Self-assembly behavior of polymer-grafted mixed ligand gold nanoparticles

Introduction & Objective

- NPs are believed to be the most versatile building blocks for the creation of new tunable materials.
- The self-assembled structures have various applications.

Experiment & Discussion

MUA-BT (Stucky method) / MUA-OT (ligand exchange)

Control sample: MUA-Protected MUA (75% MUA)

Preparation of protected MUA

Polymer grafting
- Reaction condition: EDC, DMF, 2days, RT
- Polymer (NH2PEG~2000)

Self-assembly
- Stock solution of polymer-grafted NPs in methanol (10mg/ml)
- Instill stock solution into diethyl ether to different concentration (stock solution/diethyl ether from 0.05% to 5%)

Conclusion & Further work

1. For MUA-BT NPs (Janus) the self-assembled nanostructure is relatively stable independent of concentration and time.
2. Once MUA-BT NPs reach a equilibrium in the selective solvent, the sphere like micelles have a diameter of approximately 60nm.
3. For MUA-OT NPs, the size of self-assembled structure increases with concentration.
4. The protected MUA used for controlling the grafting ratio of homo-ligand batch can be synthesized by oxidation of di-thiol MUAs by iodine.

- Larger range of self-assembly of MUA-OT-PEG
- Self-assembly behavior of homo-ligand NPs as control
- Self-assembly in other solvent
- Cryo-TEM for detection on morphology of self-assembled nanostructures under the native environment
- SAXS can be used for more precise size characterization

Real ligand ratio from NMR

<table>
<thead>
<tr>
<th>Ratio</th>
<th>MUA-BT</th>
<th>MUA-DT</th>
<th>MUA: MUA9p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>1:1</td>
<td>1.2</td>
<td>1:1</td>
</tr>
<tr>
<td>Real</td>
<td>1:5.2</td>
<td>1:1.4</td>
<td>10.4</td>
</tr>
<tr>
<td>MUA%</td>
<td>77%</td>
<td>67%</td>
<td>42%</td>
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</tbody>
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Cleanness of grafted NPs from NMR

Size distribution from DLS

Effect from concentration

Sizes of self-assembled structure in different concentrations

MUA-BT: Independent of concentration

MUA-OT: Increase with concentration

Challenges: Understand and control self-assembly

- Two distinct ligands
- Patchiness
- Specific surface functionalization
- Surface properties of NPs
- Control over the self-assembly

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