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[Pt₁Ag₃₇(SAdm)₂₁(Dppp)₃Cl₆]²⁺: intercluster transformation and photochemical properties†

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Ligand-exchange-induced structure transformation has been exploited as an effective approach to dictate the size and structure of nanoparticles with atomic precision. However, phosphine ligand induced intercluster transformation remains rarely explored. Herein, we report the controllable preparation and the structural elucidation of a [Pt₁Ag₃₇(SAdm)₂₁(Dppp)₃Cl₆]²⁺ nanocluster (Pt₁Ag₃₇; where Dppp is 1,3-bis(diphenylphosphino)propane and HSAdm is 1-adamantanethiol). Notably, the reaction of Pt₁Ag₃₇ with PPh₃ triggers an intercluster transformation, giving rise to a stable and smaller-sized nanocluster, [Pt₁Ag₂₈(SAdm)₁₈(PPh₃)₄]²⁺ (Pt₁Ag₂₈). Such an intercluster transformation is systematically monitored with ESI-MS and UV-vis. The photochemical properties of Pt₁Ag₃₇ and Pt₁Ag₂₈ nanoclusters are further investigated. Of note, in the presence of chiral Bdpd diphosphines (Bdpd = 2,4-bis-(diphenylphosphino)pentane), the enantiomeric Pt₁Ag₃₇(SAdm)₂₁(R/S-Bdpd)₃Cl₆ (R/S-Pt₁Ag₃₇) are obtained, and such chiral nanoclusters displayed obvious optical activity. The results in this work hopefully shed light on the future preparation of metal nanoclusters for customized applications.

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1 Introduction

Atomically precise metal nanoclusters are a class of molecular-like nanomaterials, which can be precisely manipulated with adjustable physicochemical properties at the atomic level.^{1–11} Such nanoclusters have rich opportunities in both fundamental studies (*e.g.*, structure-dependent properties) and promising applications (*e.g.*, medicine, sensing, catalysis and energy).^{7,12–15} Several efficient synthesis methods have been proposed to controllably prepare nanoclusters with molecular purity, including size focusing, ligand exchange, and intermolecular assembly.^{16–21} Among them, the ligand exchange induced structure transformation (LEIST) is a highly versatile strategy for correlating the surface motifs/organic–metal interface with the reactivity of nanoclusters.^{21–29} In the past decade, the LEIST of thiolated gold nanoclusters has been widely

studied.^{30–33} Jin *et al.* reported transformation of rod-like bicosahedral Au₃₈(SCH₂CH₂Ph)₂₄ to a tetrahedral Au₃₆(TBBT)₂₄ nanocluster.³⁴ The transformation from Au₂₃(SCy)₁₆ to Au₃₆(TBBT)₂₄ *via* Au₂₈(TBBT)₂₀ that activated by the presence of bulky 4-*tert*-butylbenzenethiol ligands was demonstrated by the Mandal group.³⁵ In addition, the transformations of alkynyl-protected gold nanoclusters have also been achieved. The Zang group reported the size conversion of a carbora-alkynyl-protected gold nanocluster Au₂₈ into a stable and smaller-sized nanocluster Au₂₃.³⁶ Indeed, the ligand exchange can be partial or complete, with or without altering the metallic kernel.

Nowadays, increasing interest is focused on the alloy nanoclusters with synergistic effect due to their potential for fundamental research.^{8,37–39} With respect to silver-rich alloy nanoclusters, especially, for doping Pt heteroatoms into Ag nanoclusters that gives rise to Pt@Ag alloy nanoclusters, several research efforts have been made for investigating the structure–property correlations at the atomic level. Despite this, a limited number of Pt doping silver-rich nanoclusters were reported, including Pt₁Ag₂₄(SPhMe₂)₁₈⁴⁰ protected by thiolates, Pt₁Ag₁₄(SR)₆(PPh₃)₈,⁴¹ Pt₁Ag₂₄(SR)₁₆(PPh₃)₃,⁴² Pt₁Ag₂₆(2-EBT)₁₈(PPh₃)₆,¹⁸ Pt₁Ag₂₈(S-Adm)₁₈(PPh₃)₄ (Pt₁Ag₂₈ for short),⁴³ Pt₁Ag₃₁(SR)₁₆(DPPM)₃Cl₃⁴⁴ coprotected by thiolates and phosphine ligands, Pt₅Ag₂₂(C≡CPh)₃₂,⁴⁵ Pt₁Ag₄₂(C≡CPhMe)₂₈,⁴⁶ stabilized by alkynyl, and so on. Among these nanoclusters, much effort has been devoted to the one-pot synthesis, such as Pt₁Ag₂₄(SPhMe₂)₁₈, Pt₁Ag₂₄(SR)₁₆(PPh₃)₃, Pt₁Ag₂₆(2-

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EBT)₁₈(PPh₃)₆, Pt₅Ag₂₂(C≡CPh)₃₂, and Pt₁Ag₄₂(C≡CPhMe)₂₈. Meanwhile, the ligand exchange strategy is a versatile approach to achieve Pt@Ag alloy nanoclusters with novel structures and distinct properties. For example, Pt₁Ag₂₈ was prepared by etching Pt₁Ag₂₄(SPhMe₂)₁₈ with both the HS-Adm and PPh₃ ligands⁴⁰ and when the Pt₁Ag₂₈ was reacted with Ag₂(Dppm)Cl₂, Pt₁Ag₃₁ was generated.⁴⁴ The fabrication of more Pt@Ag alloy nanoclusters is of great significance for further investigating the structure–property correlations in detail, rendering the future preparation of metal nanoclusters or cluster-based nanomaterials with customized structures and properties.

Herein, we report the synthesis of a [Pt₁Ag₃₇(SAdm)₂₁(Dppp)₃Cl₆]²⁺ (denoted as Pt₁Ag₃₇) nanocluster co-protected by 1,3-bis(diphenylphosphino)propane (Dppp) and 1-adamantanethiol (HS-Adm) ligands. The phosphine ligand-exchange-induced structure transformation of Pt₁Ag₃₇ to [Pt₁Ag₂₈(SAdm)₁₈(PPh₃)₄]²⁺ (denoted as Pt₁Ag₂₈) nanocluster was fulfilled in the presence of PPh₃. The intercluster conversion was monitored by ESI-MS and UV-vis absorption spectra. Furthermore, both Pt₁Ag₃₇ and Pt₁Ag₂₈ nanoclusters were emissive. Compared to Pt₁Ag₃₇, the photoluminescence (PL) lifetime of Pt₁Ag₂₈ was largely increased from 17.53 ns to 3.97 μs,⁴⁷ which might be attributed to different PL mechanism induced by different electronic structure in Pt₁Ag₃₇ and Pt₁Ag₂₈, respectively.⁴⁸ Additionally, chiral *R/S*-Pt₁Ag₃₇ nanoclusters were obtained *via* substituting achiral Dppp with homologous *R/S*-Bdpp ligands, which showed exciting CD activity and CPL response.

2 Experimental Methods

Chemicals

Hexachloroplatinic(IV) acid (H₂PtCl₆·6H₂O, 99.99%, metals basis), silver nitrate (AgNO₃, 99%, metals basis), 1-adamantanethiol (AdmSH, C₁₀H₁₆S, 99%), 1,3-bis(diphenylphosphino)propane (Dppp, 98%), triphenylphosphine (PPh₃, 99%), (2*S*,4*S*)-(–)-2,4-bis(diphenylphosphino)pentane ((2*S*,4*S*-Bdpp, purity 99%), (2*R*,4*R*)-(+)-2,4-bis(diphenylphosphino)pentane (2*R*,4*R*-Bdpp, purity 99%), tetraphenylboron sodium (NaBPh₄, 98%), and sodium borohydride (NaBH₄, 99.9%). Methylene chloride (CH₂Cl₂, HPLC), methanol (CH₃OH, HPLC), acetonitrile (CH₃CN, HPLC) and *n*-hexane (Hex, HPLC grade).

Synthesis of the [Pt₁Ag₃₇(Dppp)₃(SAdm)₂₁Cl₆]²⁺ nanocluster

AgNO₃ (60 mg, 0.36 mmol) was dissolved in 10 mL of CH₃OH and 2 mL CH₃CN under vigorous stirring. After 5 min, 1,3-bis(diphenylphosphino)propane (Dppp, 20 mg, 0.048 mmol) and 1-adamantane mercaptan (AdmSH, 30 mg, 0.178 mmol) were added. H₂PtCl₆·6H₂O (4 mg, 0.0075 mmol) was dissolved in 5 mL of CH₃OH and added to the reaction mixture. After half an hour, a freshly prepared sodium borohydride (NaBH₄, 20 mg, 0.14 mmol) was added to methanol solution of 50 μL of NEt₃. The solution changed from white to dark brown. This reaction lasted for 5 h at room temperature. The crude product was obtained by rotary evaporation and centrifugation 3 min

at 11 000 rpm. The precipitate was washed with excess *n*-hexane and collected by centrifugation again. The crystals were crystallized from CH₂Cl₂/hexane at room temperature and afford red block crystals after 7 days. The yield was calculated as 14.6% based on the Pt element for Pt₁Ag₃₇.

Transformation from [Pt₁Ag₃₇(SAdm)₂₁(Dppp)₃Cl₆]²⁺ to [Pt₁Ag₂₈(SAdm)₁₈(PPh₃)₄]²⁺

5 mg of [Pt₁Ag₃₇(SAdm)₂₁(Dppp)₃Cl₆]²⁺ (0.5 μmol) was dissolved in 15 mL of CH₂Cl₂, to which solution the PPh₃ ligand (5.2 mg, 20 μmol) was added. The reaction was allowed to proceed for 360 min at room temperature. Time-dependent UV-vis and ESI-MS spectra were monitored.

Synthesis of the chiral Pt₁Ag₃₇(SAdm)₂₁(*R/S*-Bdpp)₃Cl₆ nanocluster

Chiral Pt₁Ag₃₇ (SAdm)₂₁(*R/S*-Bdpp)₃Cl₆ nanocluster was obtained referring to the preparation of Pt₁Ag₃₇(SAdm)₂₁(Dppp)₃Cl₆, using 18 mg (2*S*,4*S*-Bdpp)/(2*R*,4*R*-Bdpp) in place of 20 mg of Dppp. All the other experimental conditions were kept unchanged.

Fitting of dynamic curves

All the dynamic curves in this study were fitted with the exponential decay function:

$$y = Ae^{(-x)/\tau} + y_0,$$

where x is the reaction time and y is variation of the absorbance at 408 nm of Pt₁Ag₃₇, the ratio of C_0 and C_t (the concentration of Pt₁Ag₃₇ at time 0 min and t min) was determined by the relative absorbance at time 0 min (A_0) and time t min (A_t). τ is the lifetime of the curve and $\tau \ln 2$ is the half-life ($T_{1/2}$).

DFT calculations

The structures of PtAg nanocluster is fully optimized by using density functional theory (DFT) method at B3LYP/def2SVP^{49,50} level of theory with Grimme D3 corrections⁵¹ and verified to be true minima by frequency check. The cubane groups in the ligands of synthesized cluster are replaced by CH₃ groups in order to reduce the computational cost. UV absorption simulations are performed at the same level by time-dependent density functional theory (TD-DFT)^{52,53} method. All calculations are carried out in Gaussian 16⁵⁴ and Multiwfn⁵⁵ package, and the Kohn–Sham orbitals are visualized in the Chemcraft program.⁵⁶

Characterization

All UV-vis spectra of the nanoclusters were recorded using an Agilent 8453, and the samples were dissolved in CH₂Cl₂ whose background correction was made using a CH₂Cl₂ blank. Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (DTG-60H, Shimadzu Instruments, Inc.) with 5 mg of the nanocluster in a SiO₂ pan at a heating rate of 10 K min^{−1} from 323 to 1073 K. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo ESCALAB 250 configured with a monochromated Al

$K\alpha$ (1486.8 eV) 150 W X-ray source, 0.5 mm circular spot size, a flood gun to counter charging effects, and an analysis chamber base pressure lower than 1×10^{-9} mbar, and the data were collected with FAT of 20 eV. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) measurements were performed on a MicrOTOF-QIII high-resolution mass spectrometer. Photoluminescence spectra were measured using a HORIBA FluoroMax+ spectrofluorometer with the same optical density (OD) of ~ 0.05 . Absolute quantum yields were measured with dilute solutions of nanoclusters (0.05 OD absorption at 410 nm) on a HORIBA FluoroMax+. Transmission electron microscopy (TEM) was conducted on a JEM-2100 microscope with an accelerating voltage of 200 kV. Data collection for single crystal X-ray diffraction was carried out using a Stoe Stadivari diffractometer under a liquid nitrogen flow at 170 K, using graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54186 \text{ \AA}$). Data reductions and absorption corrections were performed using SAINT and SADABS programs, respectively. CD spectra were recorded with a BioLogic MOS-500 CD spectropolarimeter in a 0.1 cm path length quartz cell. The spectra were recorded in diluted solutions of dichloromethane and the signal of the blank solvent was subtracted. PL intensity and polarization spectra were measured on a JASCO CPL-300 circularly polarized luminescence spectrophotometer.

3 Results and discussion

Synthesis and characterization of Pt_1Ag_{37} nanocluster

The Pt_1Ag_{37} nanocluster was synthesized *via* a one-pot procedure. Red block crystals were obtained after the cultivation in DCM/Hex for seven days (Fig. S1a†). TEM image showed that the Pt_1Ag_{37} was uniform with an average size of 1.69 nm (Fig. S1b†). The UV-vis spectra of Pt_1Ag_{37} in CH_2Cl_2 displayed two strong peaks centered at 408 nm and 475 nm, and two weak shoulder peaks at 327 and 435 nm, in good agreement with the time-dependent density functional theory (TDDFT) calculated spectrum (Fig. 1a). Based on computed excitation energies and Kohn-Sham (KS) orbitals, we further assigned the orbital transition modes of four distinct absorption peaks which were shown in Fig. S2.† To verify the formula of Pt_1Ag_{37} , the electrospray ionization mass spectrometry (ESI-MS) was performed that showed an intense peak at m/z of 4574.8 Da, corresponding to the characteristic peak of $[Pt_1Ag_{37}(SAdm)_{21}(Dppp)_3Cl_6]^{2+}$ (Fig. 1b), with a weak peak at 3891.16 Da corresponding to the $[Pt_1Ag_{32}(SAdm)_{16}(Dppp)_2Cl_6(CH_2Cl_2)_4(CH_3CN)_2]^{2+}$, with a loss of Ag_5S_5 motif and one Dppp ligand of Pt_1Ag_{37} . The experimental isotopic distributions matched perfectly with the simulation model. The free electron count of Pt_1Ag_{37} was calculated as $8e$ (*i.e.*, 37 (Ag)- 21 (SR)- 6 (Cl)- 2 (charge) = $8e$), the same as that of the reported $Pt_1Ag_{24}(SR)_{16}(PPh_3)_3$,⁴² $Pt_1Ag_{26}(2\text{-EBT})_{18}(PPh_3)_6$,¹⁸ and $Pt_1Ag_{28}(SAdm)_{18}(PPh_3)_4$ ⁴³ nanoclusters. The X-ray photoelectron spectroscopy (XPS) result revealed the presence of Pt, Ag, P, Cl, C and S in the nanocluster (Fig. 1c). An expanded view of the Pt 4f spectrum showed two peaks centered at 71.08

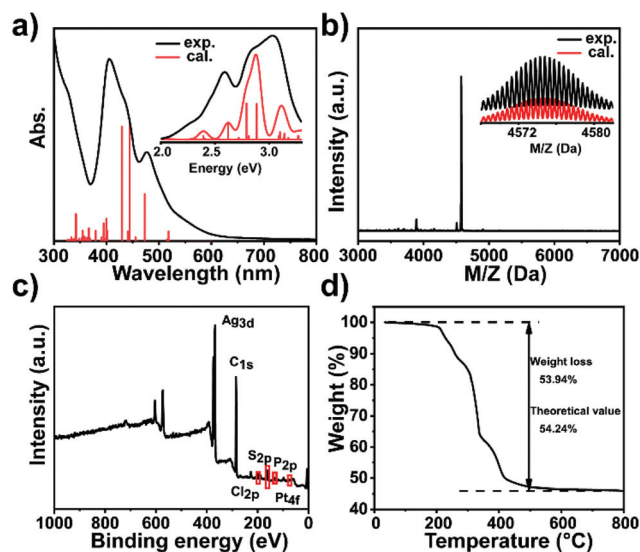


Fig. 1 (a) Experimental UV-vis spectrum of Pt_1Ag_{37} (black) and its excitation energies calculated by TD-DFT (red). Inset: The corresponding UV-vis data on the energy scale; the red curve was constructed *via* Lorentzian broadening of 0.1 eV. (b) ESI-MS result in a positive mode. (c) XPS, and (d) TGA results of Pt_1Ag_{37} .

eV and 74.41 eV, corresponding to characteristic peaks of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ for Pt^0 , respectively (Fig. S3†).^{57,58} Thermogravimetric analysis (TGA) was also performed with a total weight loss of 53.94 wt% (Fig. 1d), consistent with the theoretical loss of 54.24 wt%. The Pt_1Ag_{37} nanocluster exhibit good thermal stability, because no decomposition was observed when stored in CH_2Cl_2 for two days (Fig. S4†).

Atomic structure

The detailed structure of Pt_1Ag_{37} could be divided into two parts, including the metal kernel and the stabilizing shell. The icosahedral kernel, *i.e.*, Pt_1Ag_{12} , was stabilized by a shell including three $Ag_3(SR)_2Cl_2$ motifs connected *via* an Ag bridge, three $Ag_5(SR)_5$ motifs, and three Dppp motifs (Fig. 2). Besides, the whole $Ag@(Ag_3(SR)_2Cl_2-Ag_5(SR)_5-Dppp)_3$ shell with a C_3 symmetry was bound onto the icosahedral kernel (Fig. S5†). From the other side, the whole trefoil-like shell was constituted of three leaf-like units connected by one Ag atom. In Pt_1Ag_{37} , the bond lengths between the central Pt and the icosahedron-shell Ag atoms varied from 2.735 to 2.789 Å, with an average distance of 2.752 Å. The Ag-Ag bond lengths ranged from 2.805 to 2.956 Å (averagely, 2.895 Å). Additionally, the remaining six Cl atoms linked to six silver atoms, and the average bond length of Ag-Cl was 2.506 Å. The P atoms of phosphine ligands were also directly attached to Ag atoms with an average bond length of 2.407 Å (Fig. S6†).

Transformation from Pt_1Ag_{37} to Pt_1Ag_{28}

The reaction between Pt_1Ag_{37} with 40-equivalent of PPh_3 gave rise to the generation of a smaller reported nanocluster, $Pt_1Ag_{28}(S-Adm)_{18}(PPh_3)_4$,⁴³ fulfilling the ligand exchange

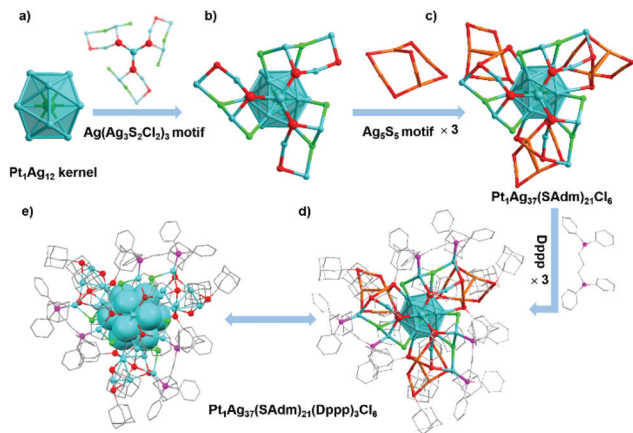


Fig. 2 (a) $\text{Pt}_1\text{Ag}_{12}$ kernel; (b) $\text{Pt}_1\text{Ag}_{12}@\text{Ag}(\text{Ag}_3\text{S}_2\text{Cl}_2)_3$ motifs; (c) $\text{Pt}_1\text{Ag}_{12}@\text{Ag}(\text{Ag}_3\text{S}_2\text{Cl}_2)_3@(\text{Ag}_5\text{S}_5)_3$ motifs. (d) The total structure of ball-stick and (e) the space-fill pattern of $\text{Pt}_1\text{Ag}_{37}$. Color labels: dark green, Pt; blue, orange, Ag; green, Cl; red, S; magenta, P; gray, C.

induced intercluster transformation. The intercluster transformation was monitored by UV-vis and ESI-MS. According to time-dependent UV-vis spectra (Fig. 3a), the peaks at 408 and 475 nm displayed the characteristic feature of $\text{Pt}_1\text{Ag}_{37}$ at 0 min. After 5 min, a new peak located at 440 nm corresponding to the $\text{Pt}_1\text{Ag}_{28}$ nanocluster appeared.⁴³ At $t = 10$ min to 300 min, the peaks at 408 and 475 nm attenuated gradually accompanied by the increase of the peak at 440 nm. After 6 hours, the peaks at 408 and 475 nm disappeared, demonstrating the complete intercluster transformation from $\text{Pt}_1\text{Ag}_{37}$ into $\text{Pt}_1\text{Ag}_{28}$. The DFT calculation results revealed a larger HOMO–LUMO energy gap for $\text{Pt}_1\text{Ag}_{37}$ relative to $\text{Pt}_1\text{Ag}_{28}$ (2.64 eV *versus* 1.76 eV; Fig. S7†), agreeing with an inverse-proportion trend to size, similar to those of $\text{Pt}_1\text{Ag}_{31}$ and $\text{Pt}_1\text{Ag}_{28}$ (1.92 eV *versus* 1.76 eV).⁴⁴

Concurrently, the time-dependent ESI-MS clearly showed ligand exchange on the $\text{Pt}_1\text{Ag}_{37}$ nanocluster along with the intercluster transformation (Fig. 3b). At the initial stage, the $\text{Pt}_1\text{Ag}_{37}$ nanocluster displayed an intense peak at 4574.8 Da. After 5 min, the peak at 4574.8 Da decreased with a new peak emerged at 3637.67 Da, corresponding to the $\text{Pt}_1\text{Ag}_{28}$ nanocluster (Fig. S8b†). Meanwhile, two new peaks with different intensities centered at 3113.12 Da and 2859.17 Da were observed, which may be identified as intermediates (*i.e.* $[\text{Pt}_1\text{Ag}_{25}(\text{SAdm})_{15}(\text{Dppp})_2]^{2+}$ and $\text{Ag}_8(\text{SAdm})_7(\text{Dppp})_2$, separately) during the ligand exchange process. As the reaction continued, the intensity of the $\text{Pt}_1\text{Ag}_{28}$ peak increased, while the intensity of these $\text{Pt}_1\text{Ag}_{37}$ and intermediates decreased (Fig. 3b, $t = 10$ and 300 min profiles). After 6 h, the mass peak of $\text{Pt}_1\text{Ag}_{37}$ disappeared, suggesting a complete intercluster transformation from $\text{Pt}_1\text{Ag}_{37}$ to $\text{Pt}_1\text{Ag}_{28}$. It is worth mentioning that with different equivalent of PPh_3 ligand, the ligand exchange process proceeded in different ways (Fig. S9†). With the addition of 20 equivalent of PPh_3 , the reaction proceeded in the same way but with different conversion rate compared with 40 equivalent of PPh_3 during the first 60 min. After that, the peak of $\text{Pt}_1\text{Ag}_{37}$ and $\text{Pt}_1\text{Ag}_{28}$ decreased simultaneously accompanied by the emer-

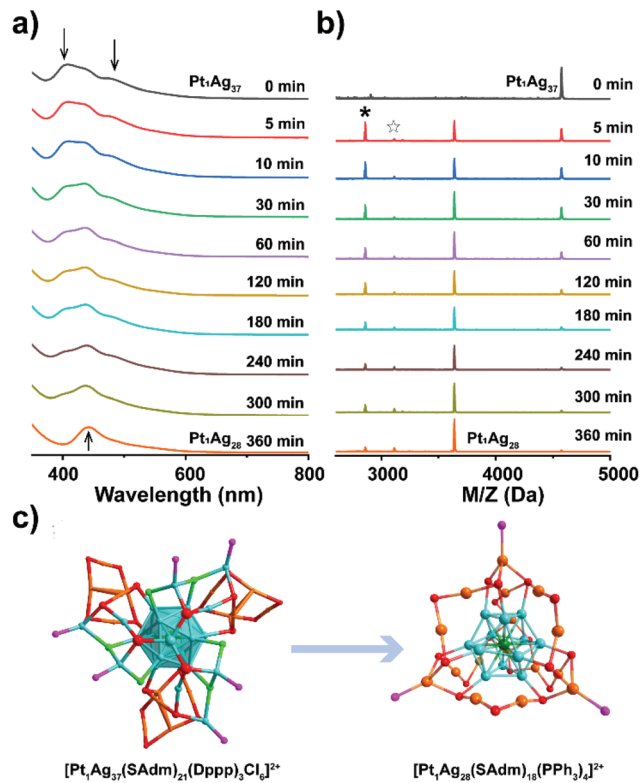


Fig. 3 (a) Time-dependent UV-vis and (b) ESI-MS results of the intercluster transformation from $\text{Pt}_1\text{Ag}_{37}$ to $\text{Pt}_1\text{Ag}_{28}$. \star and \star may be identified as intermediates (*i.e.* $[\text{Pt}_1\text{Ag}_{25}(\text{SAdm})_{15}(\text{Dppp})_2]^{2+}$ and $\text{Ag}_8(\text{SAdm})_7(\text{Dppp})_2$, separately). (c) Intercluster transformation from $\text{Pt}_1\text{Ag}_{37}$ to $\text{Pt}_1\text{Ag}_{28}$. Color labels: dark green, Pt; blue, orange, Ag; green, Cl; red, S; magenta, P.

gence of new fragment peaks at the range of 3000–3500 Da, indicating the disassociation of both $\text{Pt}_1\text{Ag}_{37}$ and $\text{Pt}_1\text{Ag}_{28}$. At $t = 360$ min, the peaks of $\text{Pt}_1\text{Ag}_{37}$ and $\text{Pt}_1\text{Ag}_{28}$ disappeared completely. When the PPh_3 ligand was increased to 60 equivalent, the reaction completed within 180 min without the appearance of intermediate peaks at the range of 2500 Da–4000 Da. The 408 nm of peak UV-vis spectra could be used for the kinetic study. After analyzing the fitting coefficients of the functions,⁵⁹ the half-life periods ($T_{1/2}$) of reaction with 40 and 60 equivalent of PPh_3 were calculated and compared, showing a sequence as 60 eq. (27.43 min) < 40 eq. (38.71 min) (Fig. S10†).

The $\text{Pt}_1\text{Ag}_{37}$ and $\text{Pt}_1\text{Ag}_{28}$ displayed significantly different structures. Along with the intercluster transformation, the icosahedral $\text{Pt}_1\text{Ag}_{12}$ kernel of $\text{Pt}_1\text{Ag}_{37}$ was converted into a face-centered cubic (FCC) $\text{Pt}_1\text{Ag}_{12}$ kernel in $\text{Pt}_1\text{Ag}_{28}$ (Fig. 3c). Besides, the surface shell was changed from three $\text{Ag}_8(\text{SR})_7\text{Cl}_2\text{Dppp}$ trefoil-like motifs to four $\text{Ag}_4(\text{SR})_6(\text{PPh}_3)_1$ cage-like motifs by sharing the terminal thiol ligands, among which the vertex Dppp ligands on $\text{Pt}_1\text{Ag}_{37}$ were peeled off. The difference in bond lengths was also observed and compared. The Pt–Ag average bond length (2.752 Å) in the $\text{Pt}_1\text{Ag}_{37}$ kernel was shorter than that of $\text{Pt}_1\text{Ag}_{28}$ (2.783 Å), suggesting the more robust Pt–Ag bond in $\text{Pt}_1\text{Ag}_{37}$ (Table S1†). Besides, the Ag

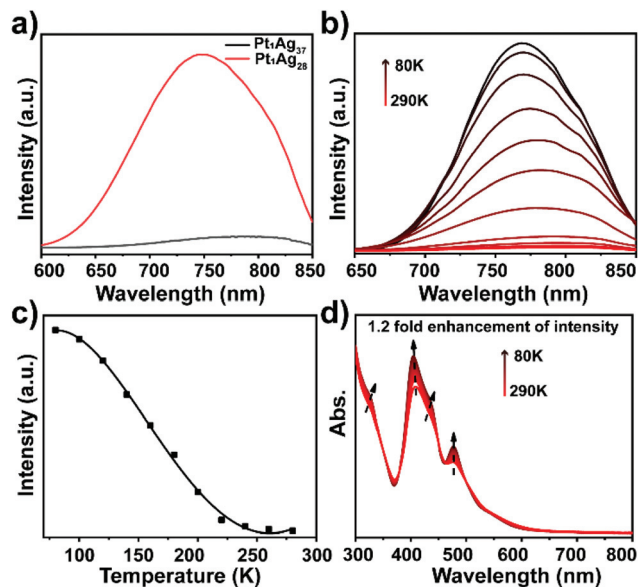


Fig. 4 (a) PL of the Pt₁Ag₃₇ and Pt₁Ag₂₈ nanoclusters at room temperature. (b) Temperature-dependent PL spectra of Pt₁Ag₃₇ nanocluster in CH₂Cl₂. (c) Variation of the PL Intensity over temperature. (d) Temperature-dependent UV-vis absorption of Pt₁Ag₃₇ in CH₂Cl₂.

(kernel)–S(motif) and Ag(motif)–S(motif) bonds in Pt₁Ag₃₇ were also shorter than those of Pt₁Ag₂₈. However, the Ag–Ag bonds of the icosahedral (averagely, 2.895 Å) and Ag(motif)–P(motif) (averagely, 2.407 Å) bonds in Pt₁Ag₃₇ were much longer than those in Pt₁Ag₂₈. The average distance between the terminal Ag and kernel Ag atom in Pt₁Ag₁₂ of Pt₁Ag₃₇ was 6.961 Å, much longer than that in Pt₁Ag₂₈ (4.290 Å), which was attributed to the bulky peripheral ligands of Pt₁Ag₃₇. The transformation of the outermost shell further caused a change towards the core–shell interaction, which altered the innermost Pt₁Ag₁₂ kernel from an icosahedral configuration of Pt₁Ag₃₇ to a FCC configuration of Pt₁Ag₂₈.

Photoluminescent property

The photoluminescence (PL) spectra of Pt₁Ag₃₇ and Pt₁Ag₂₈ was analyzed and compared (Fig. 4a). The excitation spectrum of Pt₁Ag₃₇ nanocluster was shown in Fig. S11.† Upon excitation at 410 nm, the Pt₁Ag₃₇ nanocluster (in CH₂Cl₂ solution) emits at 789 nm, with a PL quantum yield (QY) of 1.49%. By comparison, the Pt₁Ag₂₈ nanocluster emits at 747 nm with a higher PL QY of 4.9% upon excitation at 360 nm.‡⁴³ Moreover,

‡In our previous works, the photoluminescence of Pt₁Ag₂₈(SR)₁₈(PR)₄ was characterized using an instrument of HITACHI (F-7000) with a photoluminescence detection limit at 750 nm, which resulted in an inaccurate emission wavelength (*i.e.*, 672 nm). In this work, we tested the PL of nanoclusters by an instrument of HORIBA Scientific (FluoroMax+) with a higher photoluminescence detection limit at 870 nm. And here, we updated the emission wavelength data of Pt₁Ag₂₈(S-Adm)₁₈(PPh₃)₄ to 747 nm. The photoluminescence quantum yields and emission lifetimes were correct in previous works since they were detected by an instrument of HORIBA Scientific (FluoroMax-4P) with a photoluminescence detection limit at 870 nm.

the PL lifetime of Pt₁Ag₃₇ was 17.53 ns measured by time-correlated single-photon counting (TCSPC) (Fig. S12†), whereas that for Pt₁Ag₂₈ was determined as 3.97 μs.⁴⁷ Such a PL enhancement may be attributed to the different PL mechanism induced by different electronic structure in Pt₁Ag₃₇ and Pt₁Ag₂₈, respectively (Fig. S7†). Specifically, the LUMO density of Pt₁Ag₃₇ was concentrated mainly on Ag core structures, while the HOMO density distributed over the metal core and SR motif structures. In this context, the PL of Pt₁Ag₃₇ might originate from the metal-to-metal-to-ligand charge transfer (MMLCT) process.⁴⁸ For Pt₁Ag₂₈, the PL was ascribed to ligand-to-metal charge transfer (LMCT) based on the excited state behavior analysis.⁴³ The temperature-dependent fluorescence of Pt₁Ag₃₇ in CH₂Cl₂ was also monitored, showing a 37.5-fold enhancement on the PL intensity along with the temperature-lowering process from 290 to 80 K and a blue-shifted emission from 789 to 768 nm (Fig. 4b and c). The increase of the fluorescence intensity may result from the restriction of intramolecular vibration as the temperature decreased.⁶⁰ Meanwhile, the red-shift of PL peak may be ascribed to the decreased molecular transition energy as the temperature increased. The temperature dependent optical absorption of Pt₁Ag₃₇ in CH₂Cl₂ was further investigated and a 1.2-fold enhancement of the peaks at 408 and 475 nm was shown in the corresponding temperature-lowering process (Fig. 4d). Additionally, two new peaks locating at 327 and 435 nm appeared and enhanced gradually in the cooling process. Accordingly, the PL QY of the Pt₁Ag₃₇ nanocluster at 80 K was enhanced from 1.49% to 46.56% (1.49% × 37.5/1.2 = 46.56%) during the temperature-lowering process.

Optical activity

Compared with the monodentate ligand PPh₃ for Pt₁Ag₂₈, the bidentate ligand Dppp for Pt₁Ag₃₇ shows more opportunities to functionalizing nanoclusters. By controlling the enantioselectivity of the peripheral Dppp ligand, the enantioselective synthesis of optically pure intrinsic chiral Pt₁Ag₃₇ nanocluster could be achieved. The chiral ligands (2*S*,4*S*)-2,4-bis(diphenylphosphino) pentane (2*S*,4*S*-Bdpp) and (2*R*,4*R*)-2,4-bis(diphenylphosphino) pentane (2*R*,4*R*-Bdpp) were exploited to substitute the achiral Dppp ligand in the nanocluster synthesis. The UV-vis spectra of the racemic Pt₁Ag₃₇ and *R/S*-Pt₁Ag₃₇ nanoclusters in CH₂Cl₂ were measured. As shown in Fig. 5a, the racemic Pt₁Ag₃₇ and two enantiomers *R/S*-Pt₁Ag₃₇ nanoclusters exhibited two strong bands at 405 and 482 nm, demonstrating their similar geometric and electronic compositions and structures. ESI-MS results demonstrated that two peaks, corresponding to [Pt₁Ag₃₂(SAdm)₁₆(Bdpp)₃Cl₆]³⁺ and [Pt₁Ag₃₂(SAdm)₁₆(Bdpp)₃Cl₇]²⁺ with a loss of an Ag₅S₅ motif, were detected (Fig. 5b and Fig. S13†).

Significantly, compared with the optically inactive Pt₁Ag₃₇, the newly obtained *R/S*-Pt₁Ag₃₇ nanoclusters displayed apparently optical activity. The circular dichroism (CD) spectra of the *R/S*-Pt₁Ag₃₇ solutions exhibited mirror-images signals around 250, 287, 326, 355, 401, 476, and 501 nm (Fig. 5c). The anisotropy factors $g = \Delta A/A = \theta[\text{mdeg}]/(32980 \times A)$ were calcu-

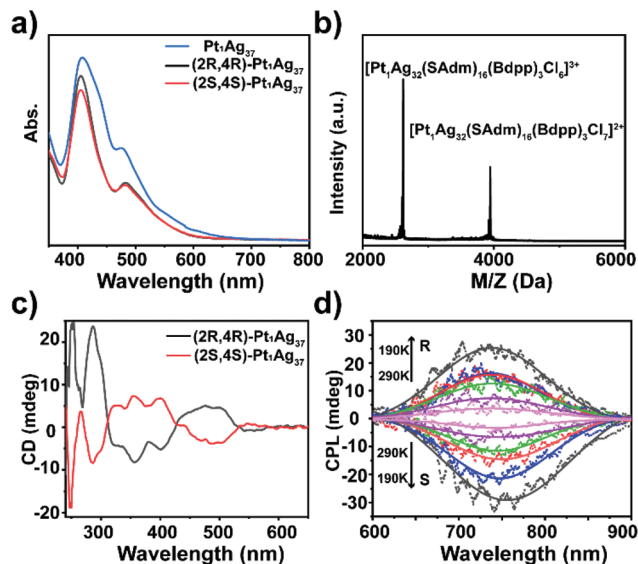


Fig. 5 (a) UV-vis spectra of *R/S*-Pt₁Ag₃₇ and *Rac*-Pt₁Ag₃₇. (b) ESI-MS spectra of *S*-Pt₁Ag₃₇ in CH₂Cl₂. CD (c) and temperature-dependent CPL spectra (d) of the enantiomers.

lated, and the maximum anisotropy factor was up to 7.0×10^{-4} at 501 nm (Fig. S14a[†]). Furthermore, the CD spectra of pure *R/S*-Bdpp ligands were quite different from that of *R/S*-Pt₁Ag₃₇ (Fig. S15[†]). These results demonstrated that the CD signals of *R/S*-Pt₁Ag₃₇ originated from the nanoclusters but not the free ligands, confirming the chirality of *R/S*-Pt₁Ag₃₇. The temperature-dependent circularly polarized luminescence (CPL) signals were then collected (Fig. 5d). The *R/S*-Pt₁Ag₃₇ performed obvious CPL responses that corresponded to their emission bands (600–900 nm) (Fig. S16[†]). Besides, the intensity of CPL signals significantly enhanced with the temperature drop process from 290 to 190 K, consistent with variation of the absorption and emission of such nanoclusters. The calculated g_{lum} values were all at the level of 10^{-3} (Fig. S14b[†]) with a highest g_{lum} value of $\pm 2 \times 10^{-3}$ at about 887 nm.

4 Conclusions

In summary, we synthesized a Pt₁Ag₃₇ nanocluster *via* a one-pot method, and operated the phosphine ligand exchange-induced intercluster transformation from Pt₁Ag₃₇ to Pt₁Ag₂₈. The UV-vis and ESI-MS were performed to track the intercluster transformation. Structurally, the Pt₁Ag₃₇ nanocluster contained an icosahedral Pt₁Ag₁₂ kernel, in contrast to the FCC Pt₁Ag₁₂ kernel of the Pt₁Ag₂₈ nanocluster. Besides, these two Pt@Ag nanoclusters presented significantly different surface motif structures. A 3.3-fold enhancement on PL QY was accomplished *via* the ligand exchange from Pt₁Ag₃₇ to Pt₁Ag₂₈. Furthermore, chiral *R/S*-Ag₃₇ nanoclusters enantiomers could be obtained by substituting achiral Dppp into chiral bidentate phosphine ligands. The chiral *R/S*-Ag₃₇ nanoclusters displayed obvious optical activity. Our results suggest that the phosphine

ligand exchange can be exploited as an efficient approach to fulfill the size evolution and fluorescence regulation of metal nanoclusters, and hopefully contributes more to the fabrication of noble metal nanoclusters, for potential biological, electronic and catalytic applications.

Author contributions

Y. Z. carried out experiments, analyzed the data and wrote the manuscript. X. K. revised the manuscript and C. X. completed DFT calculations. S. J. assisted the X-ray structure analysis. C. F. assisted the measurements of UV-vis and ESI-MS. M. Z. and D. H. designed the project, analyzed the data, and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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