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Electronic Supplementary Information (ESI) for the paper

Thirty-fold photoluminescence enhancement induced by secondary ligands

in monolayer protected silver clusters

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Synthesis of [Ag₂₉(BDT)₁₂] (Ia) and [Ag₂₉(BDT)₁₂(X)₄] (where, X: 3PPh₃, DPPM, DPPE, DPPP, TTP, TFPP and TCPP) (Ib, II, III, IV, V, VI and VII, respectively)

For the synthesis of $[Ag_{29}(BDT)_{12}(PPh_3)_4]$ (**Ib**), ~20 mg of AgNO₃ was dissolved in MeOH (5 mL) and then DCM (~9 mL) was added to the solution.¹ The solution was then kept for stirring. After ~5 min, 13.5 µl of 1,3-BDT was added which resulted in the formation of a yellow colored silver-thiolate complex. Then, ~200 mg of PPh₃ (in 0.5 mL of DCM) was added to the reaction mixture after 5 min. A colorless silver-thiolate-phosphine complex was formed which was further reduced by ~11 mg of NaBH₄ (in 0.5 mL of ice-cold H₂O), turning the color of the solution to dark brown and then bright orange. The reaction mixture was kept at room temperature under stirring for 3 h in dark. After completion of the reaction, the precipitate was collected by centrifuging the mixture, and the supernatant was discarded. The precipitate was then washed thrice with methanol to remove the unreacted byproducts and the orange colored cluster was extracted with DMF. The $[Ag_{29}(BDT)_{12}]$ (**Ia**) cluster was synthesized following the same synthetic method without the PPh₃ ligand.

For the synthesis of $[Ag_{29}(BDT)_{12}(DPPM/DPPE/DPPP)_4]$ (**II**, **III** and **IV**), the above-mentioned procedure was used. In these cases, ~50 mg of DPPM/DPPE/DPPP and ~22.5 mg of NaBH₄ were used. After 3 h of reaction, clear reddish orange color solutions were formed which were first concentrated under rotavapor and then the clusters were precipitated using MeOH. The precipitates were collected

after centrifugation and washed repeatedly using MeOH. The clusters were then dissolved in DCM, DMF etc.

In spite of direct synthesis method, $[Ag_{29}(BDT)_{12}(X)_4]$ where, X= PPh₃, DPPM, DPPE, DPPP (II, III and IV) were also synthesized by ligand addition method from Ia and Ib. In this case, the absorbance of the stock solution of Ia/ Ib was kept at ~0.07 absorbance (at 450 nm) and 5 mg of PPh₃, DPPM, DPPE, DPPP were added in 3 mL of cluster solution, respectively. Following the ligand exchange (LE) method V, VI and VII were synthesized from Ib.

Synthesis of [Ag₅₁(BDT)₁₉(PPh₃)₃] (VIII)

The cluster was synthesized adopting an already reported method.² About 20 mg of AgNO₃ was dissolved in 5 mL of methanol and then 9 mL of CHCl₃ was added. After few mins, ~13.5 μ L of BDT (0.5 mL of CHCl₃) was added to the solution. After 5 min of stirring in dark, ~200 mg of PPh₃ (in 0.5 mL of CHCl₃) was added to the mixture. Then, 0.5 mL of an ice-cold aqueous solution containing ~11 mg of NaBH₄ was added which resulted in the immediate color change of the solution from colorless to dark brown. The reaction was kept for 3 h under dark. Then, the supernatant (green color) was collected by centrifugation (for 10 min at high speed) and the concentrated solution was collected by rotary evaporation. The cluster was precipitated using hexane after washing several times with mQ water. Then the precipitate was collected by centrifugation and dissolved in DMF for further characterizations.

Ligand exchange (LE) synthesis of [Ag₅₁(BDT)₁₉(X)₃] (where, X: DPPM, DPPE, DPPP) (IX, X and XI)

The **IX**, **X** and **XI** clusters were synthesized by ligand exchange method from **VIII** using DPPM, DPPE, and DPPP.

Quantum yield (QY) measurements

Luminescence QYs of as-synthesized Ag₂₉ clusters using different phosphines (**II**, **III**, **IV**, **V**, **VI** and **VII**) were determined by the integrated luminescence intensity method by comparing the PL emission

with the **Ib** (QY is 0.9%). The luminescence of a sample can be written in a formula with related parameters

$$F = K\varphi C\sigma lI$$

where 'F' is the PL QY of the sample, 'C' is the number density of fluorophores (concentration of the sample), ' σ ' is the one-photon absorption cross section, 'l' is the path length traversed by photons are absorbed, 'I' is the flux of incident photons (photons cm⁻² s), 'F' is the integrated luminescence signal in the emission region, and 'K' is an instrumental parameter. The samples were excited at ~450 nm wavelength and all experimental conditions were kept constant. Then the QY of clusters can be measured using following formula,

$$\varphi_s = \frac{F_s}{C_s \, \sigma_s} \times \frac{C_r \sigma_r}{F_r} \times \varphi_r$$

where 's' and 'r' refer to clusters and the reference, respectively. $C\sigma'$ represents absorption of the sample hence, replaced by 'A' where A is the absorbance at excitation wavelength. Thus, the formula can be rewritten as,

$$\varphi_s = \frac{F_s}{A_s} \times \frac{A_r}{F_r} \times \varphi_r$$

The absorbance of all the samples along with the reference were measured at \sim 446 nm and were set as 0.07. After that, luminescence intensities of the samples were measured.

Computational details

The structural, electronic and optical properties such as optical absorption and emission of **Ib**, **II**, **III** and **IV** were calculated using density functional theory (DFT), as implemented in Grid-Based Projector Augmented Wave method (GPAW).^{3, 4} To include only the interactions of the valence electrons, the PAW setup was considered as $Ag(4d^{10}5s^{1}5p^{6})$, $S(3s^{2}3p^{4})$, $P(3s^{2}3p^{3})$, $C(2s^{2}2p^{2})$ and $H(1s^{1})$ with scalarrelativistic effects included for Ag. The geometry optimizations of all clusters were performed using PBE exchange functional⁵ in real-space finite difference (FD) mode in GPAW.51 having a grid spacing of 0.2 Å and the convergence criterion for the forces on each atoms was set to 0.05 eV/Å. The initial structures of **Ib** was from the reported crystal structure and the other structures were build up by addition of different diphosphines. Also, the above optimized structures were re-optimized after simplification by replacing each benzene ring of the phosphine ligands by a reduced methyl (CH₃) model ligand, in order to greatly reduce the computational cost and time in time-dependent DFT (TDDFT) calculations. Further, these structures were taken for the investigation of electronic, optical absorption and emission properties. The optical absorption spectra were calculated by time-dependent DFT (TDDFT) using GPAW.⁶ The calculated emission spectra were plotted with a Gaussian width of 0.05 eV. All visualizations were created with Visual Molecular Dynamics (VMD) software.⁷





Fig. S1 (A) The expanded ESI MS of **Ia** (m/z 1603). The isotopic distribution shows that the separation between two peaks is 0.33 which denotes 3⁻ charge state of the cluster. (B) The theoretical (red) and experimental (black) spectra of **Ib**, **II**, **III** and **IV**. The experimental spectra in some regions overlap with other features due to other species or their fragments.



Fig. S2 The NMR spectra of **Ib** (black), **II** (red), **III** (blue) and **IV** (pink). Corresponding phosphine ligands, PPh₃, DPPM, DPPE and DPPP show ³¹P peaks at -5.3, -26.2, -12.7 and -17.2 ppm, respectively and the corresponding clusters, **Ib**, **II**, **III** and **IV** display peaks at ~ 1.4, -3.3, -0.1, 0.4 ppm, respectively which confirm the formation of Ag-P bonds.





Fig. S3 (A) XPS spectra of **Ib**, **II**, **III** and **IV**. All clusters exhibits peaks correspond to Ag 3d, S 2p and P 2p. (B) The time-dependent absorption spectra of **Ib** and **IV** after 3 weeks. The decrease in intensity is almost the same in both the clusters (7.7% and 7.4% for **Ib** and **IV**, respectively). (C) The cone voltage (CV) dependent fragmentation study from ESI MS of **Ib** and **IV** which shows that the loss of all PPh3 from **Ib** occurs at CV 40 while at CV 70 all DPPP ligands get detached from **IV**.





Fig. S4 UV-vis absorption spectra (A and C) and emission spectra (B and D) of **Ib** and **III** before (black) and after (red) DPPE and PPh₃ addition, respectively. The changes in both the absorption and emission spectra reveal the ability of DPPE ligand to replace PPh₃ which result in the formation of **III** ligand exchanged from **Ib**. But the vice versa is not occurred. UV-vis absorption spectra (E and G) and emission spectra (F and H) of **Ib** and **II** before (blue) and after (pink) DPPM and PPh₃ addition, respectively.



Fig. S5 The theoretical absorption spectra of **Ib**, **II**, **III** and **IV** using the reduced model (benzene ring of phosphines are replaced by -CH₃ ligand) to minimize the computational cost. The peak 1 (absorption maxima) of **II**, **III** and **IV** are blue-shifted than that of **Ib** and peak 2 are gradually red-shifted which are quite similar to the experimental observations.



Fig. S6 The shape of the K-S MOs of **Ib** (A), **II** (B) and **III** (C) which denote the strongest electronic transitions related to peak 1 and 2.

Supplementary Table S1

A)

System	Transition energy/eV	Transition energy/nm	MO transitions (eigen value)	Orbitals contibutions
Іb	2.782	445.7	HOMO-14 -> LUMO+8 HOMO-14 -> LUMO+9 HOMO-13 -> LUMO+7 HOMO-13 -> LUMO+9 HOMO-2 -> LUMO+11	0.116 0.192 0.116 0.45 0.0709
П	2.896	428.12	HOMO-8 -> LUMO+10 HOMO-6 -> LUMO+10 HOMO-4 -> LUMO+11 HOMO-4 -> LUMO+13 HOMO-1 -> LUMO+14	0.0604 0.246 0.0726 0.0748 0.0741
III	2.919	424.75	HOMO-16 -> LUMO+6 HOMO-7 -> LUMO+10 HOMO-5 -> LUMO+12 HOMO-4 -> LUMO+12 HOMO-2 -> LUMO+13 HOMO-1 -> LUMO+17	0.0913 0.13 0.0613 0.0826 0.0638 0.0946
IV	2.932	422.87	HOMO-10 -> LUMO+10 HOMO-8 -> LUMO+10 HOMO-7 -> LUMO+10 HOMO-4 -> LUMO+12 HOMO-2 -> LUMO+13	0.0544 0.0727 0.247 0.179 0.0863

B)

System	Transition energy/eV	Transition energy/nm	MO transitions (eigen value)	Orbitals contibutions
Ib	2.520	492.0	HOMO-4 -> LUMO+9	0.374
			HOMO-3 \rightarrow LUMO+8	0.371
			HOMO-3 -> LUMO+9	0.101
II	2.399	516.8	HOMO-19 -> LUMO+1	0.112
			HOMO-15 -> LUMO+3	0.0753
			HOMO-9 -> LUMO+7	0.212
			HOMO-8 -> LUMO+8	0.396
	2 200	516.0		0.102
111	2.399	516.8	HOMO-19 -> LUMO	0.182
			HOMO-19 -> LUMO+2	0.074
			HOMO-18 -> LUMO	0.173
			HOMO-17 -> LUMO+2	0.0626
			HOMO-16 -> LUMO+3	0.199

IV	2.381	520.7	HOMO-19 -> LUMO+2	0.0589
			HOMO-18 -> LUMO+3	0.182
			HOMO-17 -> LUMO+4	0.0905
			HOMO-16 -> LUMO+3	0.0743
			HOMO-16 -> LUMO+4	0.317

C)

System	Transition	Transition	MO transitions	Orbitals
	energy/eV	energy/nm		contibutions
	00			
Ib	2.276	492.0	HOMO-14 -> LUMO+4	0.156
			HOMO-13 -> LUMO+3	0.156
			HOMO-8 -> LUMO+5	0.319
			HOMO-7 -> LUMO+5	0.127
	2.148	577.2	HOMO-11 -> LUMO+4	0.205
			HOMO-10 -> LUMO+4	0.244
			HOMO-9 -> LUMO+3	0.244
			HOMO-3 -> LUMO+5	0.079
	2.100	590.4	HOMO-12 \rightarrow LUMO+2	0.0556
			HOMO-10 -> LUMO+1	0.0772
			HOMO-9 -> $LUMO+2$	0.0766
			HOMO-8 -> $LUMO+3$	0.0852
			HOMO-7 -> LUMO+3	0.0633
			HOMO-5 -> LUMO+4	0.0628
	0.044			0.0.001
	2.244	552	HOMO-14 \rightarrow LUMO+4	0.0691
			HOMO-13 -> LUMO+3	0.0691
			HOMO-7 -> LUMO+5	0.677
IV	2.099	520.7	HOMO-13 -> LUMO+1	0.119
	,		HOMO-13 -> LUMO+3	0.0636
			HOMO-12 -> LUMO+2	0.0486
			HOMO-9 -> LUMO+5	0.0542
			HOMO-7 -> LUMO+5	0.0891
			HOMO-6 -> LUMO+5	0.164
	1.884	658.0	HOMO-11 -> LUMO	0.131
			HOMO-10 -> LUMO	0.105
			HOMO-10 -> LUMO+2	0.0593
			HOMO-9 -> LUMO	0.178
			HOMO-9 -> LUMO+2	0.0521
			HOMO-6 -> LUMO+1	0.0616
			HOMO-2 -> LUMO+4	0.0646
	2 000	500		0.110
	2.099	590	HOMO-13 \rightarrow LUMO+1	0.119
			HOMO-13 -> LUMO+3	0.0636
			HOMO-9 -> LUMO+5	0.0542
			HOMO-/ \rightarrow LUMO+5	0.0891

	HOMO-6 -> LUMO+5	0.164

Table S1 (A) The list of MO transitions contribute to the absorption maxima (peak 1) and (B) absorption onset (peak 2) of **Ib**, **II**, **III** and **IV**. (C) The MO transitions correspond to the peaks arise at lower energy range of **Ib** and **IV**. The transitions above 0.05 orbital contribution are considered and the strongest electronic transitions are highlighted here.



Fig. S7 DLS particle size distribution of **Ib** and **IV** at higher (A) and lower (B) concentrations. (C) Emission spectra of **Ib** and **IV** at lower concentration having no aggregation (~0.05 absorbance). In the very low concentration **IV** display significant emission while **Ib** has no emission.



Fig. S8 The Ag₁₃ icosahedral metal core of **Ib** (A), **II** (B), **III** (C) and **IV** (D). The view along Cartesian coordinates X, Y and Z axes are shown in a, b and c, respectively.



Fig. S9 The emission spectra of IV after purging N_2 (A) and CO_2 (B) which show increased luminescence. (C) The emission spectra of IV at different concentrations of O_2 . With increasing O_2 concentration, PL intensity decreased gradually.

Supplementary Table S2

Cluster	τ_1 ns [%]	τ_2 ns [%]	$ au_{avg}(ns)$
Ib	99.65(51)	336.48(49)	214.90
II	108.44(17)	589.94(83)	510.49
III	120 (4)	1133.46(96)	1096.76
IV		6196.04 (100)	6196.04

Table S2 The lifetime values of **Ib**, **II**, **III** and **IV**. Each composed of two lifetime components and average lifetime increases with the longer phosphine ligands.



Fig. S10 ESI MS of **V** (red), **VI** (blue) and **VII** (pink) which is compared with that of **Ib** (black). Similar to **Ib**, other clusters are showing systematic phosphine loss.



Fig. S11 UV-vis absorption (A) and emission (B) spectra of **VIII** (black), **IX** (red), **X** (blue) and **XI** (pink). Inset: Photographs under visible light and UV light which show gradual increase in the PL intensity. Spectra for **IX**, **X** and **XI** are vertically shifted for clarity.



Fig. S12 UV-vis absorption (A) and emission (B) spectra of XI before (black) and after (red) O_2 purging.

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