Supporting Information:

Steady-State and Time-Resolved Near-Infrared Photoluminescence of $[M_1Ag_{24}(SR)_{18}]^{n-}$ (M = Ag, Au, Pt, Pd, Ni) Nanoclusters

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EXPERIMENTAL

Chemicals

Silver nitrate ($AgNO_3$, ≥99.9%, Aldrich), Chloroauric acid ($HAuCl_4 \cdot 3H_2O$, >99.99%, Aldrich), Sodium tetrachloroplatinate(II) hydrate ($K_2PtCl_4.xH_2O$, Aldrich), Palladium(II) acetate ($Pd(OAc)_2$, 98%, Aldrich), Nickel(II) chloride ($NiCl_2$, 98%, Aldrich), 2,4-Dimethylbenzenethiol (2,4-DMBT, >96.0%, TCI), Tetraphenylphosphonium bromide (PPh_4Br, ≥97%, Aldrich), Triphenylphosphine (PPh_3, 99%, Acros Organics), Sodium borohydride ($NaBH_4$, Aldrich). Phase-transfer agents: Tetraoctylammonium bromide (TOAB, Aldrich). Solvents: Dichloromethane (ACS reagent, ≥99.5%, Aldrich), Acetonitrile (HPLC grade, ≥99.9%, Aldrich), Methanol (MeOH, ACS reagent), Tetrahydrofuran (THF, ≥99.9%, Aldrich), Hexanes (≥95%, Aldrich), Ethyl alcohol (≥95.0%, Aldrich). All chemicals were used without further purification. Deionized water was prepared with a Barnstead NANOpure Diamond system (resistivity 18.2 MΩ cm).

Synthesis Procedures

Synthesis of $AuClPPh_3$. $HAuCl_4 \cdot 3H_2O$ (10.0 mg, 0.0254 mmol) was dissolved in 2 mL of degassed ethanol under ambient conditions. To this solution, PPh_3 (13.3 mg, 0.0508 mmol) was added, and the mixture was stirred at room temperature for 2 hr. During this period, the characteristic yellow color of $HAuCl_4$ gradually faded, and a white precipitate formed. The resulting solid was collected by vacuum filtration, washed with cold ethanol three times, and dried under vacuum to yield $AuClPPh_3$ as a white powder.[1]

Synthesis of $[Ag_{25}(2,4\text{-DMBT})_{18}]^-$. $AgNO_3$ (38.0 mg, 0.223 mmol) was dissolved in 2.0 mL of methanol under sonication. To this solution, 2,4-dimethylbenzenethiol (100 μL, 0.745 mmol) was added, resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 5 min at room temperature, followed by the addition of 15.0 mL of dichloromethane (DCM). After stirring for 30 min in an ice bath, a solution of PPh_4Br (7.0 mg, 0.017 mmol) in 0.5 mL of methanol was introduced. Subsequently, ice-cold aqueous $NaBH_4$ (17.0 mg, 0.449 mmol in 0.5 mL of water) was added dropwise under vigorous stirring, leading to a gradual color change from yellow to dark brown. The reaction mixture was stirred for an additional 6 hr at ambient temperature and then aged overnight in a refrigerator. The solvents were removed under reduced pressure using rotary evaporation, and the crude product was washed four times with methanol to remove excess thiol and byproducts. The pure nanocluster was extracted from the residue using acetonitrile. Single crystals of $[Ag_{25}(2,4\text{-DMBT})_{18}]^-$ were grown via slow liquid–liquid diffusion of hexane into a dichloromethane (DCM) solution of the purified nanocluster.[2]

Synthesis of $[AuAg_{24}(2,4\text{-DMBT})_{18}]^-$. A solution of $[Ag_{25}(2,4\text{-DMBT})_{18}]^-$ (20.0 mg, 0.00386 mmol) was dissolved in 5.0 mL of DCM. To this solution, $AuClPPh_3$ (1.6 mg, 0.00323 mmol) was added under ambient conditions. The reaction mixture was stirred for 2 hr, during which the color changed from dark reddish-brown to dark green, indicating the progression of the metal exchange process. After completion, the mixture was centrifuged to remove the precipitated AgCl, unreacted $AuClPPh_3$, and other insoluble side products (e.g., Ag-thiolate complexes). The resulting supernatant was concentrated under reduced pressure using rotary evaporation. The crude product was then extracted with acetonitrile to remove excess organic impurities. Single crystals of $[Ag_{25}(2,4\text{-DMBT})_{18}]^-$ were grown via slow liquid–liquid diffusion of hexane into a DCM solution containing the purified nanocluster.[1]

Synthesis of $[PtAg_{24}(2,4\text{-DMBT})_{18}]^{2-}$. Pt-doped silver NC was synthesized via a modified co-reduction protocol based on the previously reported methods.[3] First, $AgNO_3$ (38 mg, 0.223 mmol) was dissolved in 2.0 mL of methanol under sonication. To this, 2,4-dimethylbenzenethiol (100 µL, 0.745 mmol) was added, resulting in the immediate formation of a yellow precipitate. The mixture was stirred for 5 min before adding 15 mL of tetrahydrofuran (THF), followed by an additional 20 min of stirring in an ice bath. A separately prepared solution of $Na_2PtCl_4 \cdot xH_2O$ (3.8 mg, 0.010 mmol) in 2 mL of a 1:1 (v/v) THF–water mixture was then added. Subsequently, PPh_4Br (7.0 mg, 0.017 mmol) dissolved in 0.5 mL methanol was introduced, followed by dropwise addition of freshly prepared ice-cold aqueous $NaBH_4$ (17 mg, 0.449 mmol in 0.5 mL deionized water). The reaction mixture gradually darkened, indicating reduction and cluster formation, and it was stirred at room temperature for 6 hours. Afterward, the reaction was kept at 4 °C overnight to promote nanocluster maturation. Solvents were removed by rotary evaporation, and the crude product was washed four times with methanol to remove excess ligands and byproducts. The purified $[PtAg_{24}(SR)_{18}]^{2-}$ nanoclusters were extracted with acetonitrile, and crystals were obtained by diffusing hexane into a dichloromethane solution of the nanocluster.

Synthesis of $[PdAg_{24}(2,4\text{-DMBT})_{18}]^{2-}$. Pd-doped silver NC was synthesized by dissolving $AgNO_3$ (38 mg, 0.223 mmol) in 2.0 mL of methanol under sonication. Subsequently, 2,4-dimethylbenzenethiol (100 µL, 0.733 mmol) was added, resulting in immediate formation of a yellow precipitate. After stirring for 5 min, 15 mL of DCM was added, followed by $Pd(OAc)_2$ (2.25 mg, 0.010 mmol). The reaction mixture was stirred in an ice bath for 30 min, after which a freshly prepared solution of PPh_4Br (7 mg in 0.5 mL methanol) was introduced. This was followed by the dropwise addition of ice-cold aqueous $NaBH_4$ (17 mg in 0.5 mL deionized water). The yellow suspension gradually darkened, and the mixture was stirred at ambient temperature for an additional 6 hr. The solution was then stored overnight at 4 °C to facilitate nanocluster aging. Solvents were removed under reduced pressure using rotary evaporation, and the resulting crude product was washed four times with methanol to eliminate excess thiol and byproducts. The nanoclusters were extracted from the residue using acetonitrile. Crystals were obtained by liquid–liquid diffusion of hexane into a DCM solution of the purified product.[1]

Synthesis of $[NiAg_{24}(2,4\text{-DMBT})_{18}]^0$ and $[NiAg_{24}(2,4\text{-DMBT})_{18}]^{2-}$. Following a reported metal-exchange protocol, $[Ag_{25}(2,4\text{-DMBT})_{18}]^-$ NC (1 mg, 0.000193 mmol) was dissolved in 1 mL of THF, and 20 µL of $NiCl_2$ stock solution (2.5 mg in 1 mL of 1:1 THF/H_2O) was added under vigorous stirring. 2 µL of freshly prepared $NaBH_4$ stock solution (3.8 mg in 1 mL deionized H_2O) was then introduced, and the mixture was stirred for 5 hr at room temperature. During this period, a gray precipitate formed, which was removed by

centrifugation. The supernatant containing the Ni-doped nanoclusters was collected and concentrated under reduced pressure, yielding the neutral $[NiAg_{24}(2,4\text{-DMBT})_{18}]^0$ product.[3]

To obtain the dianionic analogue, the isolated $[NiAg_{24}(2,4\text{-DMBT})_{18}]^0$ (~1 mg) was redissolved in 1 mL of THF and treated with 4 μL of PPh_4Br stock solution (4.2 mg in 1 mL of MeOH), followed by addition of 4 μL of aqueous $NaBH_4$ stock solution (3.8 mg $NaBH_4$ in 1 mL of H_2O). The mixture was stirred for 1 hr at room temperature. This procedure reduces the Ni-doped nanocluster by two electrons to yield the dianionic $[NiAg_{24}(2,4\text{-DMBT})_{18}]^{2-}$ species, which was isolated as a PPh_4^+ salt using a TLC plate saturated with trioctylamine (TOA).

Characterization

Steady-State UV-Vis-NIR Measurements. The UV–Vis–NIR spectra of Ag_{25} and doped ones (in solutions) were measured on a UV-3600 Plus spectrophotometer (Shimadzu) with a wavelength range of 185-3300 nm.

Steady-state Photoluminescence Measurements. Photoluminescence spectra were measured using an Edinburgh FLS-1000 spectrofluorometer. Near-infrared PL was measured using a wide range InGaAs-based PMT-1700 detector (wavelength range: 500-1700 nm) cooled by liquid nitrogen down to -80°C.

Time-Resolved Photoluminescence Measurements. Time-resolved PL measurements were performed using an EPL-450 picosecond pulsed diode laser (~100 ps, Edinburgh Instruments) in multi-channel scaling (MCS) mode. The excitation wavelength from EPL-450 was 450 nm with a variance smaller than 5 nm. The pulse frequency was set at 100 kHz, and the detection wavelength was set at 1000 nm.

Relative Quantum Yield Determination. The relative quantum yield (Φ_S) of the nanoclusters was measured by using the rod-shaped $Au_{25}(SR)_5(PPh_3)_{10}Cl_2$ (Φ_R=8%) as the standard and was calculated by using:

$$\phi_S = \phi_R \left(\frac{I_S}{I_R}\right)\left(\frac{1-10^{-A_R}}{1-10^{-A_S}}\right)\left(\frac{n_S}{n_R}\right)^2$$

In this context, Φ_R denotes the quantum yield of the reference (standard), *I* represent the integrated photoluminescence (PL) intensity, *A* corresponds to the absorbance of the solution at the excitation wavelength, *n* stands for the refractive index of the solvent, and the subscripts (*S* and *R*) distinguish between the sample and the reference, respectively.

SUPPORTING FIGURE:

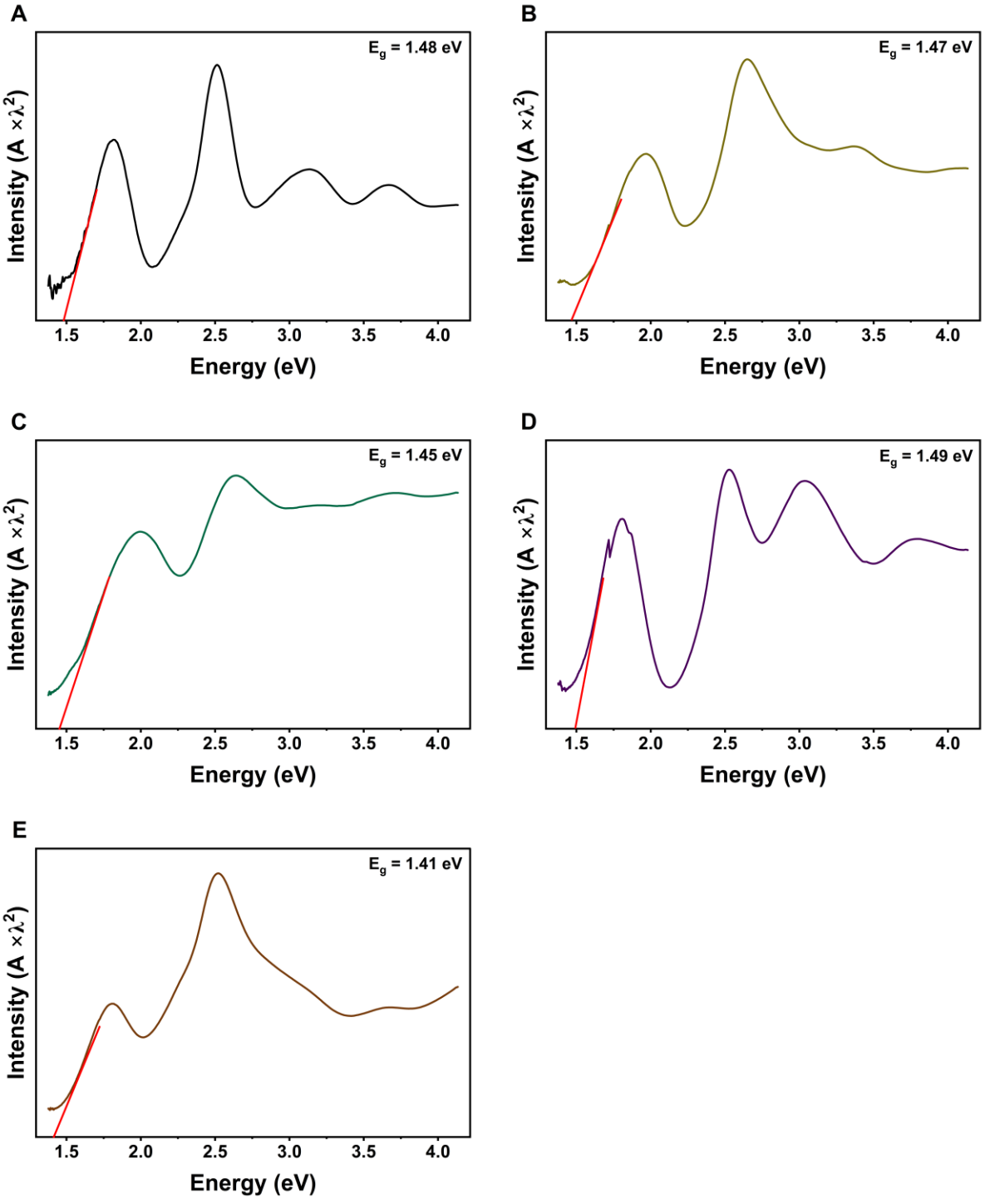

Figure S1. *Bandgap values extracted from Tauc plots for Ag_{25} (A), $AuAg_{24}$ (B), $PtAg_{24}$ (C), $PdAg_{24}$ (D), and $NiAg_{24}$ (E), showing dopant-induced modulation of the optical HOMO–LUMO gap.*

SUPPORTING REFERENCES

(1) Bootharaju, M. S.; Joshi, C. P.; Parida, M. R.; Mohammed, O. F.; Bakr, O. M. Templated Atom-Precise Galvanic Synthesis and Structure Elucidation of a $[Ag_{24}Au(SR)_{18}]^-$ Nanocluster. *Angew. Chem.* **2016**, *128* (3), 934–938. https://doi.org/10.1002/ange.201509381.

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