ESI material for:

Assembly of anionic silver nanoclusters with controlled packing structures through site-specific ionic bridges

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Materials. Silver nitrate ($AgNO_3$, 99.8%) and triphenylphosphine (TPP, >95%) were purchased from Fujifilm Wako Chemical Corp. Benzene-1,3-dithiol (BDT, >95%), sodium borohydride ($NaBH_4$, >95%) and potassium borohydride (KBH_4, >98%) were obtained from TCI Co. Ltd. Cesium borohydride ($CsBH_4$, >98%) was purchased from Katchem Ltd. All chemicals were used as received.

Synthesis of $Ag_{29}(BDT)_{12}(TPP)_4$ NCs (Ag_{29}-Na, Ag_{29}-K, and Ag_{29}-Cs NCs). Ag_{29} NCs with varied alkali metal cations were prepared according to a method reported in the literature[S1] expect that dichloromethane was used as a solvent in place of chloroform. Briefly, in a 50 mL glass vial, 36 μL of BDT was added to 28 mL of chloroform. To this solution, 13 mL of $AgNO_3$ solution in methanol (24 mM) was injected followed by the addition of TPP solution in chloroform (560 mg in 2.4 mL). The resulting mixture was allowed to stir for 15 min before the addition of an aqueous solution of reductant ($NaBH_4$, 28 mg; KBH_4, 39 mg; $CsBH_4$, 109 mg in 1.4 mL water). The mixture was stirred overnight (ca. 12h) to give orange precipitate. The precipitated NCs from the chloroform reaction solution were washed with methanol. The purified NCs were left to dry overnight under vacuum.

Crystallization of Ag_{29}-Na, -Cs, -K, -K' NCs. 1 mL of pyridine solution with 3 mg Ag_{29} NCs in a 2 mL glass vial was put in a 50 mL glass vial. 2 mL of ether was added to around the 2 mL of glass tube and sealed. After few weeks, a few red crystals were obtained.

Crystallization of Ag_{29}- K" NCs. Ag_{29}-K' crystals were soaked in toluene for a week.

Characterization. UV-vis absorption spectra were recorded with a JASCO V-670 spectrophotometer. PL spectra were measured by a JASCO FP8500. All the PL spectra were electronically corrected for instrumental response in FP8500 in the range of $\lambda_{PL} < 950$ nm. Single crystal X-ray diffraction (SCXRD) analyses was carried out using a Rigaku AFC/Mercury CCD diffractometer with Mo *Kα* radiation monochromated by graphite at 110 K. The crystal structures were solved by a direct method using SHELXT 2018/2 and refined by the full-matrix least-squares method on F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-2018/3. PL spectra of single-crystals were measured with an Olympus BX-51 polarizing microscope connected to a Hamamatsu PMA-11 photodetector (< 800 nm) through an optical fiber. Excitation to the crystals was performed with a high-pressure mercury lamp through a band path filter (330-385 nm) and the emission band was collected through a long path filter (>420 nm). PL decay measurement was performed on a Horiba Delta Flex time-correlated single-photon-counting (TCSPC) instrument with a 370 nm LED excitation light source.

Notification. The obtained crystals need careful handling because of rapid evaporation of ether and subsequent dissolution of NCs with pyridine molecules existing in the crystals.

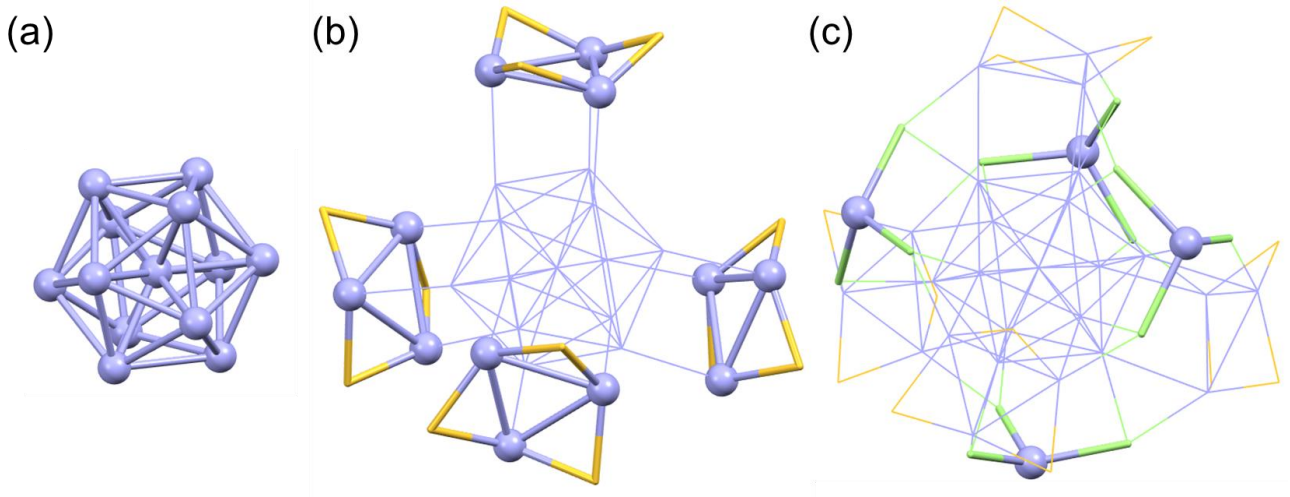

Fig. S1 X-ray crystal structure of $Ag_{29}(BDT)_{12}$ highlighting the Ag_{13} core and two motifs in the shell: (a) Ag_{13} centered icosahedral core; (b) 4 $Ag_3\mu_2$-S_3 crowns (c) 4 $Ag_1\mu_3$-S_3 motifs. Color code; violet, Ag; yellow, μ_2-S; light green, μ_3-S.

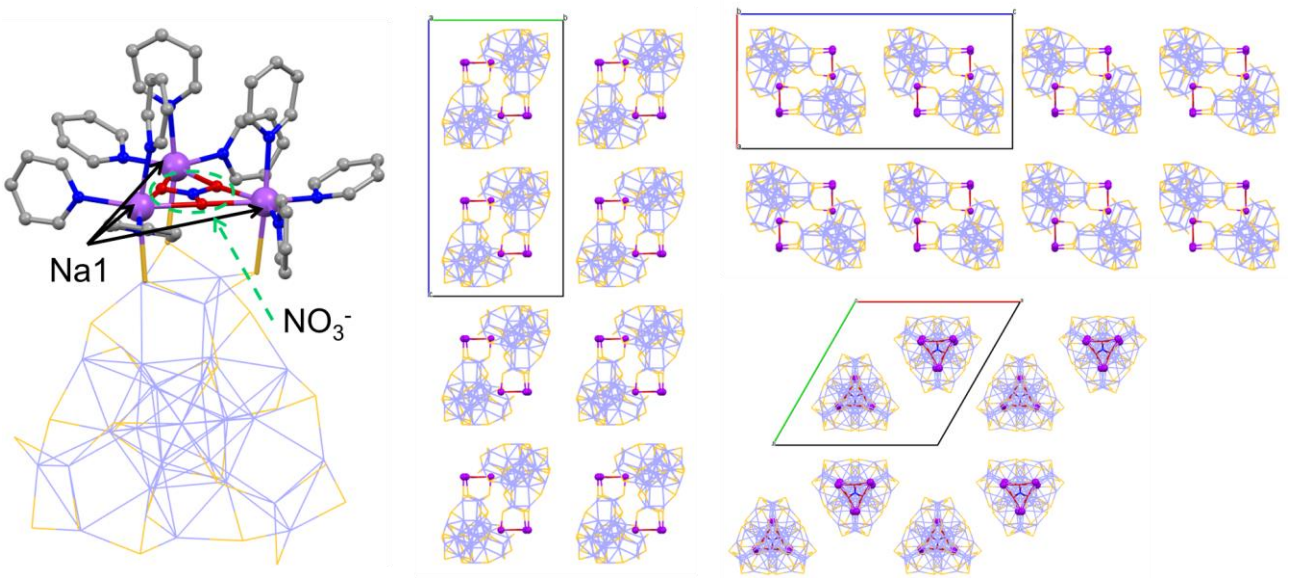

Fig. S2 Crystal structure and crystalline packing mode of **Ag_{29}-Na** NCs. The solvents, unbound Na ion, C, N atoms in NC ligands and H atoms are omitted for clarity. Color code; violet, Ag; yellow, S; purple, Na; blue, N; red, O.

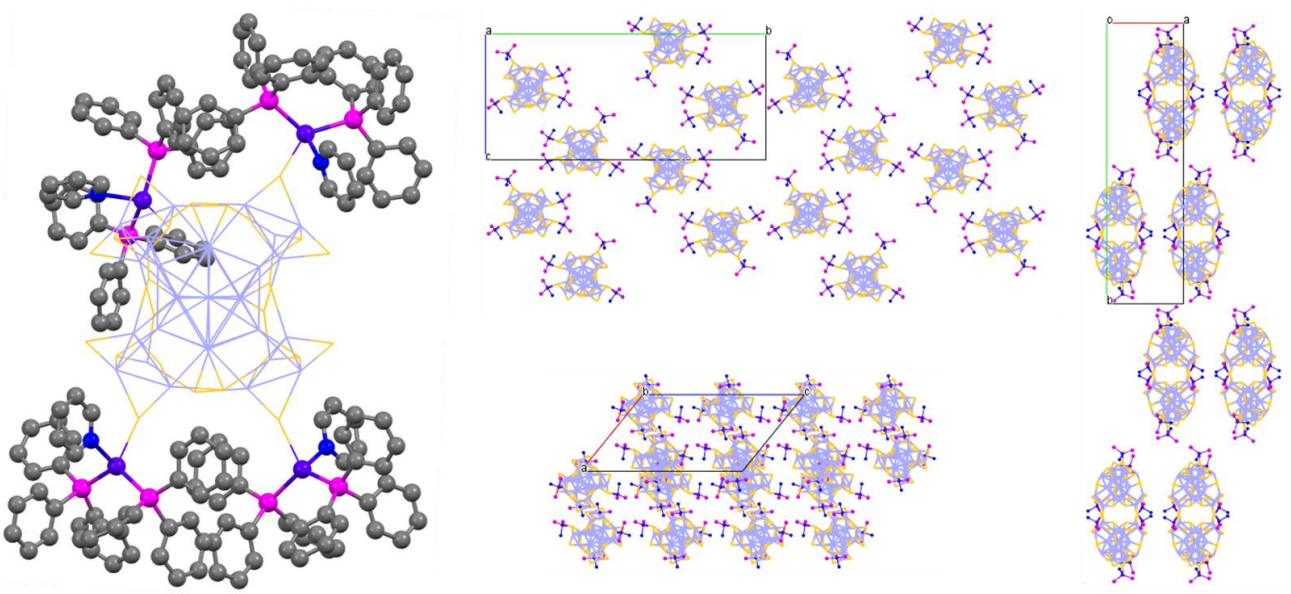

Fig. S3 Crystal structure and crystalline packing mode of Ag_{29}+Ag NCs. The solvents, C, N, P atoms in NC ligands and H atoms are omitted for clarity. Color code; violet, purple, Ag; yellow, S; blue, N; pink, P.

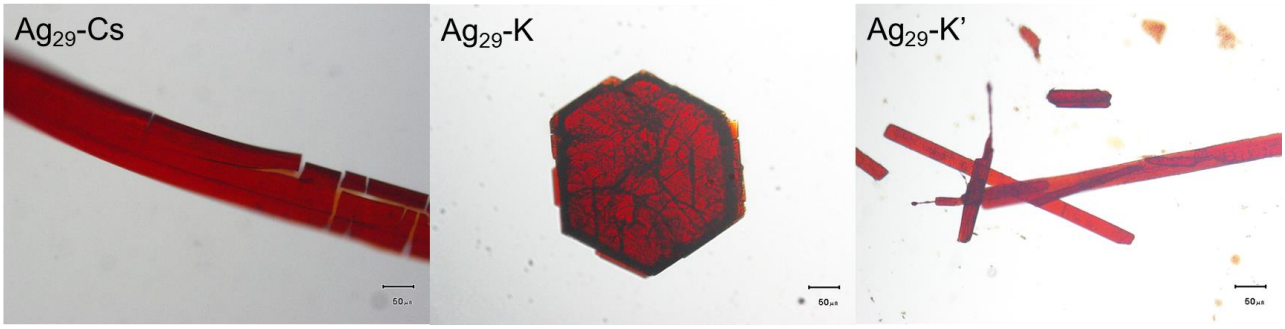

Fig. S4 Optical microscopic images of **Ag_{29}-Cs, K, K'** NCs crystals.

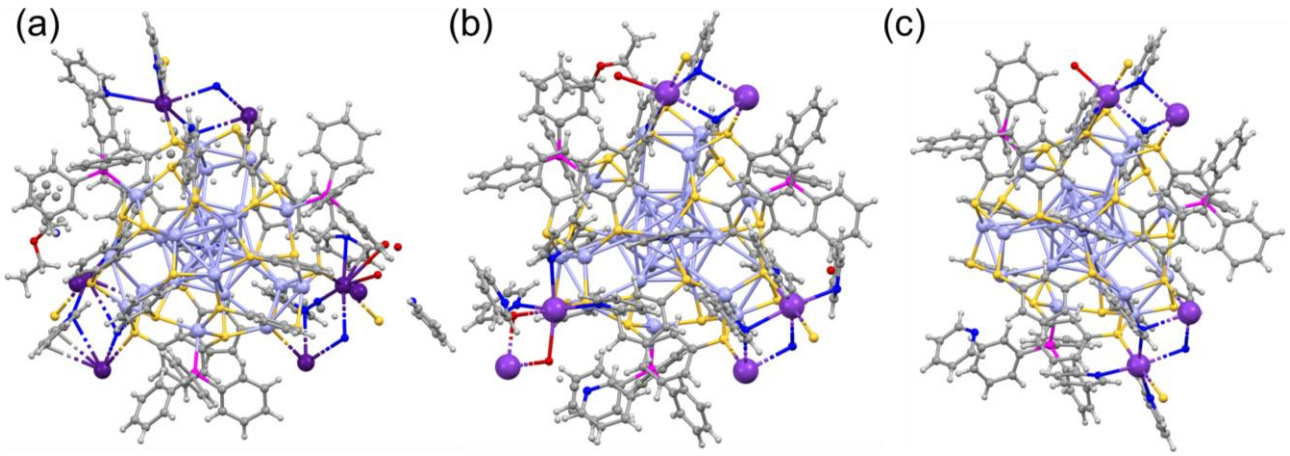

Fig. S5 Full structure of **Ag_{29}-Cs, K, K'**. Color code; violet, Ag; yellow, S; purple, Cs or K; blue, N; red, O.

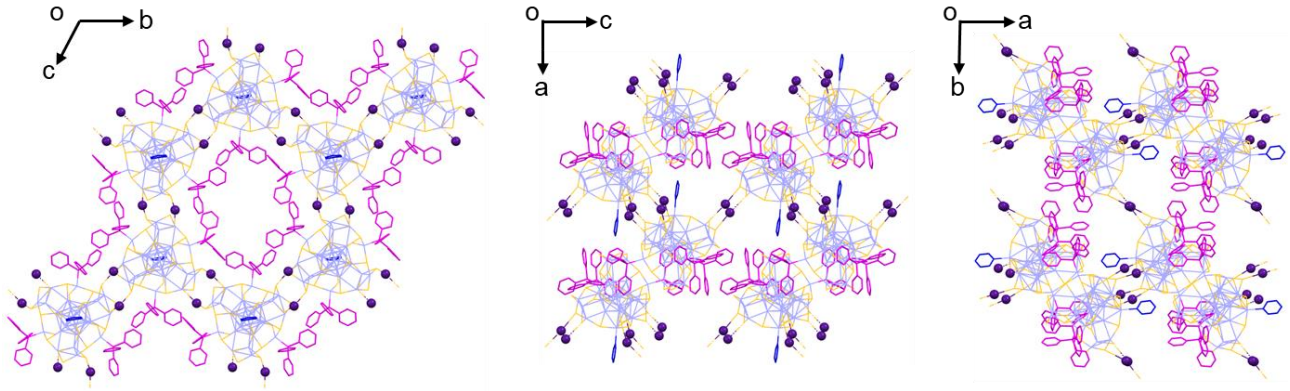

Fig. S6 Packing structure of **Ag_{29}-Cs** from different axis highlighting the TPP and pyridine sub ligands. Color code; violet, Ag; purple, Cs; yellow, S; pink, TPP; blue, pyridine.

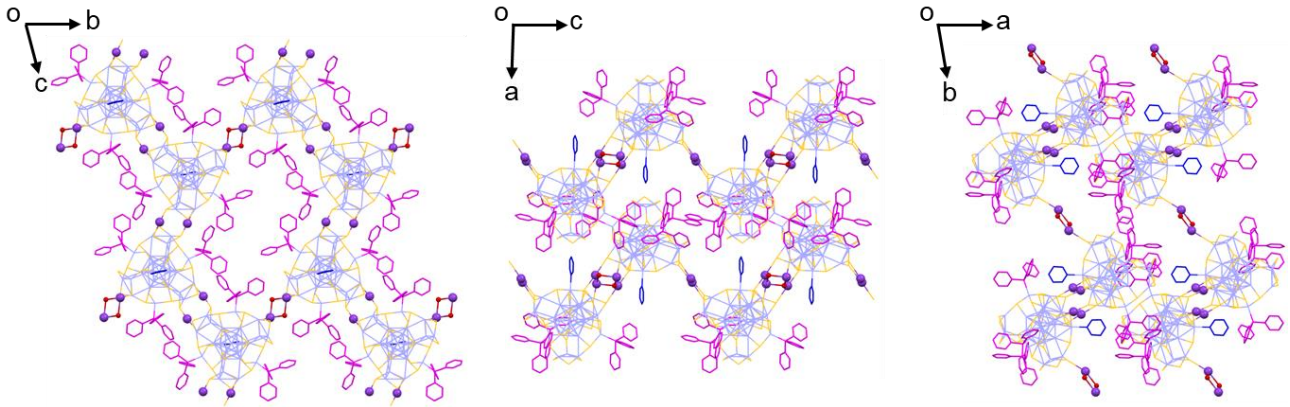

Fig. S7 Packing structure of **Ag_{29}-K** from different axis highlighting the TPP and pyridine sub ligands. Color code; violet, Ag; purple, K; yellow, S; pink, TPP; blue, pyridine; red, O.

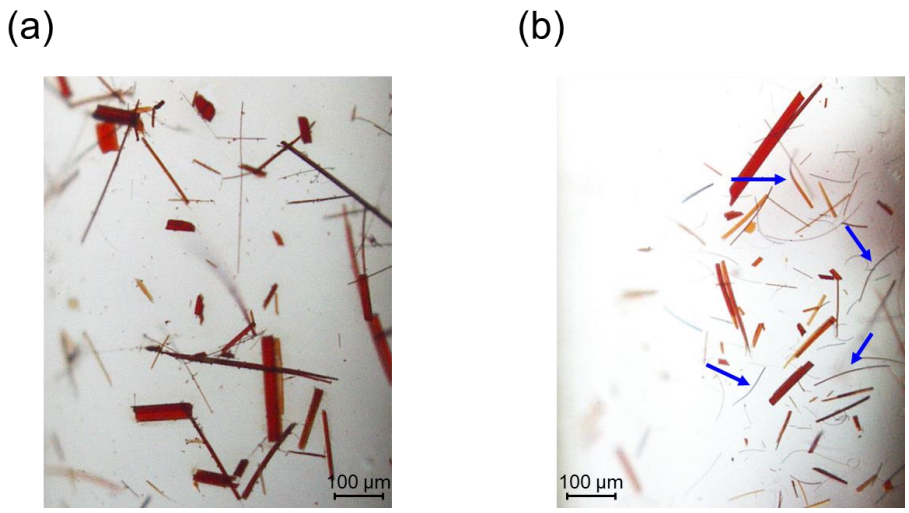

Fig. S8 Optical microscopic images of **Ag_{29}- K'** NCs crystals (a) before and (b) after toluene soaking.

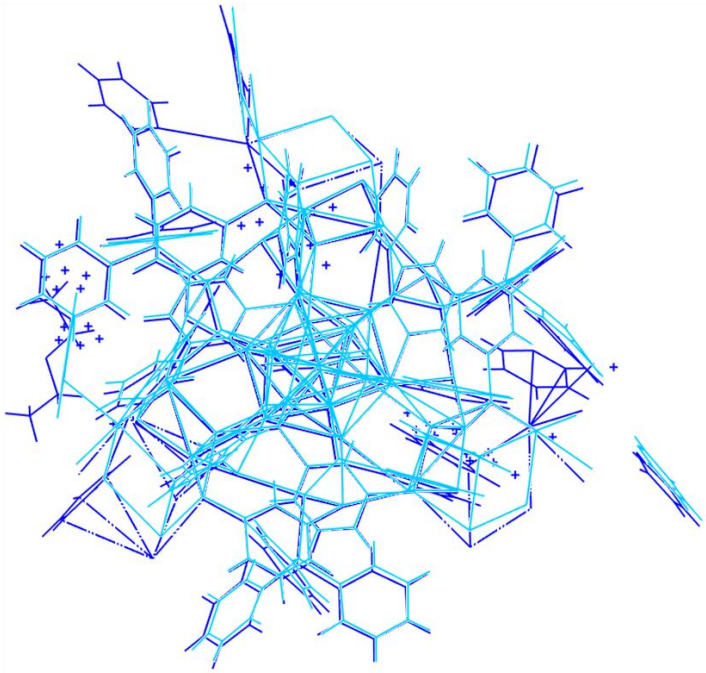

Fig. S9 Overlapping image of the unit structure of **Ag_{29}-K"** (light blue) and **Ag_{29}-Cs** (blue).

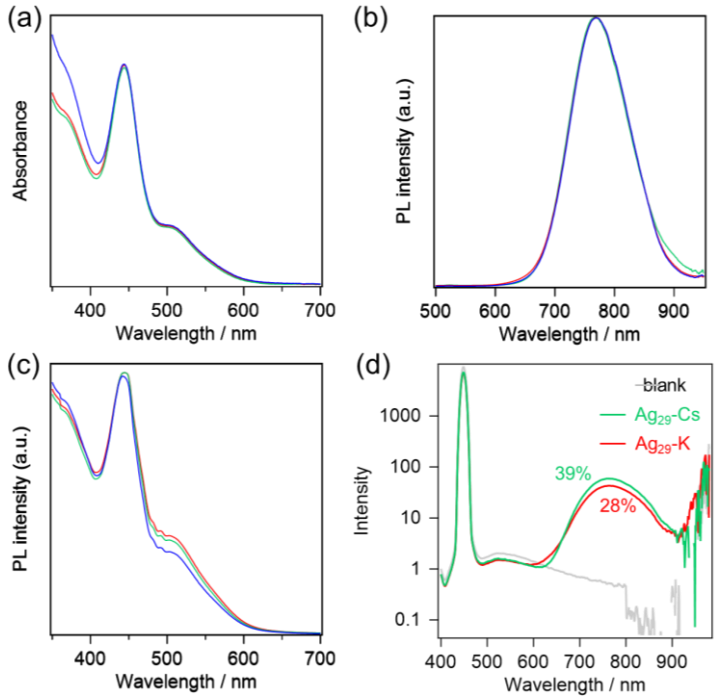

Fig. S10 (a) Absorption, (b) PL, and (c) excitation spectra of Ag_{29}-Cs (green), K (red) and Na (blue) NCs in pyridine. (d) PL spectra of Ag_{29}-Cs and K NCs in pyridine for the estimation of PLQY with the absolute method.

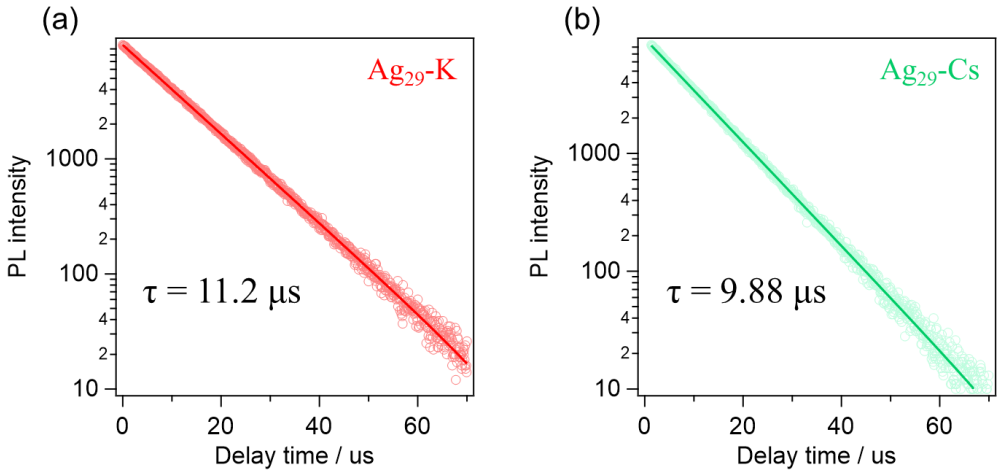

Fig. S11 PL lifetime measurement of (a) Ag_{29}-K and (b) Ag_{29}-Cs NCs in pyridine.

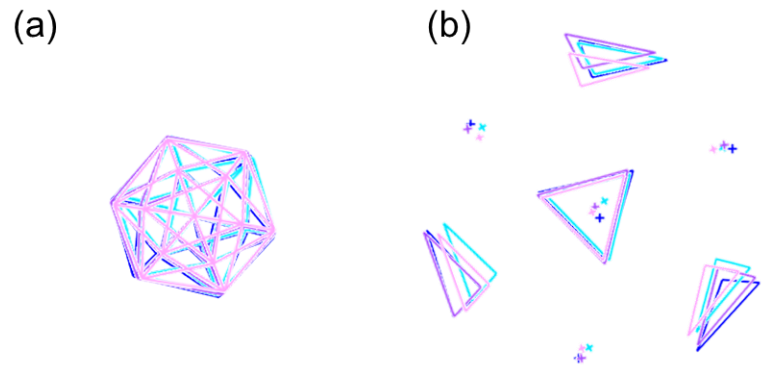

Fig. S12 Overlapping image of the (a) core and (b) shell structure of **Ag_{29}-Cs** (blue), **Ag_{29}-K** (pink), **Ag_{29}-K'** (purple) and **Ag_{29}-K"** (light blue). Only silver atoms were shown.

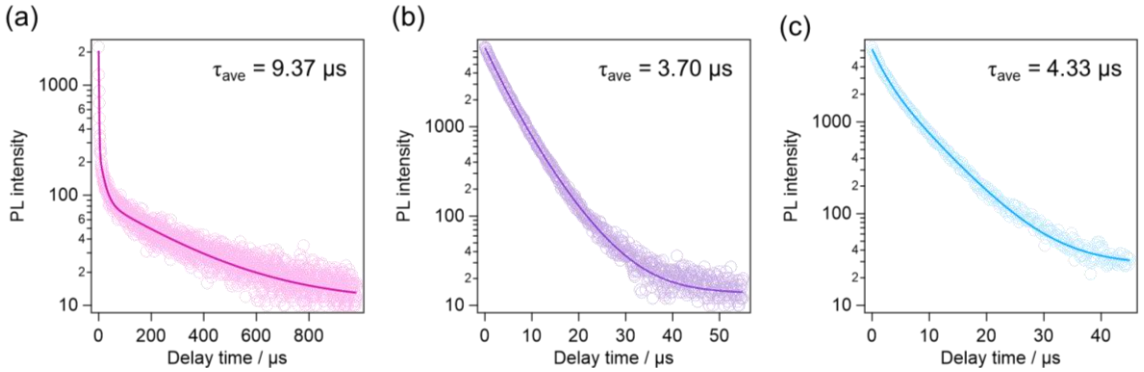

Fig. S13 Crystal PL lifetime measurement of **Ag_{29}-K** (pink), **Ag_{29}-K'** (purple) and **Ag_{29}-K"** (light blue).

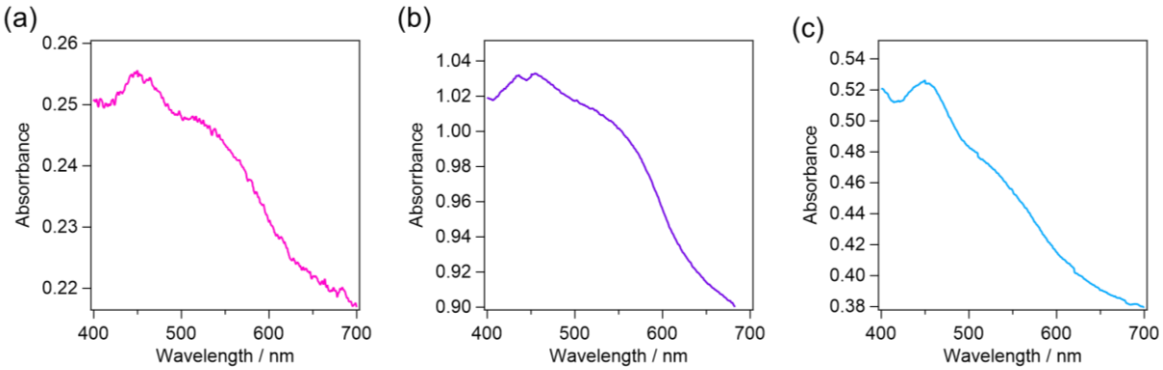

Fig. S14 Crystal absorption spectra of **Ag_{29}-K** (pink), **Ag_{29}-K'** (purple) and **Ag_{29}-K"** (light blue).

Table S1. Crystal data and structure refinement details.

	Ag_{29}-Na	Ag_{29}-Cs	Ag_{29}-K	Ag_{29}-K'	Ag_{29}-K"
Formula	$C_{132}H_{93}Ag_{29}N_{13}Na_3O_3S_{24}$, Na	$C_{170.3}H_{146.46}Ag_{29}Cs_3N_{8.06}O_{2.58}P_3S_{24}$	$C_{178.25}H_{152.15}Ag_{29}K_3N_{10.05}O_{2.45}P_3S_{24}$	$C_{161}H_{129}Ag_{29}K_2N_{75}O_{0.5}P_3S_{24}$	$C_{166}H_{135}Ag_{29}K_3N_8OP_3S_{24}$
Formula weight	5898.82	6736.39	6582.02	6238.48	6365.69
Molecular formula	$C_{87}H_{63}Ag_{29}N_3S_{24}$, $Na_3(C_5H_5N)_3$ NO_3, Na	$C_{131}H_{98}Ag_{29}NP_3S_{24}$, $Cs(C_5H_5N)_2$, $Cs(C_5H_5N)_{2.53}$, $Cs_{0.58}(C_5H_5N)_{1.16}$ $(H_2O)_{1.16}$, $Cs_{0.42}(C_5H_5N)_{0.42}$ $(H_2O)_{0.42}$, $C_4H_{10}O$, $(C_5H_5N)_{0.95}$ + solvent	$C_{131}H_{98}Ag_{29}N_1P_3S_{24}$, $K(C_5H_5N)_{2.55}(H_2O)_{0.45}$, K $(C_5H_5N)_2(H_2O)_{0.5}$, $K(C_5H5N)_3(H_2O)$, $(C_5H_5N)_{1.5}$, $(C_4H_{10}O)_{0.5}$ + solvent	$C_{131}H_{98}Ag_{29}NP_3S_{24}$, $K(C_5H_5N)_2(H_2O)_{0.5}$, $K(C_5H_5N)_3$, C_5H_5N + solvent	$C_{131}H_{98}Ag_{29}N_1P_3S_{24}$, $K(C_5H_5N)_2$, $K(C_5H_5N)_3$, $K(C_5H_5N)(H_2O)$, C_5H_5N + solvent
Crystal system	Trigonal	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-3c1	*P*-1	*P*-1	*P*-1	*P*-1
a (Å)	24.9668 (12)	18.8237 (2)	18.7241 (2)	18.6217 (3)	18.5877 (3)
b (Å)	24.9668 (12)	25.9820 (5)	25.7569 (2)	24.4444 (3)	26.3303 (4)
c (Å)	44.2740 (11)	27.2295 (5)	26.7364 (3)	27.0076 (4)	27.0946 (5)
α (deg)	90	117.517 (2)	75.7260 (10)	84.7969 (11)	117.9701 (17)
β (deg)	90	90.4220 (10)	89.4250 (10)	89.5296 (11)	90.7695 (13)
γ (deg)	120	90.8230 (10)	80.7010 (10)	82.4959 (11)	90.4463 (13)
V (Å^3)	23900 (2)	11808.1 (4)	12326.0 (2)	12138.2 (3)	11709.1 (4)
Z	4	2	2	2	2
ρ (g cm^{-3})	1.639	1.895	1.773	1.707	1.806
μ (mm^{-1})	2.564	3.070	2.557	2.574	2.688
F (000)	11164	6405	6321	5956	6088
Crystal size (mm)	0.3 × 0.3 × 0.03	0.35 × 0.03 × 0.03	0.63 × 0.18 × 0.03	0.48 × 0.10 × 0.03	0.48 × 0.11 × 0.03
Final R indices ($I >= 2\sigma(I)$)	R_1 = 0.0867, wR_2 = 0.2944	R_1 = 0.0703, wR_2 = 0.1889	R_1 = 0.0384, wR_2 = 0.1097	R_1 = 0.0750, wR_2 = 0.1935	R_1 = 0.1502, wR_2 = 0.3696
Final R indices (all)	R_1 = 0.1174, wR_2 = 0.3369	R_1 = 0.0918, wR_2 = 0.1982	R_1 = 0.0421, wR_2 = 0.1115	R_1 = 0.0937, wR_2 = 0.2137	R_1 = 0.1819, wR_2 = 0.3902*
CCDC number	2076349	2298858	2298942	2298943	2298944

Table S2. Comparison of bond lengths (average).

	Ag_{29}-Na	Ag_{29}-Cs	Ag_{29}-K	Ag_{29}-K’	Ag_{29}-K”
kernel Ag– icosahedral Ag	2.772 Å	2.771 Å	2.771 Å	2.771 Å	2.770 Å
icosahedral Ag– icosahedral Ag	2.914 Å	2.914 Å	2.913 Å	2.913 Å	2.913 Å
icosahedral Ag– crown Ag (Ag_3S_3)	3.159 Å	3.142 Å	3.151 Å	3.152 Å	3.139 Å
icosahedral Ag– motif Ag (Ag_1S_3)	3.065 Å	3.375 Å	3.367 Å	3.320 Å	3.383 Å
icosahedral Ag– motif Ag bound to pyridine (Ag_1S_3)	3.091 Å	3.069 Å	3.051 Å	3.039 Å	3.039 Å
icosahedral Ag– motif Ag bound to TPP (Ag_1S_3)	—	3.477 Å	3.472 Å	3.413 Å	3.498 Å
crown Ag (Ag_3S_3)– crown Ag (Ag_3S_3)	3.113 Å	3.163 Å	3.125 Å	3.112 Å	3.119 Å
crown Ag (Ag_3S_3)– crown μ_2-S (Ag_3S_3)	2.463 Å	2.460 Å	2.468 Å	2.469 Å	2.460 Å
crown Ag (Ag_3S_3)– crown μ_3-S (Ag_3S_3)	2.465 Å	2.479 Å	2.486 Å	2.484 Å	2.487 Å
crown S (Ag_3S_3)– alkali metal	2.928 Å	3.492 Å	3.296 Å	3.282 Å	3.263 Å

Table S3. Absolute PLQY and PL lifetime of Ag_{29}-Na, K, Cs and Ag NCs in pyridine solutions.

Sample	λ_{PL}	PLQY	Lifetime
Ag_{29}-Na[S2]	770 nm	33%	9.16 μs
Ag_{29}-K	770 nm	28%	11.2 μs
Ag_{29}-Cs	770 nm	39%	9.88 μs
Ag_{29}+Ag[S3]	770 nm	39%	9.77 μs

Table S4. Fitting results of PL lifetime data of **Ag_{29}-K**, **Ag_{29}-K'** and **Ag_{29}-K"**.

Sample	τ_1 (μs)	A_1[1]	τ_2 (μs)	A_2[1]	τ_3 (μs)	A_3[1]	τ_{ave} (μs)[2]
Ag_{29}-K	1.41	0.92	18.4	0.06	277	0.03	9.37
Ag_{29}-K'	2.19	0.37	4.60	0.63	-	-	3.70
Ag_{29}-K"	2.05	0.49	6.54	0.51	-	-	4.33

[1] A_1, A_2: Normalized pre-exponential factor

[2] The averaged decay time is defined by: $\tau_{ave} = \frac{\sum_j A_j t_j}{\sum_j A_j}$

Reference

S1. L. G. AbdulHalim, M. S. Bootharaju, Q. Tang, S. Del Gobbo, R. G. AbdulHalim, M. Eddaoudi, D. E. Jiang and O. M. Bakr, *J. Am. Chem. Soc.*, 2015, **137**, 11970–11975

S2. W. Ishii, S. Katao, Y. Nishikawa, Y. Okajima, A. Hatori, M. Ehara, T. Kawai and T. Nakashima, *Chem. Commun*., 2021, **57**, 6483–6486.

S3. W. Ishii, Y. Okayasu, Y. Kobayashi, R. Tanaka, S. Katao, Y. Nishikawa, T. Kawai and T. Nakashima, *J. Am. Chem. Soc.,* 2023, **145**, 11236–11244.