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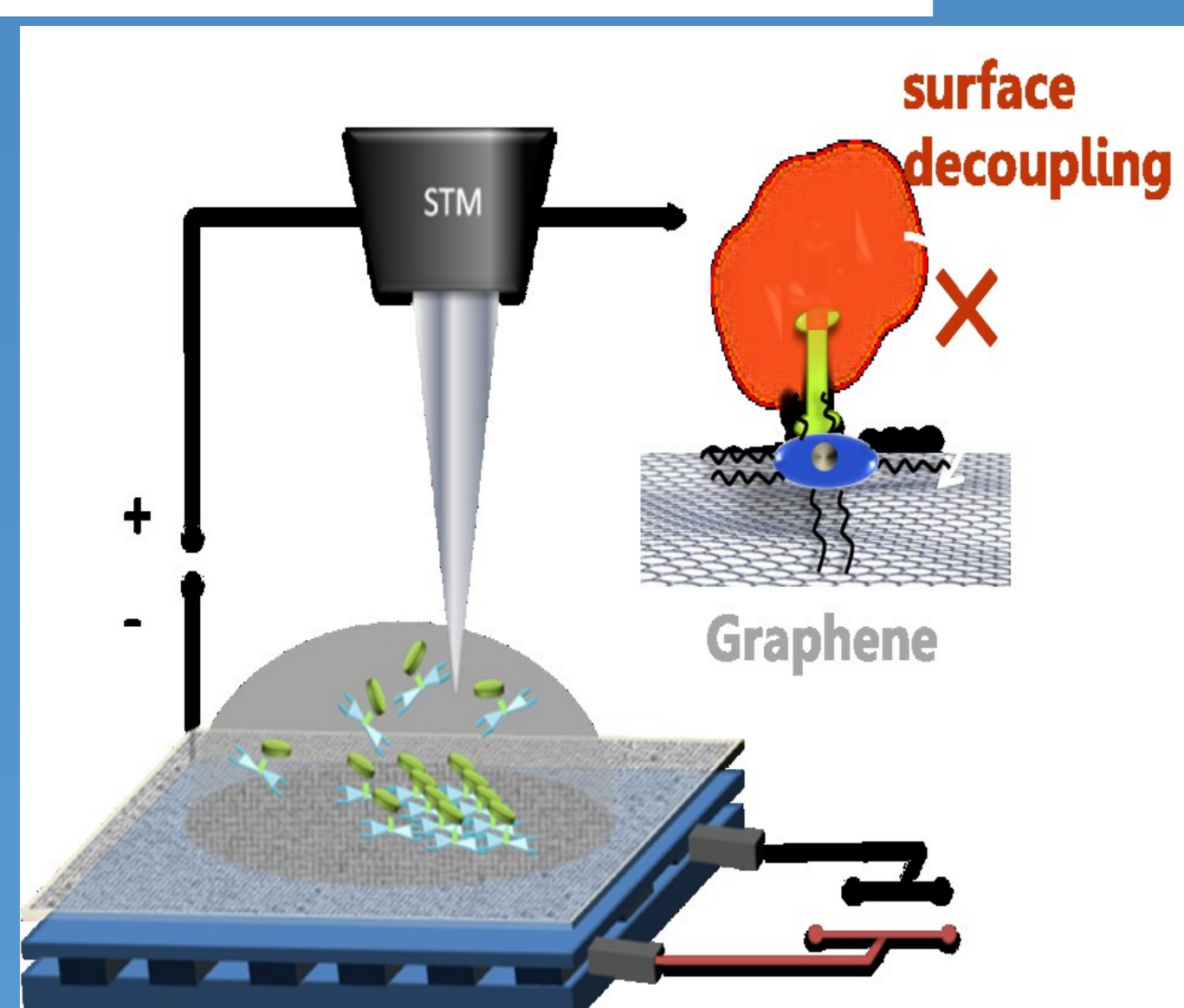
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From molecules in solution to molecules on surfaces – using supramolecular dyads to form functional self-assembled networks on graphene

Quentin Fernez^a, Shiva Moradmand^b, Michele Mattera^a, William Djampa-Tapi^c, Céline Fiorini-Debuisschert^c, Fabrice Charra^c, **David Kreher**^{a,d}, Fabrice Mathevet^a, Imad Arfaoui^b and Lydia Sosa Vargas^a

^a Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire (IPCM), F-75005, Paris, France ; ^b Sorbonne Université, CNRS, Laboratoire de la Molécule aux Nano-Objets: Réactivité, Interactions et Spectroscopies (MONARIS), F-75005, Paris, France ; ^c Université Paris-Saclay, CEA-CNRS, Service de Physique de l'état condensé (SPEC-91191), Gif-sur-Yvette, France; ^d Université Paris-Saclay, UVSQ-CNRS UMR 8180, Institut Lavoisier de Versailles (ILV), F-78035, Versailles, France

INTRODUCTION and GOALS



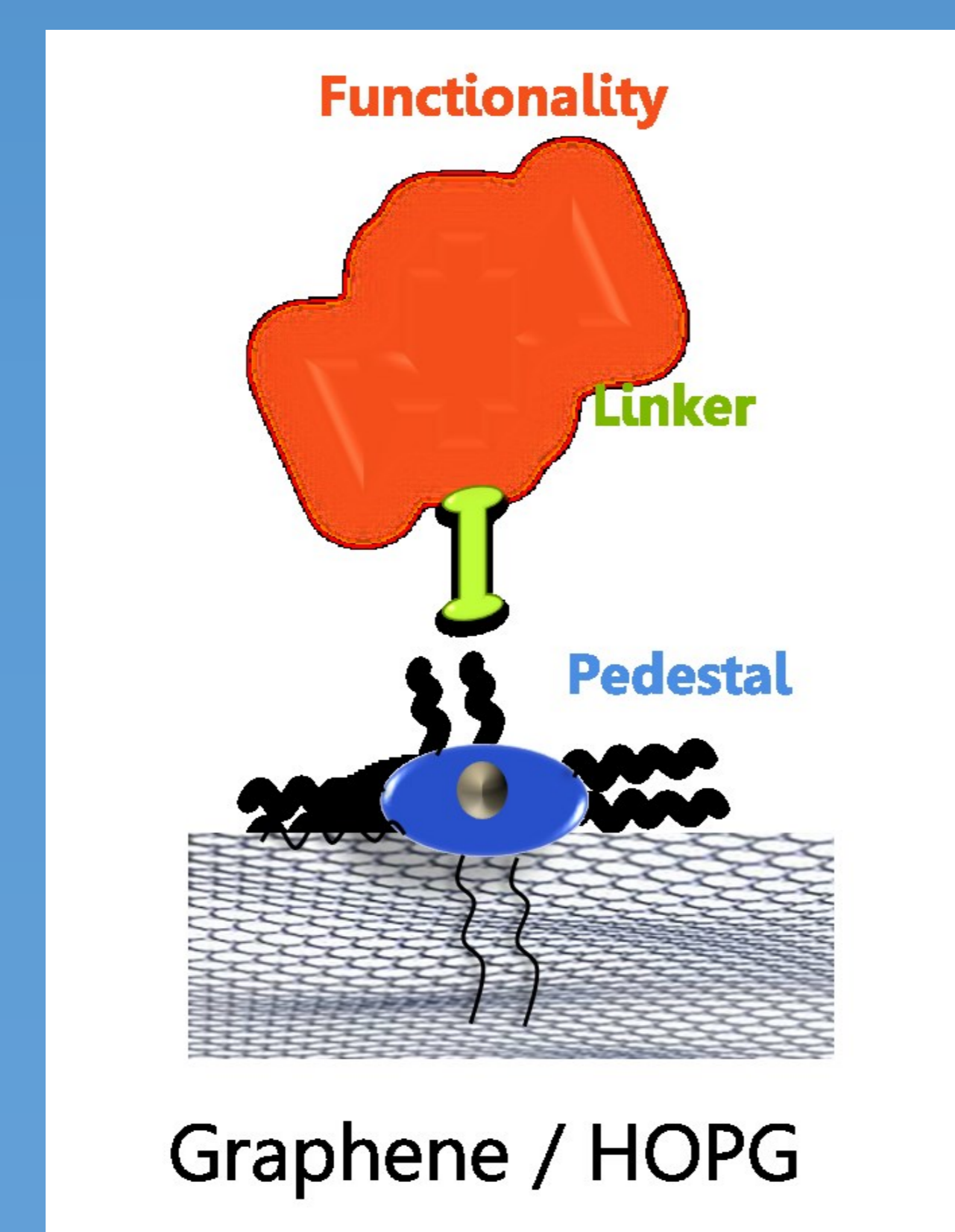
To develop new functional materials, nanoscopic scale architecture control is necessary¹. As a bottom-up synthesis strategy, molecular self-assemblies on surface have been explored, and have demonstrated good control of patterning on various surfaces². From these surfaces; graphene is of interest due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

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

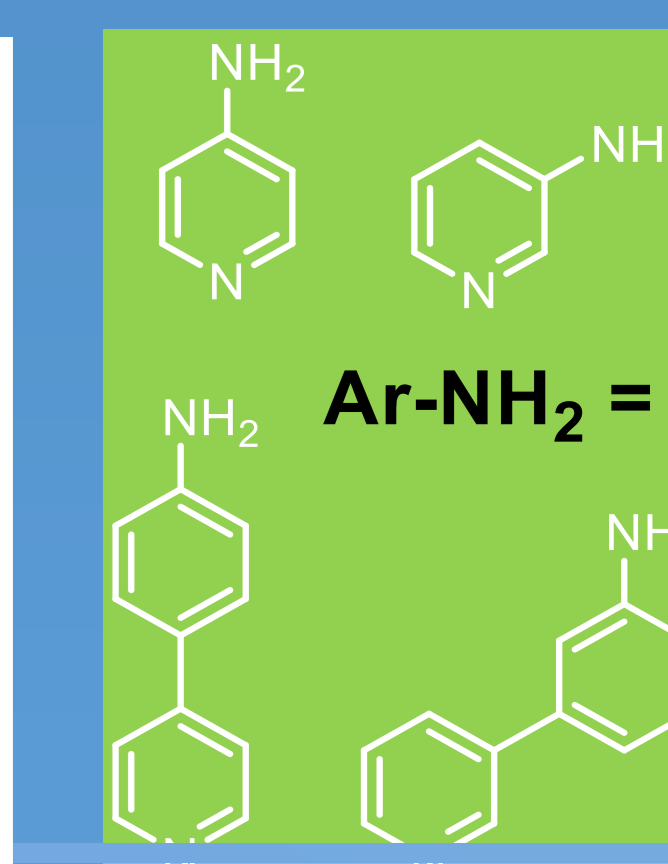
Q. Fernez et al., *J. Mat. Chem. C*, 2022, just accepted

DESIGN STRATEGY



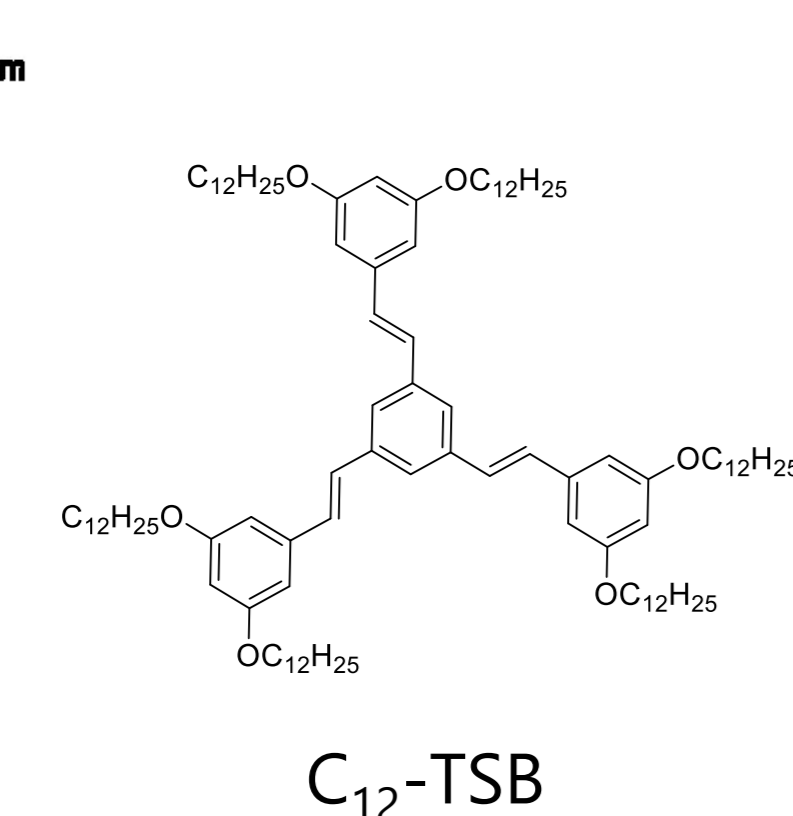
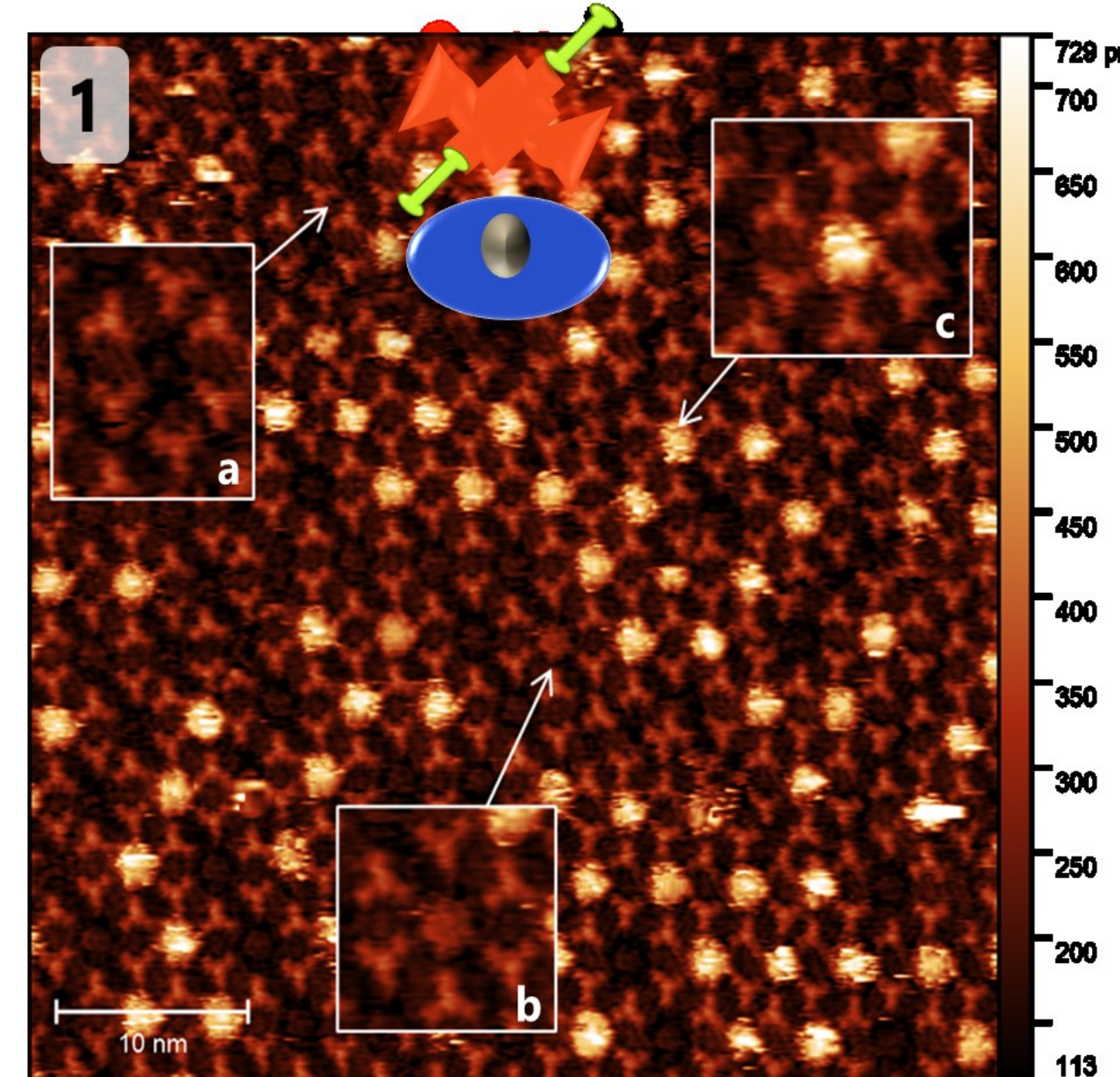
These 'smart' **building-blocks** were designed with the aim to develop a **homogeneous, functional, integrated self-assembly** on a graphenoid surface. With this molecular design strategy we are able to **fine-tune** the self-assembly, **orientation** and **functionality** via modification of:

- **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**; decouple 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.



SELF-ASSEMBLY PROPERTIES

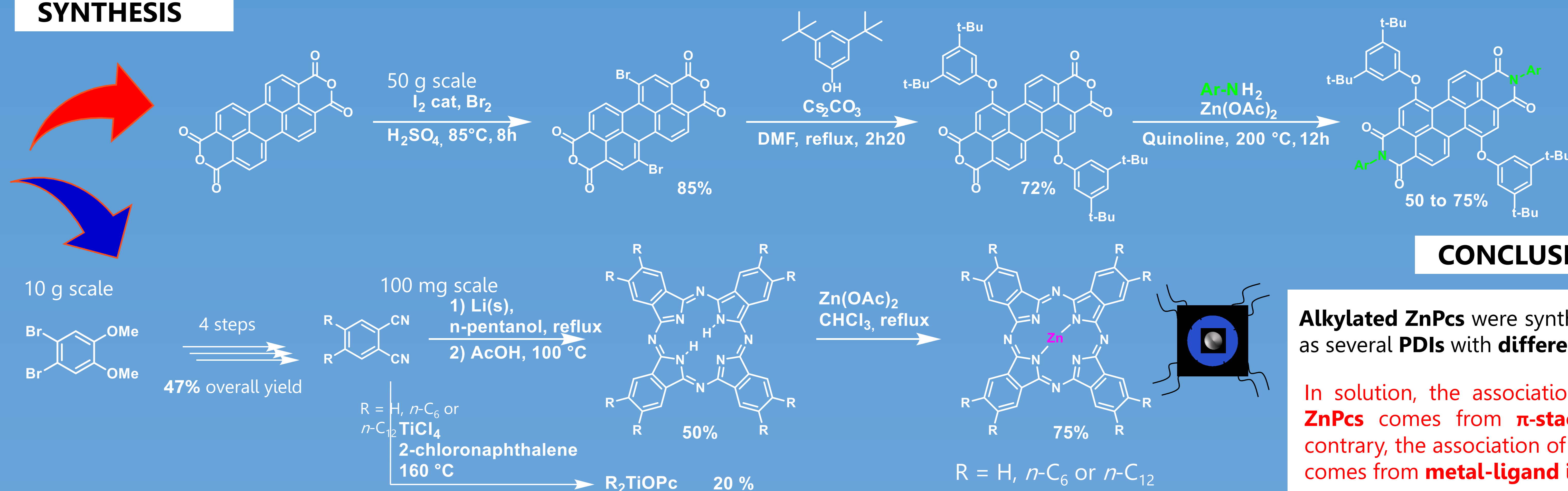
STM images are monolayers of several molecular pedestals on Highly Oriented Pyrolytic Graphite (HOPG) surfaces.



- **Host-guest network**
- **Orientation** of PDI with respect to ZnPc and HOPG surface is **unknown**
- After deposition of ZnPc-PDI (1-1) in C₁₂-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: -1,0 V, Current: 25 pA, Solid-liquid interface in phenyloctane

SYNTHESIS



CONCLUSIONS

Alkylated ZnPcs were synthesized as well as several **PDIs** with **different linkers**.

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