Carbon Nanodots as Versatile Materials for the Synthesis of Novel Protocells

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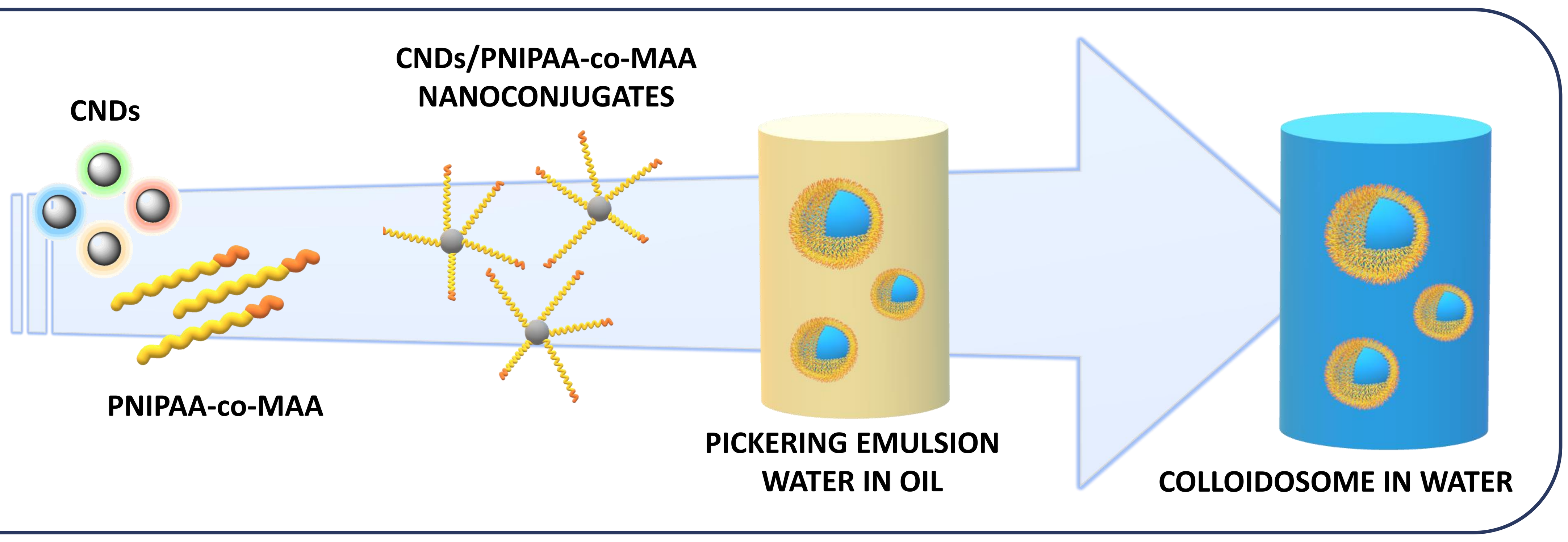
Carbon Nanotechnology Group

1. ABSTRACT

Artificial cells or "**protocells**" fabricated from different nanomaterials have drawn increasing interest due to their repercussions in diverse areas of science and technology.[1]

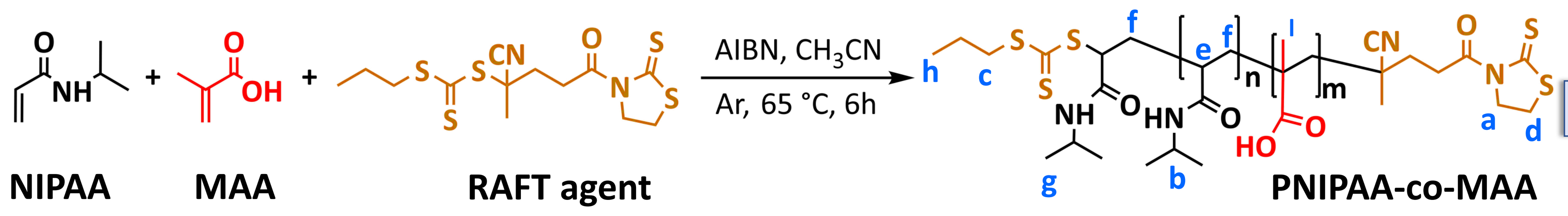
Carbon nanodots (CNDs) are quasi-spherical nanoparticles with a size below 10 nm and unique electronic features.[2]

The objective of this study is to use CNDs as nano-building blocks to develop novel protocell membranes with appealing features, such as the low costs of production, biocompatibility, and intrinsic fluorescence emission. To achieve this, we will use the **Pickering emulsion technique**. This requires the hydrophilic CNDs to be functionalized with the temperature-responsive polymer, **poly(N-isopropylacrylamide)-co-methacrylic acid** (**PNIPAA-co-MAA**), to make them amphiphilic and stabilize water-in-oil microdroplets.

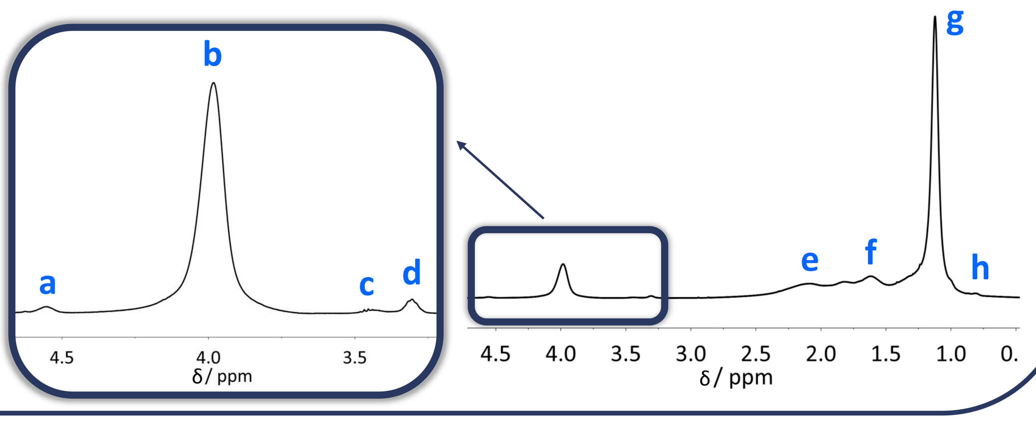


2. SYNTHESIS OF PNIPAA-co-MAA BY RAFT* POLIMERIZATION

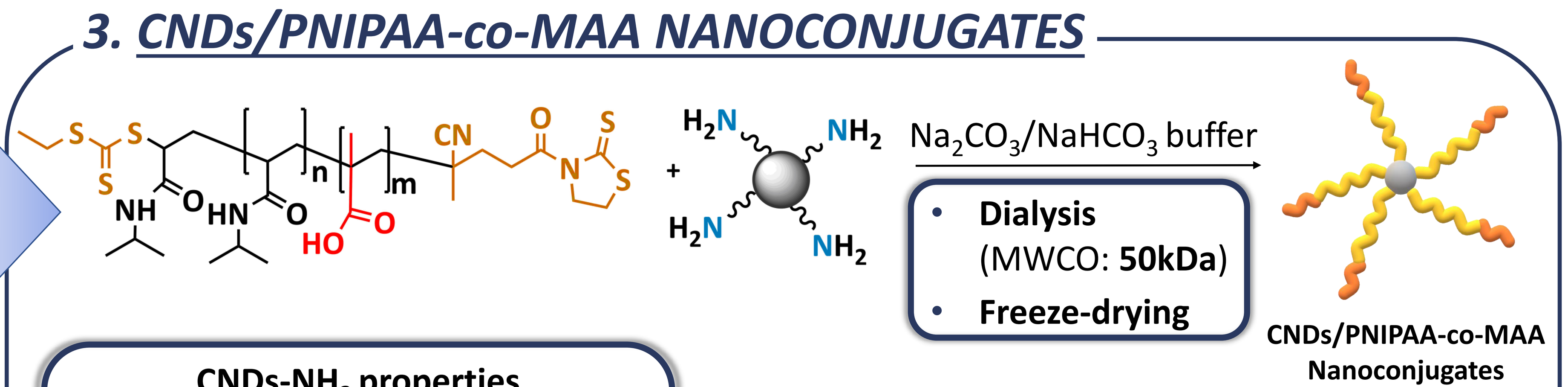
*Reversible Addition–Fragmentation chain-Transfer



- **Degree of polymerization:** 78%
- ***Đ***: 1.2 [3]
- M_n ≈ 11 kDa
- M_w ≈ 13 kDa
- **LCST** = 37 °C [3]



3. CNDs/PNIPAA-co-MAA NANOCONJUGATES



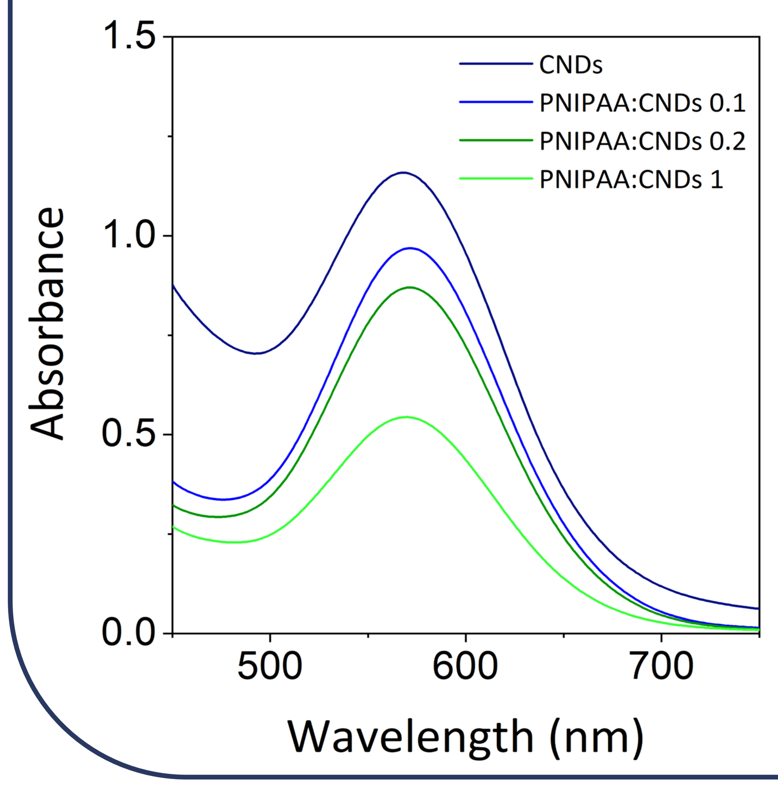
CNDs-NH_2 properties

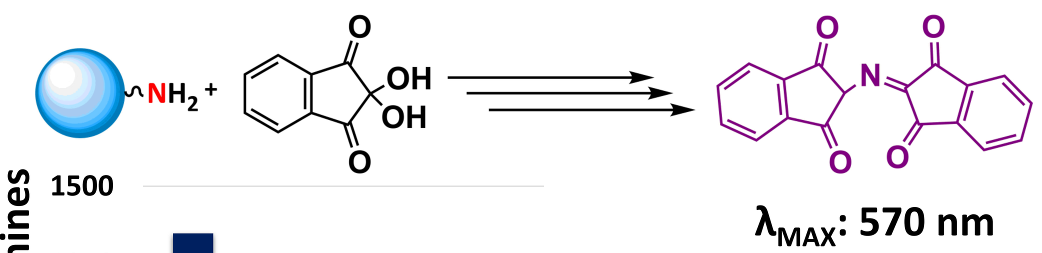
- **Amine-rich surface**
- Intrinsic **blue fluorescence**
- **Excitation wavelength-dependent** emissive behaviour

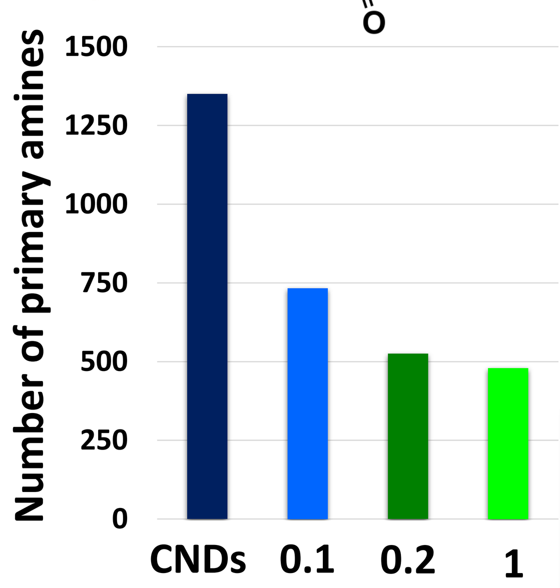
CNDs, which are synthesised following a well-established procedure,[4] are made **amphiphilic** by grafting onto them PNIPAA-co-MAA chains. This process leads to the synthesis of **CNDs/PNIPAA-co-MAA nanoconjugates**.

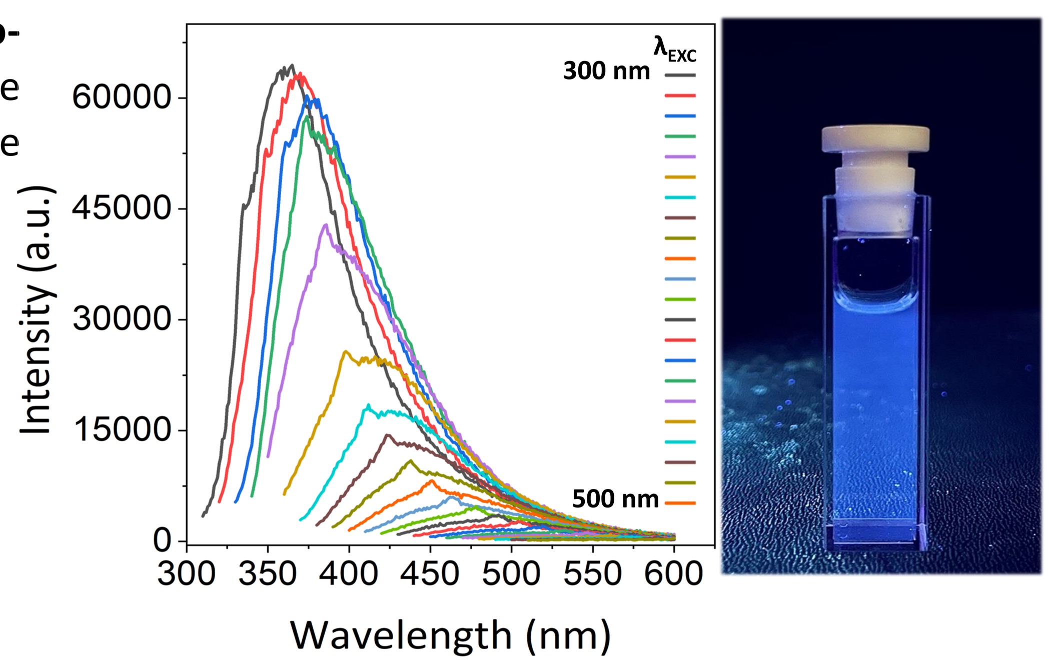
3.1. CHARACTERIZATION OF CNDs/PNIPAA-co-MAA NANOCONJUGATES

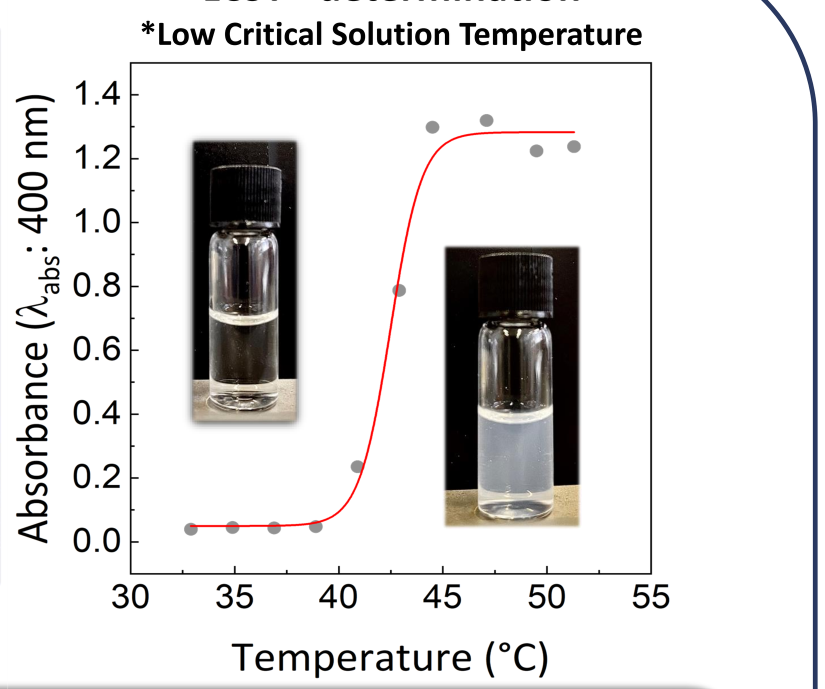
Different CNDs/PNIPAA-co-MAA nanoconjugates are synthesized, using **increasing PNIPAAM-co-MAA:CNDs molar ratio** (0.1, 0.2 and 1). The number of primary amines left on the surface of the nanoparticles after the coupling reaction is quantified by **Kaiser Test** (all the samples have the same concentration).









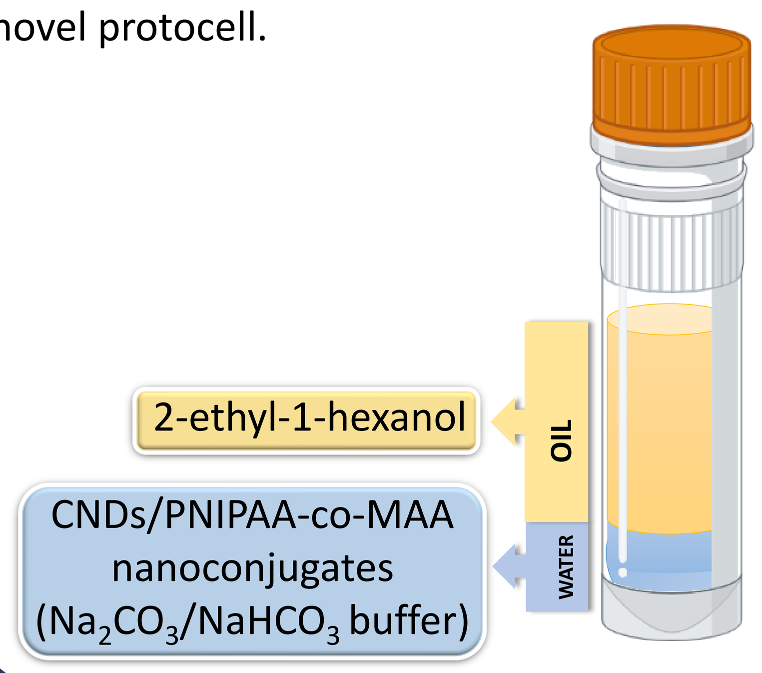


- Number of **primary amines** on the CNDs **decreases** by **increasing** the amount of polymer used in the conjugation step. This indicates **successful polymer conjugation** and the possibility to **control** the **number** of polymer chains per CND.
- Fluorescence of pristine CNDs[3] is retained after conjugation as shown by the **excitation wavelength-dependent emission profile** of CNDs/PNIPAA-co-MAA nanoconjugates.
- **LCST** of the CNDs/PNIPAA-co-MAA nanoconjugates is **42 °C**, which is higher than that of the PNIPAA-co-MAA.

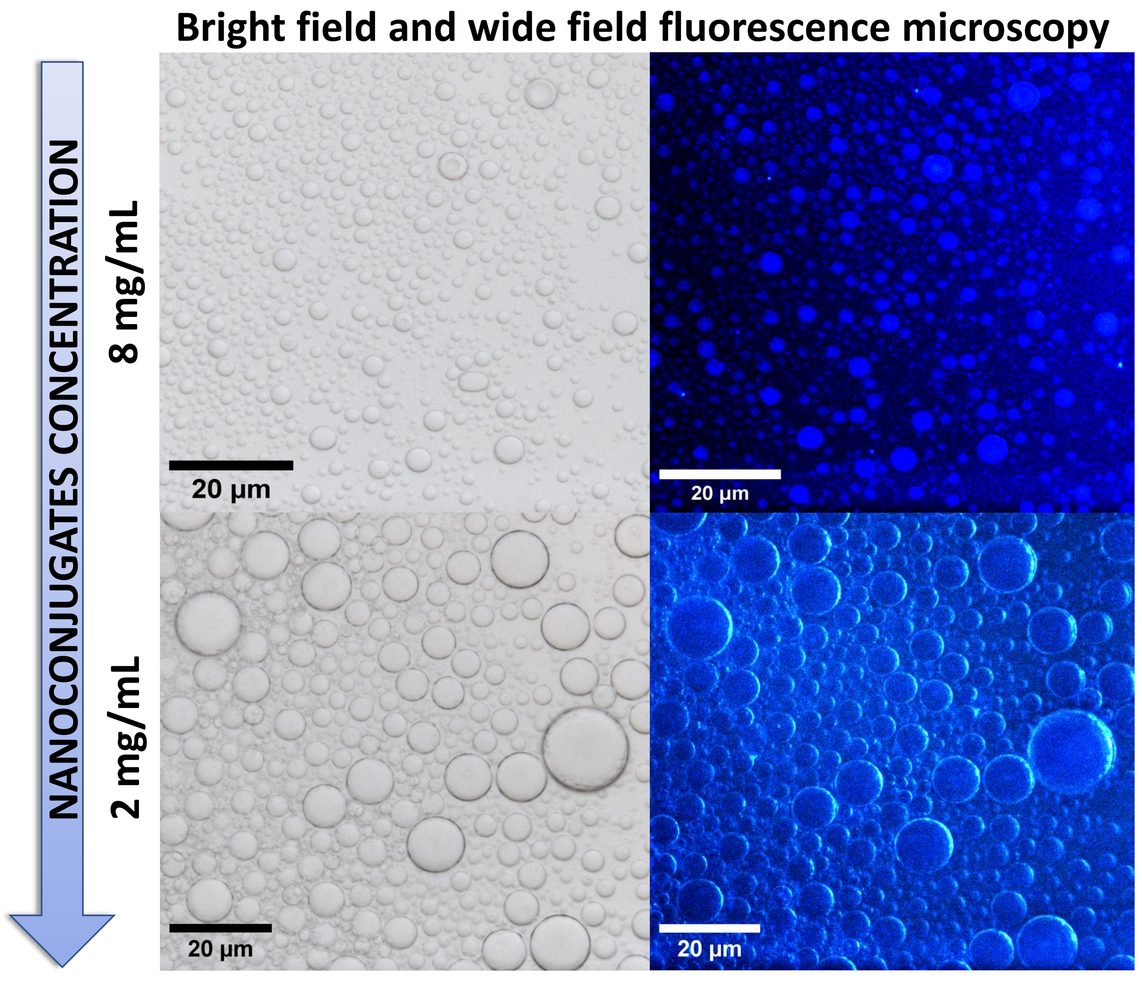
4. PICKERING EMULSIONS

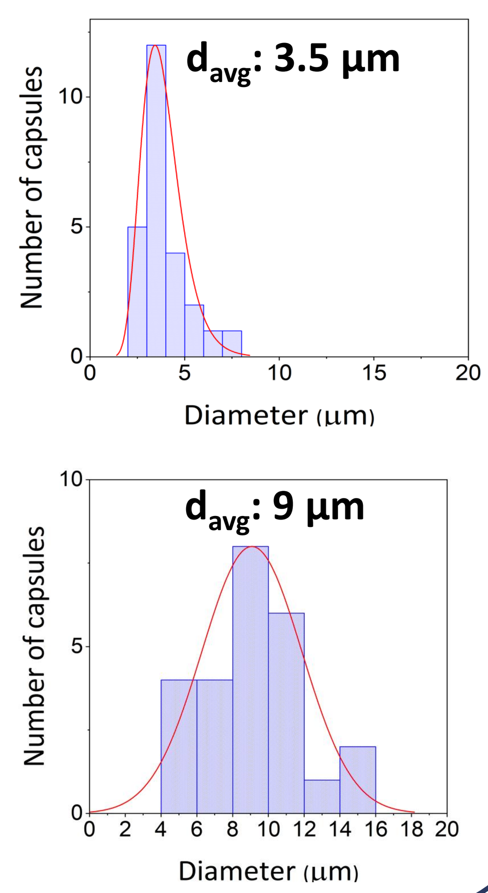
The most promising CNDs/PNIPAA-co-MAA nanoconjugate seems to be the one with the **greater amount of free primary amines** (PNIPAAM-co-MAA:CNDs molar ratio 0.1). This is pivotal for the final step of **cross-linking** the colloidosomes and transferring them to water.

We used the **Pickering emulsion technique** to assemble the CNDs/PNIPAA-co-MAA nanoconjugates into novel protocell.



- **All emulsions** are **stable for months**
- **Diameter** of the water-in-oil droplets can be **controlled**
- **Water-in-oil microdroplets** are blue fluorescent





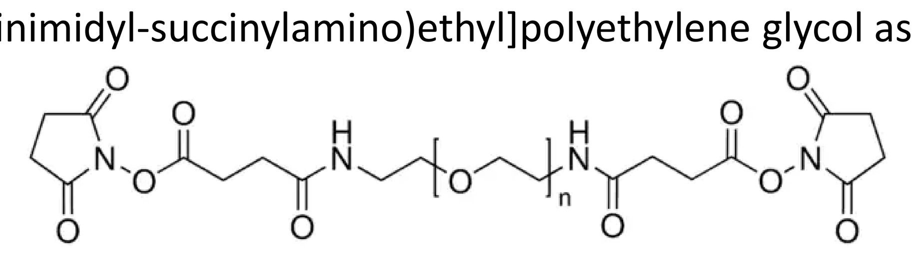
5. CONCLUSIONS AND FUTURE PERSPECTIVES

We achieved the successful synthesis of the **first CNDs/PNIPAA-co-MAA nanoconjugates**, which are effective in the formation of **highly stable Pickering emulsions**.

As next step, we will perform a **complete characterization** of CNDs/PNIPAA-co-MAA nanoconjugates.

Our final goal is to **cross-link** the CNDs/PNIPAA-co-MAA nanoconjugates at the water-in-oil interface into a **continuous membrane** to form **colloidosomes** that can be transferred into an aqueous solution and studied.

To achieve this, we will exploit the **residual free primary amine** left on the CND/PNIPAA-co-MAA core, and use O,O′-Bis[2-(N-Succinimidyl-succinylamino)ethyl]polyethylene glycol as **cross-linker**.



6. REFERENCES

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[4] Arcudi et al., *Angew. Chem. Int. Ed.*, 2016, **128**: 2147 –2152

ACKNOWLEDGEMENTS

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