On the Mechanism of Alkylammonium Ligands Binding to the Surface of $CsPbBr_3$ NCs

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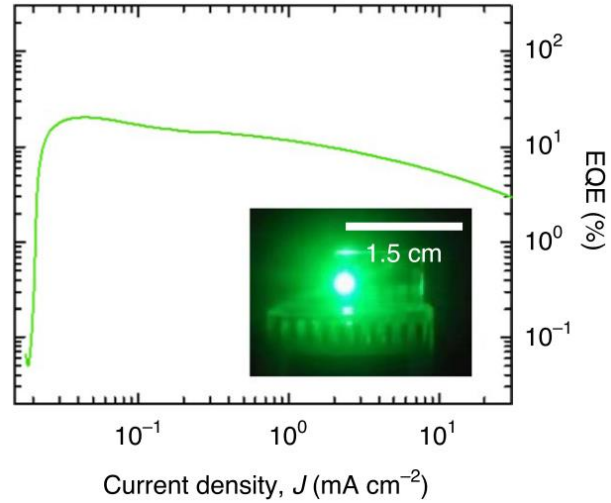
Motivation

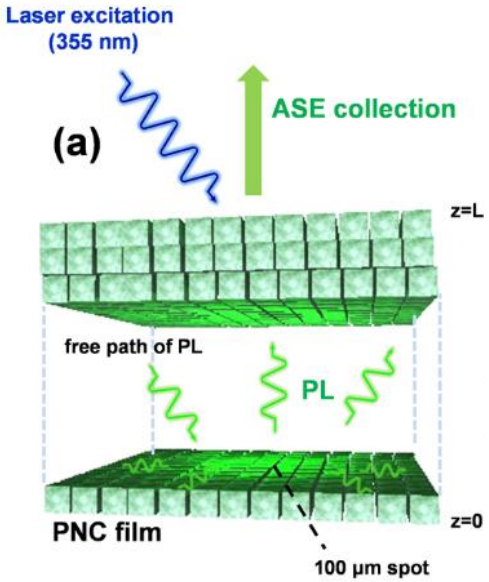
Applications of $CsPbX_3$ NCs

[2]

[1]



[3]



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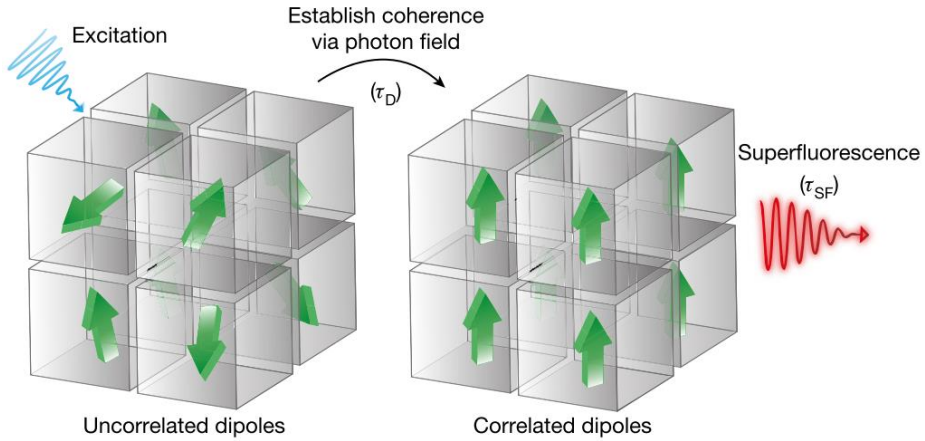
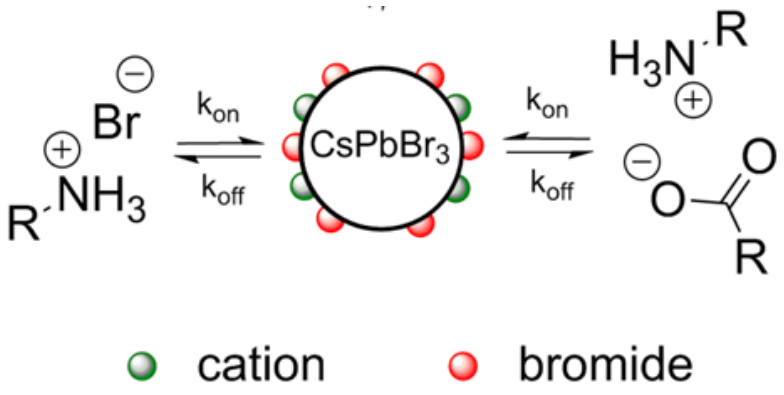


[1]Liu, et al. *Nat. Photonics* 2021, **15**, 379-385.
[2]Fei, et al. SID Symposium Digest of Technical Papers, Wiley Online Library: 2020; pp 219-221.
[3]Navarro-Arenas et al. *J. Phys. Chem. Lett.* 2019, **10 (20)**, 6389-6398.
[4]Raino, et al. *Nature* 2018, **563 (7733)**, 671-675.

Motivation

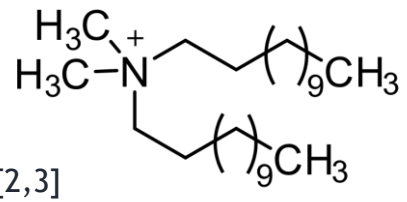
Highly dynamic ligand binding

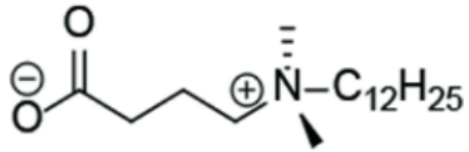
[1]



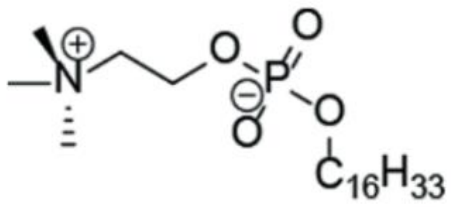
More stable surface capping

[2,3]

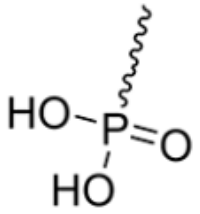


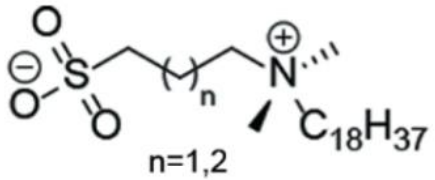


[5]



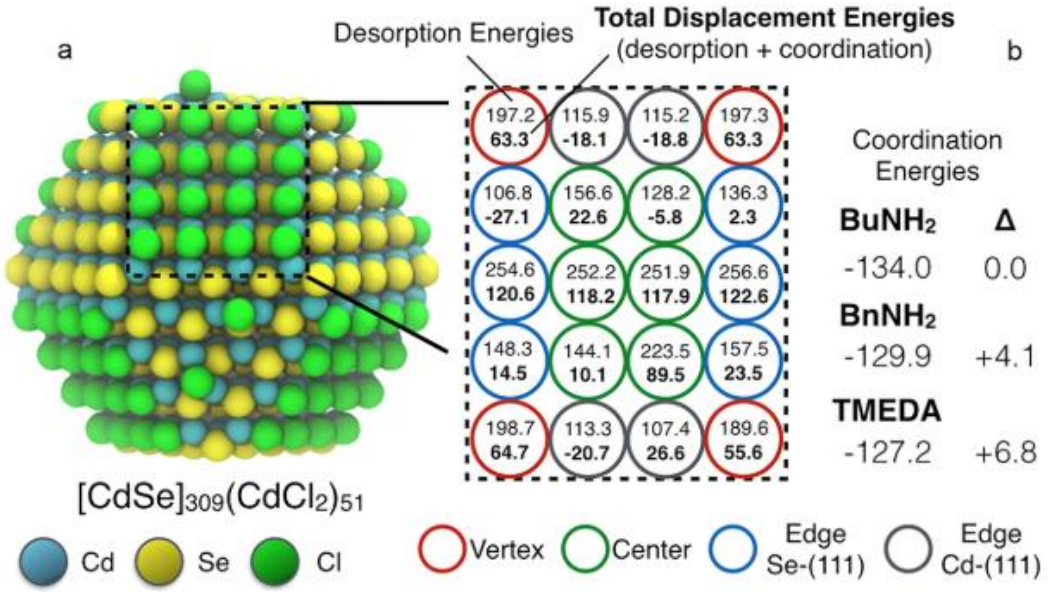
[4]



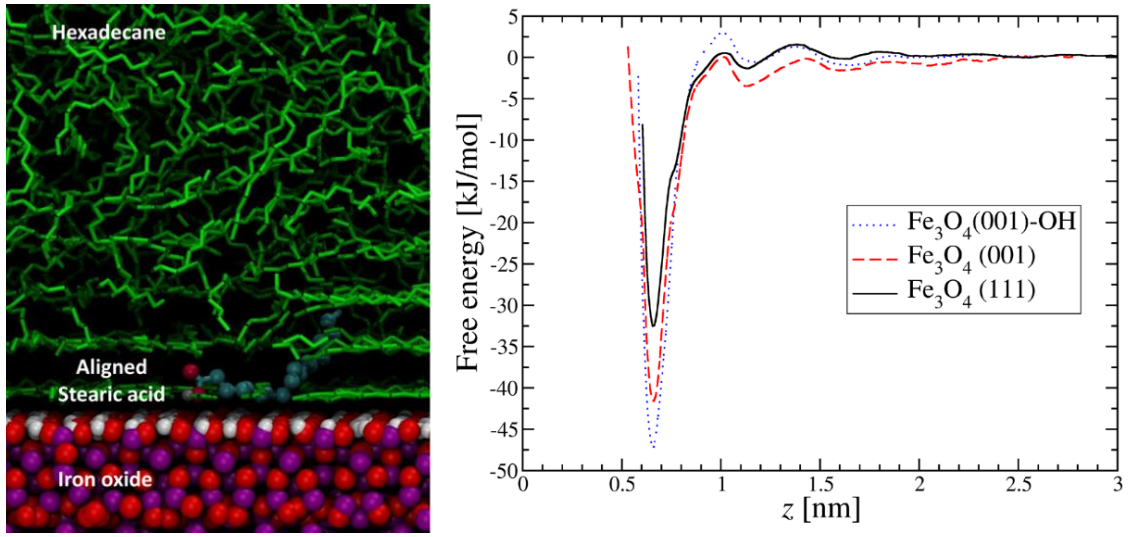


[1] De Roo, et al. *ACS Nano* 2016, **10 (2)**, 2071-2081.
[2] Bodnarchuk et al. *ACS Energy Lett*. 2019, **4 (1)**, 63-74.
[3] Imran, et al. *ACS Energy Lett*. 2019, **4 (4)**, 819-824.
[4] Zhang, et al. *Chem. Mater*. 2019, **31 (21)**, 9140-9147.
[5] Krieg, et al. *ACS Energy Lett*. 2018, **3 (3)**, 641-646.

Exploring ligand adsorption using computer simulations



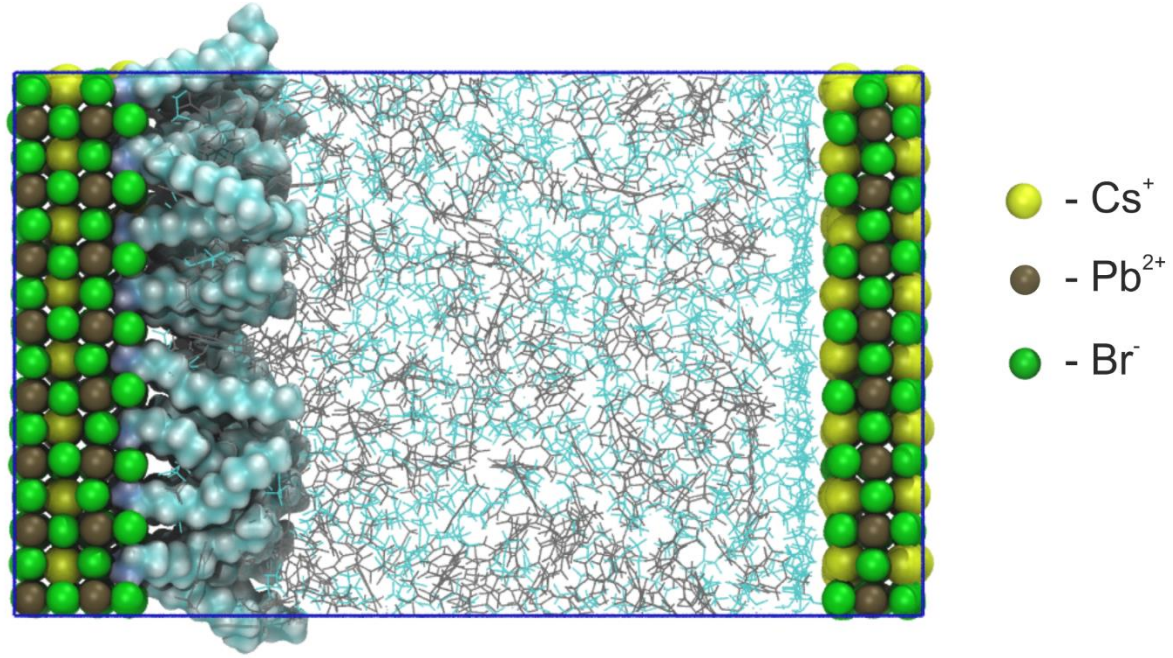
$CdCl_2$ ligand displacement energies computed at the DFT/PBE level of theory[1]



Free-energy profiles as a function of the distance between stearic acid in heptane and the solid Fe_3O_4 surface calculated using classical MD simulations[2]

[1]Drijvers, et al. *Chem. Mater.* 2018, **30 (3)**, 1178-1186.
[2]Jaishankar, et al. *Langmuir* 2019, **35 (6)**, 2033-2046.

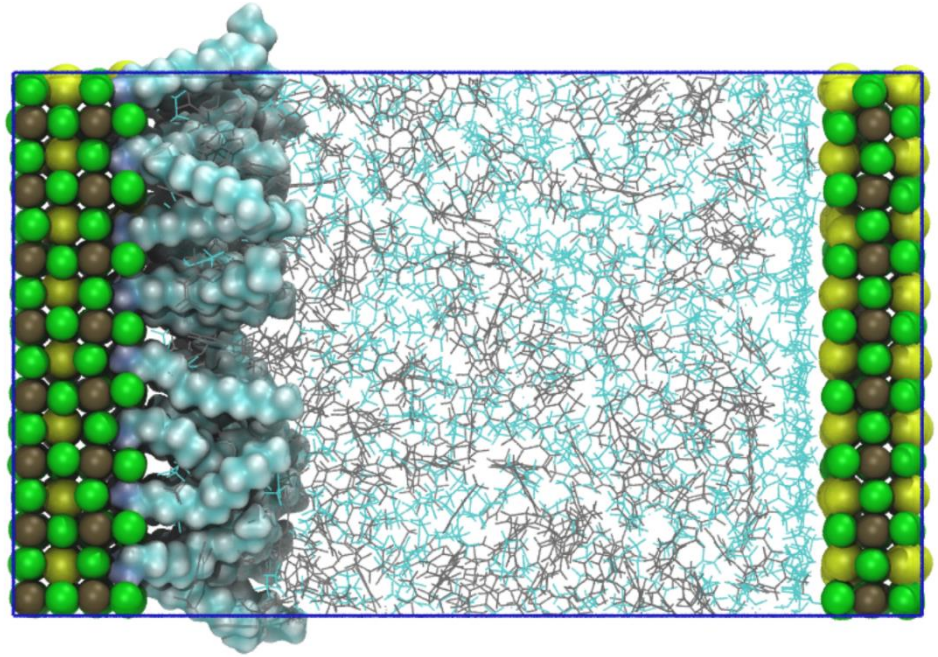
Model and methods



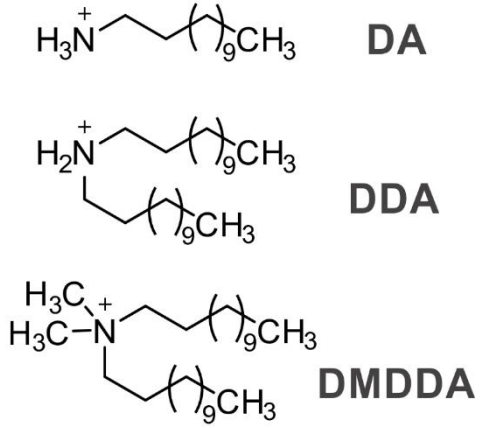
- 8×8×3.5 slab of cubic $CsPbBr_3$, terminated with CsBr-rich (100) crystallographic planes
- Interactions between ions comprising the slab modelled with Coulomb and LJ potentials[1,2]

[1]Joung, et al. *J. Phys. Chem. B.* 2008, **112 (30)**, 9020-9041.
[2]Li, et al. *J. Chem. Theory Comput*. 2013, **9 (6)**, 2733-2748.

Model and methods



- Cs^+
- Pb^{2+}
- Br^-



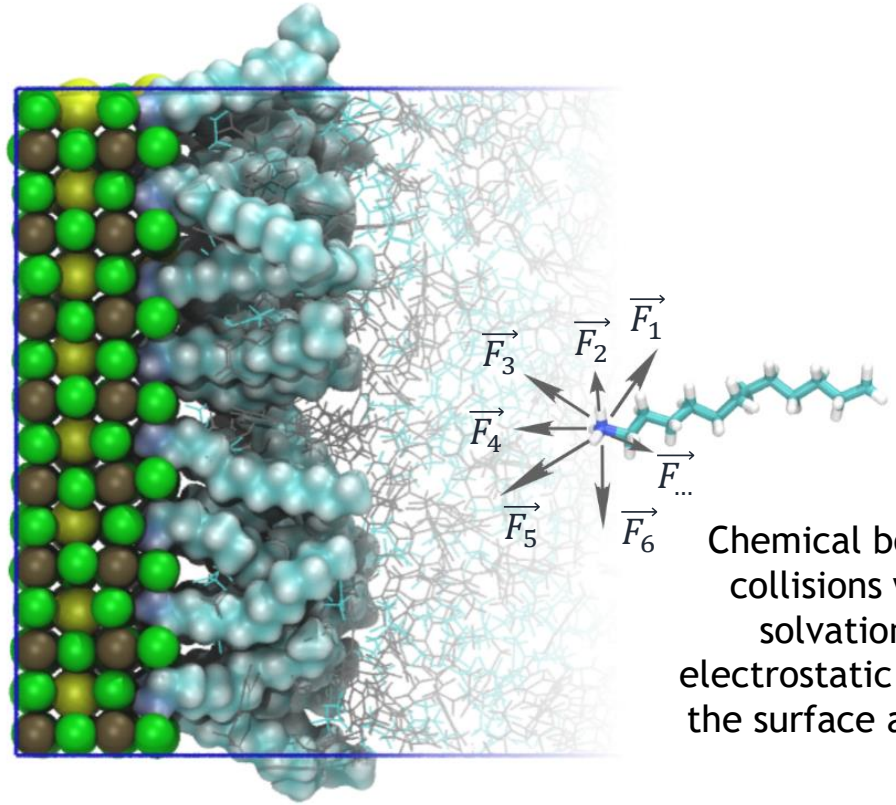
toluene : acetone = 1 : 1 (vol.)

- 8×8×3.5 slab of cubic $CsPbBr_3$, terminated with CsBr-rich (100) crystallographic planes
- Interactions between ions comprising the slab modelled with Coulomb and LJ potentials[1,2]
- Some surface Cs^+ ions replaced with alkylammonium ligands
- All-atom CHARMM General Force Field for the organic part[3]

[1]Joung, et al. *J. Phys. Chem. B.* 2008, **112 (30)**, 9020-9041.
[2]Li, et al. *J. Chem. Theory Comput*. 2013, **9 (6)**, 2733-2748.
[3]Vanommeslaeghe, et al. *J. Comput. Chem.* 2010, **31 (4)**, 671-690.

Model and methods

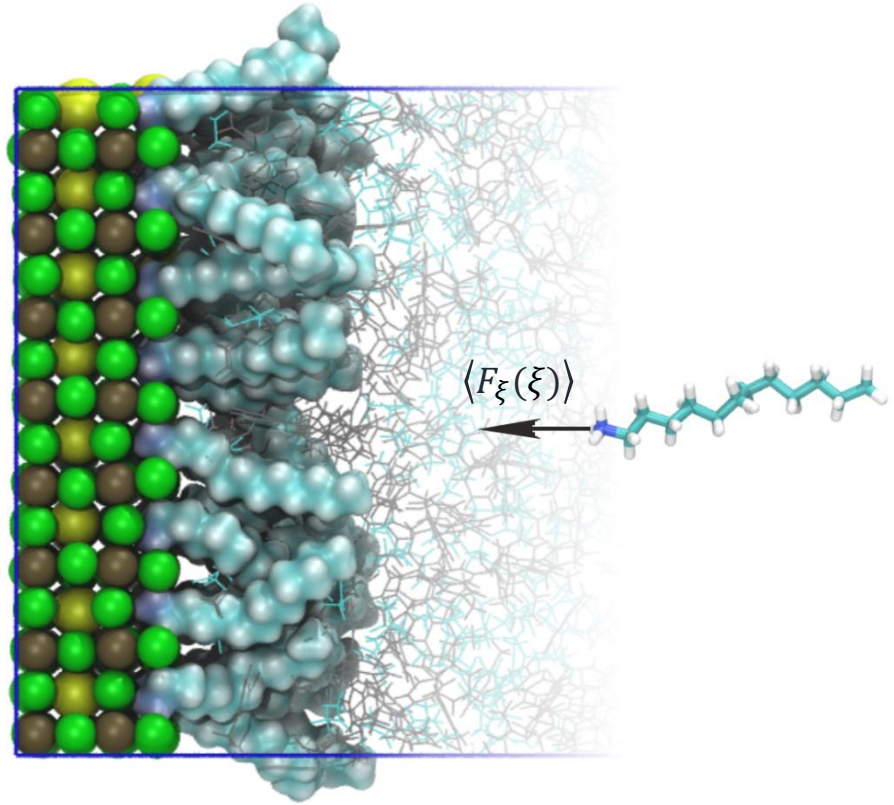
Potential of mean force



Chemical bonding within the ligand, collisions with solvent molecules, solvation/desolvation effects, electrostatic and vdW interactions with the surface and neighboring ligands, …

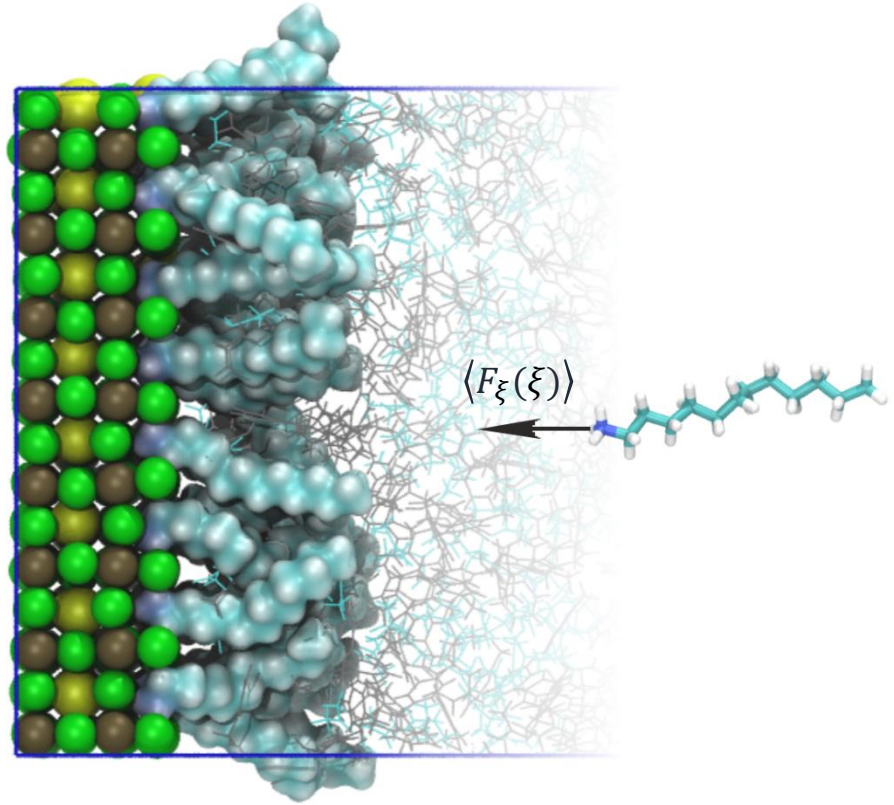
Model and methods

Potential of mean force



Model and methods

Potential of mean force



Integration

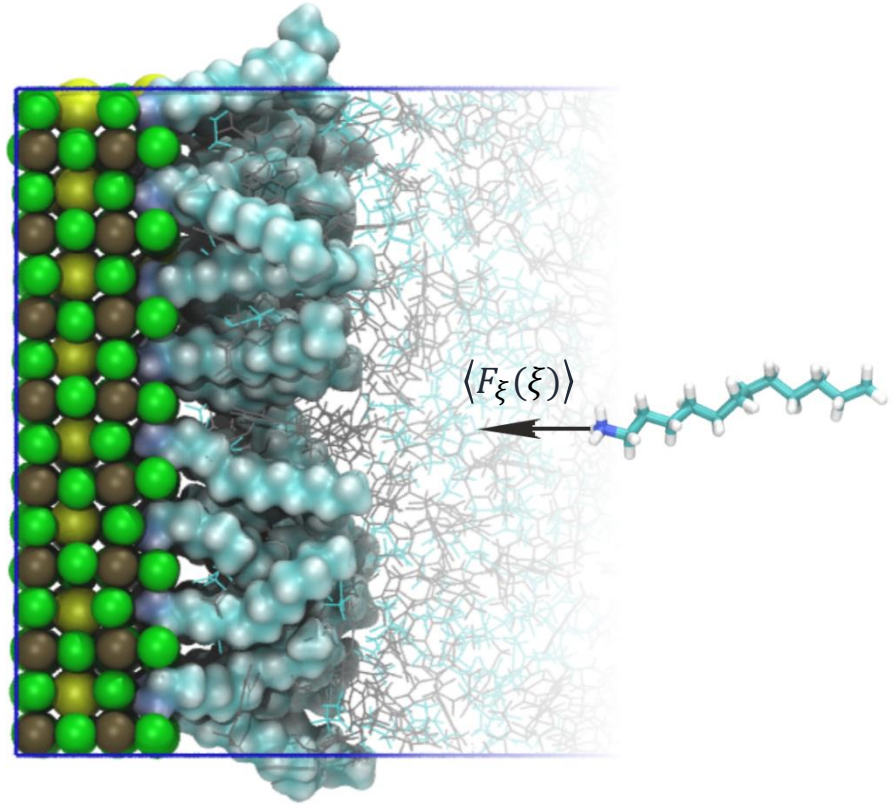
Potential of mean force (PMF)

$$\mathcal{W}(\xi) = \int \langle F_\xi(\xi) \rangle \, d\xi$$

Effective ligand-slab interactions

Model and methods

Potential of mean force



Integration

Potential of mean force (PMF)

$$\mathcal{W}(\xi) = \int \langle F_\xi(\xi) \rangle \, d\xi \quad \equiv \quad \mathcal{W}(\xi) = \mathcal{W}(\xi^*) - k_B T ln \left[\frac{\langle \rho(\xi) \rangle}{\langle \rho(\xi^*) \rangle} \right]$$

Effective ligand-slab interactions

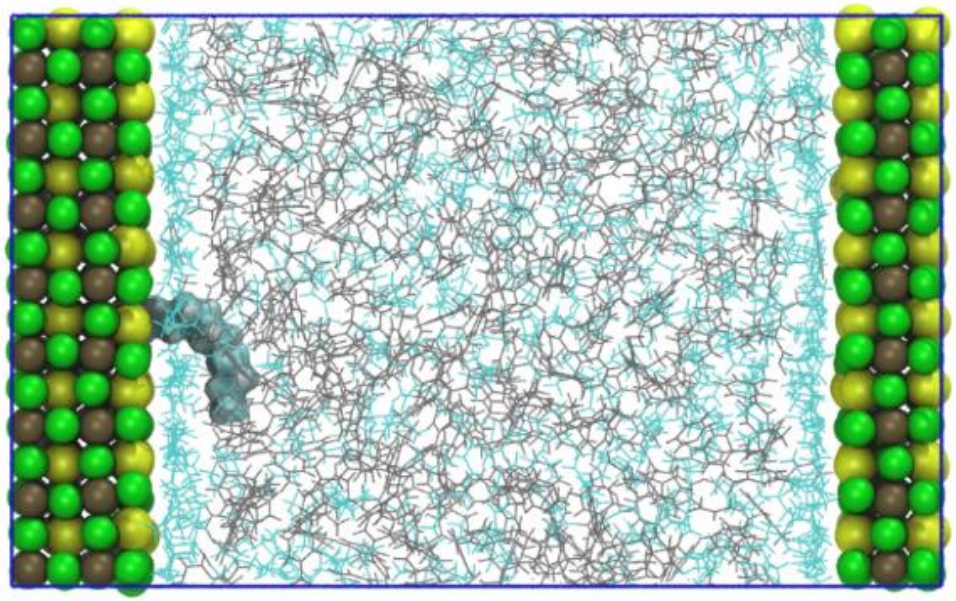
Free energy change along the chosen reaction coordinate

PMF, $F(d_{slab-N})$, was computed using umbrella sampling technique[1]

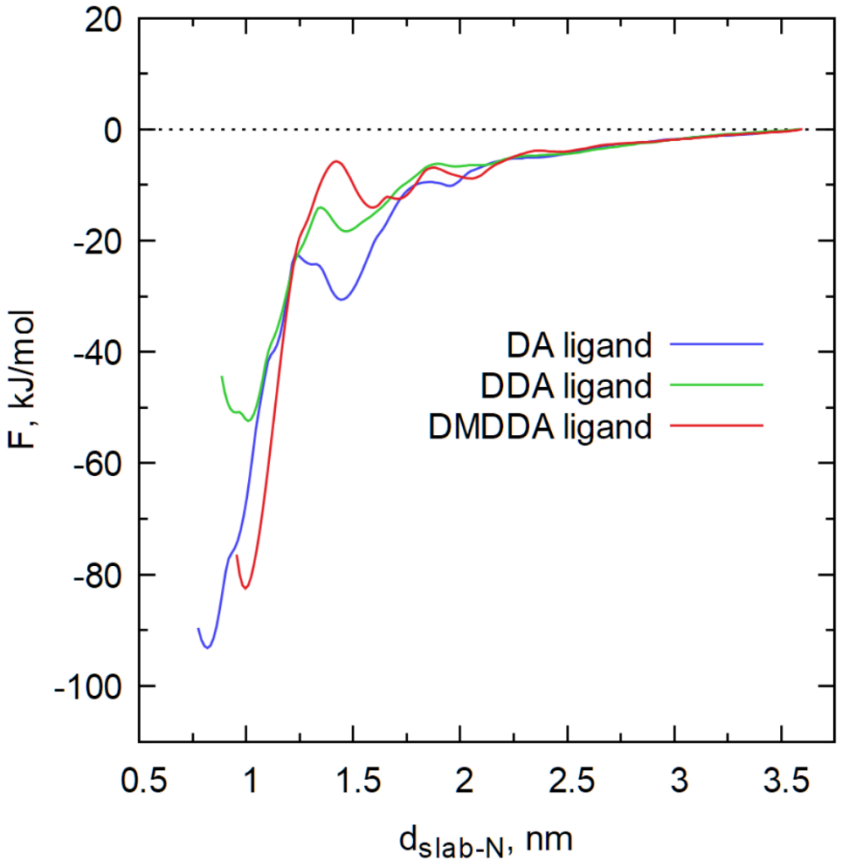
[1]Torrie, et al. *J. Comput. Phys.* 1977, **23 (2)**, 187-199.

Binding at infinitely small surface coverage ($\sigma \rightarrow 0$)

Simulation box



PMF profiles



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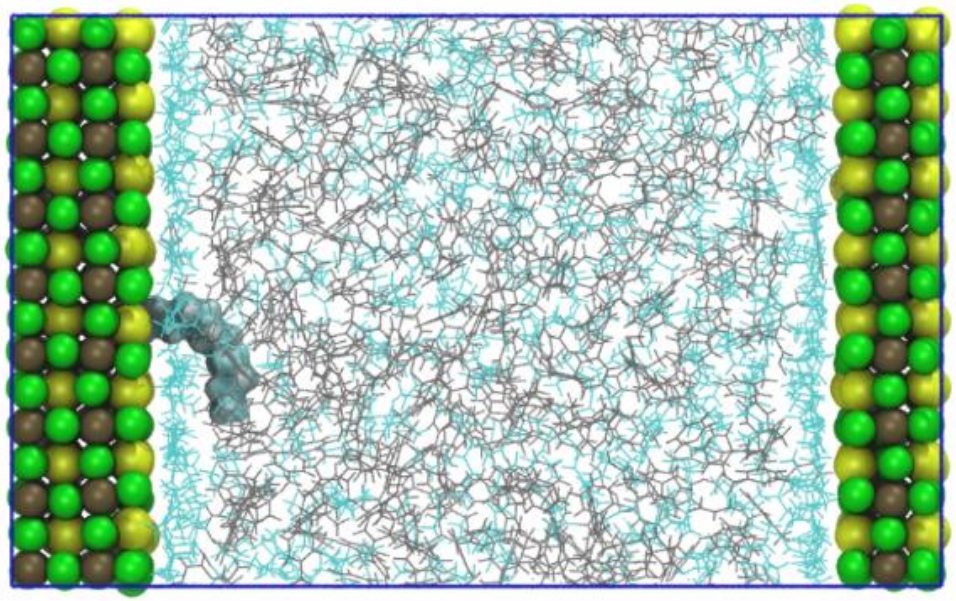
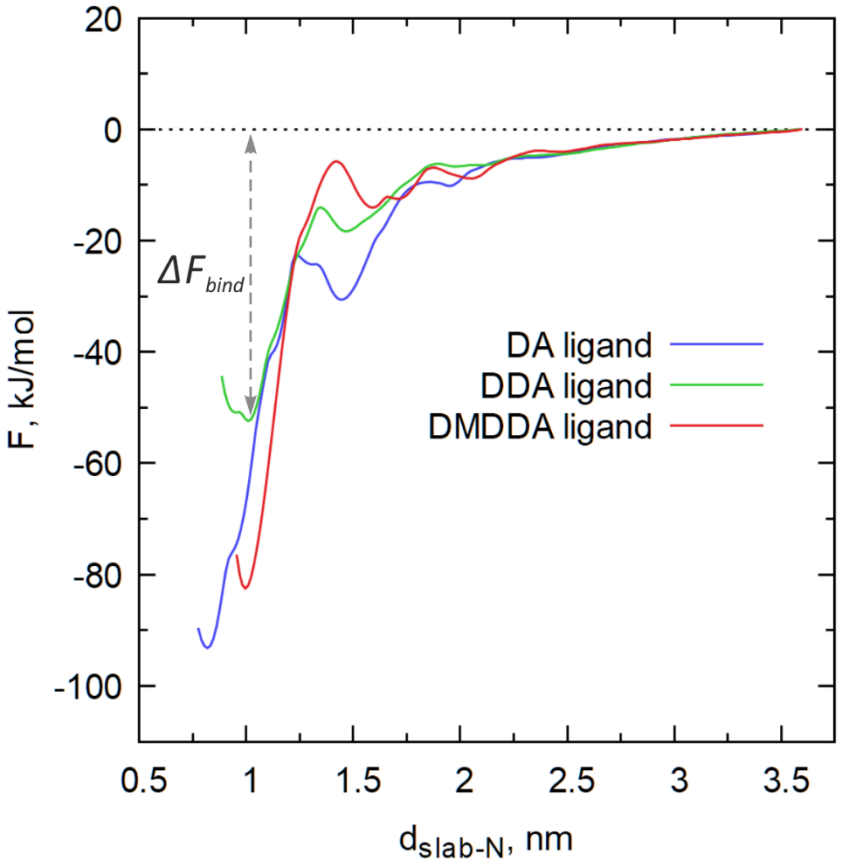
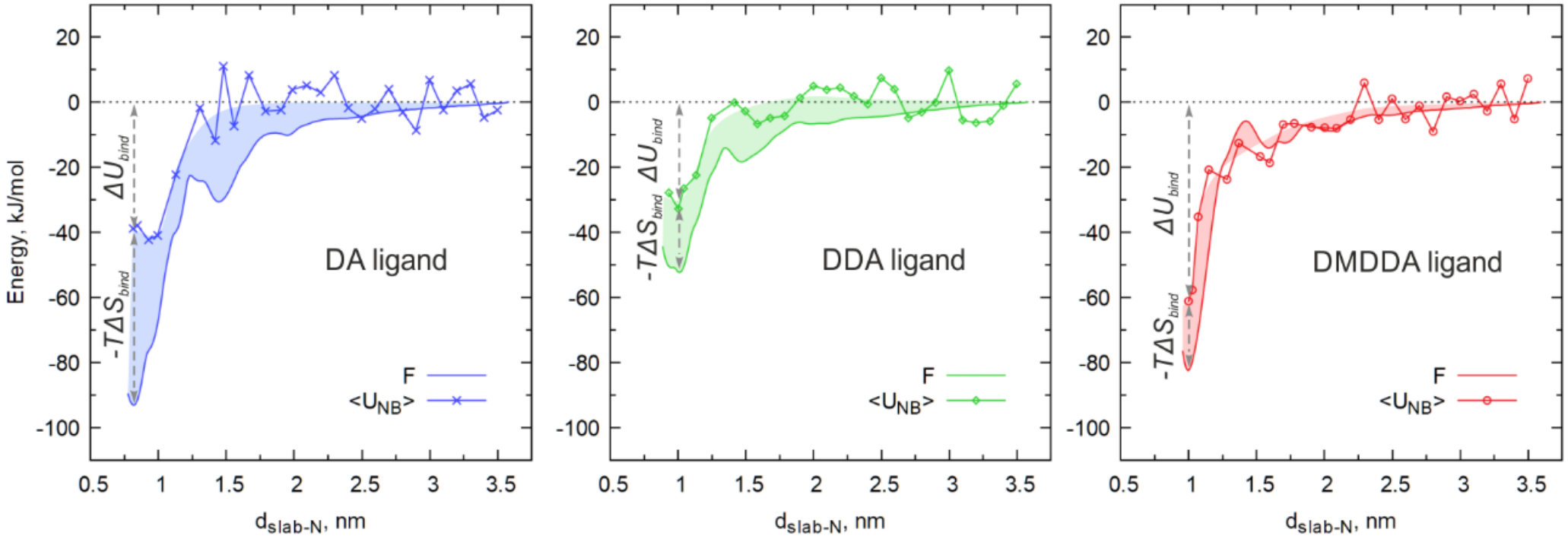


PMF profiles

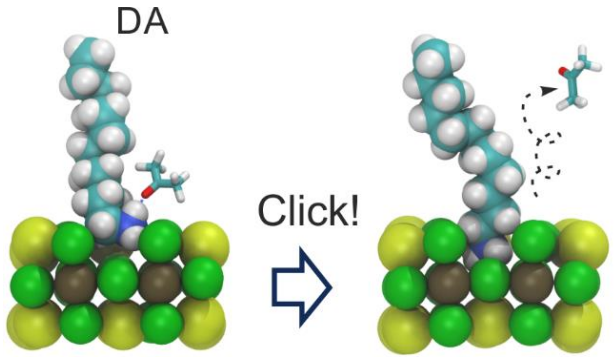


Binding at infinitely small surface coverage ($\sigma \rightarrow 0$)

Energetic and entropic contributions



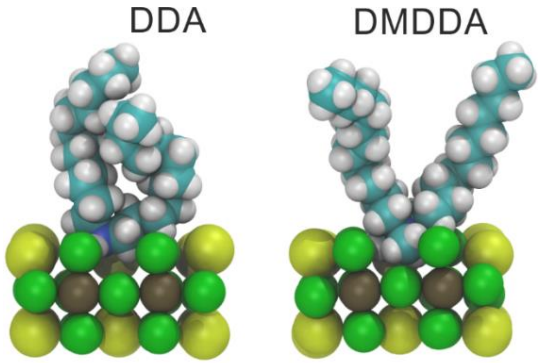
Geometric fit and head-group desolvation



Complete desolvation

Looses on average 1.1 acetones

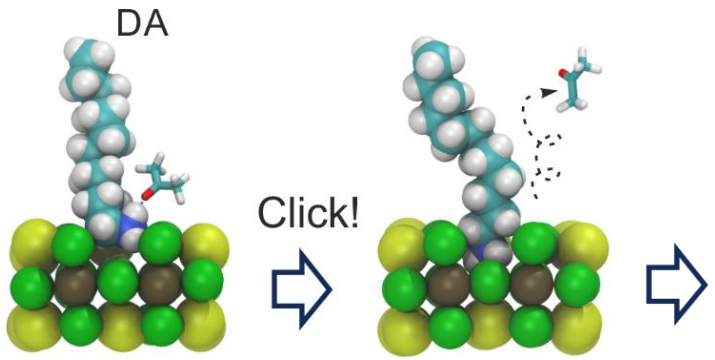
Estimated entropy gain is
$-T\Delta S \approx -20$ kJ/mol



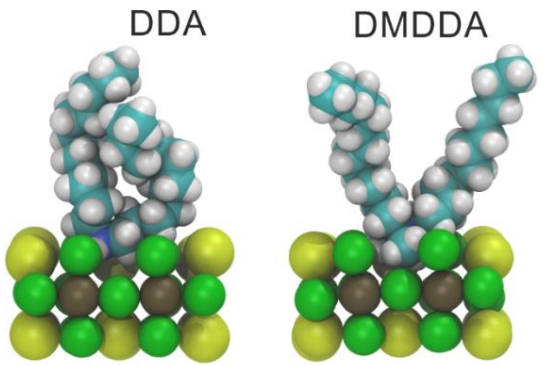
*Residual solvation is not shown

Bad geometric fit
Partial desolvation

Geometric fit and head-group desolvation



Complete desolvation



Bad geometric fit
Partial desolvation

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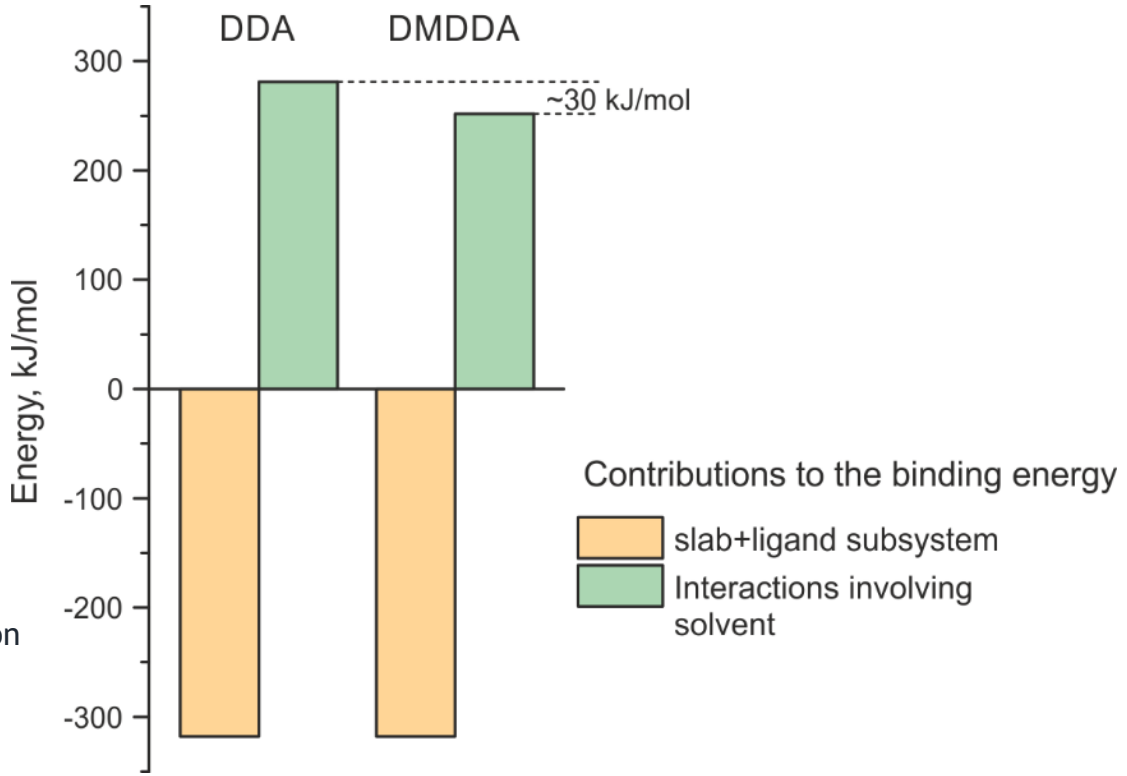
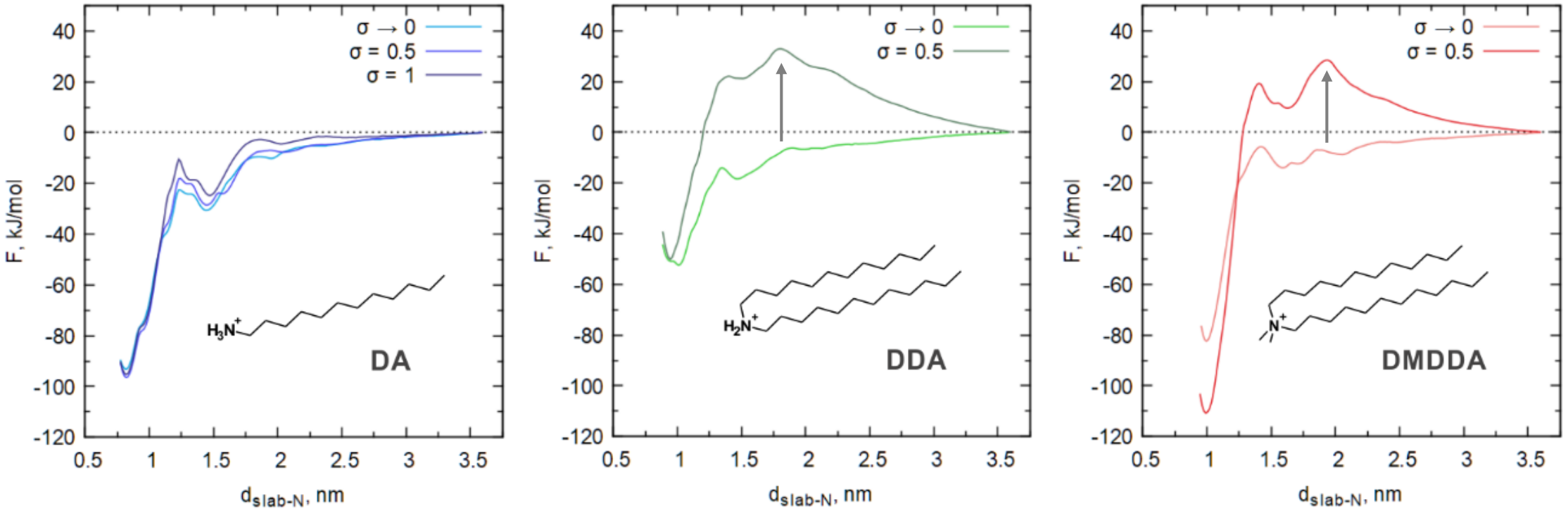
Binding of DDA and DMDDA ligands

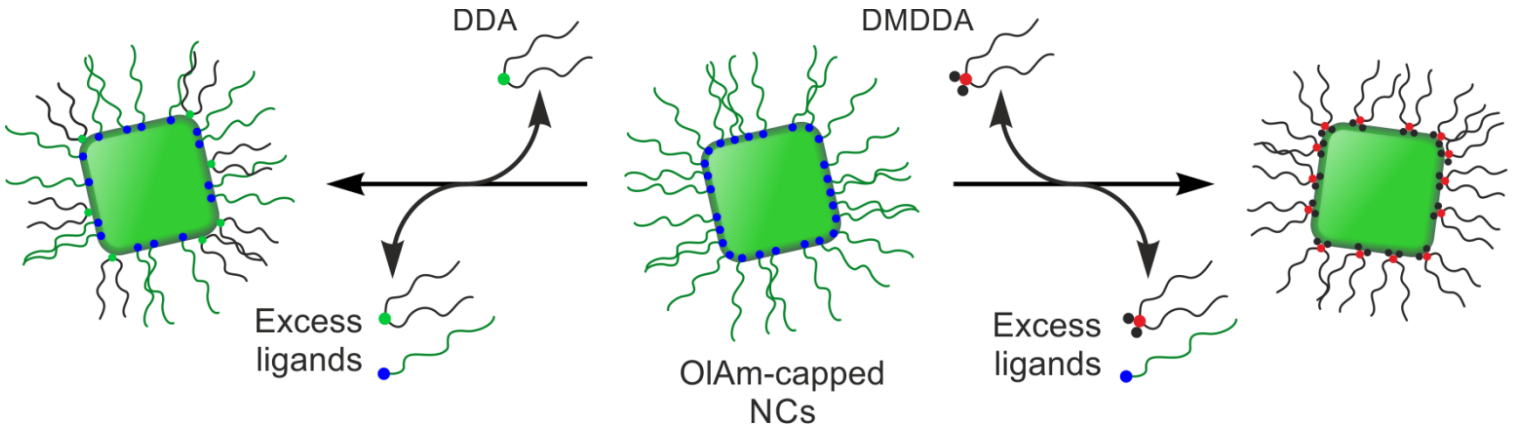


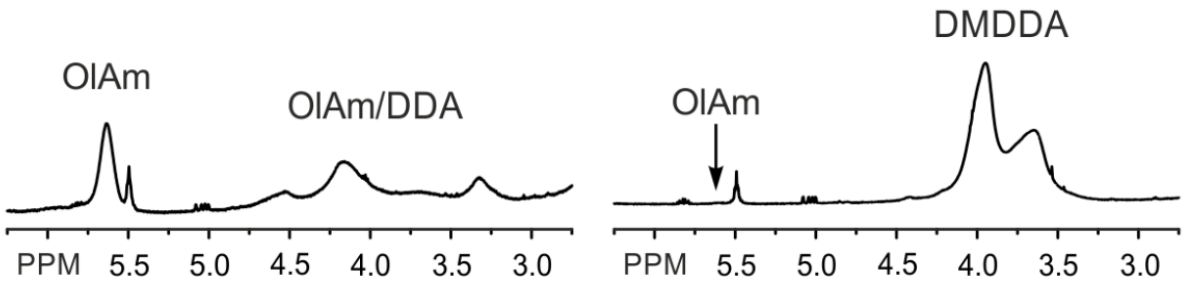
Binding at finite surface coverages

PMF profiles



Comparison with ligand-exchange experiments





^{1}H-NMR spectra of purified colloids

Ligand composition

Species	Concentration (mM)	Surface coverage (%)
Binding sites	7.4	-
DDA	1.5 – 1.8	20 – 24
OlAm	3.6 – 3.0	49 - 41
OLA (free)	0.3	-

Species	Concentration (mM)	Surface coverage (%)
Binding sites	7.2	-
DMDDA	3.1	43
OlAm	0.03	≤ 0.5
OLA (free)	0.3	-

Conclusions

Three main factors that govern effective ligand-substrate interactions

	DA	DDA	DMDDA
Geometric fit	✓	✗	✗
Low desolvation cost	✗	✗	✓
Kinetic barrier at finite coverage	✗	✓	✓

- Theoretical findings agree with the results of ligand-exchange experiments (DDA loosely binds to the $CsPbBr_3$ surface; DMDDA capping is more stable than capping with primary oleylammonium)

[1]Stelmakh, et al. *Chem. Mater.* 2021, **33, 15**, 5962-5973.

Conclusions

Three main factors that govern effective ligand-substrate interactions

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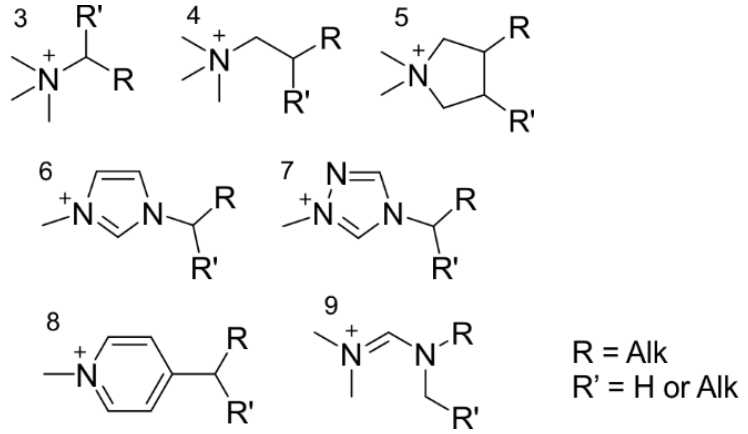
- Theoretical findings agree with the results of ligand-exchange experiments (DDA loosely binds to the $CsPbBr_3$ surface; DMDDA capping is more stable than capping with primary oleylammonium)
- Ligands with compact, yet fully substituted head-groups are expected to provide even more stable capping of $CsPbBr_3$ NCs:



[1]Stelmakh, et al. *Chem. Mater.* 2021, **33, 15**, 5962-5973.

Acknowledgements

- Prof. Dr. Maksym V. Kovalenko[1,2]
- Dr. Andrij Baumketner[3]
- Marcel Aebli[1,2]
- Dr. Maryna Bodnarchuk[1,2]
- Kovalenko Group

Thank you for your attention!

[1]Laboratory of Inorganic Chemistry, Department of Chemistry & Applied Biosciences, ETH Zürich, Switzerland
[2]Empa – Swiss Federal Laboratories for Materials Science and Technology, Switzerland
[3]Institute for Condensed Matter Physics, NAS of Ukraine

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