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Sandia National Laboratories

Harnessing Carbon Dots for Multifunctional Materials: From Synthesis to Applications

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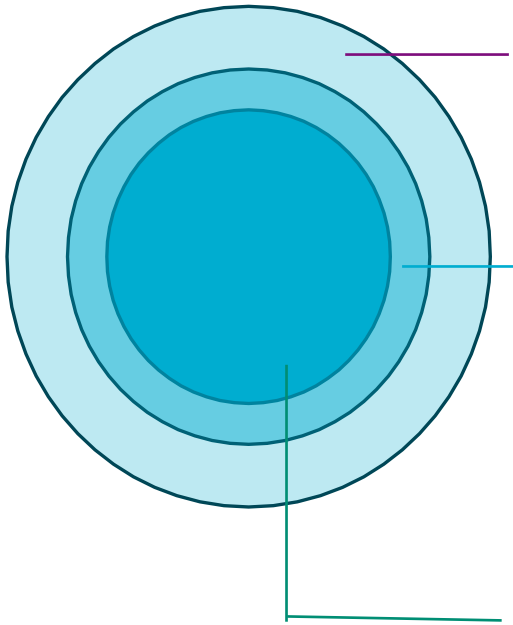
Carbon dots “organic analog” of quantum dots

Quantum dots

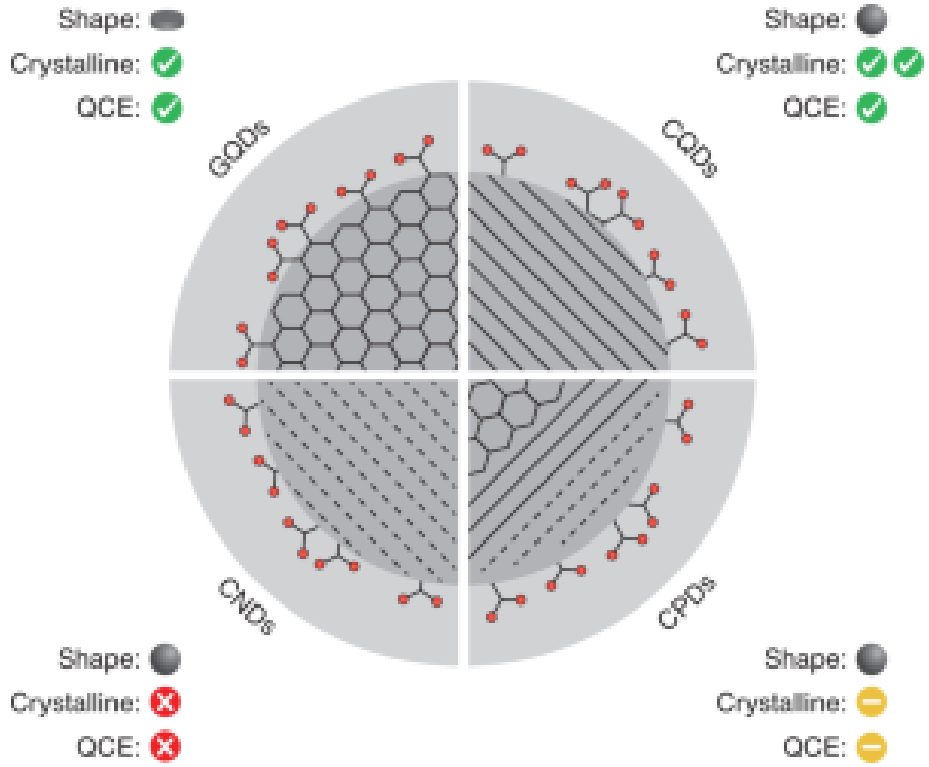


Variable outer layer, depending on needed surface functionalization

Second semiconductor layer (e.g., ZnS).

Variable inorganic metal core (e.g., CdSe, CdTe).

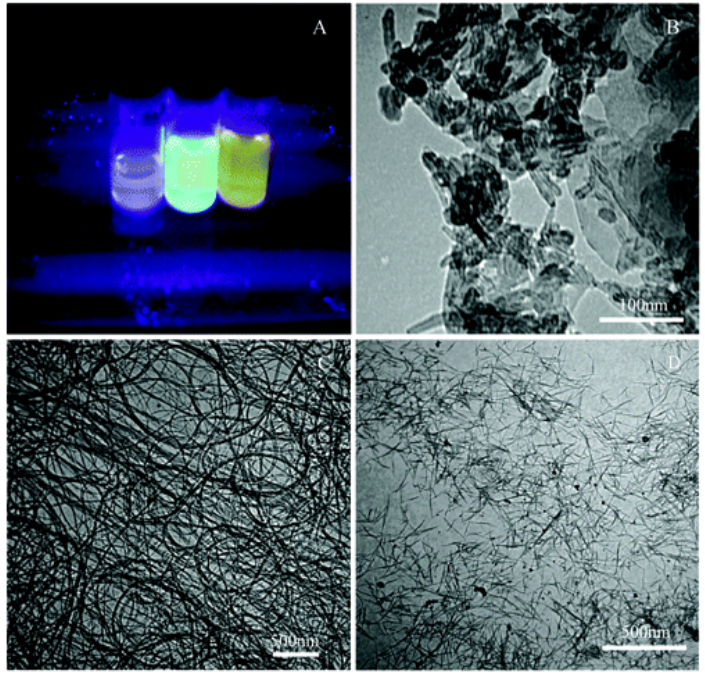
Carbon dots



Đorđević, L., Arcudi, F., Cacioppo, M. *et al.* A multifunctional chemical toolbox to engineer carbon dots for biomedical and energy applications. *Nat. Nanotechnol.* **17**, 112–130 (2022). https://doi.org/10.1038/s41565-

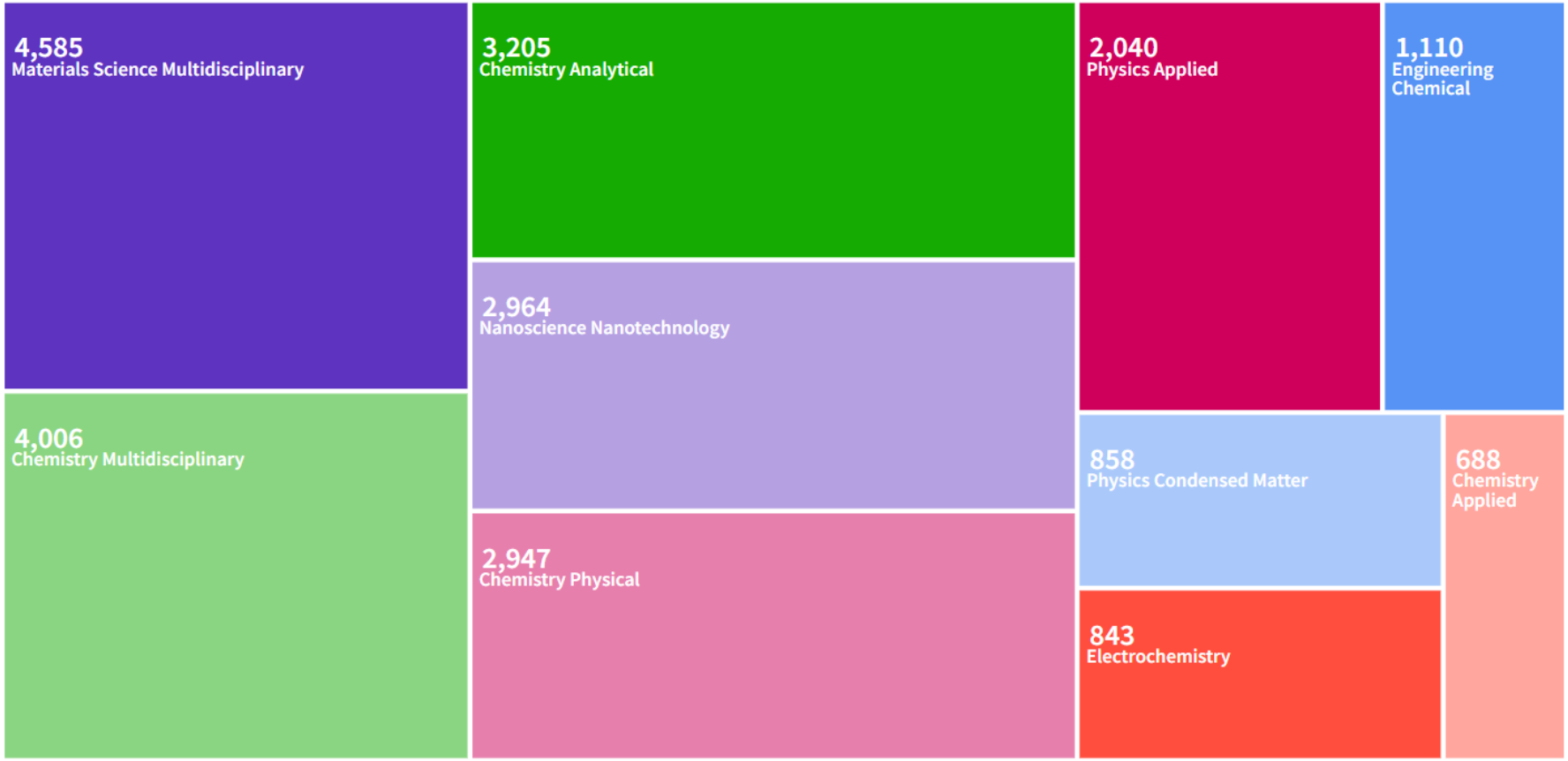
First report of carbon dots

"Arc-synthesized single-walled carbon nanotubes have been purified through preparative electrophoresis in agarose gel and glass bead matrixes. Two **major impurities** were isolated: **fluorescent carbon** and short tubular carbon."



Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments
Xiaoyou Xu, Robert Ray, Yunlong Gu, Harry J. Ploehn, Latha Gearheart, Kyle Raker, and Walter A. Scrivens
Journal of the American Chemical Society 2004 126 (40), 12736-12737
DOI: 10.1021/ja040082h

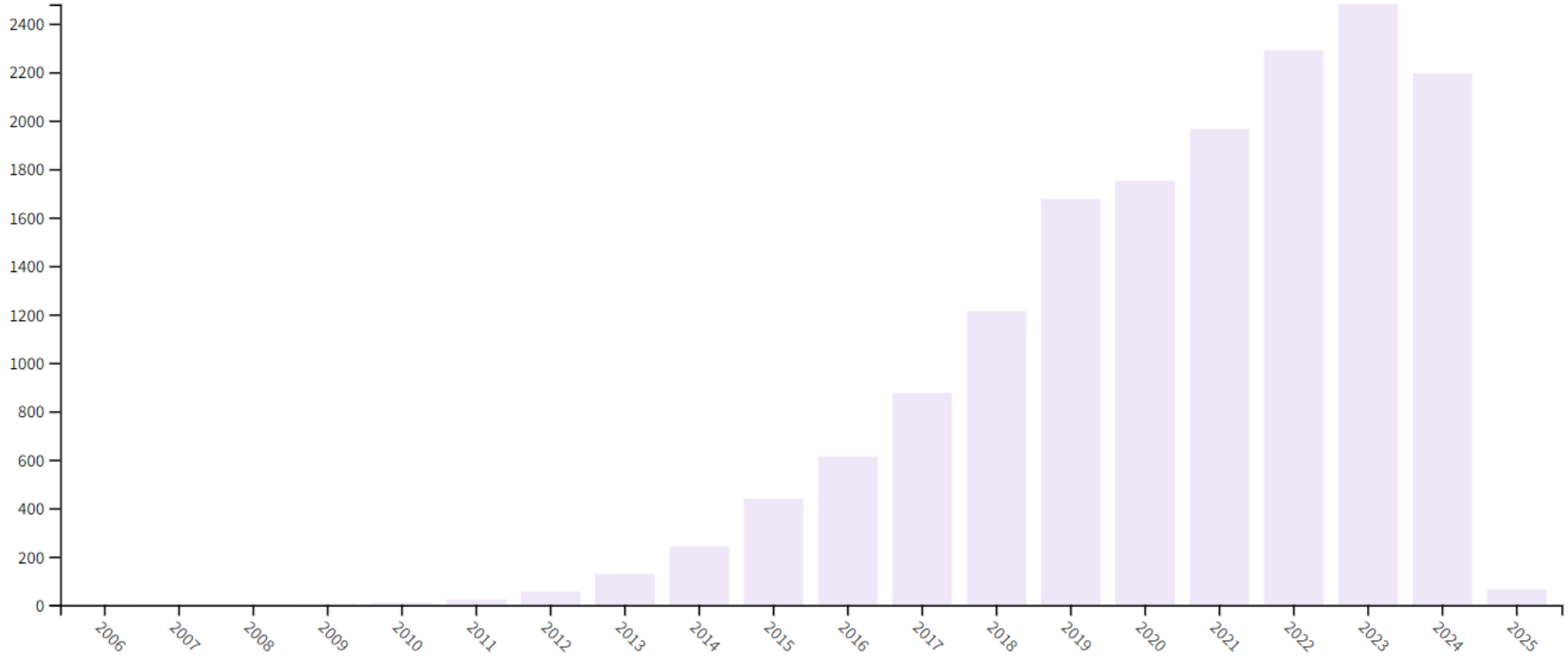
Evolution of carbon dots



Key search word: “carbon dots” on web of science, 16,000+ hits

Search conducted: 10/10/2024, 6:21 PM

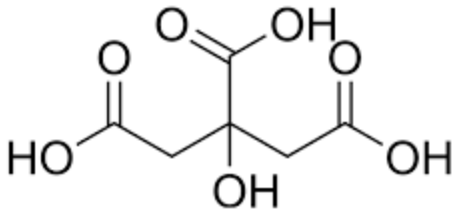
Popularity of carbon dots in scientific community

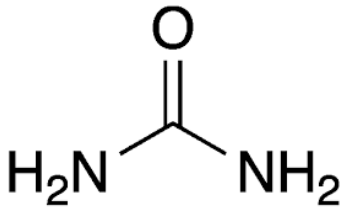


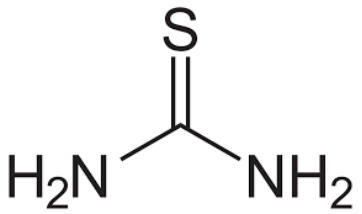
Key search word: “carbon dots” on web of science

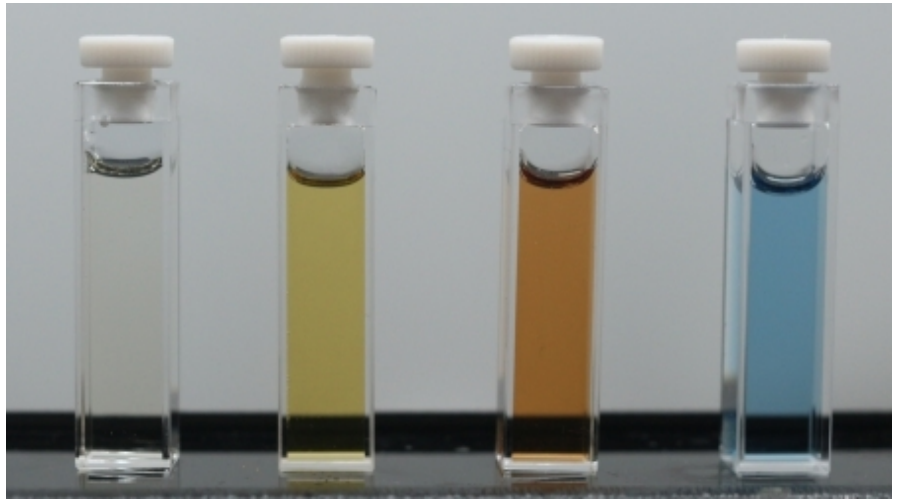
Search conducted: 10/10/2024, 6:21 PM

Carbon dots in our lab

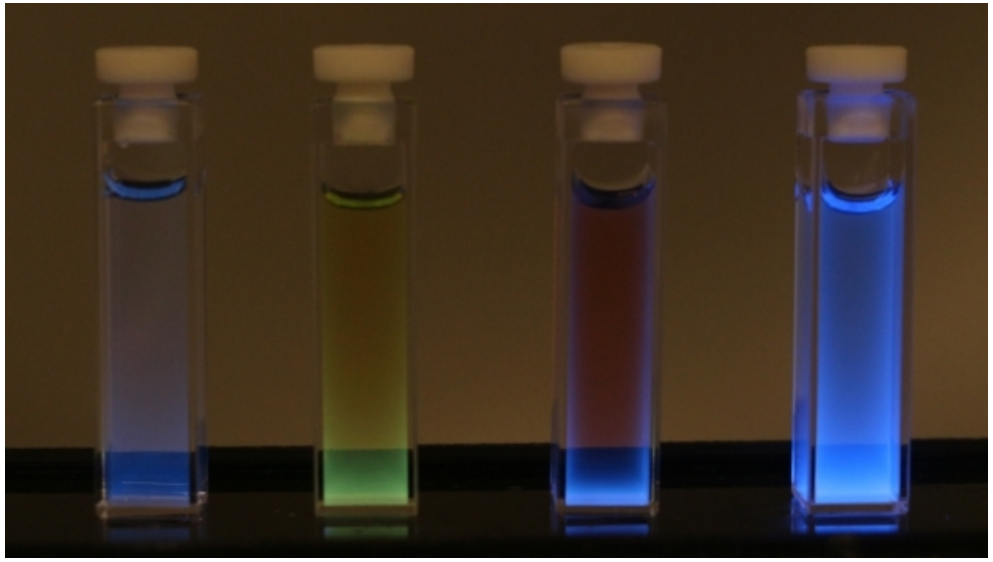








Ambient Light



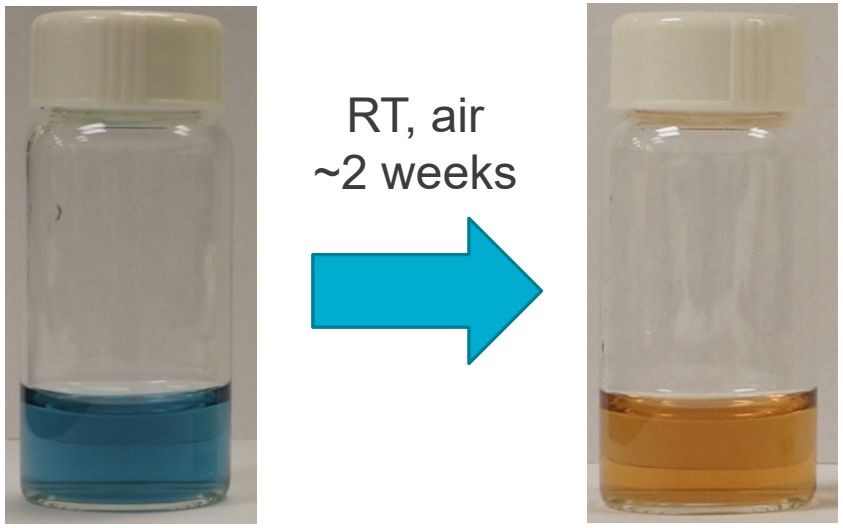
365 nm Irradiation

Self-assembled structures with carbon dots

Terefe G. Habteyes, Eric R. Westphal, Kenneth M. Plackowski, Paul G. Kotula, Melissa L. Meyerson, Stephanie L. White, W. Cody Corbin, Koushik Ghosh, and John K. Grey
Nano Letters **2023** *23* (20), 9474-9481
DOI: 10.1021/acs.nanolett.3c02977

Carbon dots in our lab

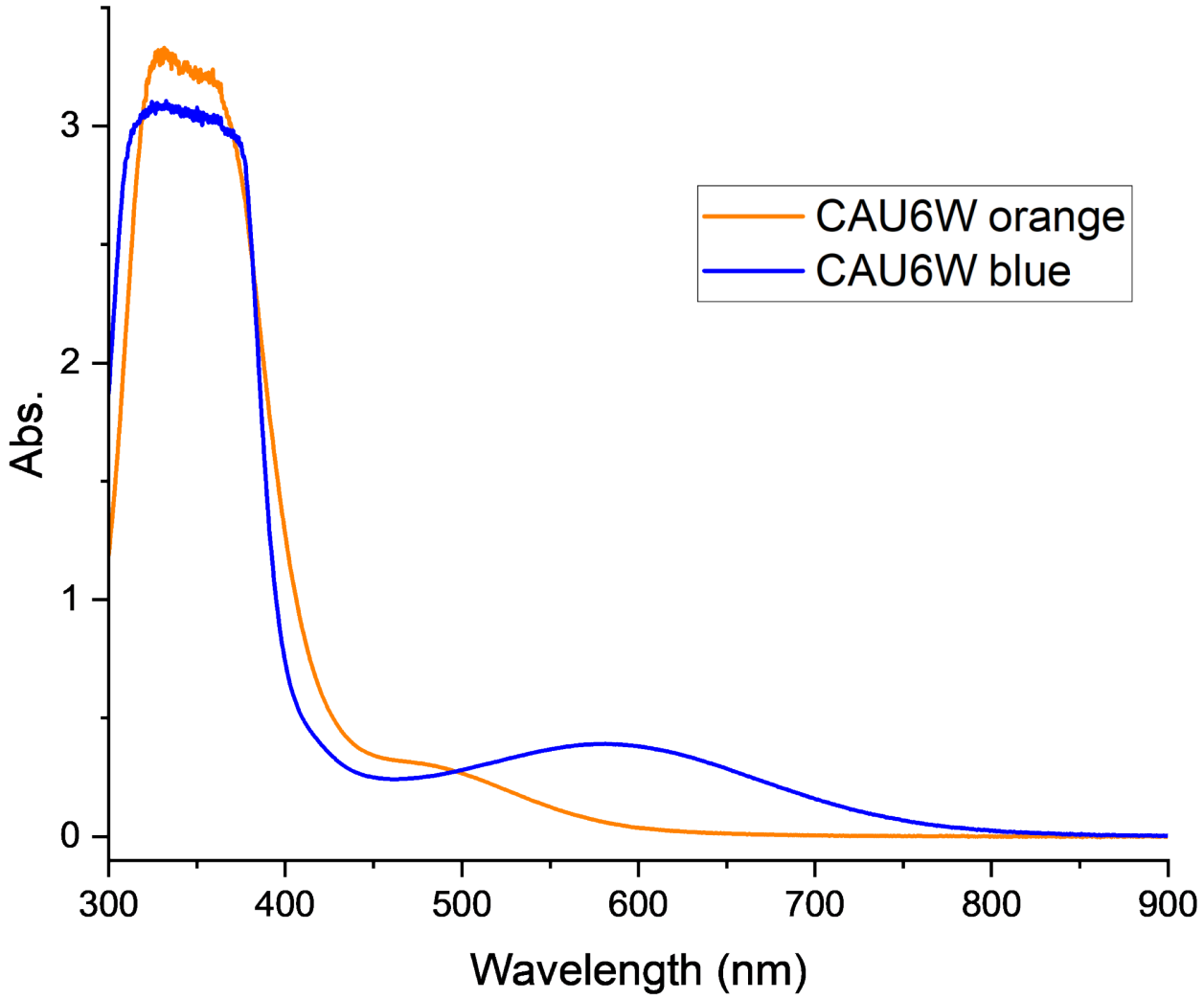
Citric acid and urea (CAU) in water (1:2 w/w)
160 ºC, 6 hours



b-CAU

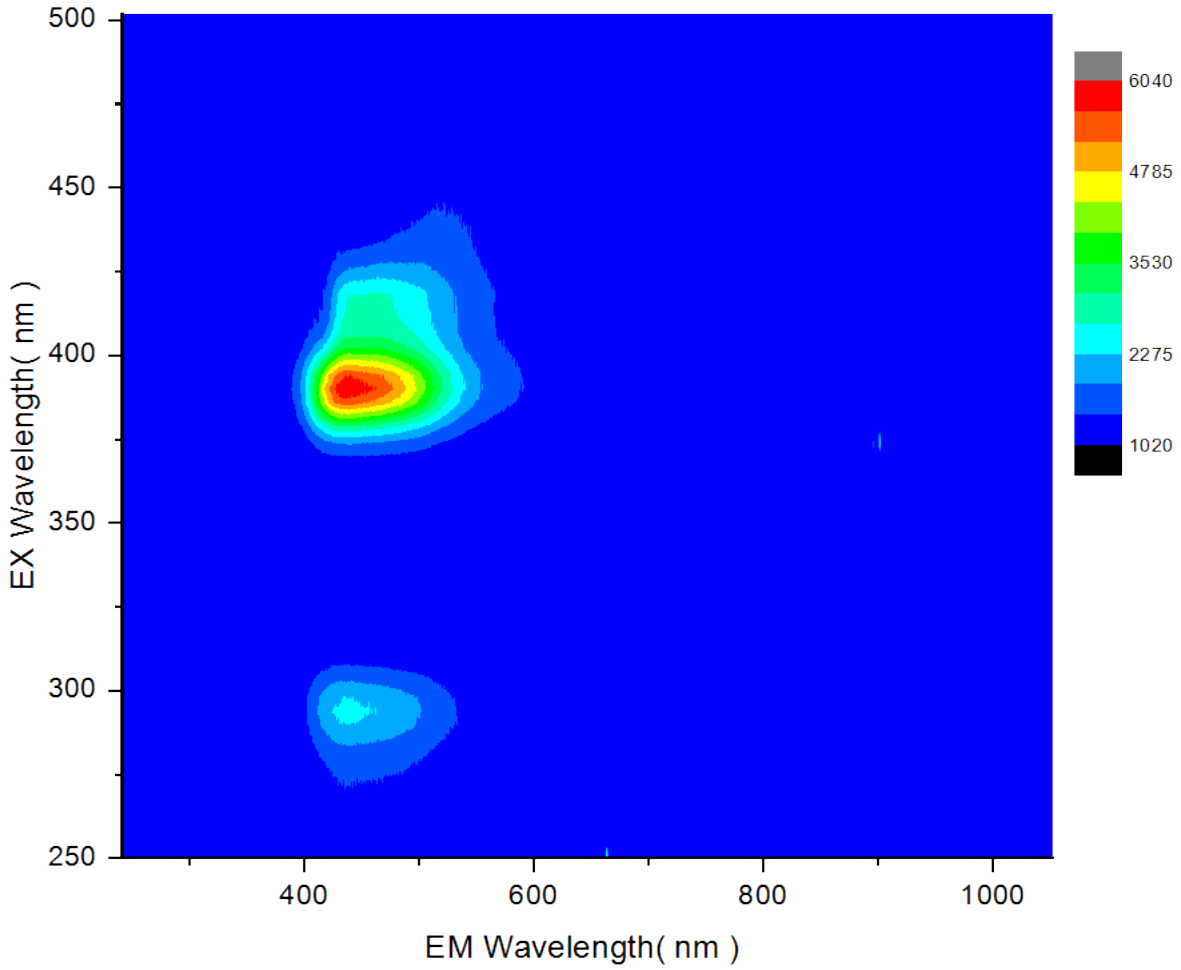
o-CAU

Absorption spectra

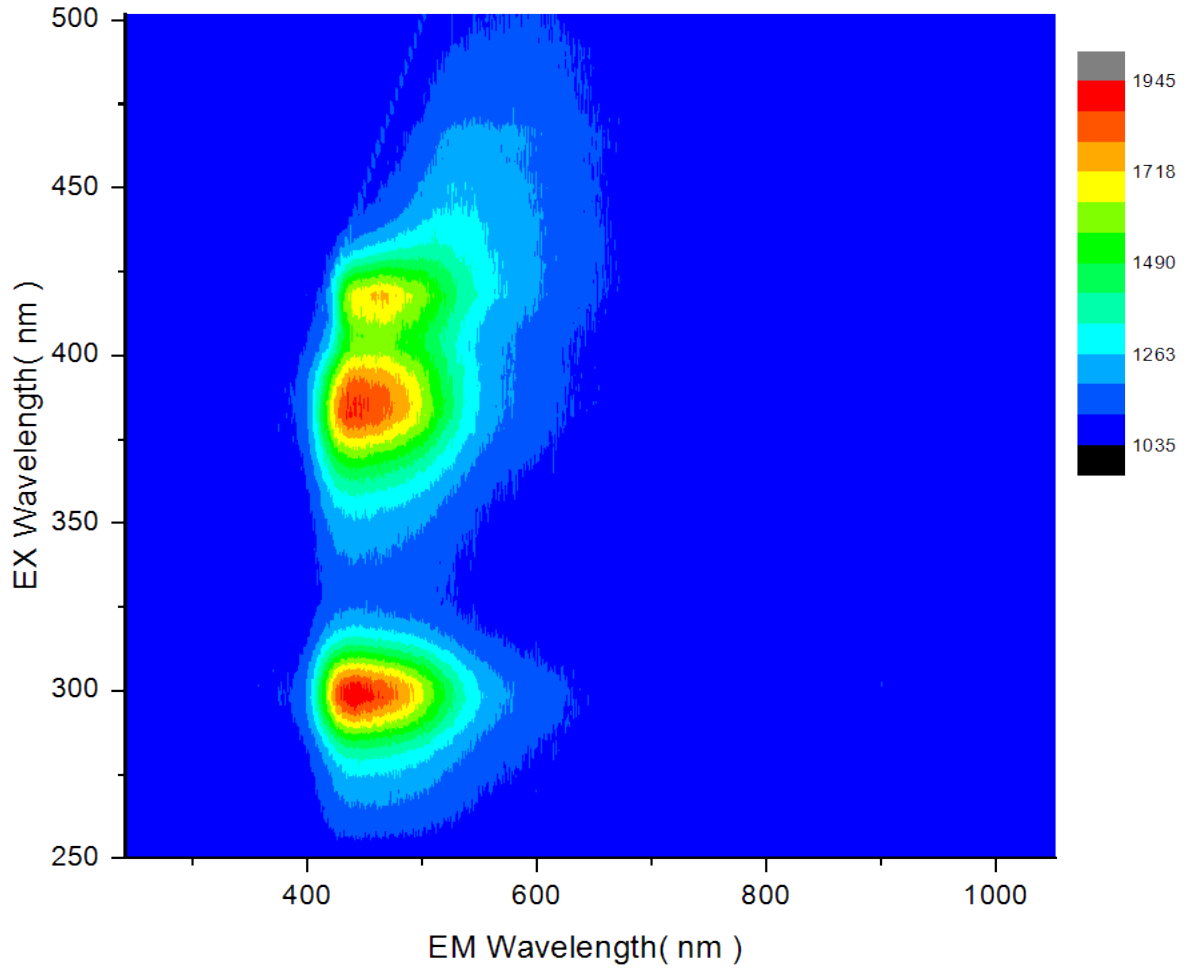


Excitation-emission maps

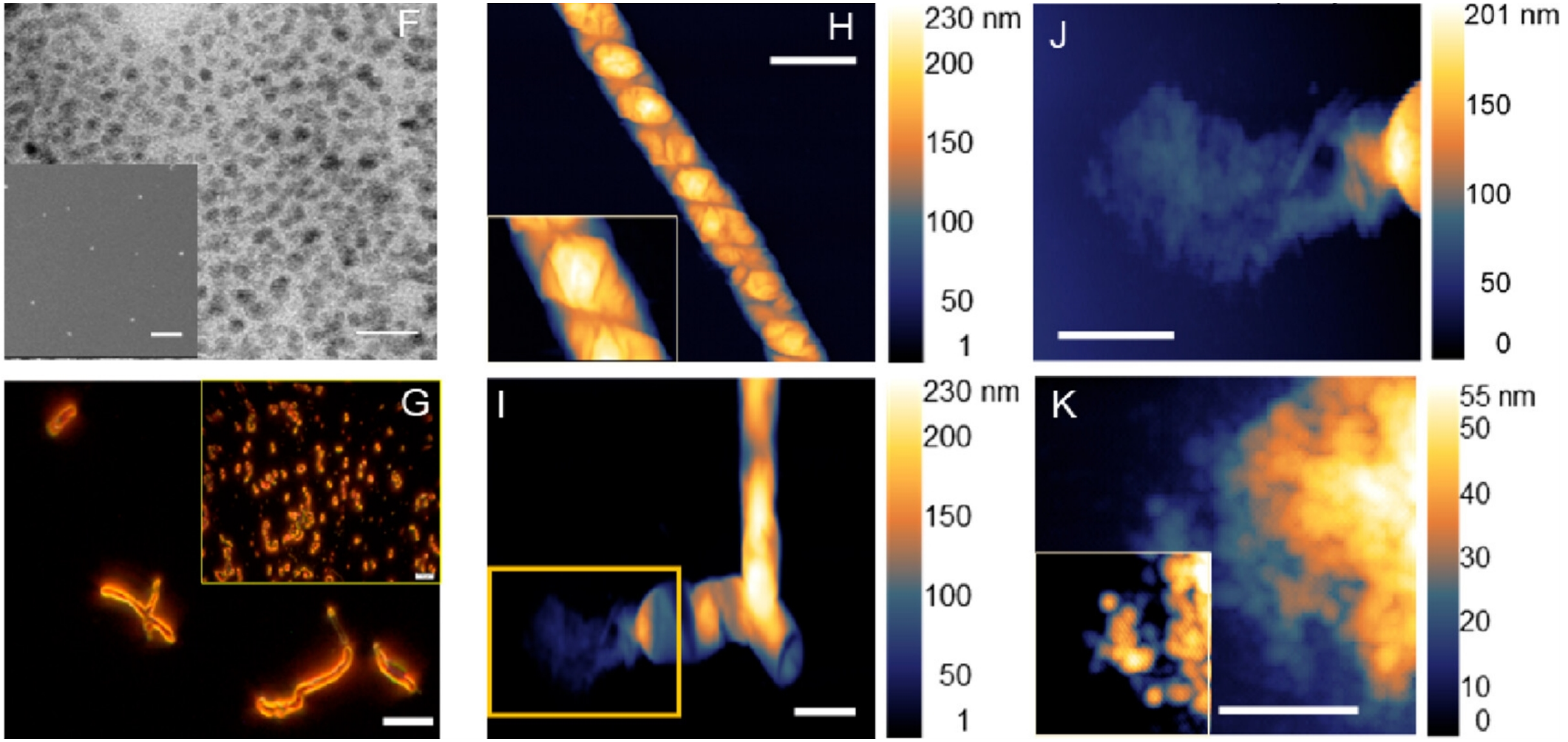
Emission from blue solution



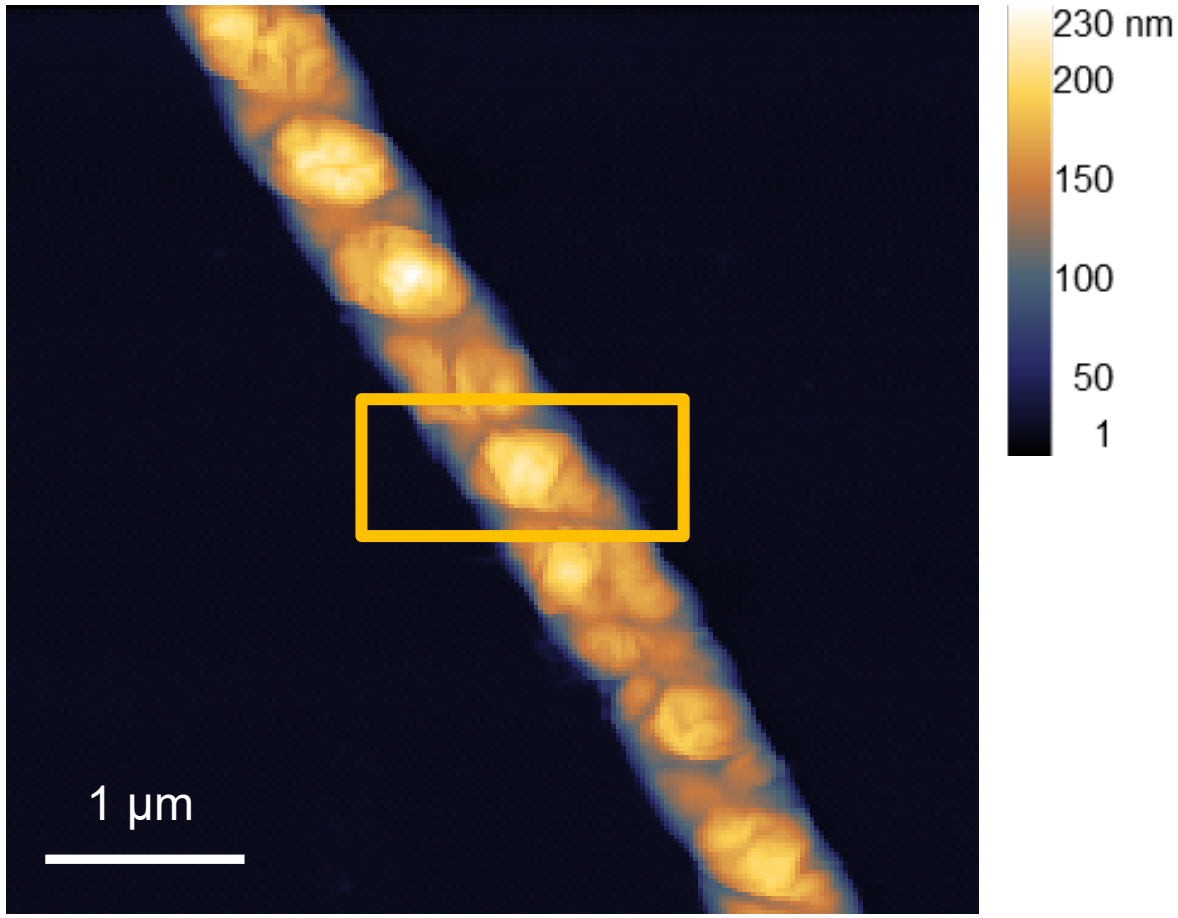
Emission from orange solution



Blue solution reveals uncontrolled agglomeration while orange solution reveals large nanowires with long-range order

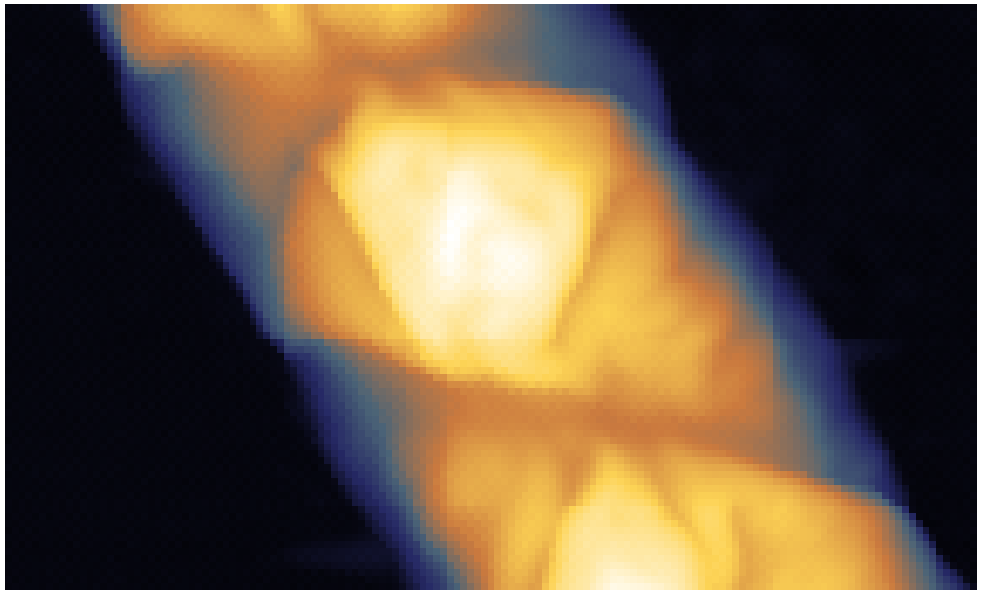


High-resolution AFM image of the o-CAU wire



- Relatively uniform wire dimensional and morphological characteristics
- High level of extended organization for a nominally heterogeneous material

→ *Self-assembly is intrinsic!*



Hierarchical, directed self-assembly

What do we know/not know?

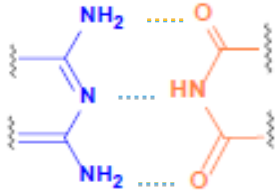
- Tautomerization is crucial for priming the material

→ *No assembly happens in b-CAU form*

→ *Aggregates form in solution but no long-range assembly*

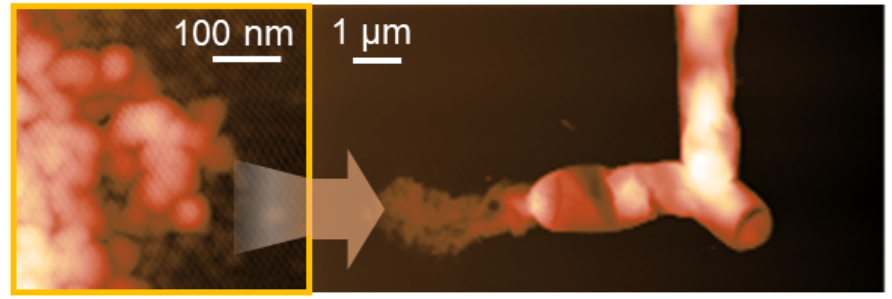
- O-CAU aggregates is a supramolecular shape synthon

→ *H-bonding provides directionality*

melamine  cyanuric acid

- Something else appears to help organize o-CAU aggregates into wire segments and regulate dimensions

→ *Need deeper insights!*

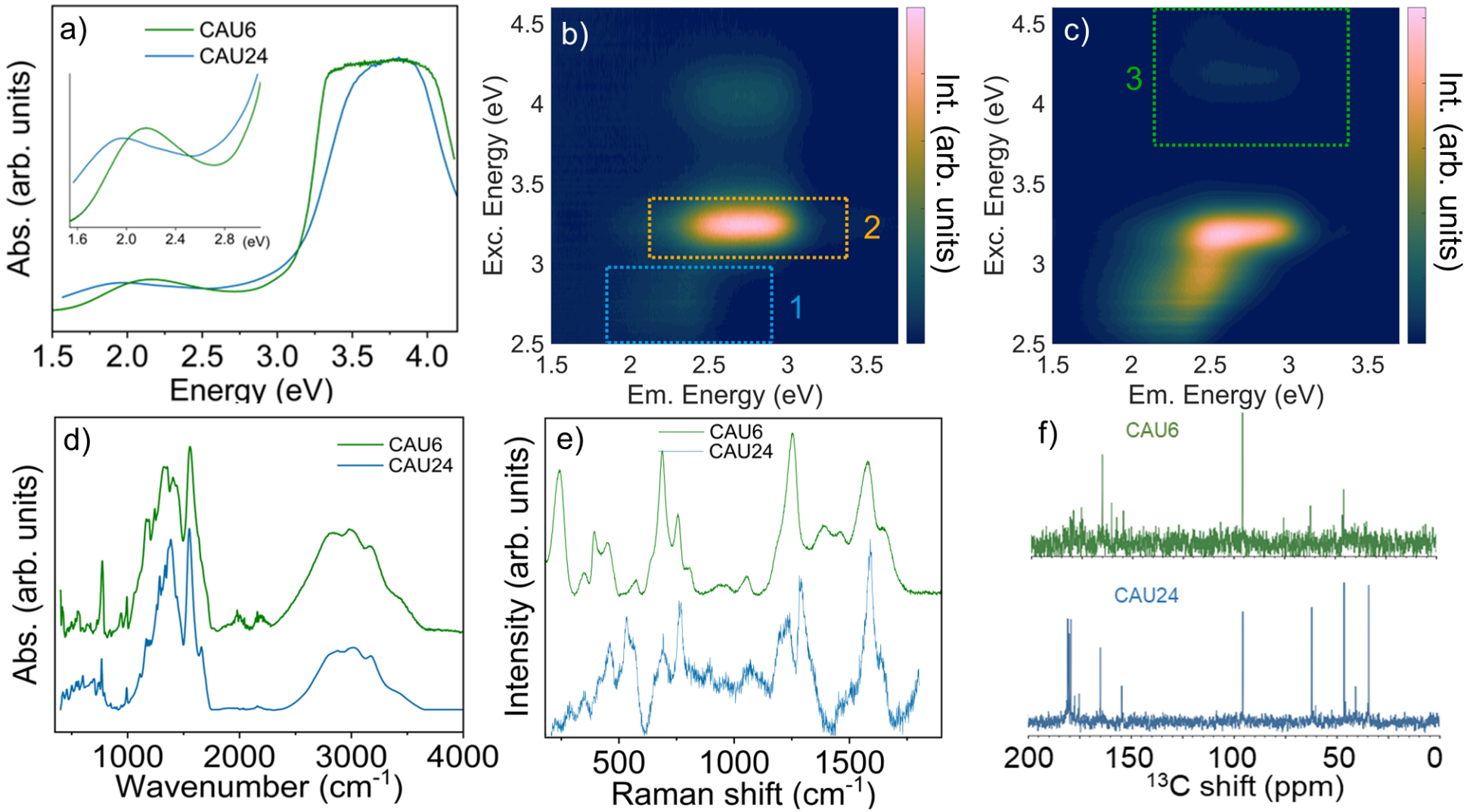


What is acting as the 'pied piper' to corral O-CAU aggregates to form large wires?

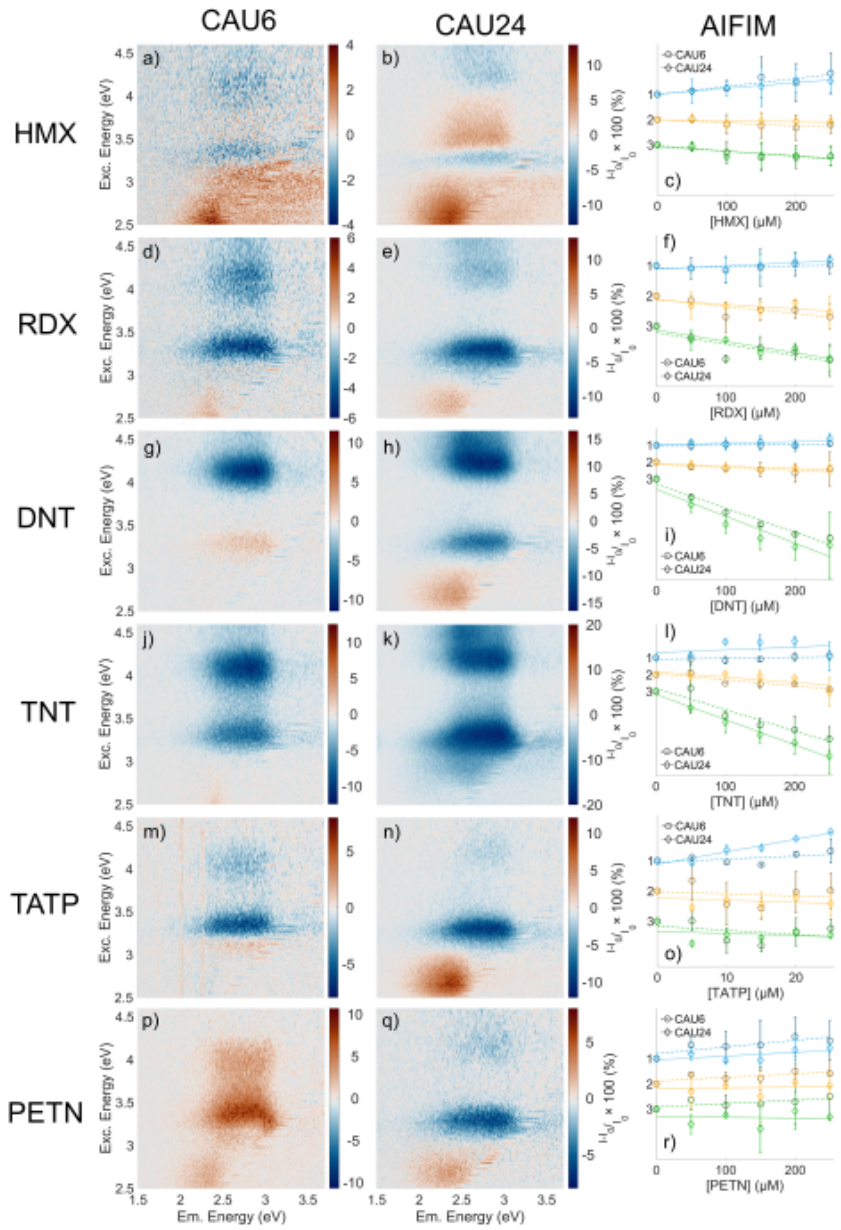
Optical sensors for explosive detection

"Influence of Carbon-Nitride Dot Emitting Species and Evolution on Fluorescence-based Sensing and Differentiation"
Author(s): Westphal, Eric; Plackowski, Kenneth; Holzmann, Michael; Outka, Alexandra; Chen, Dongchang; Ghosh, Koushik; Grey, John ACS Sensors, Accepted

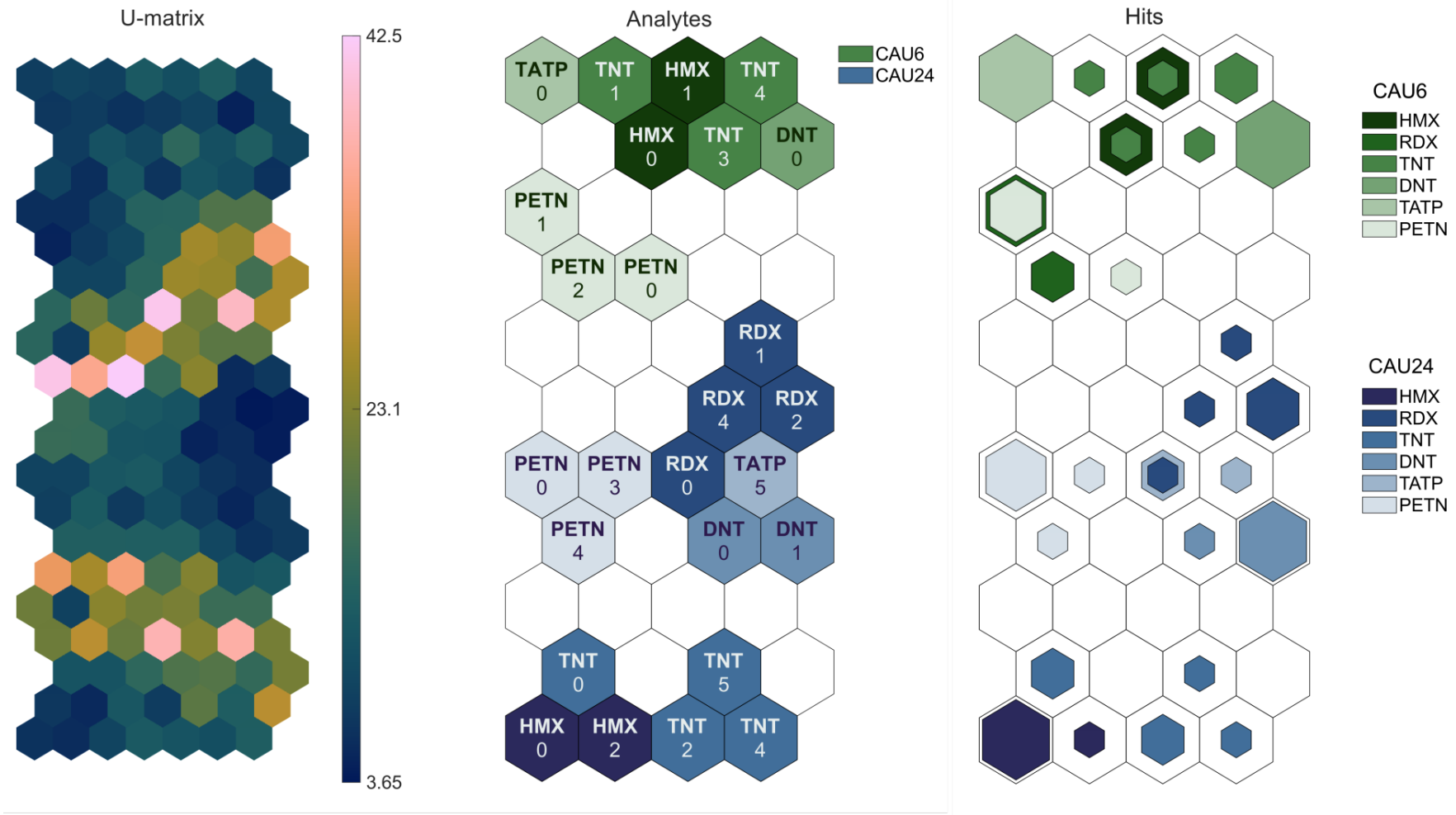
Different reaction times result in different types of carbon dots



Different regions of excitation-emission map showing different responses to analytes



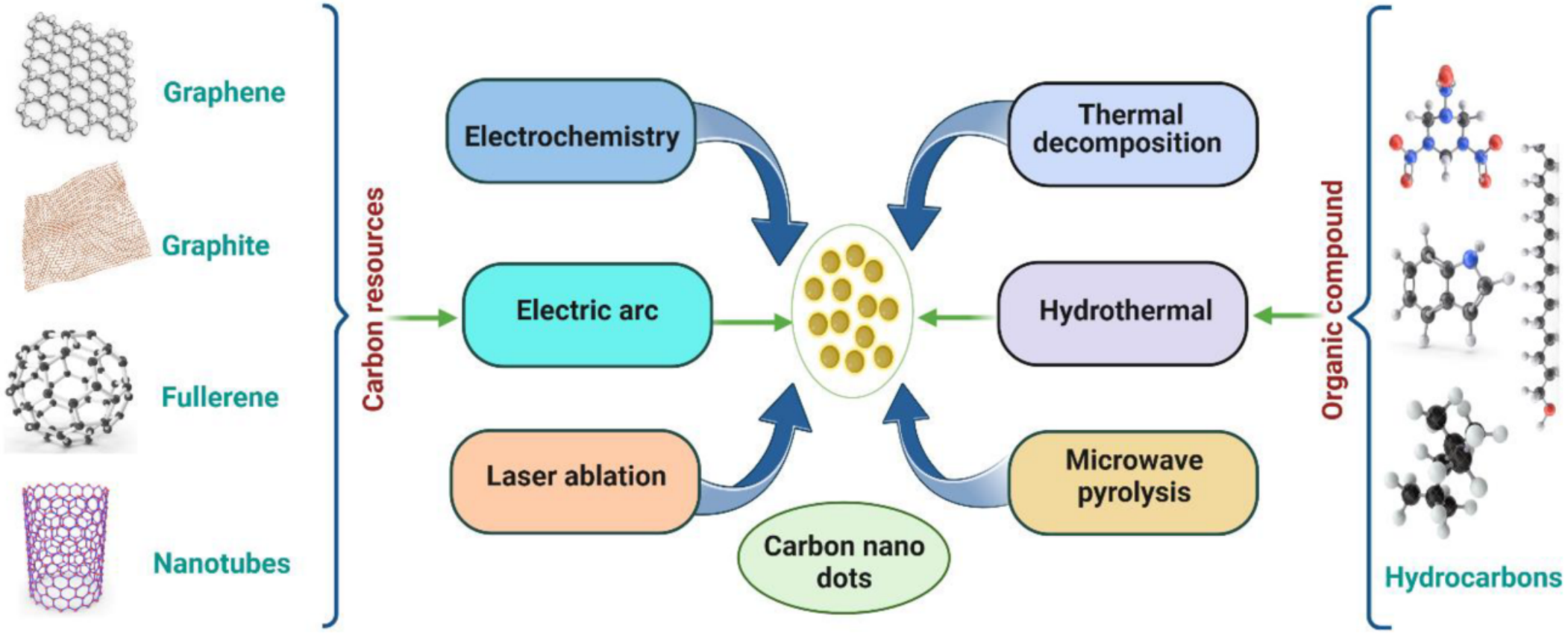
Self-organizing map (SOM) analysis of fluorescence Excitation-Emission Map



Toward Structure-Function Relationship

Publication in preparation

Top-down vs. Bottom-up synthesis of carbon dots



Multi-variable synthetic space of bottom-up carbon dot synthesis

1. Nature of the reactants

2. Ratio

Before reaction

3. Heating method

4. Reaction time

5. Temperature

During reaction

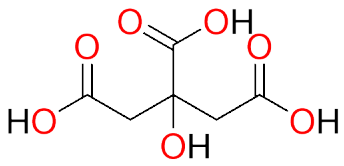
6. Purification

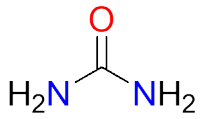
7. Drying

8. Storage

After reaction

Different fractions of Carbon Dots

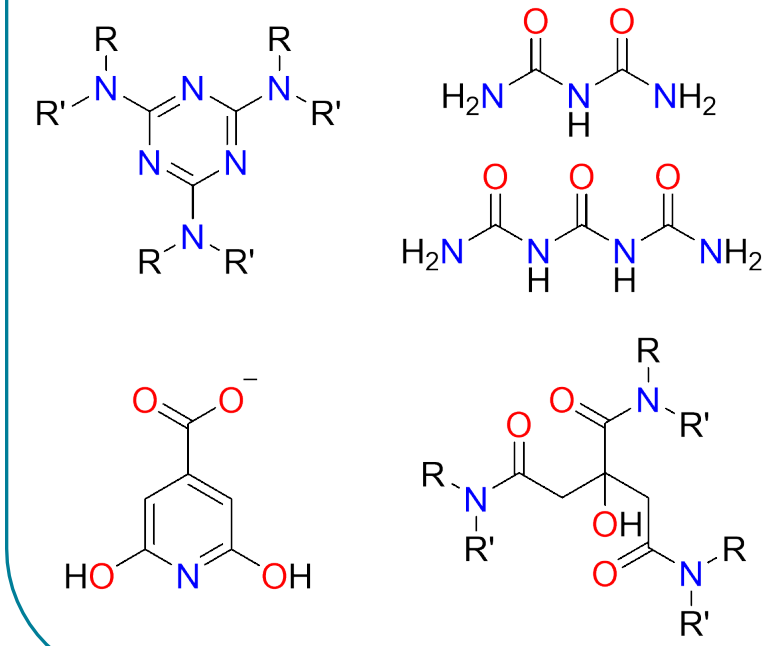




160°C,
24 hrs

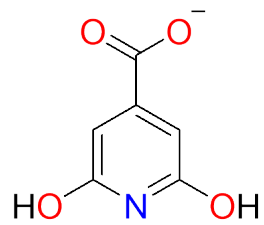
H_2O

CA-U Heterogeneous Reaction Mixture

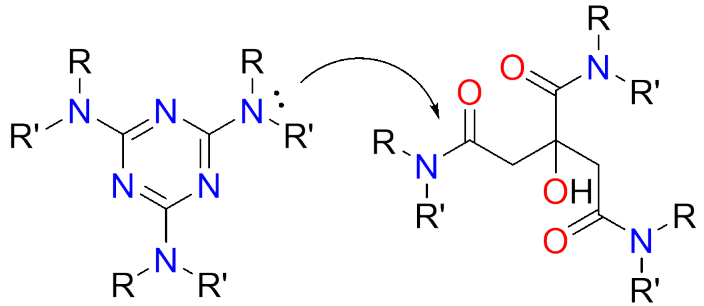


Precipitate in ethanol and centrifuged

Ethanol fraction

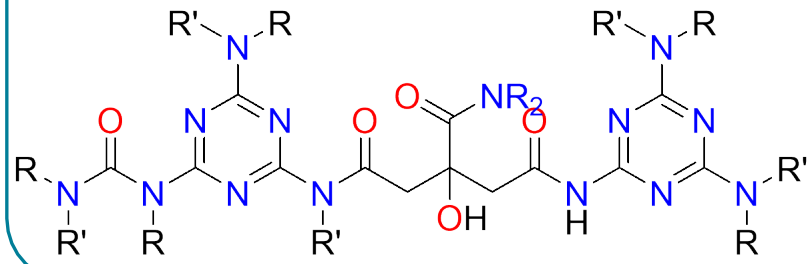


Precipitate: CAU Wet

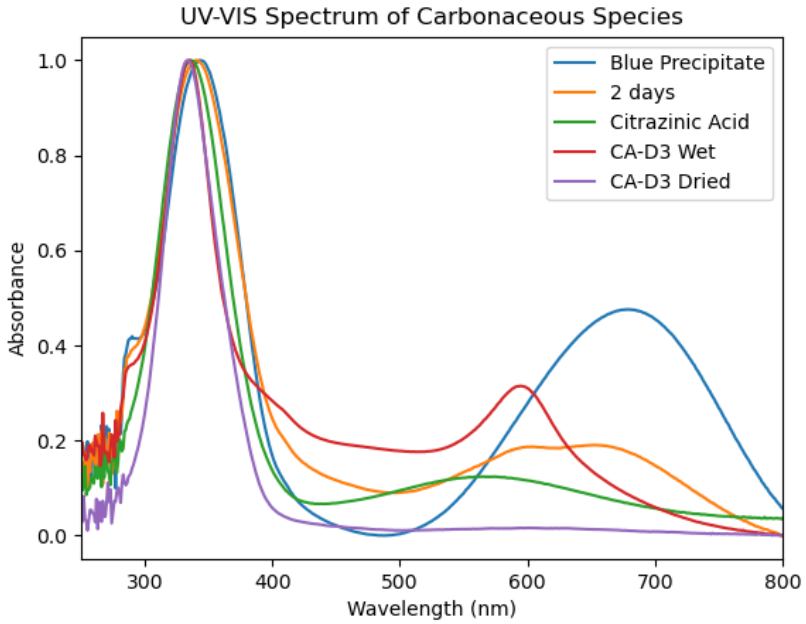


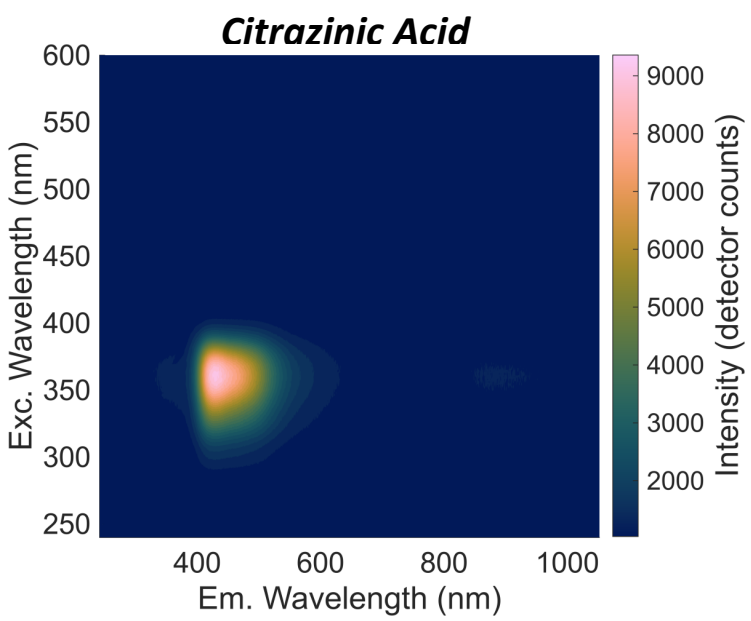
Drying of solid

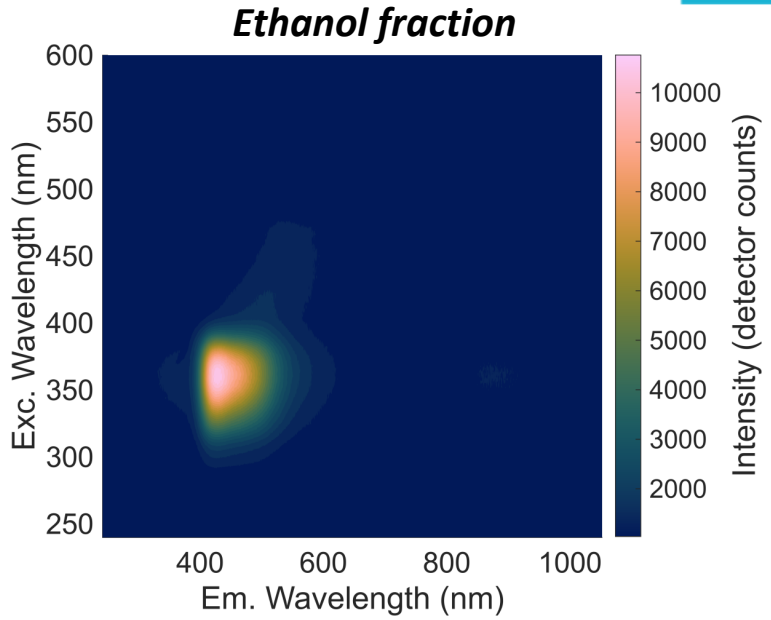
CAU Dry

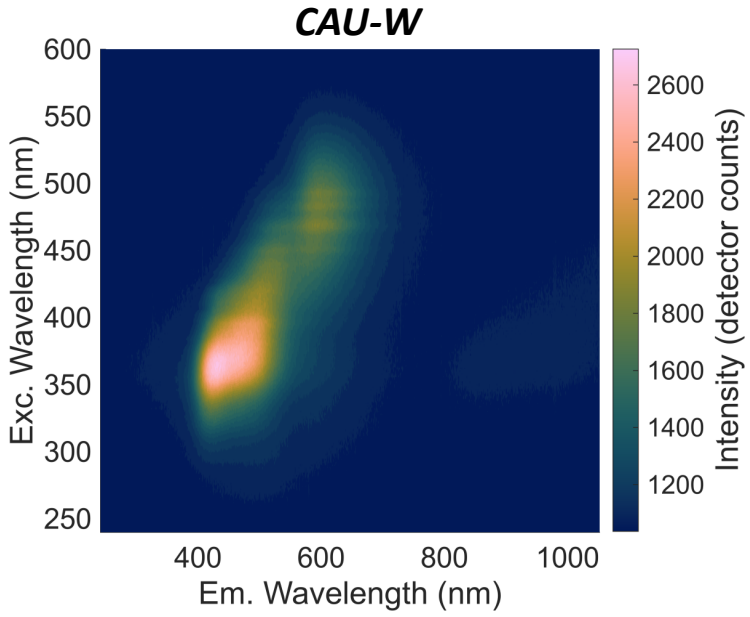


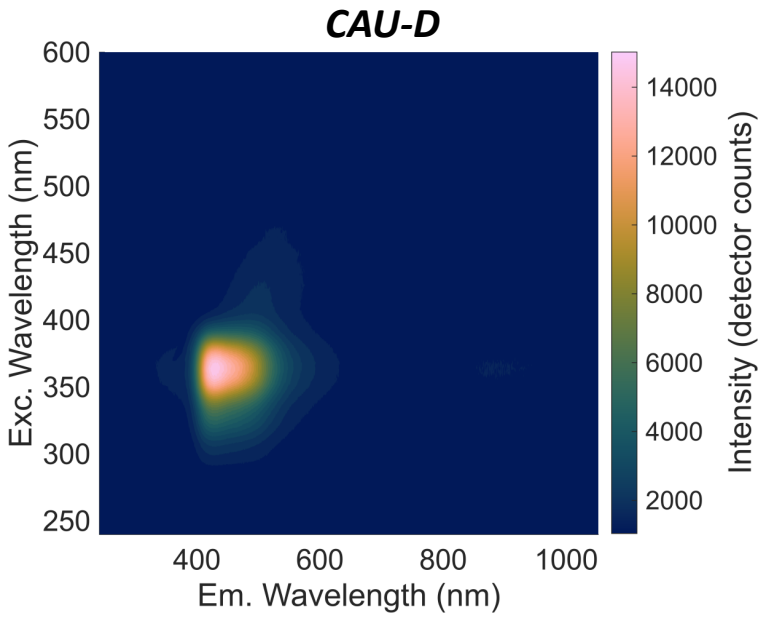
Excitation-dependent emission pattern of different fractions



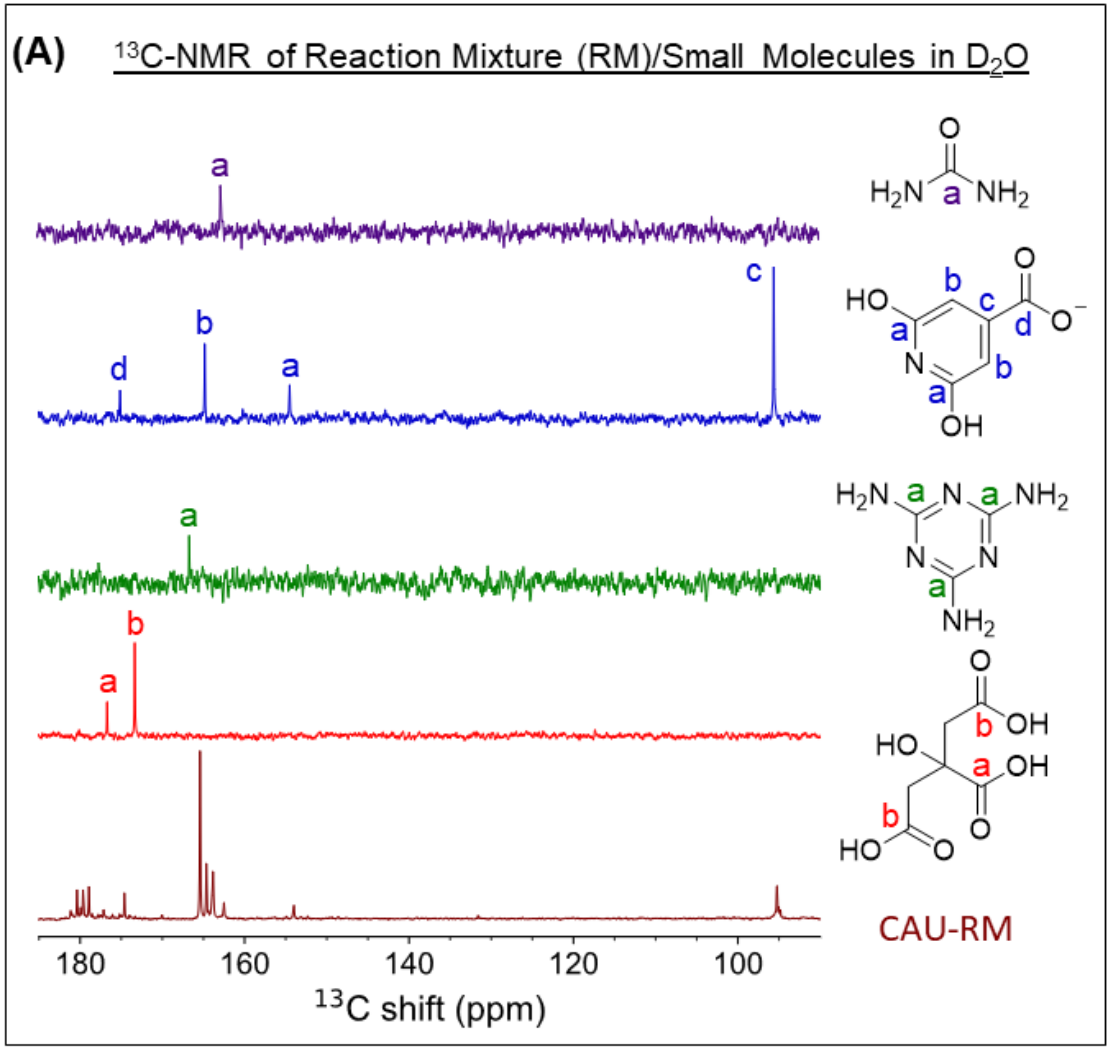


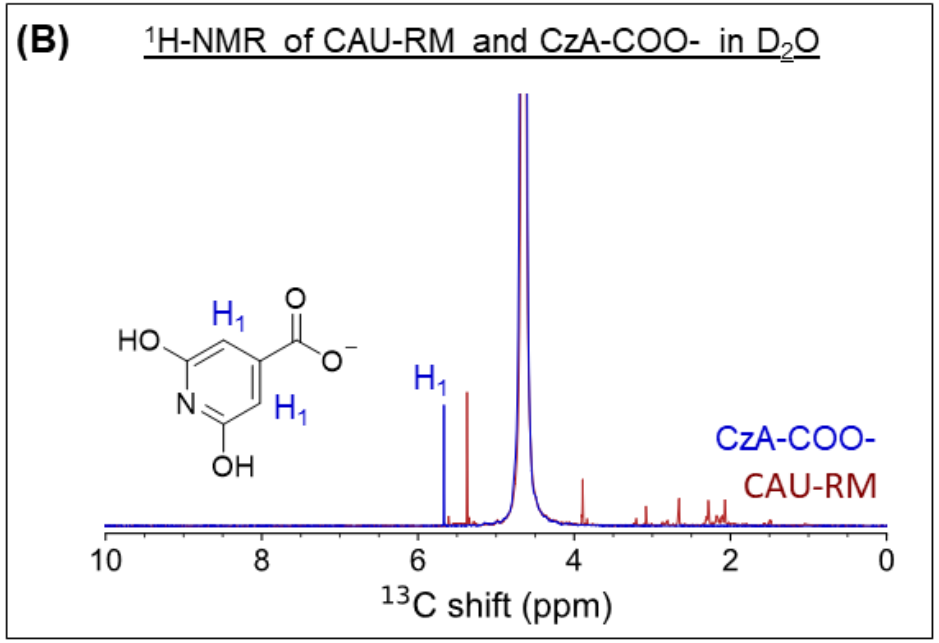




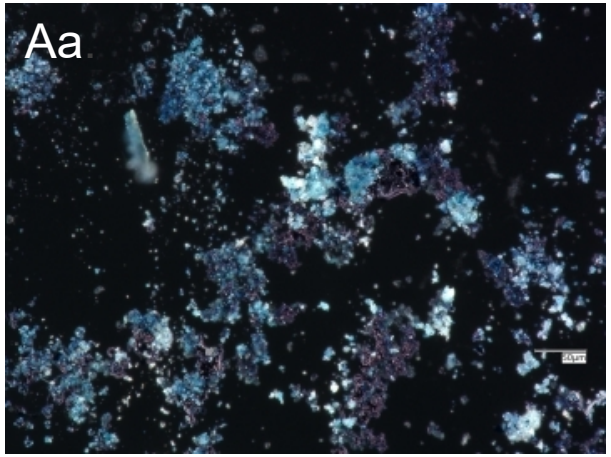


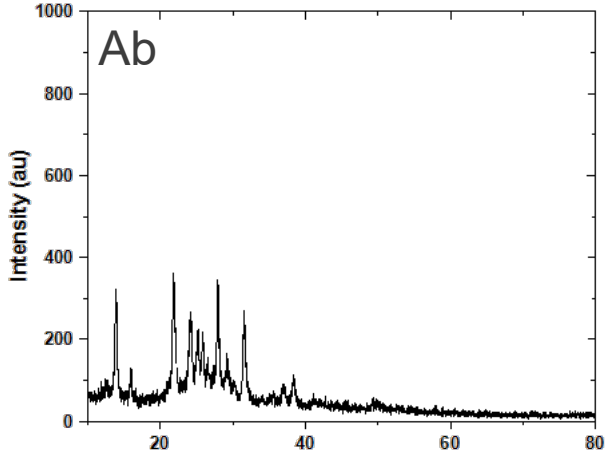
NMR show two different fractions: one with citrazinic acid rich and another with triazine rich



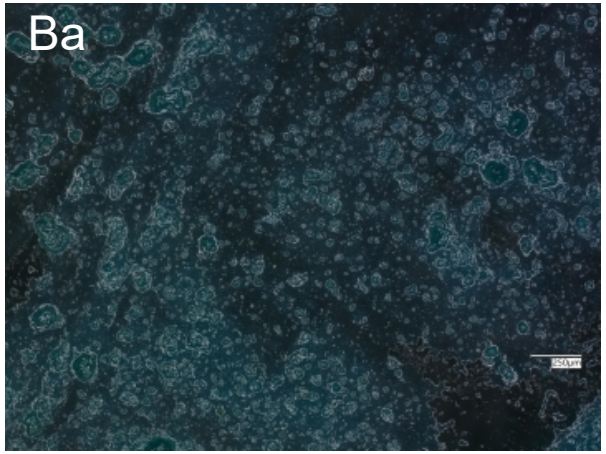


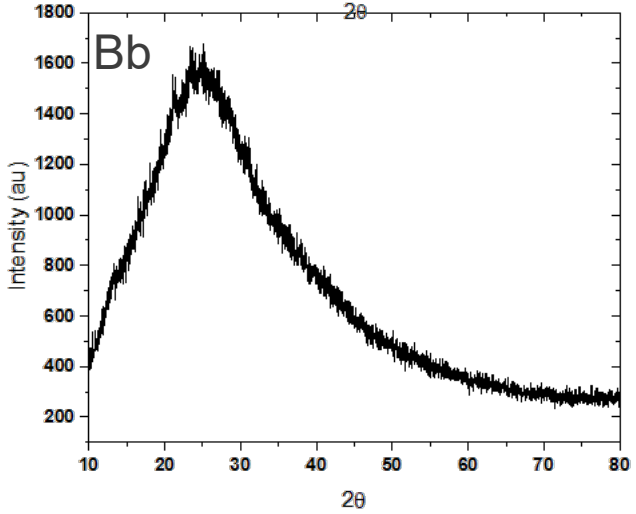
Different fractions give different particle morphology





Small-molecule hybrid

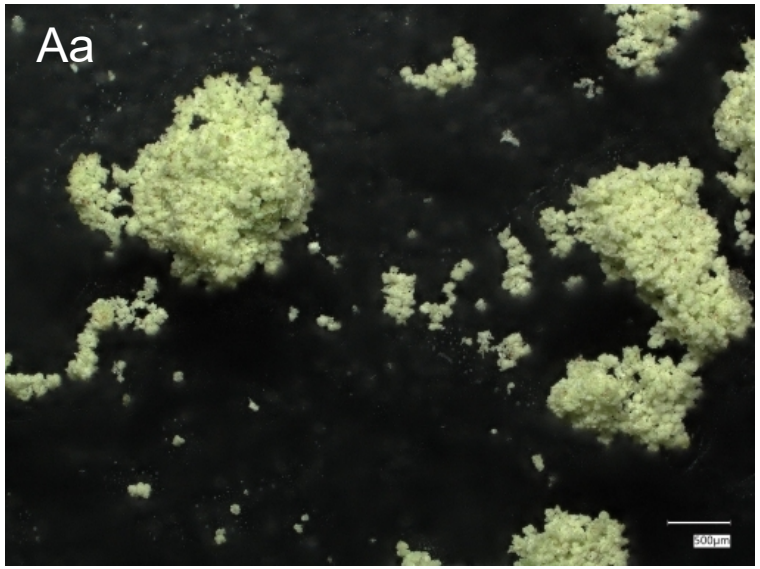


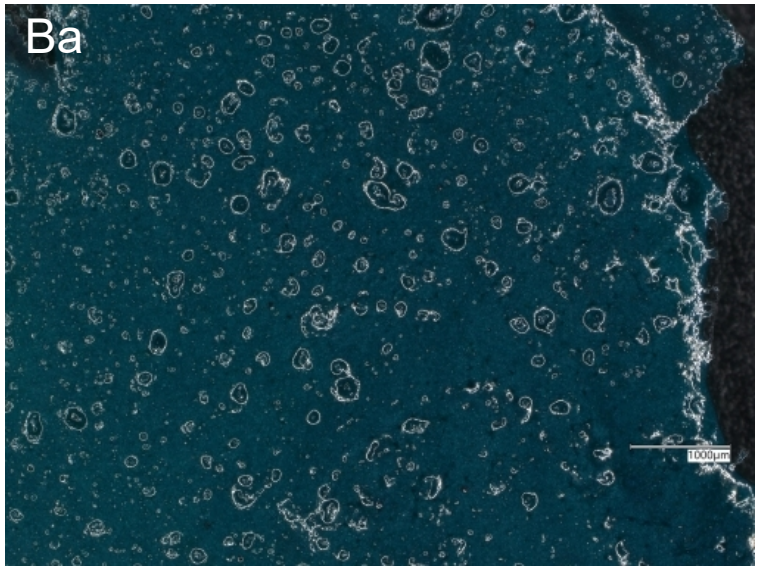


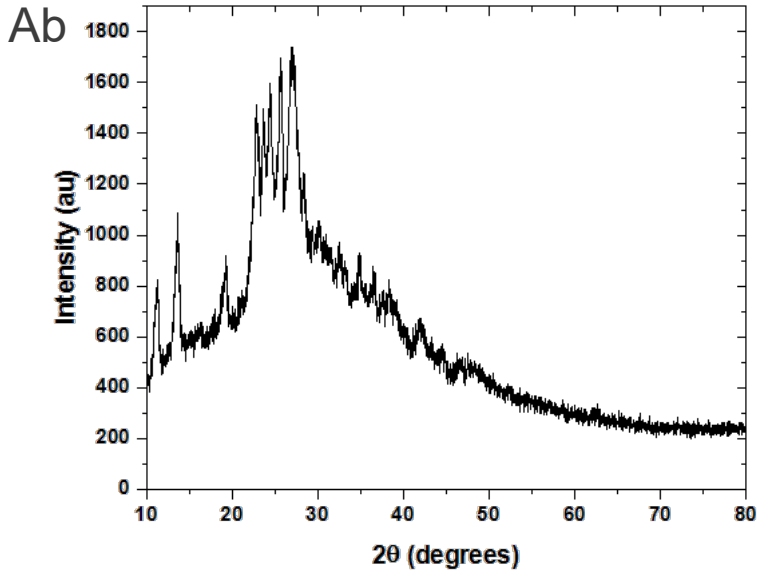
Carbonized triazine

Optical microscopy (Aa and Ba) and corresponding XRD (Ab and Bb) of ethanol fraction (Ab) and carbon nitride dot solid precipitate (Bb). While ethanol fraction consists of citrazinic acid rich crystalline structure, the solid precipitate consists of amorphous carbon nitride structure

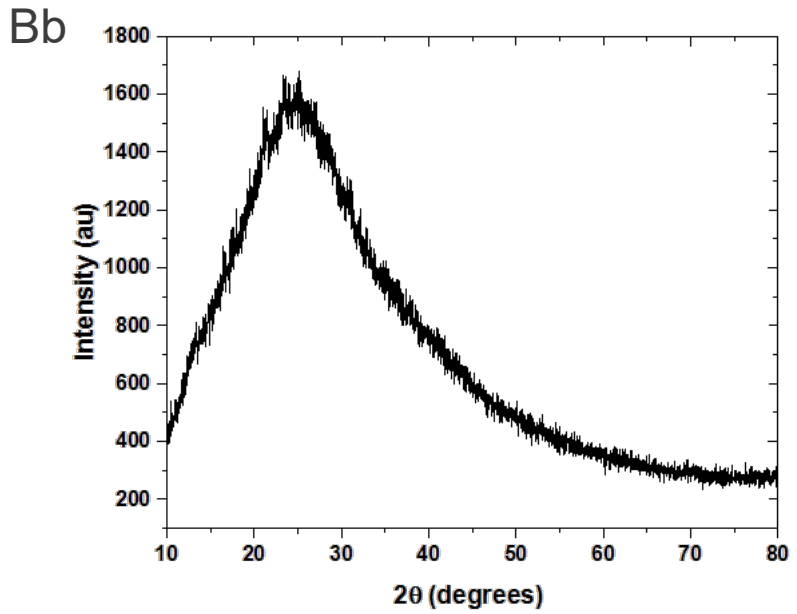
Different reaction-time gives different particle morphology







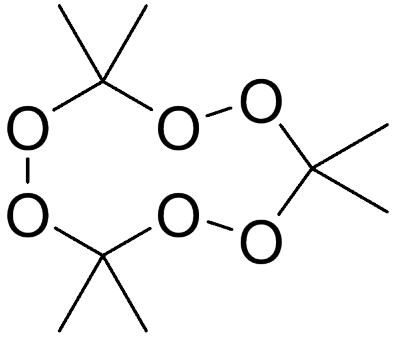
6-hour



24-hour

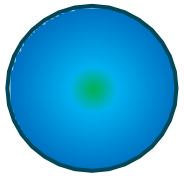
Different fractions give different responses to analytes

Tuning carbonization & CzA content for sensing applications

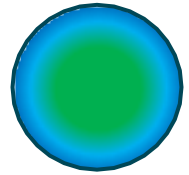


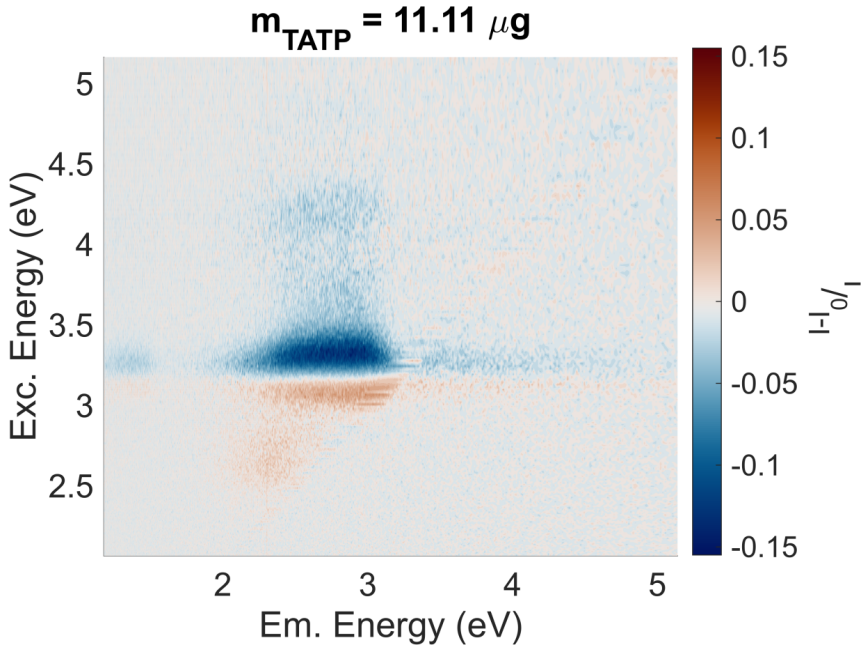
TATP

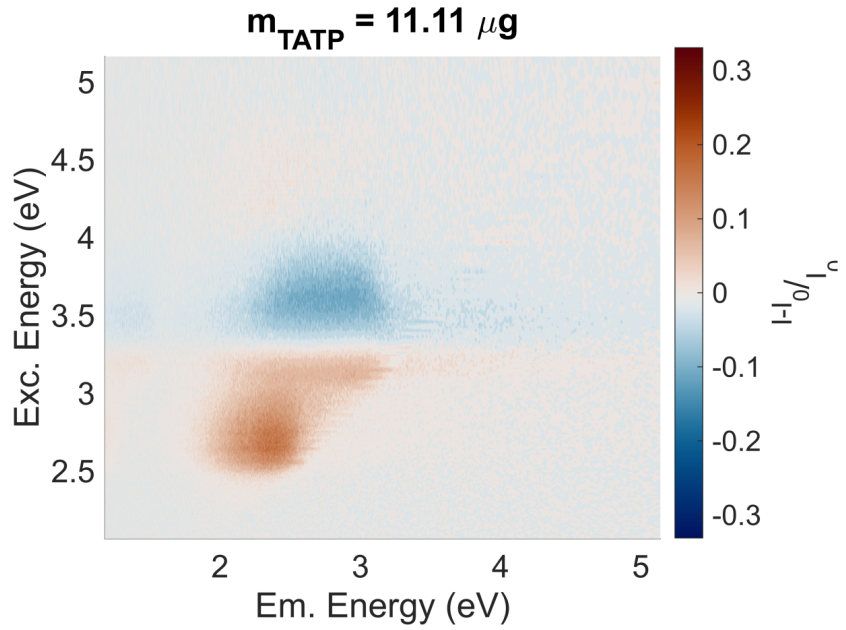
CAU-Eth



CAU-D







Key takeaways

Heterogeneity in Synthesis

- Understanding metastable structures
- Opportunities for unique properties

Excitation-Dependent Emission

- Varies with different regions
- Customizable analyte responses

Structure-Function Insights Needed

- Popularity outpaces understanding
- Essential for targeted applications