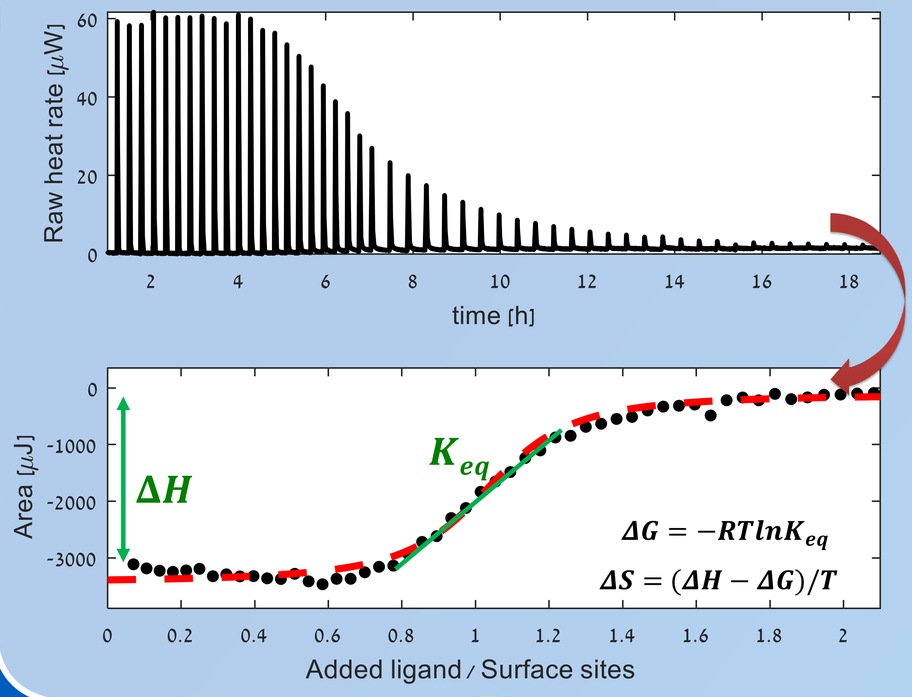
Ordering the entropy: Thermodynamics of ligand exchange in semiconductor nanocrystals

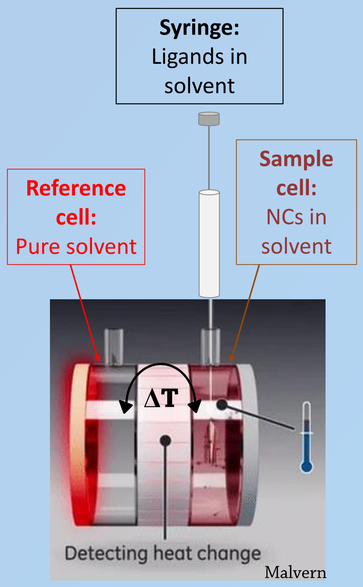
Orian Elimelech-Goldstein[1], Omer Aviv[1], Meirav Oded[1], Daniel Harries[1,2], and Uri Banin[1]

(1) The Institute of Chemistry , The Center for Nanoscience and Nanotechnology, and (2) The Fritz Haber Center. The Hebrew University of Jerusalem, Israel.

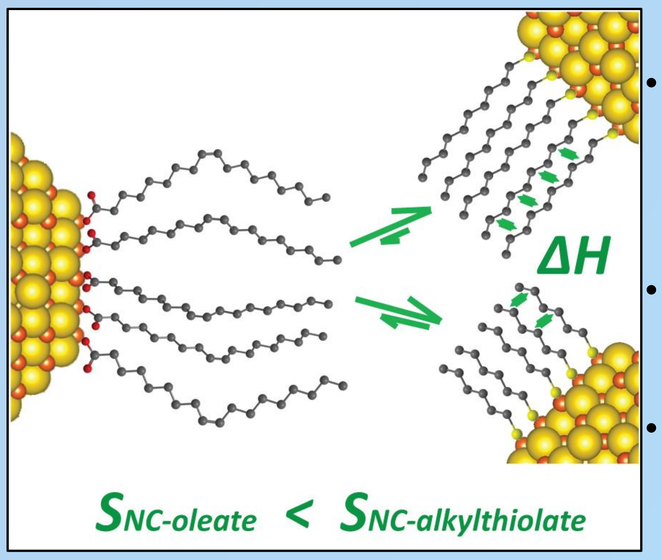
Abstract Surface ligands of nanocrystals (NCs) are central for determining their properties and for their implementation in diverse applications, yet NC-ligand interactions remain under explore. Hence, we studied the thermodynamics of ligand exchange reactions in CdSe NCs from oleate to linear and branched alkylthiols by isothermal titration calorimetry (ITC). Mean-field calculations of conformational entropy changes upon ligand binding were employed to gain an additional insight on the ligand organization contribution to the overall entropy change. This work is a starting point for achieving fundamental understanding of NCs surface physico-chemical properties and their dependence on various parameters, paving the way for smart NC surface design that can impact all NCs-based applications.

1. Ligand exchange reaction by ITC



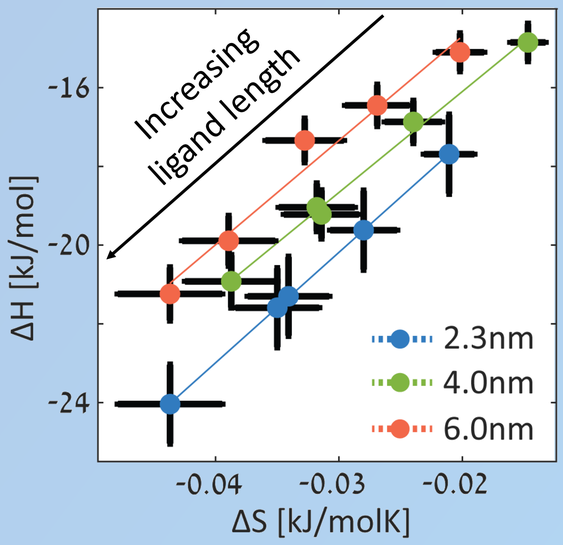


$$NC - Oleate + RSH \rightleftharpoons NC - SR + OA$$



- **ΔG<0** → Higher affinity of Cd^{2+} surface sites to the thiol binding group.
- **ΔH<0** → Thiol is a stronger binding group.
- **ΔS<0** → More organized packing of the alkylthiols.

2. Ligand length effect

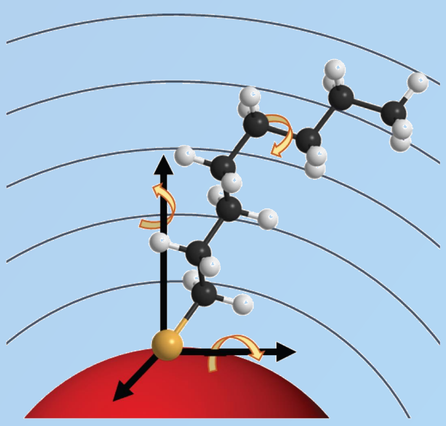


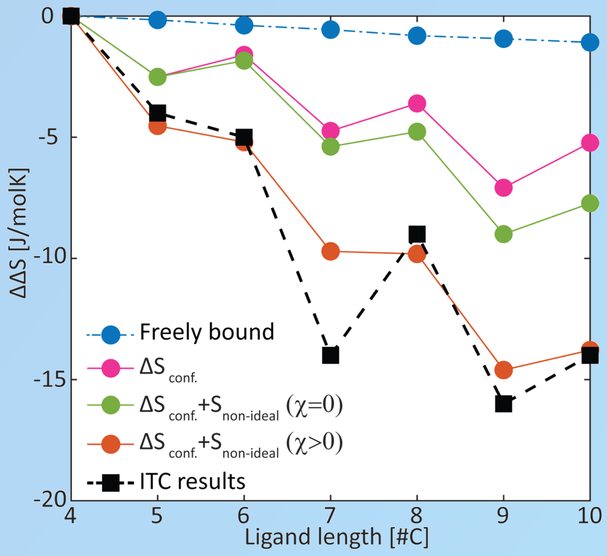
Enthalpy-Entropy compensation.
Increasing ligand length:

- Increasing **entropy loss**→ Higher loss of **degrees of freedom**.
- Increasing **exotermicity** → More inter-chain **Van der Waals interactions.**

Nano Lett. 2020, 20, 9, 6396–6403

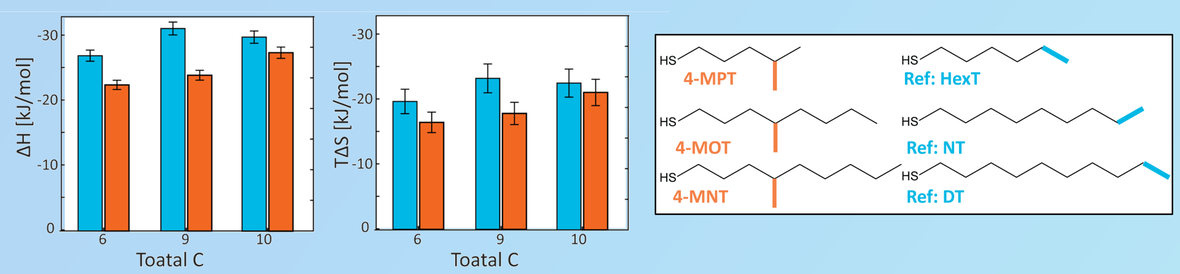
3. Conformational entropy calculations





- **Freely bound ligand** model (no packing constrain) already presents a decrease in the entropy loss with increasing ligand length.
- **Constrained chain** model (constant density in the ligand shell), mirrors the experimentally observed odd-even effect (due to inter-chain interactions).
- Addition of **Flory Huggins mixing entropy** with **entropy interaction parameter (χ)**, reproduces the experimental data.

4. Ligand exchange with branched alkylthiols



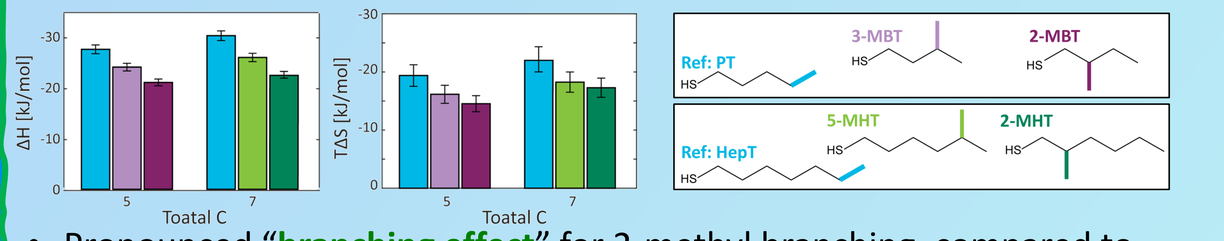
"**Branching effect**":

- Lower exothermicity
- Lower entropy loss

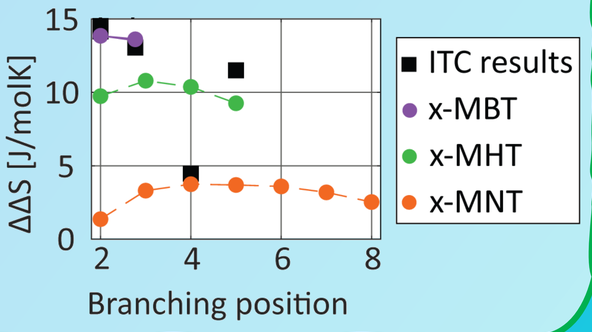
} Steric hindrance for ligand packing.

- Ligand length effect is also observed for branched ligands (increasing exothermicity and entropy loss upon increasing ligand length).

5. Branching position effect



- Pronounced "**branching effect**" for 2-methyl branching, compared to the iso position.
- Conformational entropy calculations reproduce the experimental data.
- The lower entropy loss is achieved when the branching group is located toward the middle of the chain.



Summary Conformational entropy, which is highly affected by structural changes in the ligand chain (backbone length, branching position, etc.), is central for determining the thermodynamics route of ligand exchange reaction. Thus, must be considered in future planning of NC surface modifications.