

Novel self-assembled supramolecular dyads on graphene Quentin Fernez, Shiva Moradmand, Michele Mattera, William Djampa-Tapi, Céline Fiorini-Debuisschert, Fabrice Charra, David Kreher, Fabrice Mathevet, Imad Arfaoui, Lydia Sosa Vargas

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SCIENCES SORBONNE UNIVERSITÉ Novel Self-assembled supramolecular dyads on graphene : Design, synthesis, photophysics & STM studies





Q. Fernez,^a S. Moradmand, M. Mattera, W. Djampa-Tapi, C. Fiorini, F. Charra, <u>D. Kreher</u>,^{ab} F. Mathevet,^a I. Arfaoui, L. Sosa Vargas.^a ^aInstitut Parisien de Chimie Moléculaire, Sorbonne-Université, France, ^bInstitut Lavoisier de Versailles, Université de Versailles Saint-Quentin-en-Yvelines, France



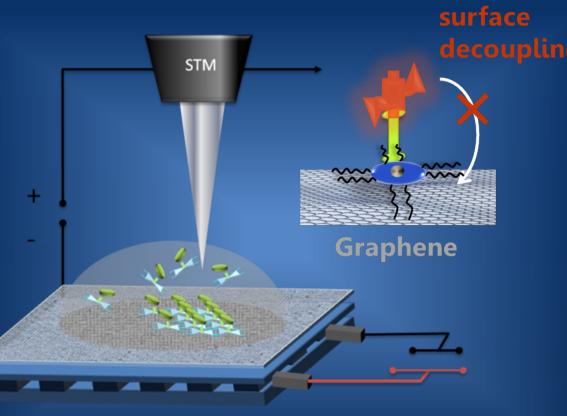


To develop new functional materials, nanoscopic scale architecture control is necessary¹. As a bottom-up synthesis strategy, molecular self-assemblies on surface have been explored, and have demonstrated good control of patterning on various surfaces². From these surfaces; graphene is of interest due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

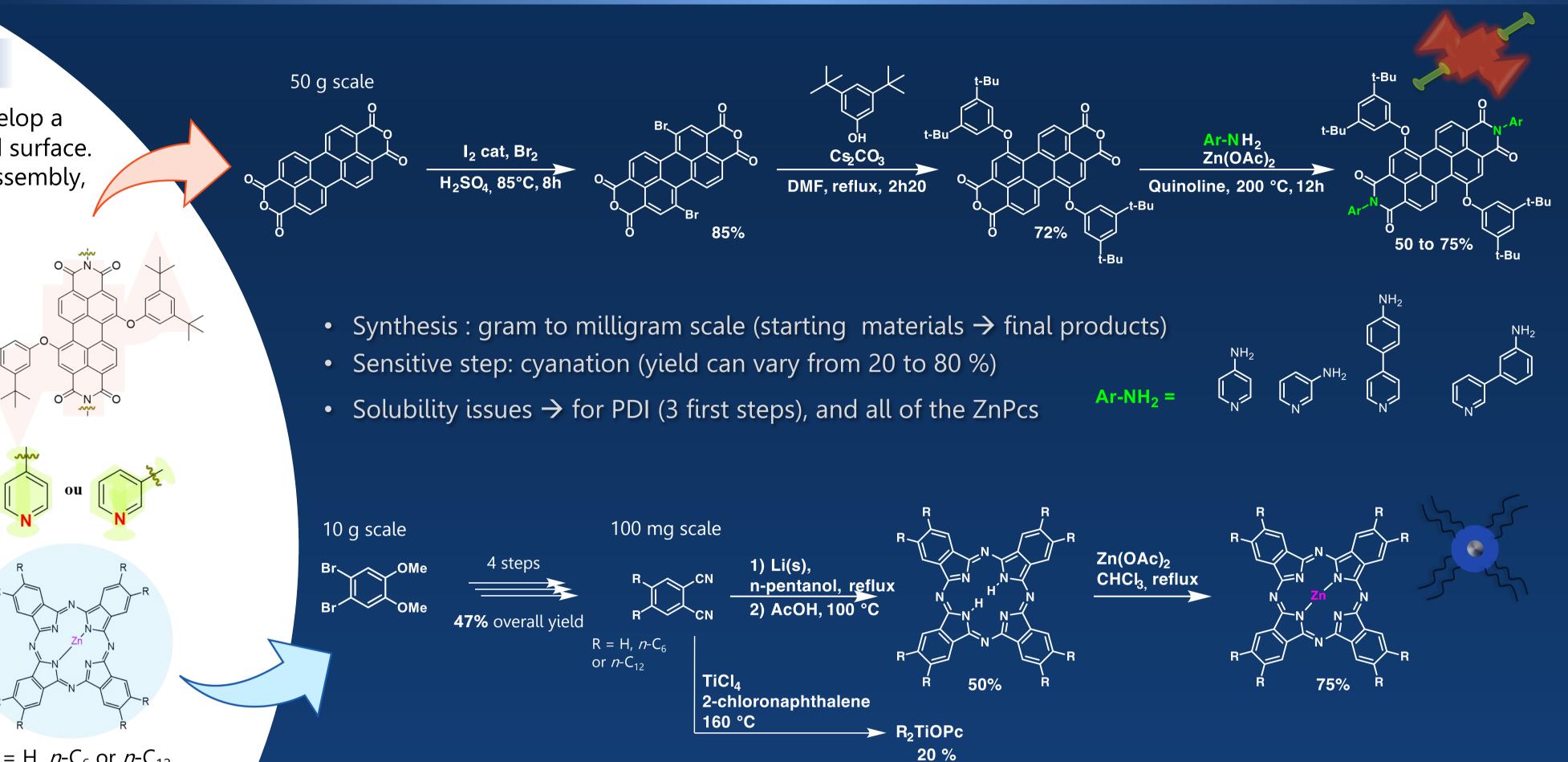
PROJECT GOALS

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



STM representation at solid-liquid interface



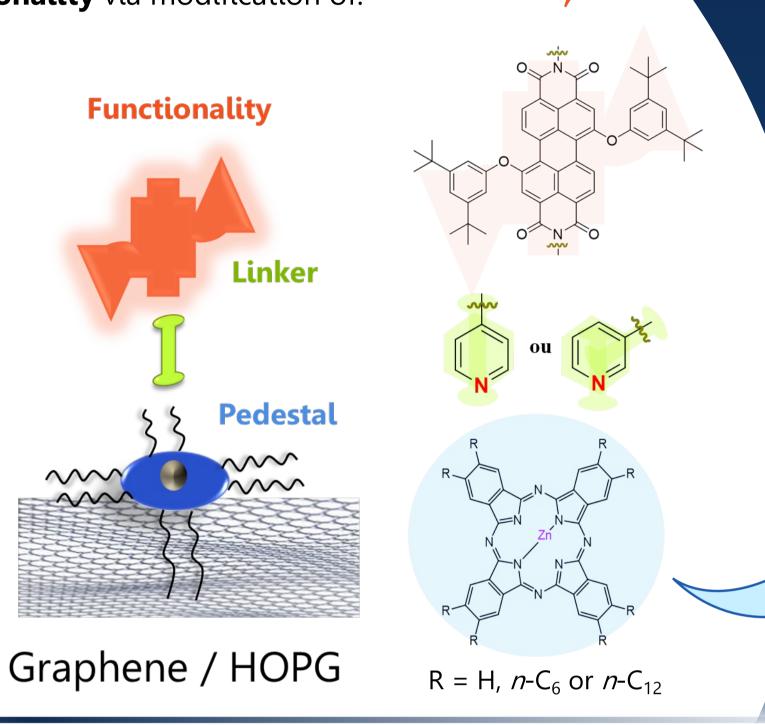
Design strategy and syntheses

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.

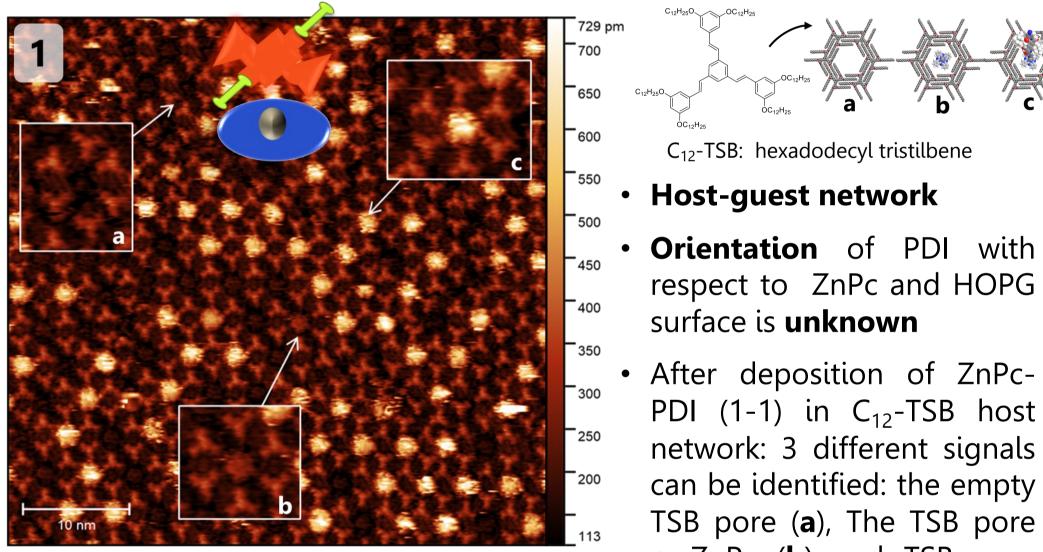
Linker: a pyridyl derivative; decouples the functionality from the surface. Orientation and distance can be controlled by modifying it.

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

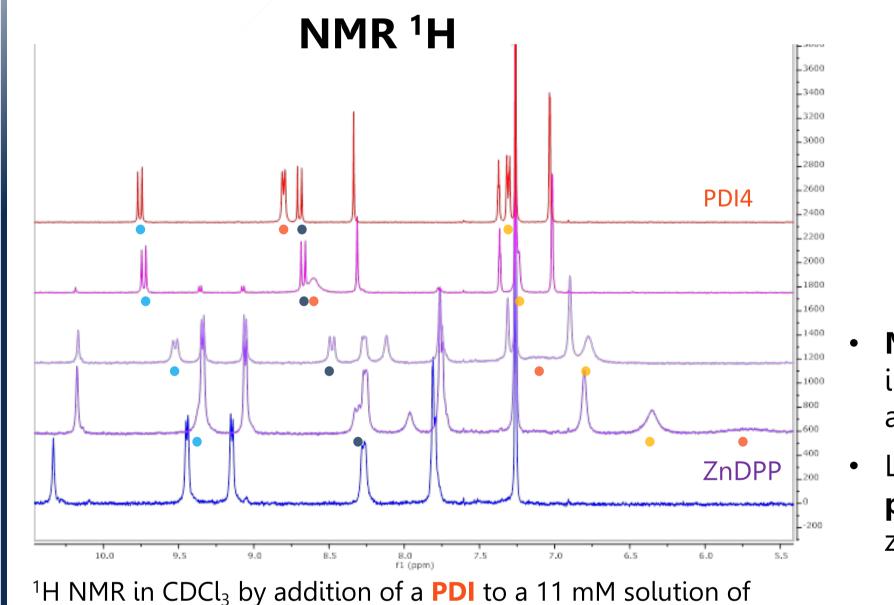


Self-assembling properties

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



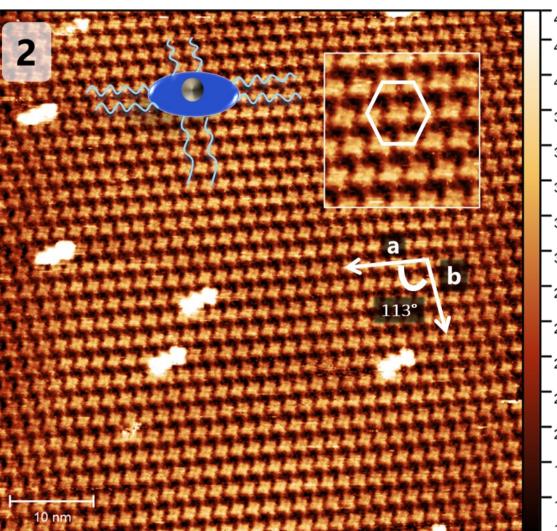
Dyad association characterization We then studied the formation of the ZnPc-PDI complexes in solution. Titration experiments were performed by ¹H NMR absorbance, and fluorescence.



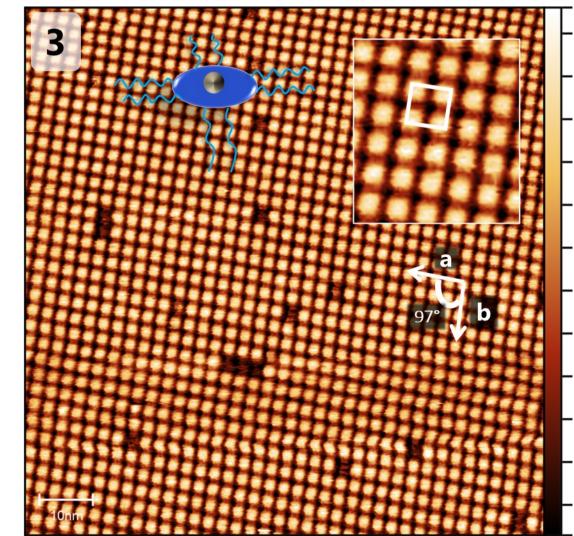
Absorbance 557 nm

150

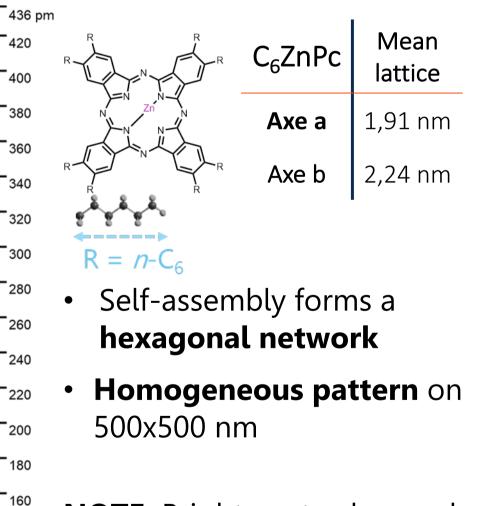
STM image: Bias: -1,0 V, Current: 25 pA, Solid-liquid interface in phenyloctane



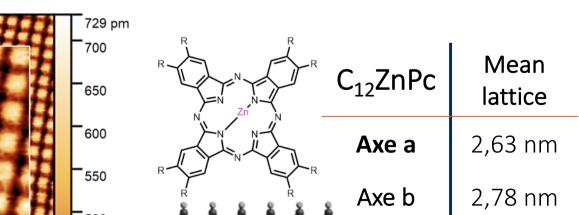
STM image: Bias: -0,55 V, Current: 20 pA, Solid-liquid interface in phenyloctane

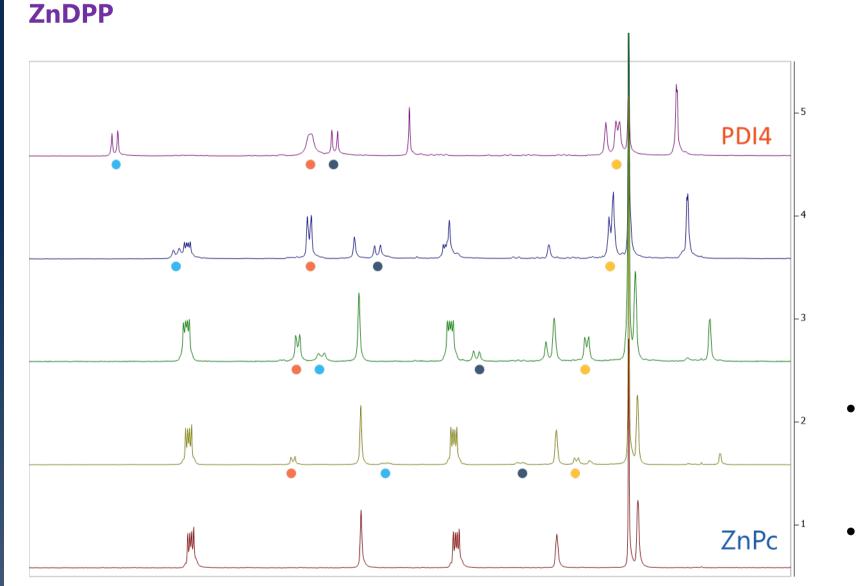


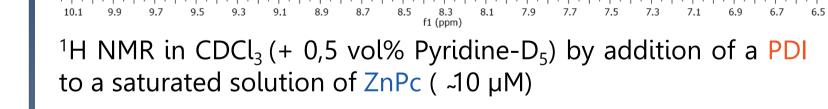
After deposition of ZnPc-PDI (1-1) in C_{12} -TSB host network: 3 different signals can be identified: the empty TSB pore (**a**), The TSB pore + ZnPc (**b**) and TSB pore hosting a ZnPc-PDI (**c**)



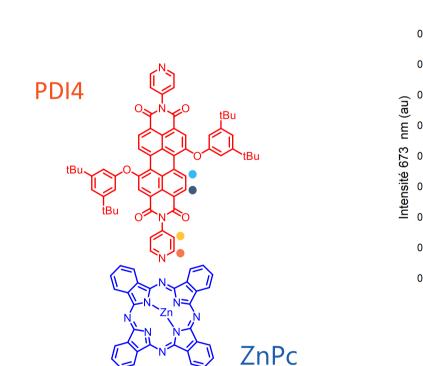
NOTE: Bright spots observed are ZnPc dimers,

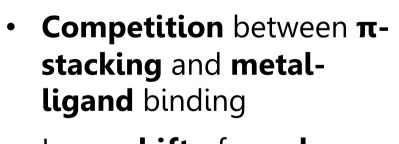




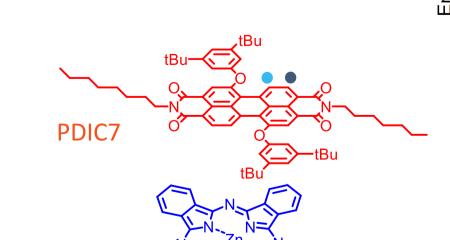


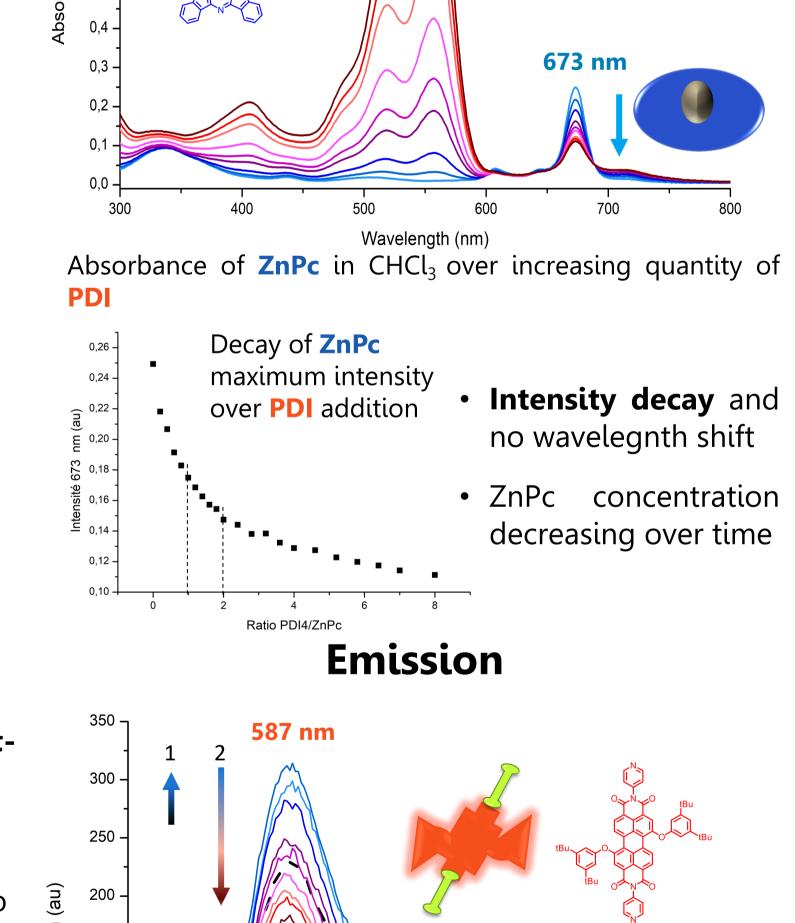
Metal- pyridyl ligand interaction between PDI and ZnDPP is dominant Large **shift** of **pyridyl** protons validates the zinc pyridyl binding





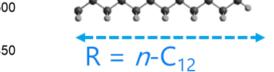
Large **shift** of **perylene** core protons compare to pyridyl ones.



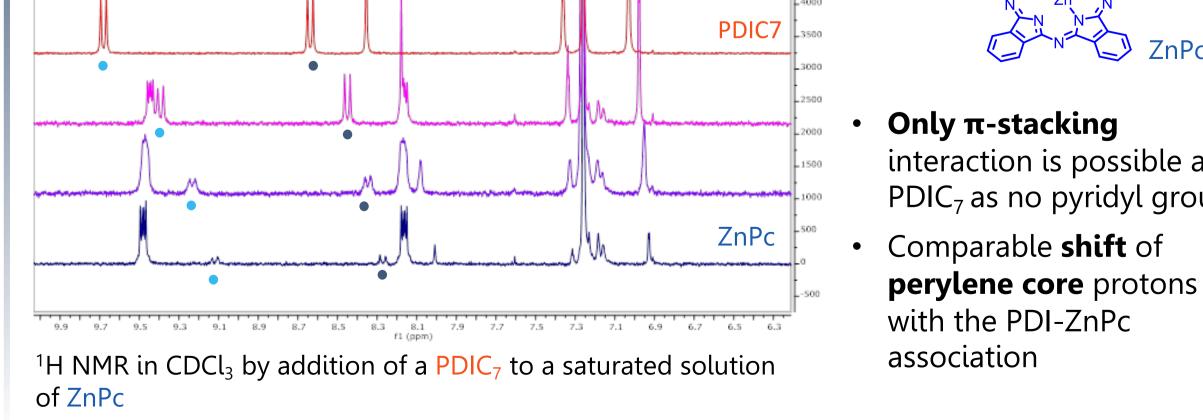


Wavelength (nm)

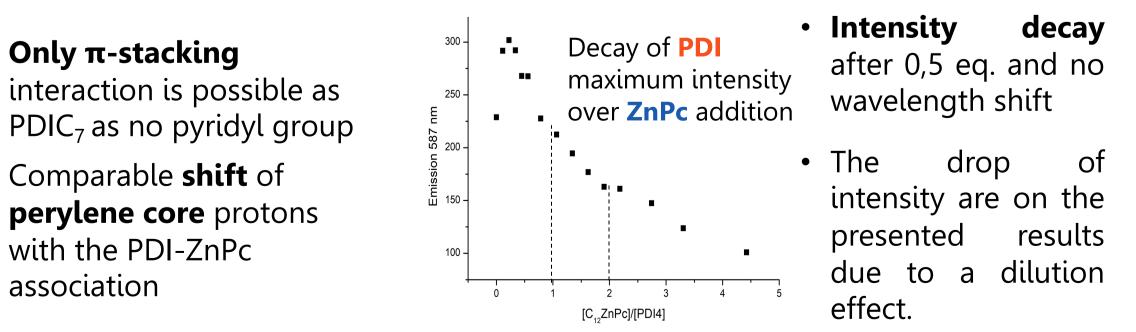
STM image: Bias: -0,95 V, Current: 9 pA, solid-liquid interface in phenyloctane



- Self-assembly forms a square network
- Homogeneous pattern on 500x500 nm
- **NOTE:** Dark spots observed are holes in the 2D network,



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



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.

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