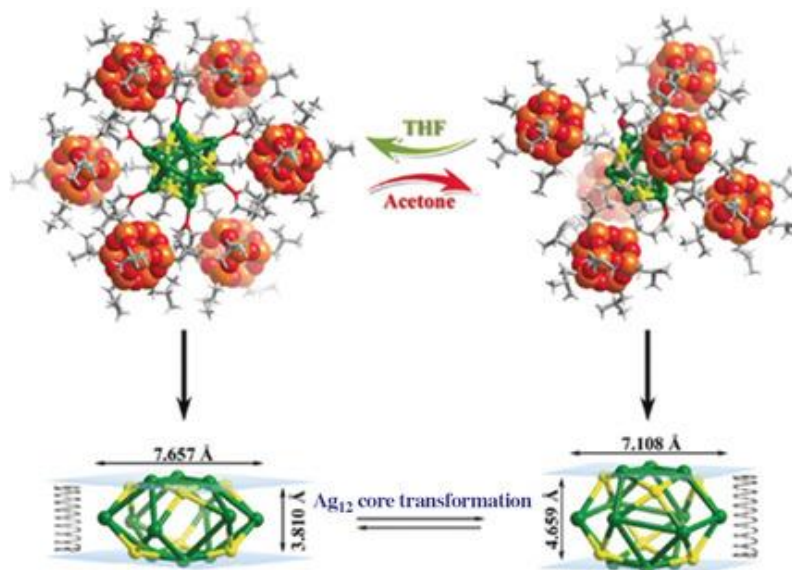


Smart Transformation of a Polyhedral Oligomeric Silsesquioxane Shell Controlled by Thiolate Silver(I) Nanocluster Core in Cluster@Clusters Dendrimers

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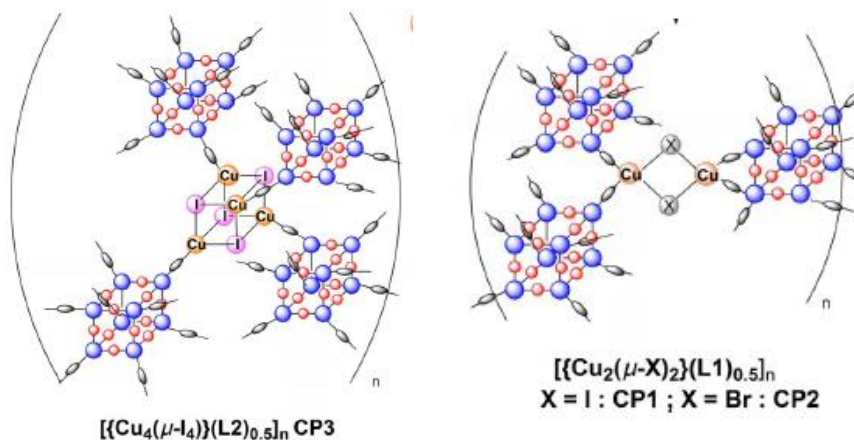


Coordination Polymers

Assembly of Coordination Polymers Using Thioether-Functionalized Octasilsesquioxanes: Occurrence of $(\text{CuX})_n$ Clusters ($\text{X} = \text{Br}$ and I) within 3D-POSS Networks

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This manuscript is dedicated in memory of our colleague Dr. Myriam Euvrard



Introduction:

- Structure-defined silver(I)nanoclusters can be synthesized by self-assembly of alkynyl, thiolate or organophosphorus ligands with silver(I)salts, of which their structures and functions can be modulated by different choice of central template anions, auxiliary ligands, or reaction conditions.
- The design of smart silver(I)clusters that can undergo a structural change upon outside stimuli still remains elusive.
- The supramolecular silver(I)nanocluster may form a smart one upon the coordination change of some shell auxiliary ligands, which can realize the shape response by outside stimuli.

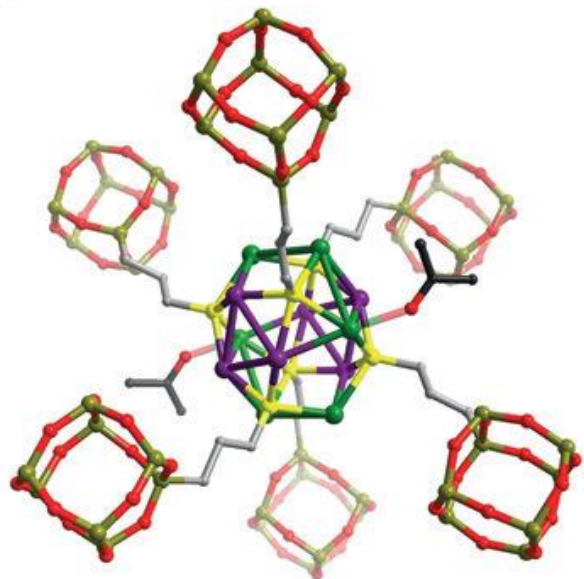
In this paper:

- Using polyhedral oligomeric silsesquioxane (POSS) modified by a thiol group as a protected ligand, atom-precise multi-heterocluster-based dendrimers $\text{Ag}_{12}@POSS_6$ (1a and 1b) were assembled.
- When such $\text{Ag}_{12}@POSS_6$ complex was stimulated by different solvents (acetone or tetrahydrofuran), the core Ag_{12} cluster underwent reversible structural transformation between flattened cubo-octahedral (in 1a) and normal cubo-octahedral (in 1b); concomitantly shell POSS clusters rearranged from pseudo-octahedral to quasi-octahedral.
- The film matrix modified by 1a or 1b showed different hydrophobicity.

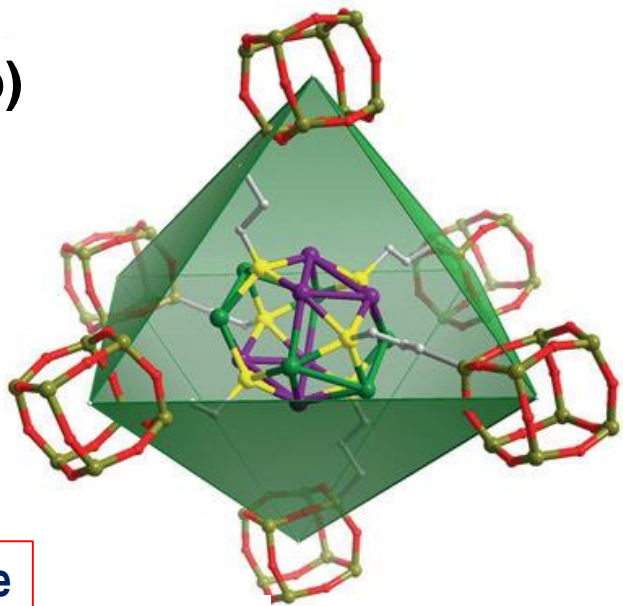
Results and discussion:



(a)



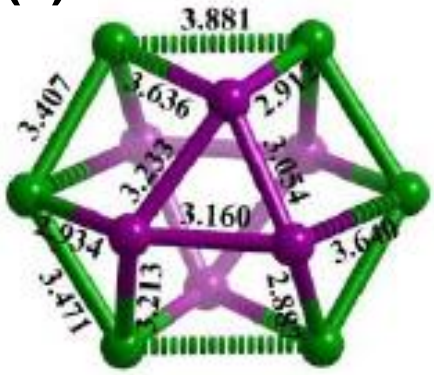
(b)



Acetone

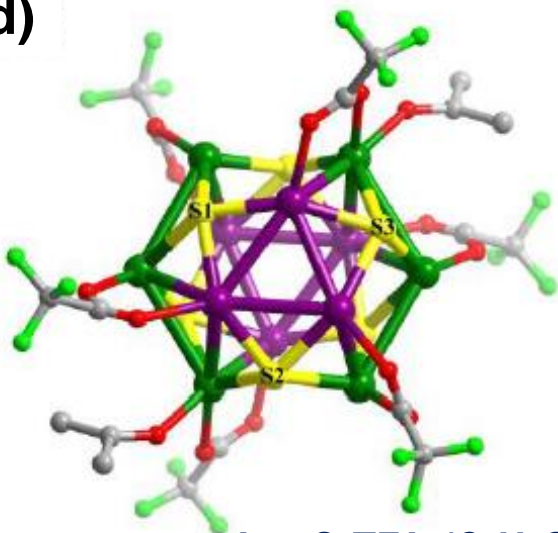
Normal cuboctahedron

(c)



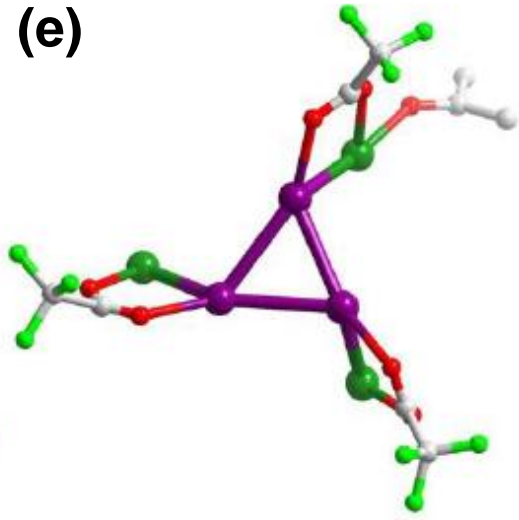
Ag₁₂ core

(d)



Ag₁₂S₆TFA₆(C₃H₆O)₂

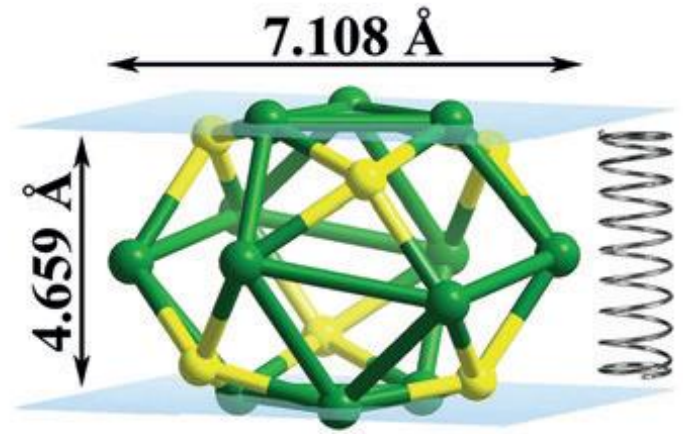
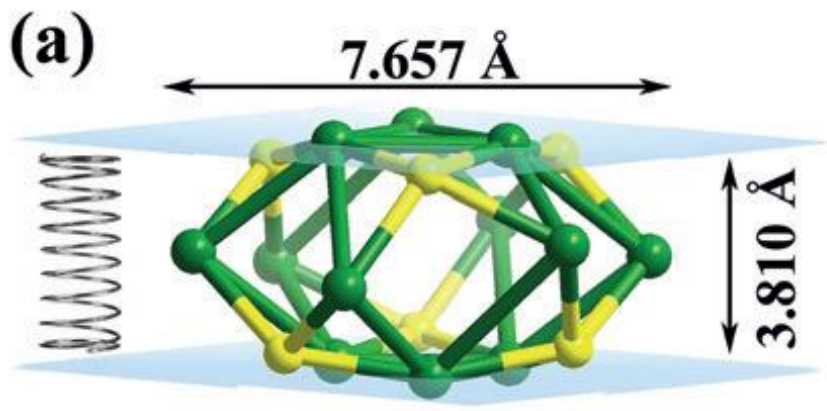
(e)



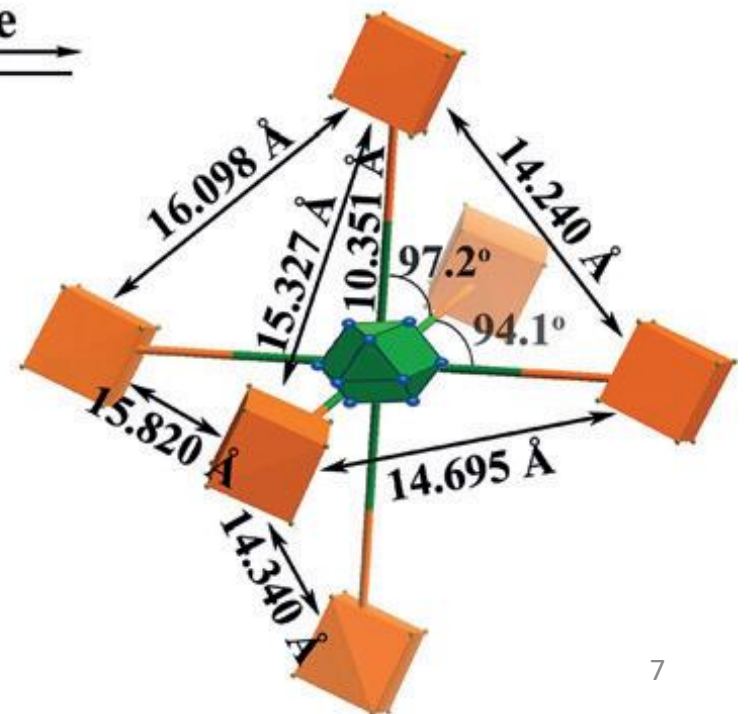
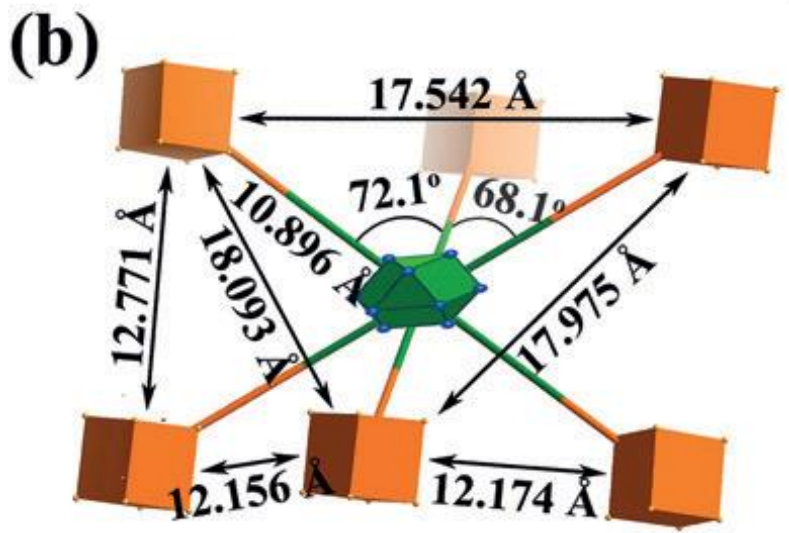
Results and discussion:

THF

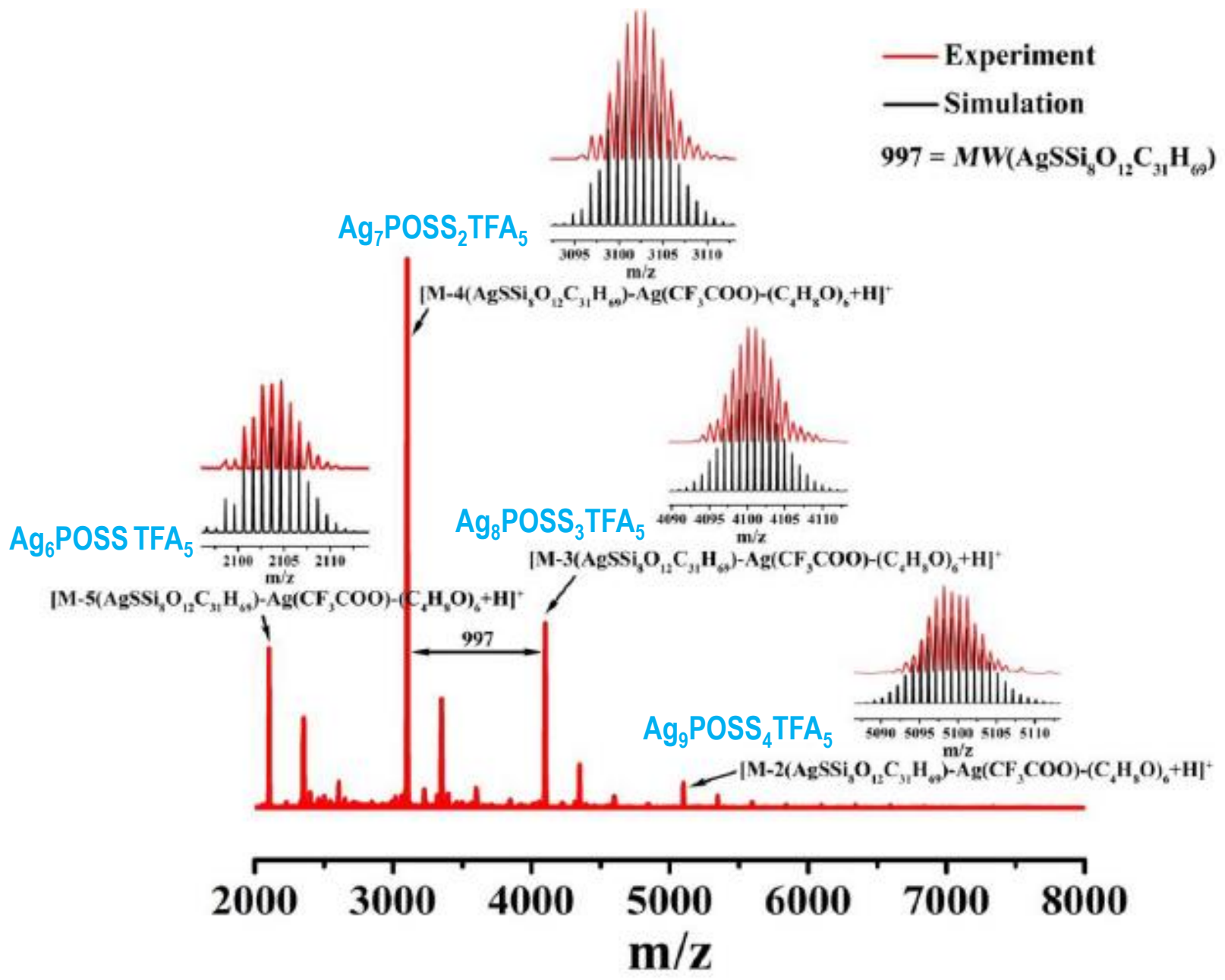
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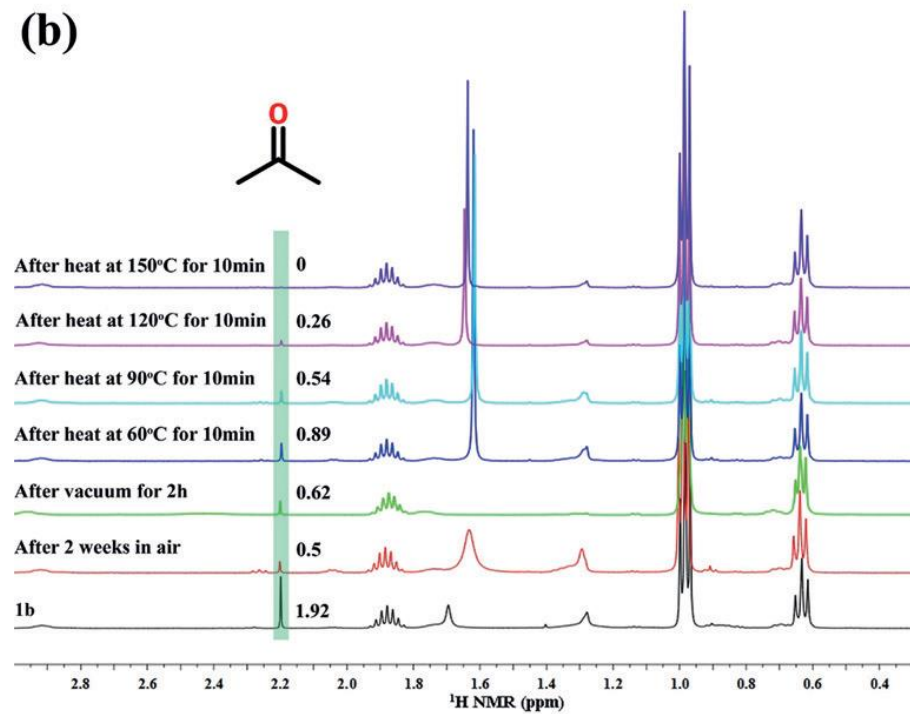
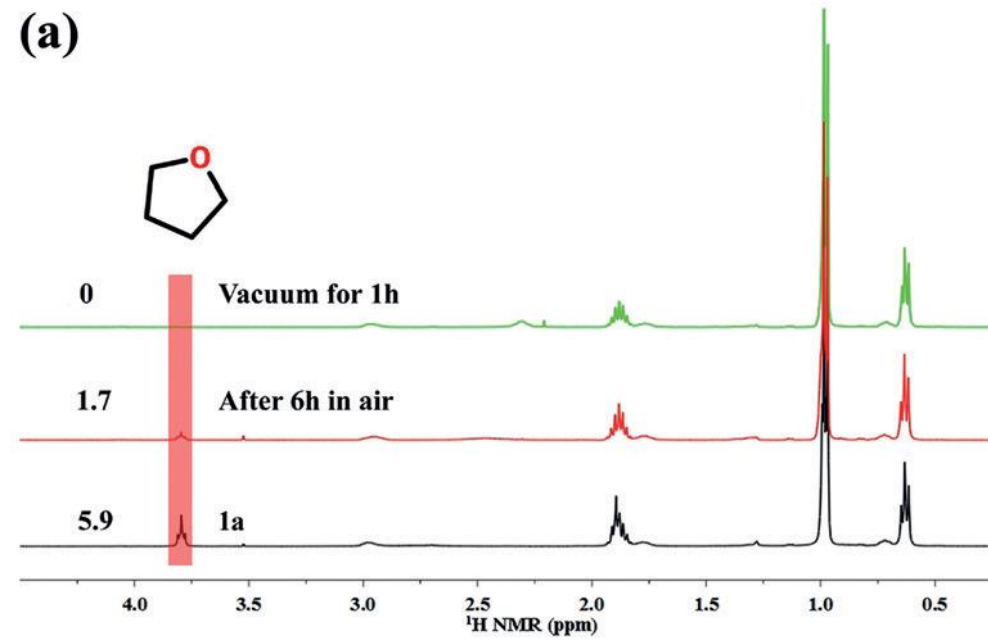
Acetone
THF



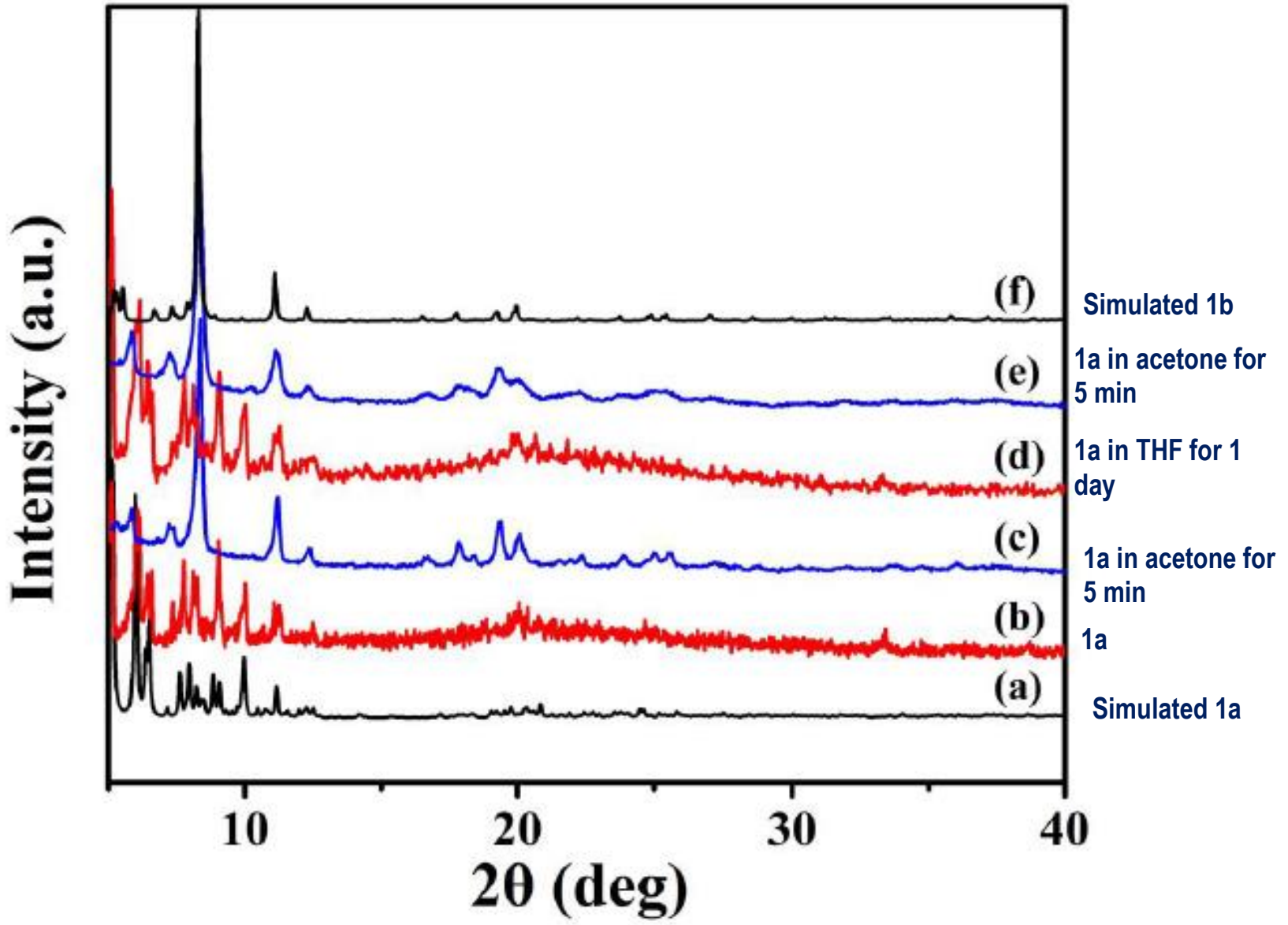
Results and discussion:



Results and discussion:



Results and discussion:



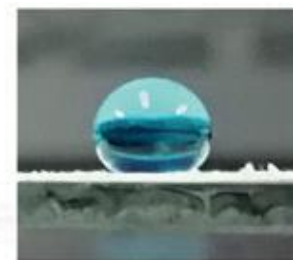
Results and discussion:

THF

Acetone

(a)

(b)



129.966°

141.447°



Conclusion:

- A novel atom-precise multiple-heterocluster based dendrimer $\text{Ag}_{12}@\text{POSS}_6$ has been designed and synthesized.
- Stimulated by different solvents (acetone or THF) enables the complex to undergo an interesting reversible central silver(I) cluster core transformation that leads to full structural change of the dendrimers.
- The shell POSS clusters arrangement variation also induces the hydrophobicity change of the complex in PMMA matrix, which firstly proposes a new way to control the hydrophobicity of silver(I)@POSS complex by regulation of coordination solvent.
- Complex 1a or 1b not only forms a new family of atom precise silver(I)@POSS complex, but also unveils a new approach to synthesize smart silver(I) clusters by shell ligand protection.



Thank you!