Chemical Science

Carboxylic acid stimulated silver shell isomerism in a triple core–shell Ag_{84} nanocluster†

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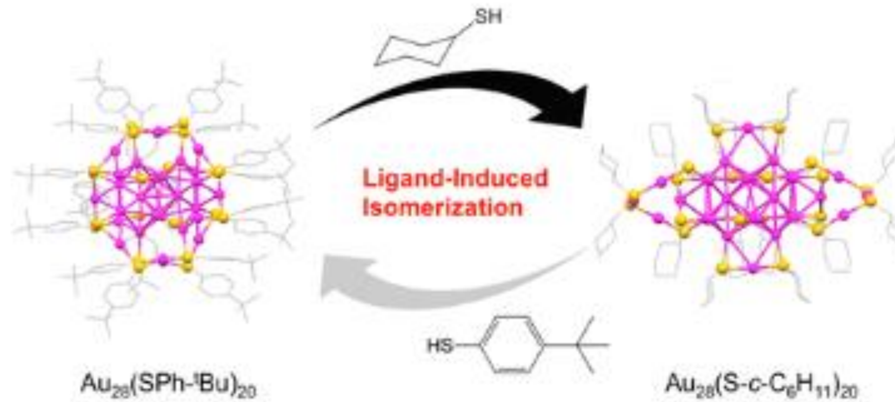
❖ Isomerism nanoclusters in the past……

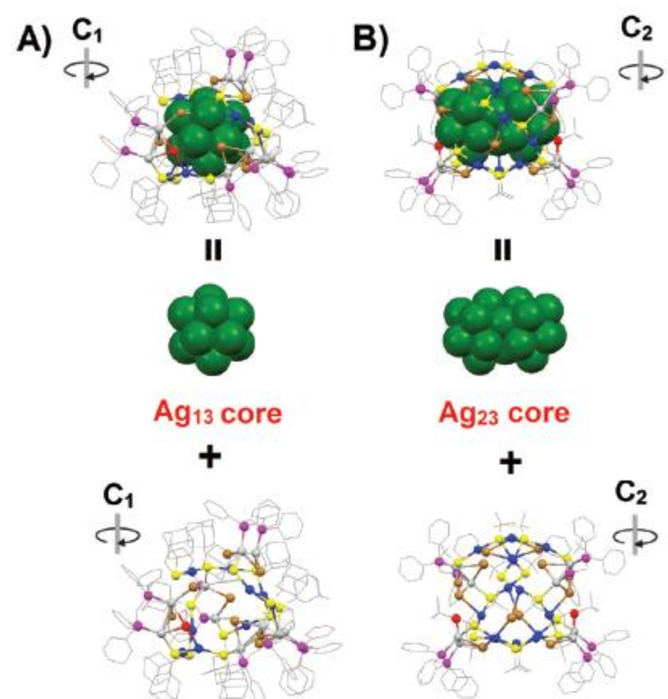
Compounds with the same atoms arranged in different manners, may deliver substantially different physicochemical properties and chemical reactivities without changing their compositions.

Ligand induced Core isomerism



Nanocluster

Anion packing induced isomerism

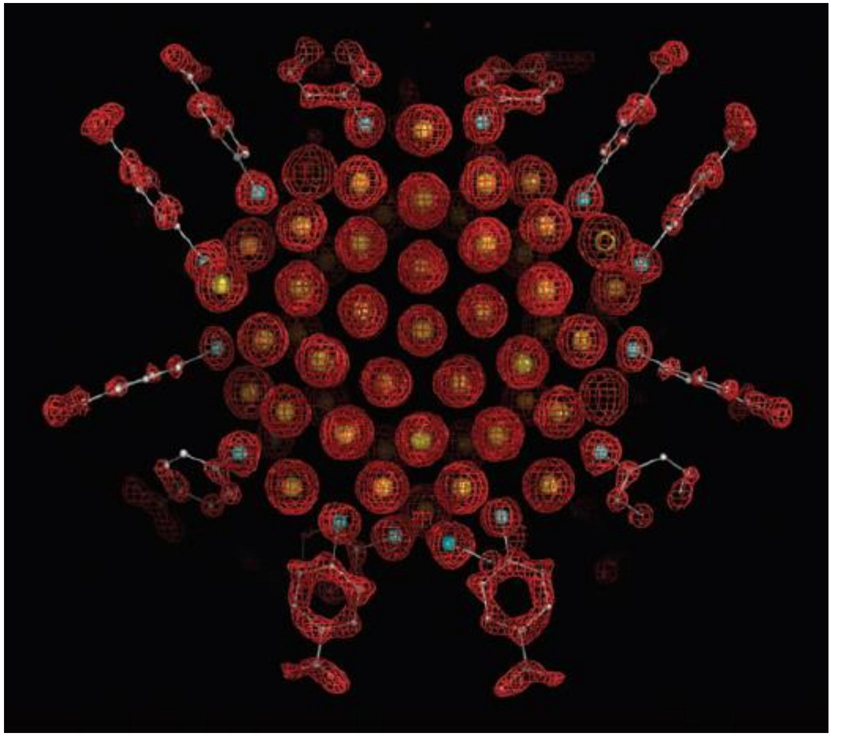


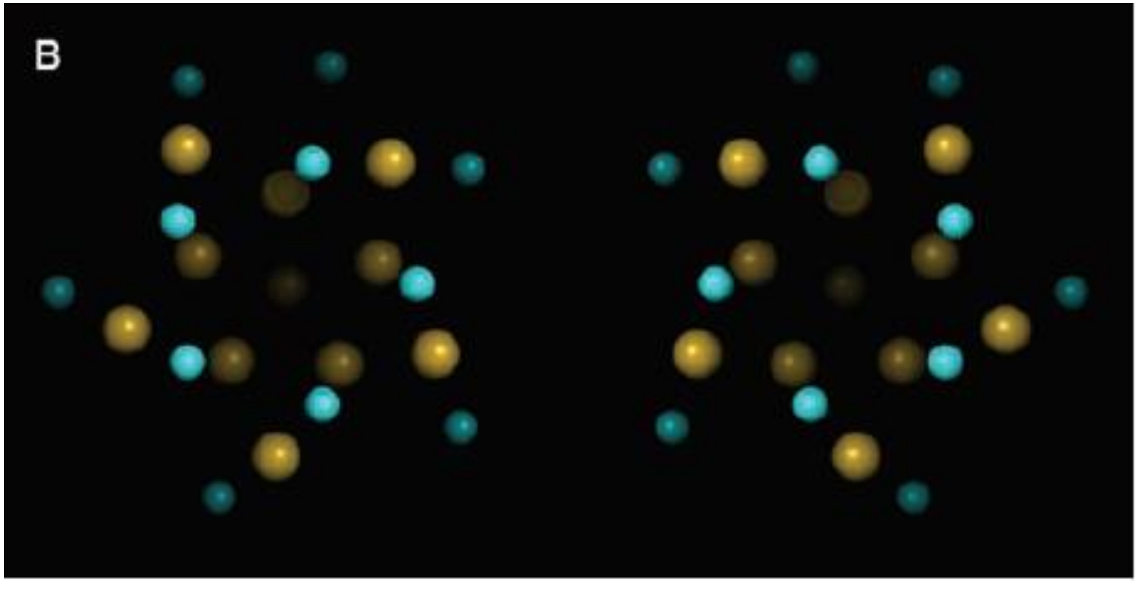
❖ **References :**

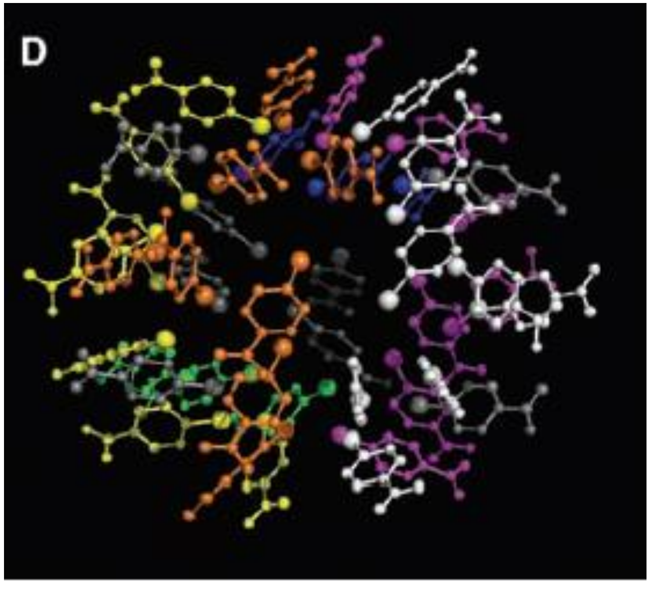
1) J. Am. Chem. Soc. 2016, 138, 1482−1485

2) Nanoscale, 2017, 9, 16800–16805

[$Au_{102}(pMBA)_{44}$]nanocluster : Science 2007

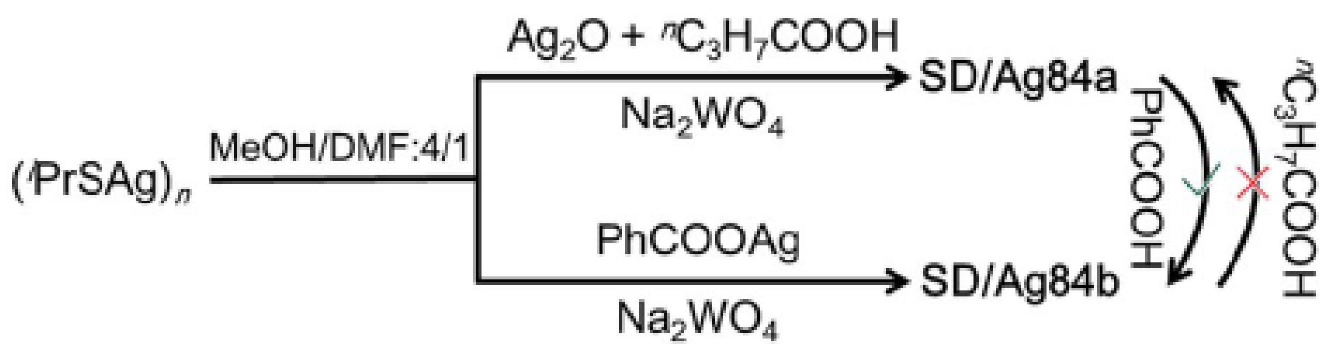




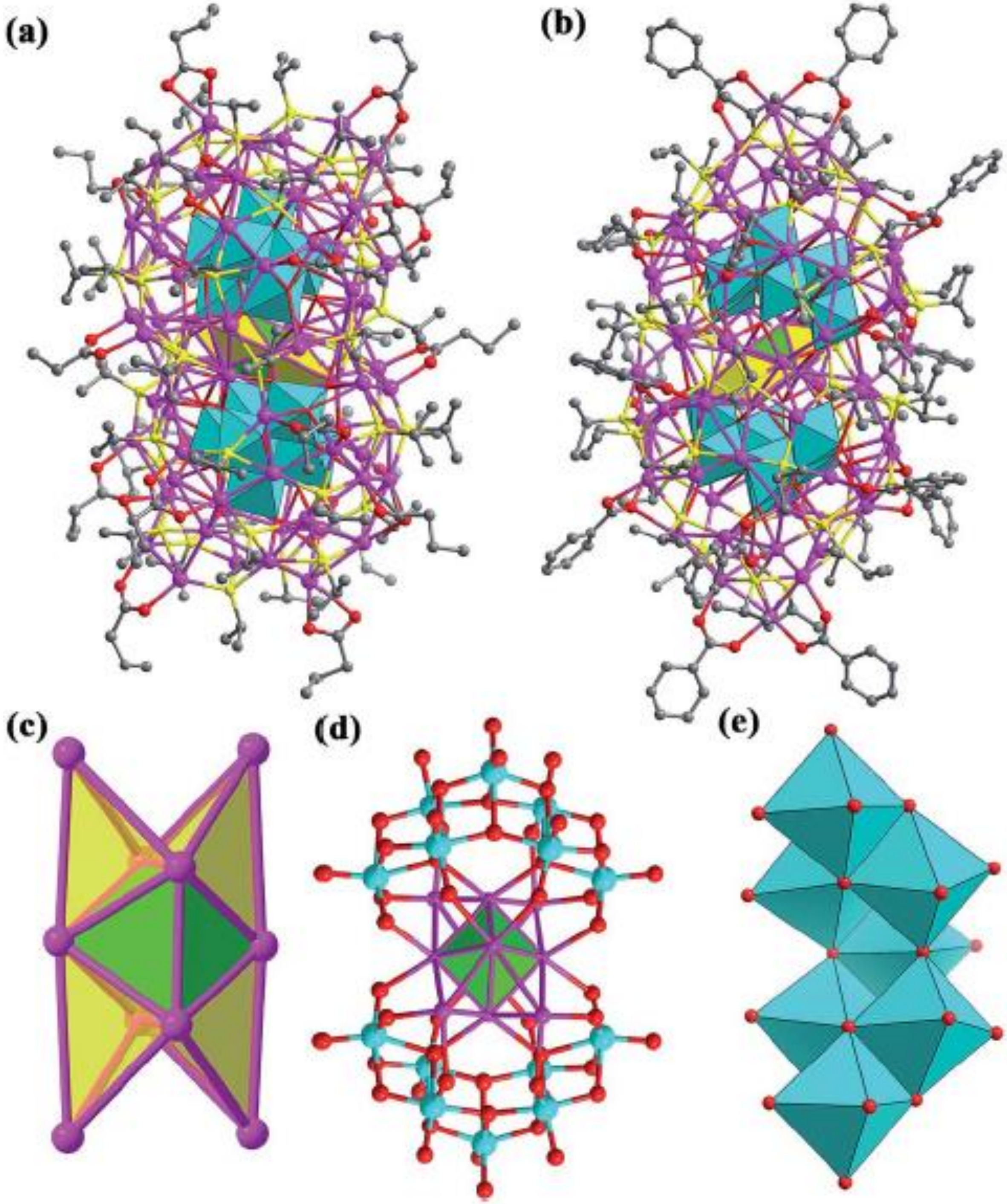


INTRODUCTION :

- Two different silver nanocluster SD/Ag84A and SD/Ag84B were synthesized by hydrothermal synthesis.
- Their impressive structures comprise a Ag10 nanocluster core, a pair of novel crescent-shaped W_7O_{26} shells and a 74-silver outer shell, thus establishing a novel common rugby-ball shaped three–shell [Ag10@(W7O26)2@Ag74] motif that differs in skeletal organization and ligand coverage at the two poles.
- Their flat headed and cuspidal prolate spherical structures, respectively are likely driven by the different steric hindrances between nPrCOO and PhCOO. Although the organic shells are different these two Ag_{84} nanocluster have identical elemental contents and hence they belongs to pseudo-isomers.



Scheme 1 Schematic representation of the assembly and conversion of SD/Ag84a and SD/Ag84b.



$[Ag_{10}@(W_7O_{26})_2@Ag_{74}S_2({}_{i}PrS)_{40}({}_{n}PrCOO)_{18}]\$2CH_3OH$

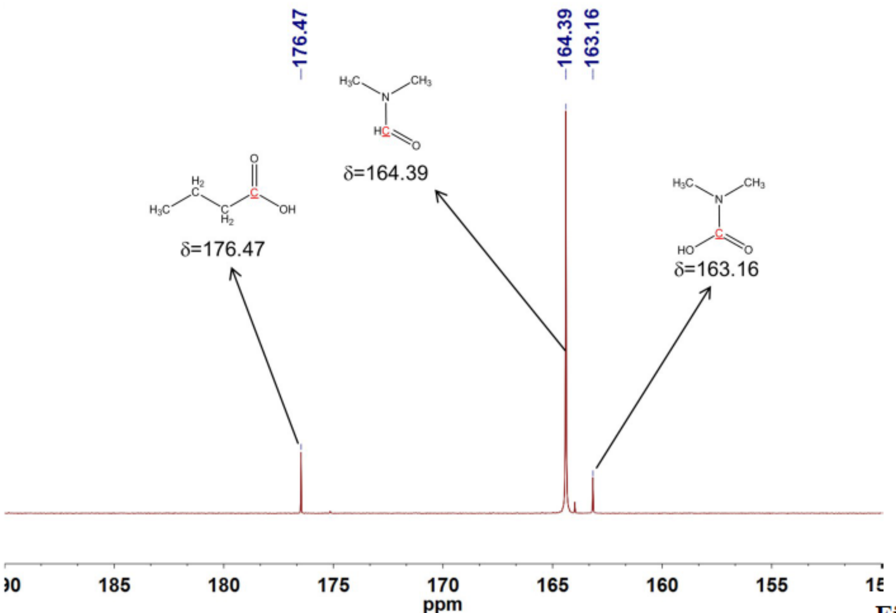
(SD/Ag84a)

$[Ag_{10}@(W_7O_{26})_2@Ag_{74}S_2({}_{i}PrS)_{40}(PhCOO)_{18}]$

(SD/Ag84b)

Fig. 1 Structures of the clusters SD/Ag84a (a) and SD/Ag84b (b). (c) The polyhedral mode showing an Ag_6 octahedron (green) capped by four additional silver tetrahedra (yellow) to form the Ag_{10} kernel; (d) two $(W_7O_{26})_{10}$ anions wrapping an Ag_{10} kernel and (e) polyhedral mode showing the structure of a $(W_7O_{26})_{10}$ anion. Color labels: purple, Ag; cyan, W; yellow, S; gray, C; and red, O.

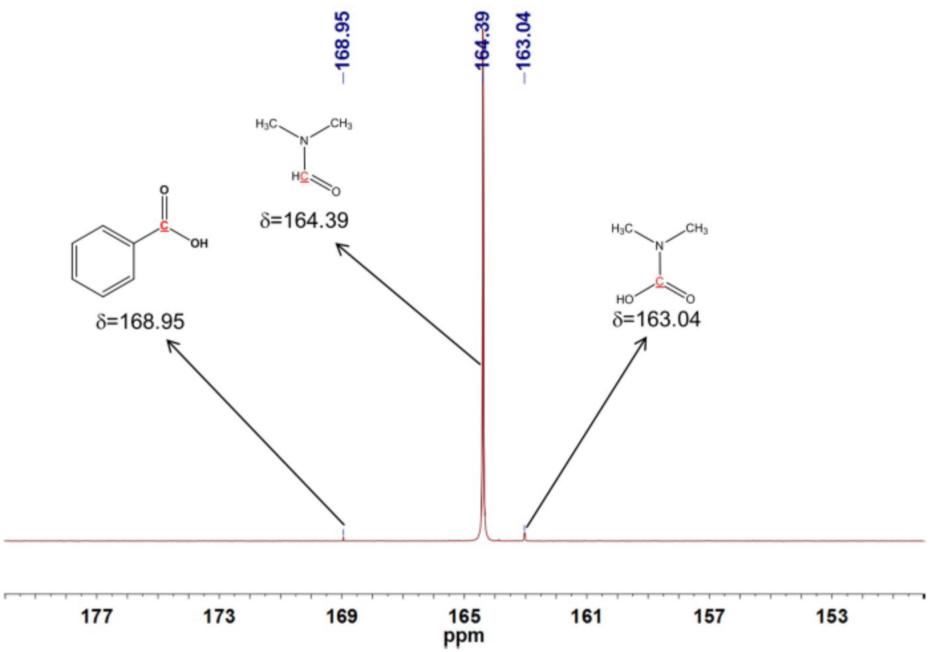
Figure S3: ^{13}C NMR of HCl digested reaction mother solution for SD/Ag84a.



$[Ag_{10}@(W_7O_{26})_2@Ag_{74}S_2(_iPrS)_{40}(_nPrCOO)_{18}]\$2CH_3OH$

(SD/Ag84a)

Figure S4: ^{13}C NMR of HCl digested reaction mother solution for SD/Ag84b.



$[Ag_{10}@(W_7O_{26})_2@Ag_{74}S_2(_iPrS)_{40}(PhCOO)_{18}]$

(SD/Ag84b)

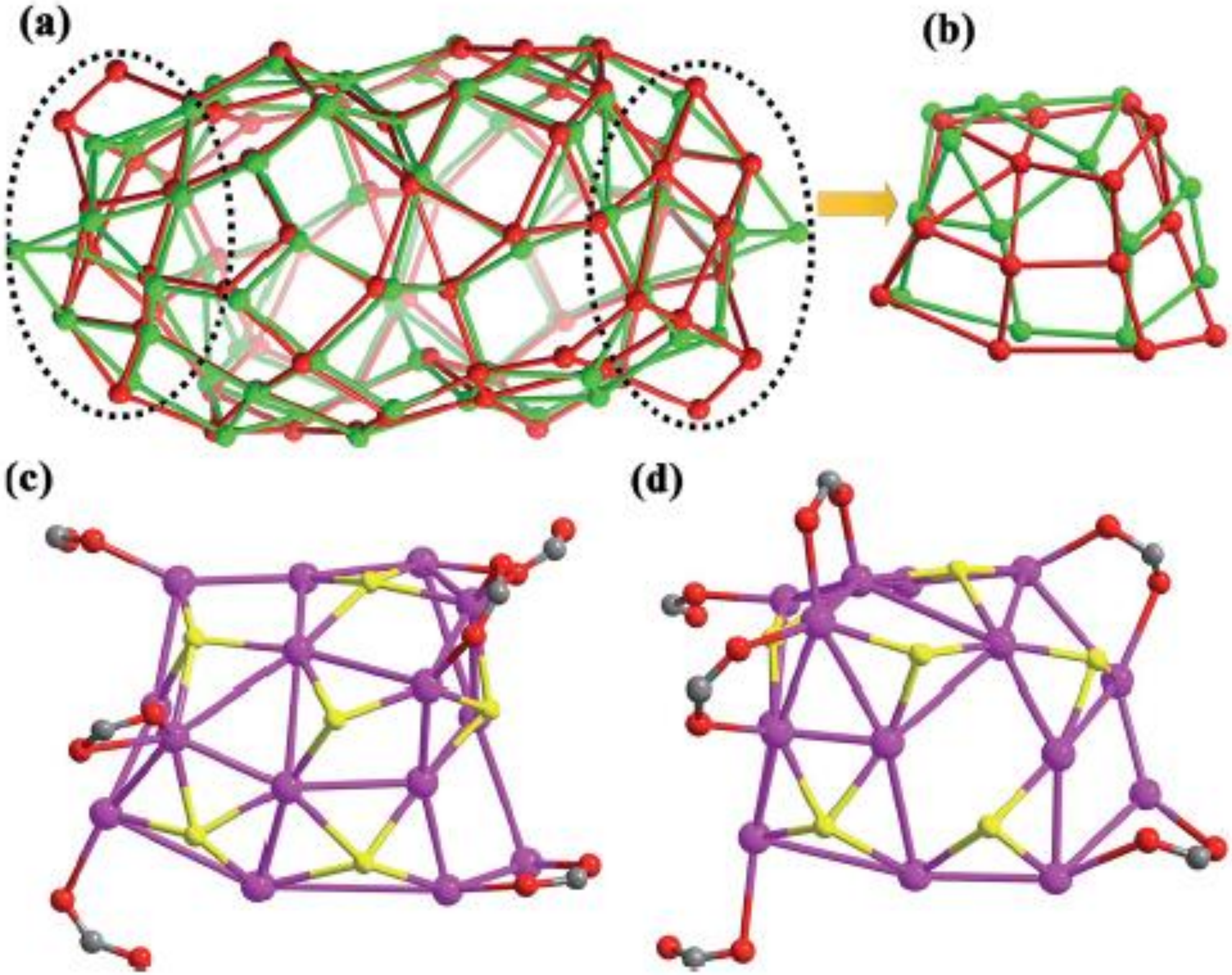
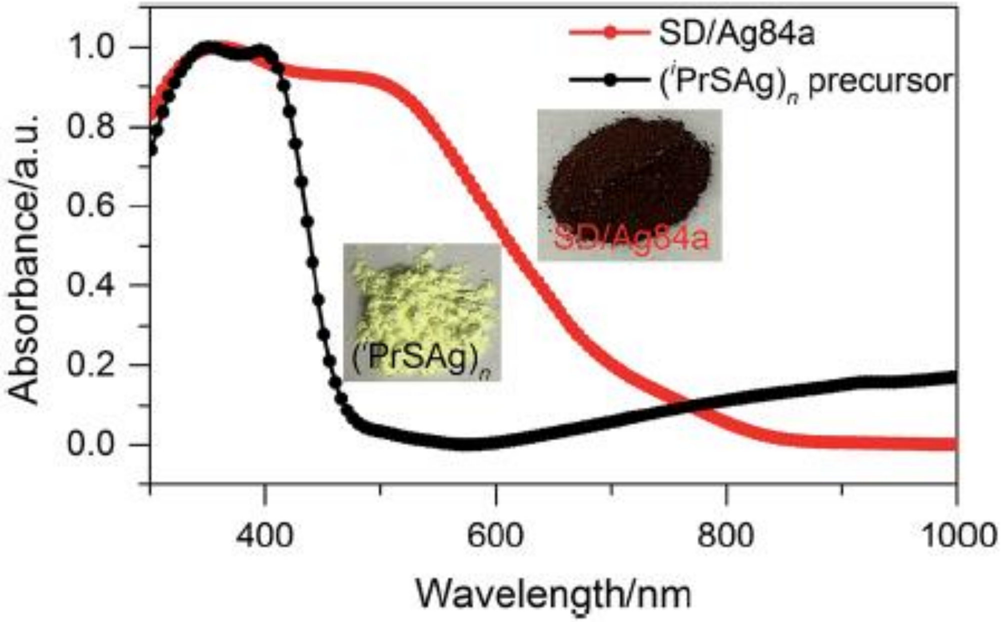
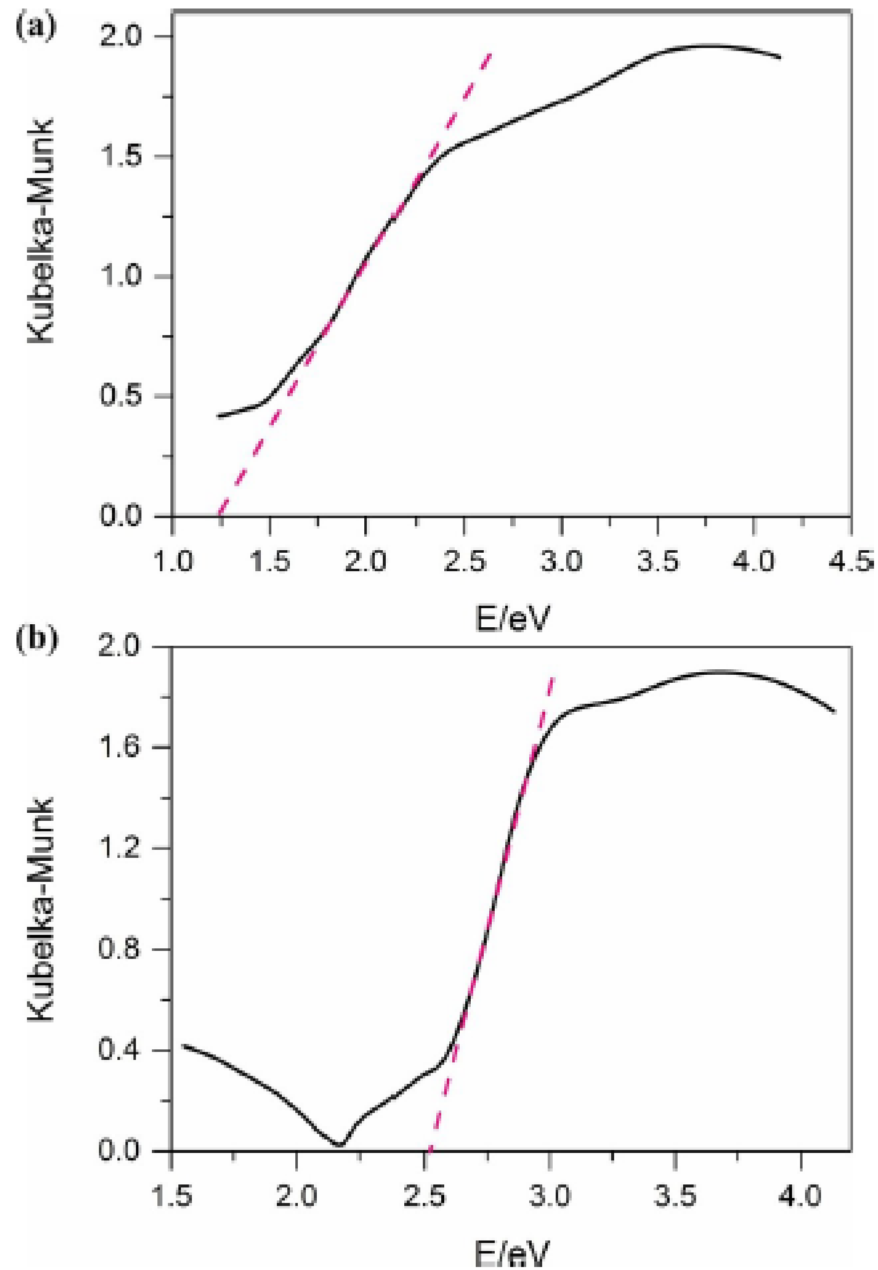
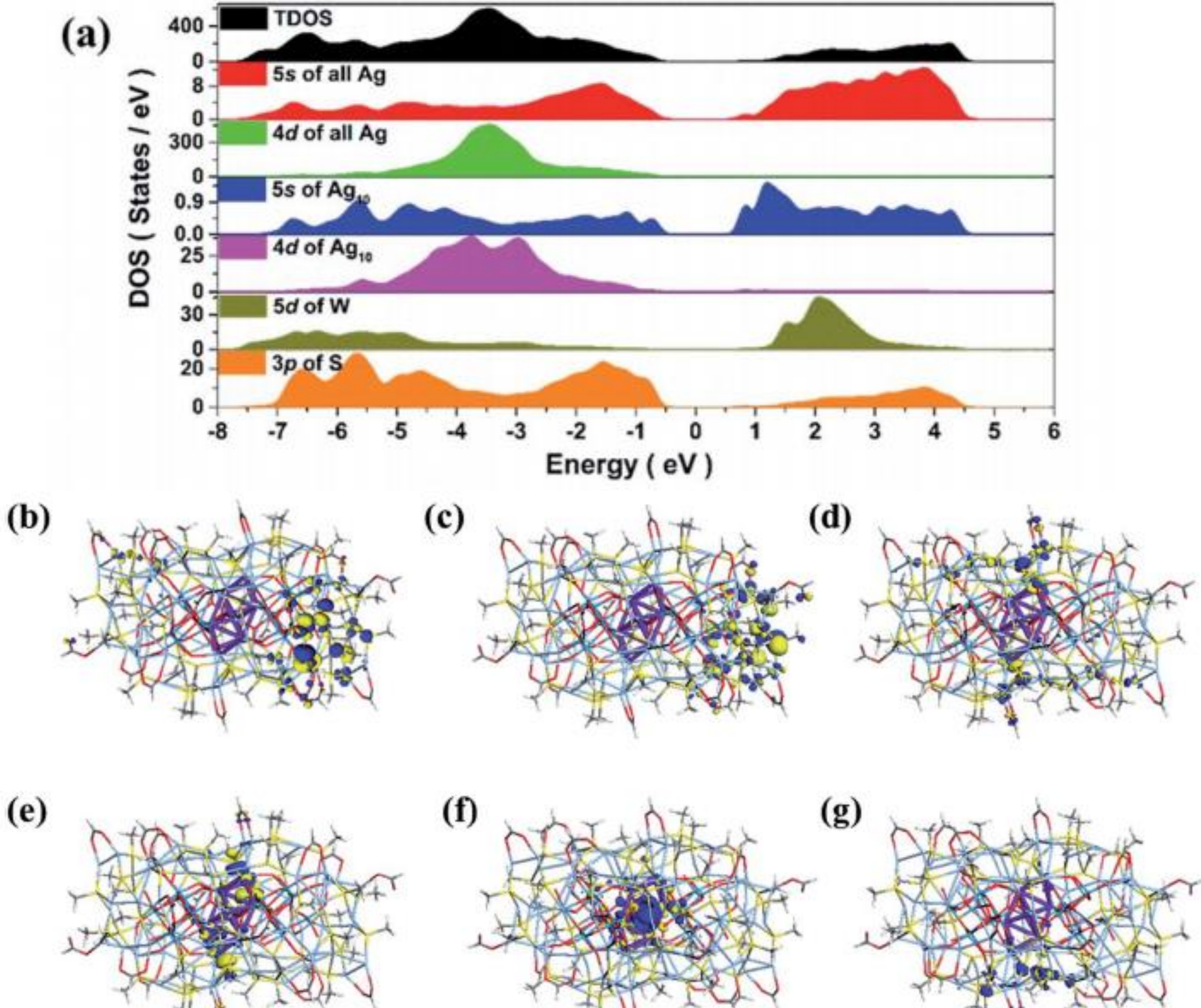


Fig. 2 (a) The superposed Ag74 shells of SD/Ag84a (red) and SD/Ag84b (green). (b) The top views of silver polygons at the pole regions of SD/Ag84a (red) and SD/Ag84b (green). The top views of ligand distributions at the pole region of SD/Ag84a (c) and SD/Ag84b (d).

UV Visible absorption spectra for the nanocluster :






(a)
TDOS
5s of all Ag
4d of all Ag
5s of Ag10
4d of Ag10
5d of W
3p of S
DOS (States / eV)
Energy (eV)
(b)
(c)
(d)
(e)
(f)
(g)

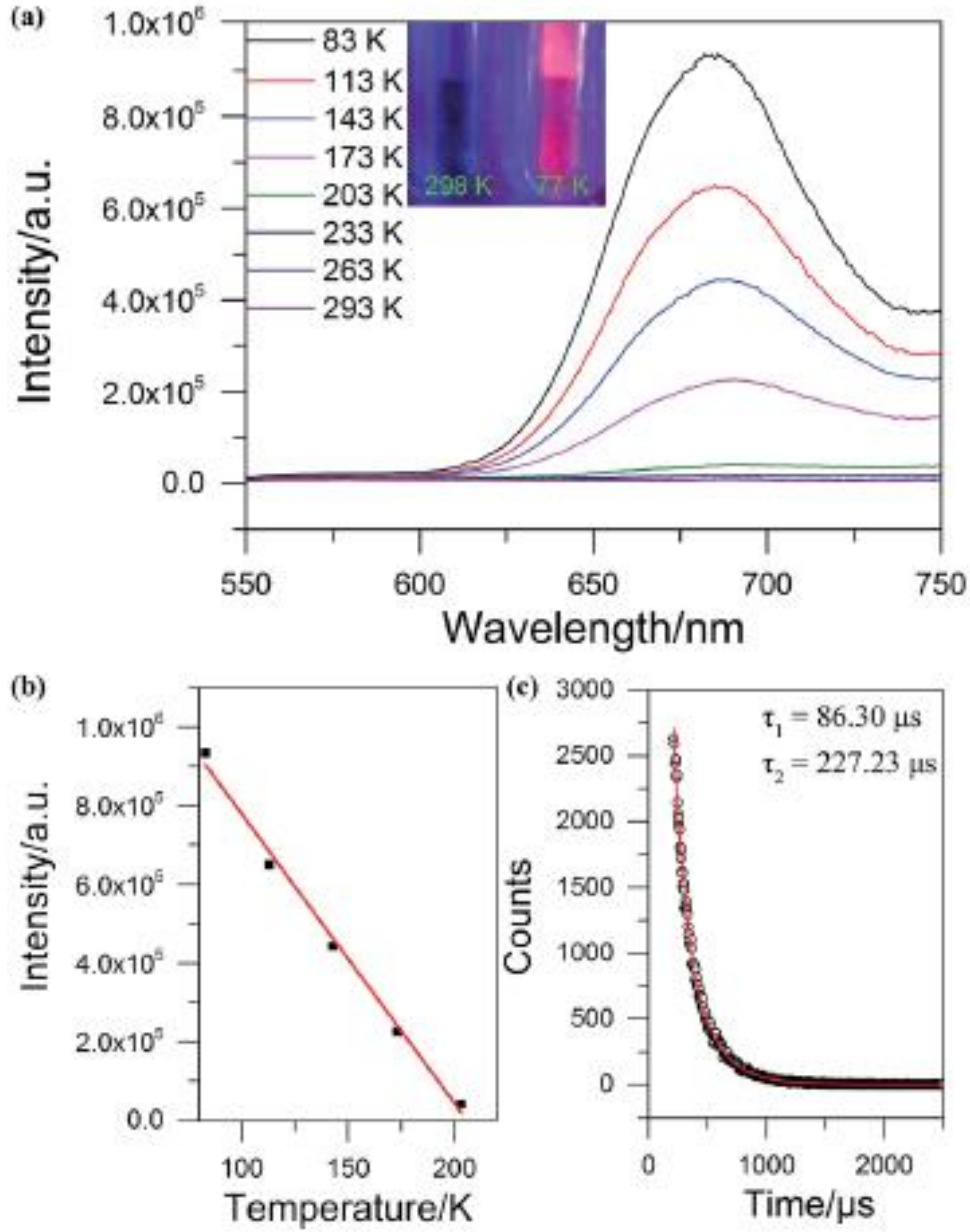


Fig. 5 (a) The temperature-dependent emission spectra of SD/Ag84a under 468 nm excitation. Insets: the photographs of SD/Ag84a irradiated with 365 nm UV light at 298 and 77 K. (b) The plot of temperature vs. maximum emission intensity (red line is the linear fitting in the range of 83–203 K). (c) Luminescence lifetime of SD/Ag84a recorded at 83 K (red line is the fitting curve).

Conclusion :

- Successful synthesis of isomeric Ag_{84} nanocluster for the first time by the combination of anion template and hard-soft ligand strategies.
- The comparative structural analysis indicated that the isomerism mainly occurred on the polar regions of the prolate spheres.
- The differences are found in both the silver skeleton and iPrS/RCOO ligand distribution. The driving force for such an isomerism is dominated by the steric hindrance of carboxylates.
- Ag_{10} core was formed by fcc face sharing of silver atom with the Ag_6 unit.

THANK YOU