The background of the slide is a dark, almost black, space filled with various colorful, glowing, and semi-transparent particles and structures. These include small red and blue dots, larger green and blue spheres, and some elongated, cylindrical structures with internal patterns. The overall effect is that of a complex, multi-colored molecular or nanoscale environment.

The Fundamental Photophysics of Fluorescent Carbon Nanodots

Alice Sciortino

A collage of various colorful and abstract images. In the top left, there's a green globe with a grid pattern and several lines radiating from it. To its right, there are two vertical rectangular objects with glowing blue and red sections. Below the globe, there's a colorful, multi-layered circular structure. In the center, there's a blue, multi-lobed structure with wavy lines extending from it. To the right, there's a large, grey, textured object with a green section. Below that, there's a green, multi-lobed structure with wavy lines. In the bottom right, there's a yellow and black striped cylindrical object. The background is dark with various other colorful shapes and patterns.

Purpose



Purpose

Understanding the
entire CDs Photocycle

Different families
of Carbon
Nanodots

Strategy

Purpose

Understanding the
entire CDs Photocycle



Different families
of Carbon
Nanodots

Strategy

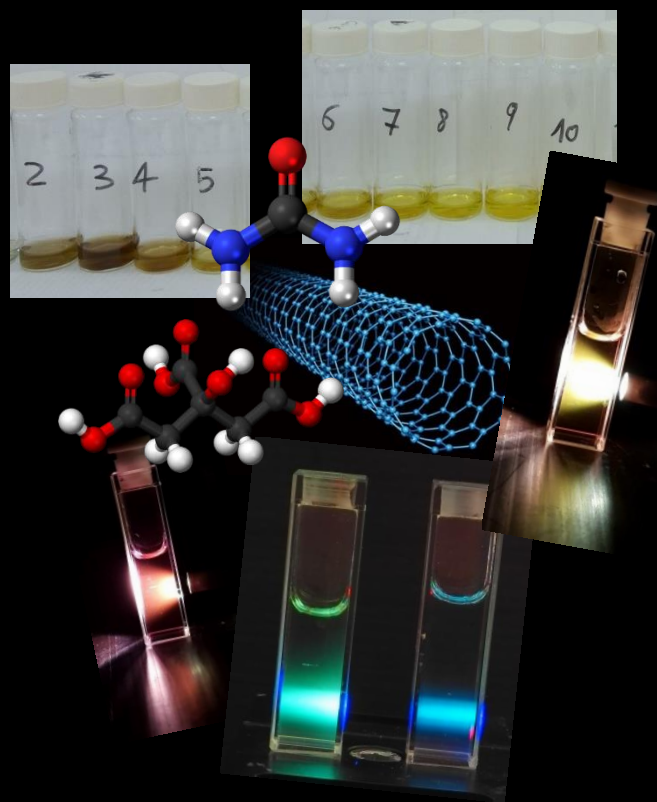
Structural &
Morphological
Characterization

Optical
Characterization

Purpose

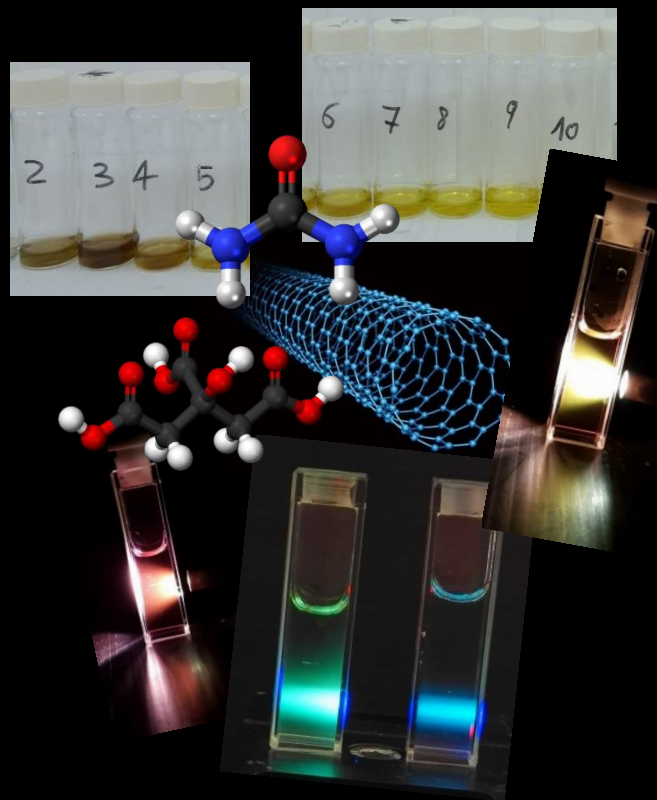
Understanding the
entire CDs Photocycle



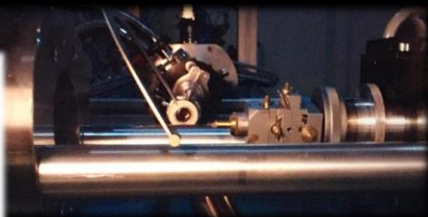


Different Synthesis
Routes

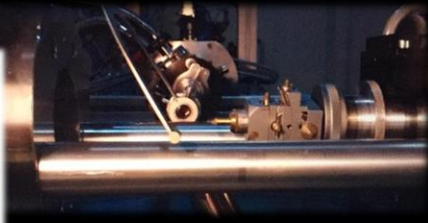
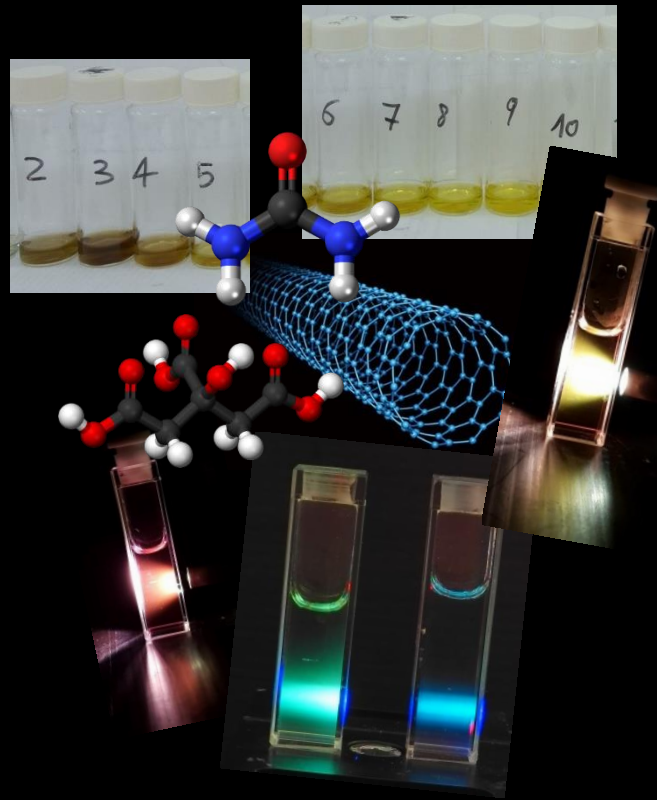
MATERIALS & METHODS



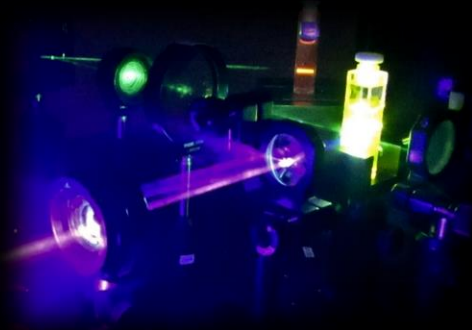
Different Synthesis
Routes
AFM, HRTEM, XRD,
...



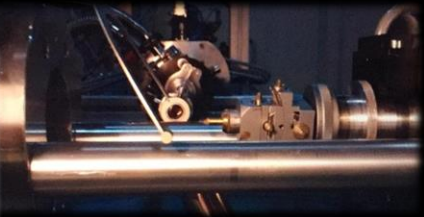
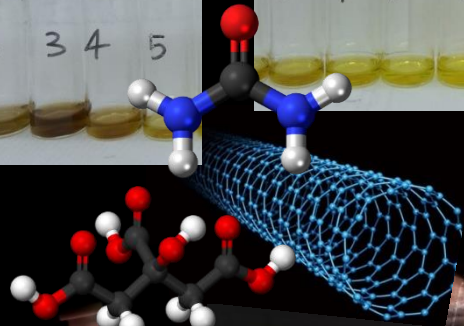
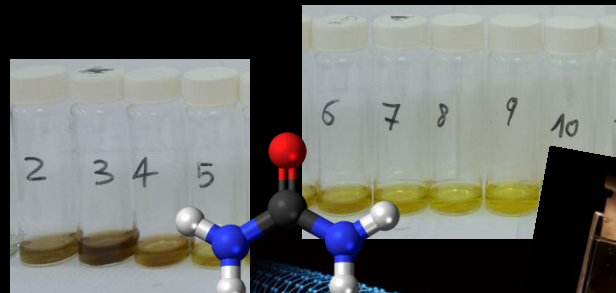
MATERIALS & METHODS



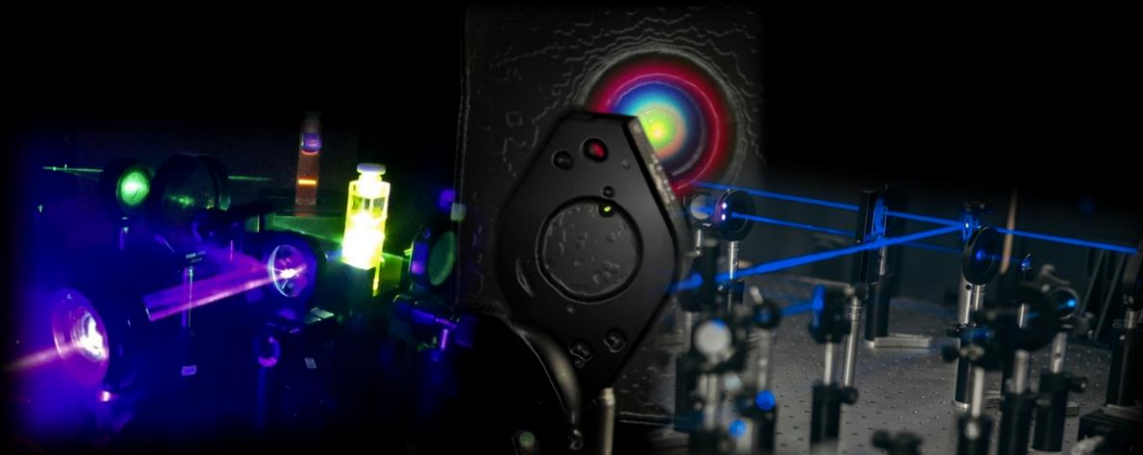
Different Synthesis
Routes
AFM, HRTEM, XRD,
...
Nanosecond Time
Resolved



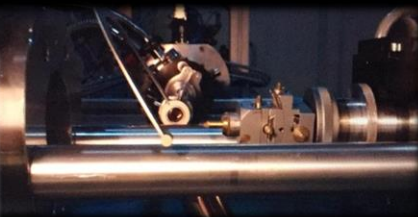
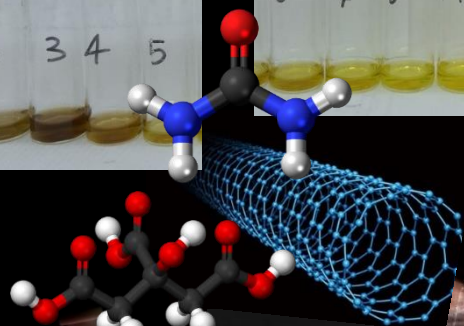
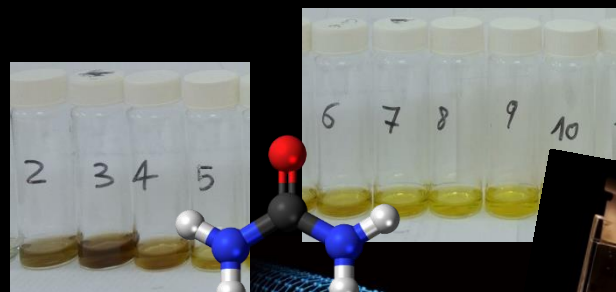
MATERIALS & METHODS



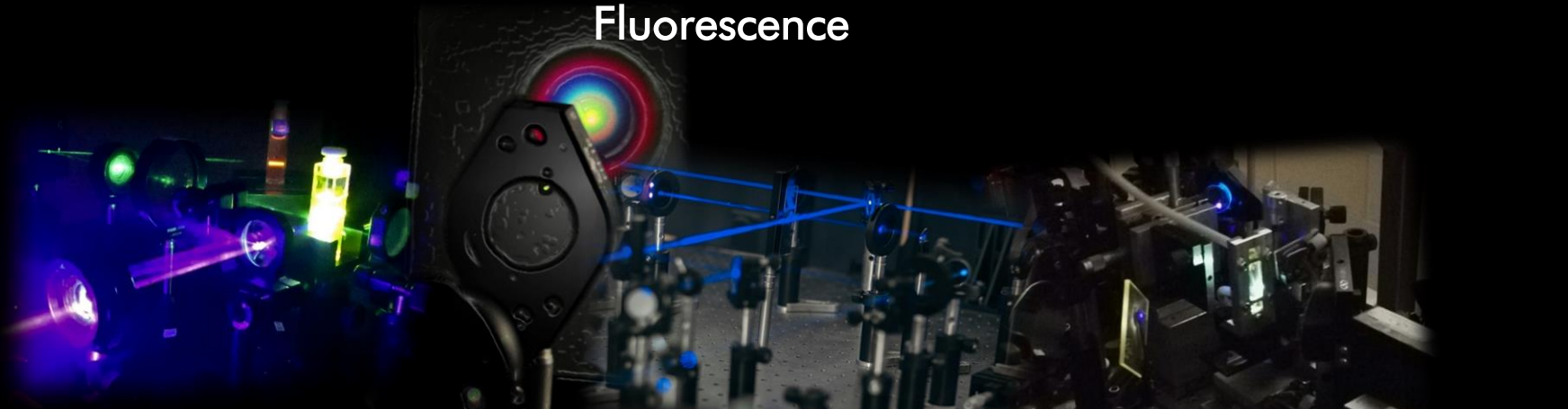
Different Synthesis
Routes
AFM, HRTEM, XRD,
...
Nanosecond Time
Resolved
Transient Absorption



MATERIALS & METHODS



Different Synthesis
Routes
AFM, HRTEM, XRD,
...
Nanosecond Time
Resolved
Transient Absorption
Ultrafast
Fluorescence



Strategy

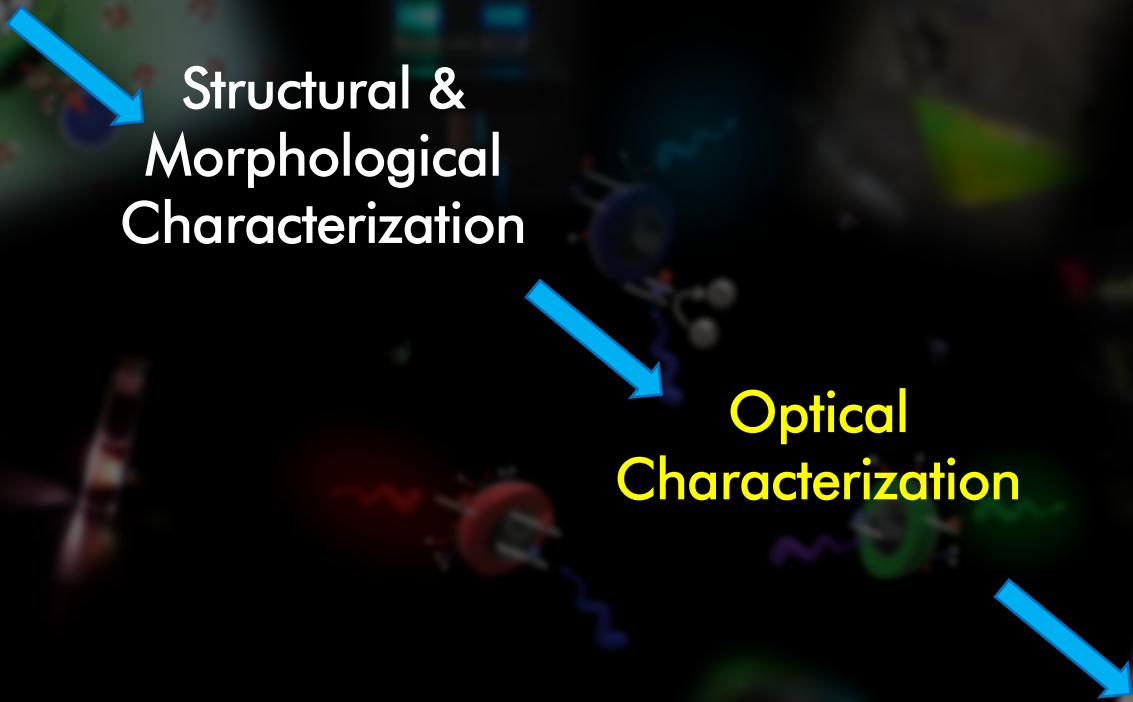
2 CDs Families:
Top Down & Bottom
Up Synthesis

Structural &
Morphological
Characterization

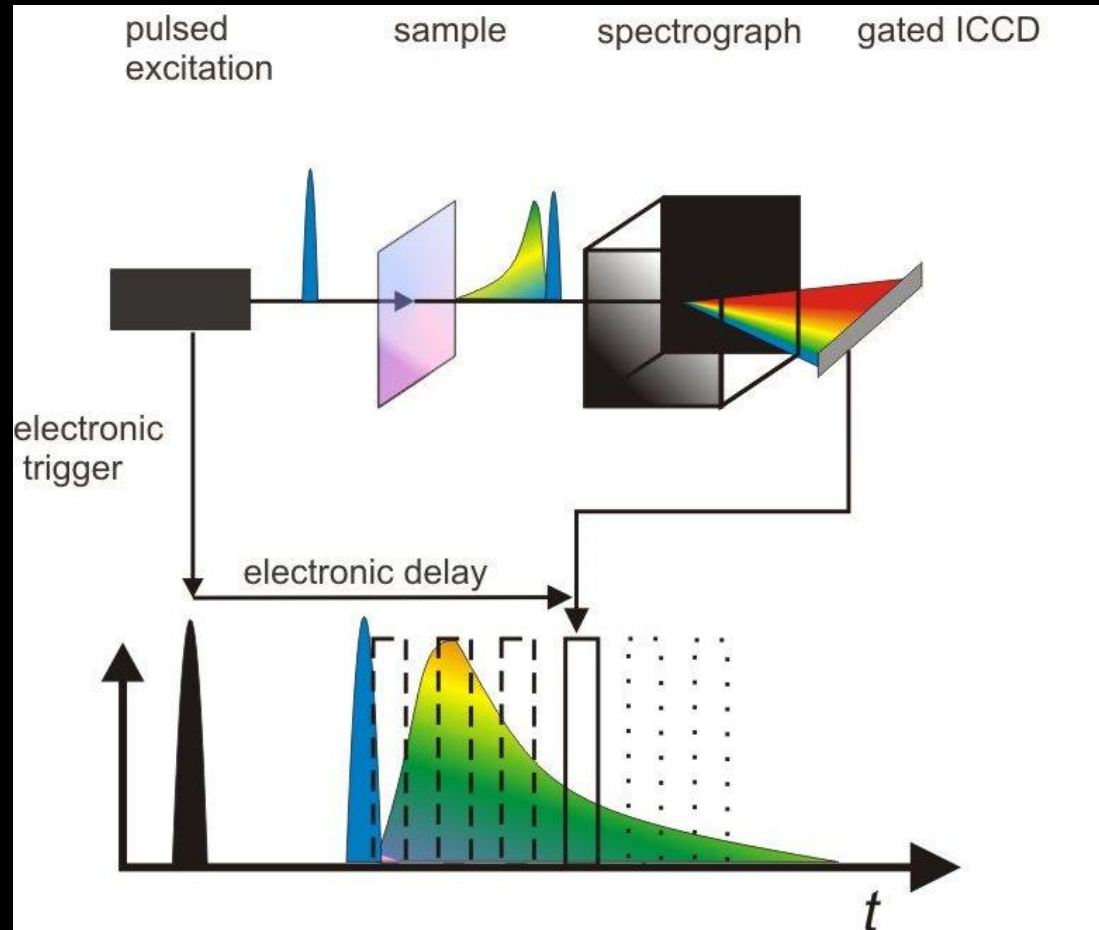
Optical
Characterization

Understanding the
entire Photocycle

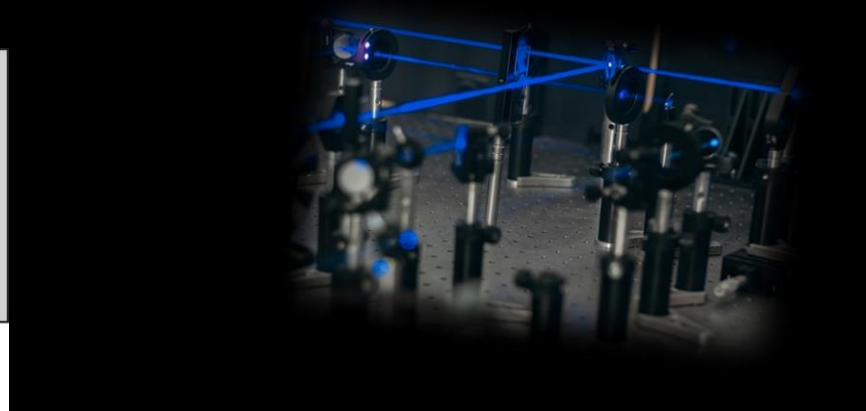
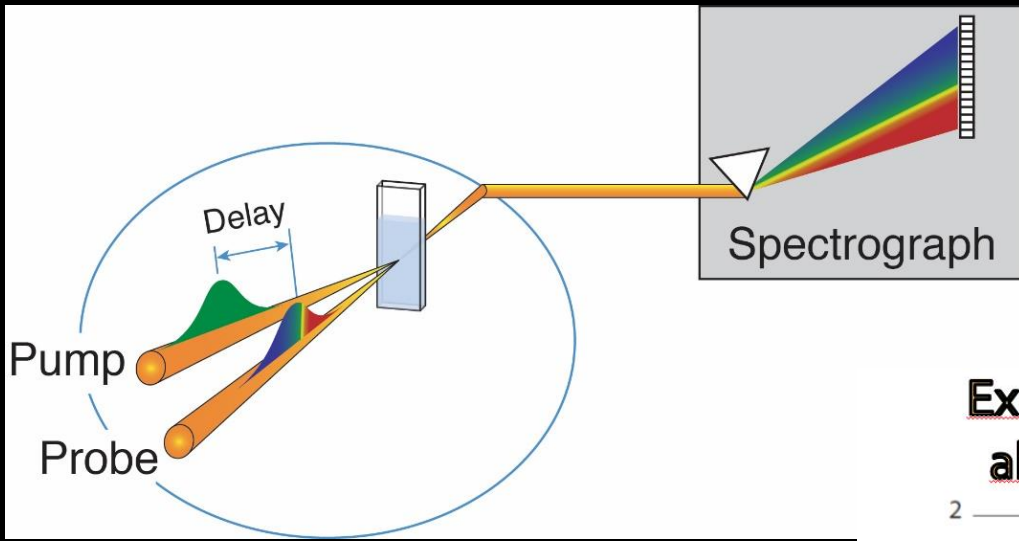
Purpose



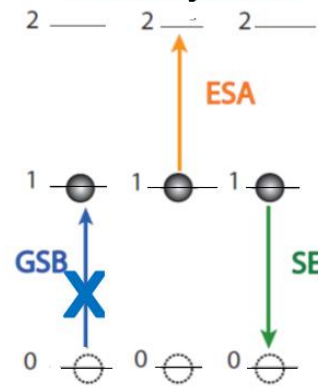
Nanosecond Time Resolved



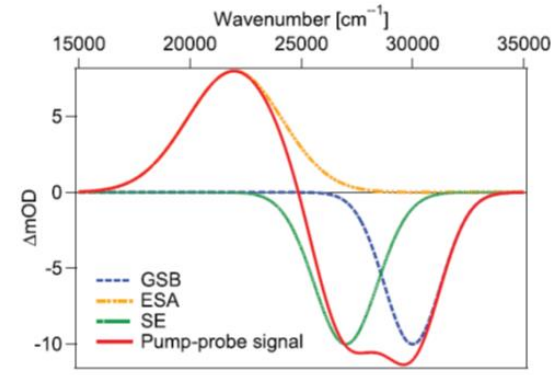
Transient Absorption



Excited state absorption

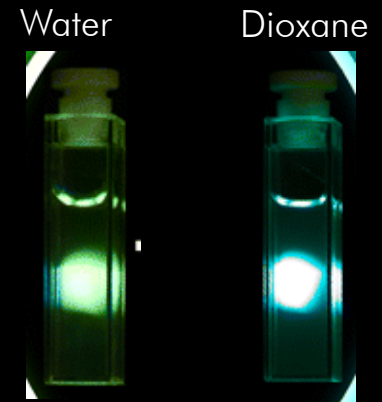


Ground state bleaching Stimulated emission



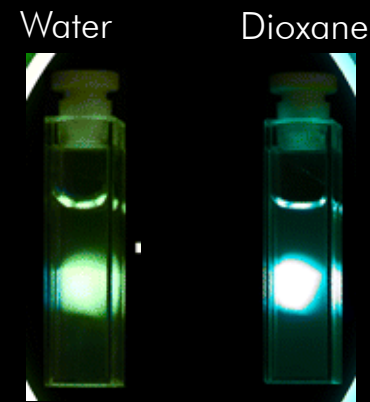
Photoluminescence Phenomenology

- Uncommon in other C-based nanomaterials
- Intense
- Tunable
- Highly sensitive to the environment: solvent, ions, pH



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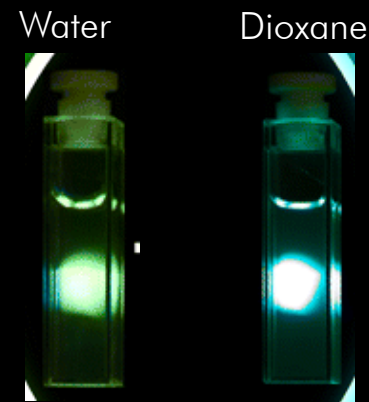


How to Explain this Phenomenology?

*Origin of the emission? Core? Surface? Size effects?
Response to the environment?
Photoinduced electron transfer mechanisms?
Tunability? Disorder? Role of crystalline structure?*

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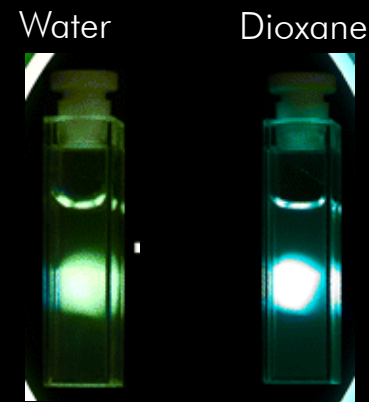


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Photoluminescence Phenomenology

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How to Explain this Phenomenology?

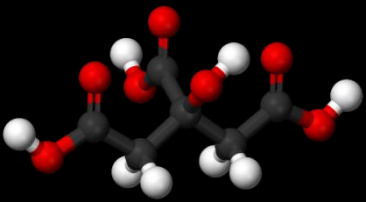
- Origin of the emission? Core? Surface? Size effects?*
- Response to the environment?*
- Photoinduced electron transfer mechanisms?*
- Tunability? Disorder? Role of crystalline structure?*

A collage of scientific illustrations on a dark background. It includes a DNA double helix, a cell diagram with various organelles, a microscope, and various molecular structures and diagrams. The text "Experimental Results" is overlaid in white at the bottom.

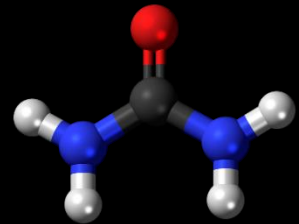
Experimental Results

BOTTOM UP SYNTHESIS

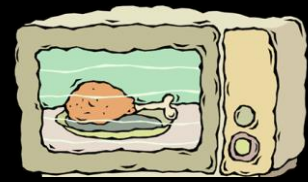
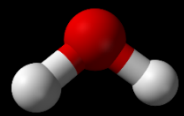
Citric Acid



Urea



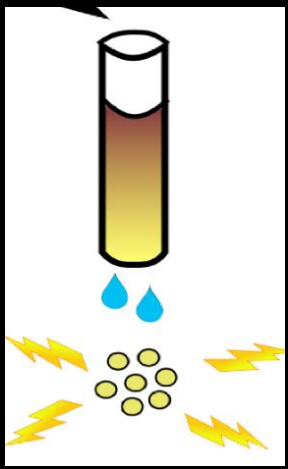
Deionized Water



Sunlight



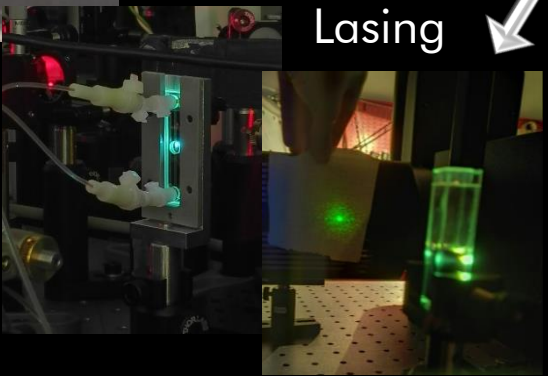
Extraordinary
Optical Properties:
High QY



Purification

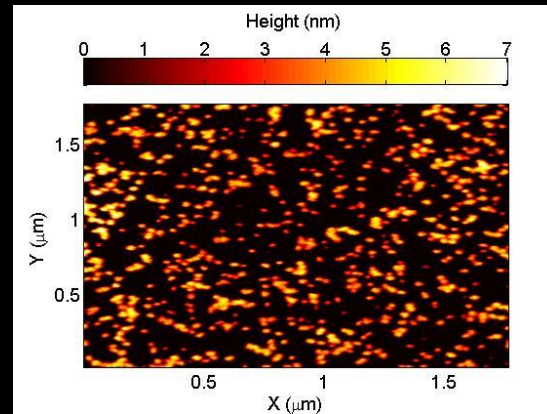
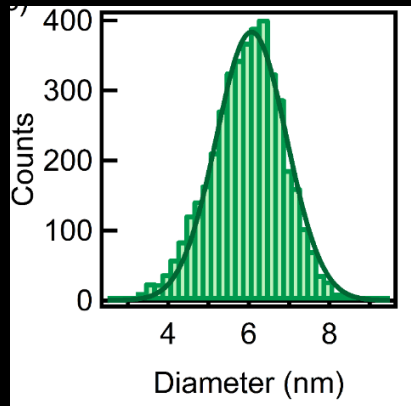
UV light

Lasing



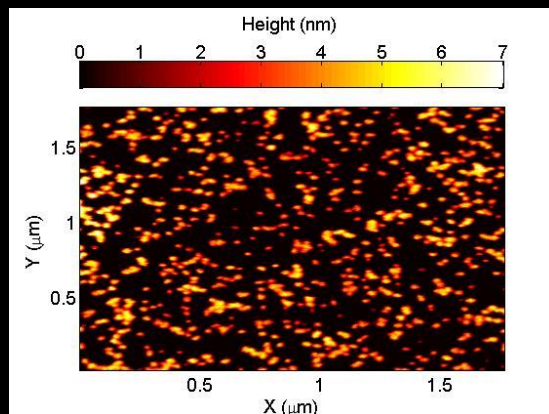
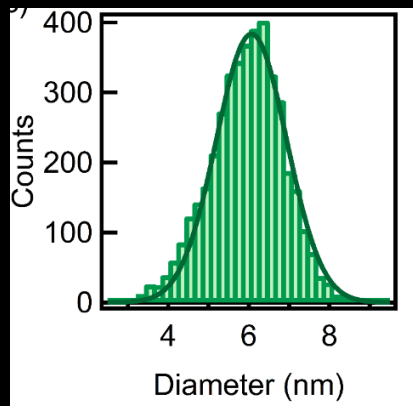
Messina et al., 2016, *J Mater Chem C*
Sciortino et al., 2018, *Chem. Mater.*

Atomic Force Microscopy



6 nm Nanoparticles

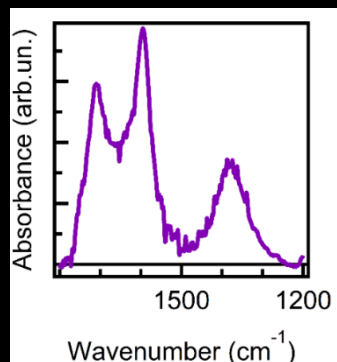
Atomic Force Microscopy



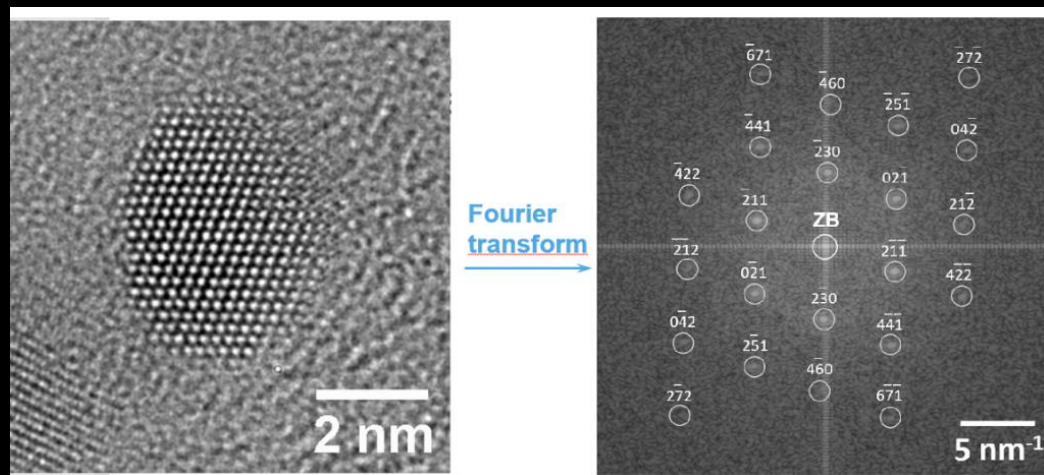
6 nm Nanoparticles

$1710\text{ cm}^{-1} \rightarrow \text{-COOH}$
 $1600\text{ cm}^{-1} \rightarrow \text{-CONH}_2$
 $1380\text{ cm}^{-1} \rightarrow \text{-CN=}$

Infrared Absorption Spectroscopy

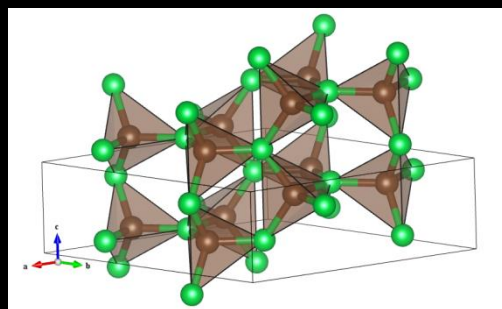


High Resolution Transmission Electron Microscopy



6 nm Nanoparticles

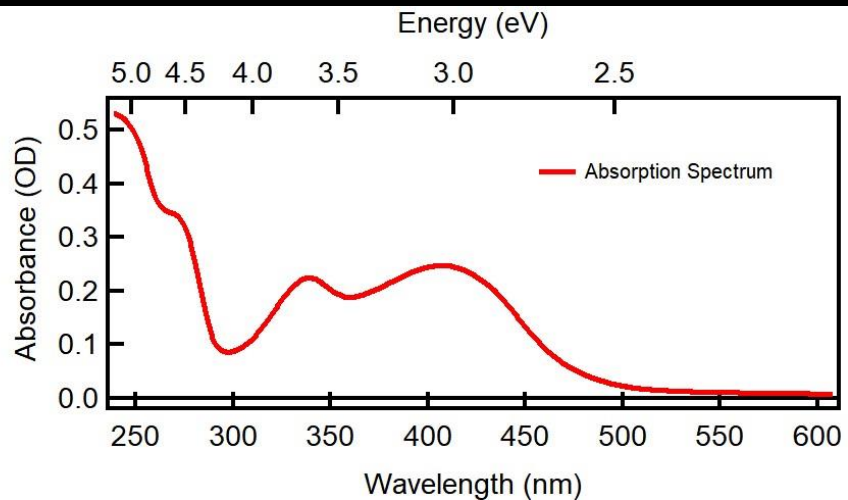
1710 cm⁻¹ → -COOH
1600 cm⁻¹ → -CONH₂
1380 cm⁻¹ → -CN=



C → sp³
N → sp²

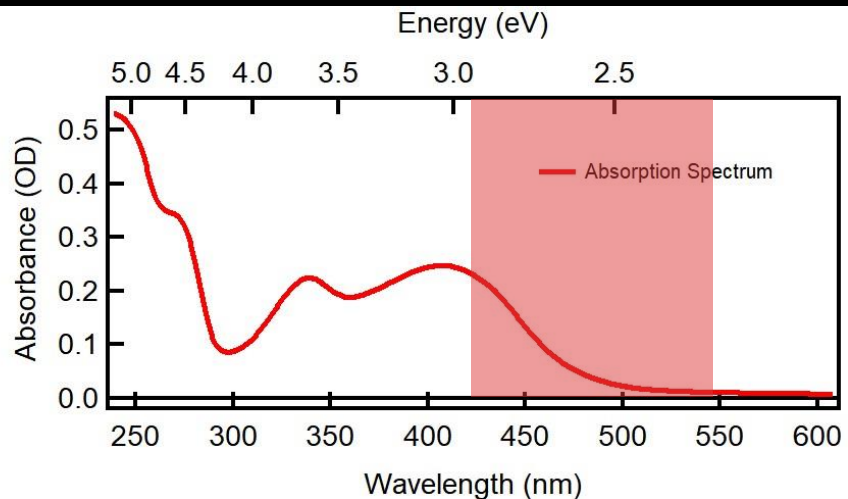
NEW STRUCTURE!
Monocrystals of β-C₃N₄

Absorption Spectrum

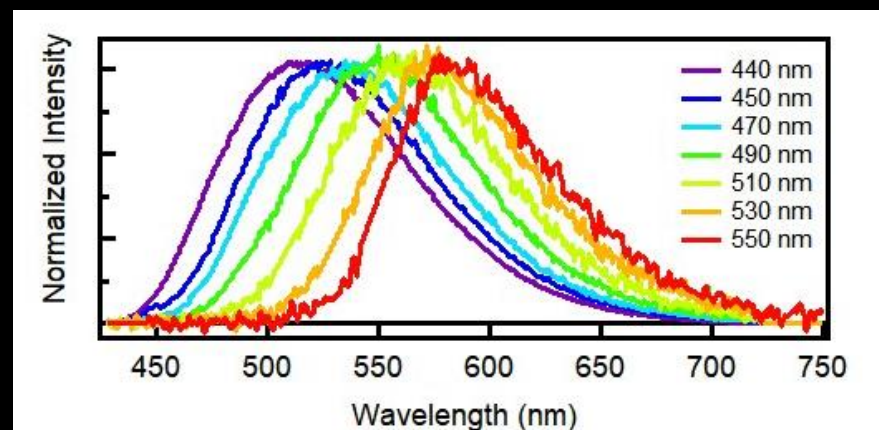


OPTICAL PROPERTIES OF β -C₃N₄

Absorption Spectrum



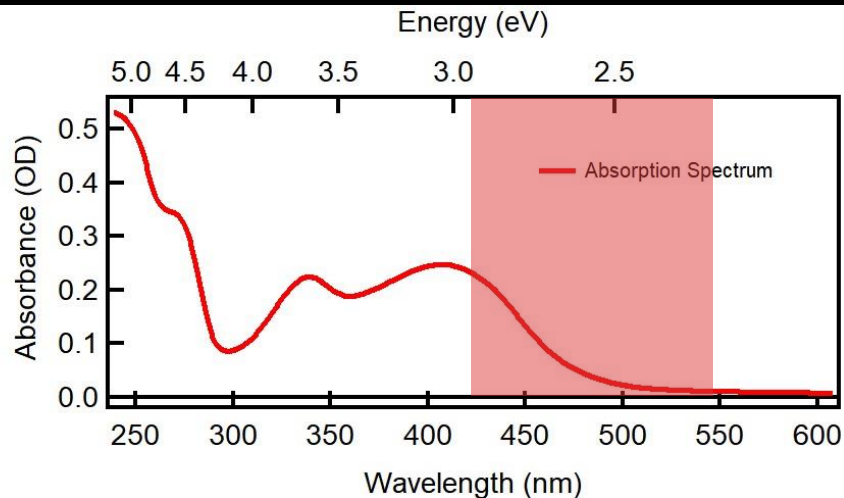
Emission Spectra



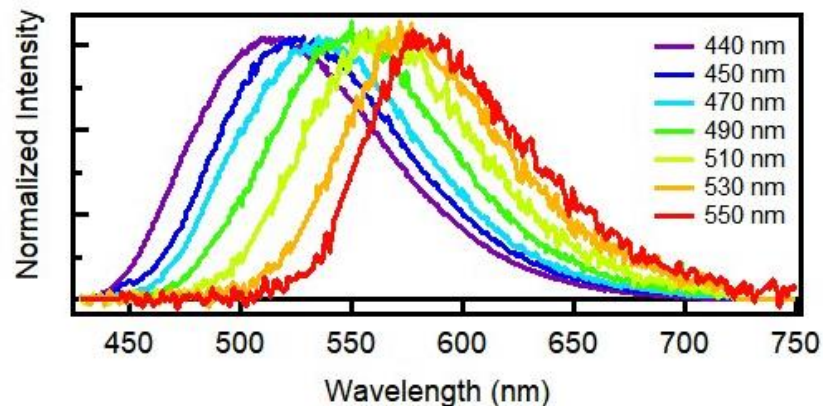
Tunable Band

OPTICAL PROPERTIES OF $\beta\text{-C}_3\text{N}_4$

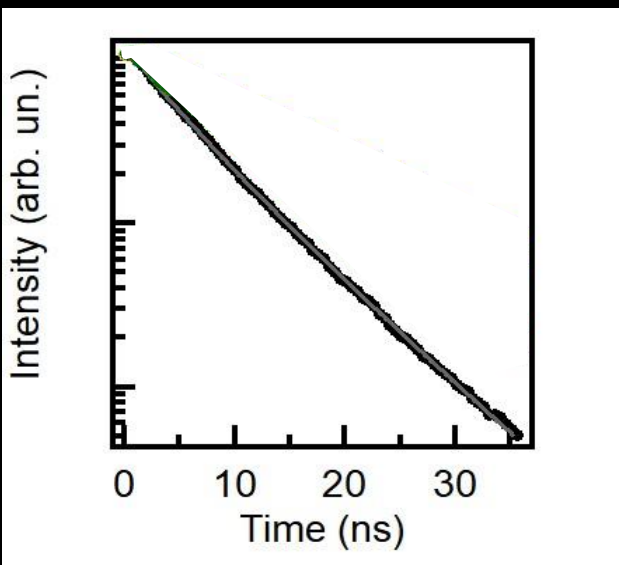
Absorption Spectrum



Emission Spectra



Tunable Band Decay Kinetics



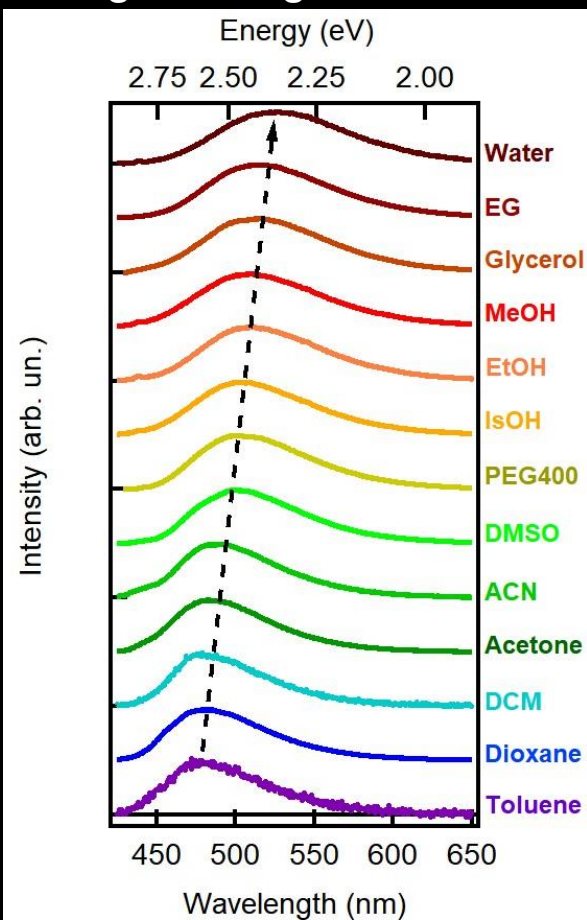
$\tau \approx 4$ ns

Tunable Band

EMISSION MECHANISM IN β -C₃N₄

EMISSION MECHANISM IN $\beta\text{-C}_3\text{N}_4$

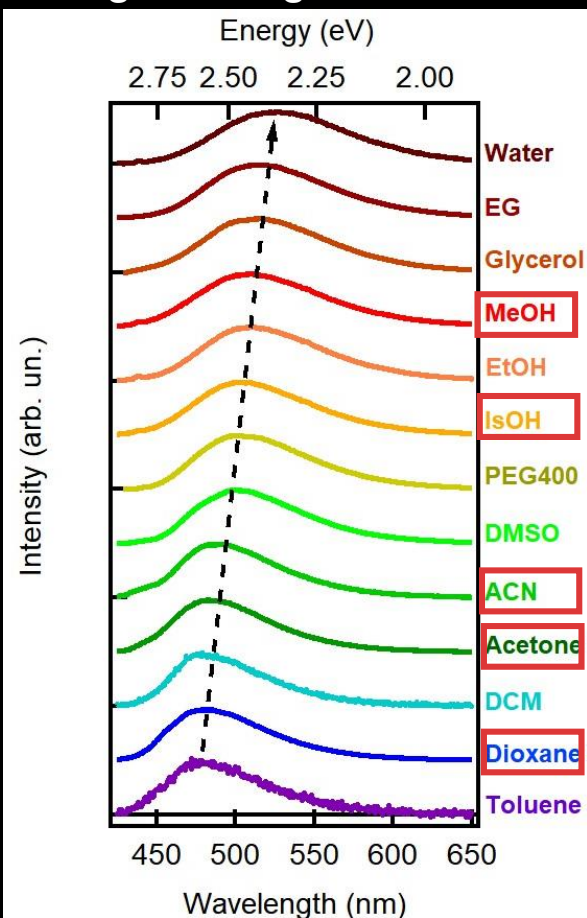
Emission Spectra: Strong and regular Solvatochromism



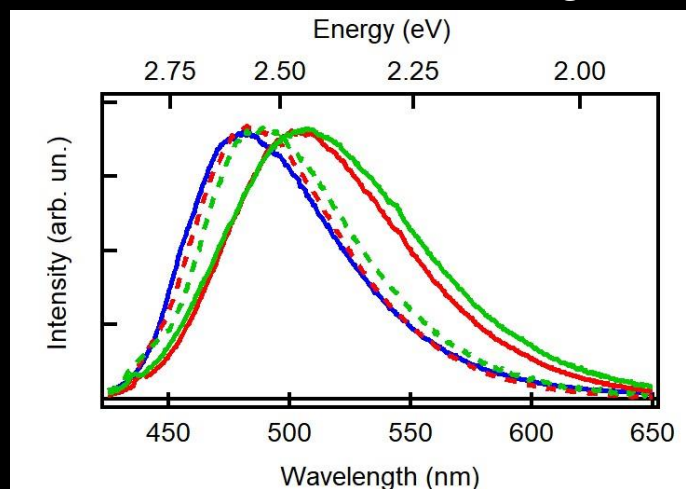
EMISSION MECHANISM IN $\beta\text{-C}_3\text{N}_4$

Emission Spectra:

Strong and regular Solvatochromism



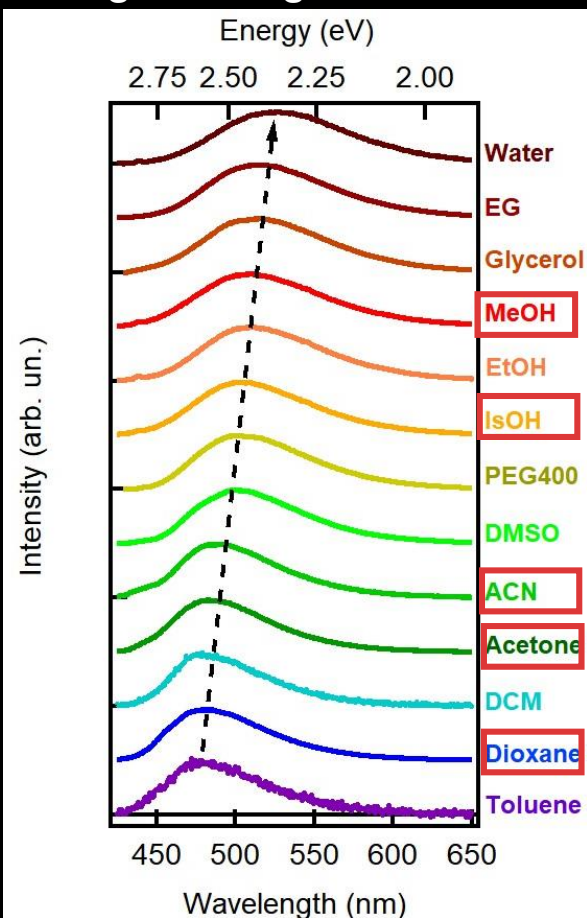
Influence of H-bonding



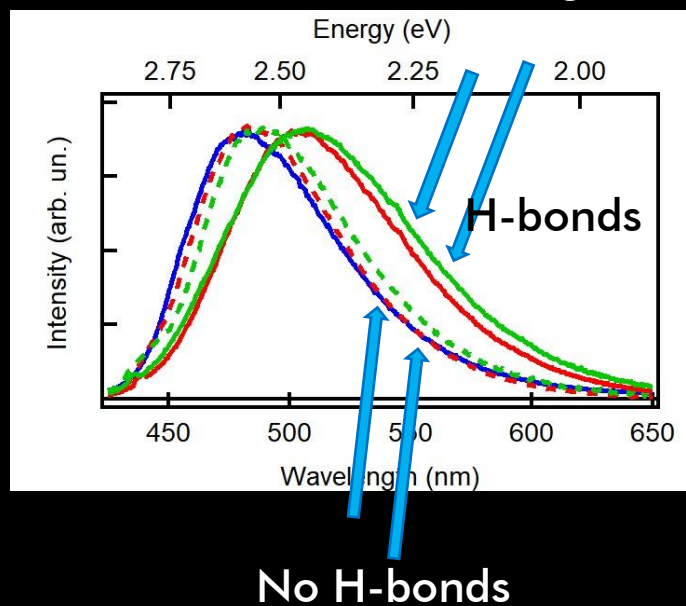
EMISSION MECHANISM IN β - C_3N_4

Emission Spectra:

Strong and regular Solvatochromism



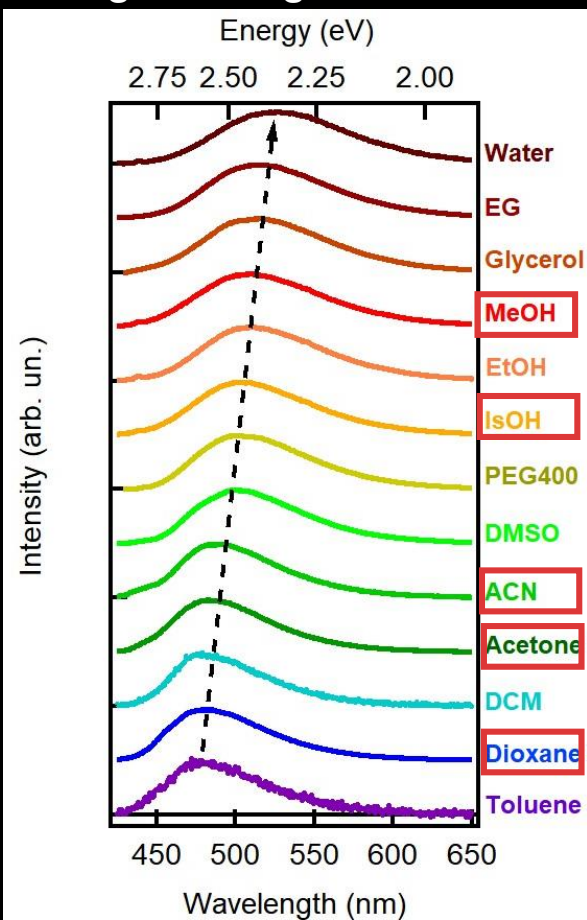
Influence of H-bonding



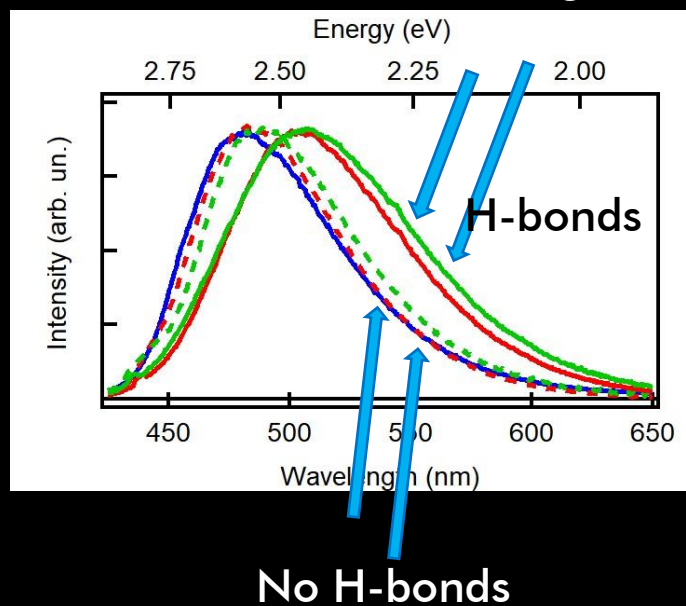
EMISSION MECHANISM IN $\beta\text{-C}_3\text{N}_4$

Emission Spectra:

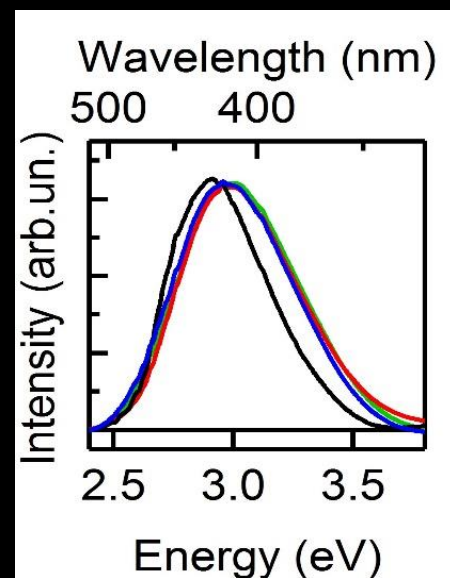
Strong and regular Solvatochromism



Influence of H-bonding

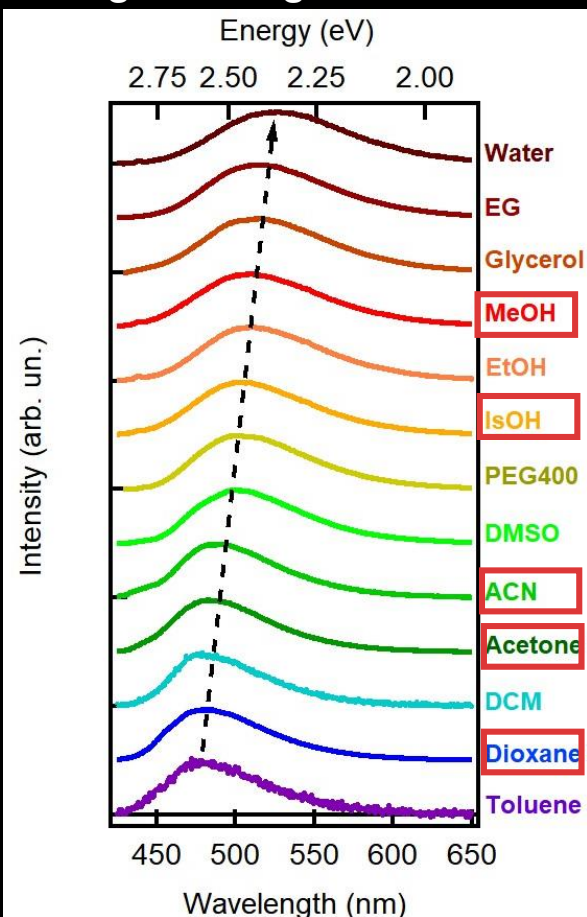


Excitation Spectra:
Hardly solvent-sensitive

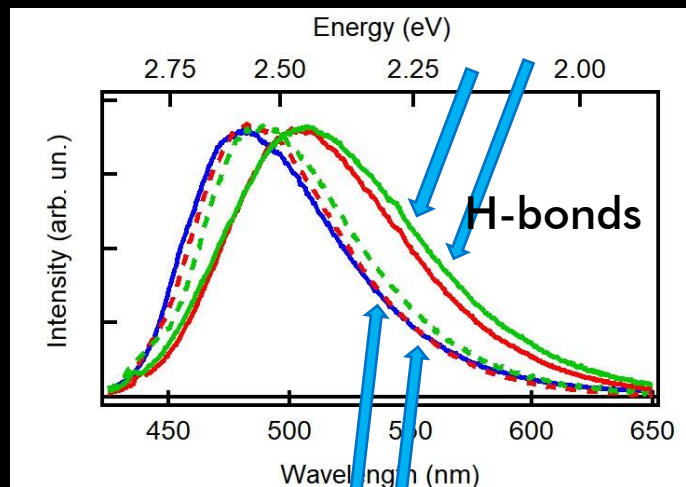


EMISSION MECHANISM IN β - C_3N_4

Emission Spectra:
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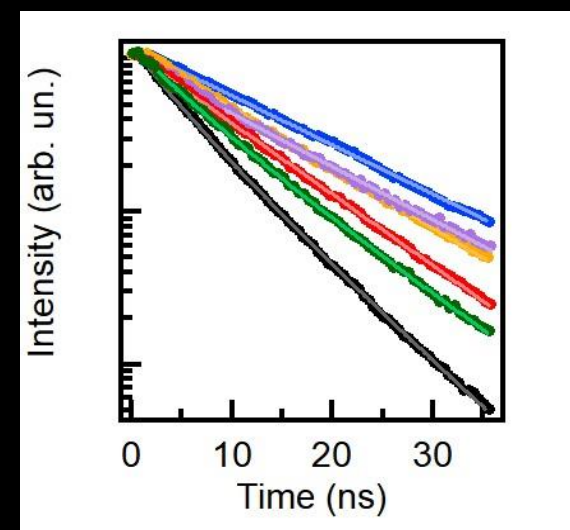
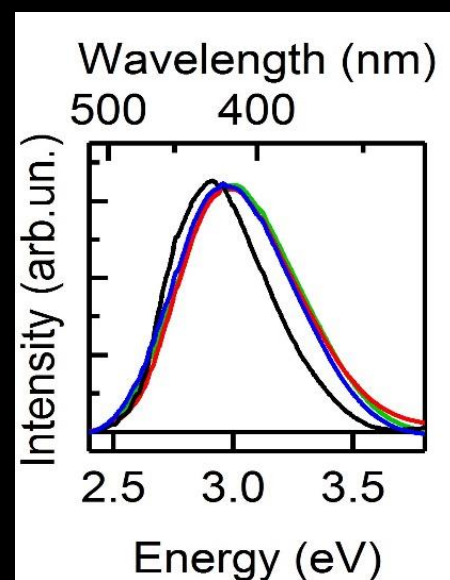
Influence of H-bonding



No H-bonds

QY values & Decay pathways are strongly solvent-dependent $\rightarrow K_{nr}$ solvent-dependent

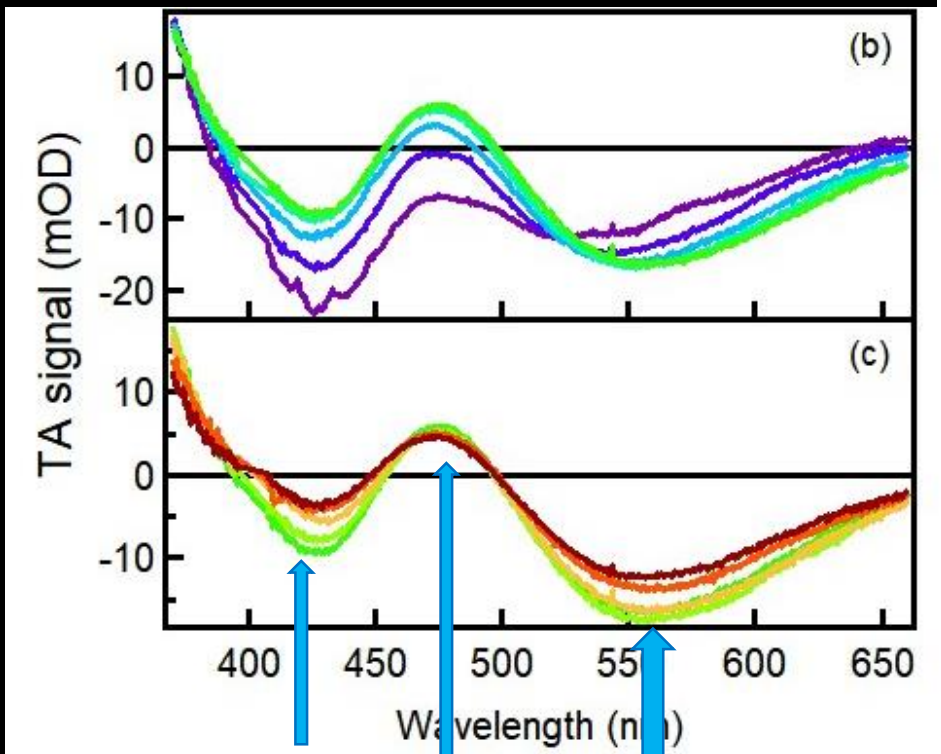
Excitation Spectra:
Hardly solvent-sensitive



ULTRAFAST TECHNIQUES TO UNRAVEL THE PHOTOCYCLE

ULTRAFAST TECHNIQUES TO UNRAVEL THE PHOTOCYCLE

Transient Absorption



- | | |
|--------|--------|
| 200 fs | 5 ps |
| 400 fs | 10 ps |
| 1 ps | 40 ps |
| 2 ps | 100 ps |
| 5 ps | 200 ps |

Times

$$\tau_1 = 0.19 \text{ ps}$$

$$\tau_2 = 2.1 \text{ ps}$$

Solvation \rightarrow Verified with other Solvents (not shown)

$$\tau_3 > 1 \text{ ns}$$

Depopulation of the excited state

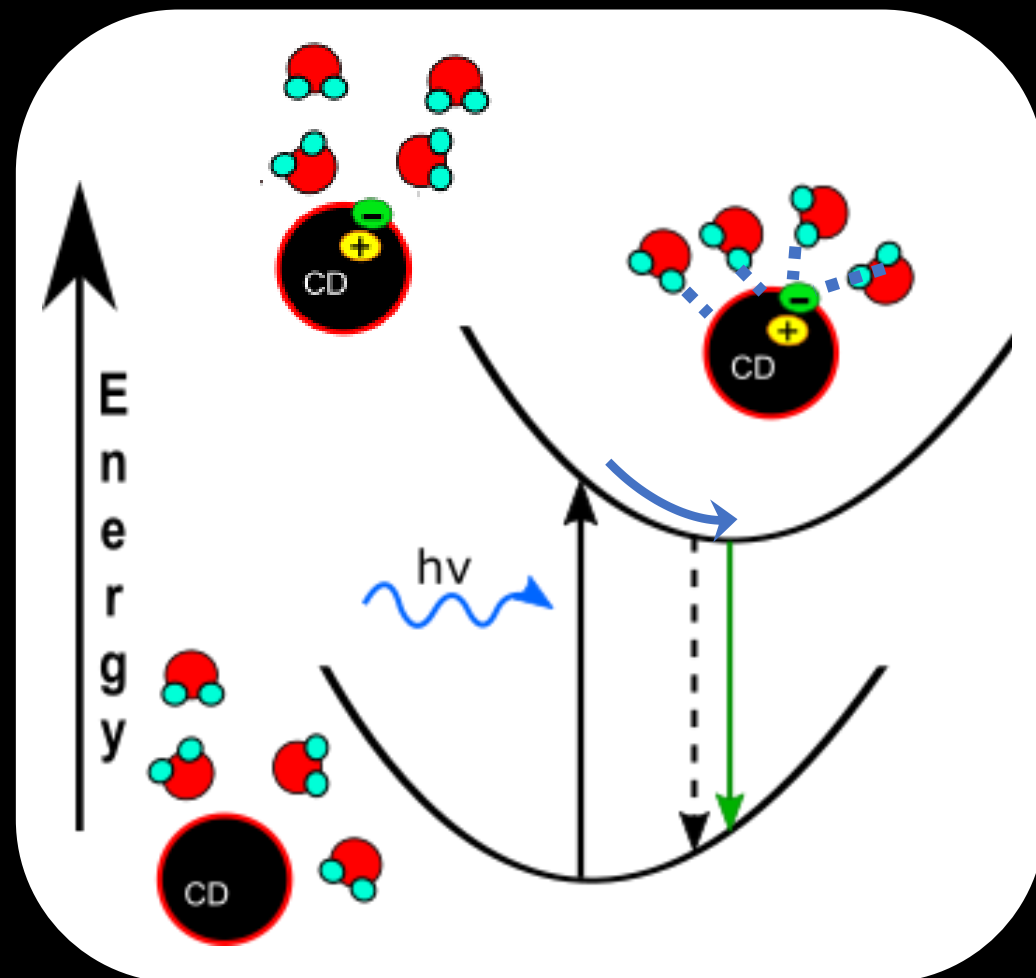
Ground State Depopulation

Excited State Absorption

Stimulated Emission

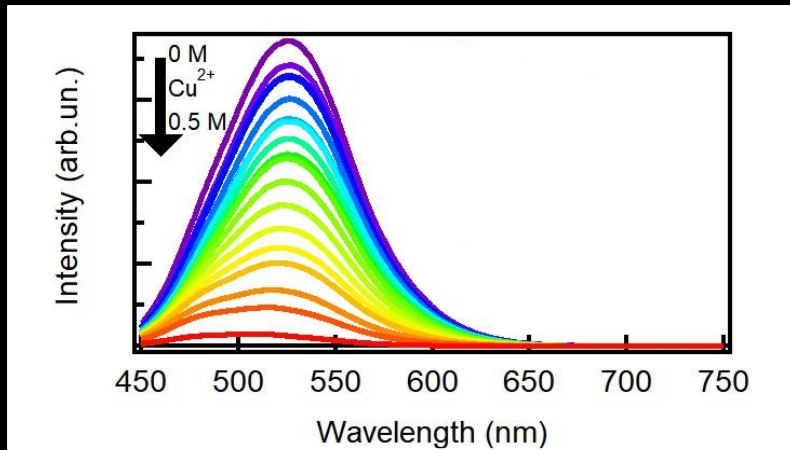
EMISSION MECHANISM IN β - C_3N_4

- Coupling between Core and Surface
 - Charge Separation
 - Localized Negative Charge Exposed to Solvent
- Direct population of the excited state
 - In sub-ns range only Solvation Relaxation
 - In ns range Depopulation of excited state



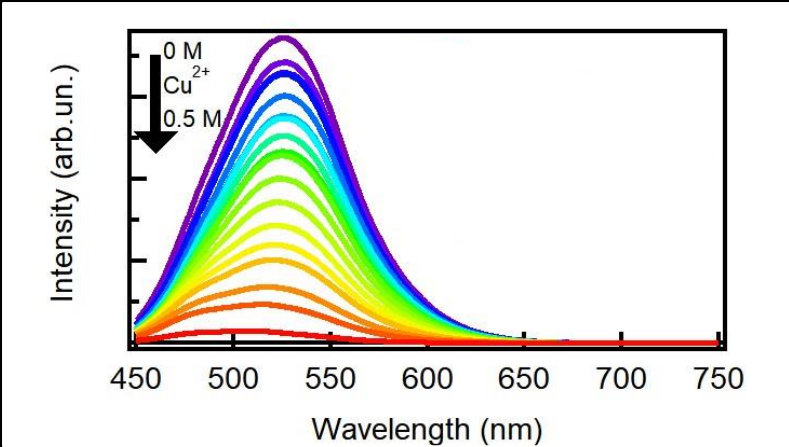
INTERACTION WITH IONS

Quenching

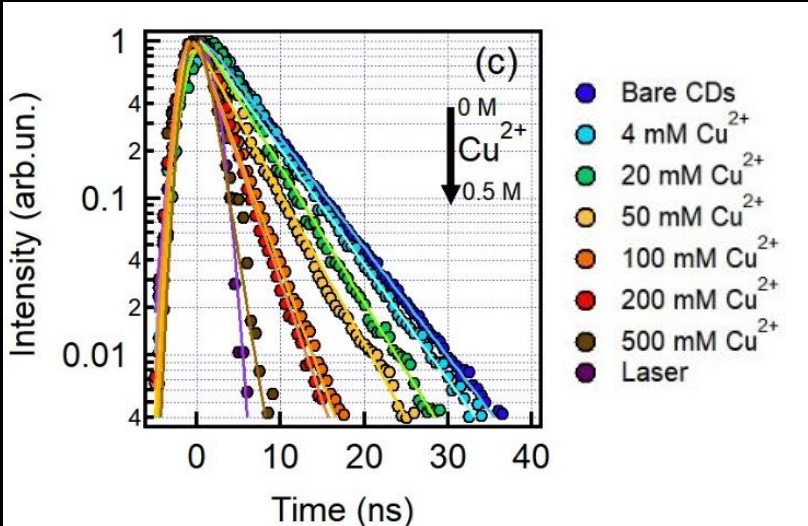


INTERACTION WITH IONS

Quenching

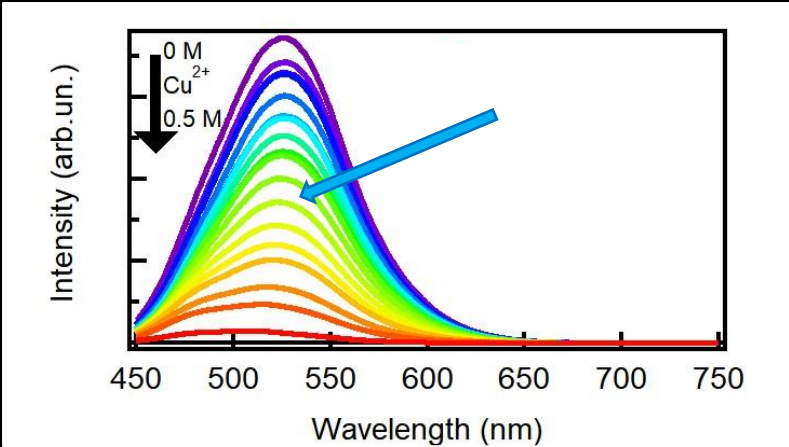


Dynamic Quenching

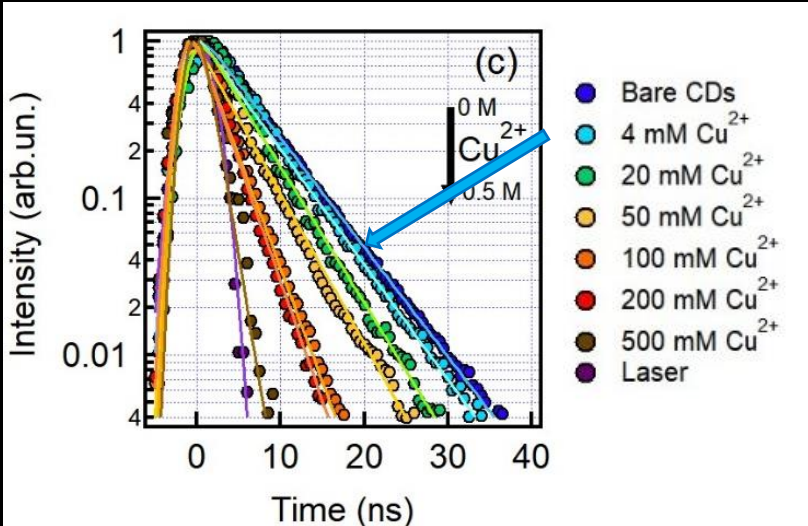


INTERACTION WITH IONS

Quenching

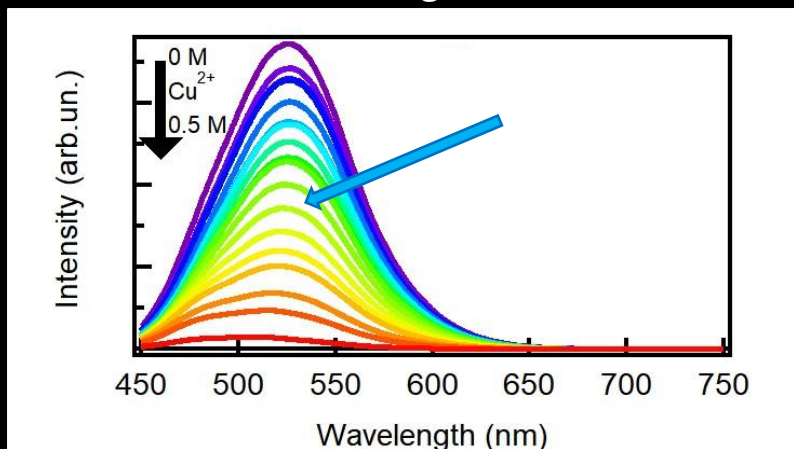


Dynamic Quenching

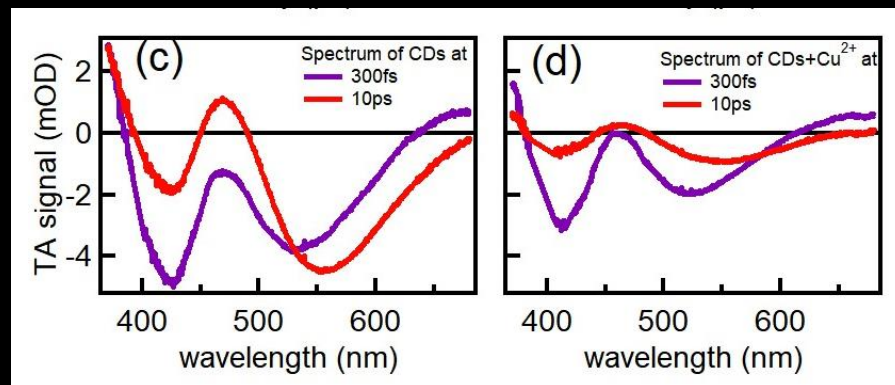
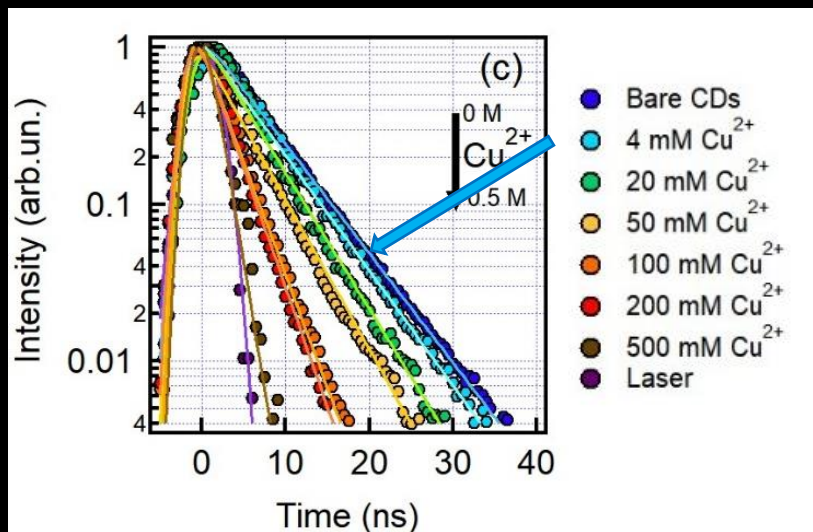


INTERACTION WITH IONS

Quenching



Dynamic Quenching



Static Quenching

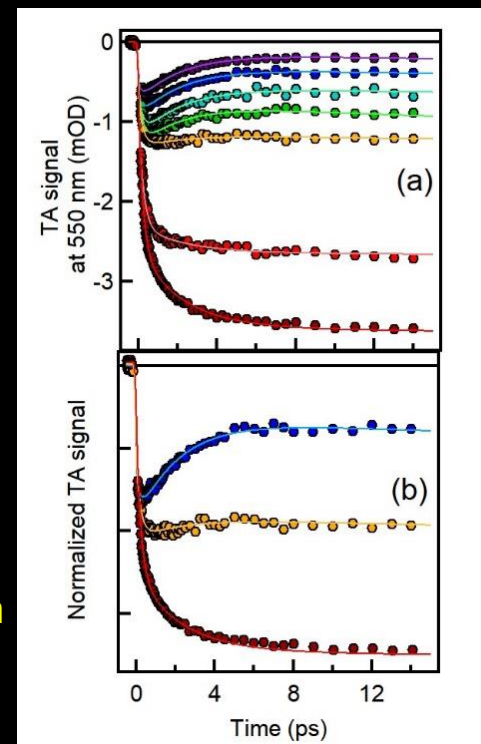
Formation of Cu^{2+} -CDs Complexes

Decay times

$$\tau_1 = 0.19 \text{ ps}$$

$$\tau_2 = 2.1 \text{ ps}$$

Decay Times Driven by Solvation

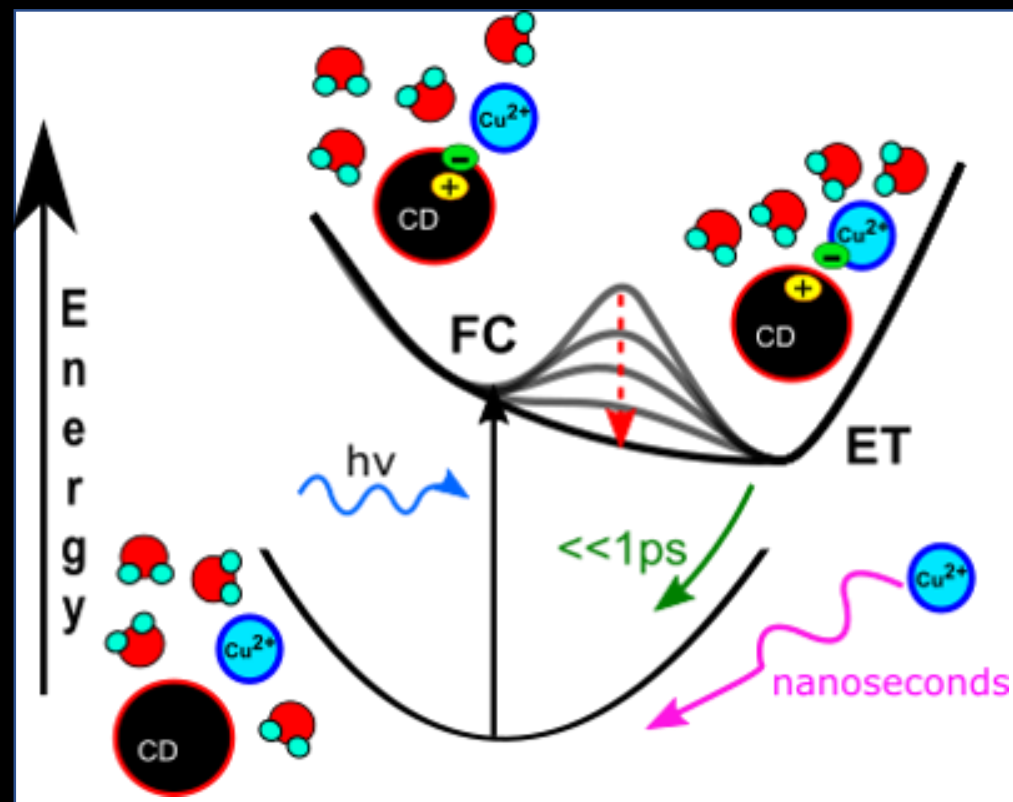


EMISSION MECHANISM IN β - C_3N_4

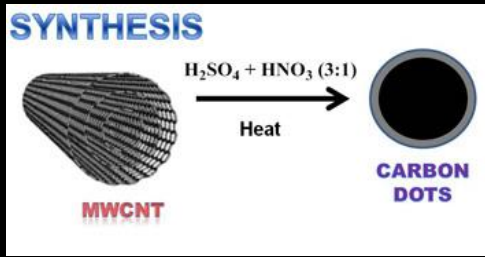
- Coupling between Core and Surface
 - Charge Separation
 - Localized Negative Charge Exposed to Solvent
- Direct population of the excited state
- In sub-ns range only Solvation Relaxation
 - In ns range Depopulation of excited state

Quenching:

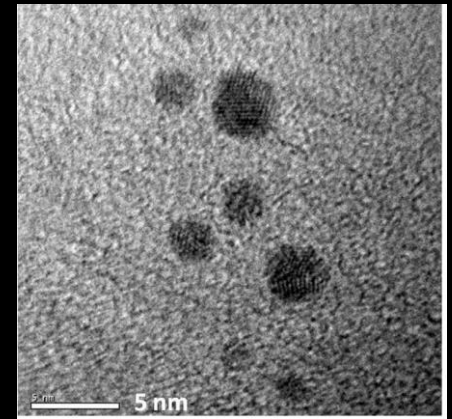
- Formation of Cu^{2+} -CDs Complexes
- Decay Times Driven by Solvation



TOP DOWN SYNTHESIS – GRAPHITIC SAMPLE

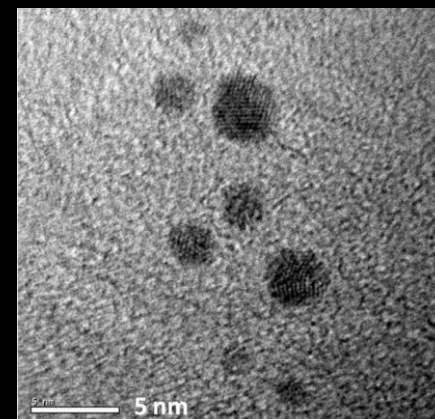
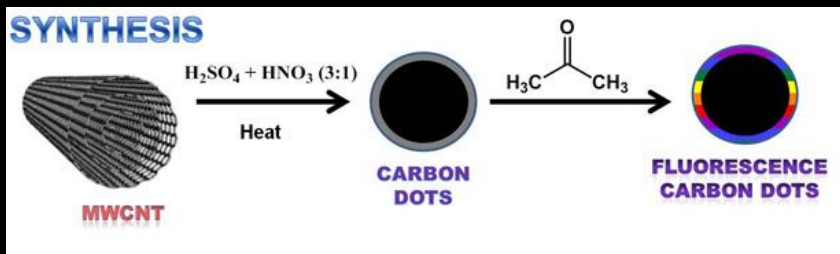


Cayuela et al., 2013, *Anal Chim Acta*



Graphitic core

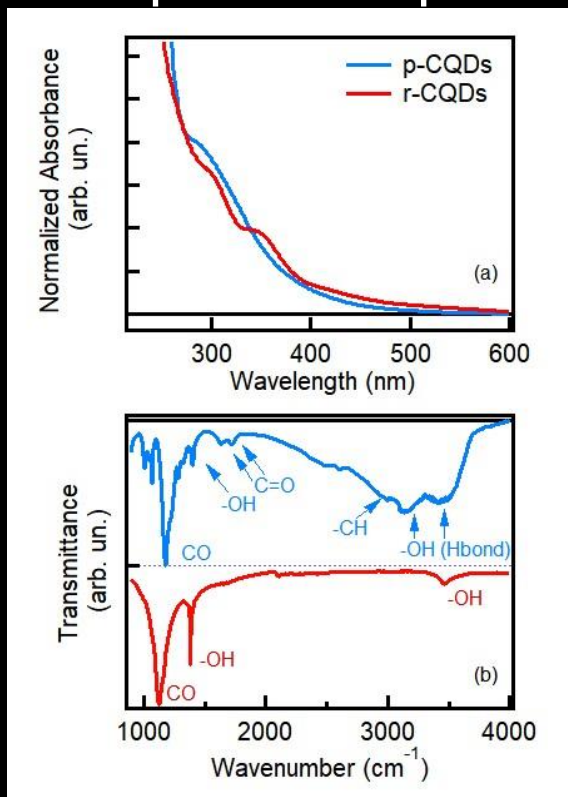
TOP DOWN SYNTHESIS – GRAPHITIC SAMPLE



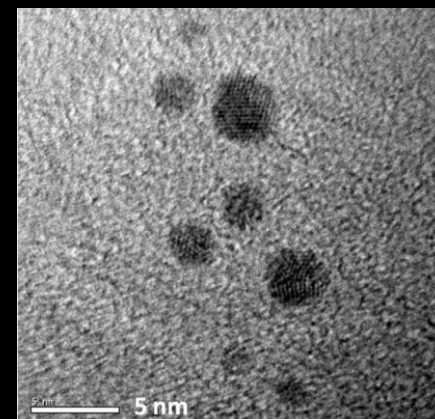
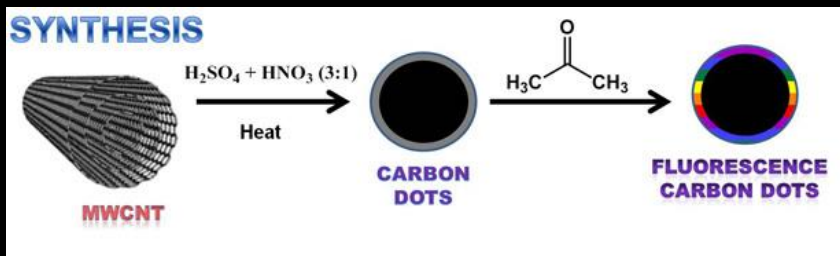
Graphitic core

Cayuela et al., 2013, *Anal Chim Acta*

Absorption & IR Spectra



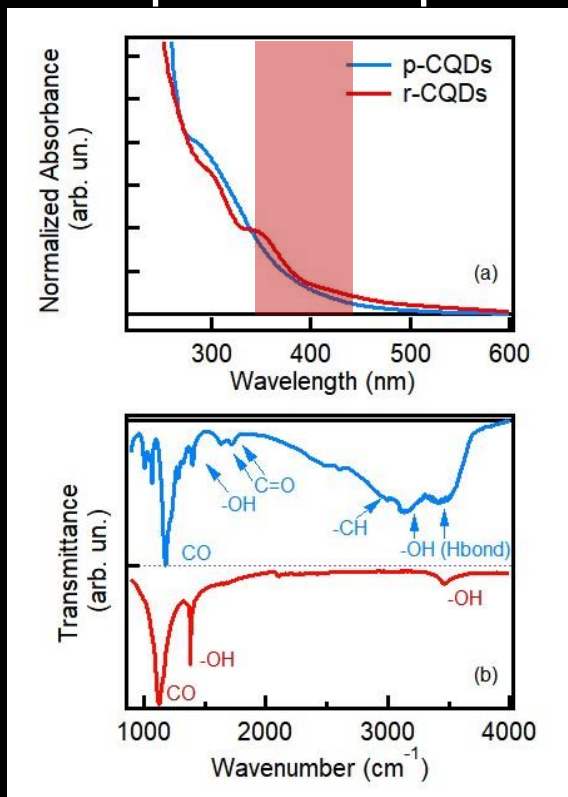
TOP DOWN SYNTHESIS – GRAPHITIC SAMPLE



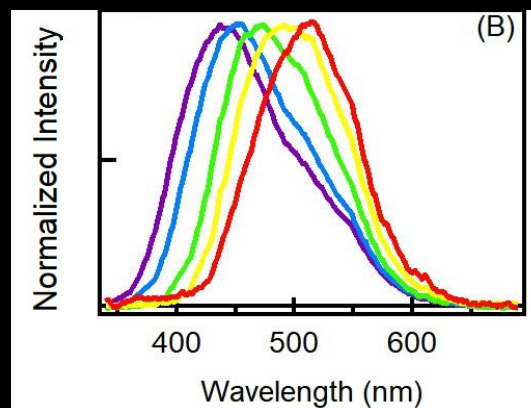
Graphitic core

Cayuela et al., 2013, *Anal Chim Acta*

Absorption & IR Spectra

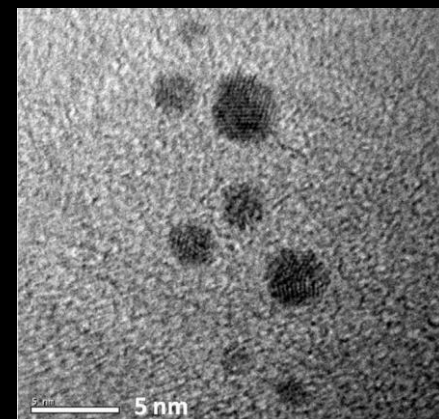
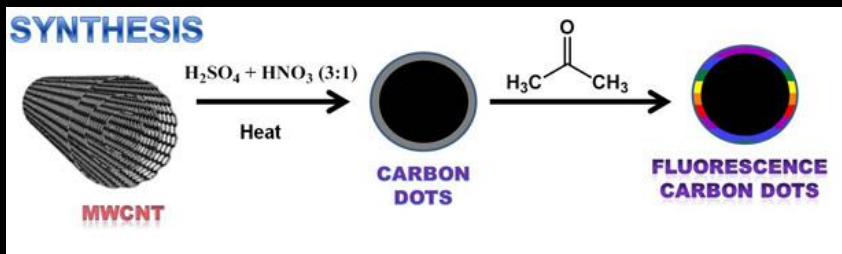


Emission Spectra



QY \approx 4%

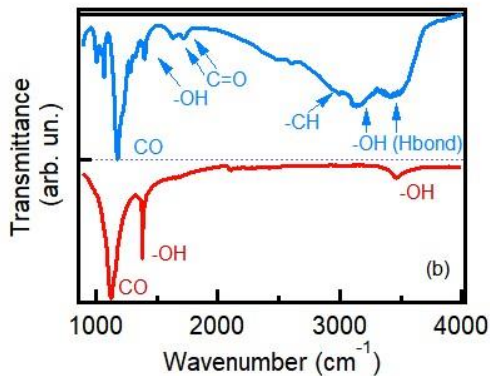
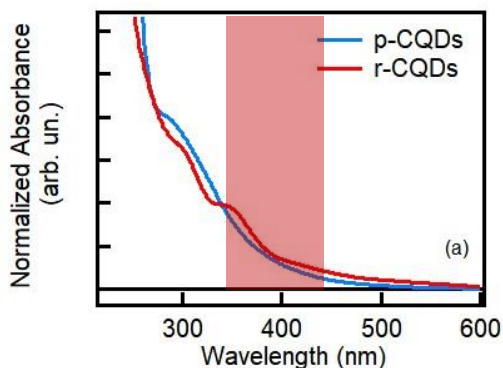
TOP DOWN SYNTHESIS – GRAPHITIC SAMPLE



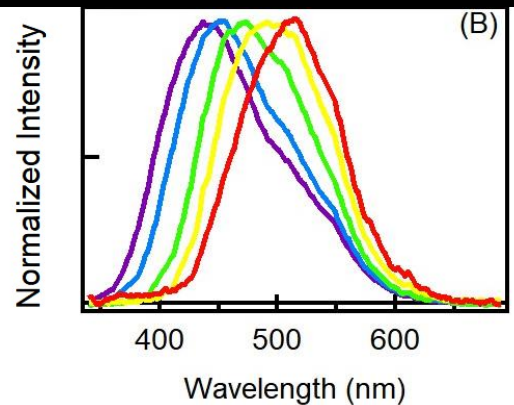
Graphitic core

Cayuela et al., 2013, *Anal Chim Acta*

Absorption & IR Spectra



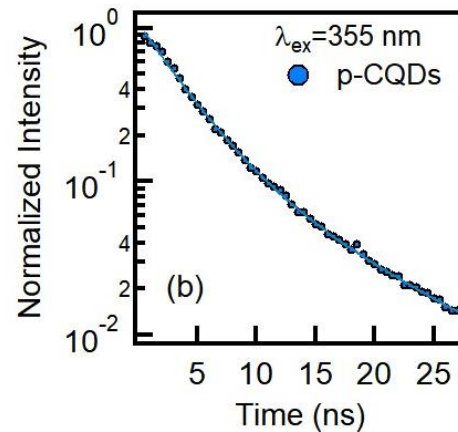
Emission Spectra



QY \approx 4%

$\tau_1 \approx 3.5$ ns
 $\tau_2 \approx 12.0$ ns

Decay Kinetics



Sciortino et al., 2017, *Phys. Chem. Chem. Phys.*

EMISSION MECHANISM IN GRAPHITIC SAMPLE

EMISSION MECHANISM IN GRAPHITIC SAMPLE

- Emission is **Activated** by Surface Passivation
- Emission is independent of core structure (not shown)

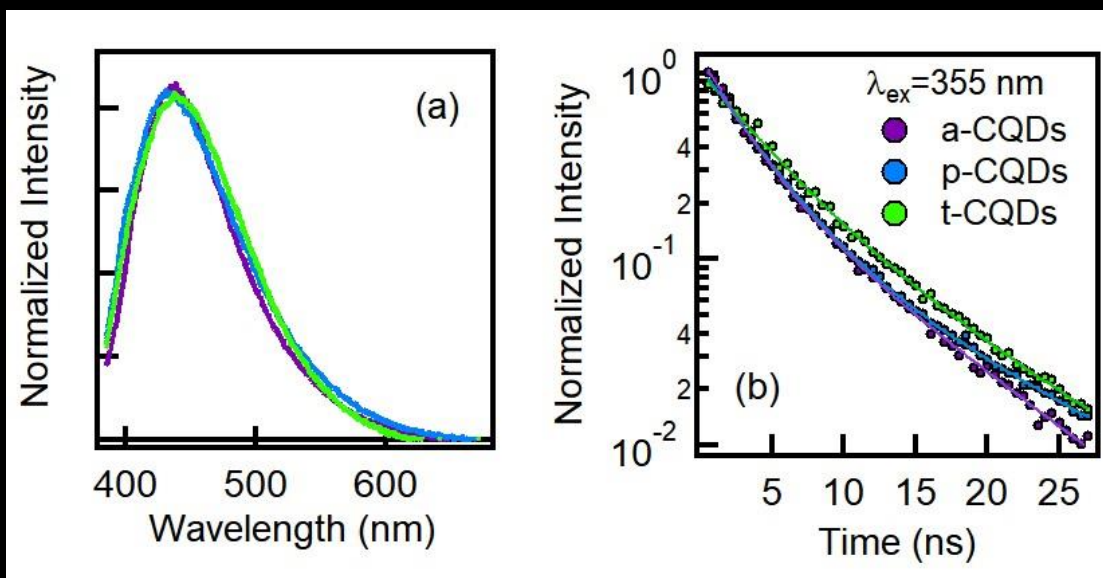
BUT...

EMISSION MECHANISM IN GRAPHITIC SAMPLE

- Emission is **Activated** by Surface Passivation
- Emission is independent of core structure (not shown)

BUT...

- Emission is **Independent** of Type of Surface Passivation

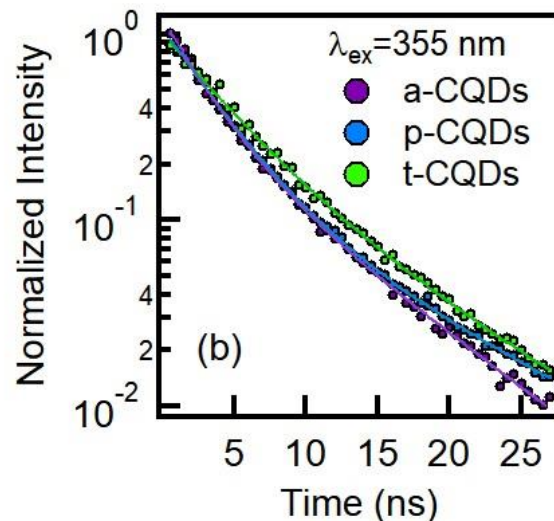
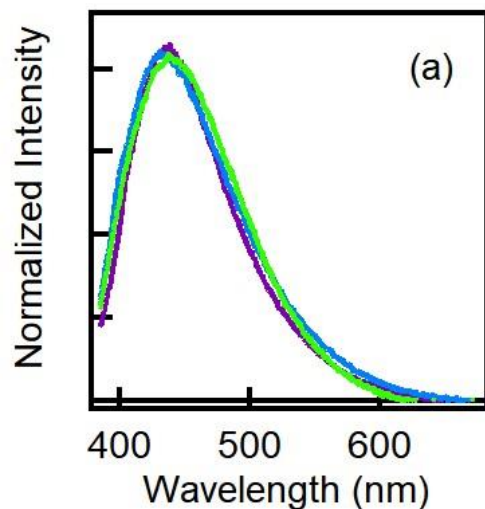
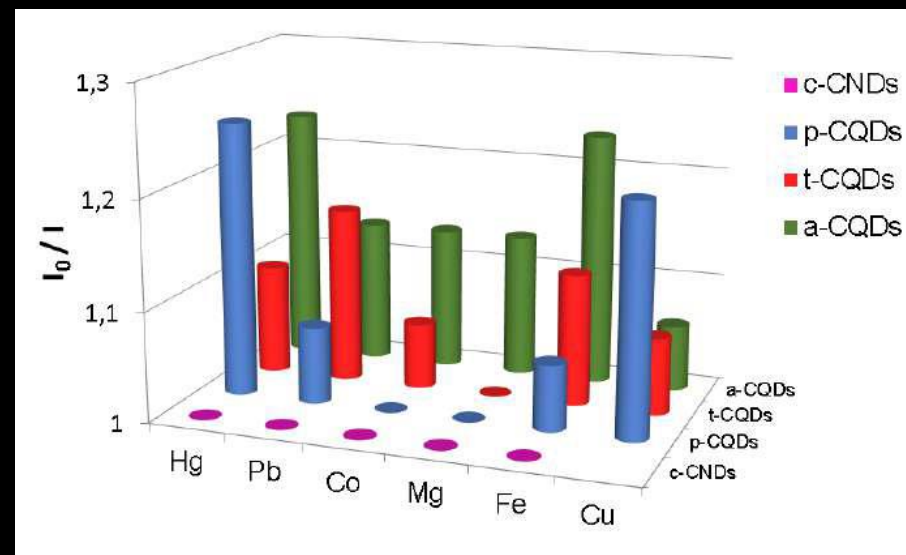


EMISSION MECHANISM IN GRAPHITIC SAMPLE

- Emission is **Activated** by Surface Passivation
- Emission is independent of core structure (not shown)

BUT...

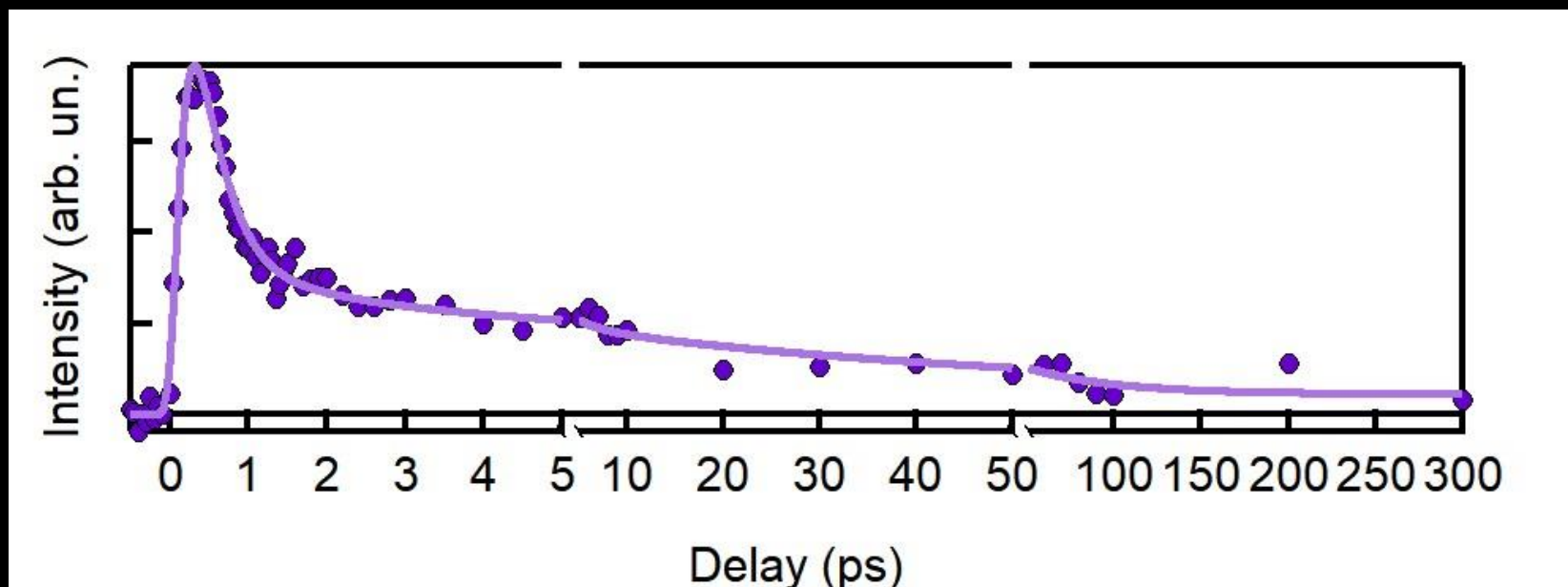
- Emission is **Independent** of Type of Surface Passivation



- Emission Quenching is **Dependent** on Type of Surface Passivation

ULTRAFAST TECHNIQUES TO UNRAVEL THE PHOTOCYCLE

Ultrafast Fluorescence



Decay times

$$\tau_1 = 0.3 \text{ ps}$$

$$\tau_2 = 2.5 \text{ ps}$$

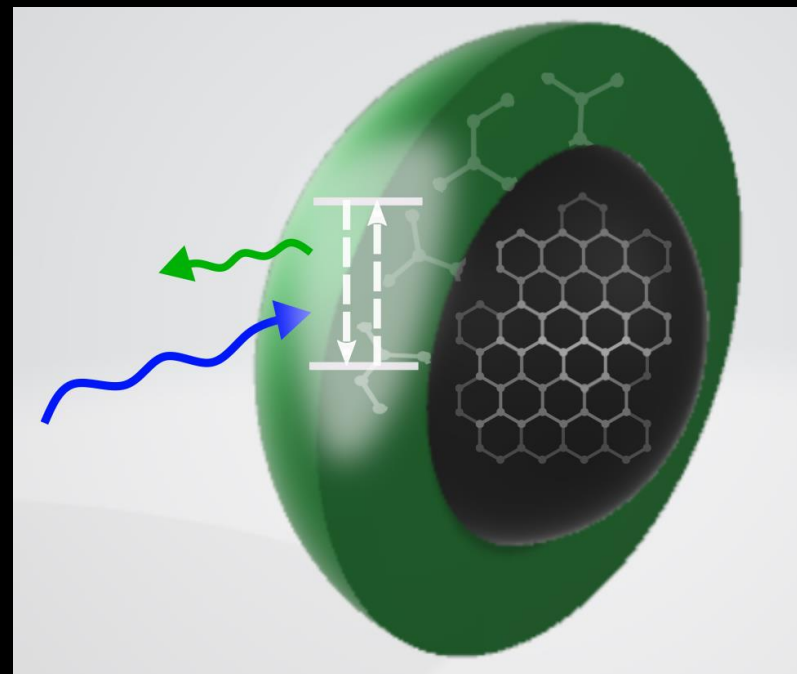
$$\tau_3 = 70 \text{ ps}$$

$$\tau_4 > 1 \text{ ns}$$

Direct population of
Excited State and its
Depopulation → QY ≈ 4%

EMISSION MECHANISM IN GRAPHITIC SAMPLE

- Passivation creates emissive states
 - Electronic Transition Involves the Surface
 - The Wavefunction is Delocalized on the Surface and involves different functional groups
- Sub-ns Depopulation of excited state which causes 4% of QY



SUMMARY

Different families
of Carbon
Nanodots



Structural &
Morphological
Characterization



Optical
Characterization



Understanding the
entire Photocycle

CDs are Different Families of
Fluorescent Carbon
Nanoparticles

Unravelled the Photophysics

Which are the Emission
Mechanisms:

Core-Surface Coupling – Electron
Transfer Character

or

Surface Delocalized States

...



Thank You