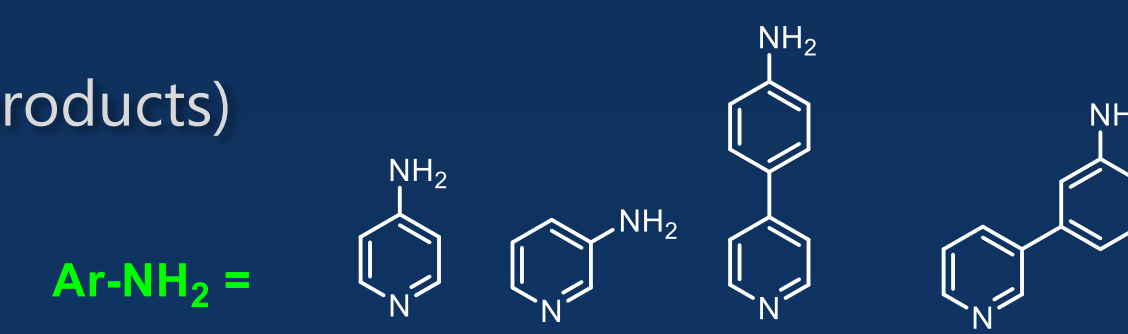
Functionality: a **perylene (PDI)**; with steric hindrance to avoid its assembly on the surface. It is a strongly fluorescent component. A donor/acceptor unit could replace it.

Linker: a **pyridyl derivative**; decouples the functionality from the surface. Orientation and distance can be controlled by modifying it.

Pedestal: a **phthalocyanine (Pc)**; functionalized on peripheral positions to enable the supramolecular self-assembly on the surface. A non-functionalized phthalocyanine was also used in host guest systems.

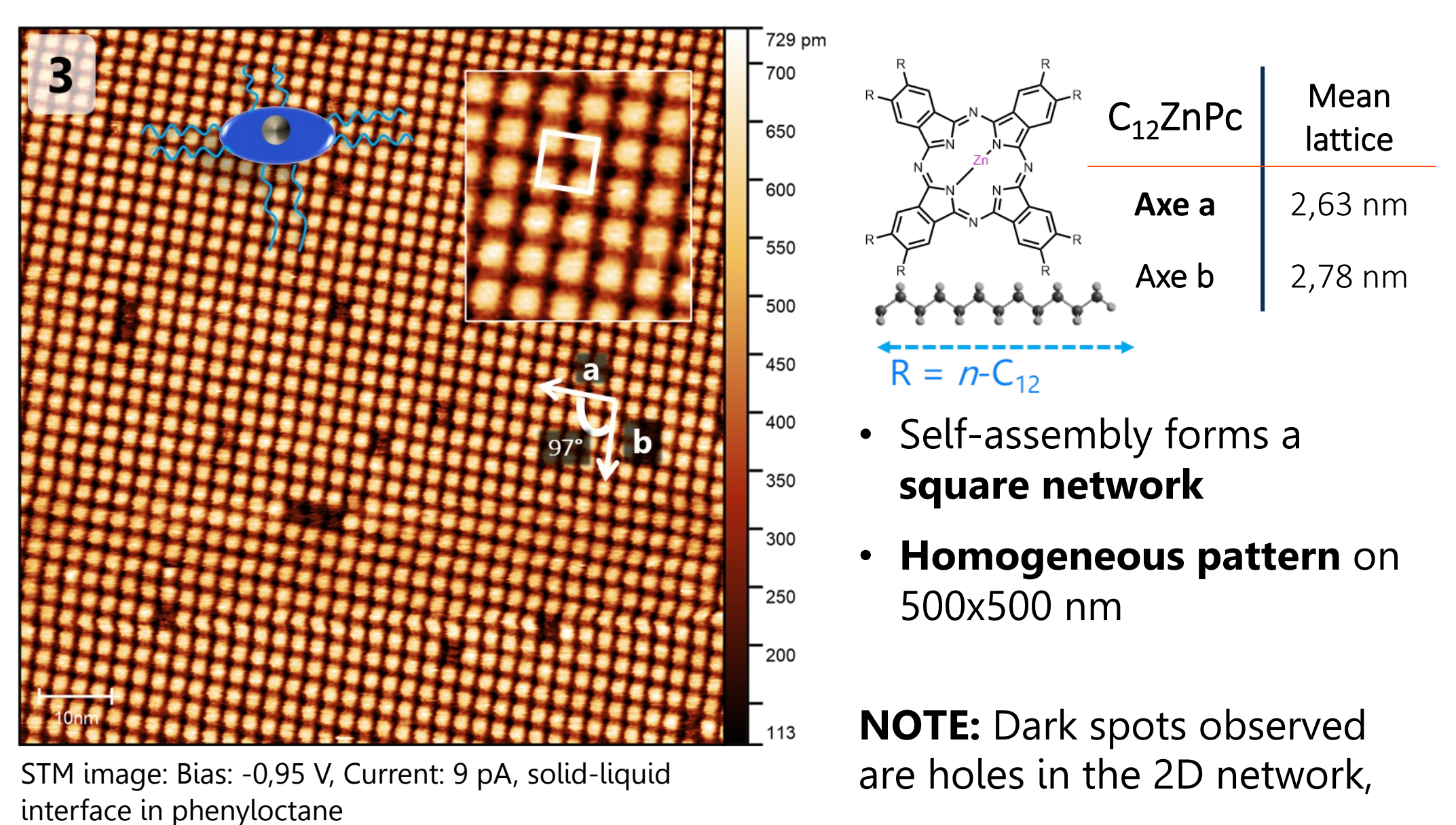
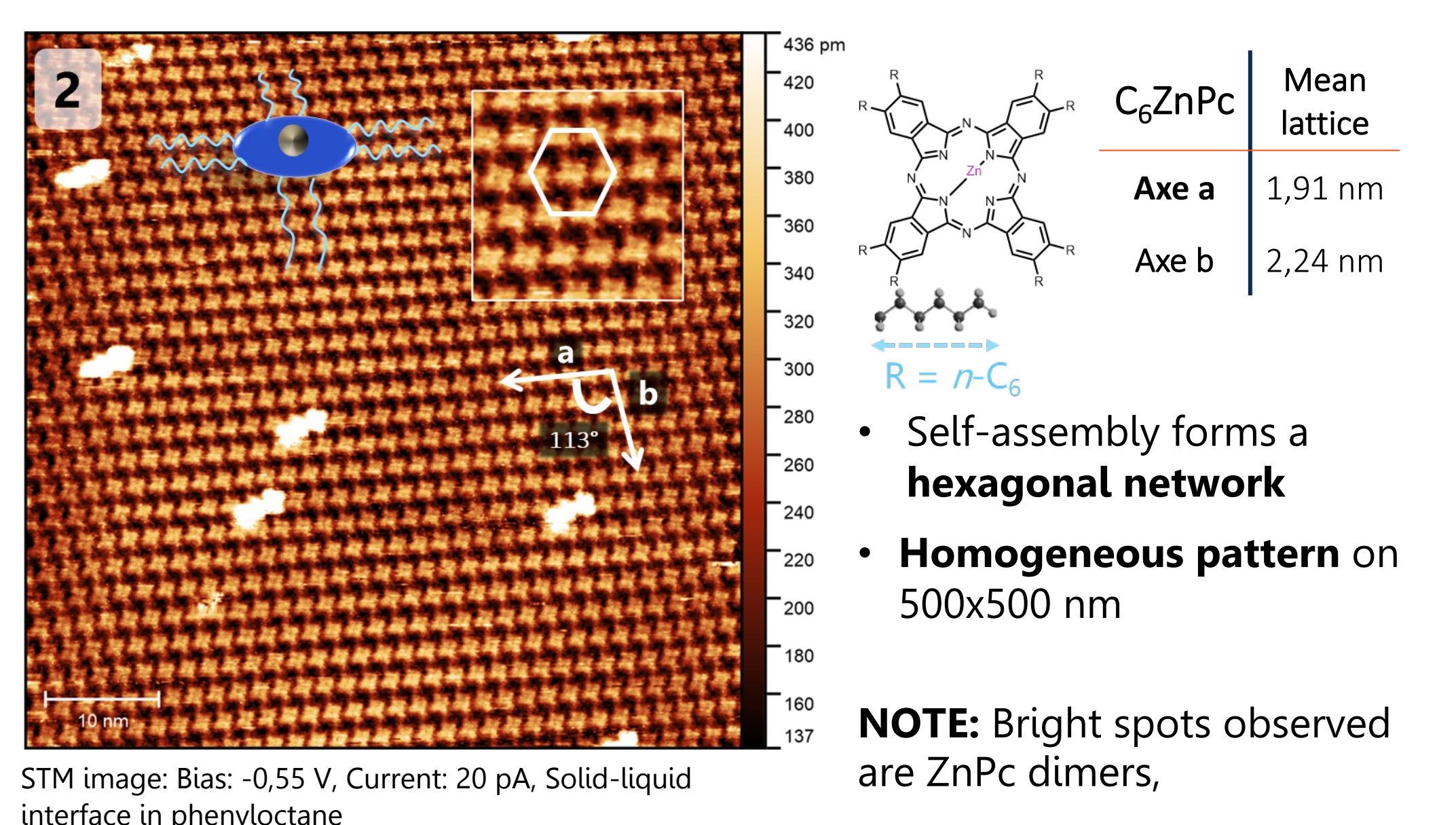
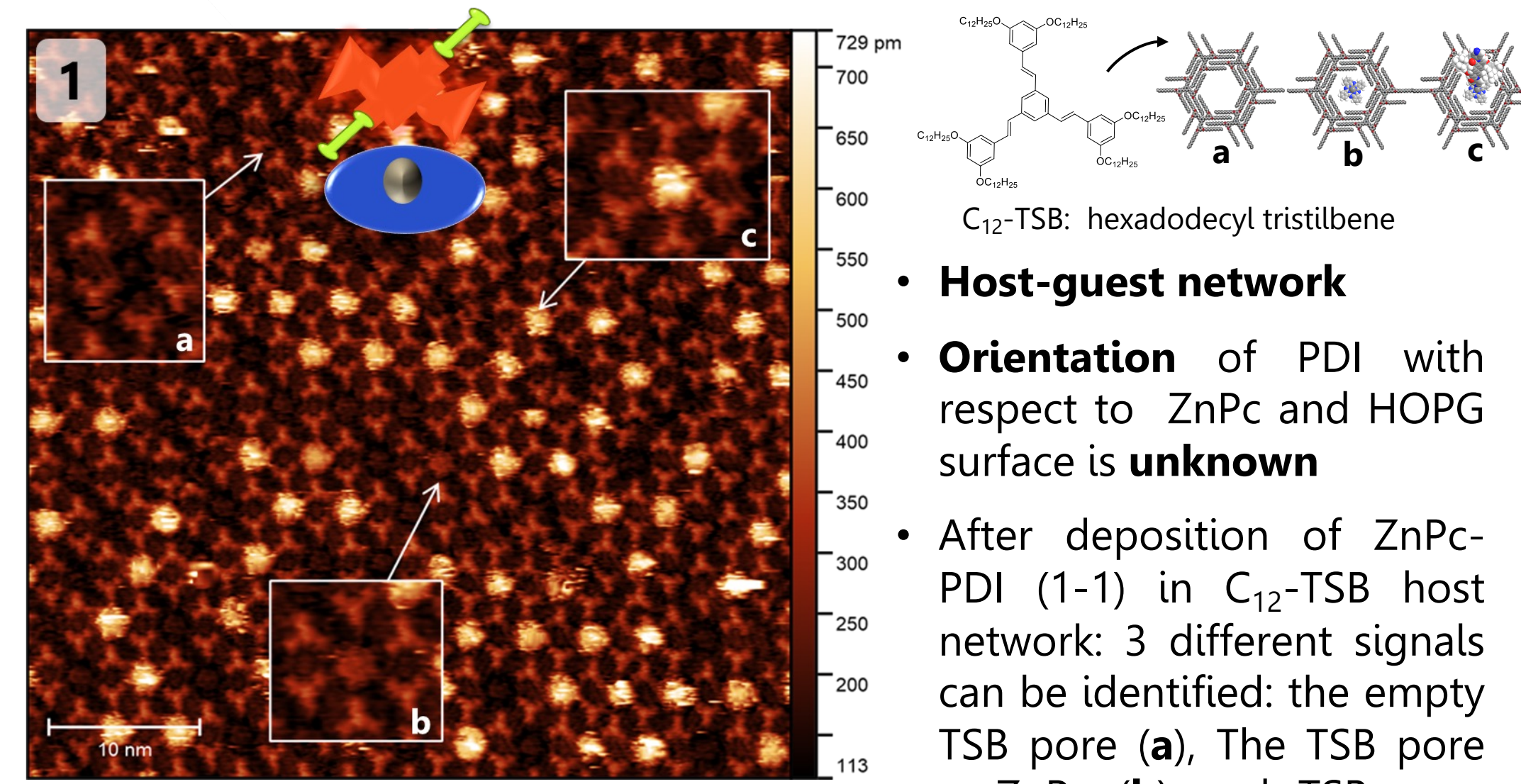


- Synthesis : gram to milligram scale (starting materials → final products)
- Sensitive step: cyanation (yield can vary from 20 to 80 %)
- Solubility issues → for PDI (3 first steps), and all of the ZnPcs



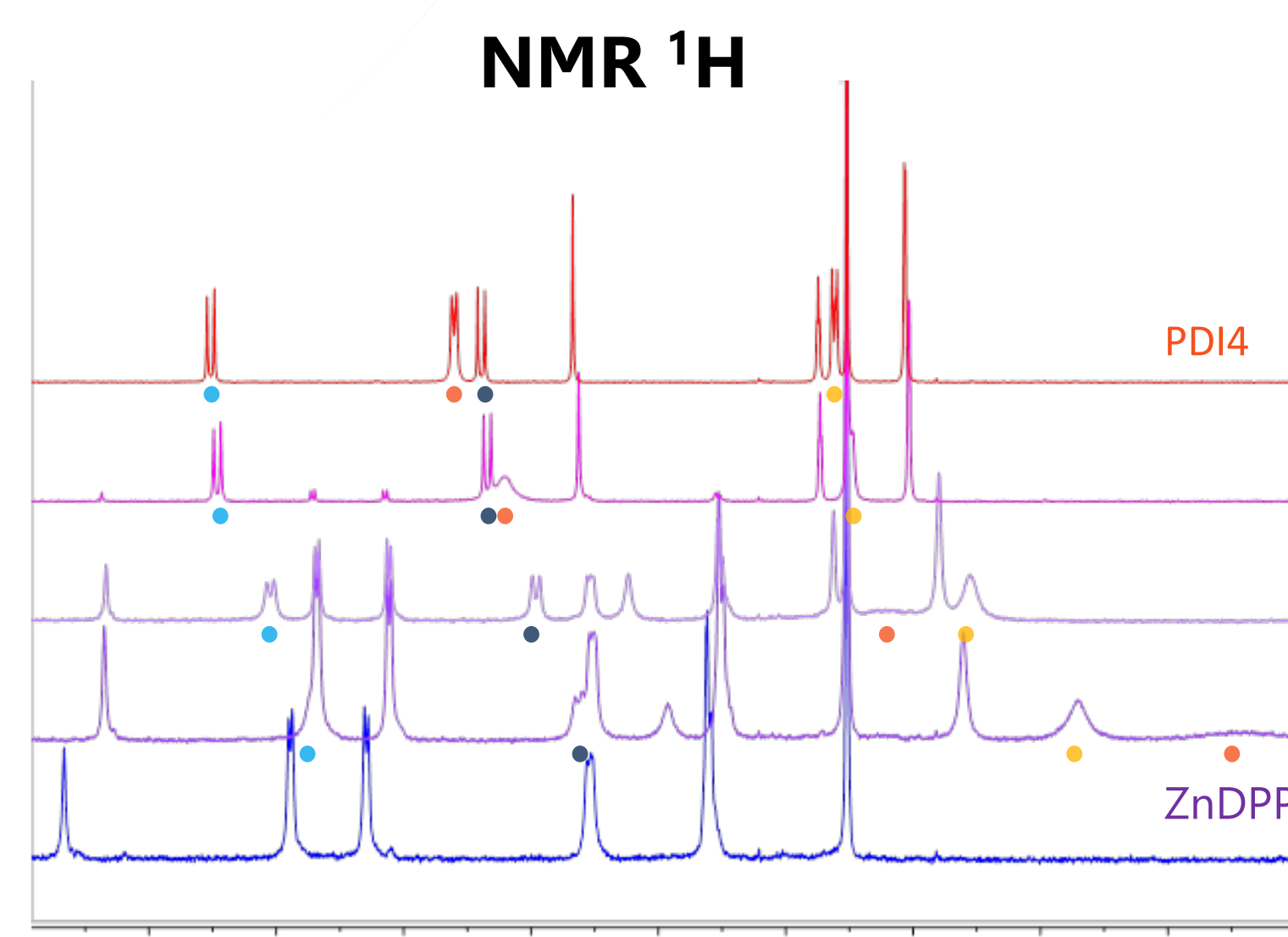
Self-assembling properties

The following STM images are monolayers of several molecular pedestals on Highly Oriented Pyrolytic Graphite (HOPG) surfaces.

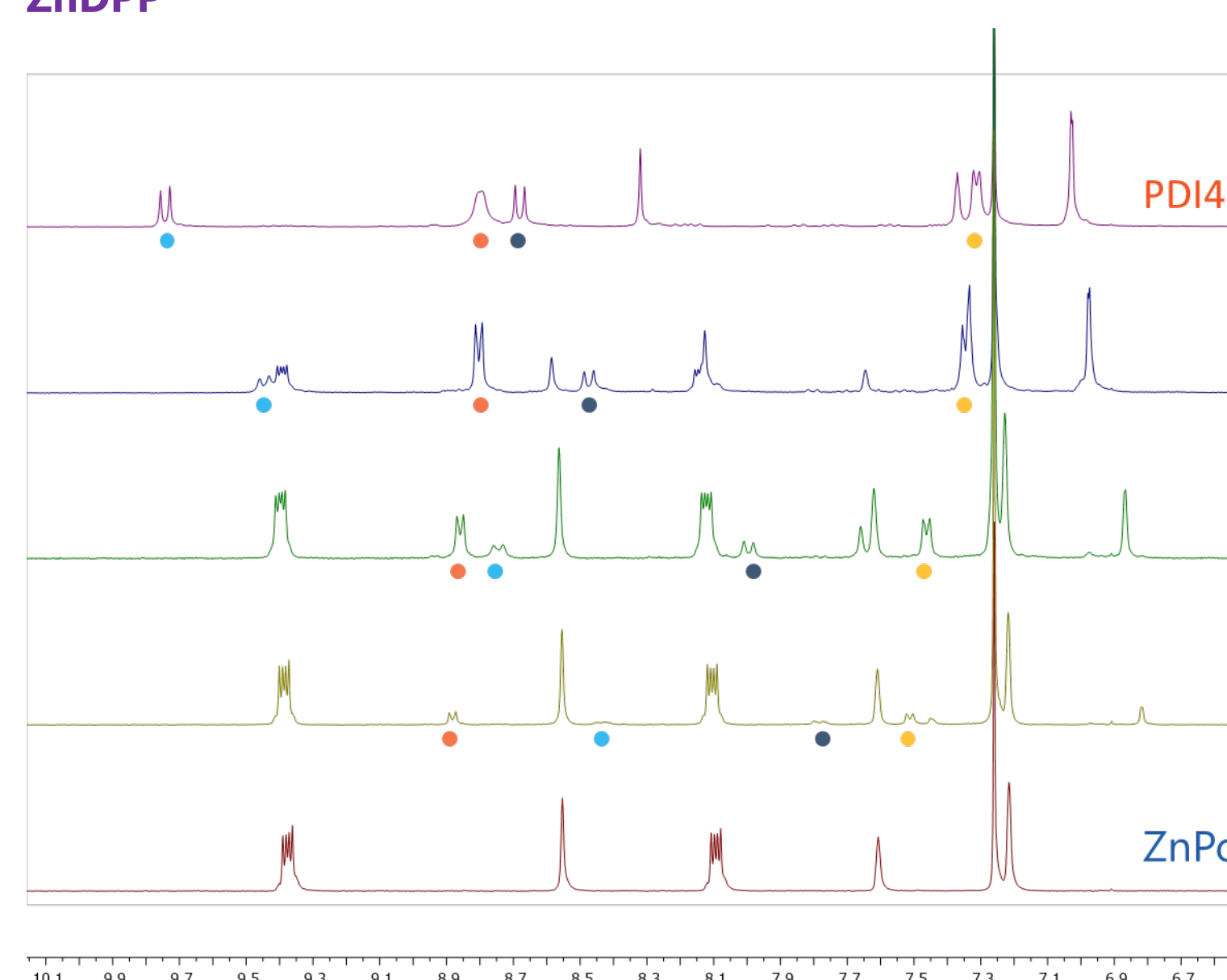


Dyad association characterization

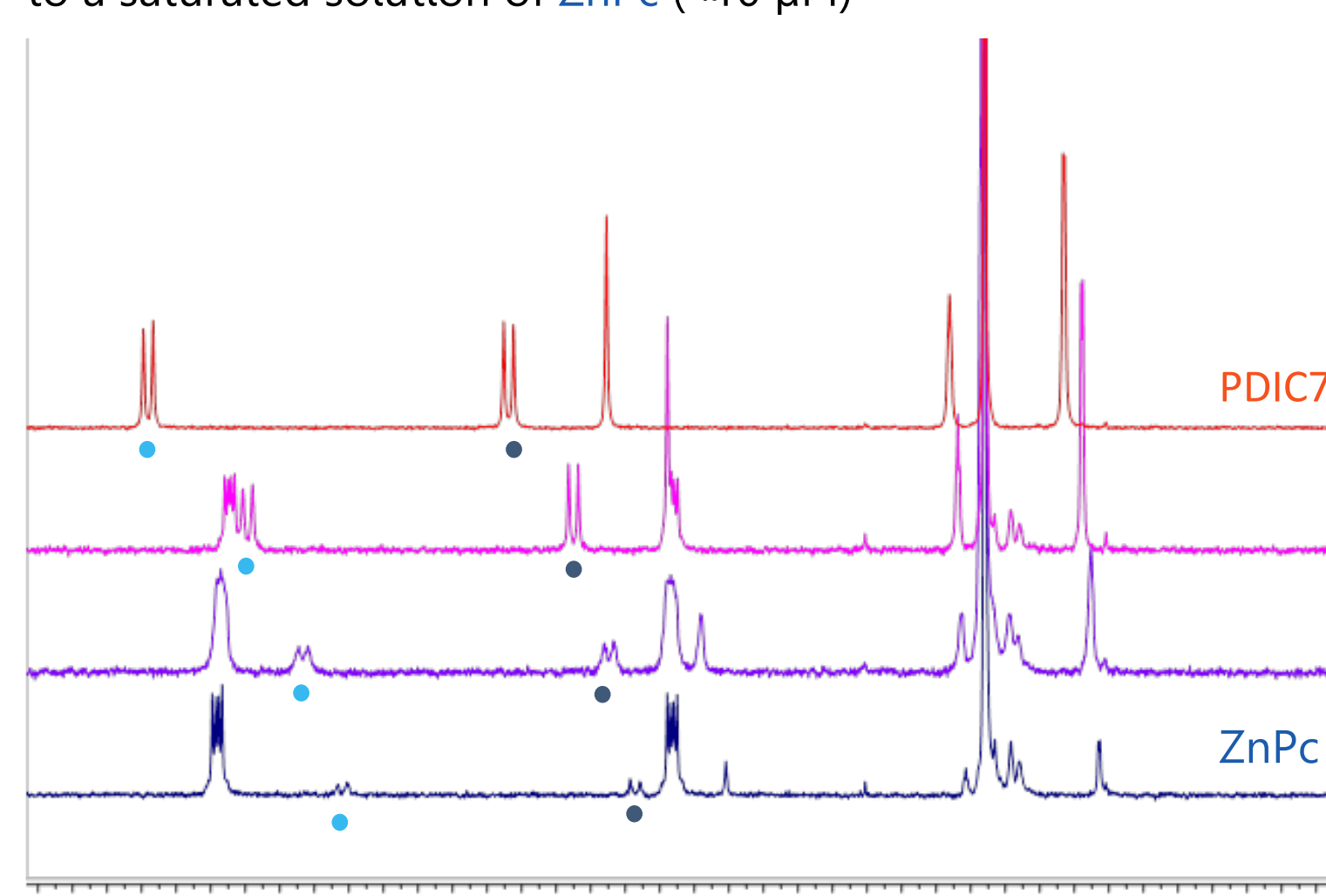
We then studied the formation of the ZnPc-PDI complexes in solution. Titration experiments were performed by ¹H NMR absorbance, and fluorescence.



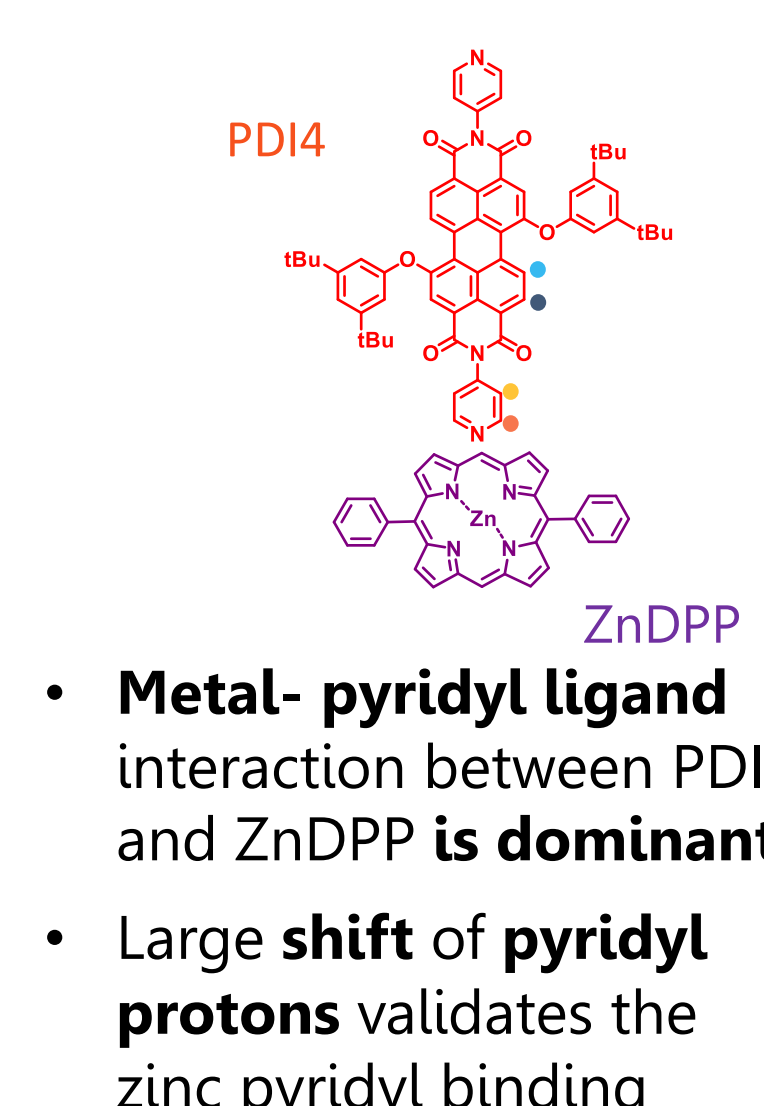
¹H NMR in CDCl₃ by addition of a PDI to a 11 mM solution of ZnDPP



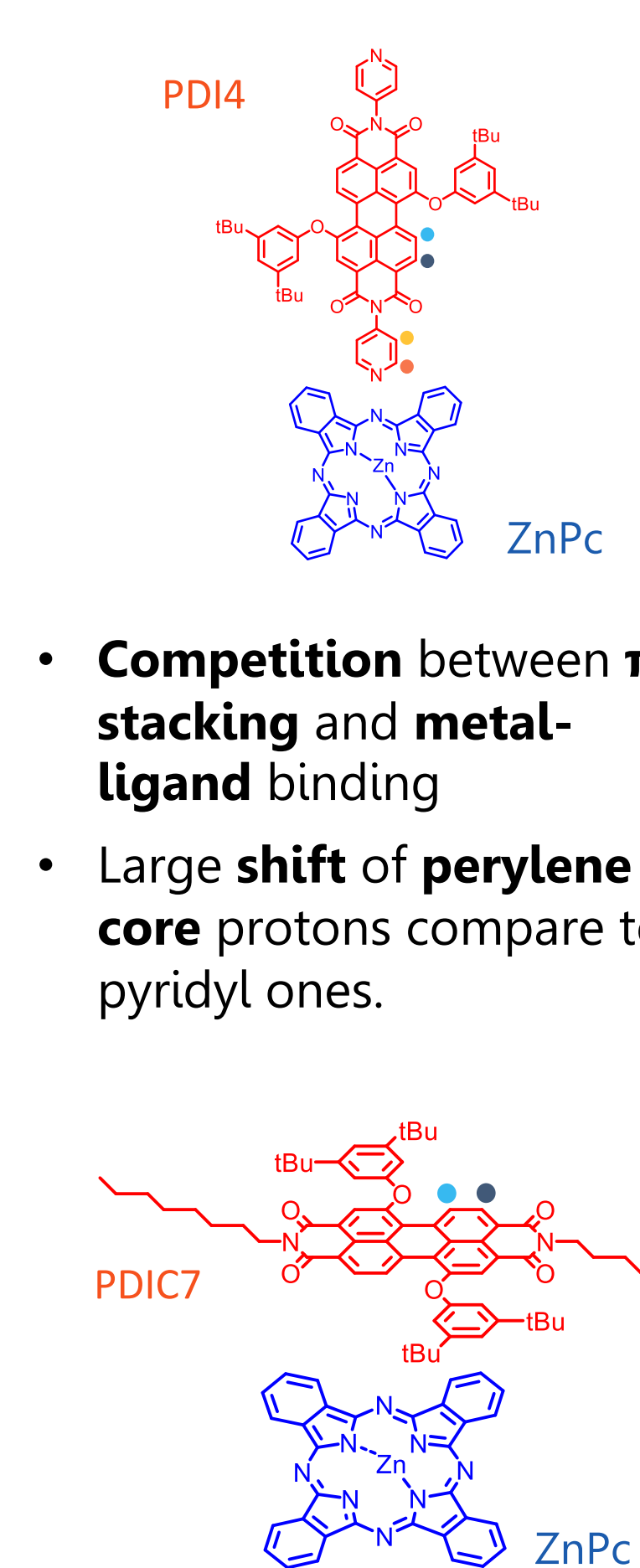
¹H NMR in CDCl₃ (+ 0,5 vol% Pyridine-D₅) by addition of a PDI to a saturated solution of ZnPc (~10 μM)



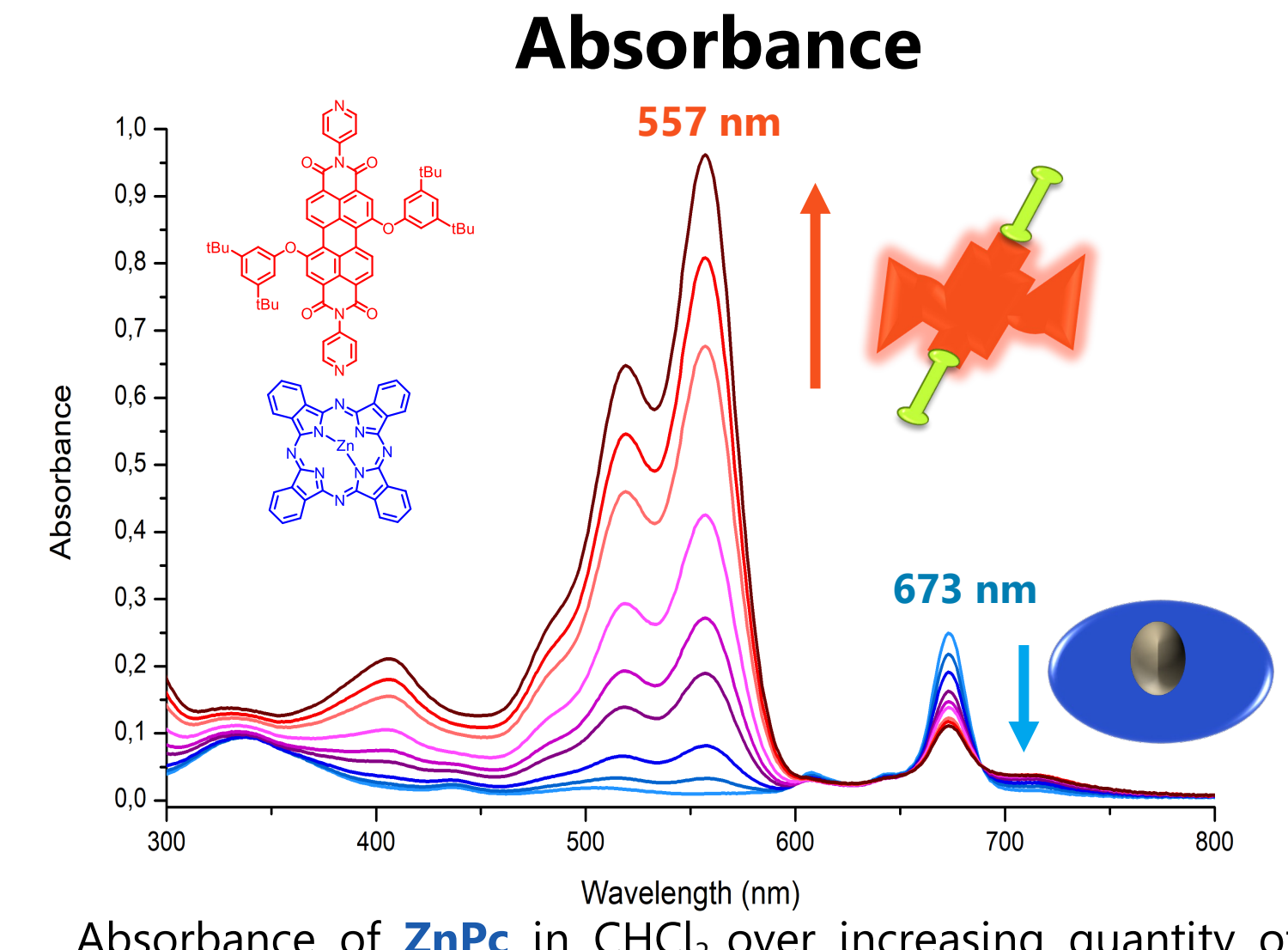
¹H NMR in CDCl₃ by addition of a PDI₇ to a saturated solution of ZnPc



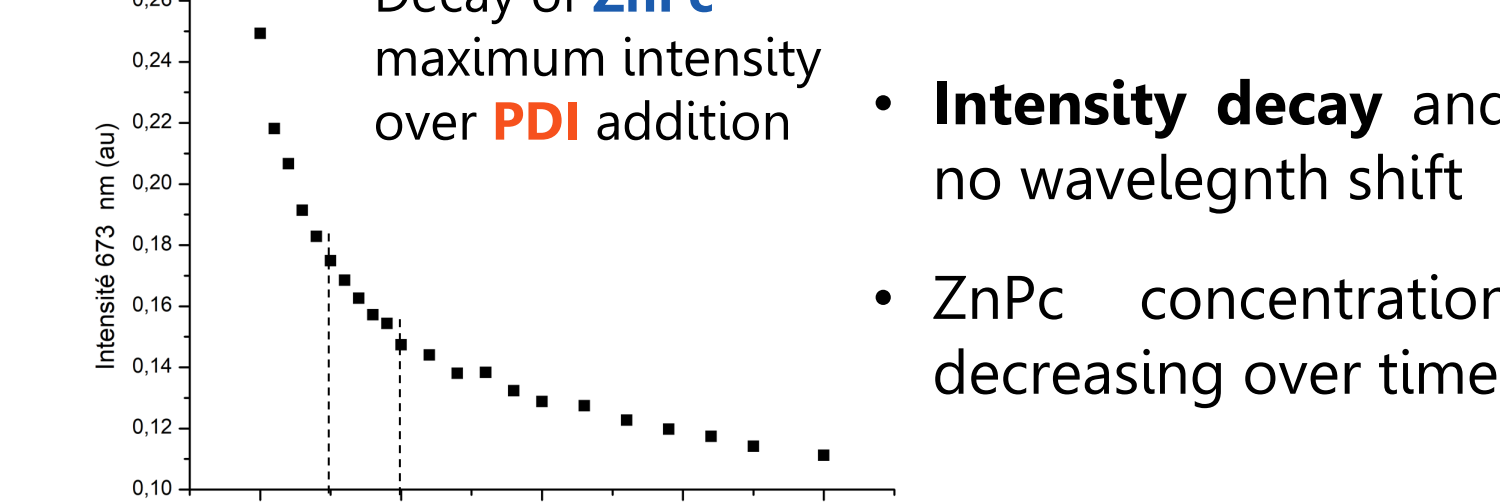
- **Metal- pyridyl ligand** interaction between PDI and ZnDPP is dominant
- Large **shift of pyridyl protons** validates the zinc pyridyl binding



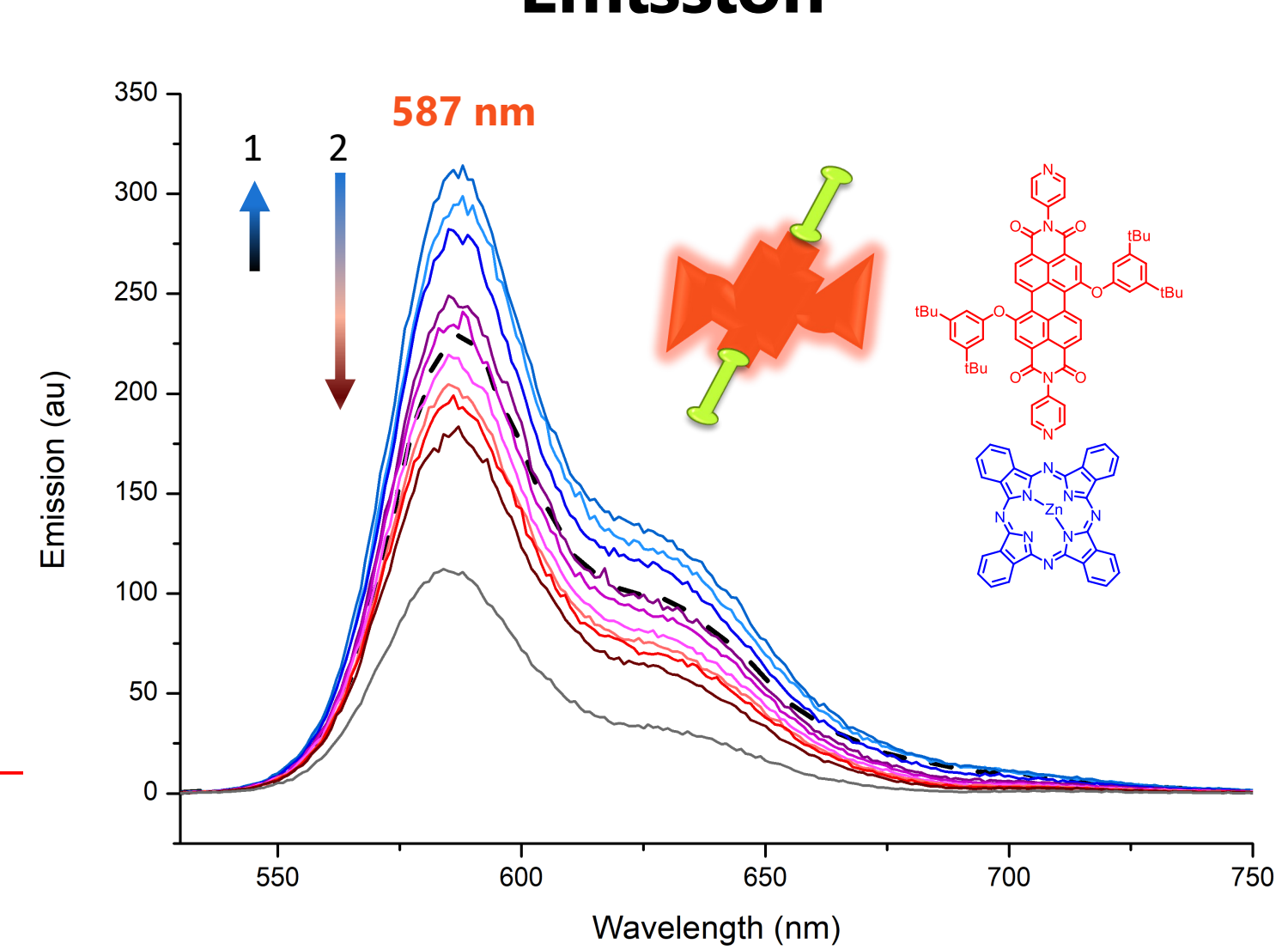
- **Competition between π-stacking and metal-ligand binding**
- Large **shift of perylene core** protons compare to pyridyl ones.
- **Only π-stacking** interaction is possible as PDI₇, as no pyridyl group
- Comparable **shift of perylene core** protons with the PDI-ZnPc association



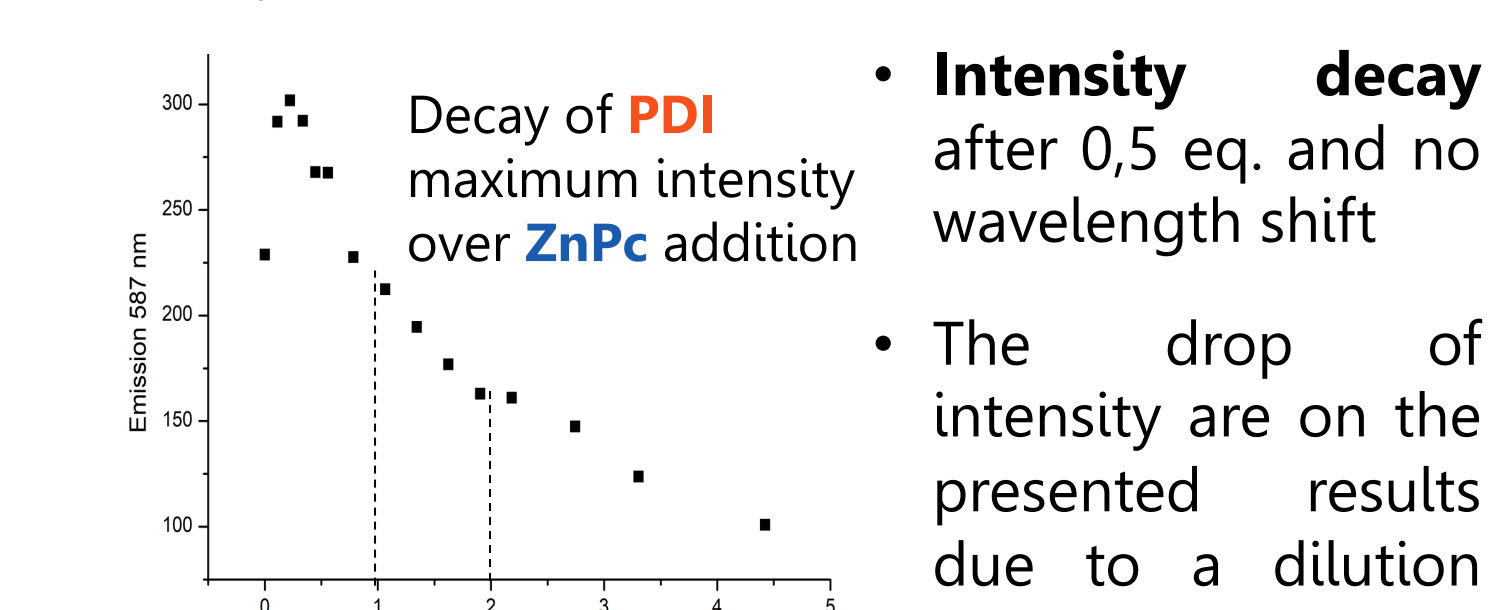
Absorbance of ZnPc in CHCl₃ over increasing quantity of PDI



Decay of ZnPc maximum intensity over PDI addition



Emission of PDI (ex. 520nm) in o-DCB over increasing quantity of ZnPc



- **Intensity decay** and no wavelength shift
- ZnPc concentration decreasing over time
- **Intensity decay** after 0,5 eq. and no wavelength shift
- The drop of intensity are on the presented results due to a dilution effect.

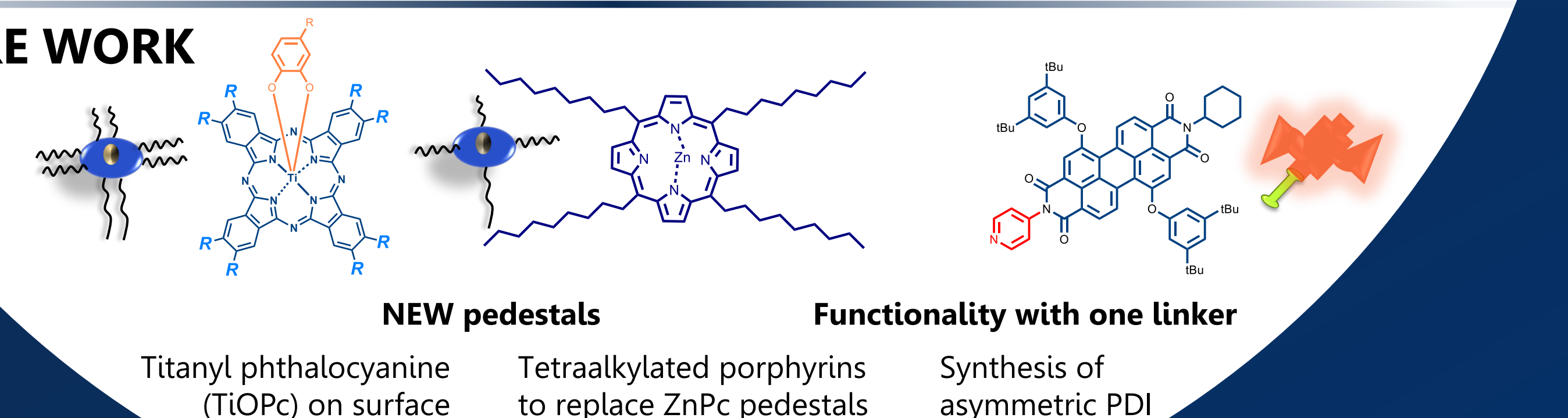
CONCLUSION

Alkylated zinc phthalocyanines were synthesized as well as several perylene diimides with different linkers.

Self-assembling networks of zinc phthalocyanine were observed on Surface by STM. The lattice parameters are as expected; proportional to the alkyl chain lengths on the zinc phthalocyanines.

In solution, the association of PDI with ZnPcs comes from π-stacking. The association of PDI with ZnPs comes from metal-ligand interactions.

FUTURE WORK



NEW pedestals
Titanyl phthalocyanine (TiOPc) on surface

Tetraalkylated porphyrins to replace ZnPc pedestals

Functionality with one linker
Synthesis of asymmetric PDI