Supporting Information

Isolation of Mixed Valence Charge-Neutral Ag12, and Dicationic Ag10 Nano-Clusters Stabilized by Carbene-Phosphaalkenides

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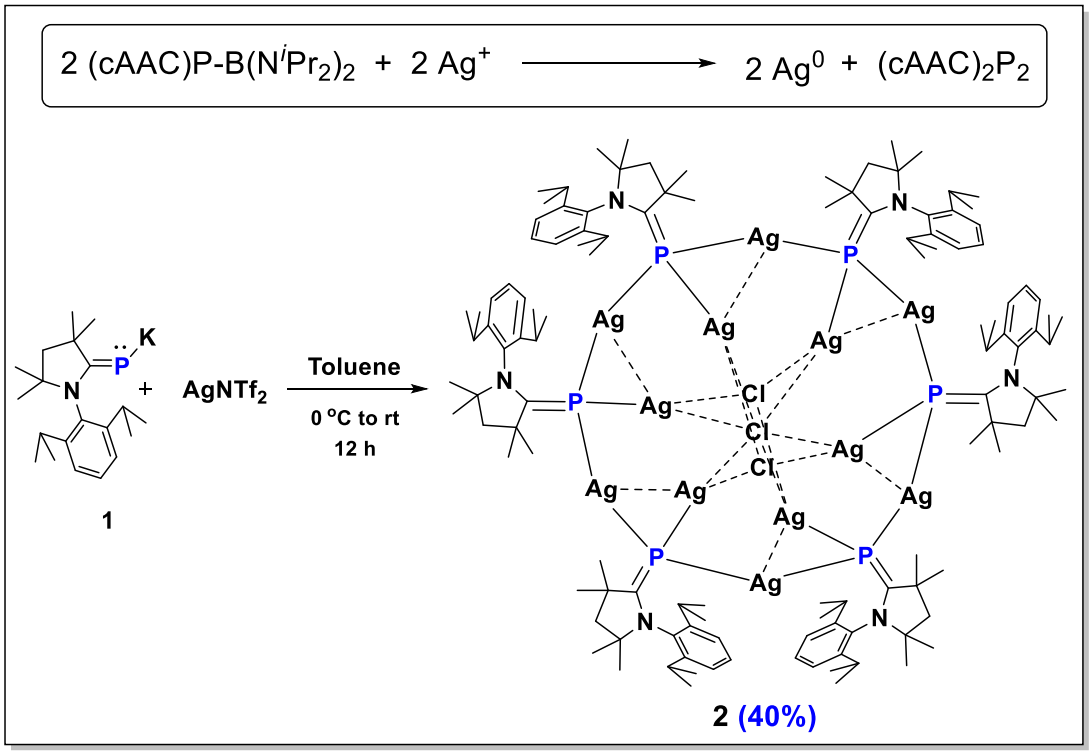
S1. General Remarks

All manipulations were performed using either standard Schlenk line techniques under inert argon atmosphere or in an argon-filled MBraun Eco Plus glove box, where O_2 and H_2O levels were kept below 0.1 ppm. All glassware were oven-dried (150 °C) prior to use. Solvents obtained from an MBraun Solvent Purification System (SPS) were further dried by standard methods of refluxing with Na/K alloy for two days, followed by vacuum distillation over 4 Å molecular sieves under argon. Cyclic alkyl(amino) carbene (cAAC) salts,[1] free cAACs,[1] cAAC=P-Cl,[2] cAAC=PK [3] and [cAAC=P-B(N^iPr_2)$_2$] [4] were synthesized according to the literature reported procedures. ^1H, ^{13}C {^1H}, and ^{31}P NMR spectra were recorded on Bruker Neo Avance 400 MHz. Melting points were measured in sealed glass tubes on a Digital Stuart Melting Point Apparatus. EPR spectra were obtained using an X-band (8.75-9.65GHz) JEOL Model JES FA200 EPR spectrometer at 293 K. UV-visible absorption spectra were recorded using an Agilent Cary-60 UV-Vis Spectrophotometer. The ESI-MS of the reported clusters were recorded on Agilent Technologies Q-TOF 6545 instruments. Single crystal X-Ray diffraction data were collected on a Bruker D8 venture Apex4 HEED diffractometer, with helios optics mono-chromated Mo-Kα (λ = 0.71073 Å) radiation at 100 K. The data was integrated using SAINT PLUS and absorption correction was done using multi-scan absorption correction method (SADABS). Thermogravimetric analysis (TGA) of the samples were performed on TA Instruments model-Q500 by loading 4.65 mg of sample onto a pan and heated from room temperature to 900 °C at a heating rate of 20 °C/min under the flow of nitrogen at the flow rate of 60 mL/min. The X-ray photo-electron spectroscopy (XPS) measurements were carried out using a Thermo Scientific K-ALPHA$^+$ X-ray photo-electron spectrometer using a mono-chromated Al Kα radiation with 6mA beam current and 12 KV.

S2. Detailed syntheses of the nano-clusters (NCs) 2 and 4

Synthesis of neutral NC [(Me$_2$-cAAC=P)$_6$Ag$_{12}$Cl$_3$] (2)



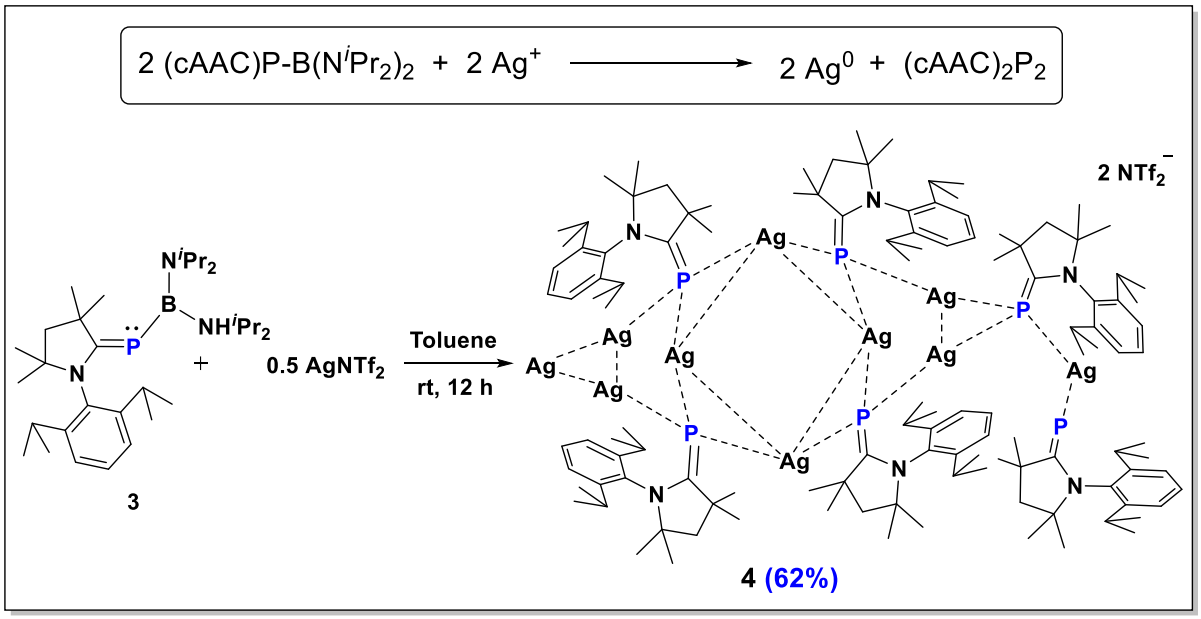
Scheme S1. Synthesis of the neutral NC [(Me$_2$-cAAC=P)$_6$Ag$_{12}$Cl$_3$] (**2**).

To an oven dried 50 mL Schlenk flask, [Me$_2$-cAAC=PK] (**1**) (190 mg, 0.534 mmol, 1 equiv) was taken, and to another 100 mL Schlenk flask, AgNTf$_2$ (142.5 mg, 0.367 mmol, 1.45 equiv) was taken. 15 mL of anhydrous toluene was added separately in each of the flasks, and stirred until clear a solution is obtained. Both the flasks were cooled to 0 °C (using liquid nitrogen/iso-propanol bath) and the AgNTf$_2$ solution was added to the flask containing [Me$_2$-cAAC=PK] through cannula under constant stirring. After this, the temperature was maintained at 0 °C for 1 h, then the reaction mixture was brought slowly to room temperature (rt) and allowed to stir for another 12 h. The color of the reaction mixture changed from orange to dark brownish-red with the formation of reddish-brown precipitate. The reaction mixture was dried, given wash with *n*-hexane, filtered, and evaporated the solvent from filtrate to complete dryness under reduced pressure. The crystalline solid was dissolved in anhydrous DCM to produce dark reddish-brown solution, which was concentrated up to 1 mL under reduced pressure and stored for crystallization in a freezer kept at -40 °C. After one-

week, dark red block shaped crystals of [(Me_2-cAAC=P)$_6Ag_{12}Cl_3$] (**2**) were obtained (65 mg, 40%).

Decomposition point of 2: 205-207 °C.

Synthesis of mono-cationic NC [(Me_2-cAAC=P)$_6Ag_{10}$](NTf_2)$_2$ (4)



Scheme S2. Synthesis of NC [(Me_2-cAAC=P)$_6$(Ag)$_{10}$](NTf_2)$_2$ (**4**).

To an oven-dried 100 mL Schlenk flask, [Me_2-cAAC=P−B(N(^{i}Pr)$_2$)$_2$] (**3**) (150 mg, 0.28 mmol, 1 equiv), and $AgNTf_2$ (58.60 mg, 0.19 mmol, 0.5 equiv) were taken. Added 10 mL of anhydrous toluene, and stirred at rt for 12 h. The reaction color changed from golden-yellow to brownish-red with the formation of greenish-brown precipitate. The reaction mixture was filtered, and the greenish-brown colored residue was completely dried under reduced pressure. The residue was then further dissolved in anhydrous DCM to obtain a greenish-yellow color solution, which was further concentrated up to 1-2 mL under reduced pressure, and stored for crystallization at 0 °C to obtain the yellow block shaped crystals of [(Me_2-cAAC=P)$_6Ag_{10}$](NTf_2)$_2$ (**4**) in 62% yield (95 mg).

Note: The redox non-innocent (cAAC=P)$^-$ ligands are *in situ* generated by the reaction of $AgNTf_2$ with the boryl-phosphaalkene (cAAC)P-B(N^{i}Pr$_2$)$_2$ (**3**) via the cleavage of the P−B bond with the help of triflate anion (OTf^-), which acts as a weak nucleophile. The equivalent numbers of the *in situ* generated $(cAAC)P^-$ anions are oxidized to produce the corresponding radical Me_2-cAACP$^\bullet$,[3] which undergoes dimerization to produce the

bis-phosphinidene $(Me_2\text{-}cAAC)_2P_2$, leading to the generation of Ag(0) atoms in solution for the formation of the mixed valence $Ag^{0/I}$ NCs. The formation of the corresponding cAAC-supported bis-phosphinidene $(Me_2\text{-}cAAC)_2P_2$ has been supported by the ^{31}P NMR spectroscopic measurements of the crude reaction mixture (55.1 ppm).

Decomposition point of 4: 165-167 °C.

S3. Cyclic voltammetry (CV) studies of NCs 2 and 4.

The cyclic voltammetry (CV) studies of NCs **2, 4** have been performed at a Metrohm-Autolab204 Potentiostat. All experiments have been performed under argon atmosphere in deoxygenated and anhydrous DCM solution of 0.1 M $[n\text{-}Bu_4N]PF_6$ or $[n\text{-}Bu_4N]PClO_4$. The setup consisted of a glassy carbon (GC) working electrode (WE), a Pt wire as the counter electrode (CE) and Ag wire as the reference electrode (RE). The recorded voltammograms have been referenced to the internal standard $(Cp)_2Fe/(Cp)_2Fe^+$, which was added after the measurements.

S3.1. Cyclic voltammetry studies of $[(Me_2\text{-}cAAC{=}P)_6Ag_{12}Cl_3]$ (2)

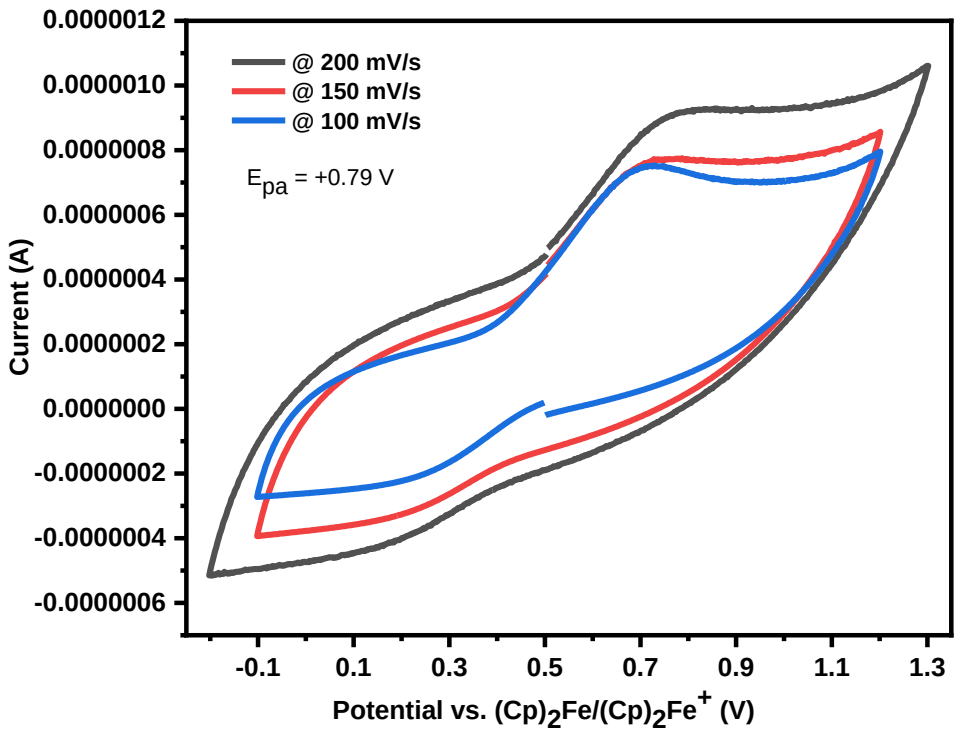


Figure S1. Cyclic voltammograms of **2** in DCM containing 0.1 M $[n\text{-}Bu_4N]PClO_4$ as the electrolyte (CE: Pt, WE: GC, RE: Ag).

S3.2. Cyclic voltammetry studies of $[(Me_2\text{-}cAAC{=}P)_6Ag_{10}](NTf_2)_2$ (4)

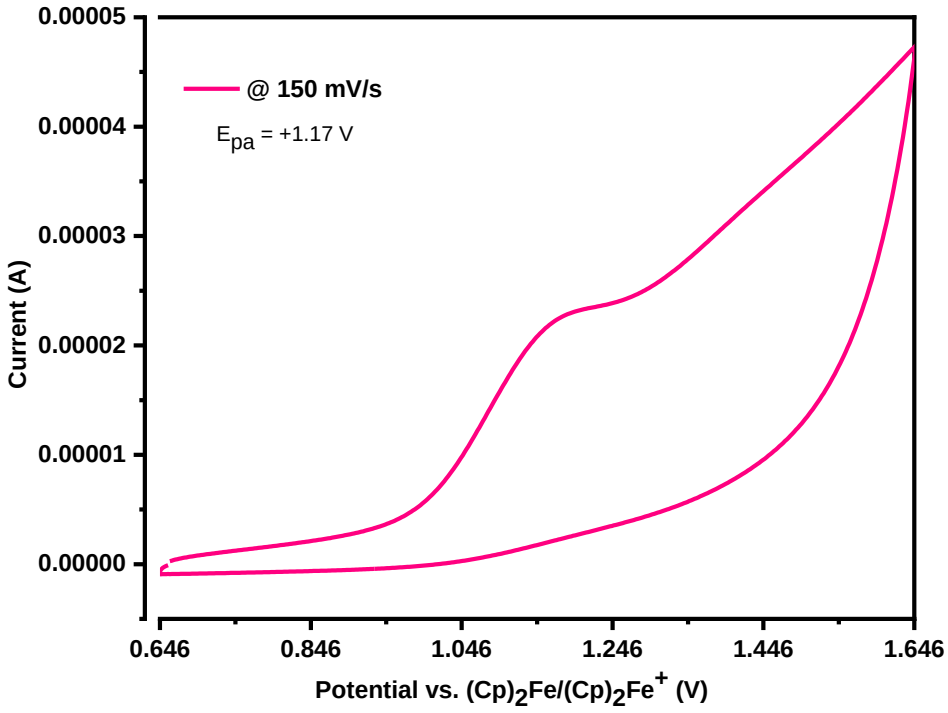


Figure S2. Cyclic voltammograms of **4** in DCM containing 0.1 M [*n*-Bu_4N]PF_6 as the electrolyte (CE: Pt, WE: GC, RE: Ag).

S4. EPR spectra of NCs 2, 4

The sample preparation was done under argon atmosphere using the glove box technique. 5 mg of each NCs **2, 4** were taken in oven-dried sample vials and added distilled DCM (0.1 mL) separately. The light greenish-yellow color solutions were further diluted by the addition of more DCM and transferred to quartz capillary tubes. The capillary tubes with the complexes used for measurements were sealed adequately using silicon grease and melted wax to maintain the argon atmosphere throughout the experiment.

S4.1. EPR spectrum of [(Me_2-cAAC=P)$_6$$Ag_{12}$$Cl_3$] (2) in DCM

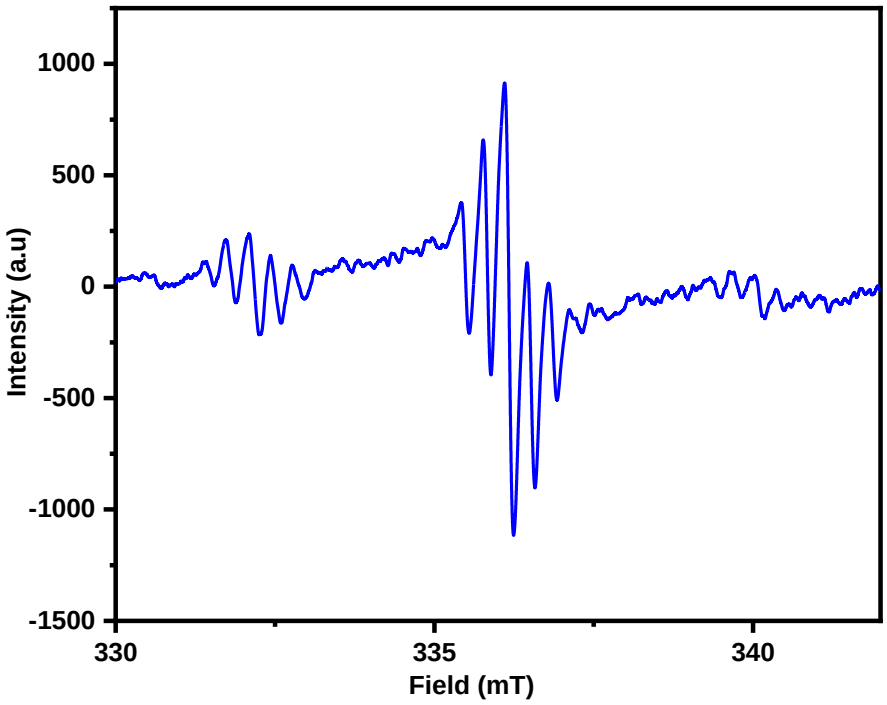


Figure S3. X-band ESR spectrum of [(Me_2-cAAC=P)$_6$$Ag_{12}$$Cl_3$] (**2**) in DCM at 293 K.

Calculation of Lande factor (*g*):

$$g = \frac{h\nu}{\mu_B H}$$

(h = Planck's constant, ν = Operating frequency, μ_B = Bohr magneton, H = Magnetic field and g = Lande factor)

h = 6.626 x 10^{-34} J.S, v = 9.436 GHz = 9.436 x 10^9 Hz, μ_B = Bohr magneton = 9.2740 x 10^{-24} J/T, H = magnetic field = data on x-axis in T = 336.1708 mT = 336.1671 x 10^{-3} T

$$g = \mathbf{2.0056}$$

S4.2. EPR spectrum of [(Me_2-cAAC=P)$_6$$Ag_{10}$]($NTf_2$)$_2$ (4) in DCM

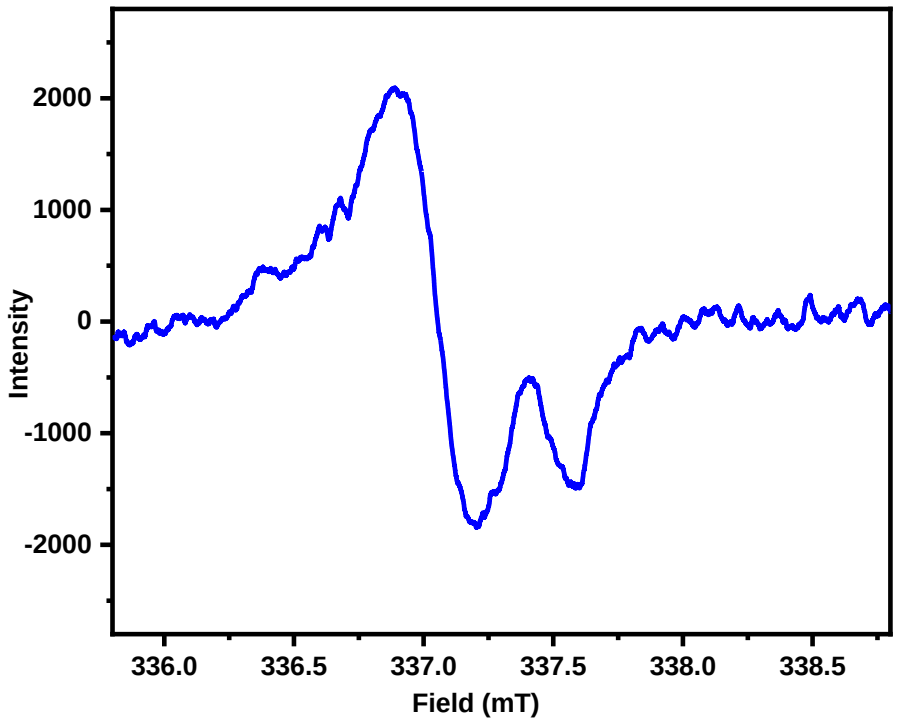


Figure S4. X-band ESR spectrum of [(Me_2-cAAC=P)$_6$$Ag_{10}$]($NTf_2$) (**4**) in DCM at 293 K.

$$\boldsymbol{g} = \frac{6.626 \times 10^{-34}\, Js^{-1} \times 9.435 \times 10^{69}\, s^{-1}}{9.2740 \times 10^{-24}\, JT^{-1} \times 337.05 \times 10^{-3}\, T}$$

$$\boldsymbol{g} = \frac{6.2520 \times 10^{-24}}{3.1258 \times 10^{-24}}$$

$$\boldsymbol{g} = \mathbf{2.0001}$$

S5. ESI-MS spectra of NCs 2, 4

S5.1. ESI-MS spectrum of complex [(Me$_2$-cAAC=P)$_6$Ag$_{12}$Cl$_3$] (2) in DCM.

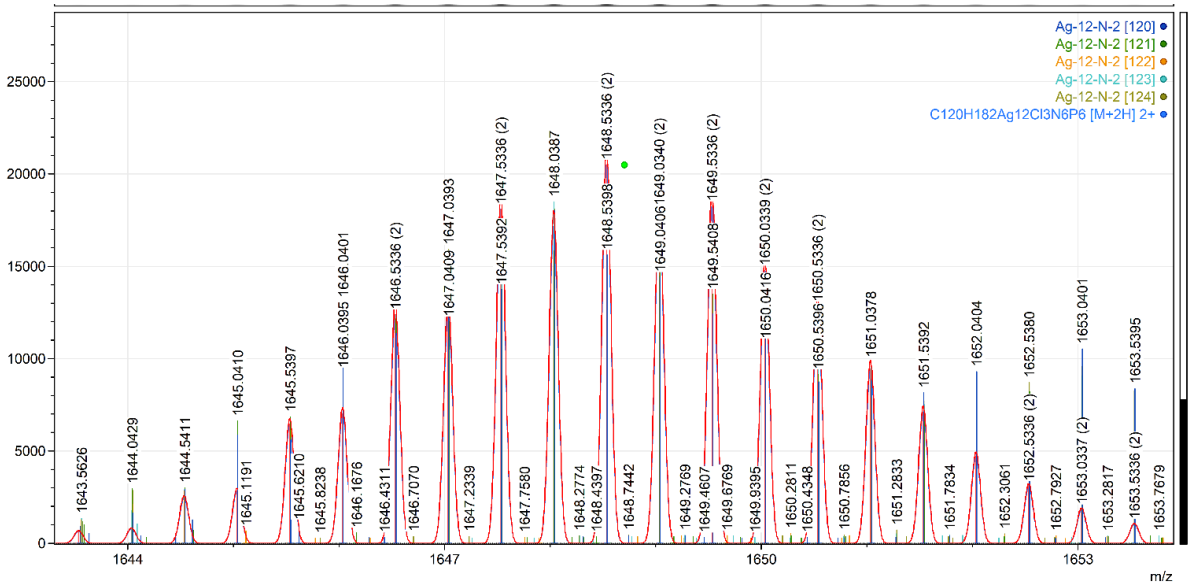


Figure S5. Experimental (green) and simulated (red) ESI-MS mass spectra of corresponding ionic fragment isotopic pattern is given by [$C_{120}H_{186}Ag_{12}N_6P_6Cl_3$ – 2H (radical)]$^{2+}$.

S5.2. ESI-MS spectrum of complex [(Me$_2$-cAAC=P)$_6$(Ag)$_{10}$](NTf$_2$)$_2$ (4) in DCM.

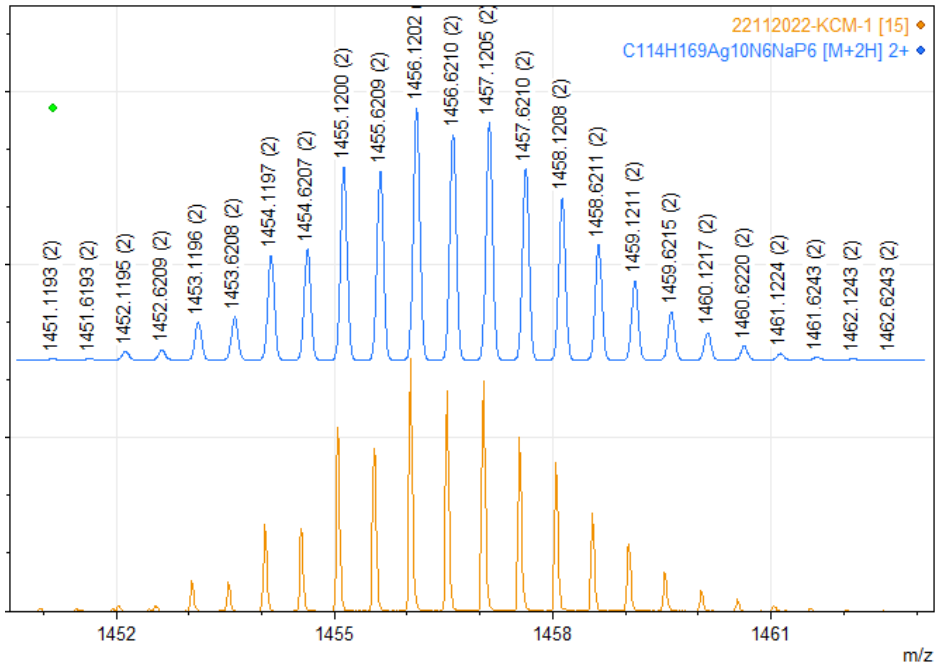


Figure S6. Experimental (bottom) and simulated (top) ESI-MS mass spectra of [(Me$_2$-cAACP)$_6$Ag$_{10}$ + Na – 2C$_3$H$_7$ – H] dication. Me$_2$-cAACP = $C_{20}H_{31}NP$.

S6.1 UV-vis absorption spectrum of [(Me_2-cAAC=P)$_6Ag_{12}Cl_3$] (2) in THF solution at room temperature (298 K)

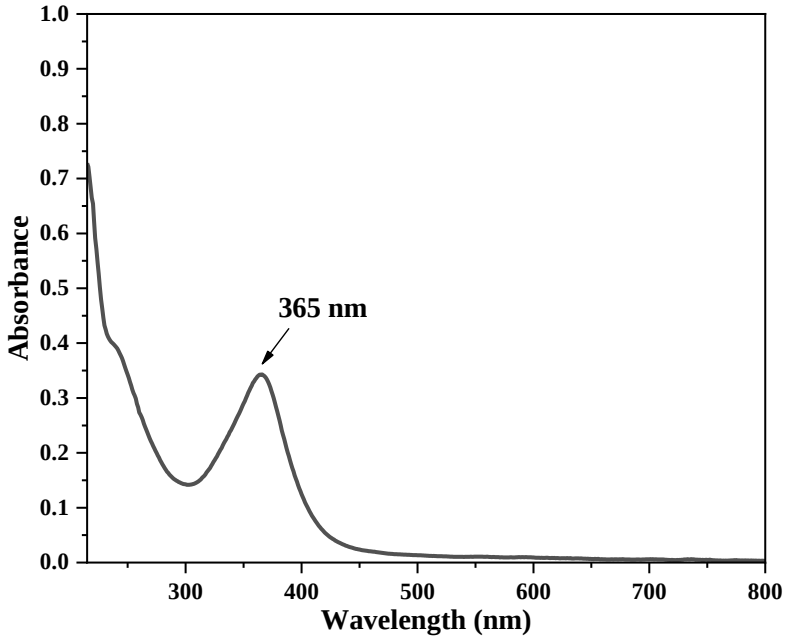


Figure S7. UV-vis Absorption spectrum of [(Me_2-cAAC=P)$_6Ag_{12}Cl_3$] (**2**) in THF solution at 298 K. The absorption maximum (λ_{max}) was observed at 365 nm.

S6.2 UV-vis absorption spectrum of [(Me_2-cAAC=P)$_6(Ag)_{10}$](NTf_2)$_2$ (4) in THF solution at 298 K

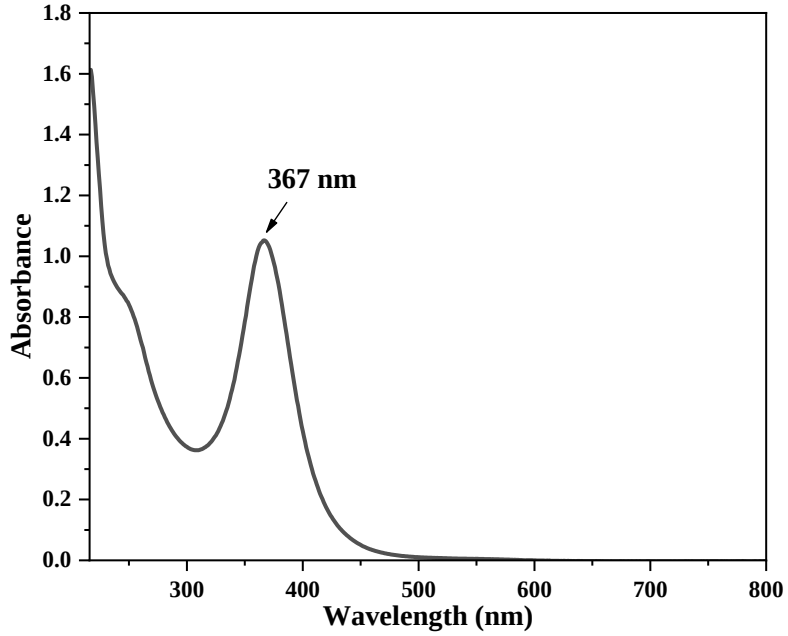


Figure S8. UV-vis absorption spectrum of [(Me_2-cAAC=P)$_6(Ag)_{10}$](NTf_2)$_2$ (**4**) in THF solution at 298 K. The λ_{max} was observed at 367 nm.

S7. X-ray crystallographic analysis of NCs 2, and 4

The single crystal X-ray data were collected on a **Bruker D8 VENTURE** diffractometer equipped with **PHOTON III C28** detector using **IμS 3.0 microfocus** sealed X-ray source with **Molybdenum Kα (λ = 0.71073 Å) radiation**. Complete data set was collected following the strategies generated using the APEX4[5] module of the Bruker software suite. The data reduction was carried out using SAINTPLUS[5] and multi-scan absorption correction was performed using the program **SADABS**.[5] The crystal structures were solved by **intrinsic phasing method (SHELXT)**[6] and was refined with full-matrix least squares on F2 using **ShelXle**[7] plug-in included in APEX4. All non-hydrogen atoms were refined anisotropically.

Table S1. X-ray crystallographic parameters for nanoclusters **2**, and **4.**

Crystal formula	**$C_{120}H_{186}Ag_{12}Cl_3N_6P_6$**	**$C_{124}H_{186}Ag_{10}F_{12}N_8O_8P_6S_4$**
Complex	**2**	**4**
M_r	3299.35	3537.56
CCDC Number	2242239	2194453
Crystal system	Trigonal	Triclinic
Space group	R -3	P -1
Temperature (K)	100	100
***a* (Å)**	32.5258(13)	16.8356(9)
***b* (Å)**	32.5258(13)	22.3238(14)
***c* (Å)**	16.6904(10)	26.6877(15)
***α* (°)**	90	70.721(2)
***β* (°)**	90	73.976(2)
***γ* (°)**	120	71.123(2)
***V* (Å^3)**	15291.6(15)	8796.2(9)
Z	3	2

λ (Å)	0.71073	0.71073
μ (mm^{-1})	1.24	1.25
R_{int}	0.051	0.059
R_1 **[I > 2σ(I)]**	0.083	0.070
$wR(F^2)$	0.276	0.235
No. of measured reflections	211782	393575
Independent reflections	6982	46090
observed [I > 2σ(I)] reflections	4867	34011
$\Delta\rho_{max}$ **(e** $Å^{-3}$**)**	1.67	3.25
$\Delta\rho_{min}$ **(e** $Å^{-3}$**)**	−1.64	−2.10
GooF	1.13	1.04

Bond length (Å) of **2**.

Ag1—Ag2^{i}	3.0244(10)	C11—H11	1
Ag1—Ag2	2.8826(10)	C11—C12	1.551(16)
Ag1—Cl1	2.4530(14)	C11—C19	1.538(12)
Ag1—Cl2	2.572(7)	C12—H12A	0.98
Ag1—P2	2.455(3)	C12—H12B	0.98
Ag2—P2^{ii}	2.379(2)	C12—H12C	0.98
Ag2—P2	2.401(2)	C13—H13	1
P2—C10	1.750(9)	C13—C14	1.552(13)
N1—C1	1.471(10)	C13—C20	1.508(13)
N1—C7	1.518(12)	C14—H14A	0.98
N1—C10	1.339(10)	C14—H14B	0.98
C1—C2	1.379(13)	C14—H14C	0.98
C1—C6	1.401(12)	C15—H15A	0.98

C2—C3	1.411(13)	C15—H15B	0.98
C2—C11	1.535(13)	C15—H15C	0.98
C3—H3	0.95	C16—H16A	0.98
C3—C4	1.436(14)	C16—H16B	0.98
C4—H4	0.95	C16—H16C	0.98
C4—C5	1.360(15)	C17—H17A	0.98
C5—H5	0.95	C17—H17B	0.98
C5—C6	1.396(13)	C17—H17C	0.98
C6—C13	1.483(14)	C18—H18A	0.98
C7—C8	1.484(14)	C18—H18B	0.98
C7—C15	1.552(18)	C18—H18C	0.98
C7—C16	1.530(16)	C19—H19A	0.98
C8—H8A	0.99	C19—H19B	0.98
C8—H8B	0.99	C19—H19C	0.98
C8—C9	1.445(13)	C20—H20A	0.98
C9—C10	1.519(12)	C20—H20B	0.98
C9—C17	1.482(17)	C20—H20C	0.98
C9—C18	1.670(19)		

Bond angle (°) of **2**.

Ag2—Ag1—Ag2^{i}	90.30(3)	C9—C8—H8A	109.1
Cl1—Ag1—Ag2	103.13(4)	C9—C8—H8B	109.1
Cl1—Ag1—Ag2^{i}	99.21(4)	C8—C9—C10	104.7(8)
Cl1—Ag1—Cl2	70.8(2)	C8—C9—C17	109.3(11)
Cl1—Ag1—P2	133.69(8)	C8—C9—C18	108.2(10)
Cl2—Ag1—Ag2	136.83(3)	C10—C9—C18	102.1(9)
Cl2—Ag1—Ag2^{i}	132.70(3)	C17—C9—C10	111.5(9)
P2—Ag1—Ag2^{i}	50.17(5)	C17—C9—C18	119.9(11)
P2—Ag1—Ag2	52.73(5)	N1—C10—P2	125.4(7)
P2—Ag1—Cl2	155.0(2)	N1—C10—C9	107.4(7)
Ag1—Ag2—Ag1^{ii}	70.08(6)	C9—C10—P2	126.8(6)
P2—Ag2—Ag1	54.45(7)	C2—C11—H11	108.5
P2^{ii}—Ag2—Ag1^{ii}	52.40(7)	C2—C11—C12	110.5(8)
P2^{ii}—Ag2—Ag1	110.99(6)	C2—C11—C19	110.6(8)

P2—Ag2—Ag1^{ii}	111.17(6)	C12—C11—H11	108.5
P2^{ii}—Ag2—P2	163.21(11)	C19—C11—H11	108.5
Ag1^{iii}—Cl1—Ag1^{ii}	92.47(3)	C19—C11—C12	110.1(10)
Ag1^{iii}—Cl1—Ag1^{iv}	87.54(3)	C11—C12—H12A	109.5
Ag1^{v}—Cl1—Ag1^{i}	87.53(3)	C11—C12—H12B	109.5
Ag1^{v}—Cl1—Ag1^{iv}	92.47(3)	C11—C12—H12C	109.5
Ag1^{v}—Cl1—Ag1^{iii}	87.53(4)	H12A—C12—H12B	109.5
Ag1^{ii}—Cl1—Ag1^{iv}	87.54(3)	H12A—C12—H12C	109.5
Ag1^{i}—Cl1—Ag1^{iii}	92.46(3)	H12B—C12—H12C	109.5
Ag1—Cl1—Ag1^{ii}	87.53(4)	C6—C13—H13	108.7
Ag1^{i}—Cl1—Ag1	87.53(4)	C6—C13—C14	112.0(9)
Ag1^{i}—Cl1—Ag1^{iv}	180	C6—C13—C20	110.6(9)
Ag1^{iii}—Cl1—Ag1	180	C14—C13—H13	108.7
Ag1—Cl1—Ag1^{iv}	92.47(3)	C20—C13—H13	108.7
Ag1^{v}—Cl1—Ag1^{ii}	180	C20—C13—C14	108.0(8)
Ag1^{i}—Cl1—Ag1^{ii}	92.47(3)	C13—C14—H14A	109.5
Ag1^{v}—Cl1—Ag1	92.47(3)	C13—C14—H14B	109.5
Ag1^{v}—Cl2—Ag1	87.1(3)	C13—C14—H14C	109.5
Ag1—Cl2—Ag1^{iv}	87.1(3)	H14A—C14—H14B	109.5
Ag1^{v}—Cl2—Ag1^{iv}	87.1(3)	H14A—C14—H14C	109.5
Ag2^{i}—P2—Ag1	77.44(7)	H14B—C14—H14C	109.5
Ag2—P2—Ag1	72.82(7)	C7—C15—H15A	109.5
Ag2^{i}—P2—Ag2	122.39(9)	C7—C15—H15B	109.5
C10—P2—Ag1	106.7(3)	C7—C15—H15C	109.5
C10—P2—Ag2^{i}	117.9(3)	H15A—C15—H15B	109.5
C10—P2—Ag2	117.4(3)	H15A—C15—H15C	109.5
C1—N1—C7	121.5(7)	H15B—C15—H15C	109.5
C10—N1—C1	123.6(7)	C7—C16—H16A	109.5
C10—N1—C7	114.8(7)	C7—C16—H16B	109.5
C2—C1—N1	117.5(8)	C7—C16—H16C	109.5
C2—C1—C6	123.6(8)	H16A—C16—H16B	109.5
C6—C1—N1	118.9(9)	H16A—C16—H16C	109.5
C1—C2—C3	117.0(9)	H16B—C16—H16C	109.5
C1—C2—C11	125.9(9)	C9—C17—H17A	109.5
C3—C2—C11	117.0(10)	C9—C17—H17B	109.5

C2—C3—H3	119.2	C9—C17—H17C	109.5
C2—C3—C4	121.6(10)	H17A—C17—H17B	109.5
C4—C3—H3	119.2	H17A—C17—H17C	109.5
C3—C4—H4	121.5	H17B—C17—H17C	109.5
C5—C4—C3	117.0(10)	C9—C18—H18A	109.5
C5—C4—H4	121.5	C9—C18—H18B	109.5
C4—C5—H5	118	C9—C18—H18C	109.5
C4—C5—C6	124.0(9)	H18A—C18—H18B	109.5
C6—C5—H5	118	H18A—C18—H18C	109.5
C1—C6—C13	124.1(9)	H18B—C18—H18C	109.5
C5—C6—C1	116.7(9)	C11—C19—H19A	109.5
C5—C6—C13	119.0(9)	C11—C19—H19B	109.5
N1—C7—C15	110.9(8)	C11—C19—H19C	109.5
N1—C7—C16	110.1(10)	H19A—C19—H19B	109.5
C8—C7—N1	99.5(7)	H19A—C19—H19C	109.5
C8—C7—C15	111.4(13)	H19B—C19—H19C	109.5
C8—C7—C16	112.6(10)	C13—C20—H20A	109.5
C16—C7—C15	111.7(11)	C13—C20—H20B	109.5
C7—C8—H8A	109.1	C13—C20—H20C	109.5
C7—C8—H8B	109.1	H20A—C20—H20B	109.5
H8A—C8—H8B	107.9	H20A—C20—H20C	109.5
C9—C8—C7	112.3(9)	H20B—C20—H20C	109.5

Symmetry codes: (i) *x*−*y*+2/3, *x*+1/3, −*z*+4/3; (ii) *y*−1/3, −*x*+*y*+1/3, −*z*+4/3; (iii) −*x*+2/3, −*y*+4/3, −*z*+4/3; (iv) −*x*+*y*, −*x*+1, *z*; (v) −*y*+1, *x*−*y*+1, *z*

Bond length (Å) of **4**.

Ag1—P2	2.332(3)	C9—C10	1.517(13)
Ag1—P1	2.434(3)	C9—C17	1.538(9)
Ag2—P3	2.348(3)	C9—C17'	1.552(9)
Ag2—P2	2.431(3)	C9—C18	1.554(12)
Ag2—Ag4	2.916(5)	C11—C12	1.531(12)
Ag3—P3	2.319(5)	C11—C22	1.559(12)
Ag3—P4	2.464(5)	C13—C14	1.499(14)
Ag3—Ag5	2.889(7)	C13—C23	1.556(13)
Ag3—Ag6	2.903(5)	C19—C32	1.515(9)
Ag4—P5	2.321(4)	C20—C40	1.490(13)

Ag4—P2	2.485(4)	C20—C41	1.513(13)
Ag5—P6	2.364(4)	C20—C21	1.532(14)
Ag5—P3	2.482(4)	C24—C27	1.543(11)
Ag5—Ag1A	3.005(7)	C25—C26	1.504(16)
Ag6—P5	2.348(4)	C25—C56	1.529(9)
Ag6—P4	2.445(4)	C25—C57	1.533(15)
Ag6—Ag1A	3.207(7)	C26—C27	1.497(10)
Ag7—P4	2.374(3)	C27—C59	1.488(15)
Ag7—Ag9	2.472(3)	C27—C58	1.532(17)
Ag7—Ag8	3.044(3)	C28—C29	1.523(7)
Ag8—P6	2.397(3)	C29—C60	1.513(10)
Ag8—Ag9	2.458(3)	C29—C61	1.529(10)
Ag1A—P5	2.368(6)	C29—C30	1.543(8)
Ag1A—P6	2.424(6)	C30—C31	1.519(9)
Ag1'—P1	2.261(8)	C31—C63	1.521(9)
Ag1'—P2	2.523(7)	C31—C62	1.531(10)
Ag2'—P2	2.312(9)	C32—C33	1.475(11)
Ag2'—P3	2.494(9)	C32—C70	1.518(11)
Ag2'—Ag4'	2.865(13)	C32—C40	1.539(12)
Ag3'—P4	2.252(11)	C34—C35	1.400(11)
Ag3'—P3	2.518(11)	C34—C39	1.421(10)
Ag3'—Ag6'	2.832(11)	C35—C36	1.397(11)
Ag3'—Ag5'	2.873(17)	C35—C71	1.530(10)
Ag4'—P2	2.239(9)	C36—C37	1.408(11)
Ag4'—P5	2.551(9)	C37—C38	1.357(12)
Ag5'—P3	2.271(9)	C38—C39	1.373(10)
Ag5'—P6	2.573(9)	C39—C73	1.492(11)
Ag5'—Ag1B	2.980(17)	C42—C43	1.540(9)
Ag6'—P4	2.328(8)	C43—C75	1.416(9)
Ag6'—P5	2.469(9)	C43—C76'	1.423(9)
Ag6'—Ag1B	3.189(16)	C43—C75'	1.451(9)
Ag7'—P4	2.277(9)	C43—C44	1.458(9)
Ag7'—Ag9'	2.630(14)	C43—C76	1.521(9)
Ag7'—Ag8'	3.094(12)	C44—C45	1.511(10)
Ag8'—P6	2.196(9)	C45—C77	1.494(12)
Ag8'—Ag9'	2.668(13)	C45—C78	1.518(10)
Ag1B—P6	2.360(12)	C46—C47	1.536(9)
Ag1B—P5	2.401(12)	C47—C86	1.518(9)
S1—O1	1.369(9)	C47—C85	1.537(9)
S1—O2	1.383(10)	C47—C48	1.546(8)
S1—N7	1.579(7)	C48—C49	1.514(11)

S1—C12A	1.781(8)	C49—C87	1.512(10)
C12A—F3	1.364(8)	C49—C88	1.550(10)
C12A—F1	1.377(8)	C50—C55	1.390(13)
C12A—F2	1.386(9)	C50—C51	1.396(12)
S1'—F1'	1.20(2)	C51—C52	1.395(13)
S1'—N7	1.456(8)	C51—C95	1.613(17)
S1'—C12B	1.788(10)	C52—C53	1.390(14)
S1'—O1	1.818(12)	C53—C54	1.401(14)
S1'—S2	2.242(10)	C54—C55	1.388(13)
C12B—F2'	1.386(10)	C55—C97	1.56(2)
C12B—F3'	1.388(10)	C97—C99	1.42(2)
C12B—F1'	1.397(10)	C97—C98	1.43(2)
F1'—F2'	1.29(4)	C99—C98	2.02(3)
S2—O3	1.402(8)	C50'—C51'	1.384(17)
S2—O4	1.405(9)	C50'—C55'	1.396(17)
S2—N7	1.595(11)	C51'—C95	0.88(3)
S2—C119	1.831(14)	C51'—C52'	1.399(17)
S3—O5	1.438(8)	C51'—C11B	1.98(3)
S3—O6	1.442(9)	C51'—C96	1.99(3)
S3—N8	1.555(9)	C52'—C53'	1.399(17)
S3—C120	1.792(16)	C52'—C95	1.96(2)
S4—O7	1.429(9)	C53'—C54'	1.375(18)
S4—O8	1.450(7)	C54'—C55'	1.405(17)
S4—N8	1.558(9)	C55'—C97'	1.55(3)
S4—C121	1.761(11)	C97'—C99'	1.76(3)
P1—C10	1.752(10)	C97'—C98	1.76(3)
P2—C19	1.791(7)	C64—C65	1.404(9)
P3—C42	1.766(6)	C64—C69	1.419(10)
P4—C24	1.756(6)	C65—C66	1.391(9)
P5—C28	1.792(5)	C65—C100	1.486(11)
P6—C46	1.769(5)	C66—C67	1.381(13)
F4—C119	1.357(16)	C67—C68	1.391(12)
F5—C119	1.281(13)	C68—C69	1.382(8)
F6—C119	1.377(17)	C69—C102	1.502(10)
F7—C120	1.317(15)	C71—C72	1.499(12)
F8—C121	1.309(12)	C71—C104	1.565(11)
F9—C120	1.330(15)	C73—C105	1.534(11)
F10—C120	1.393(17)	C73—C74	1.568(10)
F11—C121	1.328(12)	C75—C76	1.69(2)
F12—C121	1.350(10)	C75'—C76'	1.38(2)
N1—C10	1.328(9)	C79—C84	1.412(7)

N1—C1	1.444(9)	C79—C80	1.417(8)
N1—C7	1.493(10)	C80—C81	1.388(9)
N2—C19	1.335(8)	C80—C106	1.519(8)
N2—C34	1.432(9)	C81—C82	1.373(10)
N2—C20	1.521(9)	C82—C83	1.402(10)
N3—C24	1.337(9)	C83—C84	1.391(9)
N3—C50'	1.38(2)	C84—C108	1.499(9)
N3—C50	1.515(15)	C89—C90	1.397(11)
N3—C25	1.534(11)	C89—C94	1.416(9)
N4—C28	1.298(7)	C90—C91	1.354(13)
N4—C64	1.464(7)	C90—C110	1.514(10)
N4—C31	1.536(6)	C91—C92	1.386(13)
N5—C42	1.310(8)	C92—C93	1.375(14)
N5—C79	1.441(7)	C93—C94	1.390(12)
N5—C45	1.544(7)	C94—C112	1.495(10)
N6—C46	1.325(7)	C95—C96	1.518(17)
N6—C89	1.448(10)	C95—C11B	1.539(9)
N6—C49	1.530(8)	C95—C11A	1.551(10)
C1—C2	1.376(12)	C100—C101	1.535(10)
C1—C6	1.421(13)	C100—C114	1.545(9)
C2—C3	1.412(13)	C102—C103	1.548(9)
C2—C11	1.513(15)	C102—C115	1.565(9)
C3—C4	1.315(18)	C106—C107	1.522(9)
C4—C5	1.407(18)	C106—C116	1.550(9)
C5—C6	1.363(14)	C108—C109	1.505(10)
C6—C13	1.536(15)	C108—C117	1.569(8)
C7—C15	1.503(13)	C110—C122	1.532(17)
C7—C16	1.509(13)	C110—C111	1.558(15)
C7—C8	1.521(13)	C112—C113	1.547(11)
C8—C9	1.497(17)	C112—C118	1.556(9)

Bond angle (°) of **4**.

P2—Ag1—P1	172.31(16)	C17'—C9—C18	106.5(9)
P3—Ag2—P2	159.89(17)	N1—C10—C9	111.0(8)
P3—Ag2—Ag4	109.35(14)	N1—C10—P1	127.4(7)
P2—Ag2—Ag4	54.48(10)	C9—C10—P1	120.4(6)
P3—Ag3—P4	162.0(2)	C2—C11—C12	113.9(8)
P3—Ag3—Ag5	55.63(13)	C2—C11—C22	109.9(9)

P4—Ag3—Ag5	111.5(2)	C12—C11—C22	109.3(7)
P3—Ag3—Ag6	110.21(18)	C14—C13—C6	109.9(9)
P4—Ag3—Ag6	53.43(13)	C14—C13—C23	107.9(9)
Ag5—Ag3—Ag6	86.64(17)	C6—C13—C23	114.8(10)
P5—Ag4—P2	169.31(19)	N2—C19—C32	110.7(5)
P5—Ag4—Ag2	123.53(17)	N2—C19—P2	124.1(5)
P2—Ag4—Ag2	52.78(9)	C32—C19—P2	125.1(5)
P6—Ag5—P3	169.6(2)	C40—C20—C41	106.5(9)
P6—Ag5—Ag3	121.5(2)	C40—C20—N2	102.0(6)
P3—Ag5—Ag3	50.46(13)	C41—C20—N2	110.6(7)
P6—Ag5—Ag1A	52.04(14)	C40—C20—C21	118.5(10)
P3—Ag5—Ag1A	119.63(17)	C41—C20—C21	106.5(7)
Ag3—Ag5—Ag1A	99.23(19)	N2—C20—C21	112.4(8)
P5—Ag6—P4	161.27(19)	N3—C24—C27	108.8(6)
P5—Ag6—Ag3	122.19(19)	N3—C24—P4	125.2(6)
P4—Ag6—Ag3	54.04(12)	C27—C24—P4	126.0(5)
P5—Ag6—Ag1A	47.42(12)	C26—C25—C56	114.8(12)
P4—Ag6—Ag1A	114.04(16)	C26—C25—C57	108.3(11)
Ag3—Ag6—Ag1A	94.44(17)	C56—C25—C57	111.0(11)
P4—Ag7—Ag9	166.97(14)	C26—C25—N3	101.0(7)
P4—Ag7—Ag8	115.75(12)	C56—C25—N3	110.1(10)
Ag9—Ag7—Ag8	51.65(7)	C57—C25—N3	111.2(8)
P6—Ag8—Ag9	164.62(14)	C27—C26—C25	109.7(9)
P6—Ag8—Ag7	113.73(11)	C59—C27—C26	110.6(9)
Ag9—Ag8—Ag7	52.08(7)	C59—C27—C58	102.1(11)
Ag8—Ag9—Ag7	76.27(9)	C26—C27—C58	112.9(10)
P5—Ag1A—P6	154.4(3)	C59—C27—C24	113.3(8)
P5—Ag1A—Ag5	108.2(2)	C26—C27—C24	103.5(7)
P6—Ag1A—Ag5	50.24(12)	C58—C27—C24	114.7(8)
P5—Ag1A—Ag6	46.90(12)	N4—C28—C29	110.8(4)
P6—Ag1A—Ag6	109.39(18)	N4—C28—P5	125.0(4)
Ag5—Ag1A—Ag6	79.48(16)	C29—C28—P5	124.2(4)
P1—Ag1'—P2	167.1(3)	C60—C29—C28	111.1(5)
P2—Ag2'—P3	156.5(4)	C60—C29—C61	108.3(6)
P2—Ag2'—Ag4'	49.9(3)	C28—C29—C61	112.6(5)

P3—Ag2'—Ag4'	106.7(3)	C60—C29—C30	112.0(5)
P4—Ag3'—P3	164.0(4)	C28—C29—C30	102.3(5)
P4—Ag3'—Ag6'	53.0(3)	C61—C29—C30	110.5(5)
P3—Ag3'—Ag6'	111.8(4)	C31—C30—C29	107.5(5)
P4—Ag3'—Ag5'	119.8(5)	C30—C31—C63	111.7(6)
P3—Ag3'—Ag5'	49.3(3)	C30—C31—C62	113.2(6)
Ag6'—Ag3'—Ag5'	88.8(4)	C63—C31—C62	109.2(5)
P2—Ag4'—P5	175.1(5)	C30—C31—N4	100.2(4)
P2—Ag4'—Ag2'	52.1(3)	C63—C31—N4	112.5(5)
P5—Ag4'—Ag2'	123.1(4)	C62—C31—N4	109.8(5)
P3—Ag5'—P6	169.9(6)	C33—C32—C19	108.6(6)
P3—Ag5'—Ag3'	57.2(3)	C33—C32—C70	106.0(7)
P6—Ag5'—Ag3'	112.8(5)	C19—C32—C70	116.2(6)
P3—Ag5'—Ag1B	128.7(4)	C33—C32—C40	116.5(8)
P6—Ag5'—Ag1B	49.7(3)	C19—C32—C40	101.6(6)
Ag3'—Ag5'—Ag1B	96.0(5)	C70—C32—C40	108.4(8)
P4—Ag6'—P5	160.7(4)	C35—C34—C39	121.0(7)
P4—Ag6'—Ag3'	50.6(2)	C35—C34—N2	119.0(6)
P5—Ag6'—Ag3'	118.7(4)	C39—C34—N2	119.9(7)
P4—Ag6'—Ag1B	112.9(3)	C36—C35—C34	118.6(7)
P5—Ag6'—Ag1B	48.2(3)	C36—C35—C71	116.3(7)
Ag3'—Ag6'—Ag1B	92.3(4)	C34—C35—C71	125.1(6)
P4—Ag7'—Ag9'	166.7(5)	C35—C36—C37	119.7(8)
P4—Ag7'—Ag8'	121.3(4)	C38—C37—C36	120.6(8)
Ag9'—Ag7'—Ag8'	54.8(3)	C37—C38—C39	122.0(8)
P6—Ag8'—Ag9'	160.9(5)	C38—C39—C34	118.1(7)
P6—Ag8'—Ag7'	110.3(4)	C38—C39—C73	117.0(7)
Ag9'—Ag8'—Ag7'	53.7(3)	C34—C39—C73	124.7(7)
Ag7'—Ag9'—Ag8'	71.5(4)	C20—C40—C32	108.5(8)
P6—Ag1B—P5	157.9(6)	N5—C42—C43	109.1(5)
P6—Ag1B—Ag5'	56.2(3)	N5—C42—P3	124.8(4)
P5—Ag1B—Ag5'	103.2(4)	C43—C42—P3	125.6(5)
P6—Ag1B—Ag6'	113.1(4)	C76'—C43—C75'	57.2(11)
P5—Ag1B—Ag6'	50.0(3)	C75—C43—C44	131.1(11)
Ag5'—Ag1B—Ag6'	80.6(4)	C76'—C43—C44	124.6(12)

O1—S1—O2	119.4(7)	C75'—C43—C44	120.4(10)
O1—S1—N7	114.6(6)	C75—C43—C76	70.3(11)
O2—S1—N7	105.0(6)	C44—C43—C76	102.4(9)
O1—S1—C12A	106.1(6)	C75—C43—C42	124.6(11)
O2—S1—C12A	103.9(6)	C76'—C43—C42	128.6(12)
N7—S1—C12A	106.6(5)	C75'—C43—C42	113.3(9)
F3—C12A—F1	108.4(9)	C44—C43—C42	104.0(5)
F3—C12A—F2	114.3(9)	C76—C43—C42	107.8(9)
F1—C12A—F2	102.0(9)	C43—C44—C45	111.6(5)
F3—C12A—S1	113.1(7)	C77—C45—C44	113.4(7)
F1—C12A—S1	106.5(7)	C77—C45—C78	109.0(7)
F2—C12A—S1	111.6(9)	C44—C45—C78	112.3(7)
F1'—S1'—N7	88.4(10)	C77—C45—N5	110.4(6)
F1'—S1'—C12B	51.3(6)	C44—C45—N5	99.8(5)
N7—S1'—C12B	138.6(10)	C78—C45—N5	111.7(6)
F1'—S1'—O1	127.0(11)	N6—C46—C47	110.9(5)
N7—S1'—O1	98.1(7)	N6—C46—P6	124.9(5)
C12B—S1'—O1	100.0(10)	C47—C46—P6	124.1(4)
F1'—S1'—S2	120.9(10)	C86—C47—C46	114.7(5)
N7—S1'—S2	45.2(5)	C86—C47—C85	110.1(6)
C12B—S1'—S2	159.7(9)	C46—C47—C85	108.3(5)
O1—S1'—S2	98.6(5)	C86—C47—C48	109.9(5)
F2'—C12B—F3'	91(2)	C46—C47—C48	100.3(5)
F2'—C12B—F1'	55.3(19)	C85—C47—C48	113.3(5)
F3'—C12B—F1'	129(2)	C49—C48—C47	108.8(6)
F2'—C12B—S1'	91.1(17)	C87—C49—C48	111.9(7)
F3'—C12B—S1'	115.5(18)	C87—C49—N6	111.7(7)
F1'—C12B—S1'	42.0(9)	C48—C49—N6	100.3(5)
S1'—F1'—F2'	132.9(18)	C87—C49—C88	109.4(6)
S1'—F1'—C12B	86.7(11)	C48—C49—C88	113.1(7)
F2'—F1'—C12B	61.9(11)	N6—C49—C88	110.1(6)
F1'—F2'—C12B	62.8(11)	C55—C50—C51	123.1(13)
O3—S2—O4	119.7(6)	C55—C50—N3	123.5(10)
O3—S2—N7	117.3(5)	C51—C50—N3	113.4(10)
O4—S2—N7	109.6(6)	C52—C51—C50	116.6(13)

O3—S2—C119	105.5(6)	C52—C51—C95	120.0(11)
O4—S2—C119	102.9(7)	C50—C51—C95	123.4(10)
N7—S2—C119	98.3(7)	C53—C52—C51	121.3(15)
O3—S2—S1'	78.3(5)	C52—C53—C54	120.8(16)
O4—S2—S1'	126.9(5)	C55—C54—C53	118.8(16)
N7—S2—S1'	40.4(3)	C54—C55—C50	119.2(15)
C119—S2—S1'	120.7(6)	C54—C55—C97	119.3(15)
O5—S3—O6	120.0(6)	C50—C55—C97	121.4(13)
O5—S3—N8	113.3(5)	C99—C97—C98	90.4(19)
O6—S3—N8	113.0(6)	C99—C97—C55	108.0(18)
O5—S3—C120	107.6(7)	C98—C97—C55	103.7(16)
O6—S3—C120	98.3(7)	C97—C99—C98	45.2(10)
N8—S3—C120	101.3(6)	N3—C50'—C51'	134(2)
O7—S4—O8	121.1(6)	N3—C50'—C55'	108.1(17)
O7—S4—N8	109.5(6)	C51'—C50'—C55'	118(2)
O8—S4—N8	115.2(5)	C95—C51'—C50'	128(2)
O7—S4—C121	100.7(5)	C95—C51'—C52'	117(2)
O8—S4—C121	103.3(4)	C50'—C51'—C52'	115(2)
N8—S4—C121	104.3(5)	C95—C51'—C11B	48.2(14)
C10—P1—Ag1'	106.9(3)	C50'—C51'—C11B	138.2(18)
C10—P1—Ag1	114.5(3)	C52'—C51'—C11B	85.4(16)
C19—P2—Ag4'	98.0(3)	C95—C51'—C96	45.8(14)
C19—P2—Ag2'	121.5(3)	C50'—C51'—C96	130.1(17)
Ag4'—P2—Ag2'	78.0(3)	C52'—C51'—C96	94.3(16)
C19—P2—Ag1	114.2(2)	C11B—C51'—C96	80.0(12)
C19—P2—Ag2	116.3(2)	C53'—C52'—C51'	123(3)
Ag1—P2—Ag2	129.24(12)	C53'—C52'—C95	146(2)
C19—P2—Ag4	94.8(2)	C51'—C52'—C95	23.6(11)
Ag1—P2—Ag4	107.93(13)	C54'—C53'—C52'	125(3)
Ag2—P2—Ag4	72.74(12)	C53'—C54'—C55'	109(2)
C19—P2—Ag1'	121.3(3)	C50'—C55'—C54'	130(2)
Ag4'—P2—Ag1'	100.3(3)	C50'—C55'—C97'	126(2)
Ag2'—P2—Ag1'	116.7(2)	C54'—C55'—C97'	104(3)
C42—P3—Ag5'	112.5(3)	C55'—C97'—C99'	114(2)
C42—P3—Ag3	111.0(2)	C55'—C97'—C98	129(2)

C42—P3—Ag2	120.8(2)	C99'—C97'—C98	111(2)
Ag3—P3—Ag2	113.65(13)	C65—C64—C69	123.0(5)
C42—P3—Ag5	109.0(2)	C65—C64—N4	119.2(6)
Ag3—P3—Ag5	73.91(17)	C69—C64—N4	117.8(5)
Ag2—P3—Ag5	119.09(14)	C66—C65—C64	117.0(7)
C42—P3—Ag2'	117.3(3)	C66—C65—C100	116.9(7)
Ag5'—P3—Ag2'	113.6(4)	C64—C65—C100	126.0(6)
C42—P3—Ag3'	112.1(3)	C67—C66—C65	121.1(7)
Ag5'—P3—Ag3'	73.5(4)	C66—C67—C68	121.0(7)
Ag2'—P3—Ag3'	120.0(3)	C69—C68—C67	120.7(7)
C24—P4—Ag3'	107.4(4)	C68—C69—C64	117.1(6)
C24—P4—Ag7'	122.6(3)	C68—C69—C102	118.4(6)
Ag3'—P4—Ag7'	109.0(4)	C64—C69—C102	124.3(5)
C24—P4—Ag6'	116.0(3)	C72—C71—C35	111.7(7)
Ag3'—P4—Ag6'	76.4(3)	C72—C71—C104	108.3(7)
Ag7'—P4—Ag6'	114.6(3)	C35—C71—C104	111.3(6)
C24—P4—Ag7	118.5(3)	C39—C73—C105	110.9(6)
C24—P4—Ag6	116.5(3)	C39—C73—C74	114.4(6)
Ag7—P4—Ag6	117.19(13)	C105—C73—C74	108.5(6)
C24—P4—Ag3	106.4(3)	C43—C75—C76	57.8(7)
Ag7—P4—Ag3	116.40(14)	C43—C76—C75	52.0(6)
Ag6—P4—Ag3	72.53(14)	C76'—C75'—C43	60.3(7)
C28—P5—Ag4	113.7(2)	C75'—C76'—C43	62.5(8)
C28—P5—Ag6	104.7(2)	C84—C79—C80	122.0(5)
Ag4—P5—Ag6	98.66(15)	C84—C79—N5	118.0(5)
C28—P5—Ag1A	125.7(2)	C80—C79—N5	120.0(5)
Ag4—P5—Ag1A	117.14(17)	C81—C80—C79	117.8(5)
Ag6—P5—Ag1A	85.68(16)	C81—C80—C106	119.2(6)
C28—P5—Ag1B	124.8(4)	C79—C80—C106	123.0(6)
C28—P5—Ag6'	101.9(3)	C82—C81—C80	121.6(6)
Ag1B—P5—Ag6'	81.8(3)	C81—C82—C83	119.7(6)
C28—P5—Ag4'	115.4(3)	C84—C83—C82	121.7(6)
Ag1B—P5—Ag4'	116.3(4)	C83—C84—C79	117.0(5)
Ag6'—P5—Ag4'	105.3(3)	C83—C84—C108	118.2(5)
C46—P6—Ag8'	117.2(3)	C79—C84—C108	124.8(6)

C46—P6—Ag1B	115.8(4)	C90—C89—C94	120.7(7)
Ag8'—P6—Ag1B	116.7(4)	C90—C89—N6	119.8(6)
C46—P6—Ag5	107.7(2)	C94—C89—N6	119.6(6)
C46—P6—Ag8	120.7(2)	C91—C90—C89	118.4(7)
Ag5—P6—Ag8	115.11(14)	C91—C90—C110	117.3(8)
C46—P6—Ag1A	112.4(2)	C89—C90—C110	124.1(7)
Ag5—P6—Ag1A	77.72(17)	C90—C91—C92	123.5(9)
Ag8—P6—Ag1A	115.17(15)	C93—C92—C91	117.1(9)
C46—P6—Ag5'	107.8(3)	C92—C93—C94	123.0(8)
Ag8'—P6—Ag5'	117.6(4)	C93—C94—C89	117.1(7)
Ag1B—P6—Ag5'	74.2(4)	C93—C94—C112	119.1(7)
C10—N1—C1	123.0(6)	C89—C94—C112	123.8(7)
C10—N1—C7	114.0(7)	C51'—C95—C96	109.7(18)
C1—N1—C7	123.0(6)	C51'—C95—C11B	106.6(19)
C19—N2—C34	125.1(6)	C96—C95—C11B	113.3(12)
C19—N2—C20	112.7(6)	C96—C95—C11A	93.5(14)
C34—N2—C20	121.9(5)	C96—C95—C51	112.3(9)
C24—N3—C50'	119.2(11)	C11A—C95—C51	136.5(16)
C24—N3—C50	122.6(7)	C51'—C95—C52'	39.6(15)
C24—N3—C25	113.8(7)	C96—C95—C52'	92.0(12)
C50'—N3—C25	123.3(11)	C11B—C95—C52'	82.6(12)
C50—N3—C25	123.0(7)	C95—C96—C51'	24.5(8)
C28—N4—C64	124.9(4)	C97—C98—C99	44.4(10)
C28—N4—C31	114.1(5)	C65—C100—C101	113.9(6)
C64—N4—C31	120.8(4)	C65—C100—C114	111.7(6)
C42—N5—C79	124.3(5)	C101—C100—C114	108.9(6)
C42—N5—C45	114.5(5)	C69—C102—C103	113.2(6)
C79—N5—C45	121.2(5)	C69—C102—C115	110.1(5)
C46—N6—C89	125.5(5)	C103—C102—C115	107.6(6)
C46—N6—C49	113.6(6)	C80—C106—C107	112.5(6)
C89—N6—C49	120.8(5)	C80—C106—C116	110.6(5)
S1'—N7—S2	94.5(7)	C107—C106—C116	108.5(6)
S1—N7—S2	122.9(7)	C84—C108—C109	111.7(6)
S3—N8—S4	126.1(5)	C84—C108—C117	111.5(5)
C2—C1—C6	122.8(8)	C109—C108—C117	109.1(6)

C2—C1—N1	120.4(8)	C90—C110—C122	109.6(9)
C6—C1—N1	116.8(7)	C90—C110—C111	110.1(8)
C1—C2—C3	116.7(11)	C122—C110—C111	112.3(8)
C1—C2—C11	124.6(7)	C94—C112—C113	110.5(7)
C3—C2—C11	118.7(9)	C94—C112—C118	111.5(6)
C4—C3—C2	121.2(11)	C113—C112—C118	109.3(6)
C3—C4—C5	121.7(11)	C95—C11B—C51'	25.2(8)
C6—C5—C4	120.1(13)	F5—C119—F4	108.7(13)
C5—C6—C1	116.9(10)	F5—C119—F6	107.4(12)
C5—C6—C13	118.6(11)	F4—C119—F6	104.3(11)
C1—C6—C13	124.4(7)	F5—C119—S2	116.2(10)
N1—C7—C15	111.5(7)	F4—C119—S2	111.7(9)
N1—C7—C16	110.6(6)	F6—C119—S2	107.8(11)
C15—C7—C16	109.3(8)	F7—C120—F9	108.6(12)
N1—C7—C8	98.8(8)	F7—C120—F10	102.8(13)
C15—C7—C8	111.4(8)	F9—C120—F10	108.4(13)
C16—C7—C8	115.0(8)	F7—C120—S3	112.6(12)
C9—C8—C7	110.6(8)	F9—C120—S3	113.7(11)
C8—C9—C10	99.4(7)	F10—C120—S3	110.1(9)
C8—C9—C17	98.5(16)	F8—C121—F11	99.3(9)
C10—C9—C17	121.9(13)	F8—C121—F12	106.9(10)
C8—C9—C17'	122.1(12)	F11—C121—F12	105.5(8)
C10—C9—C17'	103.4(10)	F8—C121—S4	113.1(7)
C8—C9—C18	112.6(8)	F11—C121—S4	116.2(8)
C10—C9—C18	112.2(9)	F12—C121—S4	114.4(7)
C17—C9—C18	110.5(12)		

S8. Computational Analyses

With the use of DFT, the complexes are optimized using hybrid functional UBP86[8,9] along with the dispersion correction term (D3(BJ))[10,11], and the Ahlrichs triple-ζ-quality basis set def2-SVP[12] using the Gaussian09[13] package in the gaseous phase. The NBO 6.0 program[14-16] is used to perform the NBO[14-16] calculations of the complexes,

spin densities, mulliken charges, HOMO-LUMO energy gap and natural bond orbitals at BP86-D3(BJ)/Def2-TZVPP.

S8.1. NBO Analysis

The NBO Analysis of **2** and **4** at neutral doublet state and dicationic triplet state respectively were performed at UBP86-D3(BJ)/Def2-SVP level of theory.

The Kohn-Sham orbitals of **2**, α-SOMO-3 and β-SOMO-3 represents the lone pair present in the P atoms. The α-SOMO-2 and β-SOMO-2 shows the π backdonation from the P–C_{cAAC}. While the α-LUMO+1 and β-LUMO+1 depicts the antibonding orbitals $\pi_{C=N}$. The P–C_{cAAC} bond shows two occupancies, where one bond is polarized towards C (62.91%) and other is polarized towards P (59.79%). This might be the presence of a double bond between them which is depicted in α-SOMO-2 and β-SOMO-2 (Figure S8), where the lone pairs on P atoms are slightly extended towards C_{cAAC}. The presence of lone pair on the P_{281}, P_{171} atoms is evident from the above given NBO results (Table S2). α-SOMO-1 and α-SOMO represents π* antibonding orbitals of C=N.

The Kohn-Sham orbitals of **4** α-SOMO-2 shows the lone pair on P atom and also π backdonation from P to C_{cAAC}. The π backdonation from P to C_{cAAC} can also be visualized in β-SOMO-3 and β-LUMO. The α-SOMO-1 and β-SOMO shows the interaction of π-type lone pair of P with Ag. α-SOMO and α-LUMO depicts the π* antibonding orbitals of C=N. The β-SOMO-1 flaunts the Ag–Ag–Ag metal interaction.

The Mulliken spin densities are primarily located on the C_{cAAC} ligands and to a lesser extent on the Ag and N atoms in **2**. In **4**, the significant contribution to the spin density comes from the P atom and Ag, with relevant contributions also observed from the C_{cAAC} ligands.

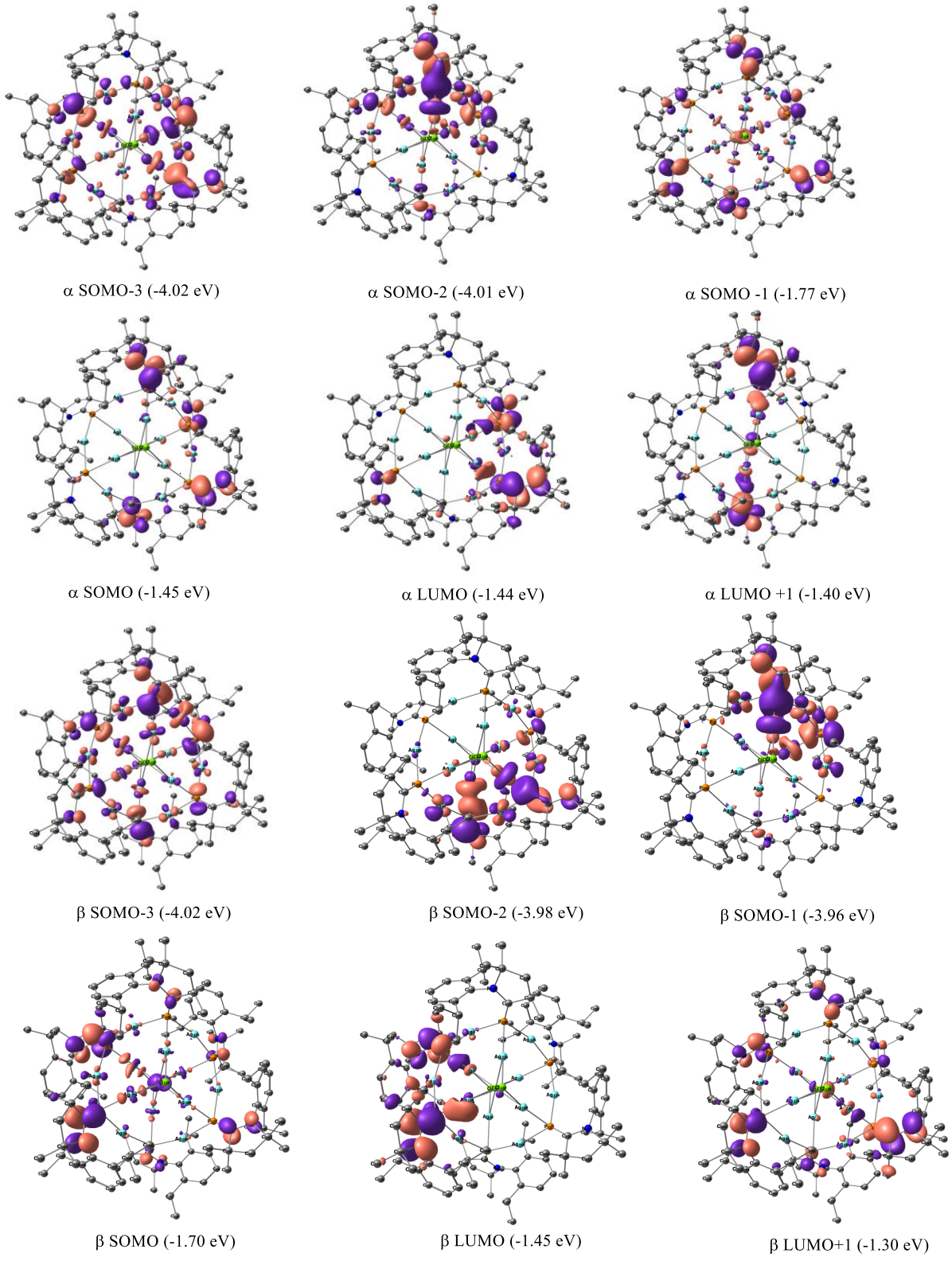


Figure S9. The selected Kohn-Sham orbitals (α/β-SOMO-3, α/β-SOMO-2, α/β-SOMO-1, α/β SOMO, α/β LUMO and a/b LUMO+1) of **2** in neutral doublet state at UBP86-D3(BJ)/Def2-SVP level of theory.

Table S2. Natural Bond Orbital (NBO) analysis of the **2** at UBP86-D3(BJ)/Def2-SVP level of theory. Occupation Number (ON) and Polarization and Hybridization.

Bond	**ON**	**Polarization and Hybridization (%)**		
Ag_{224}-Ag_{225}-P_{226}	0.906	Ag:10.2 s (51.72) p (46.86) d (1.40)	Ag:12.54 s (42.02) p (56.37) d (1.54)	P:77.24 s (35.10) p (64.87) d (0.03)
P_{226}-C_{242}	0.979	P:37.09 s (21.74) p (77.81) d (0.45)		C:62.91 s (38.20) p (61.76) d (0.04)
	0.91	P:59.79 s (3.81) p (95.95) d (0.24)		C:40.21 s (0.50) p (99.46) d (0.04)
P Lone pair	0.715	P_{281} s (36.78) p (63.19) d (0.03)		
	0.772	P_{171} s (3.47) p (96.52)		
	0.702	P_{171} s (60.77) p (39.20)		

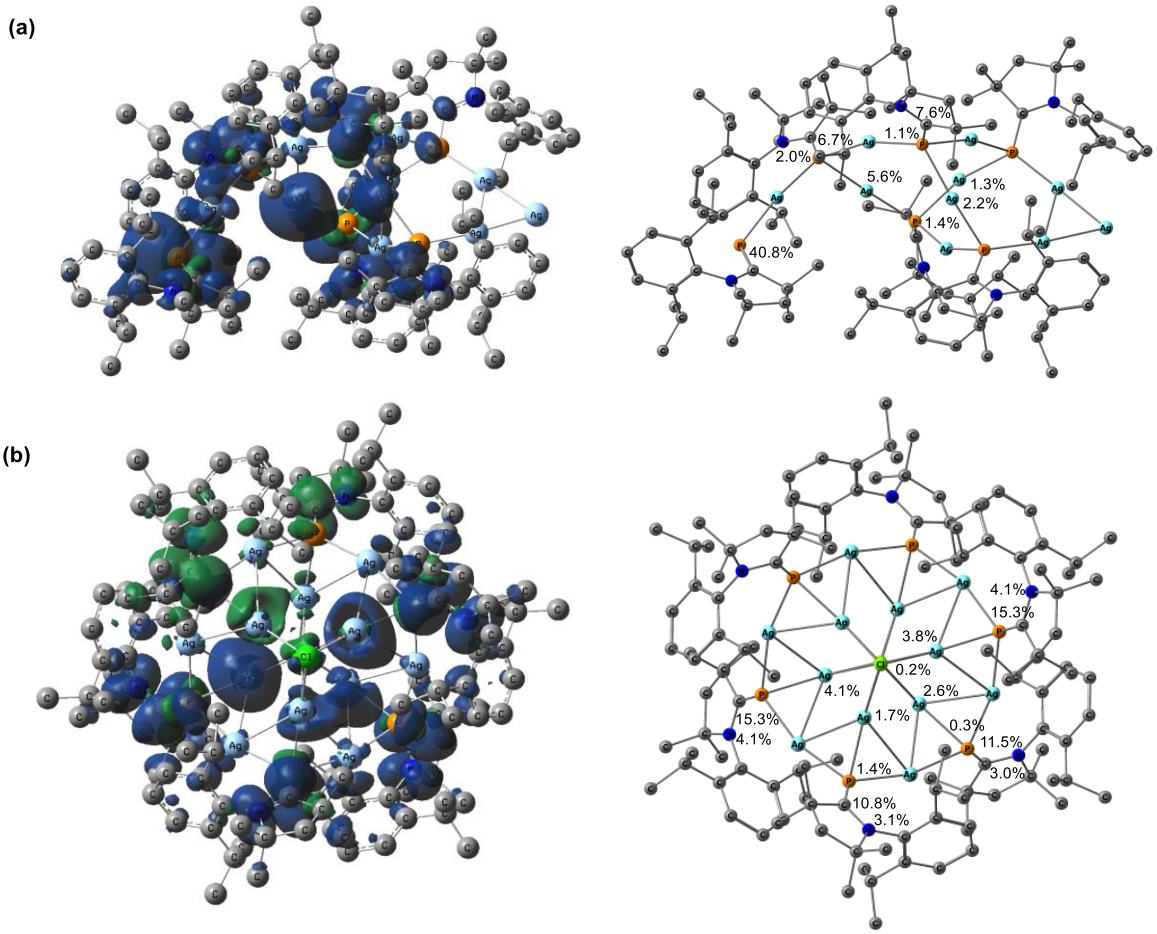


Figure S10. Mulliken α-spin densities of **2** (top) and **4** (bottom). The individual contribution of selected atoms to the total α-spin density are in %.

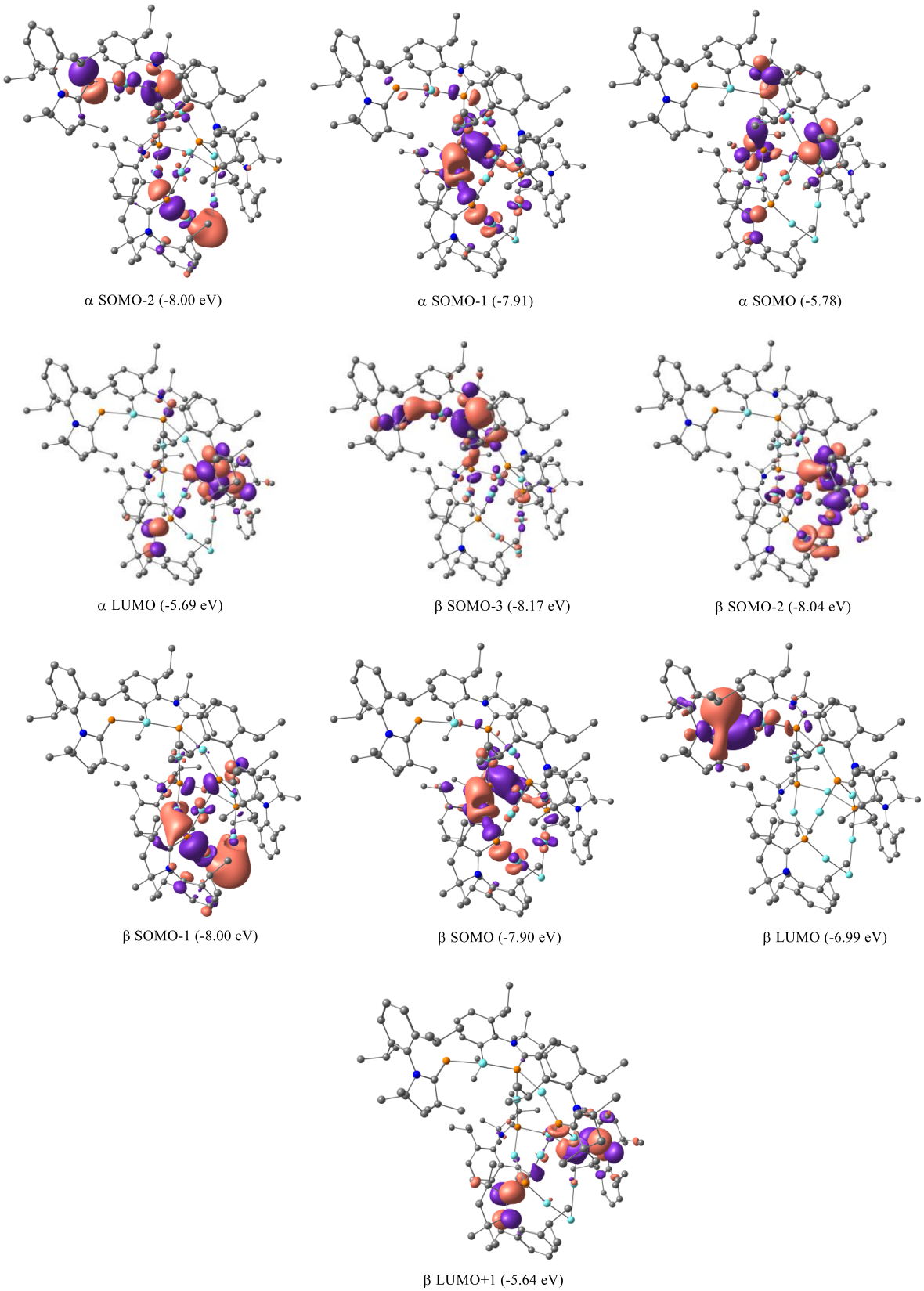


Figure S11. The selected Kohn-Sham orbitals (α/β-SOMO -3, α/β-SOMO-2, α/β-LUMO+1) of **4** in dicationic triplet state at UBP86-D3(BJ)/Def2-SVP level of theory.

Table S3. Natural Bond Orbital (NBO) analysis of **4** at UBP86-D3(BJ)/Def2-SVP level of theory. Occupation Number (ON) and Polarization and Hybridization

Bond	ON	Polarization and Hybridization (%)			WBI
Ag_1-P_{12}	0.93	Ag:18.91 s (88.90) p (7.14) d (3.95)		P:81.09 s (37.49) p (62.48) d (0.03)	0.51
Ag_2-Ag_4-P_{12}	0.913	Ag:11.35 s (41.93) p (56.66) d (1.32)	Ag:7.91 s (25.98) p (73.23) d (0.75)	P:80.75 s (41.66) p (58.31) d (0.03)	Ag_4-P_{12} =0.44 Ag_2-P_{15} = 0.49
Ag_2-Ag_4-P_{15}	0.89	Ag:1.79 s (0.41) p (99.41) d (0.17)	Ag:15.14 s (69.19) p (28.08) d (2.69)	P:83.07 s (33.88) p (66.10) d (0.03	Ag4-P15= 0.49
Ag_2-P_{13}	0.90	Ag:12.86 s (54.10) p (43.06) d (2.77)		P:87.14 s (39.30) p (60.68) d (0.02)	0.47
Ag_3-Ag_5-P_{13}	0.92	Ag:11.57 s (47.88) p (50.47) d (1.63)	Ag:11.76 s (48.21) p (50.47) d (1.53)	P:76.67 s (39.10) p (60.87) d (0.03)	Ag_5-P_{13} =0.45 Ag_3-P_{13}=0.48
Ag_3-Ag_6-P_{14}	0.93	Ag:10.59 s (41.25) p (57.43) d (1.31)	Ag:13.96 s (77.40) p (20.10) d (2.49)	P:75.45 s (35.25) p (64.72) d (0.04)	Ag_3-P_{14}=0.45 Ag_6-P_{14} = 0.44
Ag_5-Ag_{10}-P_{16}	0.92	Ag:10.88 S (44.42) p (54.04) d (1.52)	Ag:10.71 s (34.21) p (64.34) d (1.42)	P:78.41 s (37.92) p (62.05) d (0.03)	Ag_5- P_{16}=0.452 Ag_{10}- P_{16}=0.47

Ag_7-Ag_8-Ag_9	0.93	Ag:27.73 s (40.65) p (58.62) d (0.73)	Ag:27.22 s (41.02) p (58.40) d (0.57)	Ag:45.05 s (94.82) p (4.99) d (0.19)	
Ag_7-P_{14}	0.91	Ag:12.63 s (56.60) p (40.67) d (2.71)		P:87.73 s (43.82) p (56.16) d (0.02)	0.44
Ag_8 -P_{16}	0.91	Ag:12.27 s (55.67) p (41.78) d (2.51)		P:87.73 s (42.19) p (57.81) d (0.01)	0.43
Ag_{10}-P_{15}	0.89	Ag: 13.51 s (60.65) p (36.53) d (2.78)		P:86.49 s (18.16) p (67.88) d (0.03)	0.50
P_{11}-C_{37}	0.98	P:32.92 s (18.16) p (81.23) d (0.61)		C:67.08 s (36.51) p (63.44) d (0.04)	1.30
P_{12}-C_{66}	0.98	P:37.49 s (21.32) p (78.20) d (0.48)		C:62.51 s (36.99) p (62.96) d (0.05)	1.21
P_{13}-C_{113}	0.98	P:37.65 s (22.04) p (77.49) d (0.47)		C:63.23 s (37.46) p (62.50) d (0.04)	0.60
P_{14}-C_{80}	0.98	P:36.77 s (21.27) p (78.24) d (0.48)		C:63.23 s (37.13) p (62.82) d (0.04)	1.25

P_{15}-C_{86}	0.98	P:38.50 s (23.30) p (76.34) d (0.45)	C:61.50 s (36.89) p (63.05) d (0.05)	1.17
P_{16}-C_{119}	0.98	P:36.96 s (20.41) p (79.11)	C:63.04 s (37.58) p (62.37) d (0.04)	1.24
P-LonePairs	0.94	P_{11} 47.49 52.56		
	0.79	P_{12} s (31.81) p (68.17)		
	0.66	P_{12} s (5.81) p (94.11)		
	0.69	P_{13} s (0.10) p (99.83)		
	0.68	P_{14} s (0.24) p (99.67)		
	0.69	P_{15} s (10.77) p (89.18)		
	0.68	P_{16} s (0.01) p (99.90)		

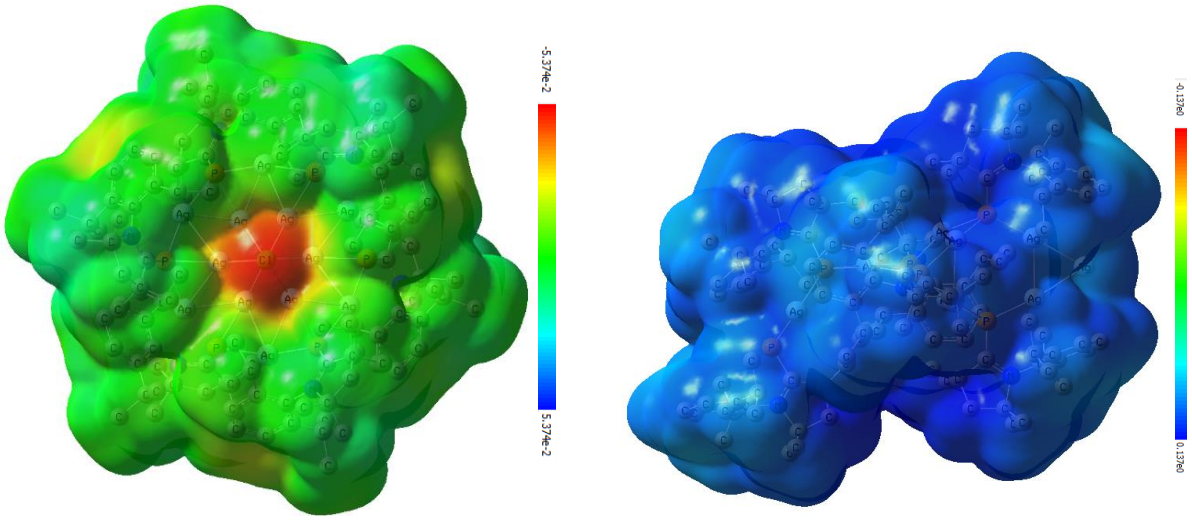


Figure S12. MEP plots of nanoclusters **2** and **4** at UBP86-D3(BJ)/Def2-SVP level of theory.

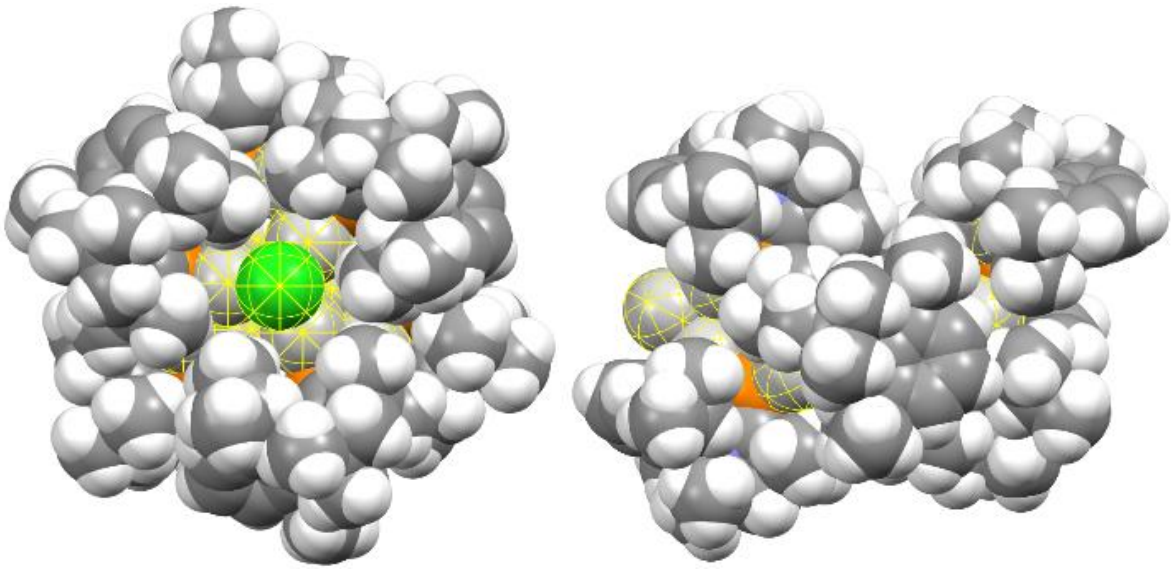


Figure S13. Space filling models of total molecule of $[(Me_2\text{-}cAAC{=}P)_6Ag_{12}Cl_3]$ (**2**) (left) and $[(Me_2\text{-}cAAC{=}P)_6Ag_{10}](NTf_2)_2$ (**4**) (right).

Coordinates of nanoclusters 2 and 4

Nanocluster 2

Ag	0.932164102	1.826751953	1.362871102
Ag	-0.076198112	4.188880969	0.050865007
Cl	0.000219021	0.000269973	-0.000227997
Cl	-0.001154055	-0.000962943	2.934417214

P	2.176060379	3.868002824	0.817019060
N	3.895569757	4.622251428	2.824421208
C	4.995617490	3.915376914	2.163127160
C	5.659692974	4.558753233	1.109819081
C	6.721156759	3.868695088	0.489203038
H	7.229293232	4.315840958	-0.302874019
C	7.116935091	2.569121719	0.919527069
H	7.908882658	2.071751113	0.462431036
C	6.414460548	1.990883759	1.961110146
H	6.693597313	1.040623568	2.283278166
C	5.333132084	2.620053119	2.606303189
C	4.102981007	5.490283757	4.053400295
C	2.658572481	5.809591373	4.390590318
H	2.391346654	5.307206738	5.276879384
H	2.561039896	6.843774430	4.568462334
C	1.737950428	5.402165796	3.285321241
C	2.628716512	4.587109117	2.350040173
C	5.282259979	5.928681495	0.534456041
H	4.475916700	6.316394955	1.095355079
C	4.829917313	5.787916220	-0.944042063
H	4.497224498	6.720803692	-1.296935093
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H	3.851381562	2.515648982	4.080627295
C	3.834345325	0.636570888	3.055248224
H	3.431355783	0.057535558	3.833580278
H	4.512598833	0.057028249	2.500428183
H	3.057775146	0.960712532	2.425258179
C	4.788736703	4.685501657	5.187424378
H	5.199957512	5.350415489	5.890028431
H	5.553917321	4.091012685	4.782726345
H	4.081829846	4.069010961	5.659534432
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H	5.919799890	6.480681418	3.536023260
C	0.601572729	4.576785435	3.832059279
H	0.096596201	4.095941368	3.045324224
H	-0.074927269	5.197288966	4.346463318
H	0.982170411	3.853732041	4.492239325
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H	1.438538426	6.495037256	1.365484100
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Nanocluster 4

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P	-0.369329000	-1.234530000	2.459973000
P	-4.077784000	-1.987346000	-0.367380000
P	-0.145174000	-0.175905000	-2.351436000
P	-2.544152000	2.608898000	0.479485000
N	7.504044000	3.324753000	0.631363000
N	4.792630000	-3.770239000	-1.815561000
N	-5.911007000	-4.070334000	-0.390069000
N	-0.503719000	0.612984000	-4.998828000
N	0.511289000	-1.733352000	5.052103000
N	-2.773570000	5.120451000	1.554862000
C	8.863005000	2.844166000	0.784776000
C	9.812568000	3.107893000	-0.245518000
C	11.142716000	2.693857000	-0.032861000
H	11.896976000	2.894992000	-0.809405000
C	11.520552000	2.019867000	1.133560000
H	12.569277000	1.718607000	1.281089000
C	10.557254000	1.708901000	2.101067000
H	10.854086000	1.141895000	2.997102000
C	9.212294000	2.098346000	1.948007000
C	7.026999000	4.673014000	1.139199000
C	5.503438000	4.549726000	0.889148000
H	4.999694000	4.249225000	1.830782000
H	5.065353000	5.515868000	0.569604000
C	5.292793000	3.437932000	-0.177357000
C	6.580417000	2.617100000	-0.035190000
C	9.450905000	3.738373000	-1.589022000
H	8.383945000	4.031810000	-1.543957000
C	10.288226000	4.997423000	-1.888438000
H	9.935923000	5.483391000	-2.821341000

H	11.359325000	4.745756000	-2.033804000
H	10.232438000	5.742238000	-1.069841000
C	8.204141000	1.644805000	2.999977000
H	7.227555000	2.115380000	2.769003000
C	8.005765000	0.115307000	2.918037000
H	7.448169000	-0.253995000	3.802976000
H	8.977653000	-0.418469000	2.893425000
H	7.441065000	-0.170113000	2.006391000
C	7.365586000	4.855168000	2.623861000
H	7.066470000	5.873772000	2.941981000
H	8.455102000	4.753761000	2.801289000
H	6.831287000	4.127303000	3.263219000
C	7.675596000	5.816603000	0.341757000
H	7.292089000	6.785591000	0.718727000
H	7.452553000	5.758460000	-0.739871000
H	8.774725000	5.815049000	0.474576000
C	5.258448000	4.011010000	-1.616968000
H	5.071540000	3.203569000	-2.351327000
H	6.214589000	4.497467000	-1.893667000
H	4.447002000	4.761595000	-1.707790000
C	4.019325000	2.623699000	0.093116000
H	3.954013000	1.735528000	-0.567070000
H	3.119670000	3.243245000	-0.090974000
H	3.990332000	2.264911000	1.137763000
C	3.765125000	-3.497890000	-0.963613000
C	4.657554000	-5.095439000	-2.542314000
C	5.719936000	-6.101546000	-2.070590000
H	5.606468000	-7.041728000	-2.646381000
H	5.616769000	-6.349423000	-0.997486000
H	6.743695000	-5.718723000	-2.248625000
C	9.593906000	2.706711000	-2.732553000
H	9.522123000	3.208353000	-3.719655000
H	8.801461000	1.934205000	-2.670782000
H	10.575310000	2.190930000	-2.688455000

C	8.626210000	2.064305000	4.421090000
H	7.835845000	1.801827000	5.152827000
H	8.816506000	3.153355000	4.495573000
H	9.552552000	1.542757000	4.739315000
C	-4.619737000	-3.675491000	-0.380740000
C	-6.117568000	-5.569666000	-0.297745000
C	-4.685255000	-6.084645000	-0.565310000
H	-4.456322000	-6.953063000	0.082207000
H	-4.594414000	-6.427352000	-1.615906000
C	-3.704074000	-4.906483000	-0.300153000
C	-0.234121000	-0.388456000	-4.110293000
C	-0.001354000	-1.708577000	-4.849919000
C	-0.422569000	-1.350063000	-6.304454000
H	0.222019000	-1.847549000	-7.055683000
H	-1.461774000	-1.694191000	-6.482646000
C	-0.366767000	0.189982000	-6.442421000
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C	3.128775000	-5.468935000	0.416977000
H	2.647110000	-6.468607000	0.405427000
H	2.747896000	-4.896133000	1.284981000
H	4.217395000	-5.610910000	0.569845000
C	5.997403000	-2.985035000	-1.970844000
C	7.072098000	-3.161400000	-1.048491000
C	8.286279000	-2.485283000	-1.294502000
H	9.126451000	-2.627179000	-0.596901000
C	8.442730000	-1.645207000	-2.402593000
H	9.398855000	-1.128646000	-2.576692000
C	7.360068000	-1.433893000	-3.264436000
H	7.472366000	-0.739115000	-4.110573000
C	6.122977000	-2.080343000	-3.067308000
C	3.222835000	-5.518913000	-2.153212000
H	3.164709000	-6.609117000	-1.966892000
H	2.524947000	-5.288198000	-2.983868000
C	4.785440000	-4.911135000	-4.059122000

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H	4.061035000	-4.165581000	-4.436758000
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C	-1.287561000	-1.151287000	6.479575000
H	-1.961273000	-2.007194000	6.689096000
H	-1.489387000	-0.380187000	7.247823000
C	0.184968000	-1.637544000	6.528039000
C	-1.951116000	4.148944000	1.101444000
C	-0.489983000	4.617660000	1.175038000
C	-0.600954000	5.838365000	2.130462000
H	-0.385844000	5.505464000	3.167031000
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C	-2.055880000	6.359151000	2.058209000
C	-7.041294000	-3.174911000	-0.324312000
C	-7.712223000	-2.812347000	-1.524550000
C	-8.867567000	-2.009799000	-1.418211000
H	-9.403428000	-1.716881000	-2.333880000
C	-9.342146000	-1.580004000	-0.171107000
H	-10.261185000	-0.976529000	-0.109672000
C	-8.634098000	-1.901095000	0.995948000
H	-8.983489000	-1.524967000	1.970048000
C	-7.462578000	-2.686247000	0.946530000
C	-6.668843000	-2.904261000	2.223572000
H	-7.282733000	-3.515253000	2.920410000
H	-5.764592000	-3.501290000	2.008447000
C	-6.263917000	-1.593419000	2.933132000
H	-5.350584000	-1.746589000	3.539104000
H	-7.058557000	-1.218129000	3.608603000
H	-6.037544000	-0.788123000	2.200186000
C	-6.632354000	-5.943596000	1.103847000
H	-6.857557000	-7.028467000	1.131777000
H	-7.568172000	-5.400398000	1.341572000

H	-5.886425000	-5.728944000	1.893061000
C	-7.112927000	-6.076930000	-1.348197000
H	-7.137465000	-7.184487000	-1.305836000
H	-6.815256000	-5.785956000	-2.371812000
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C	-2.571923000	-4.877916000	-1.342401000
H	-1.958906000	-5.799077000	-1.256660000
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H	-2.971831000	-4.817359000	-2.374678000
C	-3.087294000	-5.003810000	1.119441000
H	-2.672607000	-6.019268000	1.286129000
H	-3.834077000	-4.798603000	1.912857000
H	-2.263087000	-4.267582000	1.237634000
C	1.479376000	-2.135778000	-4.767651000
H	1.656707000	-3.045416000	-5.378952000
H	1.760222000	-2.355682000	-3.715138000
H	2.154103000	-1.338113000	-5.129601000
C	-0.876690000	-2.847638000	-4.291176000
H	-0.759119000	-3.763261000	-4.908282000
H	-1.949235000	-2.562415000	-4.283663000
H	-0.585304000	-3.088589000	-3.248692000
C	0.973731000	0.673483000	-7.022725000
H	1.094463000	0.288103000	-8.055114000
H	1.836823000	0.324445000	-6.422830000
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C	-1.507102000	0.732915000	-7.310067000
H	-1.338235000	0.435544000	-8.364519000
H	-1.549229000	1.840039000	-7.273568000
H	-2.487067000	0.328383000	-6.996338000
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C	0.265362000	2.865289000	-4.316808000
C	-0.053101000	4.197793000	-3.986569000
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C	-1.381935000	4.632943000	-3.923750000

H	-1.612449000	5.682676000	-3.682539000
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H	-3.460270000	4.043078000	-4.059306000
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C	1.318804000	-4.372878000	-0.927913000
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H	6.163120000	-2.390029000	1.485091000
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C	4.964474000	-1.721249000	-3.990328000
H	4.108360000	-2.365808000	-3.710106000
C	5.301769000	-1.942275000	-5.476952000
H	4.450883000	-1.634930000	-6.119021000
H	5.537846000	-2.999124000	-5.705513000
H	6.176018000	-1.331947000	-5.783394000
C	-2.981261000	-0.901275000	4.567311000
H	-3.689598000	-0.950961000	5.419384000
H	-3.012757000	-1.880071000	4.043140000
H	-3.352069000	-0.139995000	3.854655000
C	-1.285432000	0.950298000	5.033470000
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H	-0.230732000	1.175109000	5.285084000
H	-1.939553000	1.463547000	5.768404000
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C	1.712031000	-2.370251000	4.578991000
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C	4.054723000	-2.233195000	3.948704000
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C	4.084388000	-3.618030000	3.747490000
H	5.016043000	-4.108556000	3.434133000
C	2.913385000	-4.369243000	3.902169000
H	2.934069000	-5.451522000	3.703555000
C	1.698606000	-3.766091000	4.287434000
C	-0.015110000	5.016605000	-0.244390000
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C	0.484740000	3.575860000	1.749943000
H	1.487959000	4.033871000	1.872163000
H	0.595840000	2.701197000	1.075528000
H	0.148576000	3.206969000	2.740411000
C	-2.583669000	6.785173000	3.431957000
H	-2.041660000	7.693604000	3.764222000
H	-2.422680000	5.996973000	4.190294000
H	-3.663600000	7.030518000	3.393428000
C	-2.209262000	7.537549000	1.081766000
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C	-4.213934000	4.989768000	1.579811000
C	-4.834457000	4.370598000	2.702837000
C	-6.242869000	4.312468000	2.737689000
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C	-7.022257000	4.818226000	1.691384000
H	-8.120736000	4.767646000	1.743912000
C	-6.393856000	5.354843000	0.562069000

H	-7.004865000	5.706788000	-0.283090000
C	-4.988330000	5.439669000	0.472377000
C	-7.164251000	-3.156278000	-2.905228000
H	-6.339619000	-3.884339000	-2.769955000
C	-6.539878000	-1.901513000	-3.545997000
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C	1.721680000	2.426974000	-4.248804000
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C	2.635747000	3.202857000	-5.217120000
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H	2.595344000	4.294359000	-5.020389000
H	2.357236000	3.048381000	-6.277263000
C	-3.338476000	1.412866000	-4.508776000
H	-2.958531000	0.411833000	-4.799049000
C	-4.417888000	1.849744000	-5.518455000
H	-5.206173000	1.073166000	-5.599784000
H	-4.003223000	2.029374000	-6.529440000
H	-4.916399000	2.786074000	-5.191148000
C	8.071809000	-5.093733000	0.298602000
H	7.669656000	-6.038383000	0.717776000
H	8.908443000	-4.777191000	0.955000000
H	8.505038000	-5.327937000	-0.693780000
C	4.516252000	-0.264843000	-3.770641000
H	3.592921000	-0.053738000	-4.346575000
H	5.297724000	0.455037000	-4.092669000
H	4.292792000	-0.070072000	-2.702465000
C	2.875405000	-0.060940000	4.507720000
H	1.875216000	0.235575000	4.880521000
C	3.934926000	0.428920000	5.510480000
H	3.859072000	1.526908000	5.653440000
H	4.958202000	0.213023000	5.141502000
H	3.829567000	-0.054285000	6.501480000

C	0.427986000	-4.613260000	4.288131000
H	-0.399641000	-3.980034000	4.666527000
C	0.048456000	-5.026922000	2.851256000
H	-0.917136000	-5.572115000	2.854356000
H	0.812217000	-5.698267000	2.406956000
H	-0.056811000	-4.138679000	2.195919000
C	-4.058336000	3.667901000	3.814403000
H	-2.974014000	3.830519000	3.636413000
C	-4.412128000	4.200050000	5.217664000
H	-3.796219000	3.693437000	5.989629000
H	-5.475235000	4.002476000	5.466160000
H	-4.248793000	5.291049000	5.309265000
C	-4.386727000	5.928366000	-0.838641000
H	-3.283892000	5.931096000	-0.732094000
C	-4.727540000	4.947437000	-1.975277000
H	-4.323307000	5.323153000	-2.935841000
H	-5.824194000	4.831659000	-2.095405000
H	-4.295872000	3.943349000	-1.780250000
C	-8.223314000	-3.781633000	-3.831143000
H	-7.758995000	-4.119260000	-4.780545000
H	-9.010847000	-3.046348000	-4.096885000
H	-8.724504000	-4.652386000	-3.363859000
C	2.239394000	2.565044000	-2.807892000
H	3.271601000	2.176541000	-2.735253000
H	1.609050000	1.992154000	-2.097972000
H	2.255400000	3.626953000	-2.486550000
C	-3.959239000	1.286107000	-3.104552000
H	-4.851488000	0.635199000	-3.126463000
H	-4.276452000	2.270580000	-2.704576000
H	-3.243062000	0.848273000	-2.378492000
C	3.071779000	0.633296000	3.145904000
H	3.082341000	1.734762000	3.280832000
H	2.252994000	0.384095000	2.439050000
H	4.031743000	0.335746000	2.670138000

C	0.547598000	-5.860799000	5.184140000
H	-0.406242000	-6.427467000	5.187136000
H	0.798435000	-5.604568000	6.231743000
H	1.334989000	-6.549002000	4.812787000
C	-4.857546000	7.350151000	-1.209753000
H	-4.255029000	7.753854000	-2.049684000
H	-4.778410000	8.056697000	-0.360503000
H	-5.917354000	7.347003000	-1.538912000
C	-4.316983000	2.147618000	3.748957000
H	-3.733771000	1.625113000	4.531496000
H	-4.032321000	1.730878000	2.760371000
H	-5.388426000	1.915227000	3.918772000

S9. TGA plot of [(Me$_2$-cAAC=P)$_6$(Ag)$_{10}$](NTf$_2$)$_2$ (4)

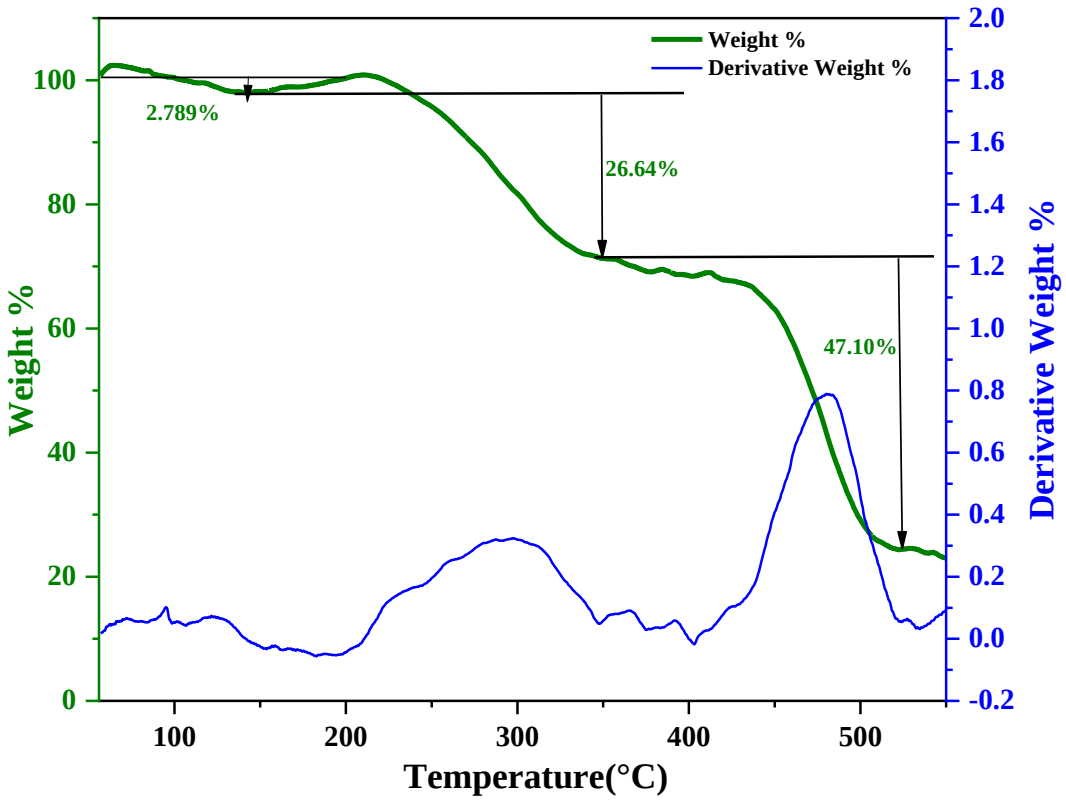

Figure S14. Thermogravimetric analysis (TGA) curve of [(Me$_2$-cAAC=P)$_6$(Ag)$_{10}$](NTf$_2$)$_2$ (**4**).

S10. X-ray photoelectron spectroscopy (XPS) Analyses under Inert Atmosphere

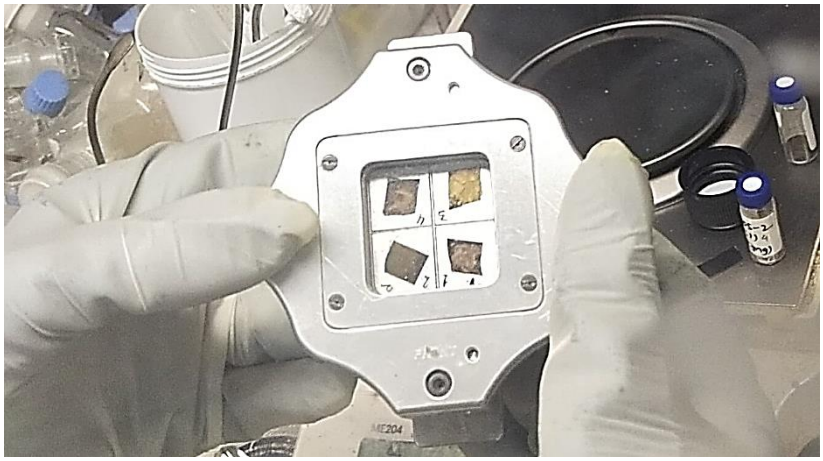

Figure S15. Sample preparation for the XPS studies.

S10.1. XPS data of [$(Me_2$-cAAC=P$)_6(Ag)_{12}(Cl)_3$] (2)

The high-resolution X-ray Photo-electron Spectroscopy (XPS) deconvolution illustrated in Figures S16-S17 offer comprehensive insights into the Ag3d region of NCs **2**, **4**. The analysis of **2** indicates distinct peaks at 367.96 eV, 368.81 eV, 373.95 eV, and 374.76 eV, which correspond to core-level transitions of Ag 3d. The peaks at 367.96 eV and 368.81 eV are attributed to the $Ag3d_{5/2}$ orbital, while those at 373.95 eV and 374.76 eV are associated with the $Ag3d_{3/2}$ orbital, exhibiting a spin-orbit splitting of approximately 6 eV. The peaks at 368.81 eV and 374.76 eV correspond to Ag^0, whereas the peaks at 367.96 eV and 373.94 eV are indicative of Ag^I.[18-20] These binding energy values suggest the presence of both Ag^+ and Ag^0 states within the samples of [$(Me_2$-cAAC=P$)_6(Ag)_{12}(Cl)_3$] (**2**).

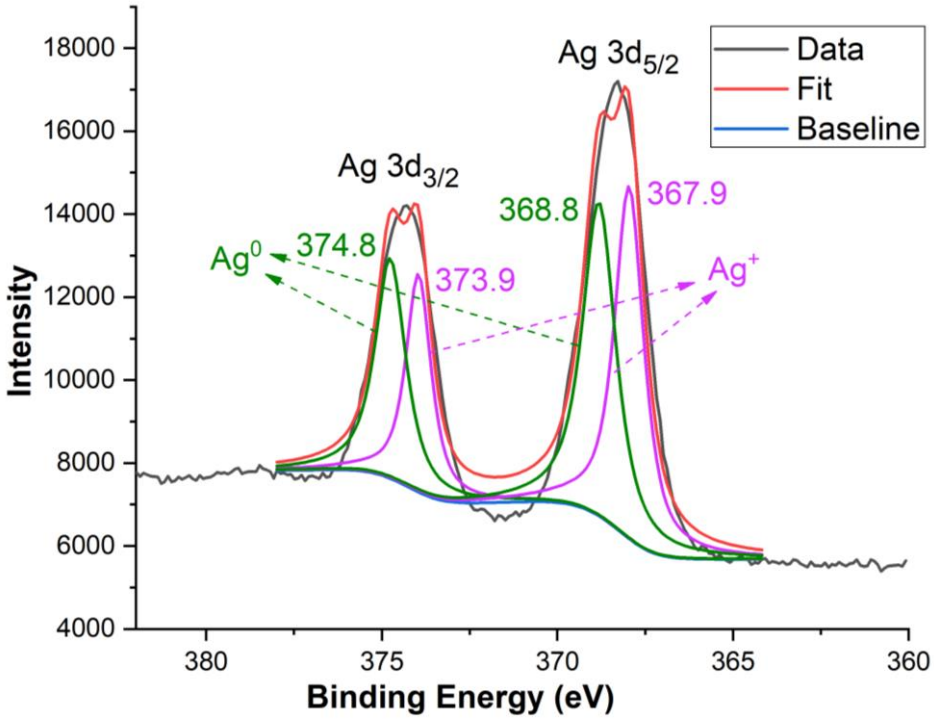

Figure S16. Ag3d high-depth deconvolution spectra of [(Me$_2$-cAAC=P)$_6$(Ag)$_{12}$(Cl)$_3$] (**2**).

S10.2. XPS data of [(Me$_2$-cAAC=P)$_6$(Ag)$_{10}$](NTf$_2$)$_2$ (4)

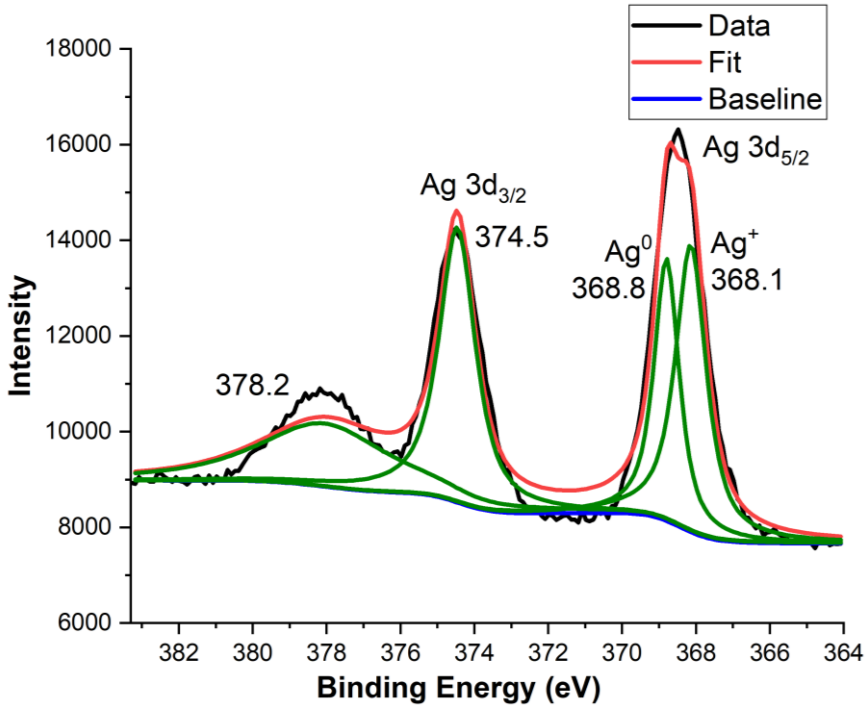

Figure S17. Ag3d high-depth deconvolution spectra of [(Me$_2$-cAAC=P)$_6$(Ag)$_{10}$](NTf$_2$)$_2$ (**4**).

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