Supplementary Information S1

Modulation of the photoelectrochemical behavior of Au nanocluster–TiO₂ electrode by doping

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Fig. S1 Electrospray ionization mass spectrometry (ESI-MS) spectra of NC-1.



Fig. S2 ESI-MS spectra of (A) NC-2, (B) NC-3, and (C) NC-4.

As shown in Figs. S1-S2, the compositional formula of the NCs is confirmed by the ESI-MS analysis. The negative ion mode ESI-MS analysis shows the existence of multiple charge states pairing with Na⁺ ions for all NCs due to the anionic nature of water-soluble noble NCs.¹



Fig. S3 UV-vis absorption spectra of the sensitization solutions of NC-1, NC-2, NC-3, and NC-

4.



Fig. S4 Extinction coefficient of $Au_{18-x}Ag_x(SR)_{14}$ NCs at various wavelengths as a function of the molar fraction of Ag⁺ precursor.

1. Electronic Structure Calculation

The HOMO and LUMO energy levels of Au₁₈(SR)₁₄ and Ag-doped Au_{18-x}Ag_x(SR)₁₄ NCs were calculated using density functional theory (DFT). It is noteworthy to mention that Au₁₈ NC models with a simplified model ligand (SCH₃) were used because of the demand of vast computational resources. As shown in Fig. S2, there are nine sites in the core of Au₁₈(SCH₃)₁₄ that can be substituted with Ag atoms. Therefore, a number of isomers can be available for each Ag-doped NC, and hence we first performed structure optimization of these isomers and determined the most plausible Ag doping sites by taking into account the substitution energy of each Au_{18-x}Ag_x(SR)₁₄. The resulting optimized structural coordinates are provided in the Supplemental Information S2. The substitution energy was calculated by the DFT calculation as below:

$$\Delta E_{Au_{18-x}Ag_{x}} = \left(E_{Au_{18-x}Ag_{x}} + x\left(\frac{1}{2}\right) E_{Au_{2}} \right) - \left(E_{Au_{18}} + x\left(\frac{1}{2}\right) E_{Ag_{2}} \right)$$
(S1)

where $E_{Au_{18-x}Ag_x}$, $E_{Au_{18}}$, E_{Au_2} , and E_{Ag_2} are the calculated energies of $Au_{18-x}Ag_x$ isomers, Au_{18} , Au₂ dimer, and Ag₂ dimer, respectively. To avoid the influence of a single valence electron of Au or Ag atoms, the energy of Au₂ or Ag₂ dimers was employed instead of those of Au or Ag atoms. When $x \ge 2$, the number of $Au_{18-x}Ag_x$ isomers increases considerably. For this reason, the major isomers of each Ag-doped $Au_{18-x}Ag_x(SR)_{14}$ were selected on the following criteria:

(i) The substitution sites having the relatively high total energy were not considered in subsequent processes when a single Ag atom was substituted.

(ii) When introducing the x^{th} Ag atom to Au_{18-x}Ag_x(SR)₁₄ ($x \ge 2$), substitution sites in the stable isomers of Au_{18-(x-1)}Ag_{x-1}(SR)₁₄ were given priority.

Since the doping occurs in the core, it can be assumed that substitution in the core would not significantly change entropy. Therefore, the thermal Boltzmann distribution (p_k) at room temperature (300 K) was calculated according to this equation:

$$p_k = e^{\left(-\frac{\Delta E_k}{k_bT}\right)} / \sum_{isomers} e^{\left(-\frac{\Delta E_i}{k_bT}\right)}$$
(S2)

where ΔE_k is the substitution energy of the k^{th} isomer and k_b is the Boltzmann constant. Fig. S6 shows the large Boltzmann population of the all the isomers calculated in this work.

	I	Γ	Γ	Γ
Isomer	Au ₁₇ Ag ₁ (SCH ₃) ₁₄	Au ₁₆ Ag ₂ (SCH ₃) ₁₄	Au15Ag3(SCH3)14	Au ₁₄ Ag ₄ (SCH ₃) ₁₄
Ι	-0.253	-0.405	-0.596	-0.721
II	-0.189	-0.402	-0.559	-0.625
III	-0.176	-0.364	-0.540	-0.611
IV	-0.176	-0.324	-0.493	-0.586
V	-0.152	-0.315	-0.491	-0.569
VI	-0.148	-0.244	-0.386	-0.431
VII	-0.012	-0.235	-0.363	-0.406
VIII	-0.005	-0.163	-0.322	-0.399
IX	0.051	-0.157	-0.316	-0.380
Х	0.091	-0.123	-0.292	-0.375
XI	0.127	-0.114	-0.274	-0.367
XII	0.131	-0.113	-0.259	-0.316
XIII	0.132	-0.109	-0.257	-0.173
XIV	0.134	-0.095	-0.256	-0.160
XV	0.134	-0.059	-0.243	-0.154
XVI	0.141	-0.055	-0.194	-0.037
XVII	0.143	0.006	-0.187	-0.006
XVIII	0.157	0.026	-0.114	
XIX		0.037	-0.091	
XX		0.055	0.109	

Table S1 Substitution energy difference (eV) between $Au_{18}(SCH_3)_{14}$ and all the calcualted isomers of $Au_{18-x}Ag_x(SCH_3)_{14}$ NCs. The energy differences of the major five isomers are shown in red.



Fig. S5 M₉ metallic core of Au₁₈(SCH₃)₁₄ and five lowest energy isomers of Au_{18-x}Ag_x(SCH₃)₁₄ with $1 \le x \le 4$. Tagging of a particular atom indicates the Ag doping sites. The energy of an isomer in a particular Ag-doped category increases from top to bottom.

Isomer $Au_{16}Ag_2$ $Au_{15}Ag_3$ $Au_{14}Ag_4$ Au_{18} $Au_{17}Ag_1$ Ι 100 83.14 45.66 72.36 94.72 Π 6.74 41.47 16.84 2.20 III 4.11 9.22 8.16 1.32 IV 4.11 1.32 0.25 1.96 1.60 V 1.19 0.50 1.39 $1.18 imes 10^{-3}$ VI 0.28 0.09 0.02 8.09×10^{-3} VII $6.92\times10^{\text{-3}}$ 6.02×10^{-2} 4.38×10^{-4} 3.31×10^{-4} VIII $5.18 imes 10^{-3}$ 3.73×10^{-3} $1.63 imes 10^{-3}$ IX 5.80×10^{-4} 2.89×10^{-3} 1.33×10^{-3} 1.61×10^{-4} 1.23×10^{-4} 7.72×10^{-4} 5.24×10^{-4} $1.30\times10^{\text{--}4}$ Х 3.02×10^{-5} 5.39×10^{-4} 2.55×10^{-4} 9.46×10^{-5} XI $2.58\times10^{\text{-5}}$ XII 5.35×10^{-4} $1.43 imes 10^{-4}$ 1.33×10^{-5} $2.47\times10^{\text{-5}}$ 4.45×10^{-4} $5.03\times10^{\text{-8}}$ XIII 1.33×10^{-4} XIV $2.35 imes 10^{-5}$ 2.60×10^{-4} 1.29×10^{-4} 2.98×10^{-8} $2.40 imes 10^{-8}$ XV $2.28\times10^{\text{-5}}$ 6.35×10^{-5} 7.50×10^{-5} $1.77\times10^{\text{-5}}$ $1.13\times10^{\text{-5}}$ $2.50\times10^{\text{--}10}$ XVI 5.47×10^{-5} 1.62×10^{-5} 5.07×10^{-6} 8.64×10^{-6} 7.37×10^{-11} XVII $9.31\times10^{\text{-}6}$ 2.37×10^{-6} 4.99×10^{-7} XVIII 1.51×10^{-6} 2.01×10^{-7} XIX XX 7.39×10^{-7} $8.17 imes 10^{-11}$

Table S2 Boltzmann distribution (%) of all the calculated isomers of $Au_{18-x}Ag_x(SCH_3)_{14}$. The abundances of the major five isomers are shown in red.



Fig. S6 Boltzmann population distribution of various isomers of $Au_{18-x}Ag_x(SCH_3)_{14}$ with $1 \le x \le 4$ in (A) log scale and (B) linear scale.

As the Au atoms in the core were replaced by Ag atoms, the HOMO-LUMO gap increased slightly. Interestingly, the increase in the HOMO-LUMO gap was mainly due to the change in LUMO, whereas the HOMO change is somewhat insensitive to the number of Ag dopants. To investigate this phenomenon, we used the Mulliken charge method² to analyze the atom site contribution to the frontier orbitals and found that the substituted Ag atoms contributed substantially to the LUMO without affecting the HOMO significantly (Figs. S7-S27, Table S3). As a result, the HOMO-LUMO gap increased with the number of Ag dopants.

Table S3 DFT calculated HOMO and LUMO energy levels and HOMO-LUMO (HL) gap of $Au_{18}(SCH_3)_{14}$ and five lowest energy isomers of $Au_{18-x}Ag_x(SCH_3)_{14}$ with $1 \le x \le 4$.

	Isomer	Substitution	Substitution energy	НОМО	LUMO	HL gap
		site	(eV)	(eV)	(eV)	(eV)
Au ₁₈ (SCH ₃) ₁₄	Au18		0	-5.396	-2.955	2.44
	Ι	C1	-0.253	-5.461	-2.88	2.581
	II	A1	-0.189	-5.445	-3.039	2.407
Au ₁₇ Ag ₁ (SCH ₃) ₁₄	III	C2	-0.176	-5.393	-2.959	2.434
	IV	A3	-0.152	-5.4	-2.847	2.553
	V	A2	-0.148	-5.391	-2.88	2.511
	Ι	C1,C2	-0.405	-5.439	-2.823	2.617
	II	A1,C1	-0.402	-5.512	-3.025	2.486
Au ₁₆ Ag ₂ (SCH ₃) ₁₄	III	A1,C2	-0.364	-5.458	-2.996	2.462
	IV	A1,A2	-0.324	-5.417	-2.91	2.507
	V	A1,A3	-0.315	-5.426	-2.908	2.519
Au ₁₅ Ag ₃ (SCH ₃) ₁₄	Ι	C1,C2,C3	-0.596	-5.411	-2.699	2.712
	II	A1,C1,C2	-0.559	-5.512	-2.921	2.591
	III	A1,C1,C3	-0.54	-5.52	-2.918	2.602
	IV	A1,A2,C1	-0.493	-5.481	-2.893	2.588
	V	A1,A3,C1	-0.491	-5.494	-2.906	2.588
Au ₁₄ Ag ₄ (SCH ₃) ₁₄	Ι	A1,C1,C2,C3	-0.721	-5.496	-2.776	2.72
	II	A1,A2,A3,C1	-0.625	-5.456	-2.71	2.746
	III	A1,A2,C1,C2	-0.611	-5.48	-2.816	2.665
	IV	A1,A2,A3,C2	-0.586	-5.405	-2.716	2.688
	V	A1,A3,C1,C2	-0.569	-5.485	-2.807	2.678



Fig. S7 Frontier molecular orbital energy levels and HOMO/LUMO distributions in Au₁₈(SCH₃)₁₄.



Fig. S8 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{17}Ag_1(SCH_3)_{14}$ with Ag doped at the C1 site of the Au₉ core.



Fig. S9 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{17}Ag_1(SCH_3)_{14}$ with Ag doped at the A1 site of the Au₉ core.



Fig. S10 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{17}Ag_1(SCH_3)_{14}$ with Ag doped at the C2 site of the Au₉ core.



Fig. S11 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{17}Ag_1(SCH_3)_{14}$ with Ag doped at the A3 site of the Au₉ core.



Fig. S12 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{17}Ag_1(SCH_3)_{14}$ with Ag doped at the A2 site of the Au₉ core.



Fig. S13 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{16}Ag_2(SCH_3)_{14}$ with Ag doped at the C1 and C2 sites of the Au₉ core.



Fig. S14 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{16}Ag_2(SCH_3)_{14}$ with Ag doped at the A1 and C1 sites of the Au₉ core.



Fig. S15 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{16}Ag_2(SCH_3)_{14}$ with Ag doped at the A1 and C2 sites of the Au₉ core.



Fig. S16 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{16}Ag_2(SCH_3)_{14}$ with Ag doped at the A1 and A2 sites of the Au₉ core.



Fig. S17 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{16}Ag_2(SCH_3)_{14}$ with Ag doped at the A1 and A3 sites of the Au₉ core.



Fig. S18 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{15}Ag_3(SCH_3)_{14}$ with Ag doped at the C1, C2, and C3 sites of the Au₉ core.



Fig. S19 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{15}Ag_3(SCH_3)_{14}$ with Ag doped at the A1, C1, and C2 sites of the Au₉ core.



Fig. S20 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{15}Ag_3(SCH_3)_{14}$ with Ag doped at the A1, C1, and C3 sites of the Au₉ core.



Fig. S21 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{15}Ag_3(SCH_3)_{14}$ with Ag doped at the A1, A2, and C1 sites of the Au₉ core.



Fig. S22 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{15}Ag_3(SCH_3)_{14}$ with Ag doped at the A1, A3, and C1 sites of the Au₉ core.



Fig. S23 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{14}Ag_4(SCH_3)_{14}$ with Ag doped at the A1, C1, C2, and C3 sites of the Au₉ core.



Fig. S24 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{14}Ag_4(SCH_3)_{14}$ with Ag doped at the A1, A2, A3, and C1 sites of the Au₉ core.



Fig. S25 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{14}Ag_4(SCH_3)_{14}$ with Ag doped at the A1, A2, C1, and C2 sites of the Au₉ core.



Fig. S26 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{14}Ag_4(SCH_3)_{14}$ with Ag doped at the A1, A2, A3, and C2 sites of the Au₉ core.



Fig. S27 Frontier molecular orbital energy levels and HOMO/LUMO distributions in $Au_{14}Ag_4(SCH_3)_{14}$ with Ag doped at the A1, A3, C1, and C2 sites of the Au₉ core.

Table S4 Loading amount of NC-1, NC-2, NC-3, and NC-4 on mesoporous TiO₂ films.

Sample	Loading Amount (×10 ⁻⁸ mol·cm ⁻²)			
NC-1	9.40			
NC-2	9.81			
NC-3	9.36			
NC-4	9.52			



Fig. S28 UV-vis absorption spectra of NC-attached, mesoporous TiO₂ films.

2. Deconvolution of Incident Photon-to-Current Efficiency (IPCE)

IPCE is composed of three factors as given by the relation below:

$$IPCE = \eta_{lhe}(\lambda) \,\eta_{sep}(\lambda) \,\eta_{coll}(\lambda) \tag{S3}$$

where η_{lhe} represents the light harvesting efficiency, η_{sep} is the charge separation efficiency, and η_{coll} is the charge collection efficiency. The value for η_{lhe} can be calculated using the following relation:^{3,4}

$$\eta_{\text{lhe}}(\lambda) = T_{FTO}(\lambda) [1 - e^{-\alpha(\lambda)d}]$$
(S4)

where T_{FTO} is the transmittance of the FTO glass substrate, *d* is the thickness of the TiO₂ film, and $\alpha(\lambda)$ is the absorption coefficient of the photoanode. The value of η_{lhe} calculated using Eq. S4 showed an increase with increased doping levels (Fig. S9A), which is in agreement with the absorbance profile of the corresponding NCs. If J_{SC} were governed solely by η_{lhe} , NC-3-SC and NC-4-SC would have produced a higher J_{SC} than NC-1-SC and NC-2-SC, but they behaved contrarily. This implies that J_{SC} in NC-3-SC and NC-4-SC was limited by either η_{sep} , η_{coll} , or both. The IPCE can be normalized by η_{lhe} to obtain absorbed photon-to-current efficiency (APCE), which can be used to analyze charge separation and collection processes in solar cells. APCE is given as:



Fig. S29 (A) Light harvesting efficiency (η_{lhe}) and (B) APCE of NC-1-SC, NC-2-SC, NC-3-SC, and NC-4-SC as a function of wavelength. It should be noted that APCE values here are only used for qualitative comparison as it is prone to wild fluctuation, especially at the long-wavelength regions where IPCE and LHE values are low. In this region, a small change in the absorbance due to the scattering effect of TiO₂ films can result in many-fold fluctuations in the APCE.

3. Charge Injection

Sample	A ₁	$ au_1$	\mathbf{A}_2	$ au_2$	•	$ au_3$	$ au_{avg}$	k_c
		ns		ns	A3	ns	ns	s ⁻¹
NC-1-TiO ₂	0.27	1.34	0.43	21.22	0.43	230.77	212.41	- 2.71×10 ⁶
NC-1-ZrO ₂	0.16	0.48	0.16	31.07	0.67	506.94	499.84	
NC-2-TiO ₂	0.20	0.45	0.38	22.27	0.42	274.73	257.37	- 2.13×10 ⁶
NC-2-ZrO ₂	0.16	0.40	0.46	31.85	0.67	588.40	568.68	
NC-3-TiO ₂	0.19	0.55	0.40	18.45	0.45	214.98	200.64	- 7.14×10 ⁵
NC-3-ZrO ₂	0.16	0.39	0.44	22.62	0.47	251.90	234.17	
NC-4-TiO ₂	0.15	0.53	0.28	18.18	0.64	206.83	199.78	- 9.93×10 ⁴
NC-4-ZrO ₂	0.14	0.48	0.31	20.78	0.57	213.68	203.83	

Table S5 PL lifetime components of TiO₂ and ZrO₂ films sensitized with NC-1, NC-2, NC-3, and NC-4 and their apparent rate constants (k_c).

The average PL lifetime (τ_{avg}) was calculated using the following equation: $\tau_{avg} = \sum_i (A\tau_i^2) / \sum_i (A_i\tau_i)$. The value for k_c was calculated using the following equation: $k_c = 1/\tau_{TiO_2} - 1/\tau_{ZrO_2}$.

4. Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were performed by applying an external bias to set the Fermi level of the TiO₂ (Fig. S30) and the obtained Nyquist plots were fitted using an equivalent circuit (Fig. S31). The voltage drop due to the series resistance (R_S) and charge-transfer resistance at the counter electrode (R_{CE}) were subtracted to obtain the actual voltage controlling the Fermi level of TiO₂ ($V_{appl} - V_S - V_{CE}$). This voltage is referred to as the Fermi voltage (V_F) and is equivalent to the shift in equilibrium Fermi level (E_{F0}) relative to the quasi-Fermi level (E_{Fn}), which is expressed by the following relation: $V_F = (E_{Fn} - E_{F0})/q$, where q is the positive elementary charge. Kinetic parameters of various solar cells can only be compared fairly if they have a similar density of electrons in the TiO₂ conduction band. Chemical capacitance (C_{μ}) is a measure of electron density in TiO₂⁵ and is related to the difference between E_{Fn} and conduction band position (E_{CB}) of TiO₂ as expressed below:⁶

$$C_{\mu} \propto \exp\left(-\frac{E_{CB}-E_{Fn}}{k_{B}T}\right)$$
 (S6)

where k_B is the Boltzmann constant, and *T* is the absolute temperature. As explained in a previous report,⁶ sensitization of TiO₂ by NCs can lead to a subtle change in C_{μ} (Fig. S32A). This change indicates a different conduction band position for the TiO₂ because E_{Fn} is set by the external bias.⁷⁻⁹ Therefore, when comparing the various parameters extracted from EIS analysis, all four MCSSCs should be tested with a similar electron density in the TiO₂ conduction band. To this end, as seen in Fig. S32B, we shifted the voltage scale for C_{μ} to obtain an equilibrium conduction band (V_{ecb}) position that ensured the same gap between E_{CB} and E_{Fn} across samples.



Fig. S30 Nyquist plots of NC-sensitized solar cells obtained at different applied bias conditions in dark: (A-B) NC-1-SC, (C-D) NC-2-SC, (E-F) NC-3-SC, and (G-H) NC-4-SC. (B, D, F, and H) are zoomed-in spectra of each cell measured at 0.50 and 0.56 V, respectively.



Fig. S31 Equivalent circuit employed for fitting EIS data.¹⁰ R_s is the series resistance, R_{CE} and C_{CE} are the charge transfer resistance and interfacial capacitance at the electrolyte counter electrode interface. R_{tr} (= r_{tr} ·d) is the transport resistance, R_r (= r_r ·d) and C_{μ} (= c_{μ} ·d)) are the recombination resistance and the chemical capacitance at the TiO₂/NC/electrolyte interface. d is the thickness of the TiO₂ film and Z_d is the Warburg coefficient for the electrolyte diffusion which was ignored during the fitting. Copyright © 2016, American Chemical Society. Reprinted with permission.



Fig. S32 Chemical capacitance (C_{μ}) as a function of (A) Fermi voltage (V_F) and (B) equivalent conduction band voltage (V_{ecb}) . (C) Small perturbation diffusion coefficient (D_n) as a function of V_{ecb} .

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