

# Mechanistic Insight into the Formation of Cationic Naked Nanocrystals Generated under Equilibrium Control

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## 1. Introduction

•Ligand coated neutral nanocrystals (NCs) dispersions combined with templating polymers are used for preparation of mesoporous films.<sup>1</sup>

•PbSe thin films are used for active layers in energy conversion materials such as Schottky-type solar cells, field effect transistors, NIR photodetectors, and thermoelectrics.

•Cationic naked NCs dispersions are more promising than ligand coated neutral NCs for preparation of mesoporous film because of their (1) energy propagating ability due to close NC-NC distance, (2) strong electrostatic interaction between NC and polar polymer enables ordered mesostructure and (3) generality of NC composition (Scheme 1).

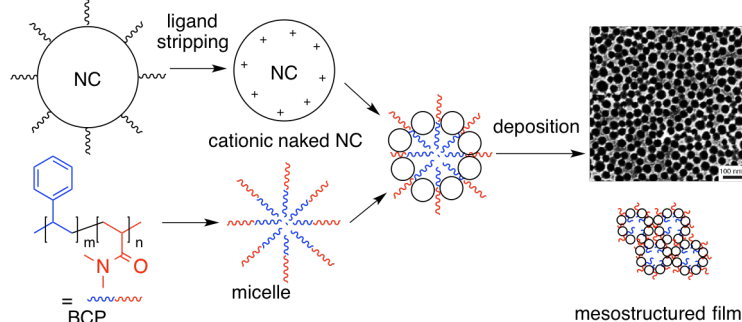
•Cationic naked NCs are usually prepared by treating ligand protected NCs with strong electrophilic reagents that irreversibly cleave bonds between native organic ligands and the NC surface (Scheme 2a).<sup>2</sup>

•If ordered cationic naked PbSe NC film is obtained, improvement as energy conversion material is expected.

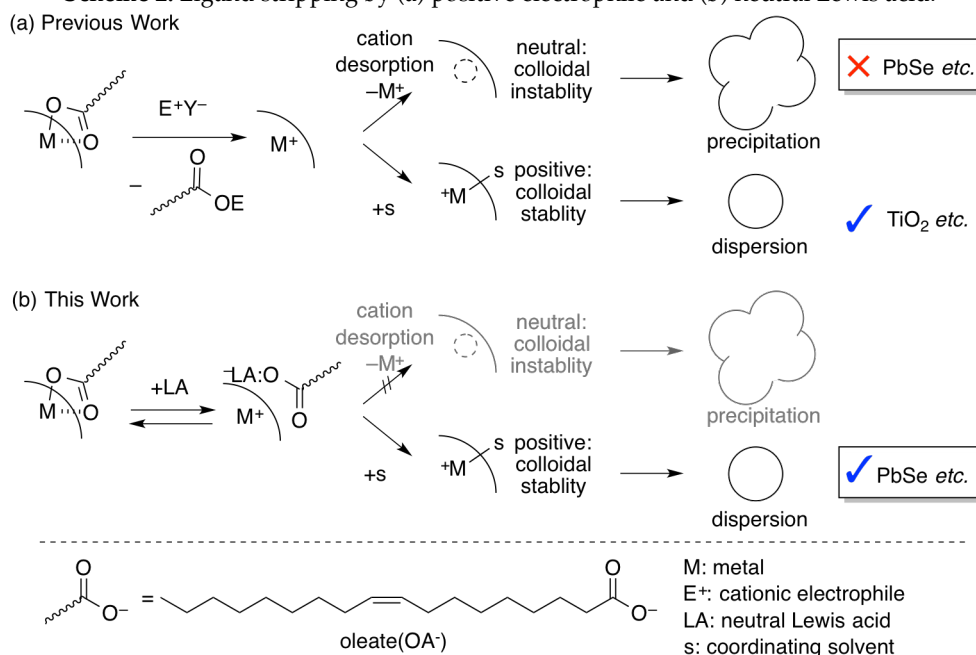
**Problem:** for some materials (including PbSe), irreversible cleaving of NC-ligand bonds cause desorption of excess metal cations which stabilize the NCs colloids, making the NCs poor dispersive as building units for mesoporous films (Scheme 2a).

**This Work:** use of relatively weak neutral Lewis acid for NC-ligand cleavage to generate reversibly physisorbing anionic species that stabilizes the NC surface until coordinating solvent is able to repassivate the surface (Scheme 2b).

**Scheme 1.** Assembly of cationic naked NC and BCP into mesoporous structure. The SEM image is TiO<sub>2</sub> NC/BCP on Si.



**Scheme 2.** Ligand stripping by (a) positive electrophile and (b) neutral Lewis acid.



## 2. Results and Discussion

### 2.1 Synthesis and Characterization of Stable Cationic NC Dispersion

•Ligand stripping of oleate coated PbSe NC in DMF was attempted with three kinds of electrophiles (Fig. 1a).

i)  $\text{NO}^+\text{BF}_4^-$  (oxidant): precipitation✖

ii)  $\text{Me}_3\text{O}^+\text{BF}_4^-$  (methylation reagent): poor dispersibility✖

iii)  $\text{Et}_2\text{O}:\text{BF}_3$  (Lewis acid): stable dispersion✓

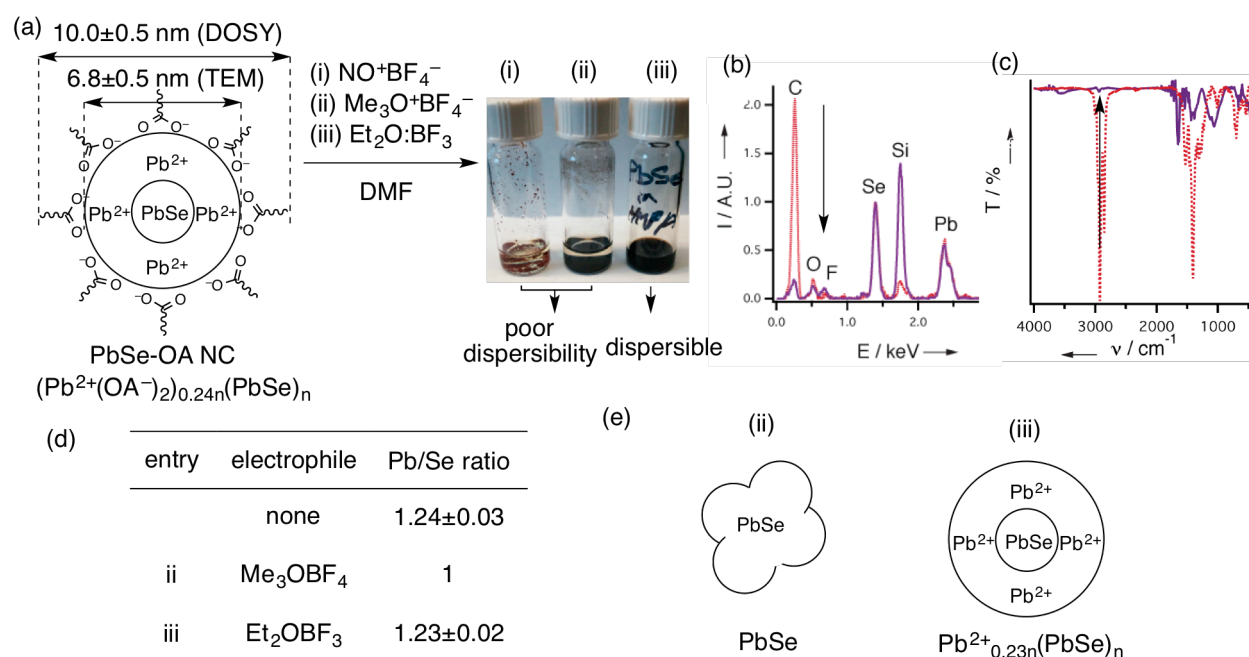
•EDX and IR analyses of PbSe-OA NC treated with  $\text{Et}_2\text{O}:\text{BF}_3$  shows large decrease in carbon signals at 0.3 keV and  $2900\text{ cm}^{-1}$ , respectively (Fig.1b,c). => PbSe-OA treated with  $\text{Et}_2\text{O}:\text{BF}_3$  is naked.

•Hydrodynamic diameter (calculated from DOSY signal of OA on the NC) of PbSe-OA NC is  $10.0\pm 0.5\text{ nm}$ . After treatment by  $\text{Et}_2\text{O}:\text{BF}_3$ , it decreased to  $6.3\pm 0.3\text{ nm}$ . It is comparable to the core diameter in TEM  $6.8\pm 0.5\text{ nm}$ .  $\text{Et}_2\text{O}:\text{BF}_3$  treated PbSe NC is not only naked but also well dispersed.

•ICP-AES (Inductively coupled Plasma Emission Spectrometry) was used for quantifying Pb and Se in isolated PbSe NCs (Fig. 1d,e).

=>  $\text{Et}_2\text{O}:\text{BF}_3$  treated PbSe NC avoided desorption of cation ( $\text{Pb}^{2+}$ ) from the surface.

•Stable cationic naked NC dispersions of ZnO,  $\text{Mn}_2\text{O}_3$ ,  $\text{Ti}_2\text{O}_3$ , and Ni also could be prepared by treatment with  $\text{Et}_2\text{O}:\text{BF}_3$ .



**Figure 1.** Ligand stripping of PbSe-OA NC by electrophiles i-iii. (a) Treatment of PbSe-OA NC and dispersiveness of the product. (b) EDX and (c) IR spectra of NCs before (red line) and after (purple line) treatment with  $\text{Et}_2\text{O}:\text{BF}_3$ . (d) Pb/Se ratio of NCs determined by ICP-AES analysis. (e) Model composition and structure of NC (ii) and (iii) calculated from Pb/Se ratio in (d).

### 2.3. Mechanism of formation of cationic naked PbSe NC

• To elucidate the stripping mechanism, titration of PbSe-OA NC by Et<sub>2</sub>O:BF<sub>3</sub> measured by <sup>1</sup>H NMR was conducted (Fig. 2a).

=> OA:BF<sub>3</sub><sup>-</sup> was formed by addition of Et<sub>2</sub>O:BF<sub>3</sub>.

• Titration of PbSe-OA by Et<sub>2</sub>O:BF<sub>3</sub> measured by <sup>1</sup>H DOSY shows time averaged diffusion constant (D) of OA moieties. At 0.2 equiv., both of OA<sup>-</sup> and OA:BF<sub>3</sub><sup>-</sup> slowly diffuse with NC core (D = 1×10<sup>-10</sup> m<sup>2</sup>s<sup>-1</sup>, Fig. 2b). At 0.5 equiv., OA<sup>-</sup> stayed same diffusivity (Fig. 2c). This means OA<sup>-</sup> is always on the NC surface regardless of Et<sub>2</sub>O:BF<sub>3</sub> addition. On the contrary, D of OA:BF<sub>3</sub><sup>-</sup> increased to 2.4×10<sup>-10</sup> m<sup>2</sup>s<sup>-1</sup>. It is intermediate value between NC and free OA moiety. That means OA:BF<sub>3</sub><sup>-</sup> rapidly exchanges on (D = 1×10<sup>-10</sup> m<sup>2</sup>s<sup>-1</sup>) and off (D = 8×10<sup>-10</sup> m<sup>2</sup>s<sup>-1</sup>) the NC.

=> OA:BF<sub>3</sub><sup>-</sup> stabilized cationic NC surface until coordination solvent is able to repassivate the surface.

### 2.4. Formation of Counter Ion BF<sub>4</sub><sup>-</sup>

• <sup>19</sup>F NMR and FT-IR of isolated cationic naked NC shows its counter ion is BF<sub>4</sub><sup>-</sup> (Fig. 3). How is it formed?

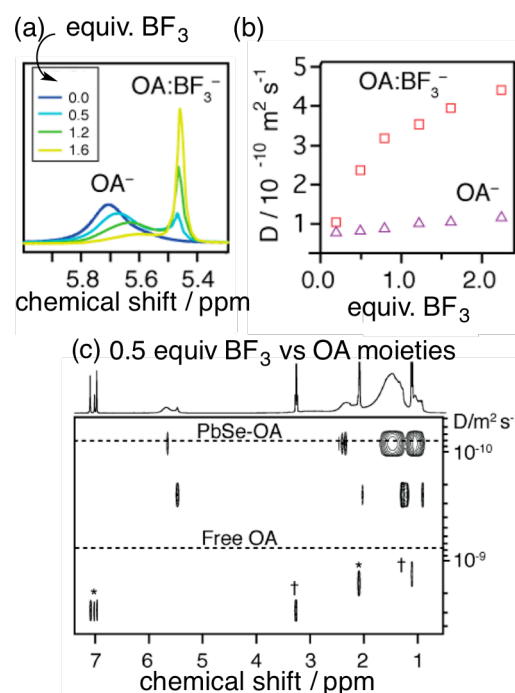
• <sup>19</sup>F NMR of Et<sub>2</sub>OBF<sub>3</sub> in DMF revealed DMF facilitated disproportionation reaction to yield BF<sub>4</sub><sup>-</sup> (Fig. 4a,b).

• Negative-ion mode ESI-MS of Pb(OA)<sub>2</sub> + Et<sub>2</sub>OBF<sub>3</sub> in benzene was conducted to find the another source of BF<sub>4</sub><sup>-</sup>. Anionic species shown in green were detected and reaction mechanism of BF<sub>4</sub><sup>-</sup> generation was predicted (Fig. 5a,b).

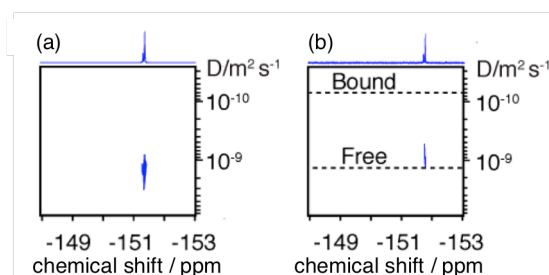
• anionic OA-B species other than OABF<sub>3</sub><sup>-</sup> generated by both mechanisms may contribute to NC stabilization

• D of BF<sub>4</sub><sup>-</sup> on the NC is comparable to D in free (Fig. 3).

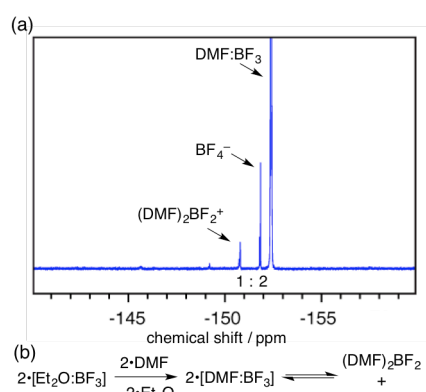
=> BF<sub>4</sub><sup>-</sup> don't interact with the NC in solution.



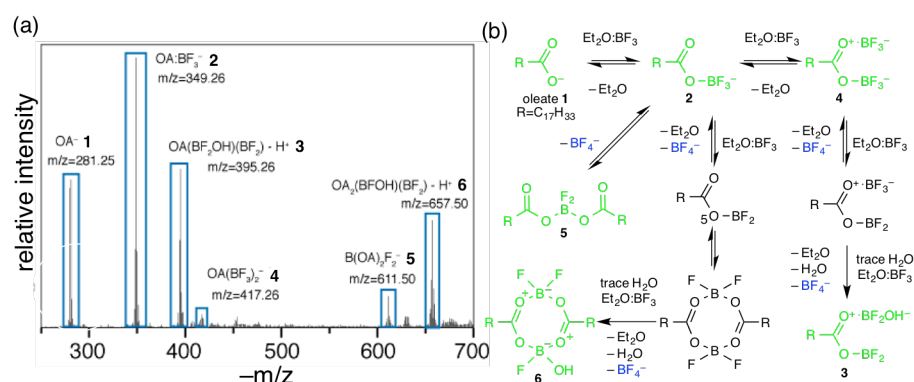
**Figure 2.** <sup>1</sup>H NMR titration study of PbSe-OA by Et<sub>2</sub>O:BF<sub>3</sub> (vs OA moiety) in DMF. (a) Generation of OA:BF<sub>3</sub><sup>-</sup> (b) Dependence of Diffusion coefficient of OA<sup>-</sup> and OA:BF<sub>3</sub><sup>-</sup> on equivalent of Et<sub>2</sub>O:BF<sub>3</sub>. (c) <sup>1</sup>H DOSY spectrum at 0.5 equiv. of Et<sub>2</sub>OBF<sub>3</sub>



**Figure 3.** Elucidation of counter ion on cationic naked PbSe NC by <sup>19</sup>F NMR (DOSY). (a) NaBF<sub>4</sub> as a reference of BF<sub>4</sub><sup>-</sup>. (b) redispersed cationic naked PbSe NC.



**Figure 4.** Reaction mechanism investigation of BF<sub>4</sub><sup>-</sup> origin by <sup>19</sup>F NMR. (a) <sup>19</sup>F NMR spectrum of Et<sub>2</sub>OBF<sub>3</sub> in DMF (b) Found species and supposed mechanism of BF<sub>4</sub><sup>-</sup> generation.



**Figure 5.** Reaction mechanism investigation of BF<sub>4</sub><sup>-</sup> origin by ESI-MS (a) ESI-MS spectrum of Et<sub>2</sub>OBF<sub>3</sub> + Pb(OA)<sub>2</sub> in benzene. (b) Proposed mechanism. of BF<sub>4</sub><sup>-</sup> generation. Found species are shown in green and numbered.

## 2.5. In Film Architecture of the Cationic Naked PbSe NC

•Cationic naked PbSe NC films were prepared using two methods.

1) Spin-coating of PbSe-OA NC dispersion on Si substrate (Fig 5a). Then removing OA ligands (Fig. 5b).

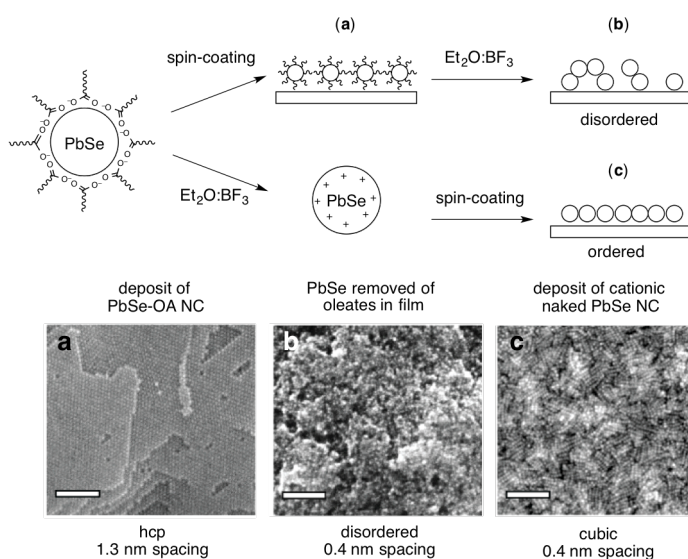
=> disordered structure

2) Preparing cationic naked PbSe NC dispersion. Then spin-coating on Si substrate (Fig 5c).

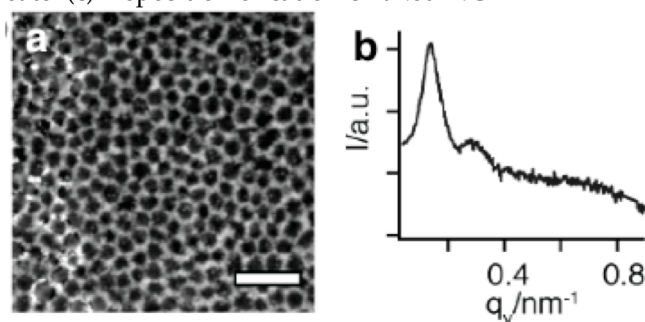
=> Newly available method 2 gives ordered structure

•cationic naked PbSe NC deposited with BCP (Scheme 1) yields highly ordered mesostructure with 45 nm periodicity (Fig. 6).

=> electrostatic interaction enables construction of a novel highly ordered mesostructure, which was unachievable by neutral NCs.



**Figure 5.** Preparation of PbSe NC films on Si substrate and their SEM images with scale bars of 100 nm. (a) Deposition before removal of oleate. (b) In film removal of oleate. (c) Deposition of cationic naked NC.



**Figure 6.** PbSe/polymer composit film (a) SEM with a scale bar of 200 nm (b) GISAX spectrum taken at an incident angle of  $0.16^\circ$ , sample-detector distance of 3.9 m and wavelength of 0.124 nm.  $q_y = 0.14 \text{ nm}^{-1}$  corresponds to 45 nm periodicity.

## 3. Conclusion

•OA ligand was stripped without cation desorption by addition of neutral Lewis acid. Stable naked cationic NC dispersion was obtained.

• $^1\text{H}$  DOSY study of PbSe-OA NC with  $\text{Et}_2\text{O}:\text{BF}_3$  shows the surface of the naked cationic NC is mainly stabilized by weak interaction with  $\text{OA}:\text{BF}_3^-$ .

•Unexpectedly, counter anion of the purified naked cationic NC turned out to be  $\text{BF}_4^-$ . Mechanistic studies of model reactions revealed its origin.

•Well dispersed cationic naked NC enabled preparation of previously unobtainable (1) ordered PbSe film with small interparticle distance and (2) mesoporous PbSe-polymer composite.

## 4. References

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