Supporting Information

Macrocycle-assisted synthesis of non-stoichiometric silver(I) halide electrocatalysts for efficient chlorine evolution reaction

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X-ray Crystallographic Analysis

Crystal data for $[Ag_4Cl(CF_3SO_3)_3(\mathbf{Py[7]})(CH_3OH)]$ (**1**, CCDC-1527294): $C_{46}H_{46}Ag_4ClF_9N_{14}O_{10}S_3$, M = 1689.08, monoclinic, space group $P2_1/n$ (No. 14), a = 24.864(5) Å, b = 10.112(2) Å, c = 24.940(5) Å, β = 114.19(3)°, V = 5720(2) Å^3, Z = 4, T = 173 K, D_c = 1.961 g cm^{-3}. The structure, refined on F^2, converged for 9994 unique reflections (R_{int} = 0.0643) and 8482 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0962 and wR_2 = 0.1894 and a goodness-of-fit = 1.225. Sliver atom Ag2 is disordered at two separated positions with a refined occupancy ratio of 0.89:0.11.

Crystal data for $[Ag_5Br(CF_3SO_3)_2(H_2O)_4(\mathbf{Py[7]})](CF_3SO_3)_2\cdot H_2O$ (**2**, CCDC-1527295): $C_{46}H_{52}Ag_5BrF_{12}N_{14}O_{17}S_4$, M = 2048.52, triclinic, space group P-1 (No. 2), a = 10.277(2) Å, b = 17.015(3) Å, c =19.143(4) Å, α = 91.21(3)°, β = 102.96(3)°, γ = 90.15(3)°, V = 3261.4(11) Å^3, Z = 2, T = 173 K, D_c = 2.086 g cm^{-3}. The structure, refined on F^2, converged for 14837 unique reflections (R_{int} = 0.0442) and 13437 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0442 and wR_2 = 0.1083 and a goodness-of-fit = 1.068. Sliver atom Ag2 is disordered at two positions with a refined occupancy ratio of 0.70:0.30. The triflate anion S4 has two orientational disorder positions with a refined occupancy ratio of 0.72:0.28.

Crystal data for $[Ag_4I(H_2O)_2(\mathbf{Py[7]})](CF_3SO_3)_3$ (**3**, CCDC-1527296): $C_{45}H_{42}Ag_4F_9IN_{14}O_{10}S_3$, M = 1764.49, orthorhombic, space group $Pnma$ (No. 62), a = 26.256(5) Å, b = 21.160(4) Å, c = 10.086(2) Å, V = 5603.6(19) Å^3, Z = 4, T = 173 K, D_c = 2.092 g cm^{-3}. The structure, refined on F^2, converged for 5068 unique reflections (R_{int} = 0.0646) and 4328 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0835 and wR_2 = 0.1439 and a goodness-of-fit = 1.209. Sliver atom Ag3 is disordered at three separated positions with a refined occupancy ratio of 0.36:0.32:0.32. The triflate anion S2 has two orientational disorder positions with a refined occupancy ratio of 0.52:0.48. A disordered atom C24 was refined isotropically.

Supporting Figures

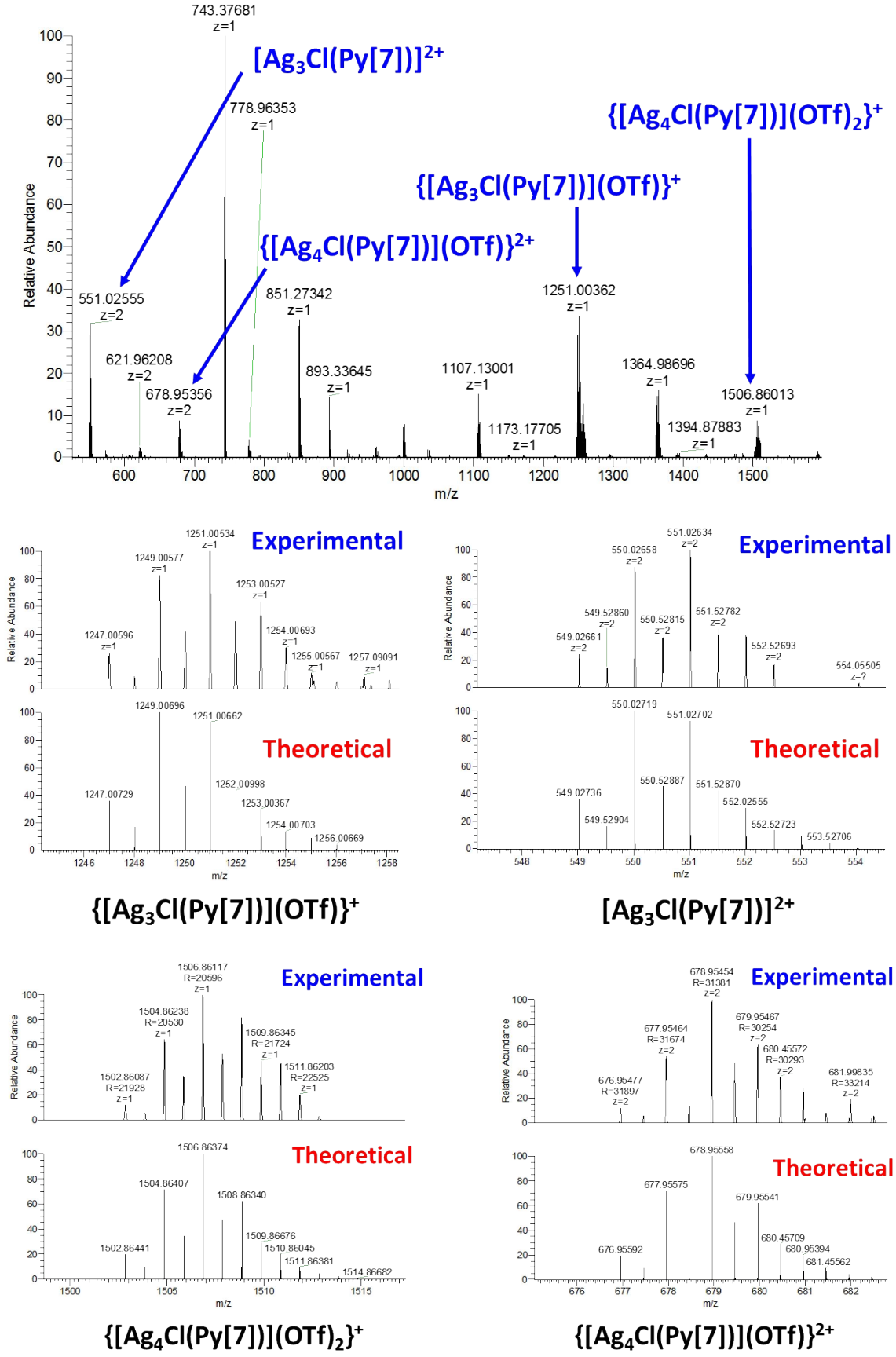

Fig. S1 High resolution ESI-MS spectra of complex **1**.

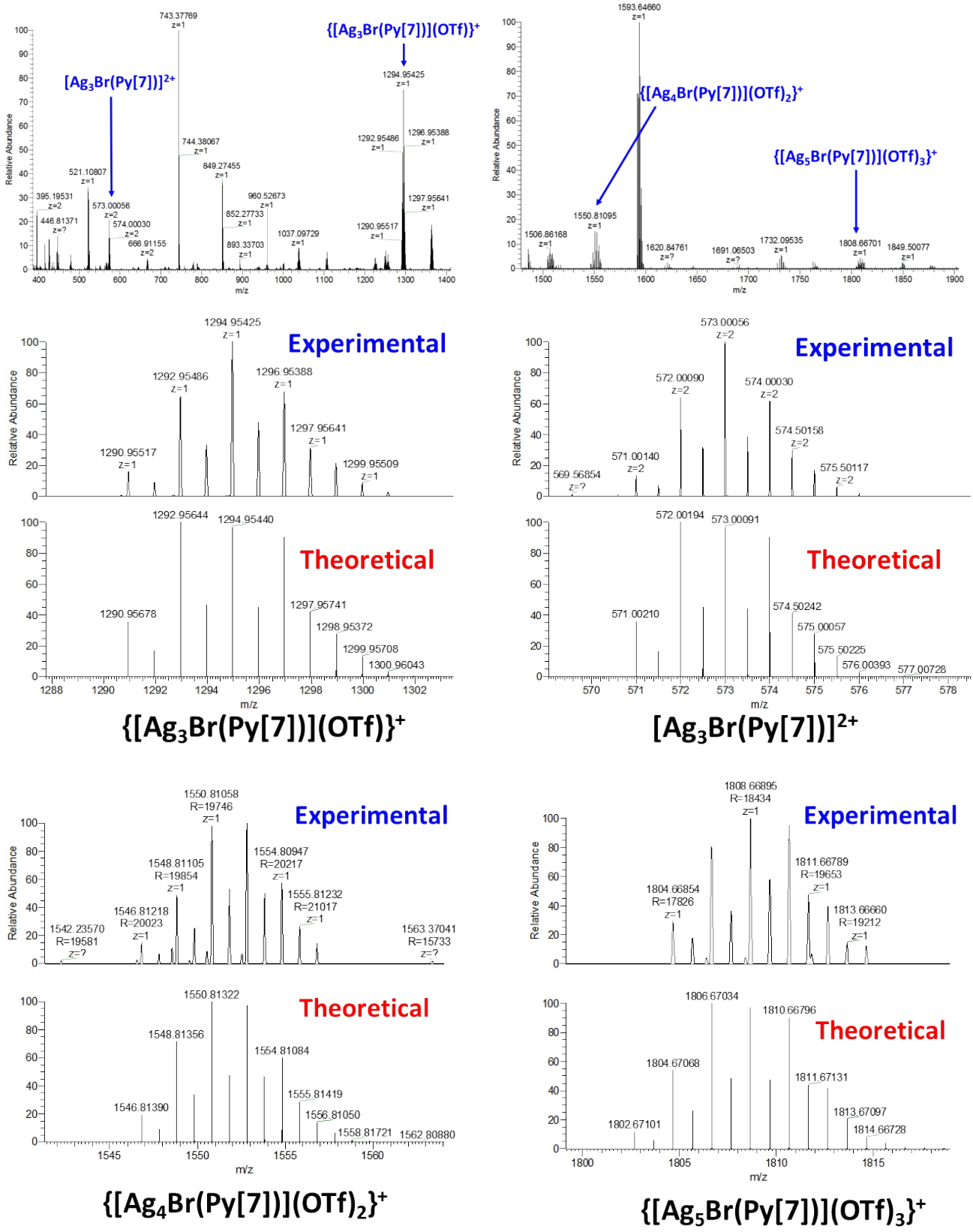

Fig. S2 High resolution ESI-MS spectra of complex **2**.

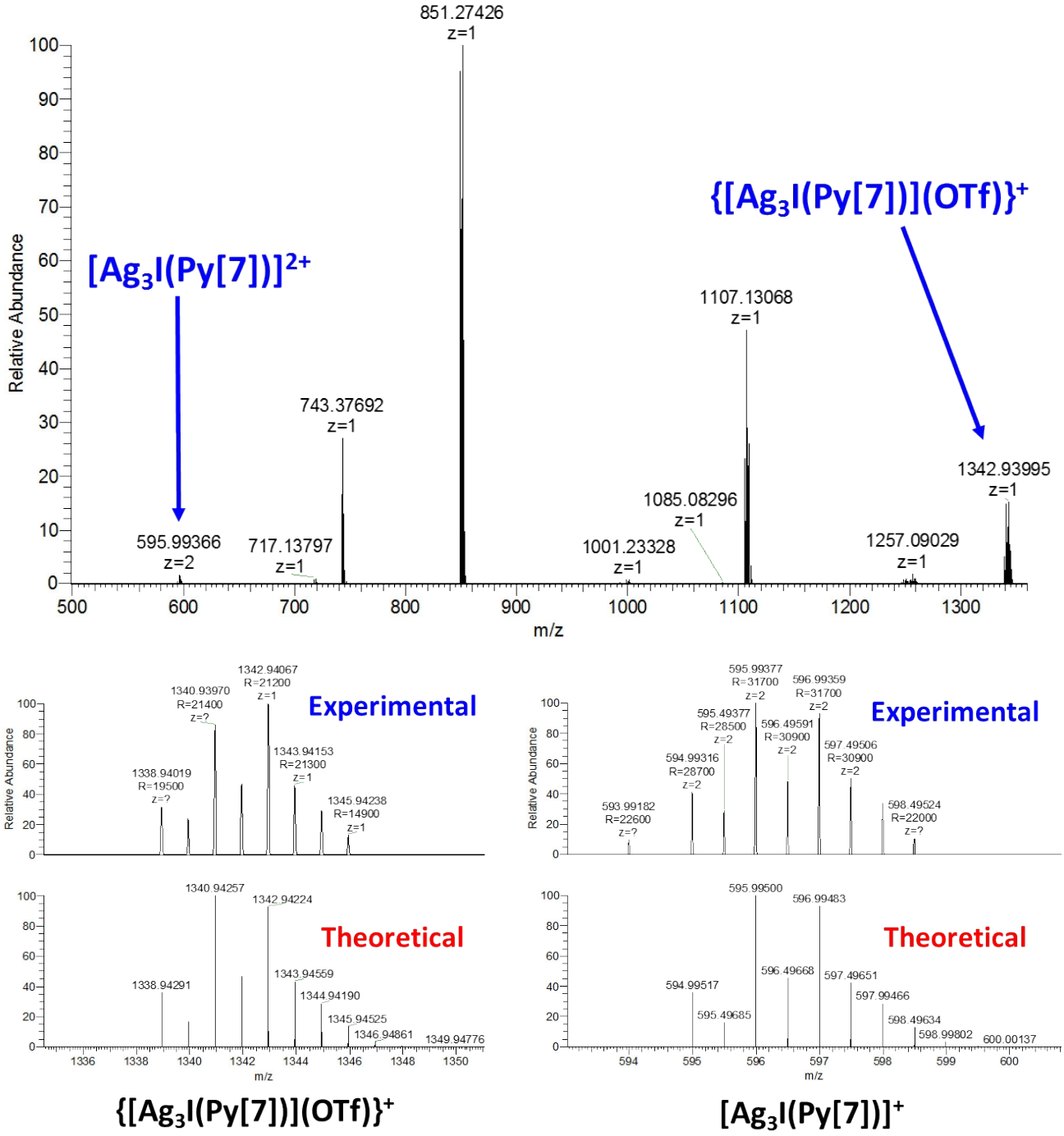

Fig. S3 High resolution ESI-MS spectra of complex **3**.

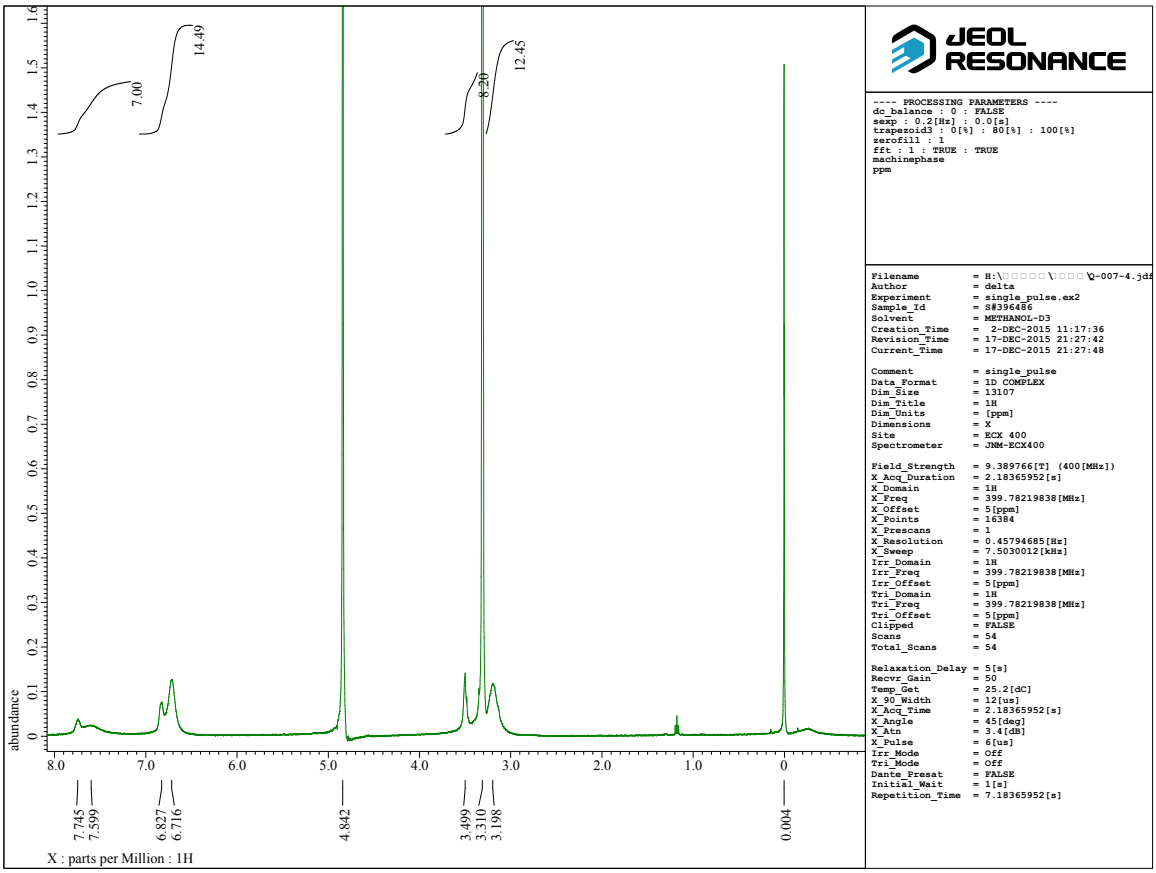

Fig. S4 ^{1}H-NMR spectrum (400MHz, methanol-d_4 : $CDCl_3$, v : v = 1 : 1) of complex **1**.

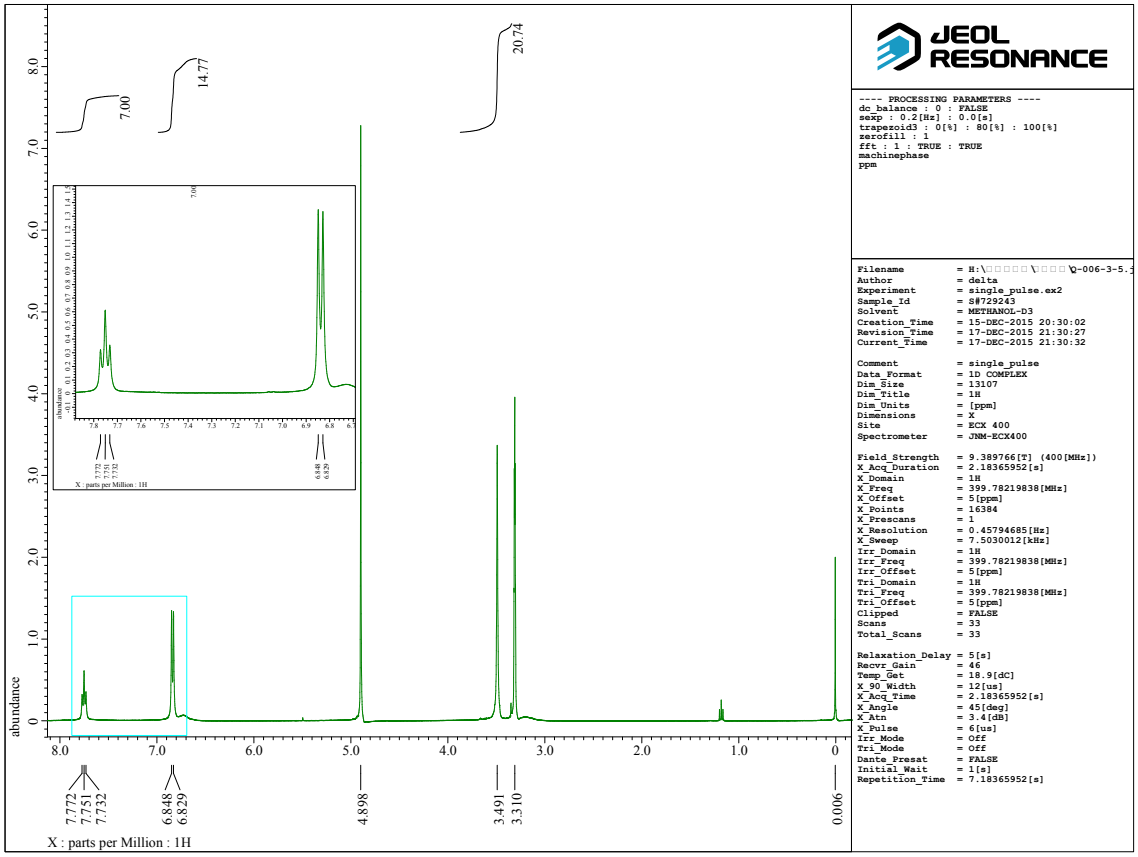

Fig. S5 ^{1}H-NMR spectrum (400MHz, methanol-d_4 : $CDCl_3$, v : v = 1 : 1) of complex **2**.

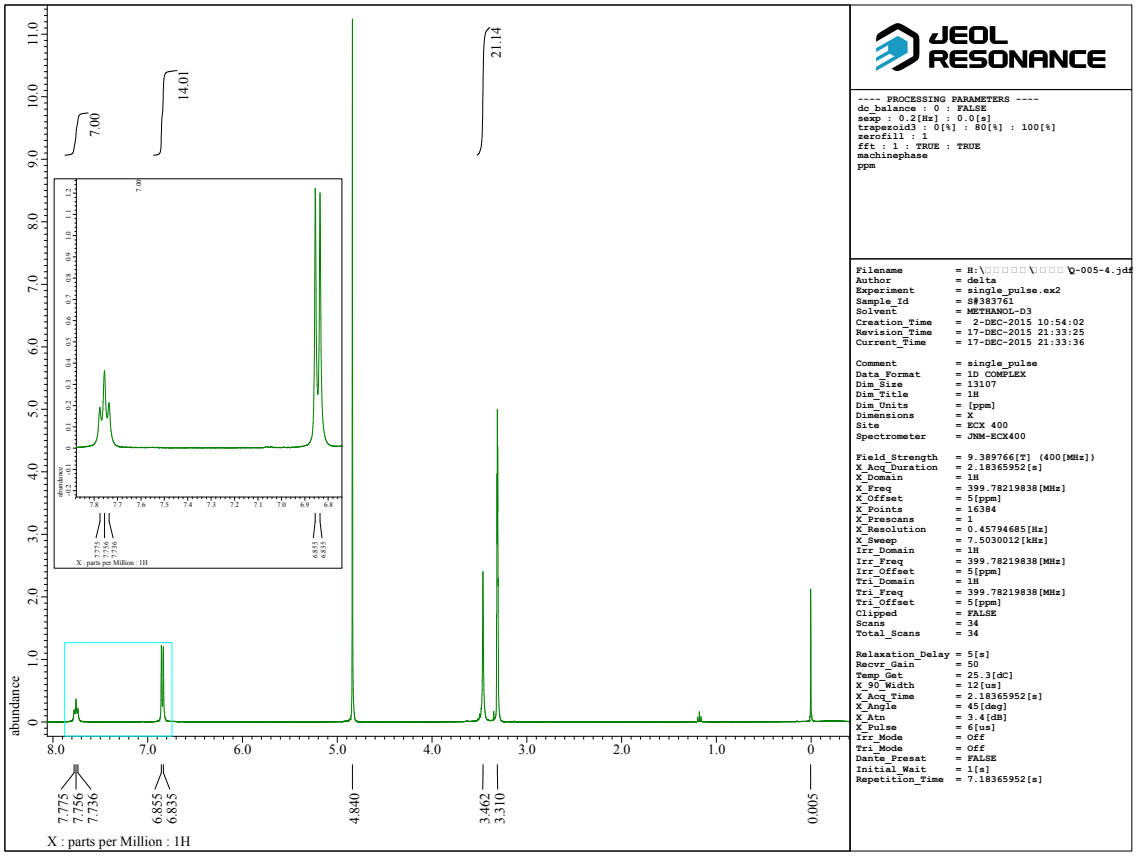

Fig. S6 ^{1}H-NMR spectrum (400MHz, methanol-d_4 : $CDCl_3$, v : v = 1 : 1) of complex **3**.

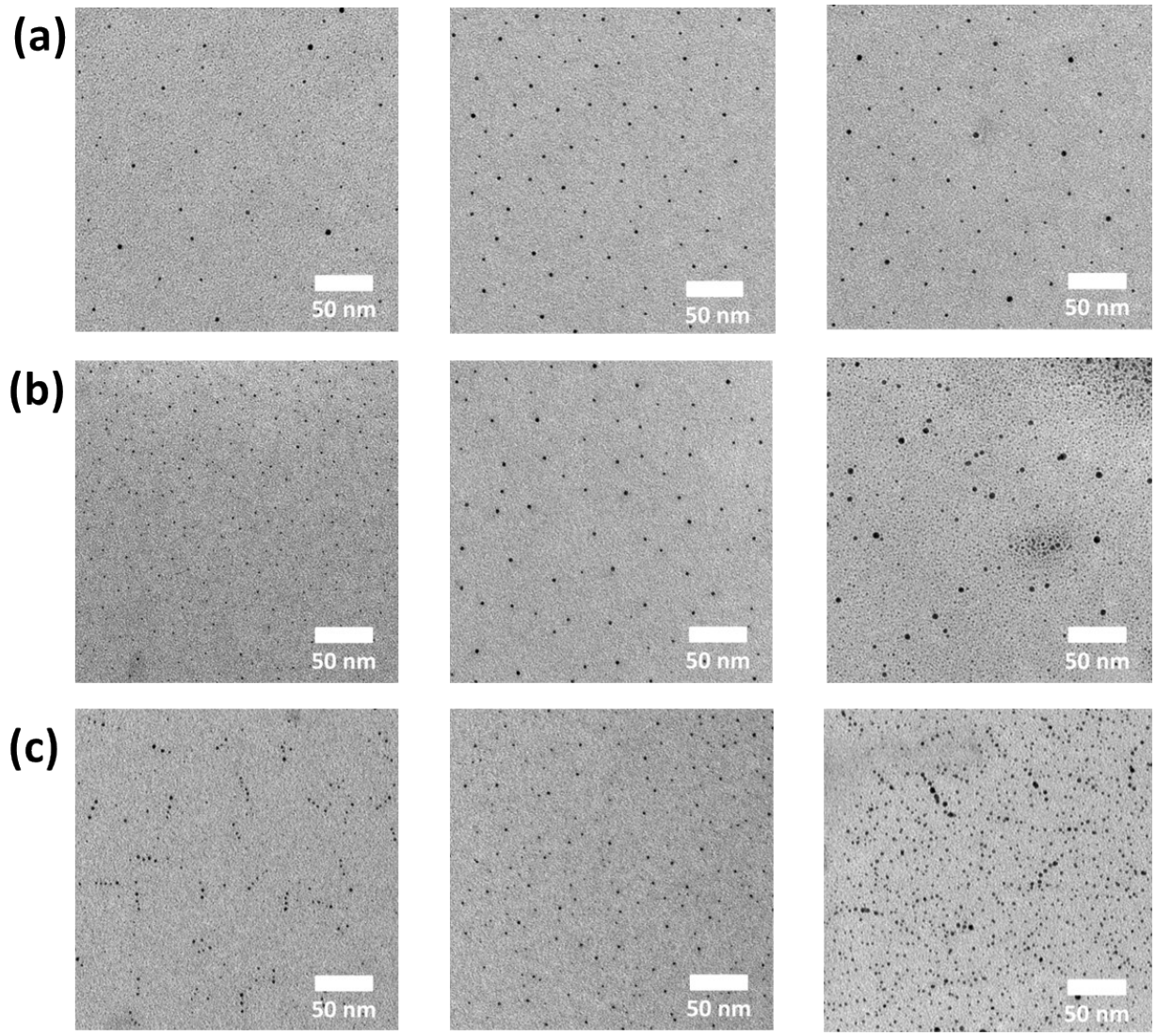

Fig. S7 TEM images for the stepwise growth of nanometer-sized particles upon adding HBF_4 into the solution of (a) complex **1**, (b) complex **2**, (c) complex **3**. From left to right: after 1, 2 and 3 minutes.

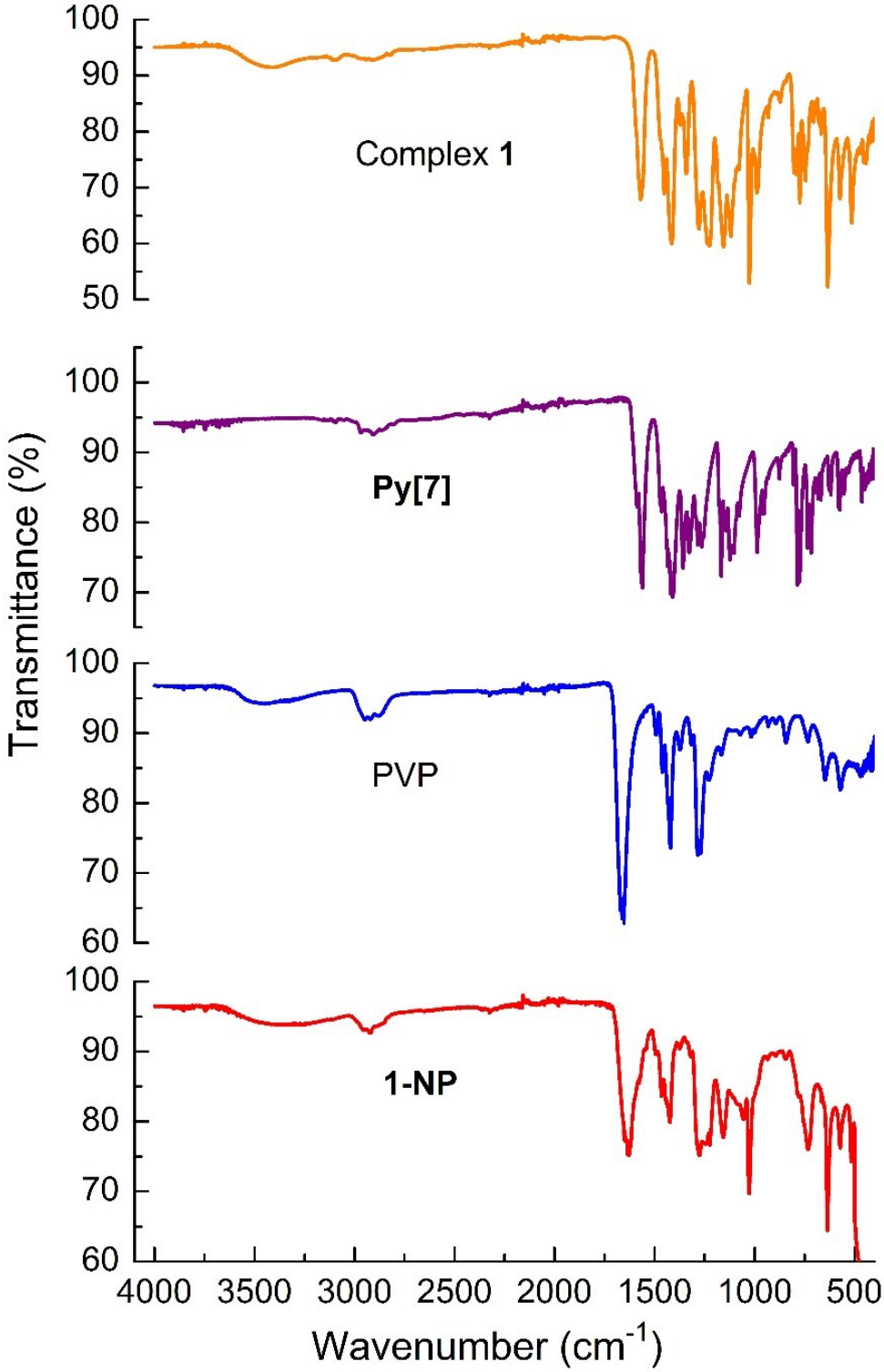

Fig. S8 FT-IR spectra of **1-NP**, PVP, macrocyclic ligand **Py[7]** and complex **1**.

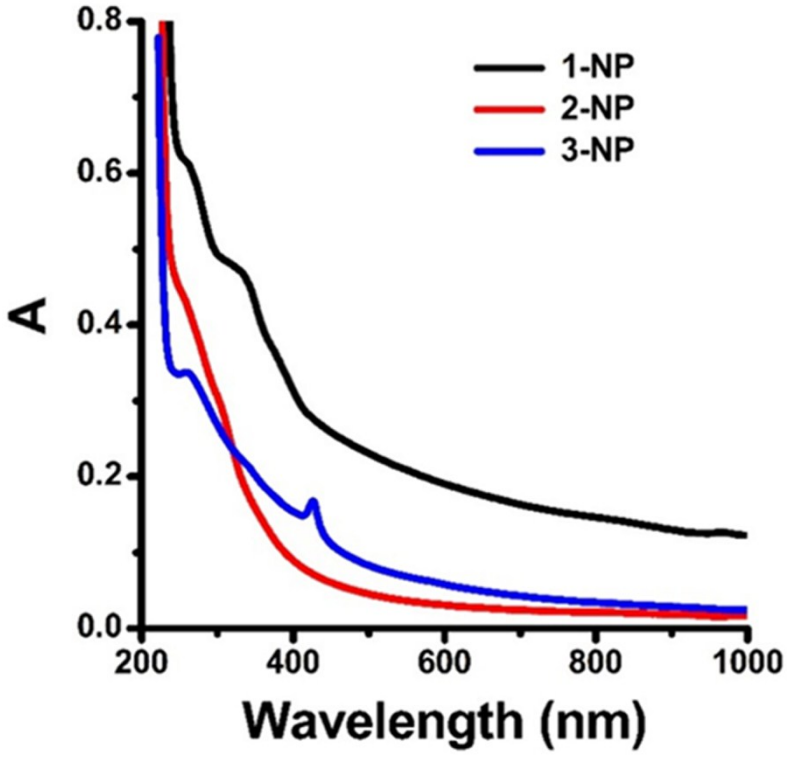

Fig. S9 UV-vis spectra of **1-** to **3-NP** in methanol at 298 K.

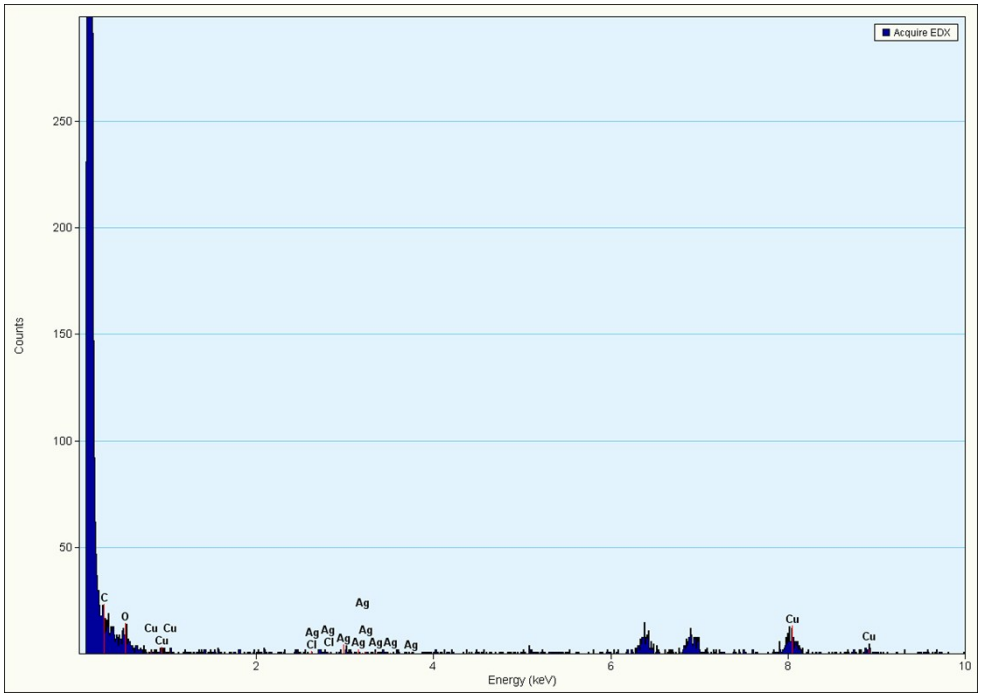

Fig. S10 EDX spectrum of **1-NP**. The Ag/Cl ratio was determined as 4.6 based on the atomic ratio of Ag-82.3% and Cl-17.7%.

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
Cl(K)	6.60	17.71	4.65	0.95	1.063
Ag(K)	93.39	82.28	42.56	0.98	6.491

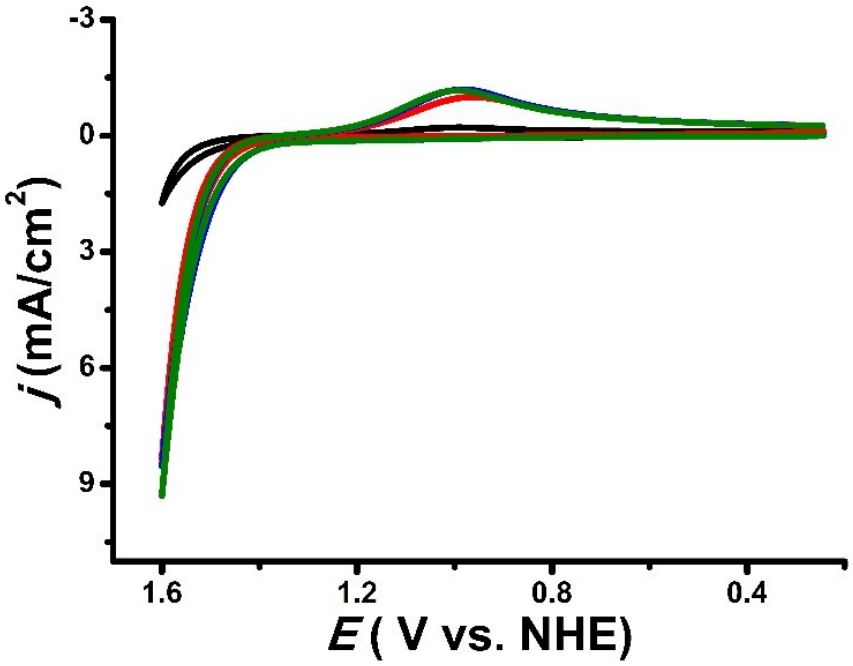

Fig. S11 CVs at a GC electrode (0.071 cm^2) in an aqueous solution of NaCl (1 M) and HNO_3 (pH ~1, 0.1 M) without (black) and with (red) **2-NP** (c_{Ag+} = 5.04 μM) and (green) **3-NP** (c_{Ag+} = 6.72 μM). Scan rate: 100 mV/s.

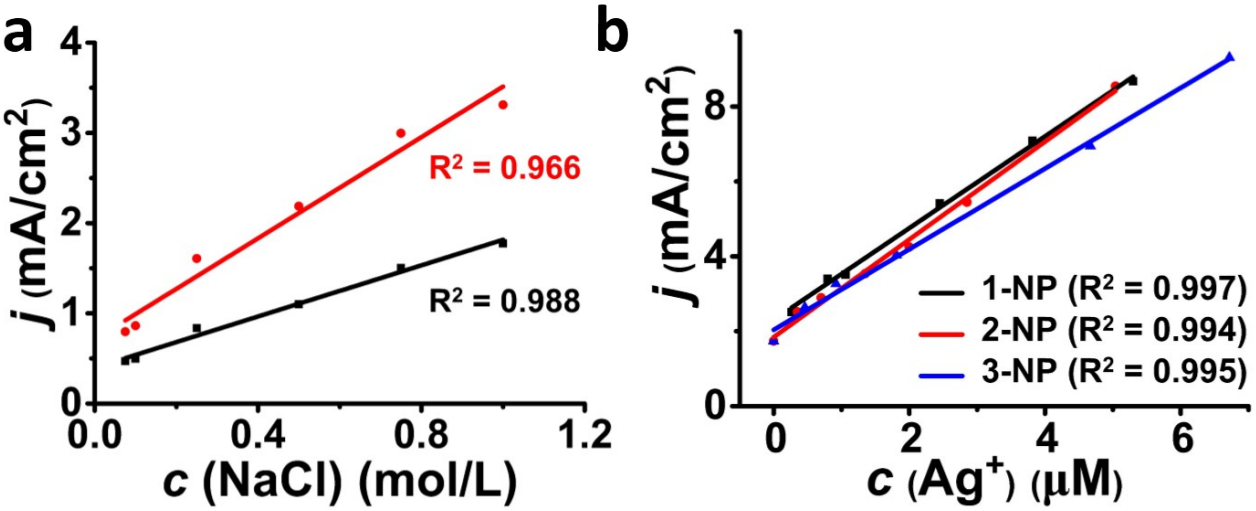

Fig. S12 (a) Plot of catalytic current density vs. NaCl concentration in 0.1 M HNO_3 solution without (black) and with (red) **1-NP** (c_{Ag+} = 0.53 μM). (b) Plot of catalytic current density vs. silver(I) concentration of **1-3-NP** (1 M NaCl, 0.1 M HNO_3).

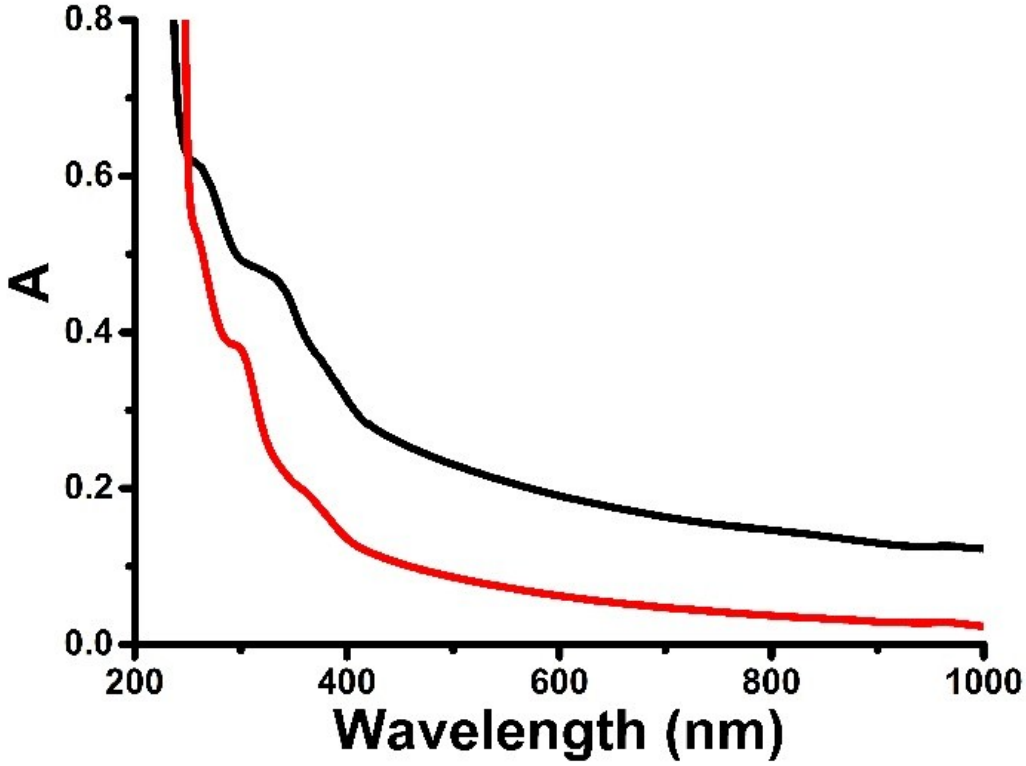

Fig. S13 UV-vis spectra of **1-NP** in (black) H_2O and (red) in an aqueous solution of NaCl (1 M) and HNO_3 (0.1 M) at 298 K.

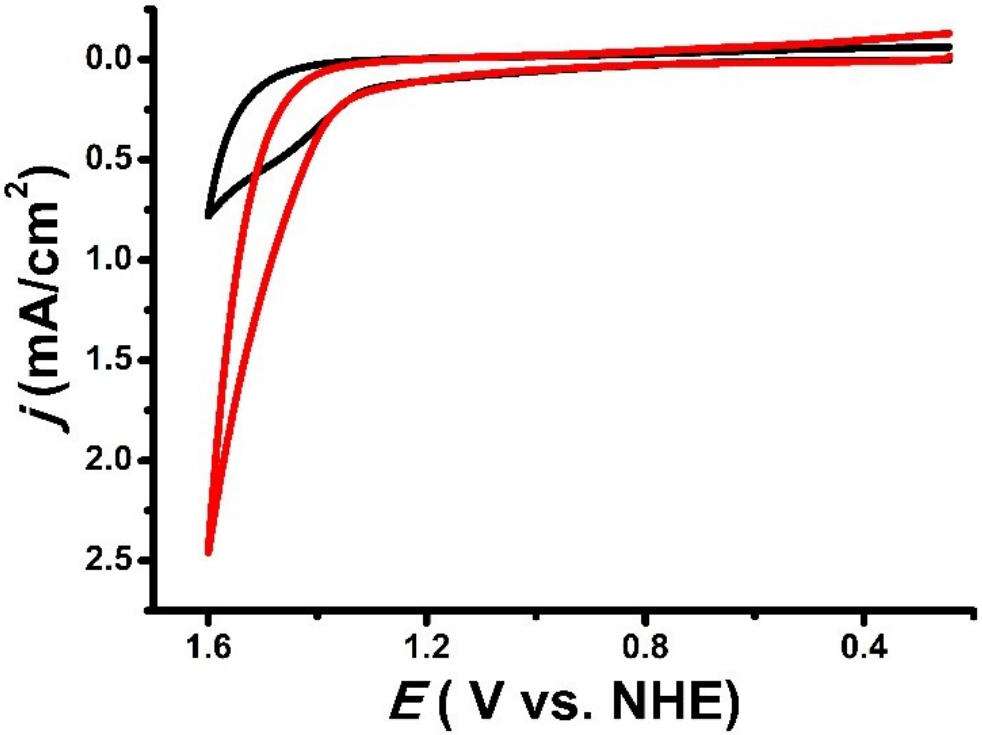

Fig. S14 CVs of a glassy carbon electrode (0.071 cm^2) in a NaH_2PO_4/Na_2HPO_4 buffer solution (0.1 M, pH~7) of NaCl (0.55 M) without (black) and with (red) **1-NP** (c_{Ag+} = 0.53 μM). Scan rate: 100 mV/s.

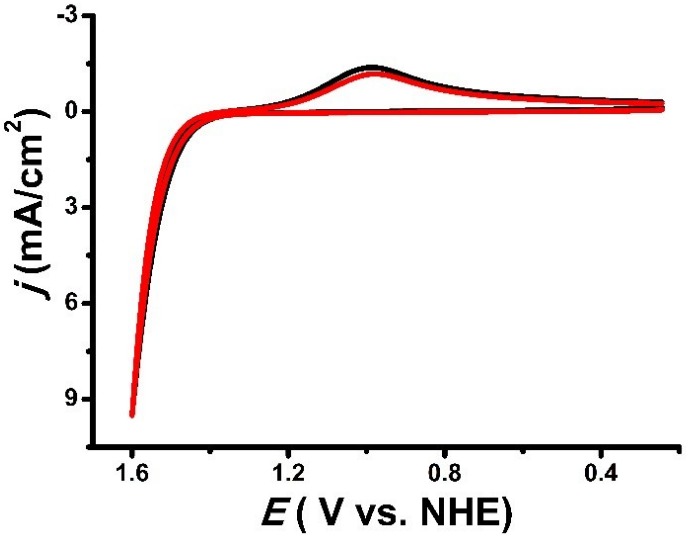

Fig. S15 CVs of a glassy carbon electrode (0.071 cm^2) in an aqueous solution of NaCl (1 M) and HNO_3 (pH ~1, 0.1 M) with **1-NP** (c_{Ag+} = 5.30 μM) (black) before and (red) after electrolysis.

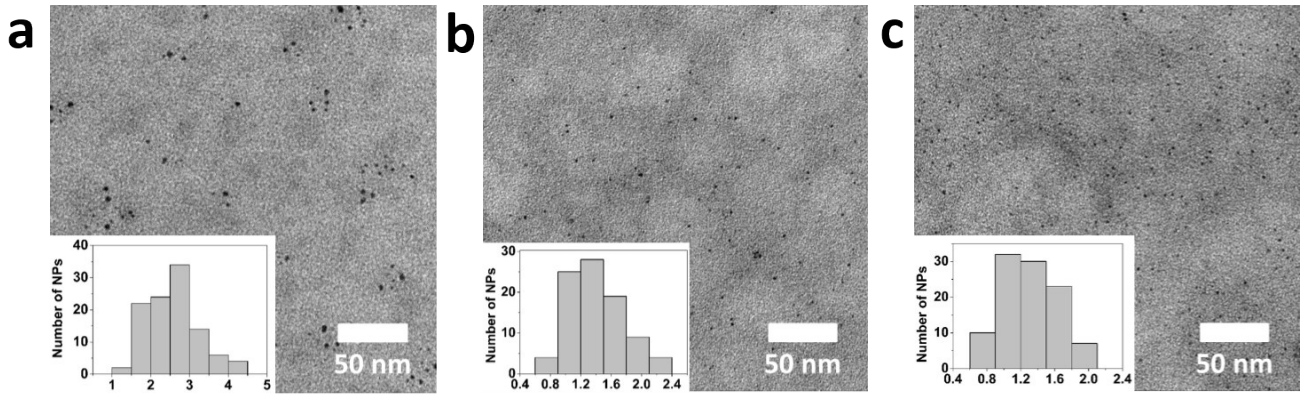

Fig. S16 TEM images and size-distribution histograms of (a) **1-NP** (2.5±1.5 nm) in 0.05 M NaCl aqueous solution, (b) **2-NP** (1.5±0.9 nm) in 1 M NaCl aqueous solution, and (c) **3-NP** (1.4±0.7 nm) in 1 M NaCl aqueous solution.

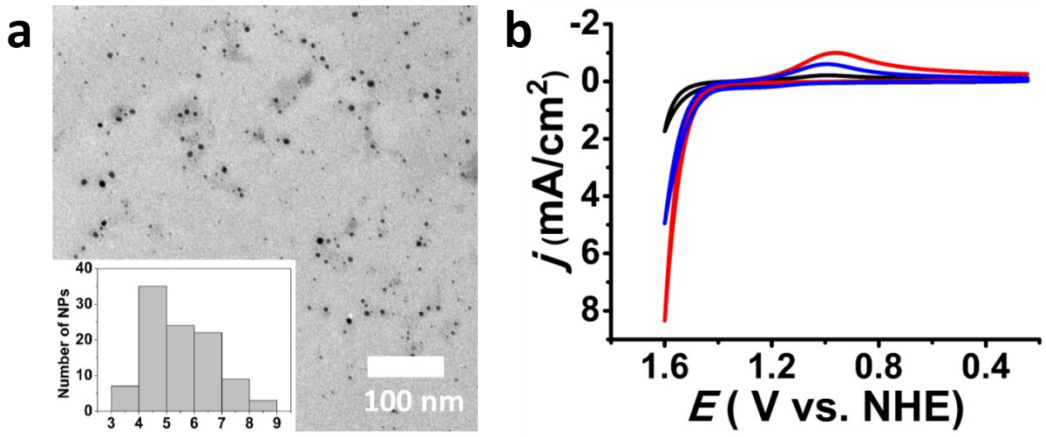

Fig. S17 (a) TEM image and size-distribution histogram of **1-NP** in larger sizes (6.0±3.0 nm). (b) CVs at a GC electrode in an aqueous solution of NaCl (1 M) and HNO_3 (pH ~1, 0.1 M) without (black) and with **1-NP** in 2.5±1.5 nm (red) and 6.0±3.0 nm (blue). Scan rate: 100 mV/s.

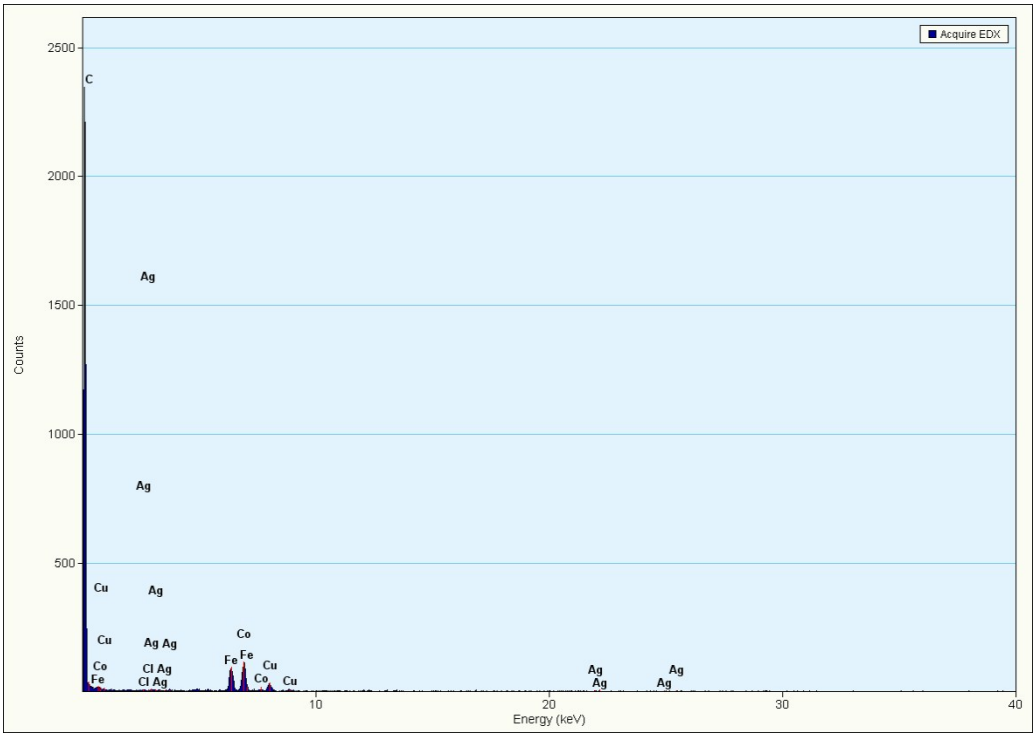

Fig. S18 EDX spectrum of **1-NP** in 1M NaCl solution . The Ag/Cl ratio was determined as 1.1 based on the atomic ratio of Ag-51.9% and Cl-48.1%.

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
Cl(K)	23.34	48.08	13.90	0.95	1.063
Ag(L)	76.65	51.91	38.48	0.95	2.617

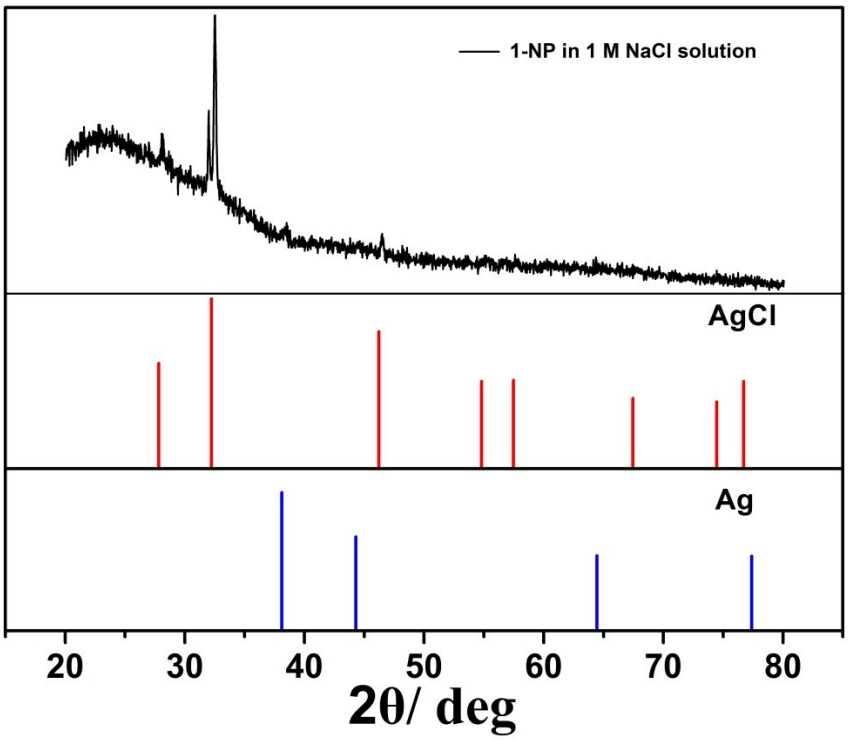

Fig. S19 XRD patterns of **1-NP** in 1M NaCl solution and the reference AgCl (JCPDS file: 31-1238) and Ag (JCPDS file: 87-0597).

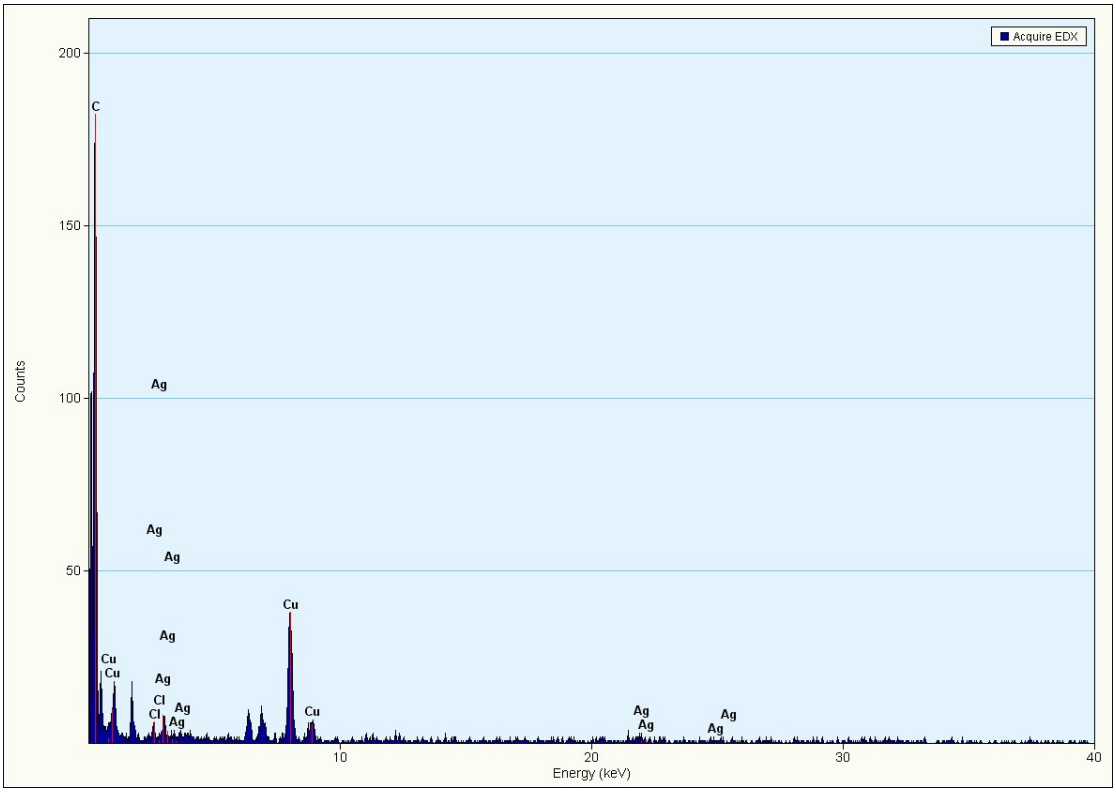

Fig. S20 EDX spectrum of **1-NP** in 1M NaCl solution after 1h controlled potential electrolysis. The Ag/Cl ratio was determined as 3.7 based on the atomic ratio of Ag-78.8% and Cl-21.2%.

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
Cl(K)	8.12	21.20	7.27	0.95	1.063
Ag(L)	91.87	78.79	20.42	0.95	2.617

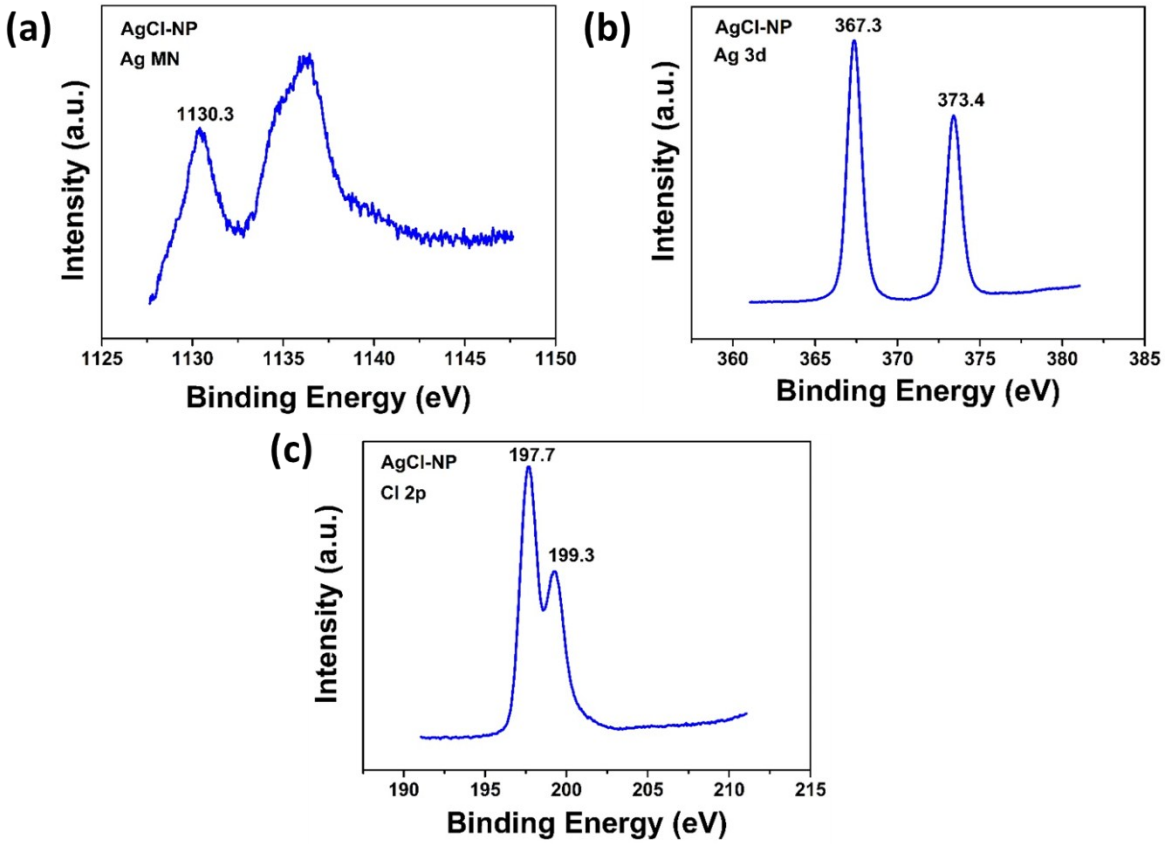

Fig. S21 Ag MN, Ag 3d and Cl 2p signals for the PVP-stabilized stoichiometric AgCl nanoparticles **AgCl-NP** (C. An, S. Peng and Y. Sun, *Adv. Mater.*, 2010, **22**, 2570-2574). The Ag MN signals were determined by AES while the binding energies for Ag 3d and Cl 2p were measured by XPS. The +1 oxidation state of silver was determined based on the Ag $3d^{5/2}$ and Ag $3d^{3/2}$ binding energy peaks at 373.4 and 367.3 eV, respectively.