UNIVERSITÀ DI PAVIA

LUXEM

Laboratory for Ultrafast X-ray and Electron Microscopy

Light-activated response in colloidal dense systems with electrons and EUV scattering

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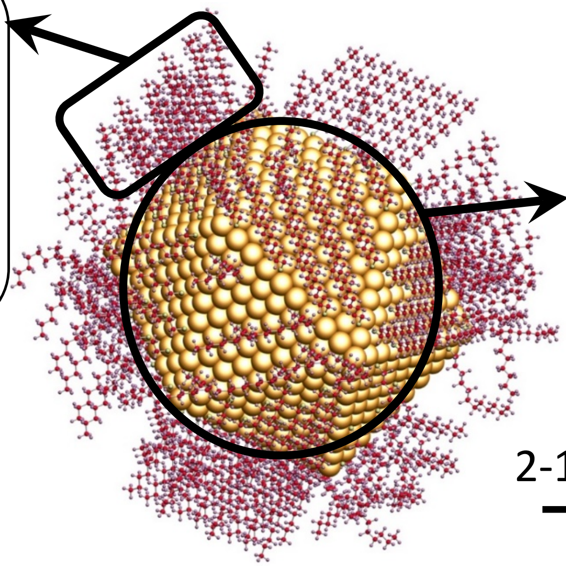
Online Workshop "Fluctuation X-Ray Scattering", EXFEL

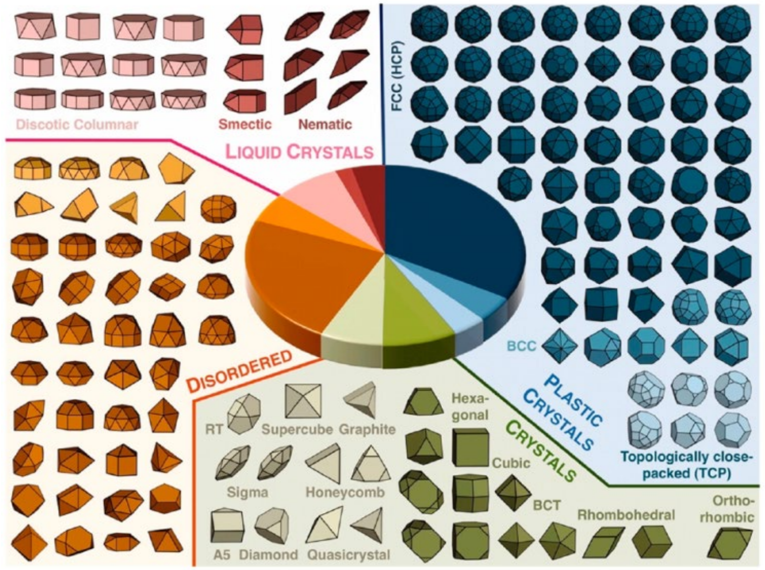
June 3rd, 2021

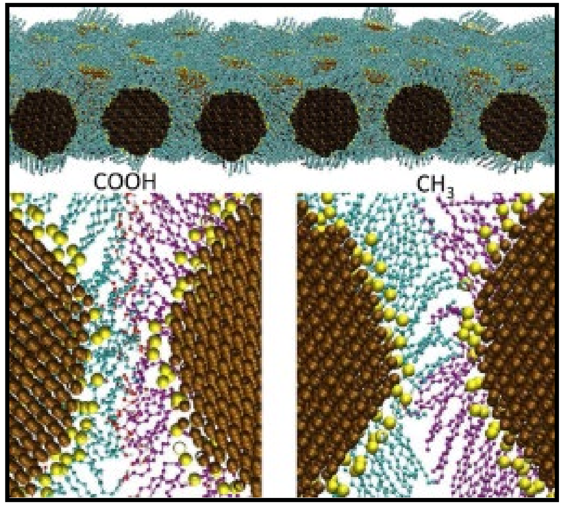
Emergent 2D & 3D nanomaterials

Tunable:
- Elastic forces
- Interaction with membrane
- Traps filling

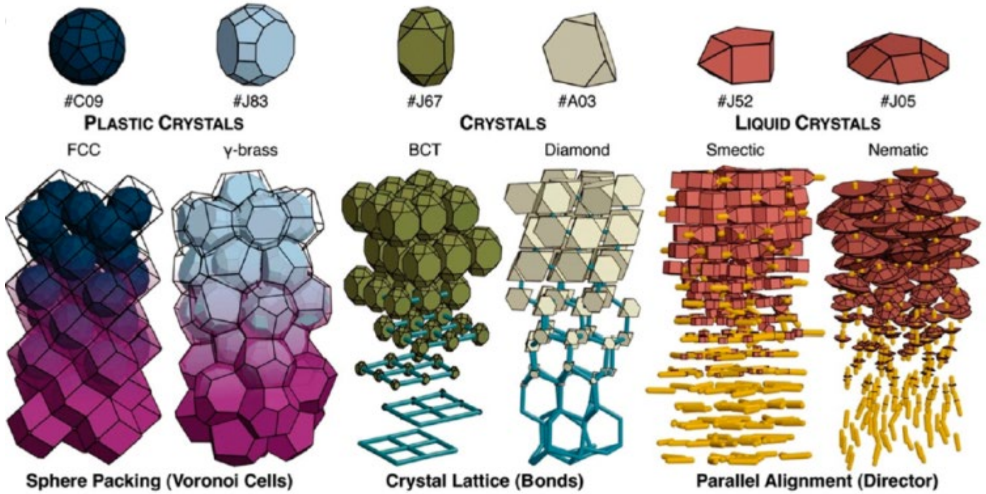


Tunable:
- Shape
- Size
- Composition





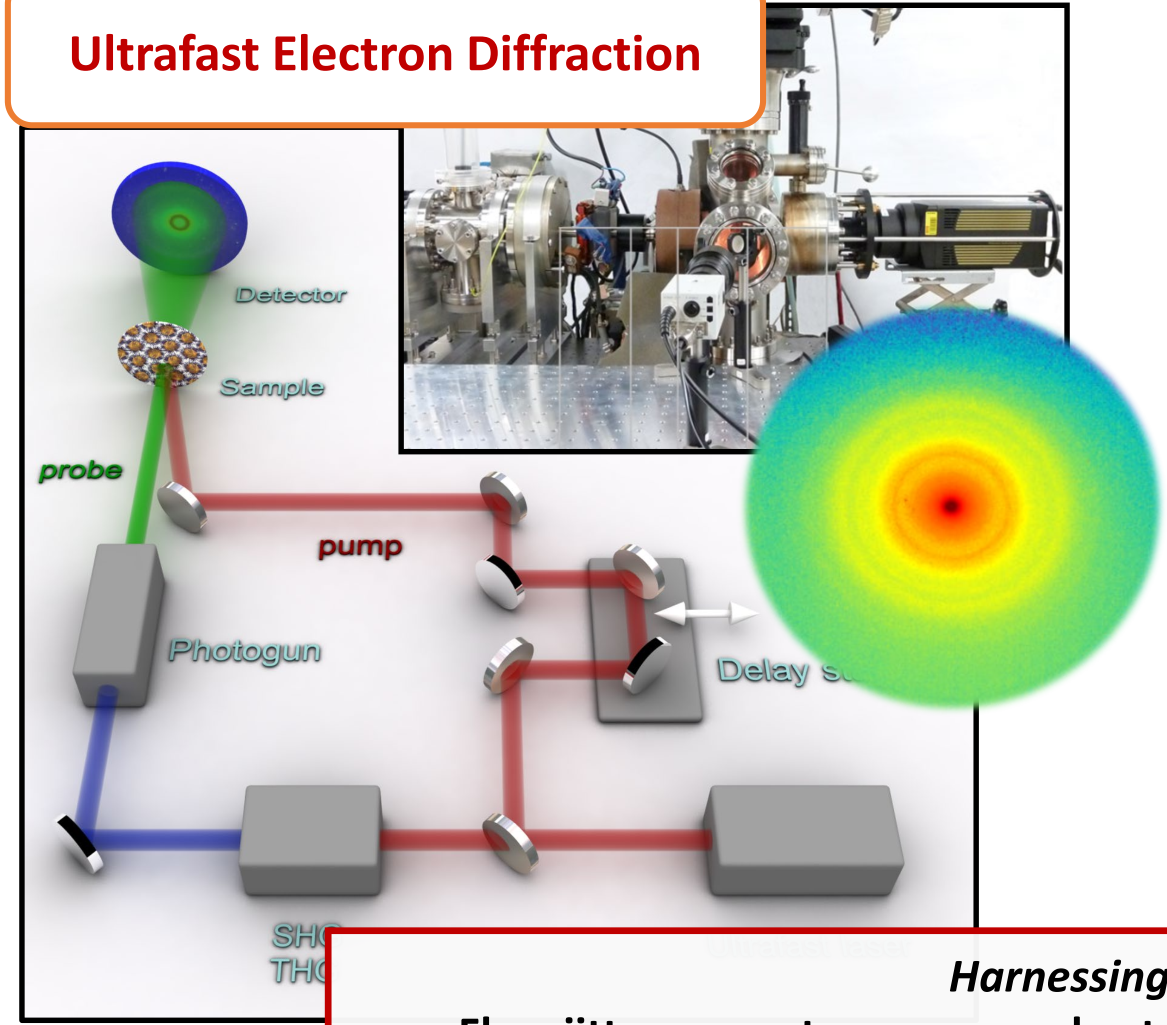
K. M. Salerno et al. Phys. Rev. Lett. 113, 258301 (2014)



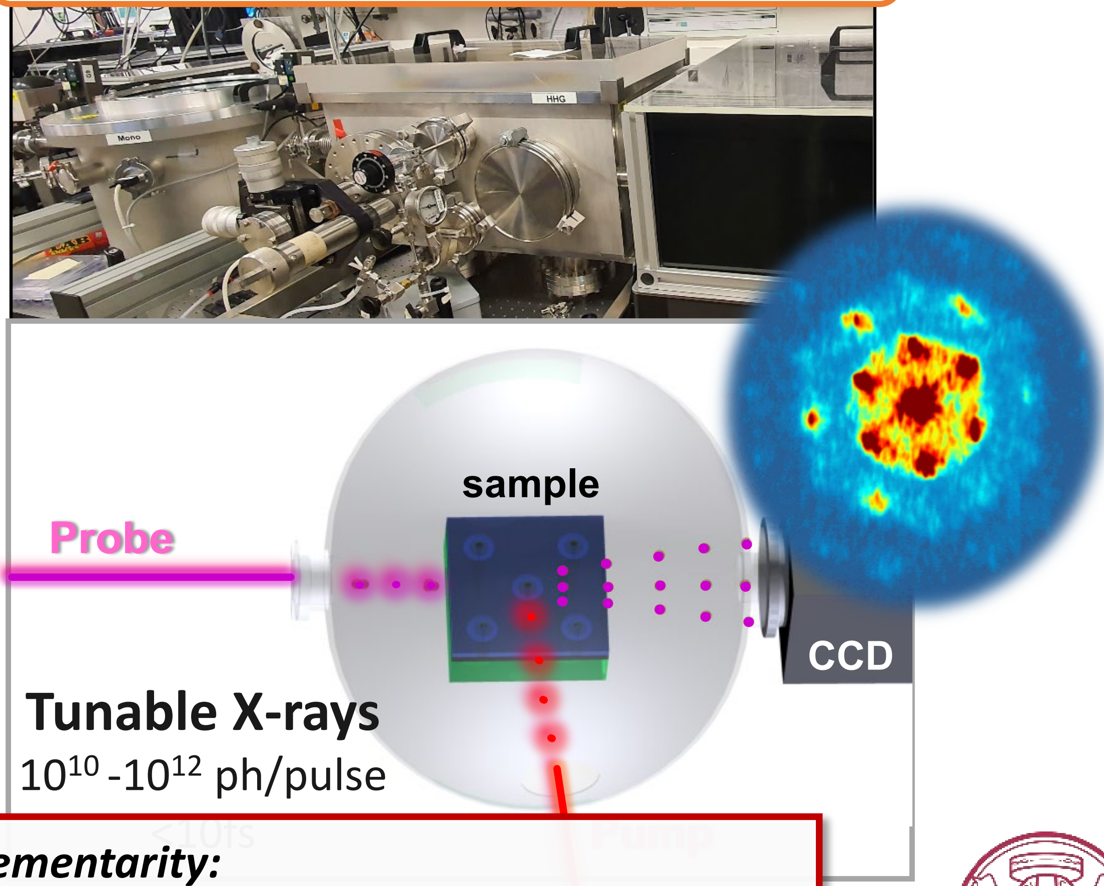
P. F. Damasceno et al., Science **337**, 453−457 (2012)

Correlative Ultrafast Methods

Ultrafast Electron Diffraction



Ultrafast EUV/soft X-ray Microscopy



Tunable X-rays

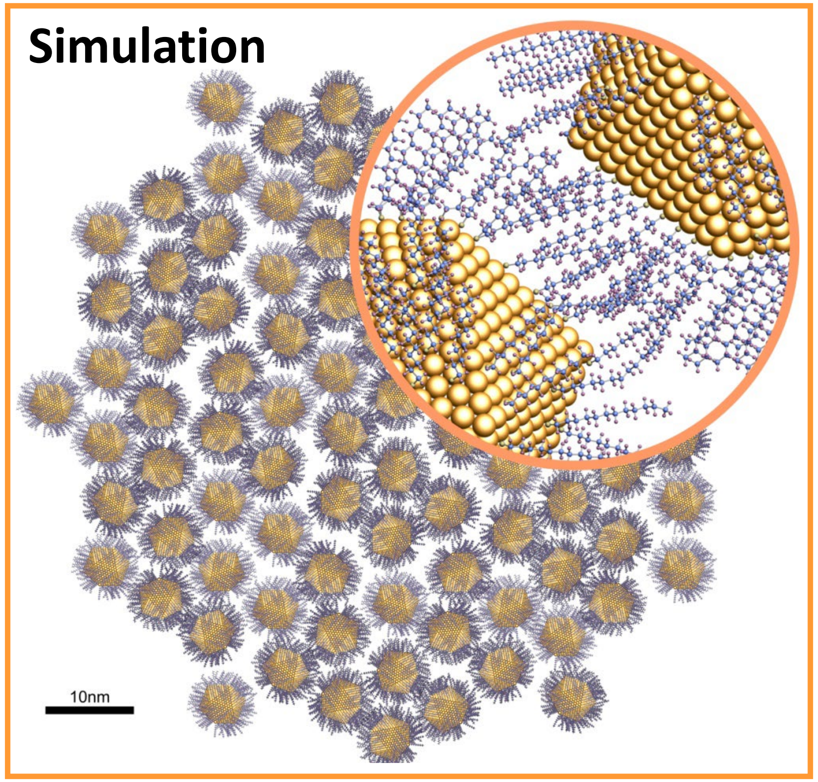
10^{10} -10^{12} ph/pulse

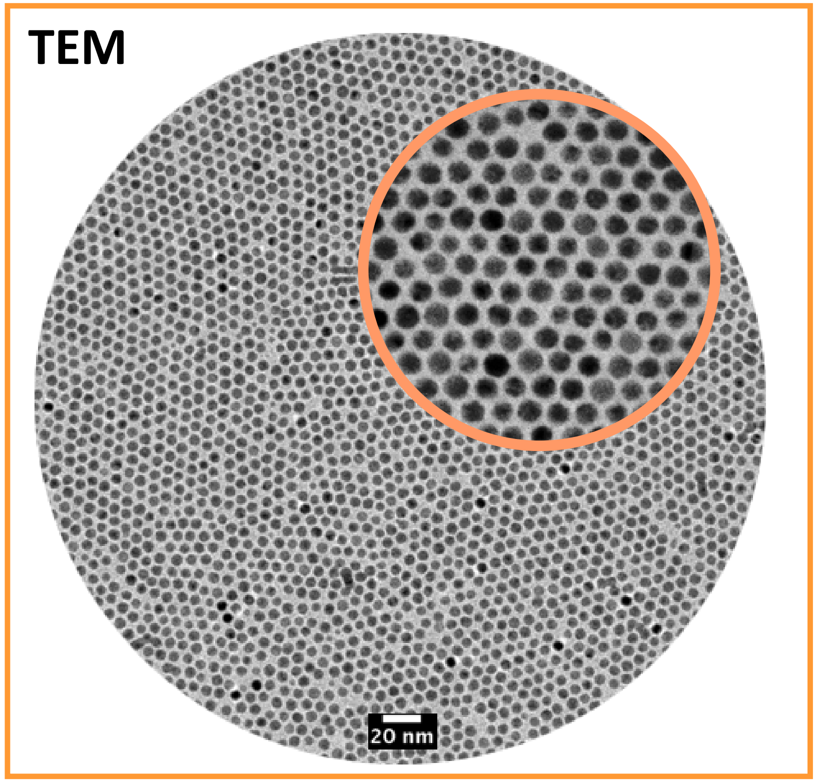
Harnessing Complementarity:

Flux, jitter, rep-rate, energy, pulse-to-pulse stability, cross-section to elements…

Visualization of ligands order

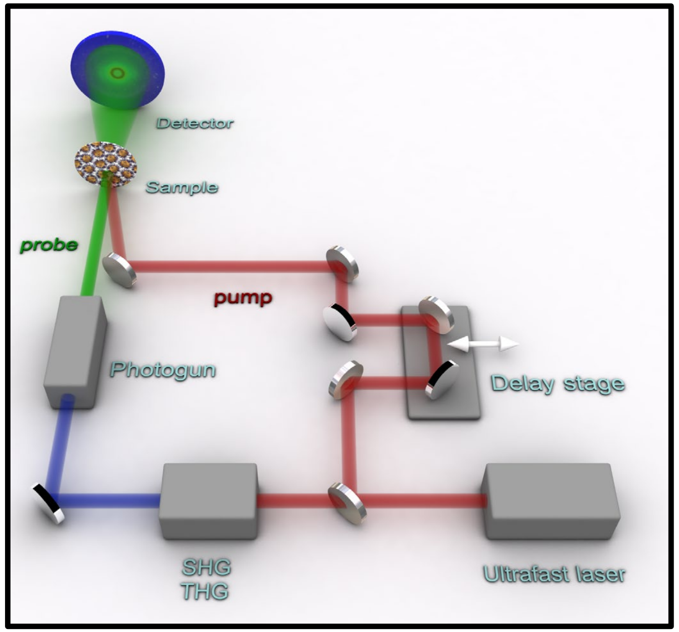
- **Dynamical interplay** between **elastic forces** and **ordering-disordering phenomena**
- 2D supracrystals ➡ **disordered elastic media**:
  - Elastic forces dependent on the ligands chemical and structural properties.



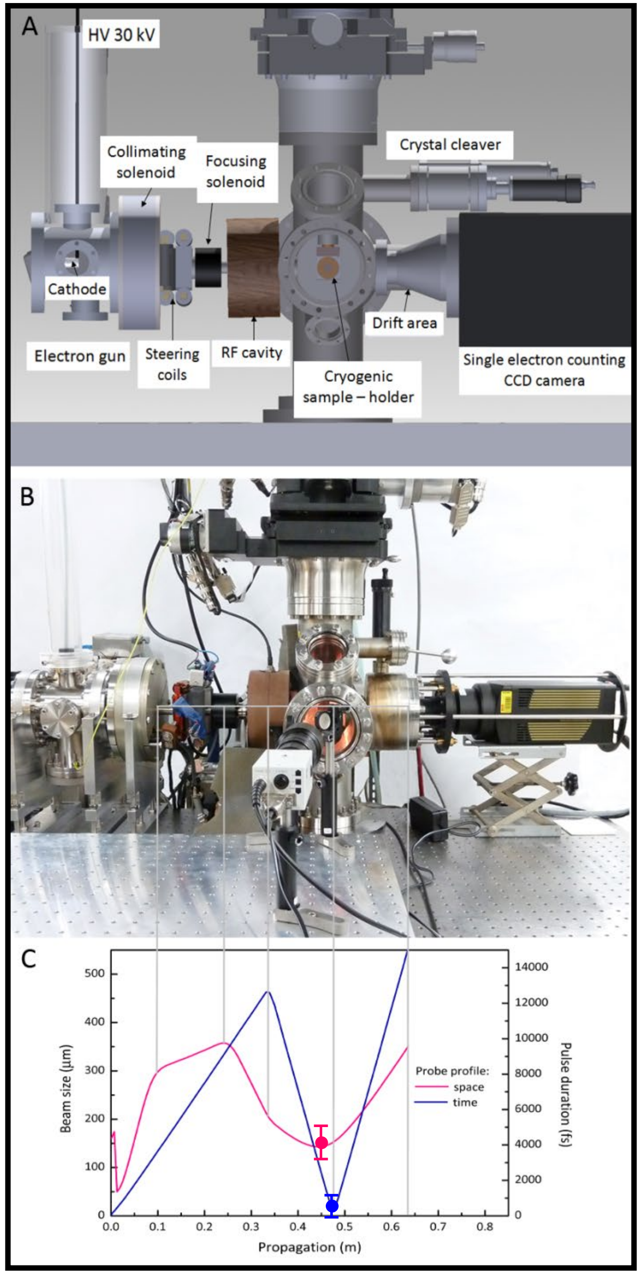


G. F. Mancini et al., NanoLett. **16** 2705 (2016)
G. F. Mancini et al., in review in Phys. Rev. Lett. (2018)
T. Latychevskaia, G. F. Mancini and F. Carbone, Sci. Rep. **5**, 16573 (2015)

Ultrafast Electron Diffraction



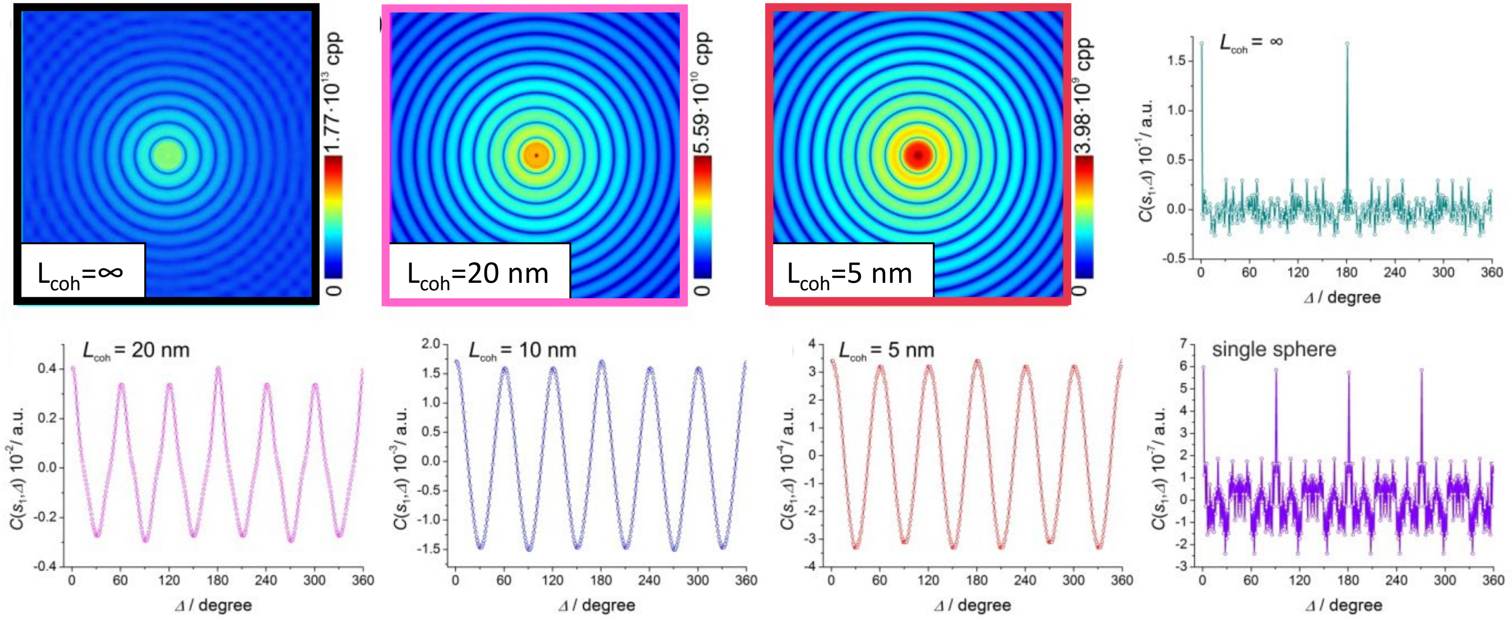
G. F. Mancini *et al.*, *Nucl. Instrum. Methods Phys. Res. A* **691**, 113 (2012)

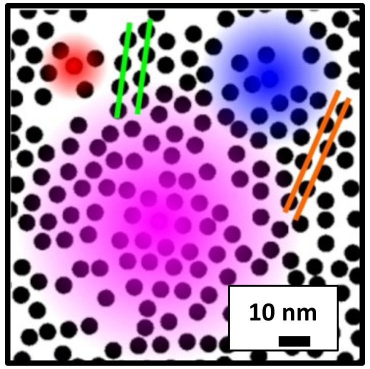


- High-flux UED: 10^9 e^- /sec
- < 250 fs time-resolution
- 10^5 electrons per pulse @ 30 keV
- 20 kHz rep-rate
- 160 µm e^- spot-size on the sample
- Transverse coherence length of e^-: ~ 5 nm

Partially coherent electrons

Mathematical explanation: **in a dense aggregate, it is sufficient that the coherence length is comparable to the NP size to be able to retrieve real-space information from diffraction**

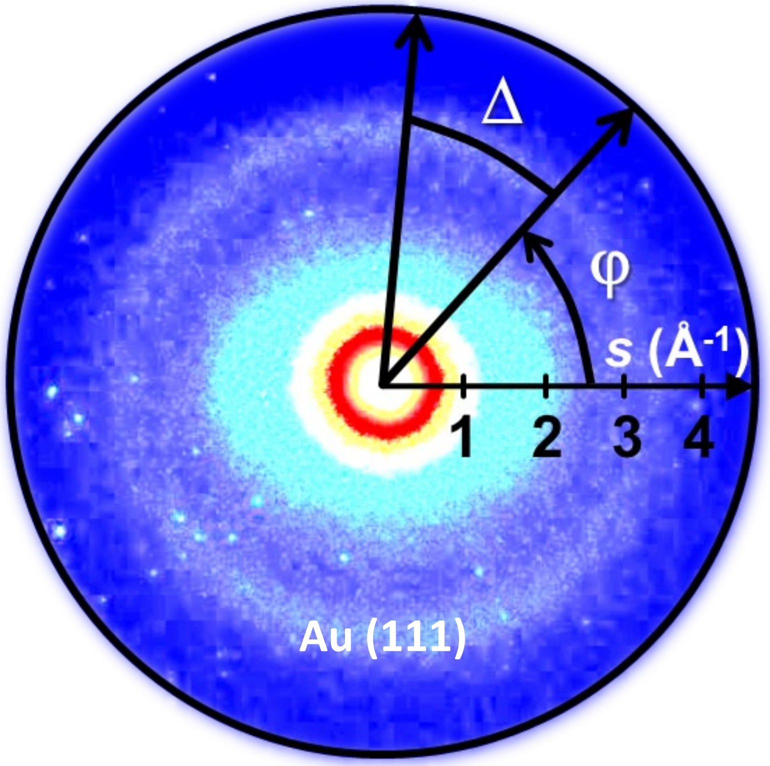




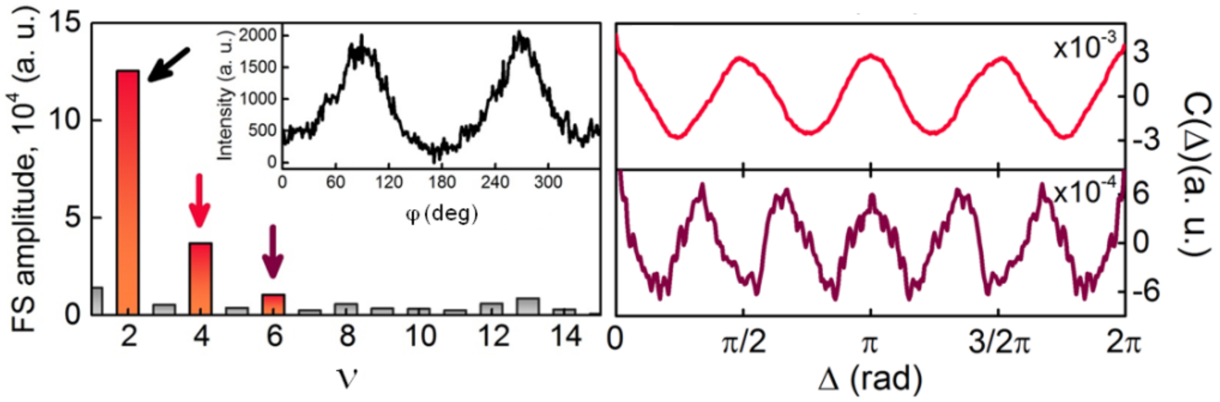
Latychevskaia, Mancini and Carbone, Scientific Reports **5**, 16573 (2015)

- ✓ Even at low coherence interference **effects among particles are not negligible**
- ✓ Infinite coherence smears out the diffraction peaks
- ✓ The **amplitude** of the **CCF** is a measure of the **degree of order** in the system

Fourier Cross-correlation analysis



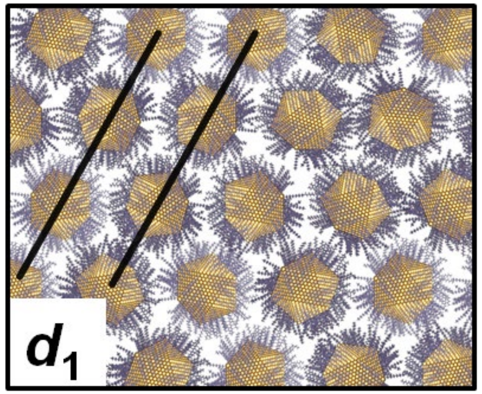
$$C(\Delta) = \langle I(s,\varphi) I(s,\varphi+\Delta) \rangle_{\varphi} = \mathrm{Re}\left(F_{\varphi}^{-1} \left(\left| F_{\varphi} \{ I(s,\varphi) \} \right|^{2} \right) \right)$$

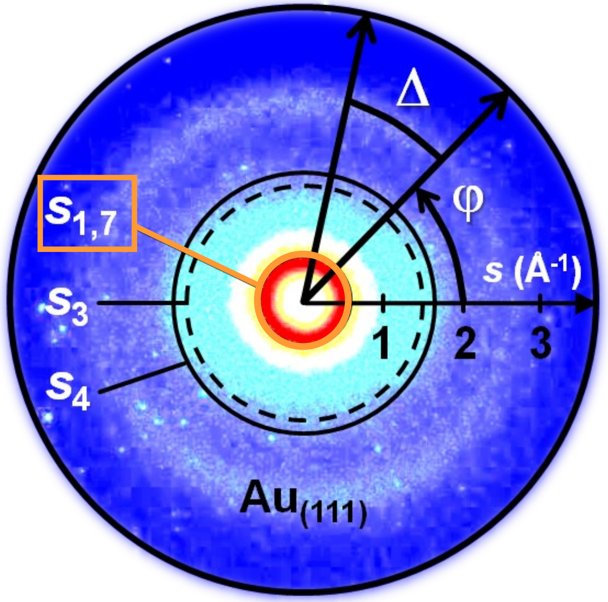


Diameter = 5.16 ± 0.58 nm
C12 ligand length = 1.56nm

Sample modulations & substrate effects are separated

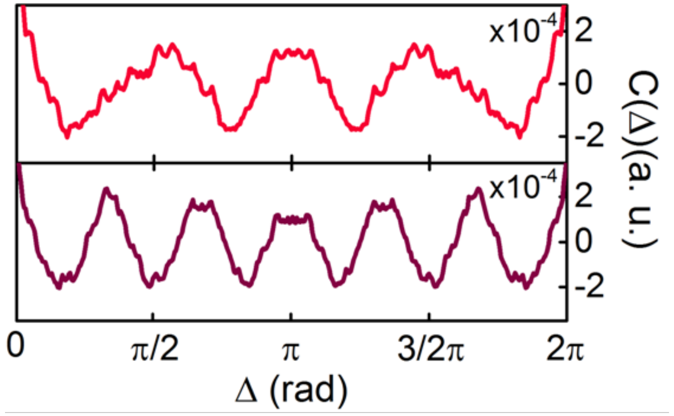
NP distribution in the supracrystal



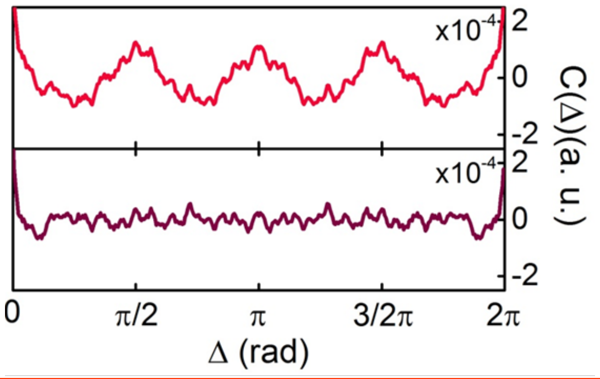


$s_{1,7}$= 0.66 Å^{-1}

Supracrystal

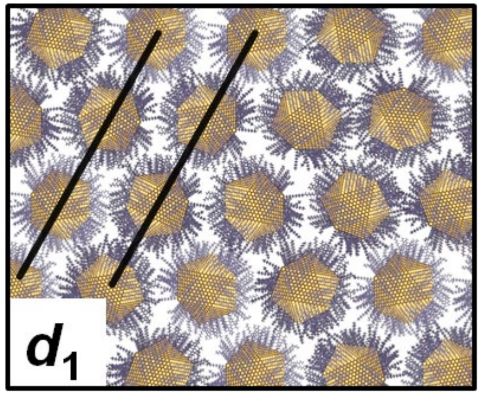


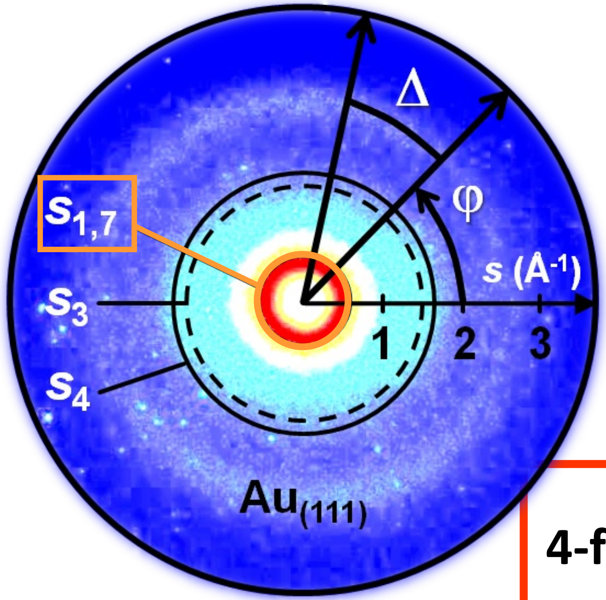
Substrate



The **modulations** are assigned to either the scattering of electrons from the **sample or** the **substrate**

NP distribution in the supracrystal





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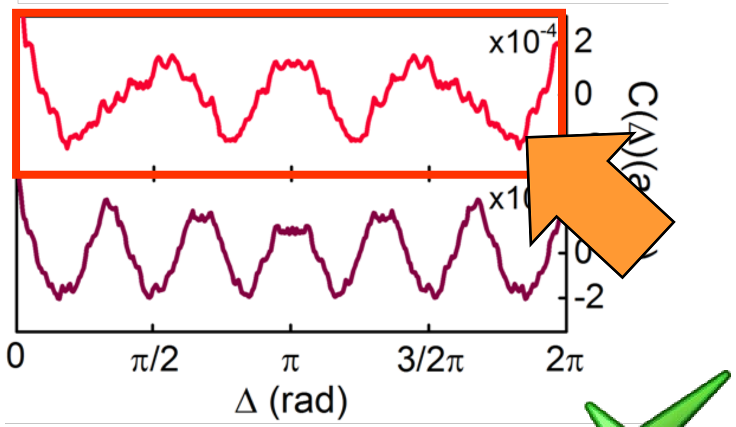
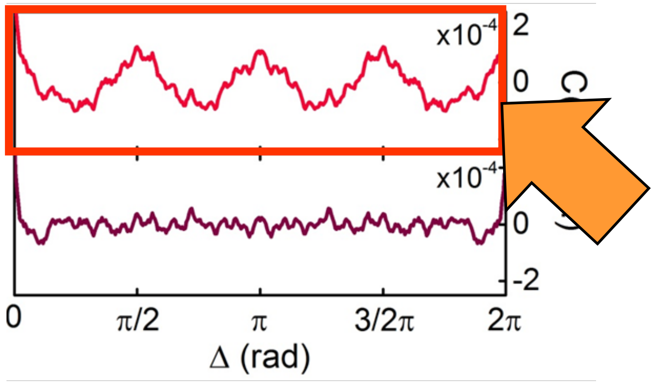
Supracrystal

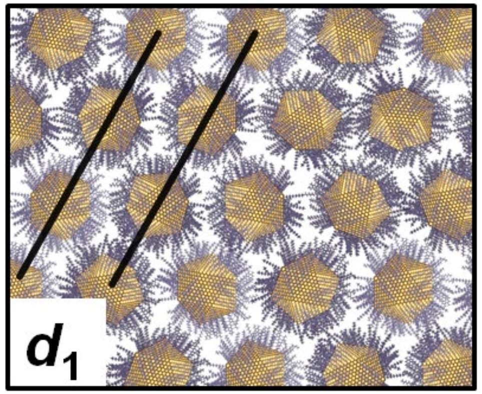


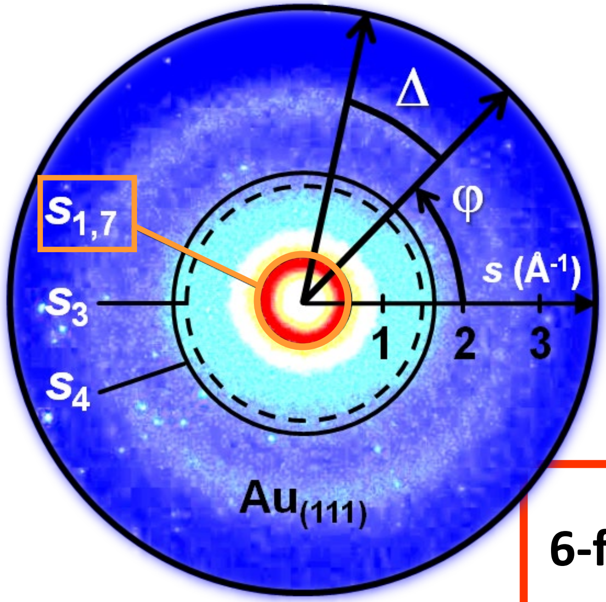
Substrate



4-fold symmetry → **Tetragonal arrangement** of the **amorphous carbon** in the **substrate**

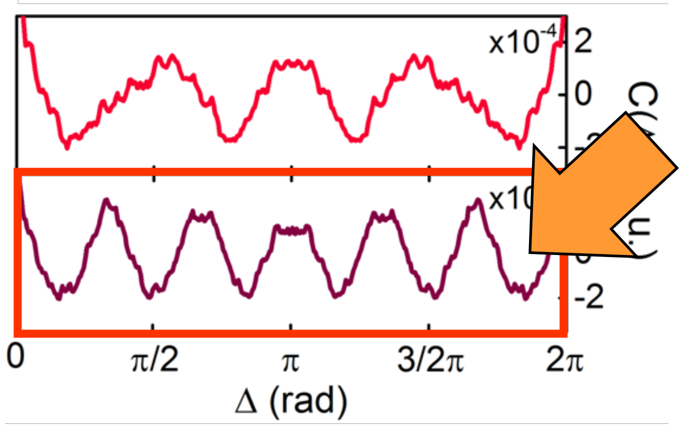
NP distribution in the supracrystal



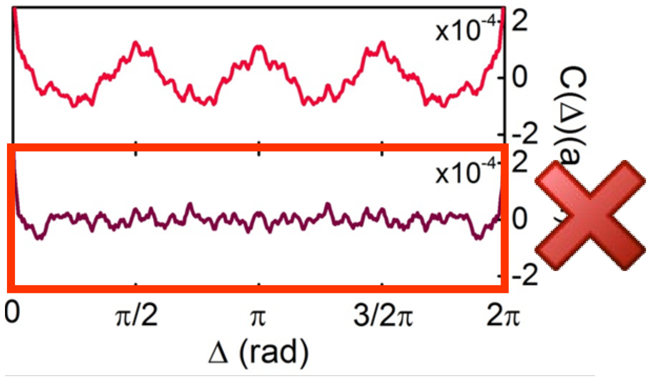


$s_{1,7}$= 0.66 Å^{-1}

Supracrystal

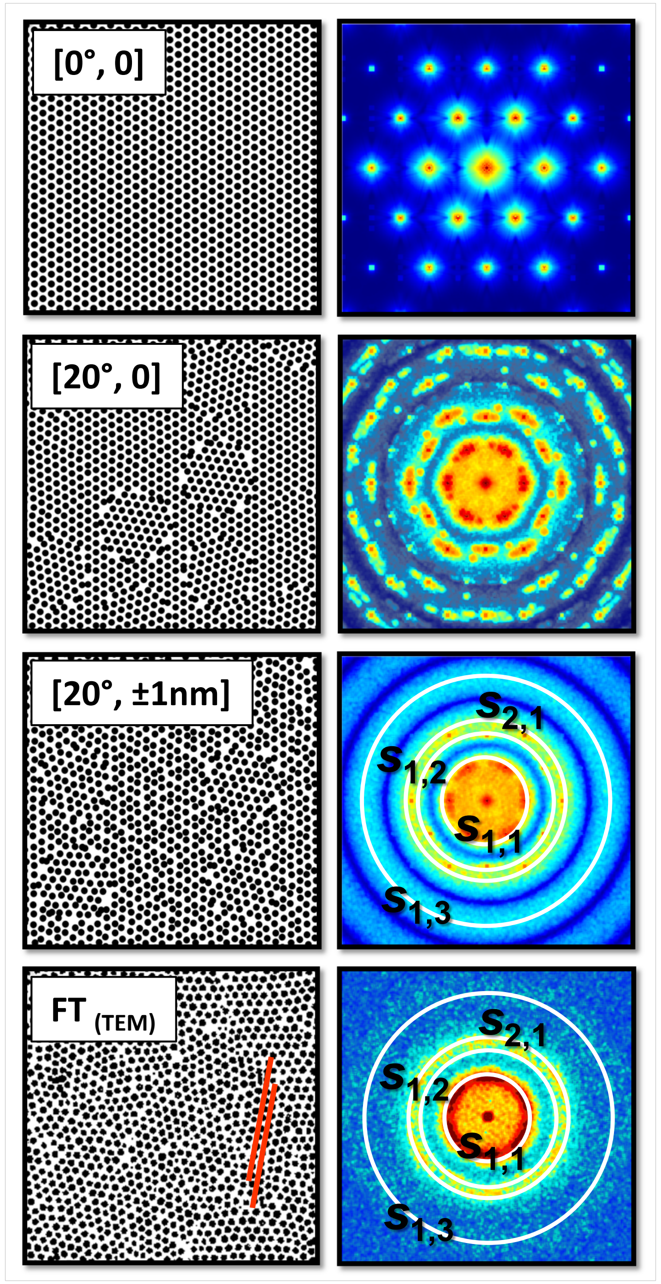


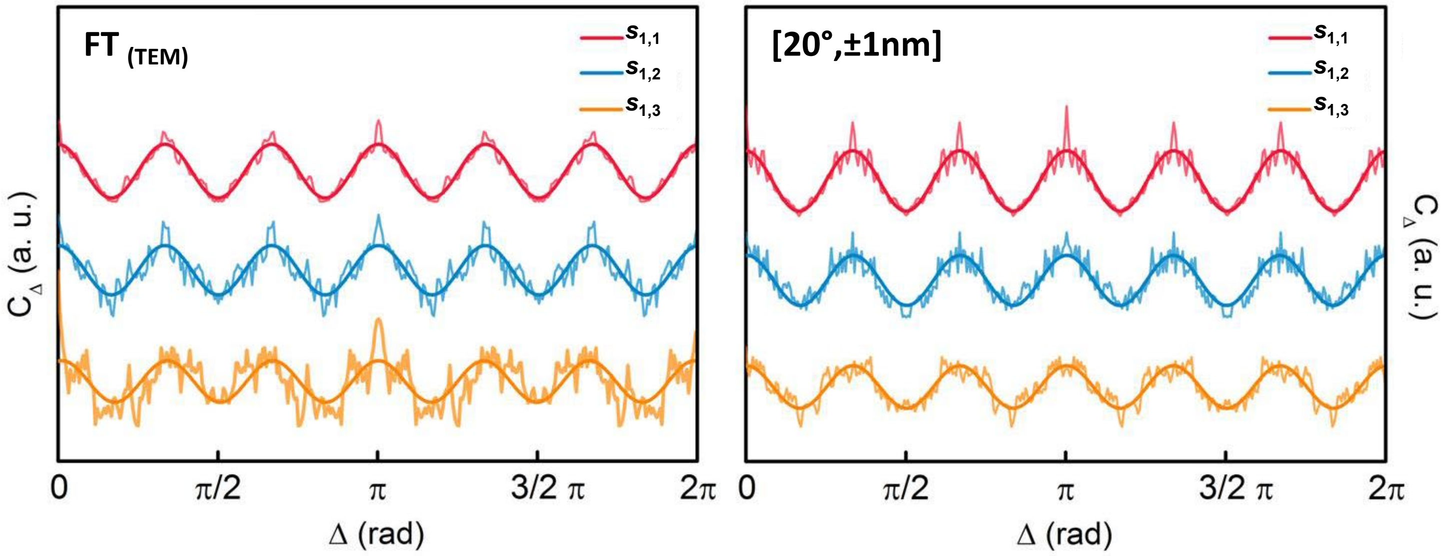
Substrate



6-fold symmetry ➡ **Hexagonal arrangement** of the **NPs** in the **supracrystal**

Supracrystal structure



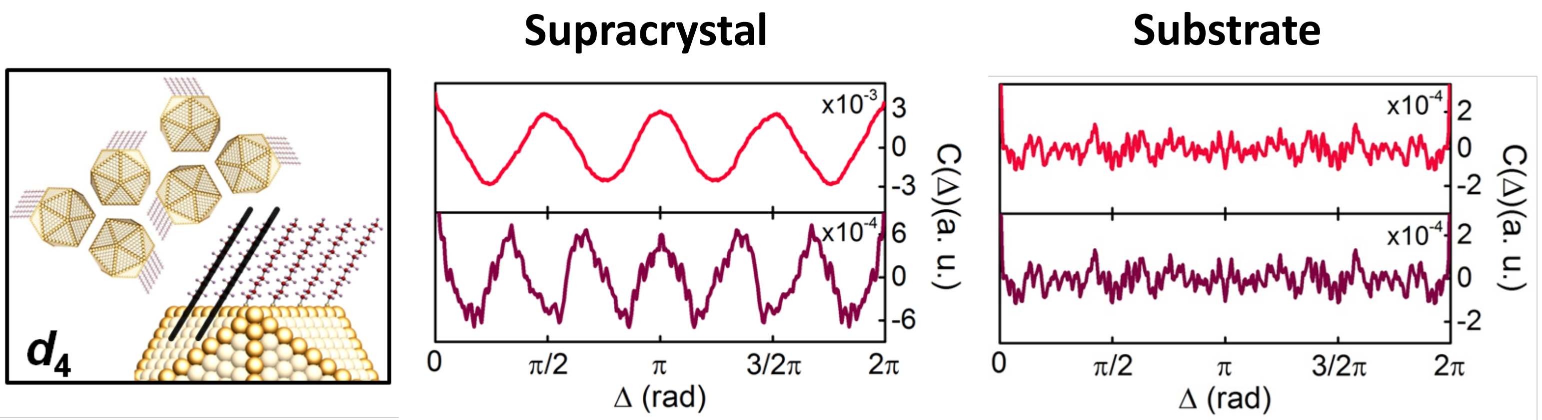


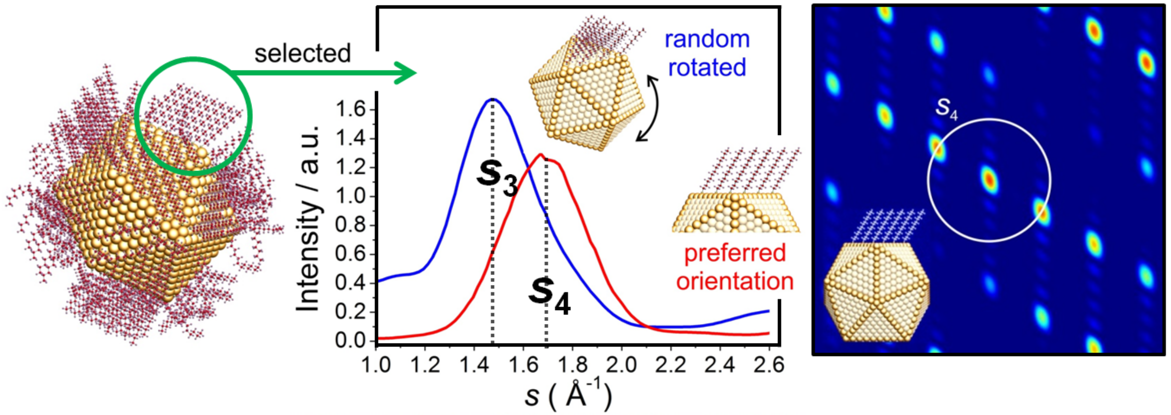
Core-core distance: d =7.63 nm
Diameter of NP: ϕ = 5.7nm

$\boldsymbol{d_1}$=6.61 nm, $\boldsymbol{d_2}$=3.82nm

C12 ligands: preferential orientation

s_4=1.68Å^{-1}
d_4=3.72Å

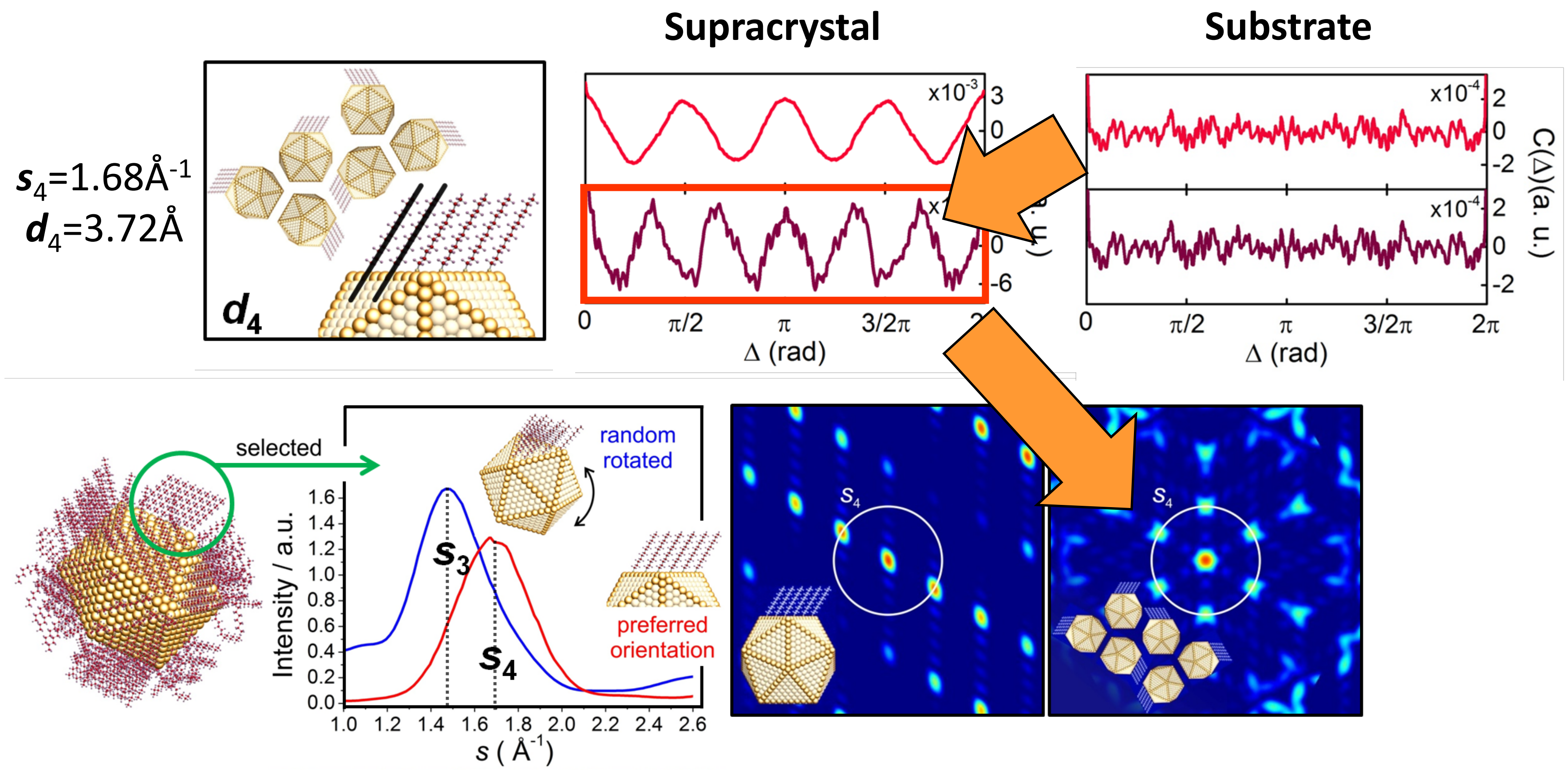




Preferential ***trans*** ligands **orientation**:

2 peaks in diffraction.

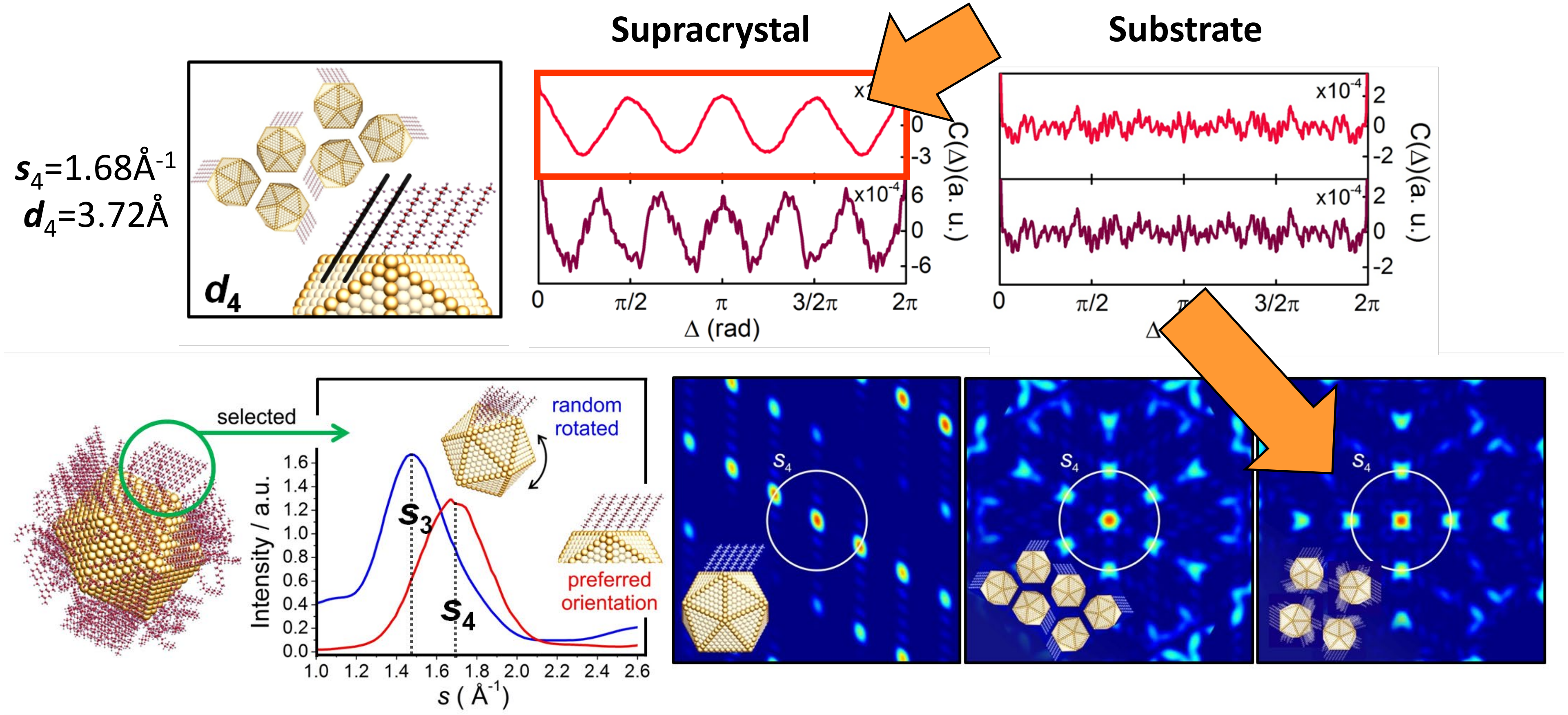
C12 ligands: preferential orientation



NPs arranged in a **hexagonal lattice**:

6 possible orientations of the NPs in the sample plane.
3 possible orientations of bunch of **ligands**:
six peaks in the diffraction pattern.

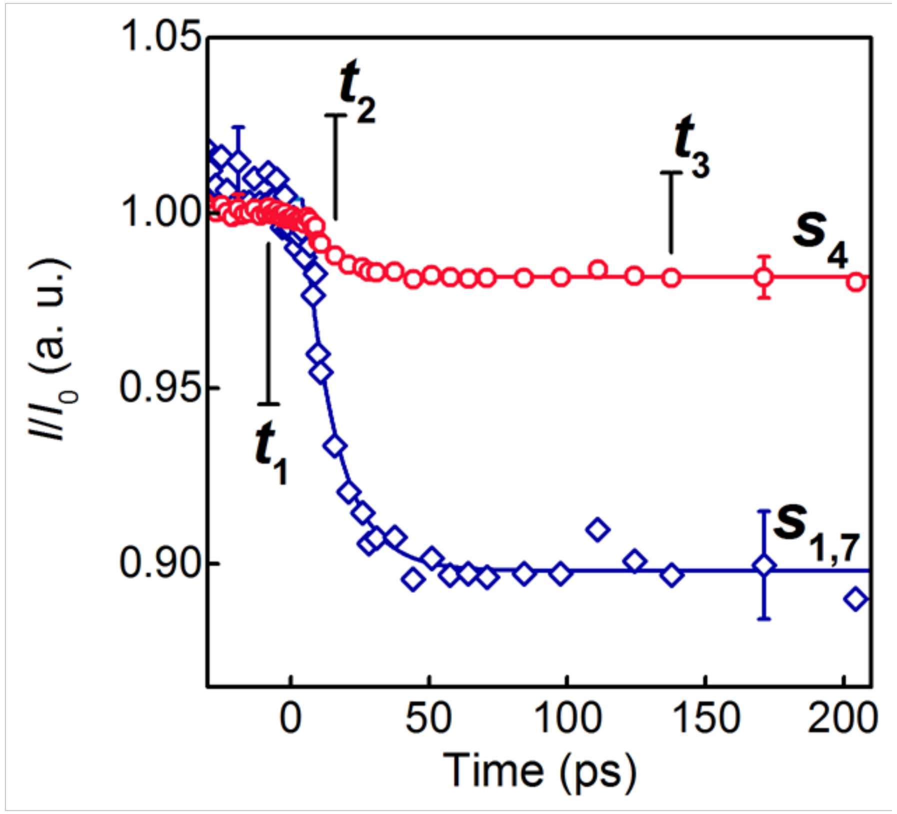
C12 ligands: preferential orientation



NPs arranged in a **tetragonal lattice**:

2 possible orthogonal **orientations** of the bunch of ligands: **4 peaks** in the diffraction pattern.

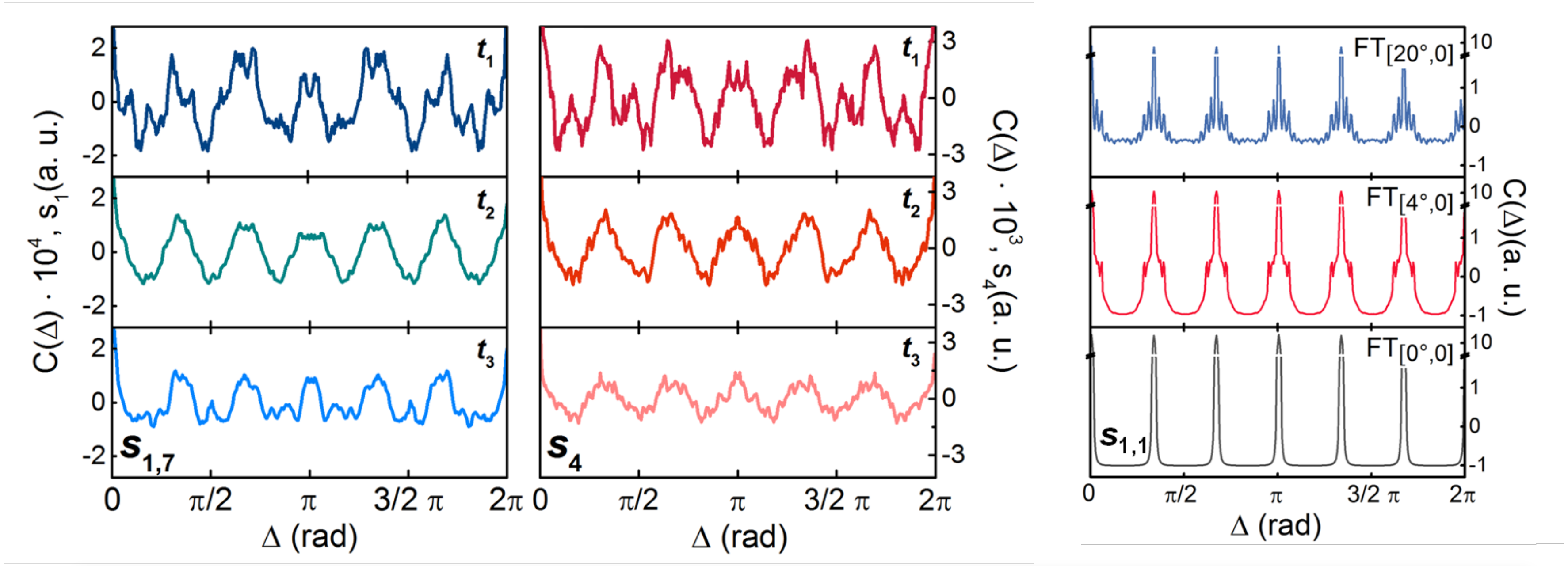
Ultrafast Dynamics: photo-induced disorder

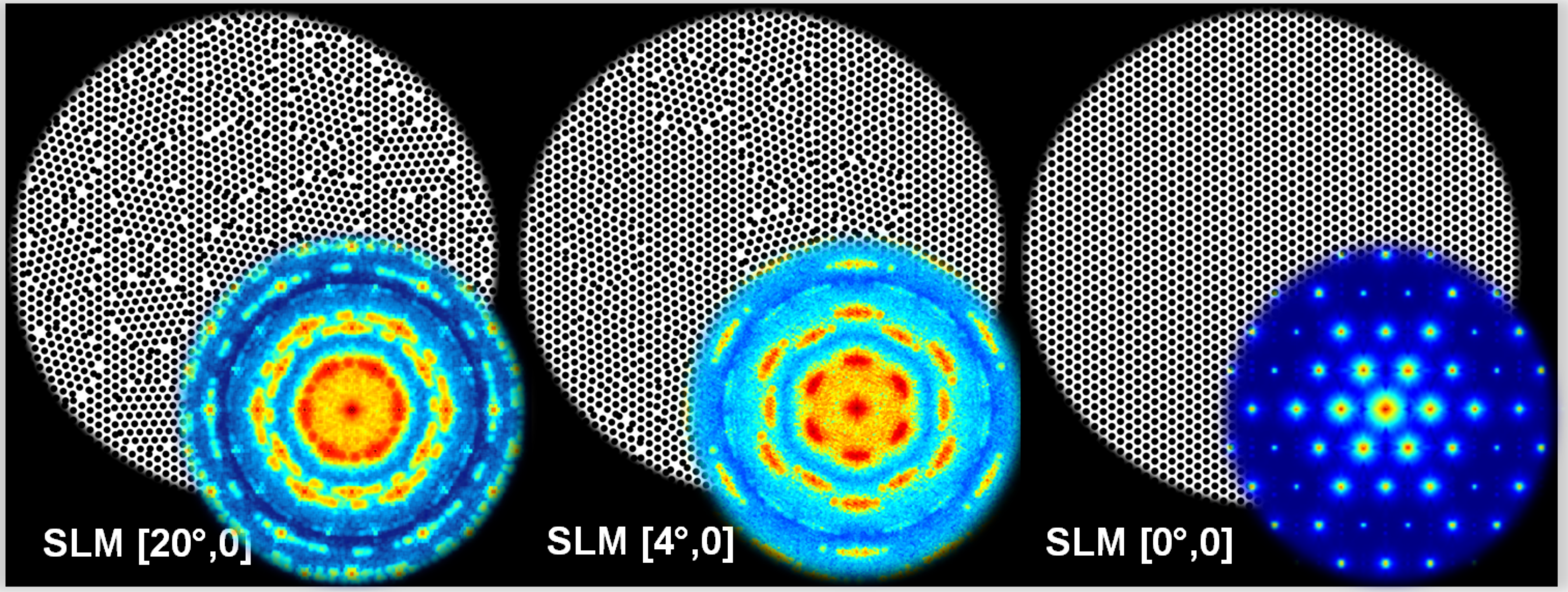


- $s_{1,7}$: 10% intensity drop
- s_4: 2% intensity drop

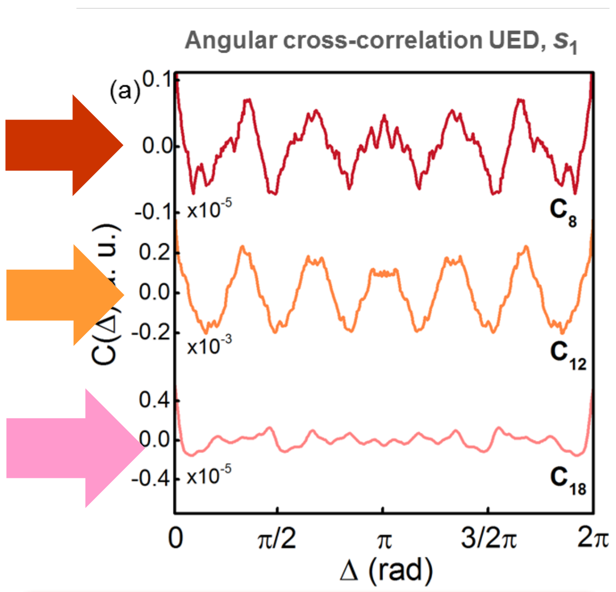
Although the **NPs** are slightly **rearranging** themselves, the **ligands** on their surfaces **preserve** the preferential **arrangement**!

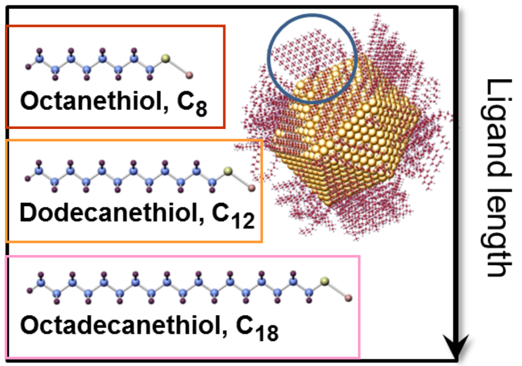
Ultrafast Dynamics: annealing

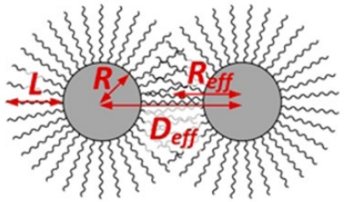




Model for 2D melting

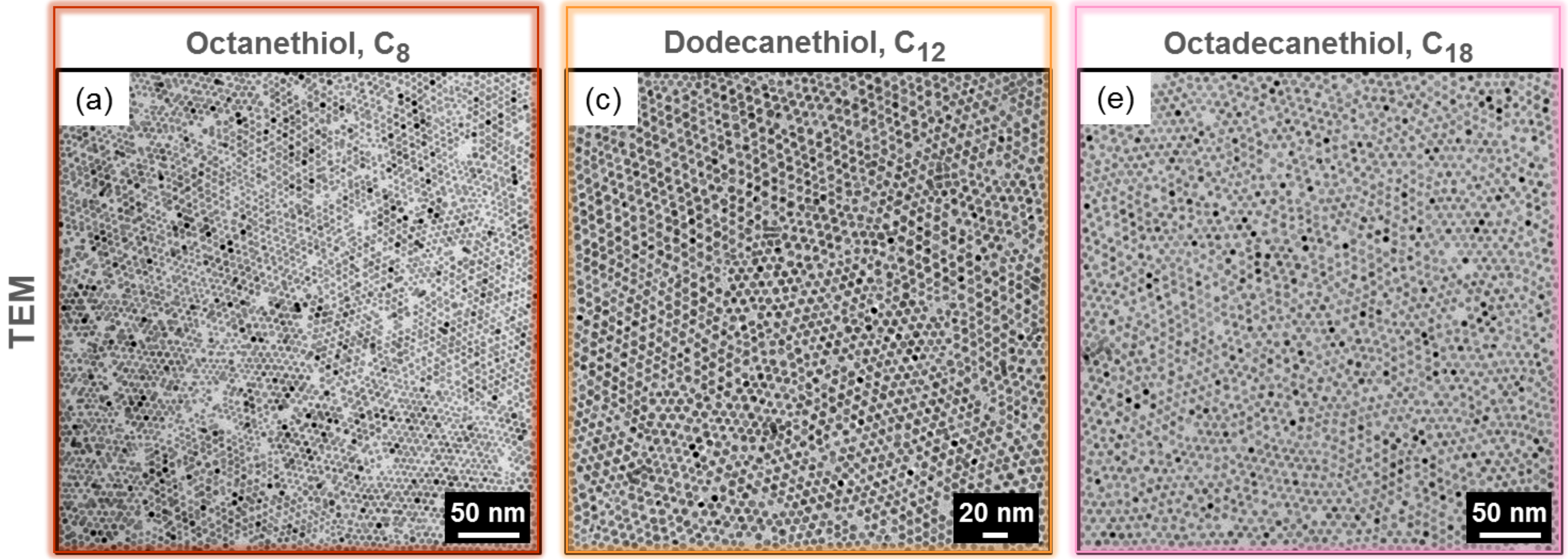






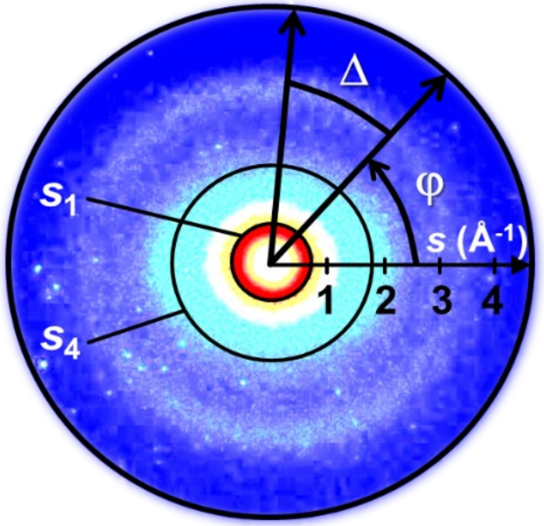
Competition between **Van der Waals** attractive interactions **and entropic** repulsive **forces**

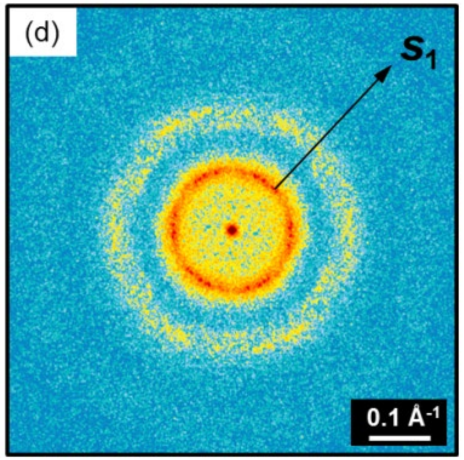
J. Y. Kim et al., Nano Lett. 16, 1352–1358 (2016)



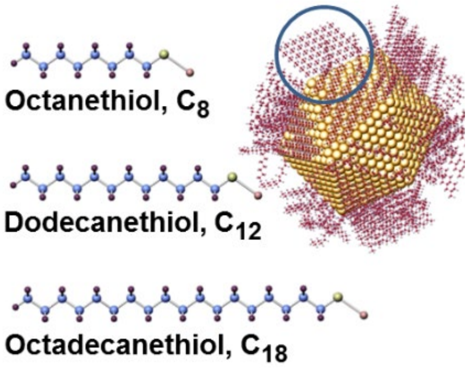
Ligand-length dependent correlations

UED exp

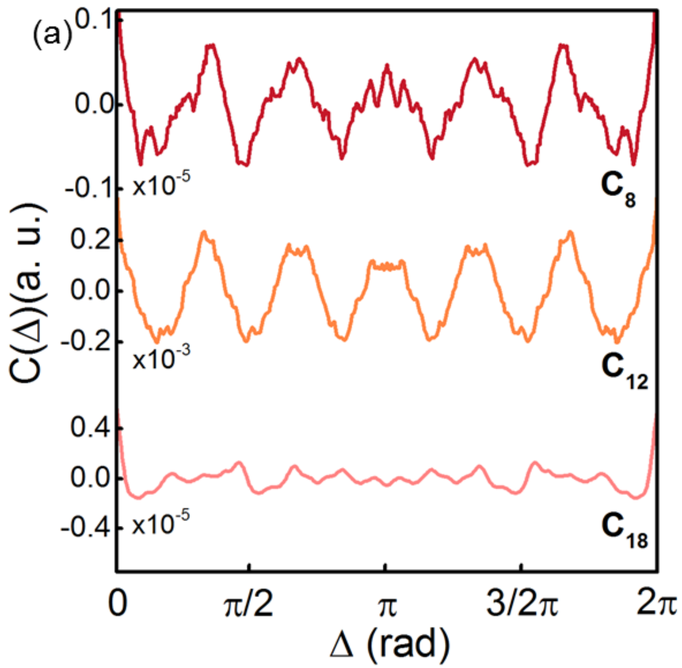




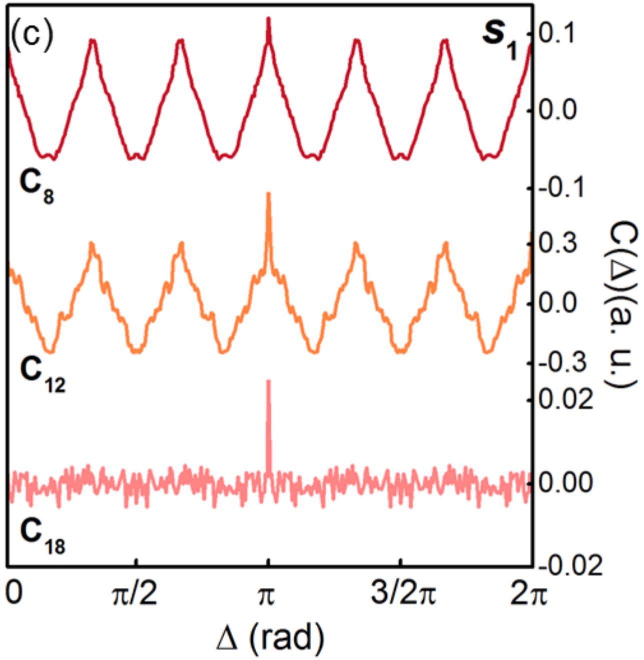
FT TEM exp



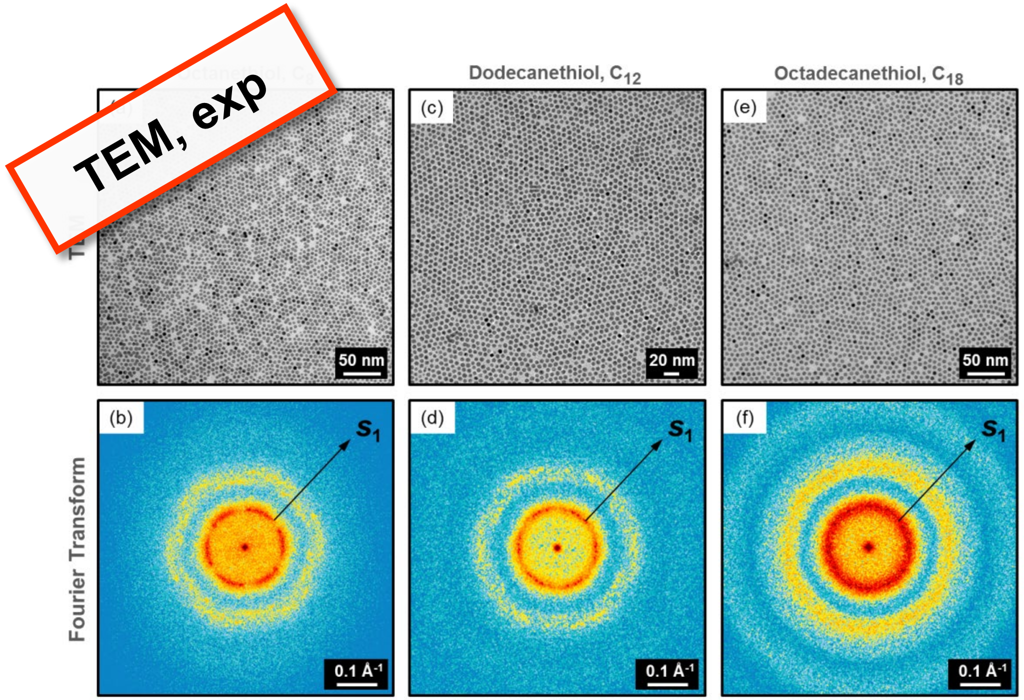
Angular cross-correlation UED, s_1

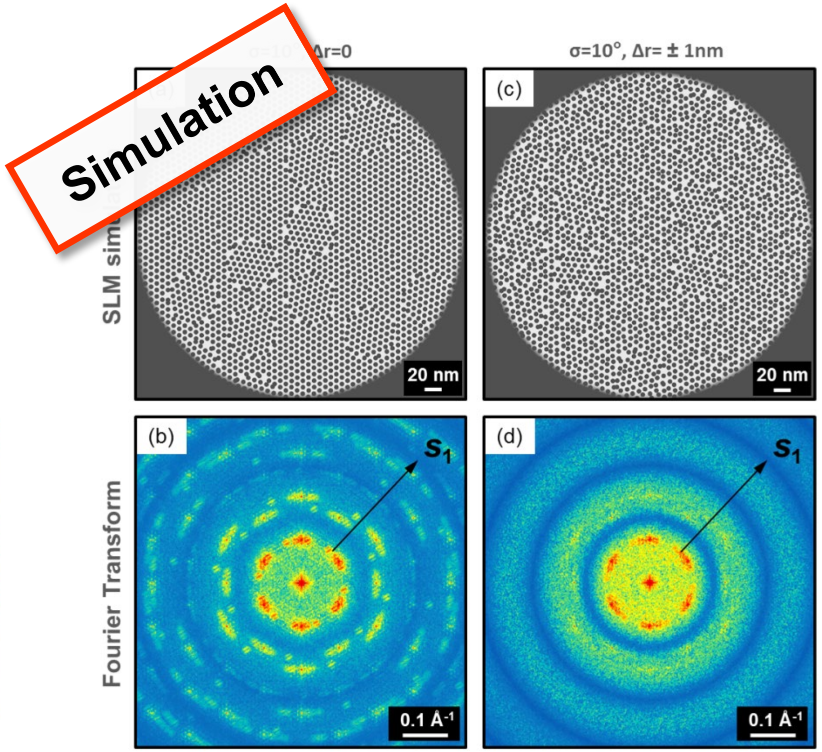


Angular cross-correlation TEM, s_1



Ligand-length and local order

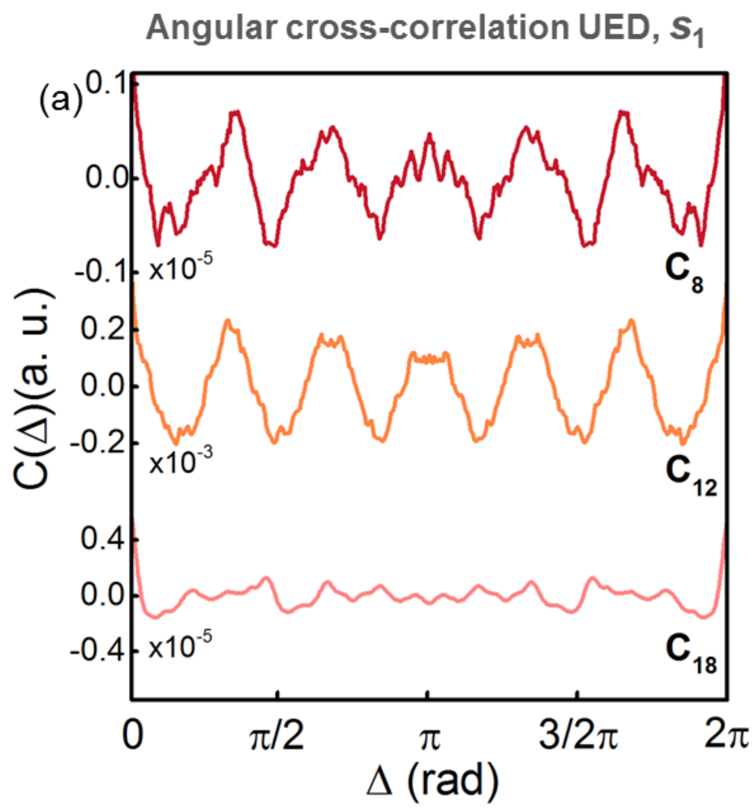


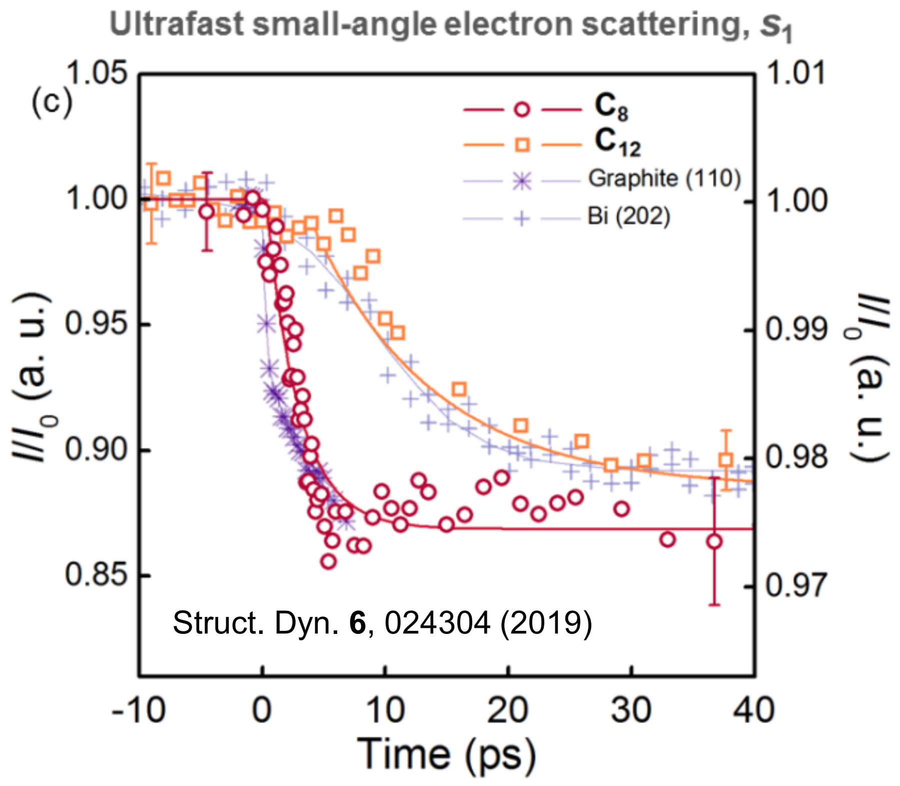


- An **increase in ligand length** limits the possible configurations for the ligand chains interdigitation, yielding and **increase in conformational disorder**.
- The **shorter** the **ligand length**, the **higher** the **crystallinity** within single grains.

Mancini et al., Struct. Dyn. **6**, 024304 (2019)

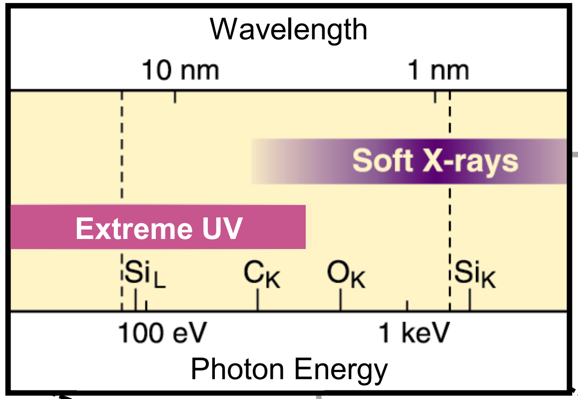
Supramolecular e⁻-ph coupling

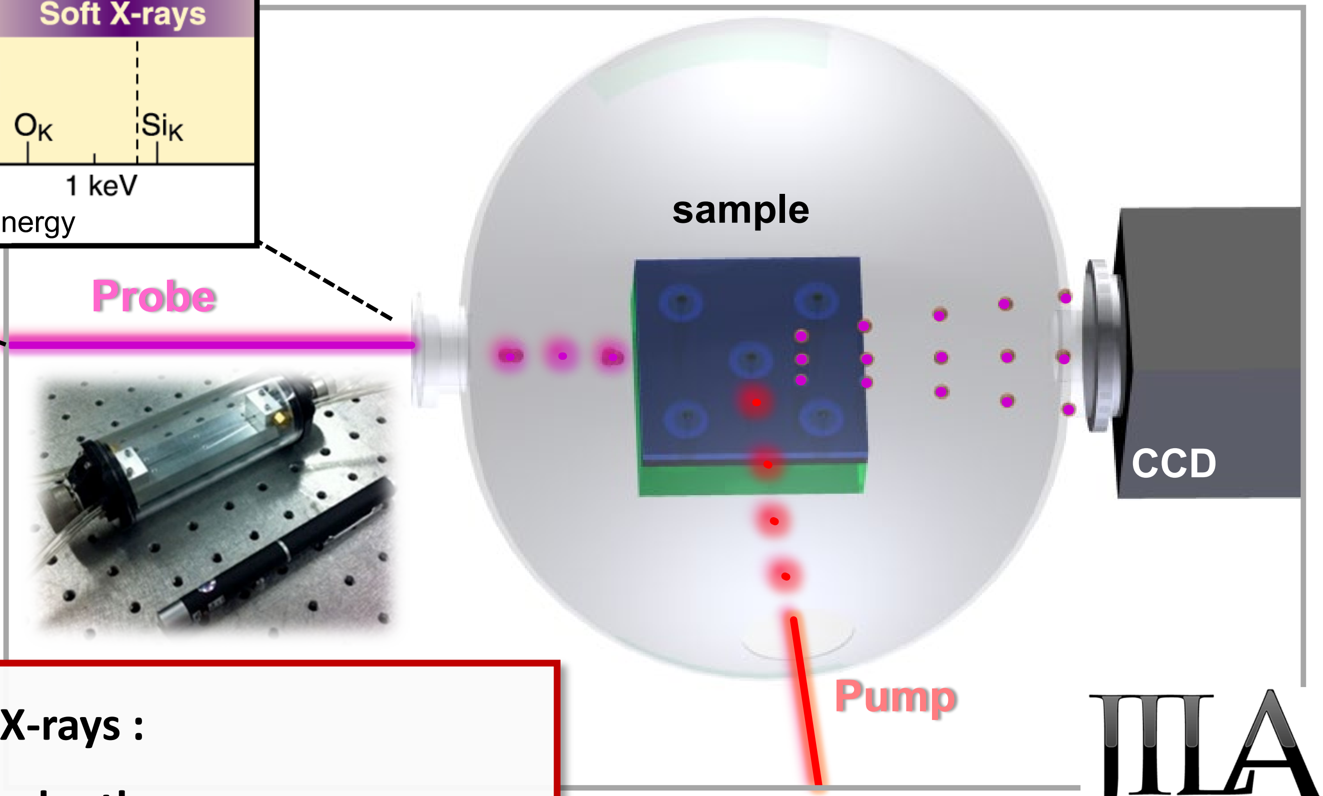




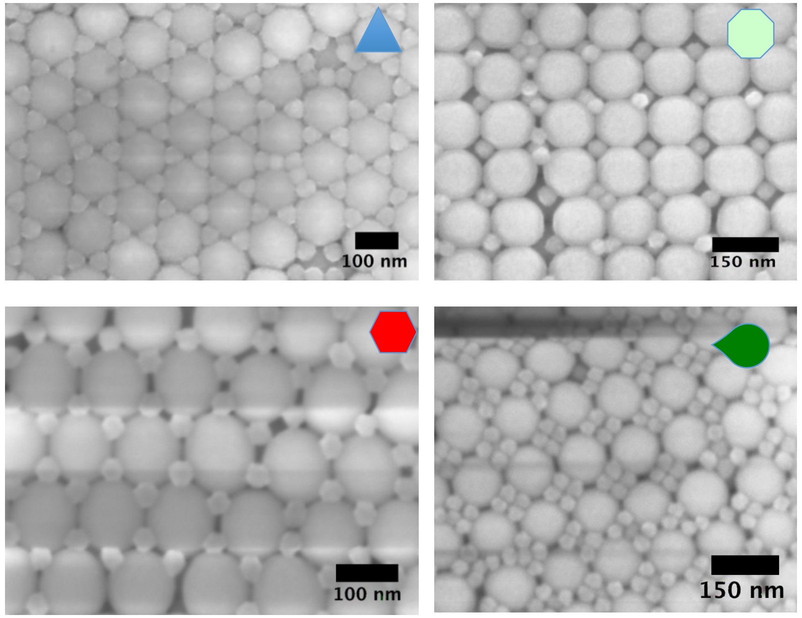
- C8 supracrystal: the **interdigitation** of the shorter ligands provides a very **efficient channel for transferring energy** between the initial electronic excitation to structural motions of the NPs.
- **Local stiffness** in a dense **supramolecular assembly** can be created by **Van der Waals** interactions up to a level **comparable** to **systems** characterized by **covalent bonding**.

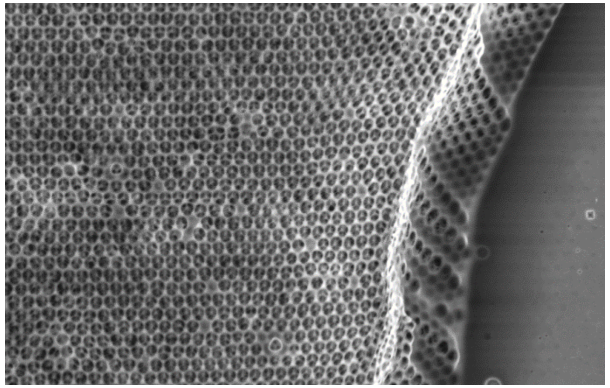
Multilayered opals lattices





Multilayers, packing
Tunable band-gap



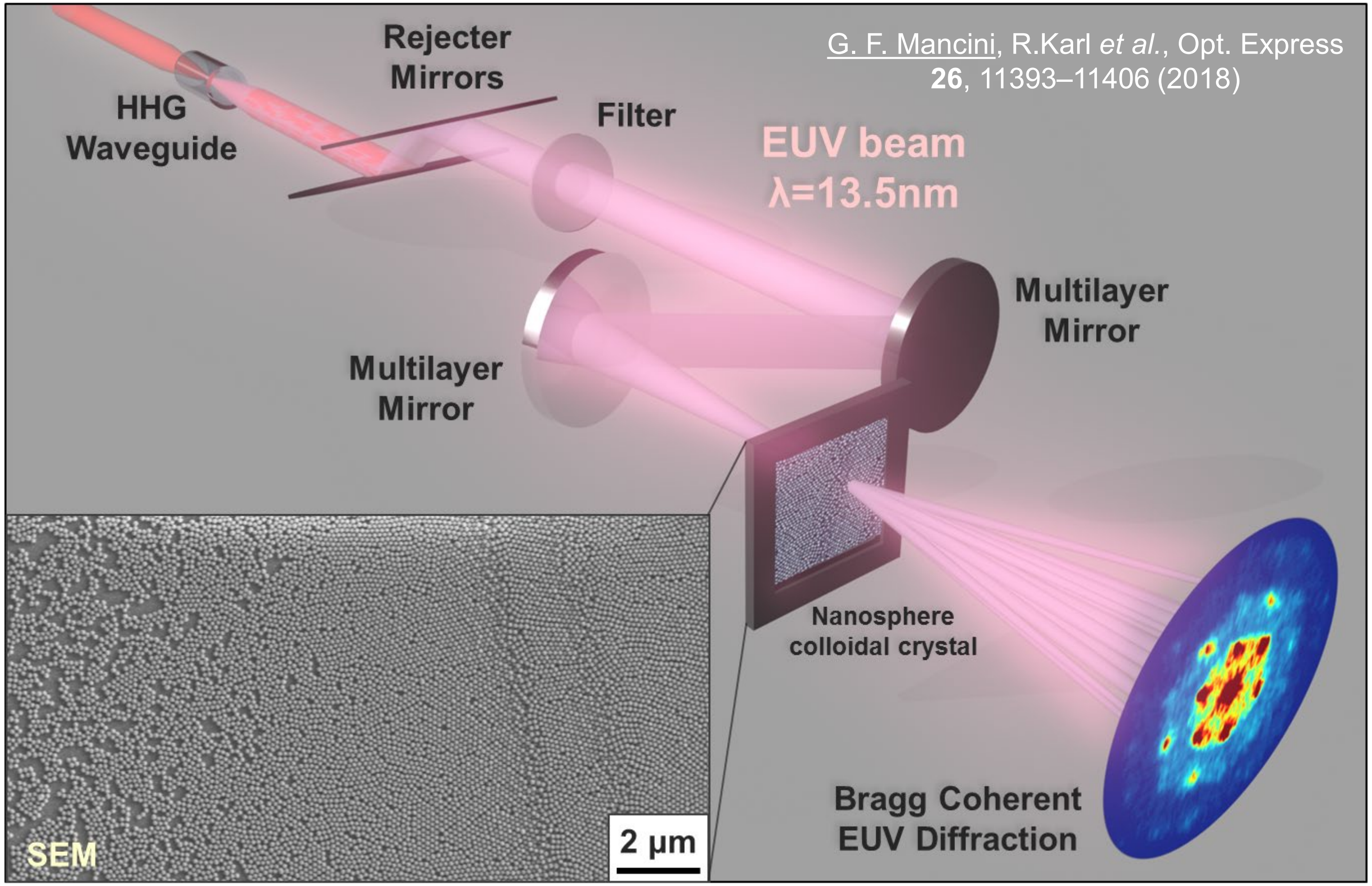


Images courtesy of J. L. Russell and J. Badding

Coherent **EUV/X-rays :**

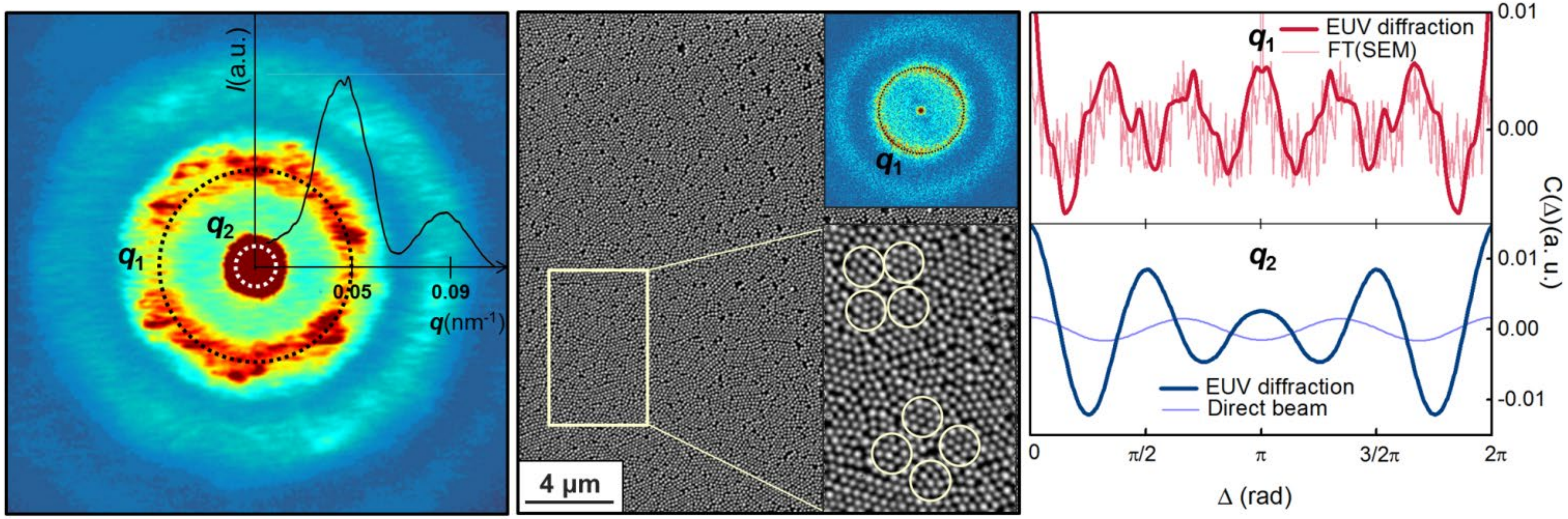
- **Penetration depth**
- **Capture dynamics** relevant to function
- High **coherence**

EUV scattering



- **Silica spheres**, core size 120 nm on **SiN membrane**, 30 nm thickness
- Estimated particle size: 123 ± 3 nm with SEM

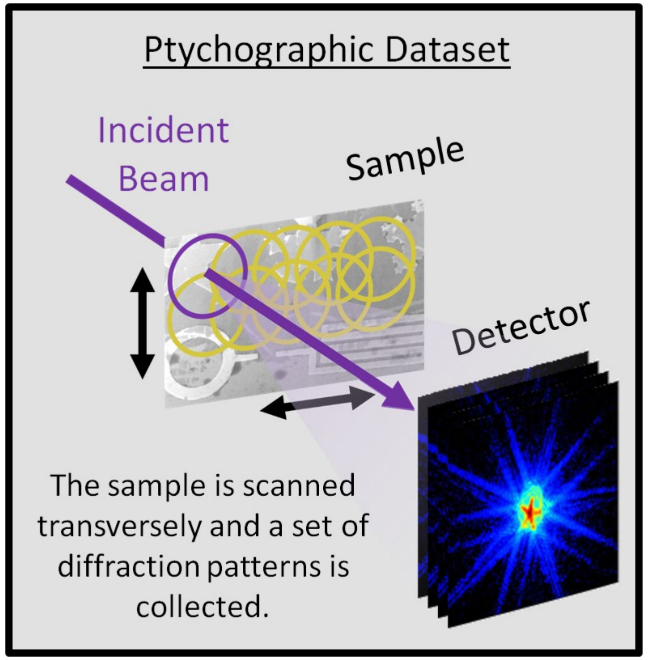
Colloidal monolayers

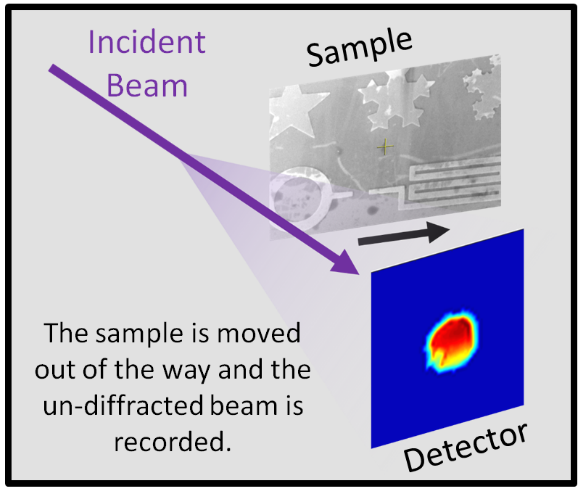


X-ray angular cross-correlation analysis: $$C_s(\Delta) = \frac{\langle I(s,\phi) I(s,\phi+\Delta)\rangle_\phi - \langle I(s,\phi)\rangle_\phi^2}{\langle I(s,\phi)\rangle_\phi^2}$$

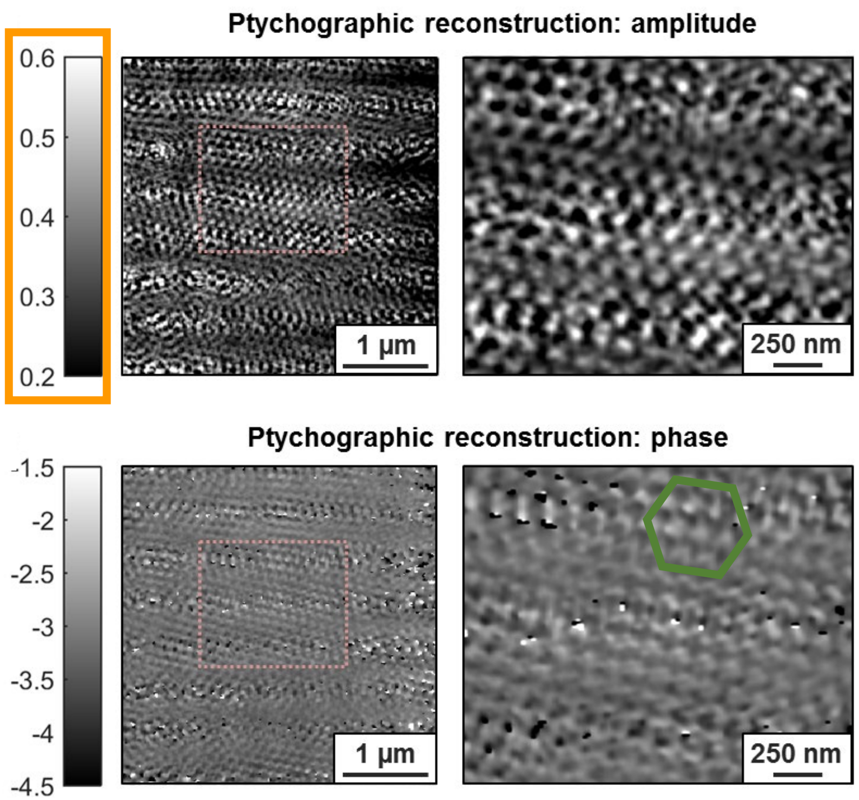
- **Small-angle Bragg scattering**:
  - Nanosphere order within single grains → 6-fold.
  - Grains symmetry in the colloidal crystals (nearest-neighbors) → 4-fold.

EUV ptychography

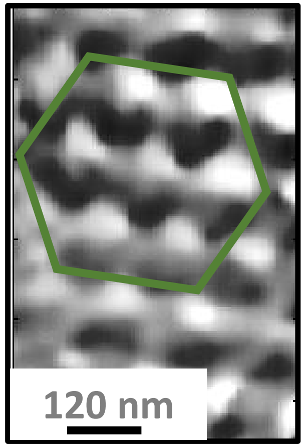




Nat. Photonics **11**, 259–263 (2017)



Lateral separation of the nanospheres = 125nm

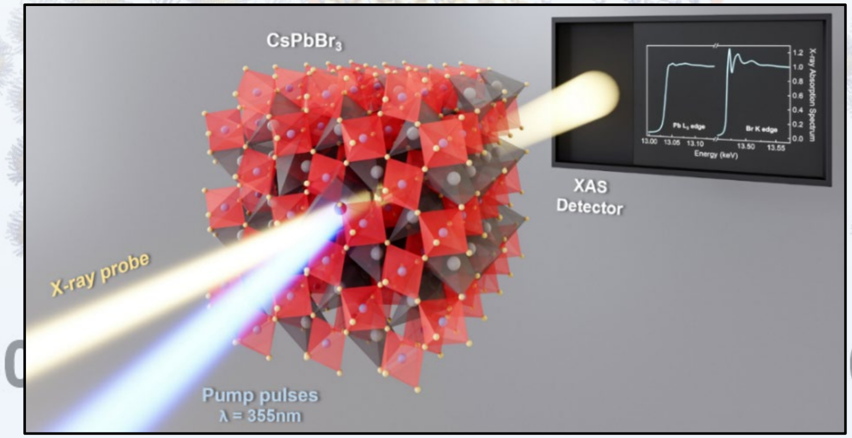


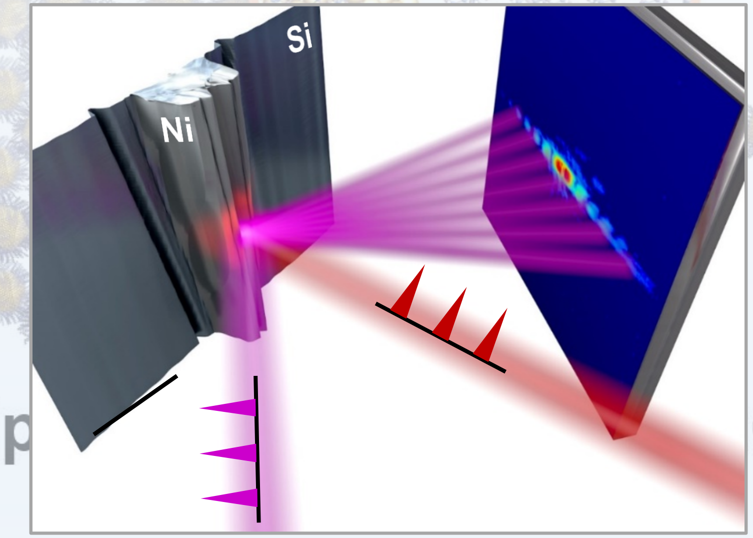
CDI Phase

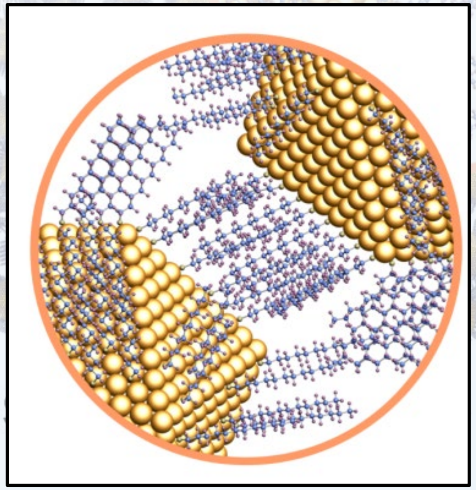
- **Quantitative** non-destructive imaging of the **number** of **layers** from transmissivity.
- **Nanosphere** estimated **thickness** from phase reconstruction (124nm±1nm) agrees well with SEM images (123±3nm).

Conclusions & Perspectives

- **CCF**: Powerful tool to characterize stiffness, thermal flow, annealing, ultrafast transport in supramolecular assemblies
- **Coherence**: can be harnessed to solve the phase problem: quantitative chemical contrast, stacking
- **Extensions**: 3D, multiple functional groups
- **New concepts**: collective modes in soft-matter

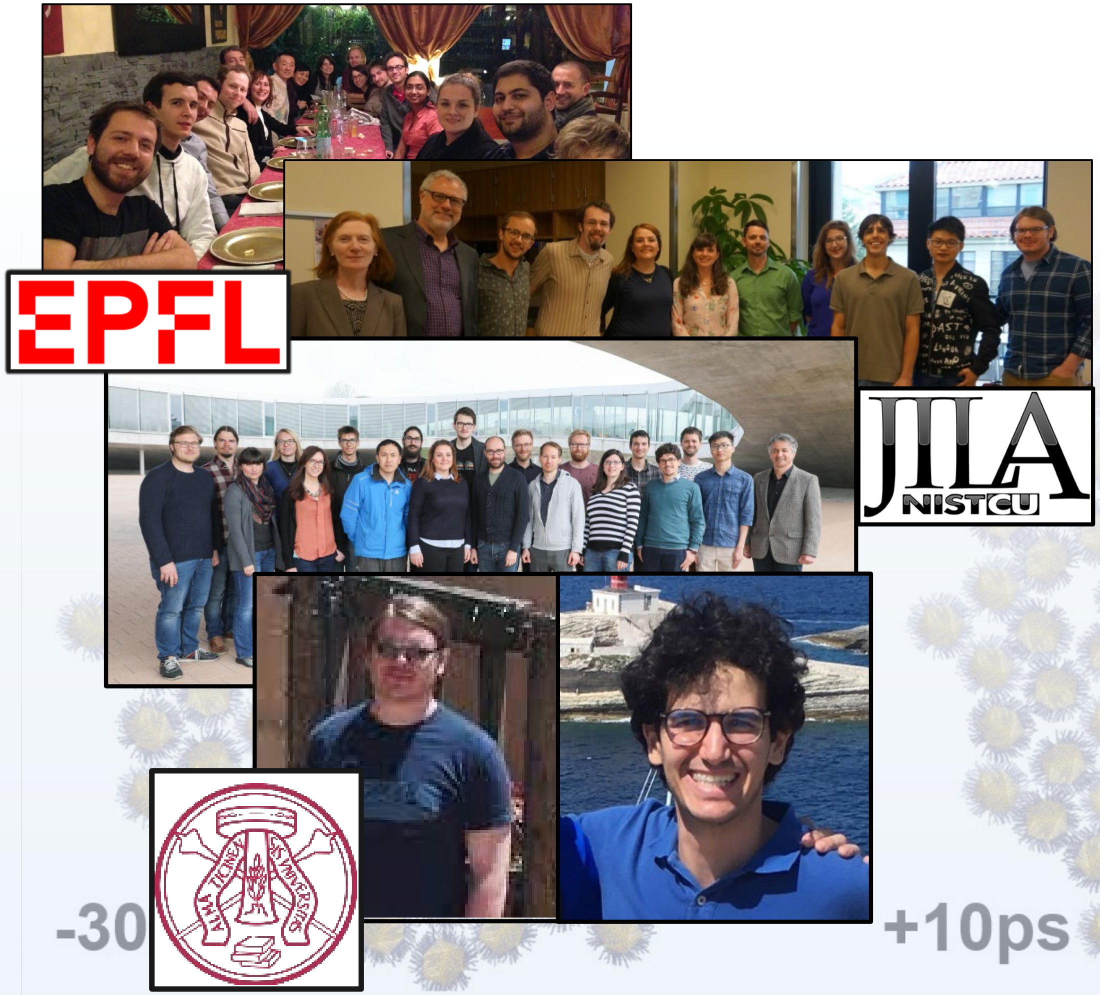






Acknowledgements

LUXEM
Laboratory for Ultrafast X-ray and Electron Microscopy



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