Molecular self-assembly on surfaces: from design and architecture to functionalized graphene

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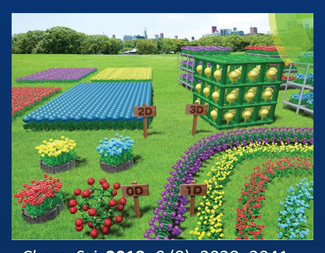
INTRODUCTION



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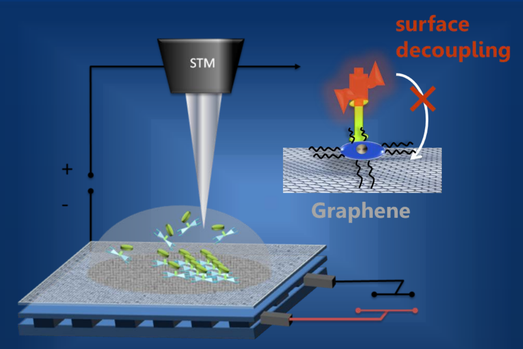
To develop new functional materials, nanoscopic scale architecture control is necessary[1]. As a bottom-up synthesis strategy, molecular self-assemblies on surface have been explored, and have demonstrated good control of patterning on various surfaces[2]. From these surfaces; graphene is of interest due to its versatility and potential in future semiconductive devices[3]. 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

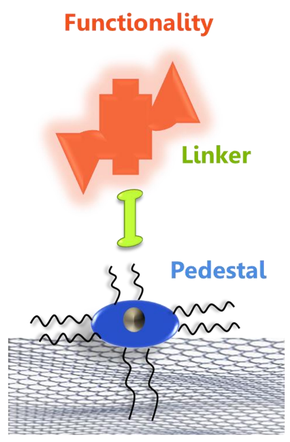
Design strategy and syntheses

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:

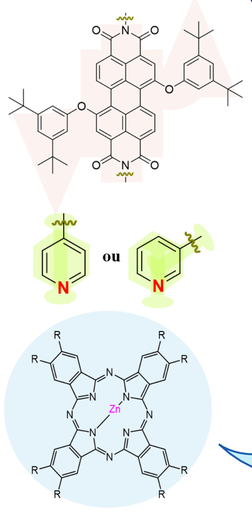
Functionality: a **perylene (PDI);** with steric hindrance to avoid its assembly on the surface. It is a strongly fluorescent component. A donor/acceptor unit could replace it.

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

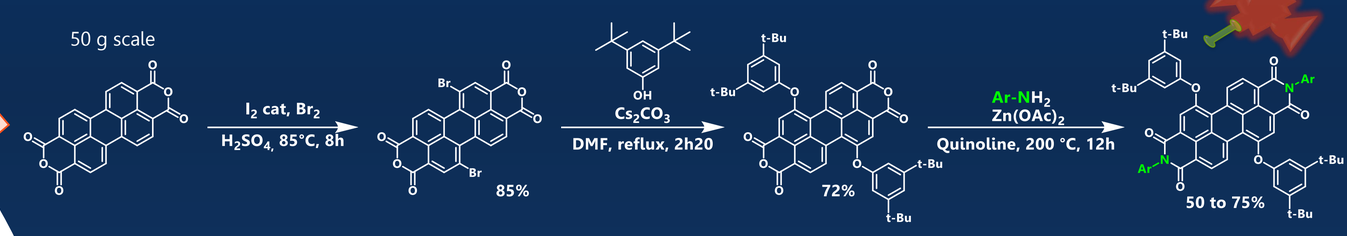
Pedestal: a phthalocyanine (Pc); functionalized on peripheral positions to enable the supramolecular self-assembly on the surface. A non-functionalized phthalocyanine was also used in host guest systems.



Graphene / HOPG

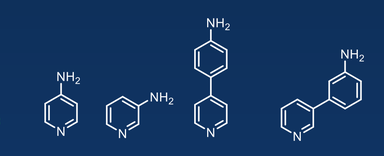


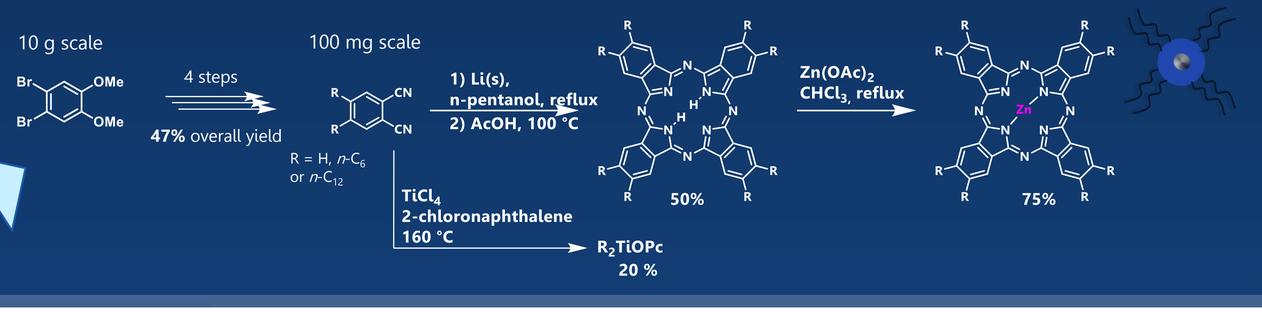
R = H, *n*-C_6 or *n*-C_{12}



- 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

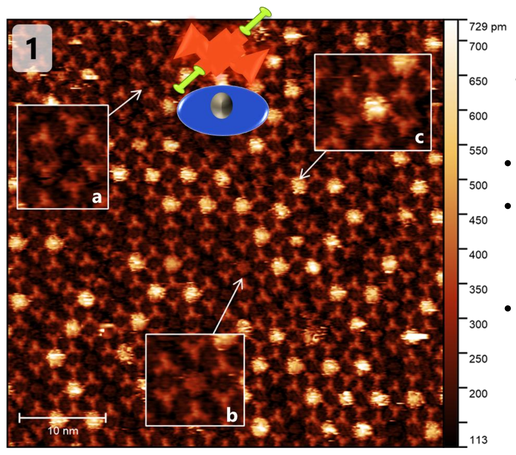
Ar-NH_2 =



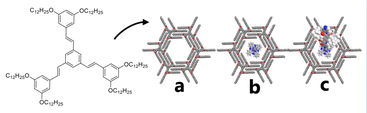


Self-assembling properties

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

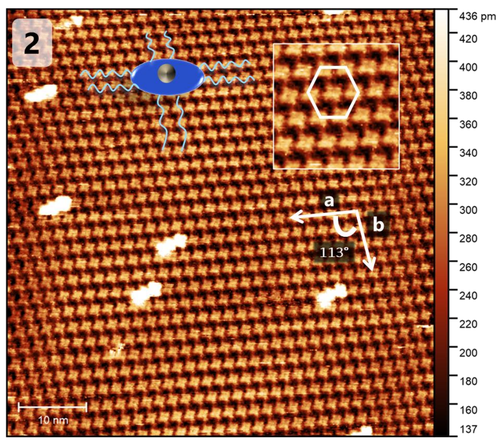


STM image: Bias: -1,0 V, Current: 25 pA, Solid-liquid interface in phenyloctane

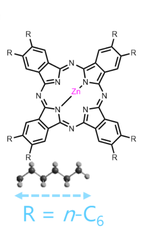


C_{12}-TSB: hexadodecyl tristilbene

- **Host-guest network**
- **Orientation** of PDI with respect to ZnPc and HOPG surface is **unknown**
- 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**)



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

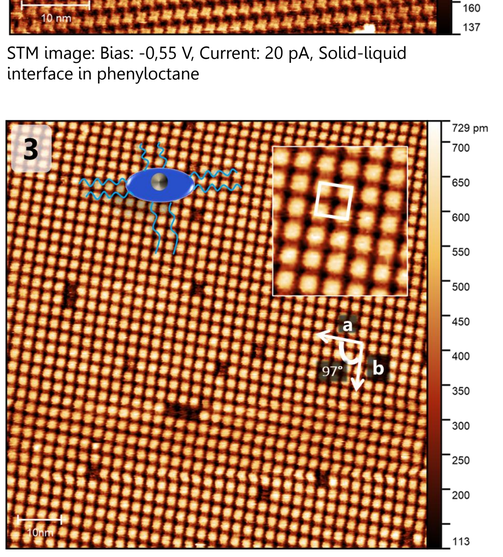


R = *n*-C_6

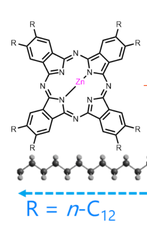
C_6ZnPc	Mean lattice
Axe a	1,91 nm
Axe b	2,24 nm

- Self-assembly forms a **hexagonal network**
- **Homogeneous pattern** on 500x500 nm

NOTE: Bright spots observed are ZnPc dimers,



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



R = *n*-C_{12}

C_{12}ZnPc	Mean lattice
Axe a	2,63 nm
Axe b	2,78 nm

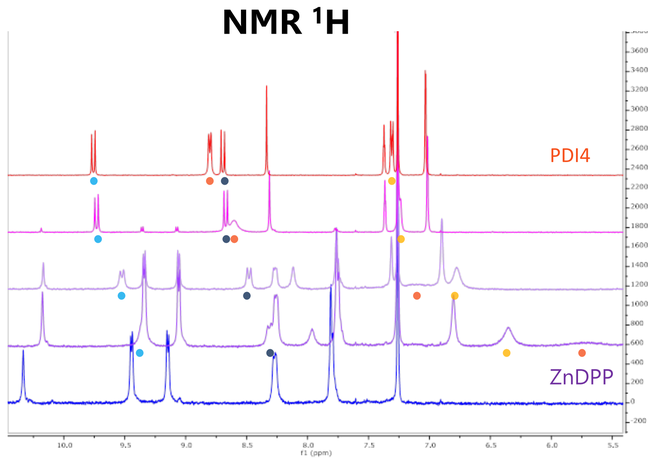
- Self-assembly forms a **square network**
- **Homogeneous pattern** on 500x500 nm

NOTE: Dark spots observed are holes in the 2D network,

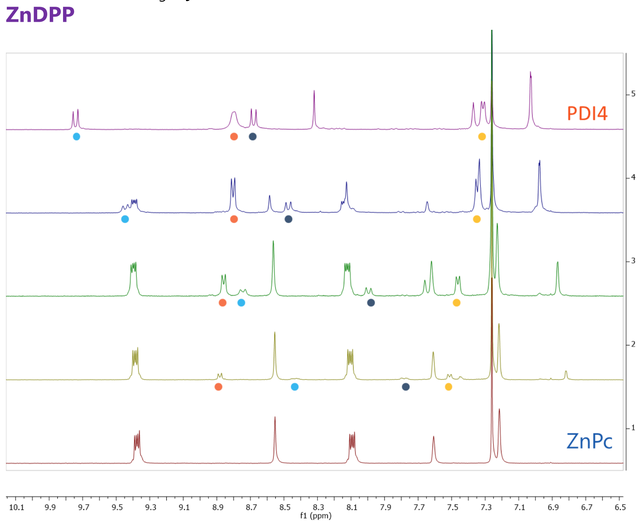
Dyad association characterization

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

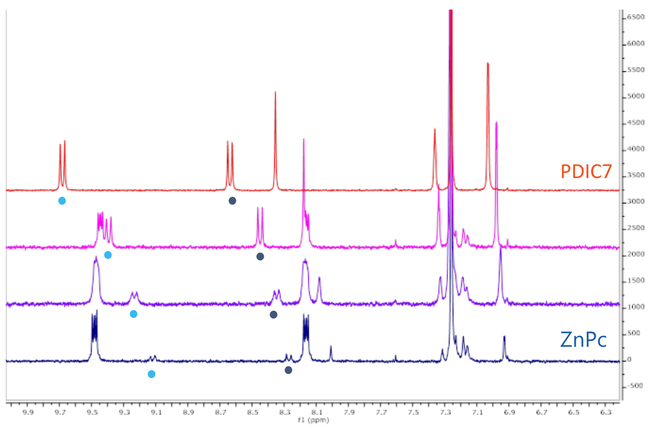
NMR ^{1}H



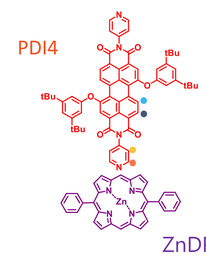
^{1}H NMR in $CDCl_3$ by addition of a **PDI** to a 11 mM solution of **ZnDPP**



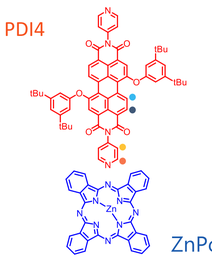
^{1}H NMR in $CDCl_3$ (+ 0,5 vol% Pyridine-D_5) by addition of a PDI to a saturated solution of ZnPc (~10 µM)



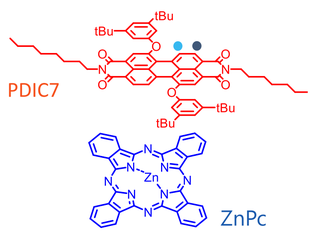
^{1}H NMR in $CDCl_3$ by addition of a $PDIC_7$ to a saturated solution of ZnPc



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

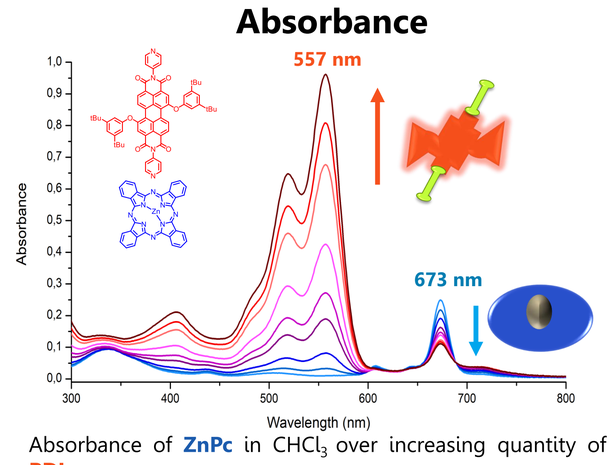


- **Competition** between **π-stacking** and **metal-ligand** binding
- Large **shift** of **perylene core** protons compare to pyridyl ones.

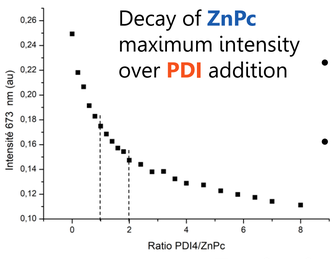


- **Only π-stacking** interaction is possible as $PDIC_7$ as no pyridyl group
- Comparable **shift** of **perylene core** protons with the PDI-ZnPc association

Absorbance

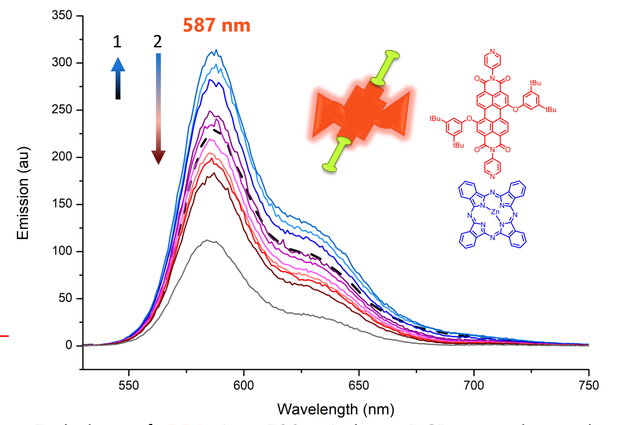


Absorbance of **ZnPc** in $CHCl_3$ over increasing quantity of **PDI**

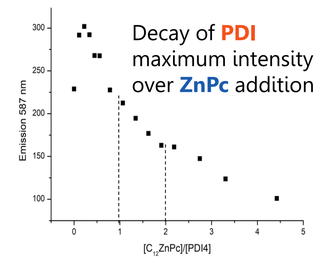


- **Intensity decay** and no wavelegnth shift
- ZnPc concentration decreasing over time

Emission



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

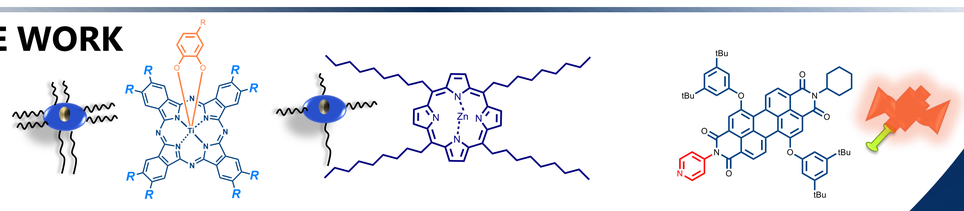


- **Intensity decay** after 0,5 eq. and no wavelength shift
- The drop of intensity are on the presented results due to a dilution effect.

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

References: **1.** *Adv. Mater.* **2016**, *28* (6), 987–988 **2.** *Mater. Horizons* **2017**, *4* (4), 570–583 **3.** *Nature* **2012**, *490* (7419), 192–200