

Controlling the Nano-particle Size by Manipulating the Diffusion Coefficient of the Solute

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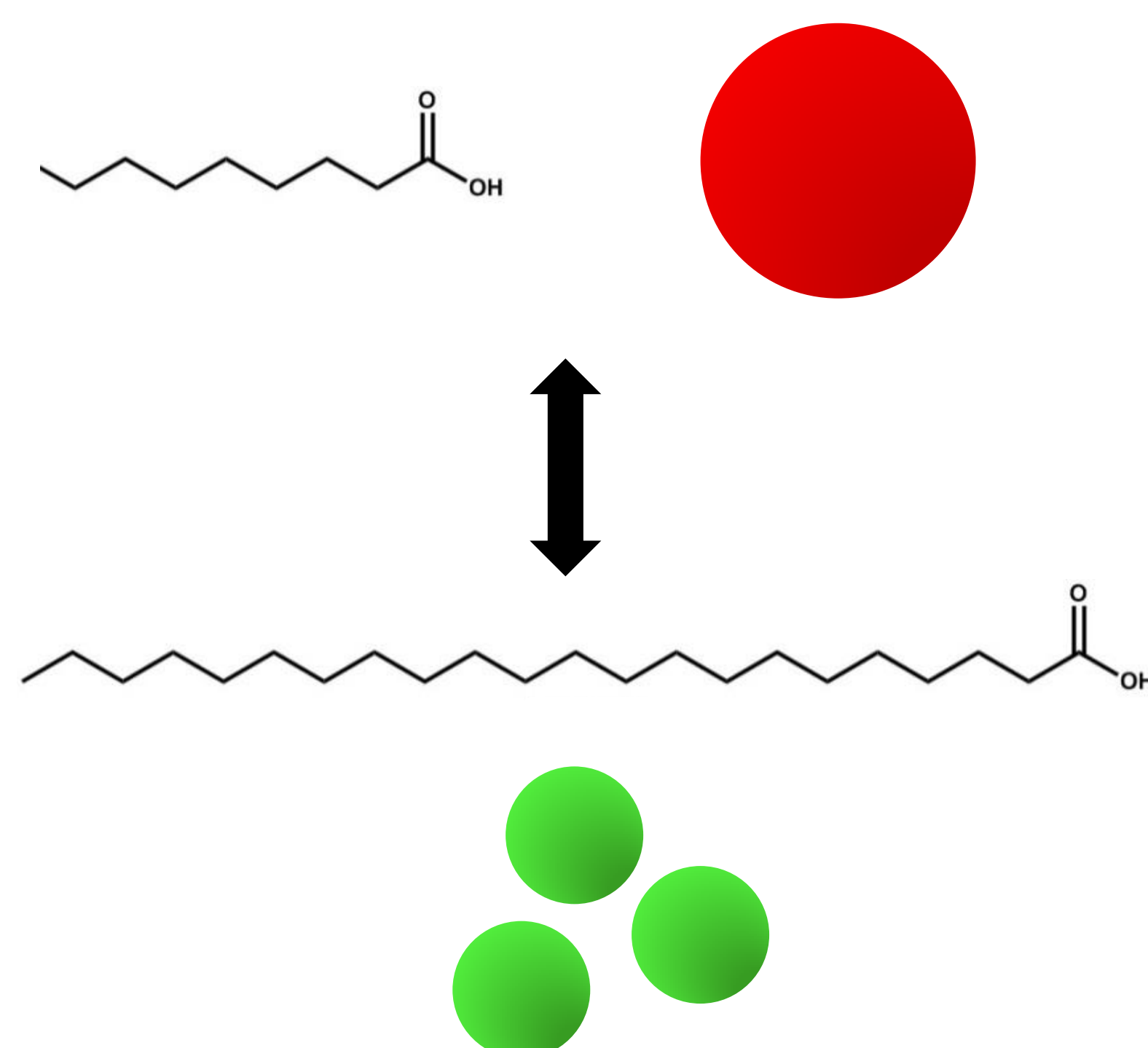
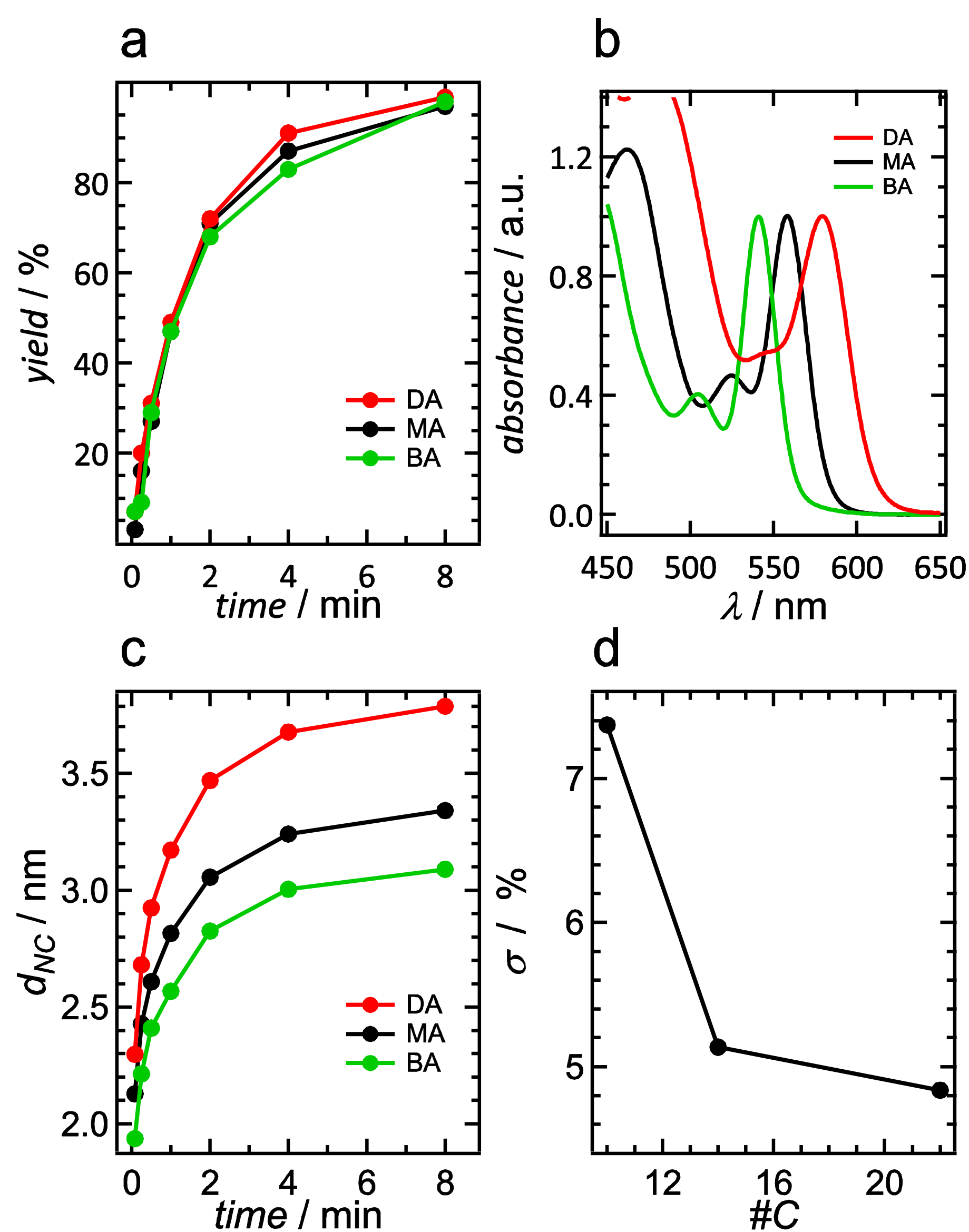
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INTRODUCTION

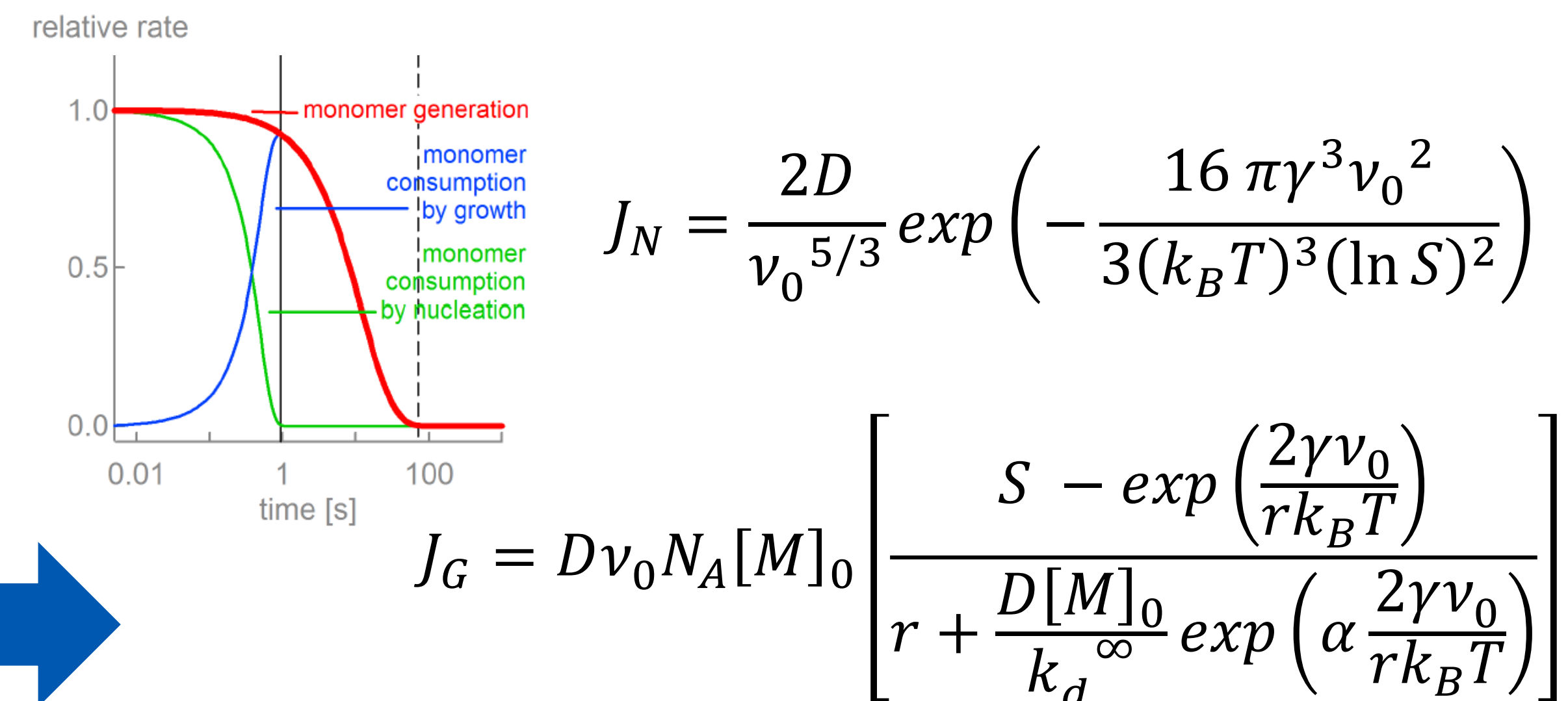
Colloidal semiconductor nanocrystals or quantum dots (QDs) are typically produced via a hot injection synthesis (HIS). For QDs to be implemented in a broad range of applications, a precise control over their size is essential. We show that efficient size tuning at high reaction yield is possible by changing the chain length of the carboxylic acid. By combining an extended experimental

reaction screening with reaction simulations, we demonstrate that this size tuning is due to a change in the diffusion coefficient and the solubility of the solute. The relation between size tuning by the ligand chain length and the coordination of the solute by the ligands is further explored by expanding the study to amines and phosphine oxides.

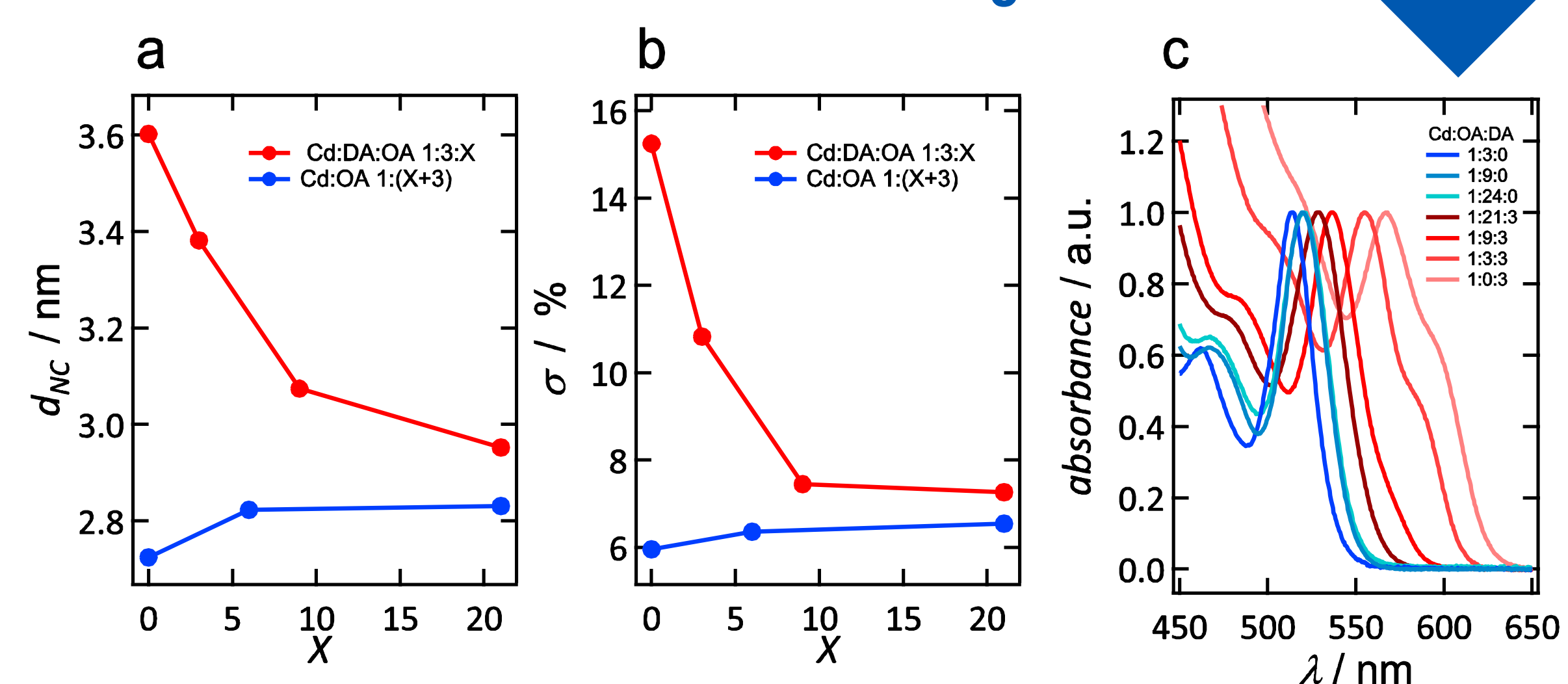
CARBOXYLIC ACIDS: LONGER CHAIN ACIDS = SMALLER NANOCRYSTALS



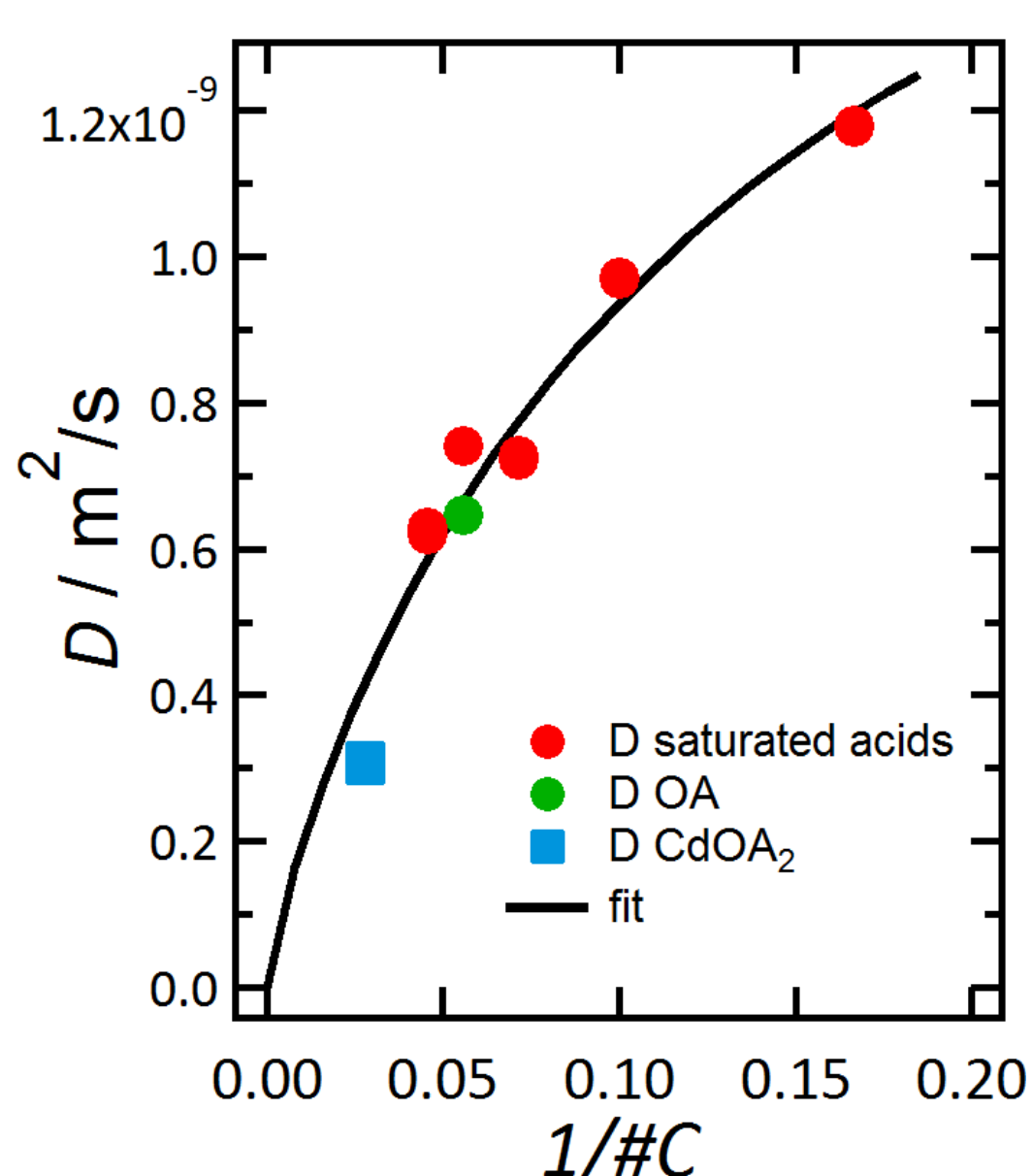
NUCLEATION AND GROWTH



MONOMER SOLUBILITY $[M]_0$

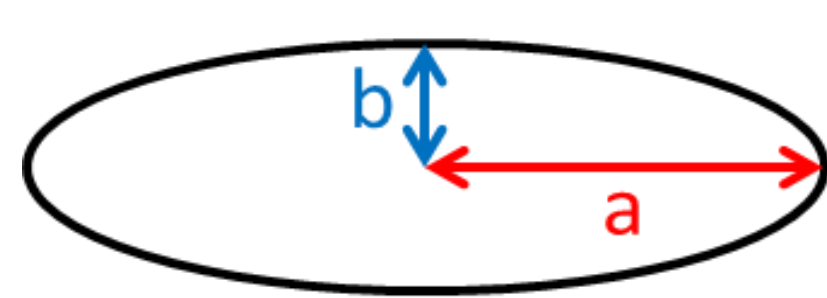


DIFFUSION COEFFICIENT D



→ D of carboxylic acids and CdOA_2 were measured with NMR
→ Correlation between D and #C of the carboxylic acids
→ $\text{Size}(\text{CdOA}_2) \approx 2 \cdot \text{size}(\text{OA})$ and $2 \cdot D_{\text{CdOA}_2} \approx D_{\text{OA}}$

$$D_{\text{rod}} = \frac{k_B T}{6\pi\eta a} \ln\left[\frac{2a}{b}\right]$$



Amount of oleic acid (OAc) ↑ in an OAc synthesis:

→ Monomer solubility $[M]_0 \uparrow$

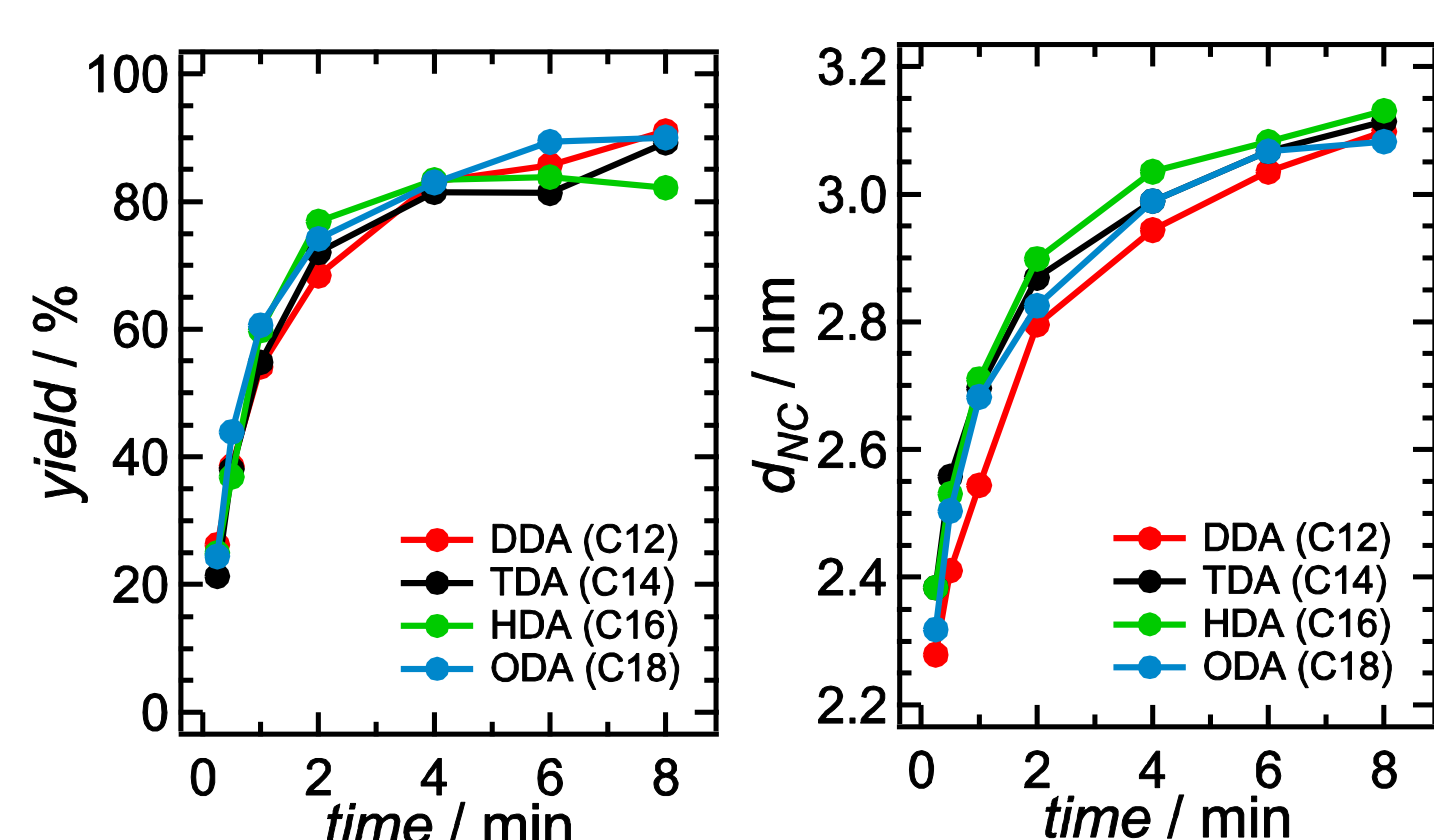
→ d_{NC} and $\sigma_d \uparrow$

Amount of oleic acid (OAc) ↑ in a DAc synthesis:

→ d_{NC} and $\sigma_d \downarrow$

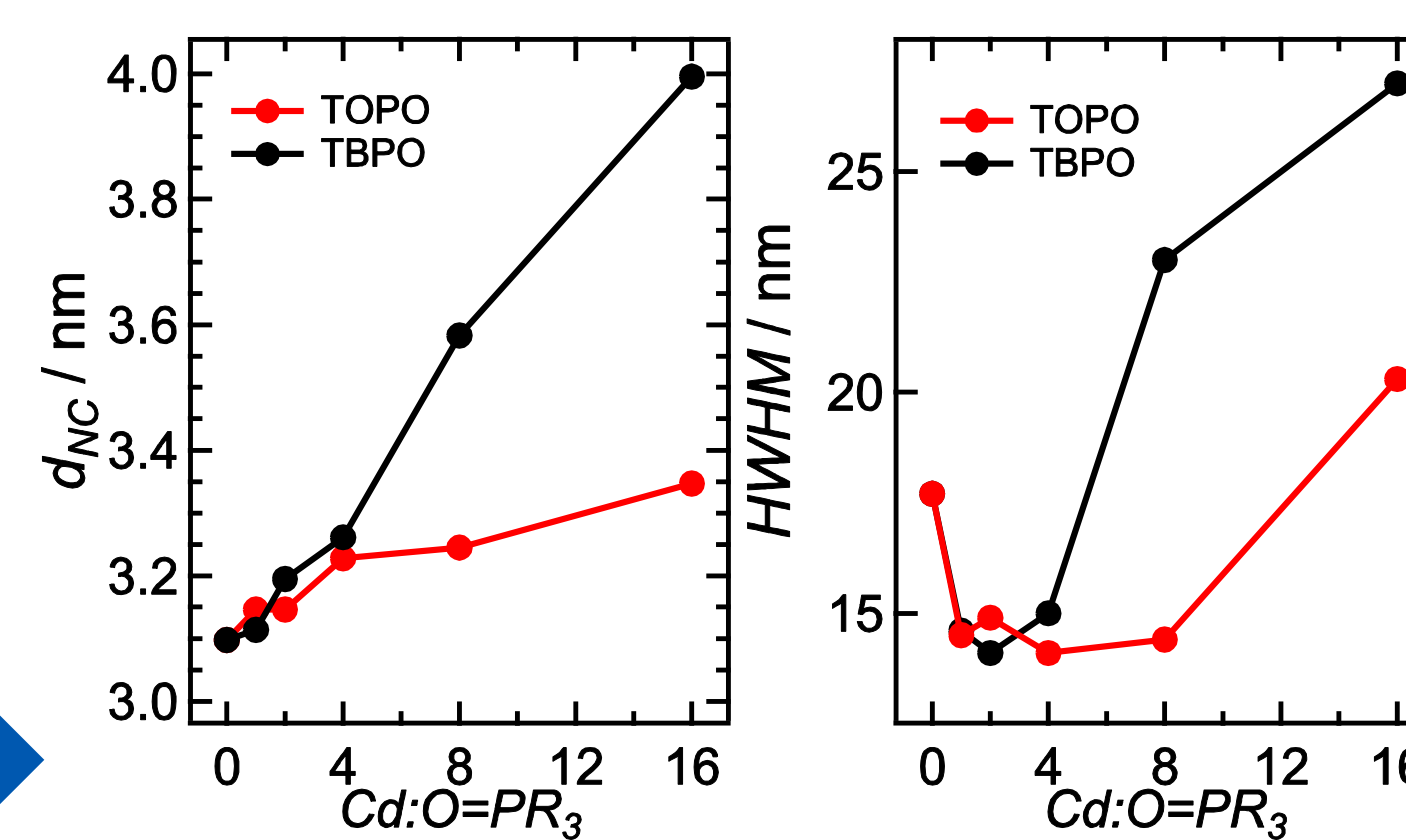
Changing the ligand chain length affects other parameters, next to the solute solubility, that have an influence on the balance between the nucleation and growth rate.

AMINE CHAIN LENGTH



→ No influence of chain length on QDs
→ No influence of amines on diffusion coefficient of CdOA_2
→ Weak coordination of CdSe QDs by amines

PHOSPHINE OXIDE CHAIN LENGTH



→ Minor effect on d_{NC} and σ_d for low concentrations.
→ Resembles amines
→ Effect rather due to a change of the solubility of the monomer and not its diffusion coefficient.

CONCLUSION

- With two different CdSe nanocrystal syntheses, we find that longer chain carboxylic acids result in smaller nanocrystals with improved size dispersions.
- This size tuning is due to a change in the diffusion coefficient and the solubility of the solute.
- In line with the weak coordination of CdSe nanocrystals by amines, no influence of the chain length on the nanocrystals is found.
- The size tuning brought about by phosphine oxides can be attributed to a solubility change.
- The ligand chain length provides a practical handle to optimize the outcome of a hot injection synthesis in terms of size and size dispersion and can be used to probe the interaction between ligands and the actual solute.

References

(1) Abe, S.; Capek, R. K.; De Geyter, B.; Hens, Z. ACS Nano 2013, 7, 943–949.



Acknowledgements

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