

Anthracene and pyrene appended Schiff bases having (N,N) donor for the synthesis of highly stable colloidal silver nano-particles: Application in selective sensing and nitroarene reduction

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NMR Data of Ligands

L1: Yield: 0.395 g (90%); NMR: (¹H, 500 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 9.52 (s, 2H); 8.49 (s, 2H); 8.44 (d, 4H, J = 10 Hz); 7.98 (d, 4H, J = 10 Hz); 7.38 (t, 4H, J = 10 Hz); 7.17-7.12 (m, 4H); 4.54 (s, 4H). ¹³C{¹H}, 125 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 159.8, 130.7, 129.6, 129.0, 128.0, 127.5, 126.1, 125.0, 124.2, 62.9. IR (cm⁻¹) **L1:** 3041, 2899, 2325, 1938, 1804, 1635, 1513, 1438, 1379, 1252, 1157, 1021, 969, 946, 879, 833, 782, 723.

L2: Yield: 0.432 g (88%); NMR: (¹H, 500 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 9.45 (s, 2H); 8.51 (d, 6H, J = 10 Hz); 8.03 (d, 5H, J = 5 Hz); 7.55-7.48 (m, 9H); 4.01 (t, 4H, J = 5 Hz); 1.75-1.72 (m, 4H). ¹³C{¹H}, 125 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 160.1, 131.3, 129.9, 129.1, 128.8, 128.2, 126.6, 125.2, 124.8, 31.0, 27.4. IR (cm⁻¹) **L2:** 3041, 2929, 2840, 1915, 1774, 1631, 1513, 1341, 1386, 1446, 1304, 1252, 1058, 1155, 946, 879, 834, 782, 723.

L3: Yield: 0.459 g (87%); NMR: (¹H, 500 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 9.35 (s, 2H); 8.71 (d, 2H, J = 10 Hz); 8.54 (d, 2H, J = 10 Hz); 8.33-7.87 (m, 14H); 7.81 (d, 2H, J = 5 Hz); 4.38 (s, 4H). (¹³C{¹H}, 125 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 162.1, 132.8, 131.1, 130.4, 129.8, 128.7, 128.4, 128.3, 127.3, 126.1, 125.9, 125.7, 125.4, 124.8, 124.7, 124.5, 122.3, 62.4. IR (cm⁻¹) **L3:** 3041, 2907, 2840, 1908, 1781, 1677, 1625, 1595, 1535, 1505, 1483, 1453, 1431, 1408, 1386, 1319, 1282, 1237, 1177, 1088, 1051, 1013, 986, 894, 745, 715, 685.

L4: Yield: 0.445 g (82%); NMR: (^1H , 500 MHz, CDCl_3 , 25 °C, TMS): δ (ppm): 9.33 (s, 2H); 8.89 (d, 2H, $J = 10$ Hz); 8.53 (d, 2H, $J = 10$ Hz); 8.24–8.01 (m, 14H); 3.90 (t, 4H, $J = 5$ Hz); 1.96 (t, 4H, $J = 5$ Hz); 1.65 (m, 4H). ($^{13}\text{C}\{^1\text{H}\}$, 125 MHz, CDCl_3 , 25 °C, TMS): δ (ppm): 159.6, 132.8, 131.4, 130.7, 129.8, 129.0, 128.6, 128.5, 127.6, 126.4, 126.2, 125.9, 125.6, 125.1, 125.0, 124.8, 122.8, 62.8, 31.2, 27.4. IR (cm^{-1}) **L4:** 3034, 2922, 2847, 1915, 1781, 1677, 1625, 1595, 1431, 1386, 1356, 1304, 1237, 1177, 1095, 1021, 969, 931, 887, 849, 820, 745, 715, 685.

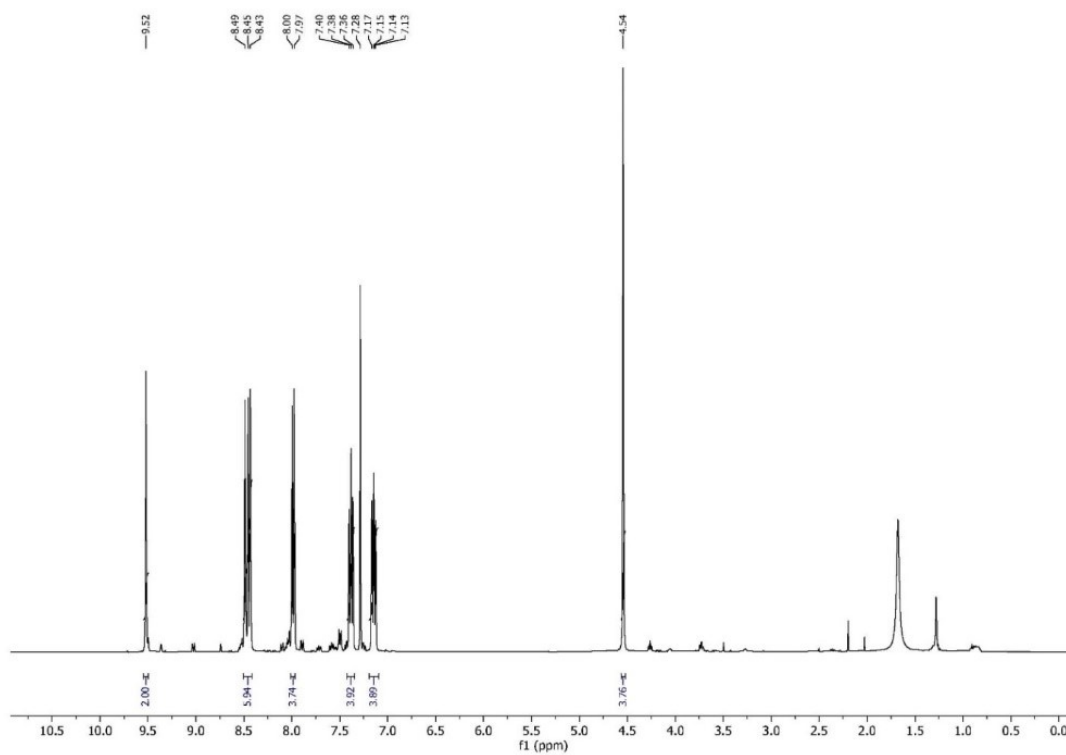


Figure S1. ¹H NMR spectra of L1

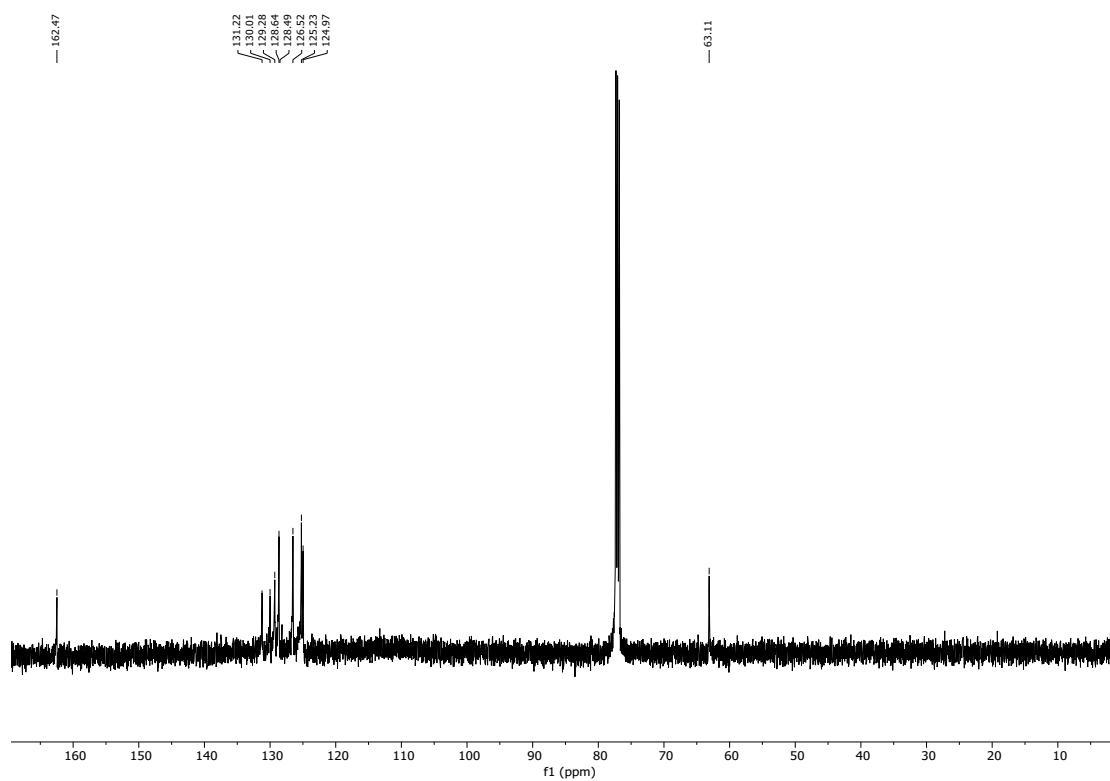


Figure S2. ¹³C{¹H} NMR spectra of L1

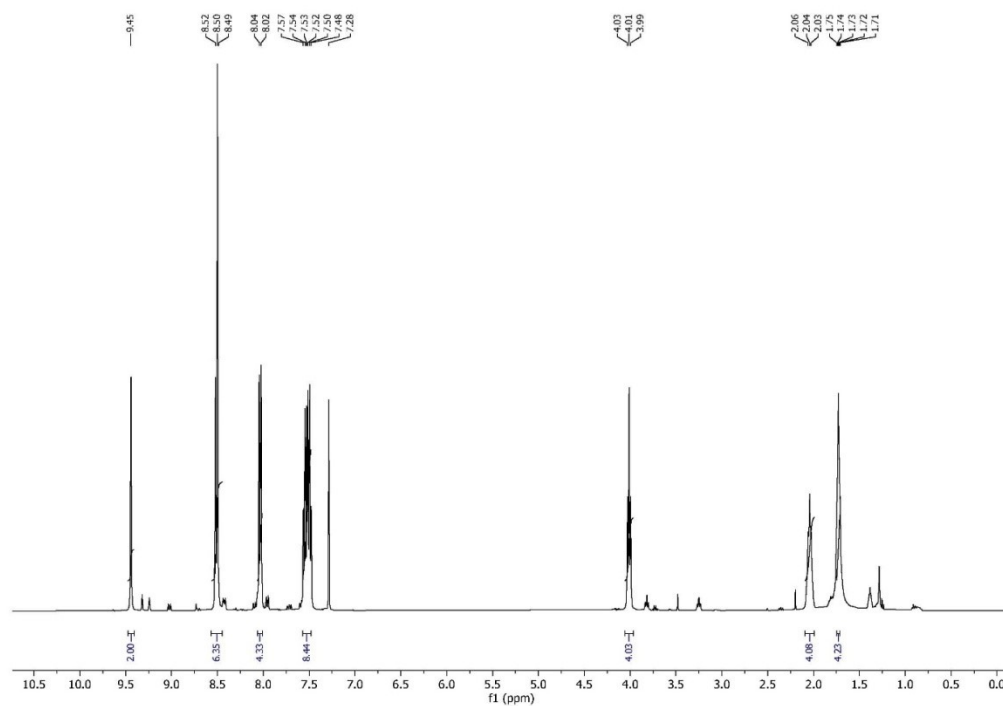


Figure S3. ^1H NMR spectra of L2

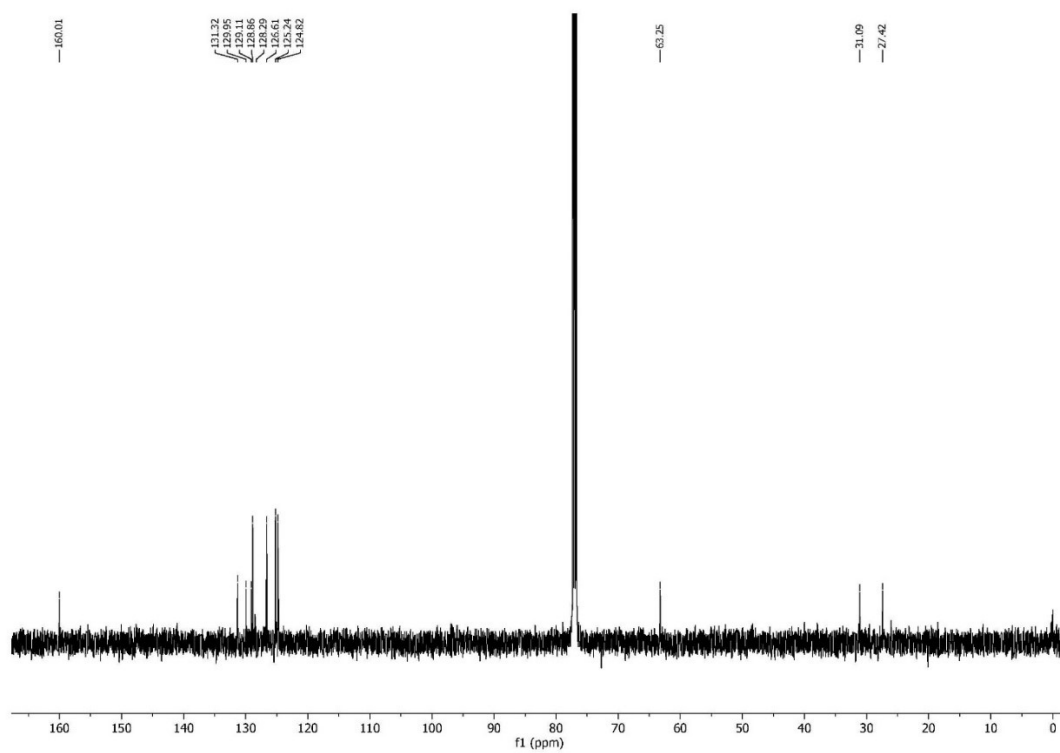


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of L2

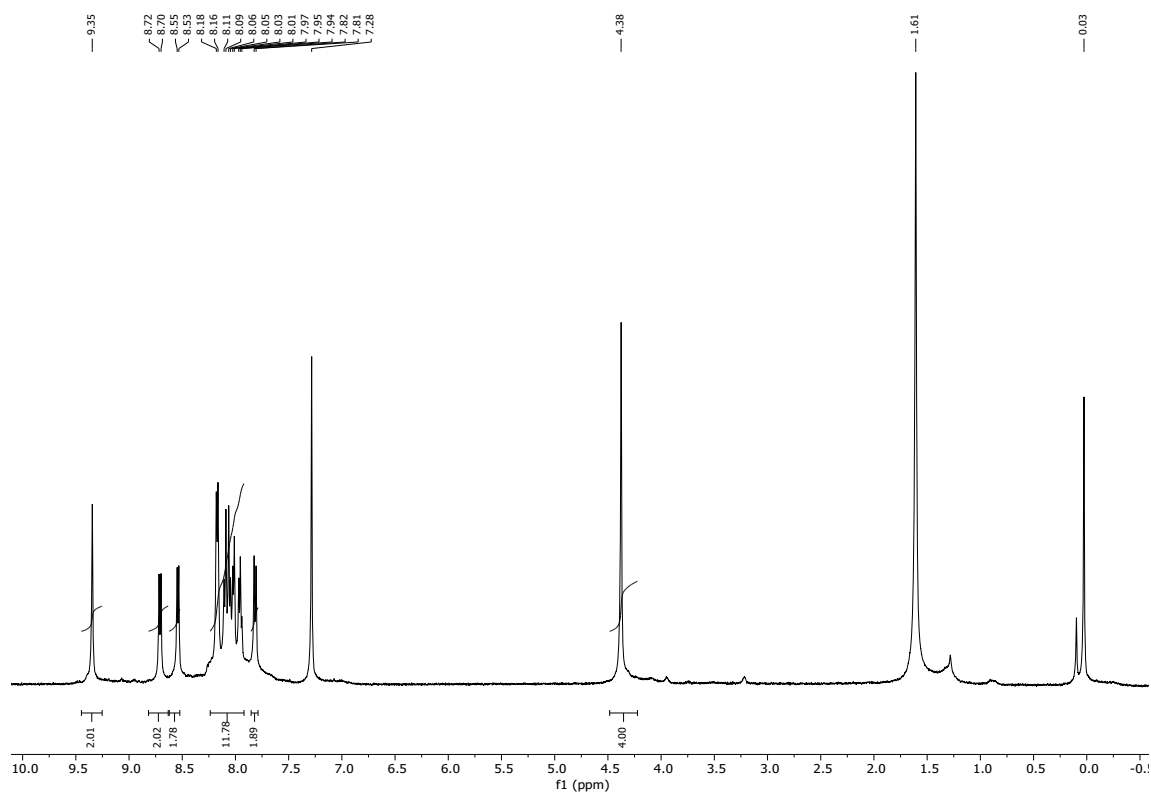


Figure S5. ^1H NMR spectra of L3

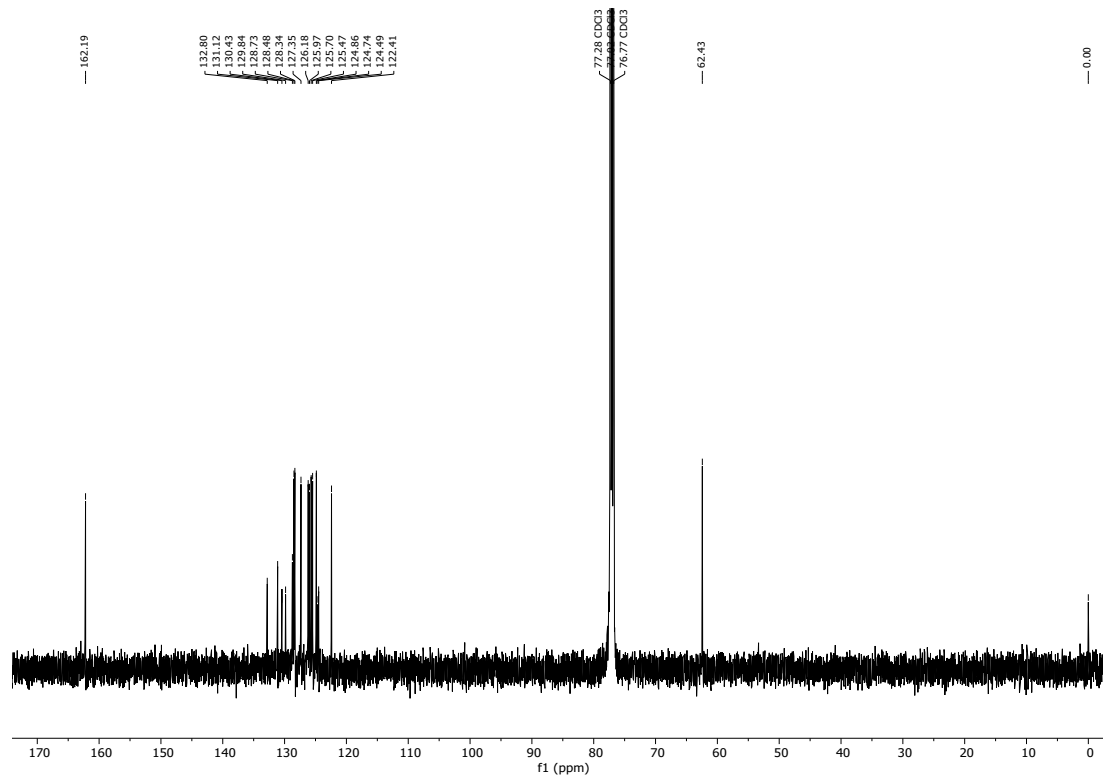


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of L3

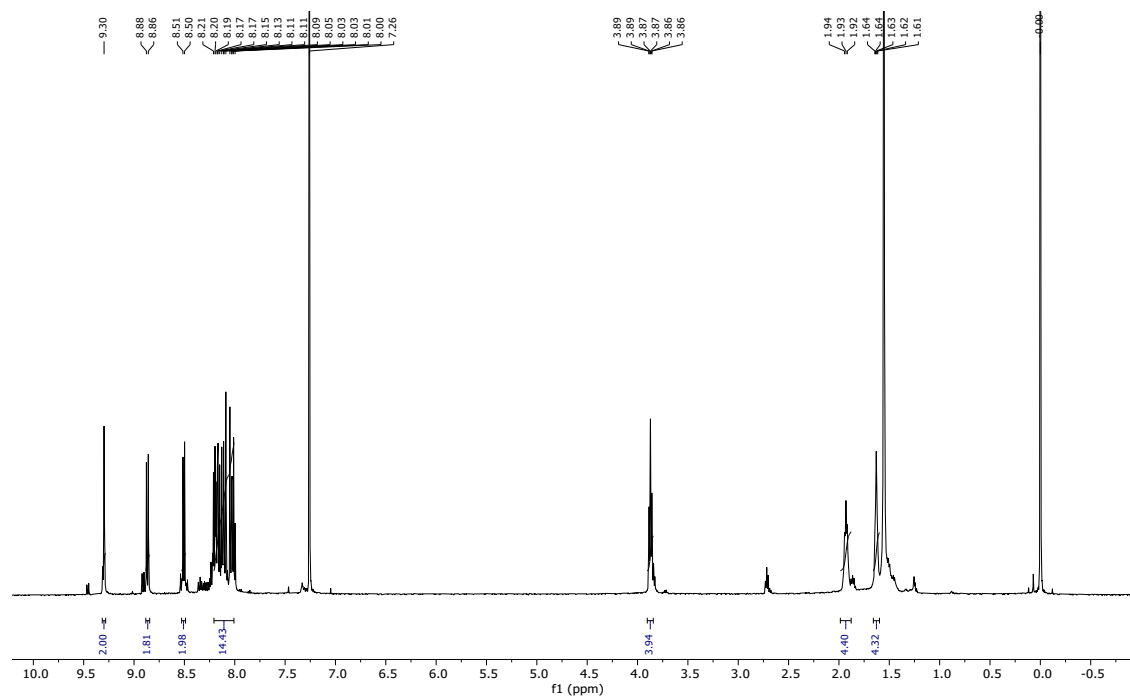


Figure S7. ¹H NMR spectra of L4

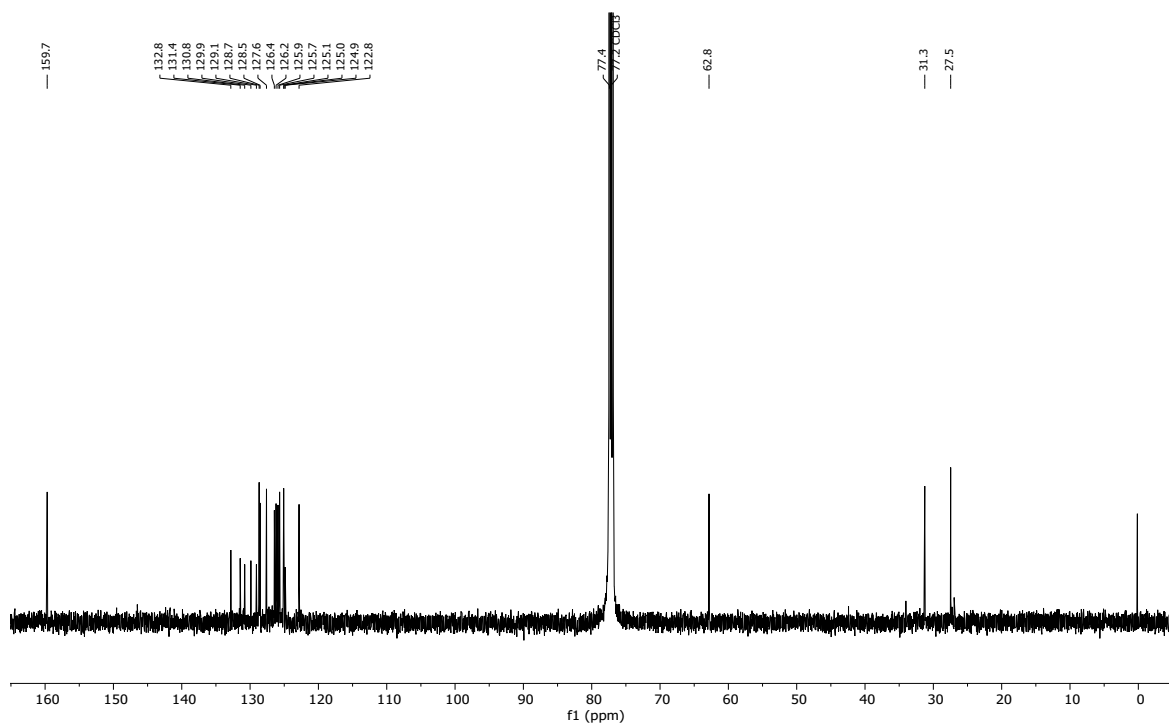


Figure S8. ¹³C{¹H} NMR spectra of L4

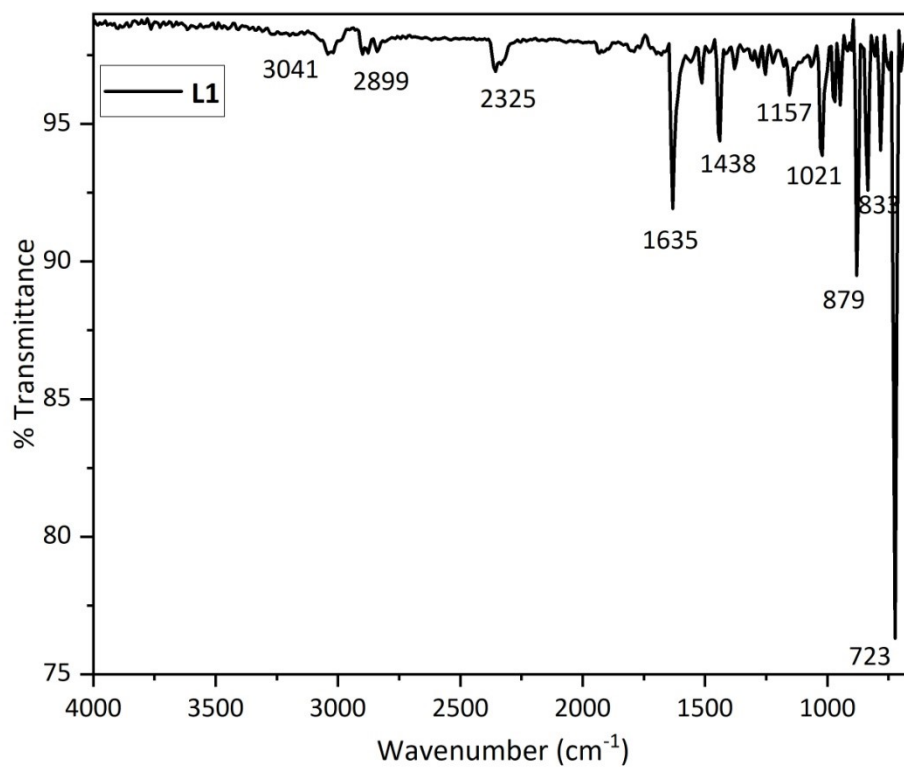


Figure S9. Infrared spectra of L1

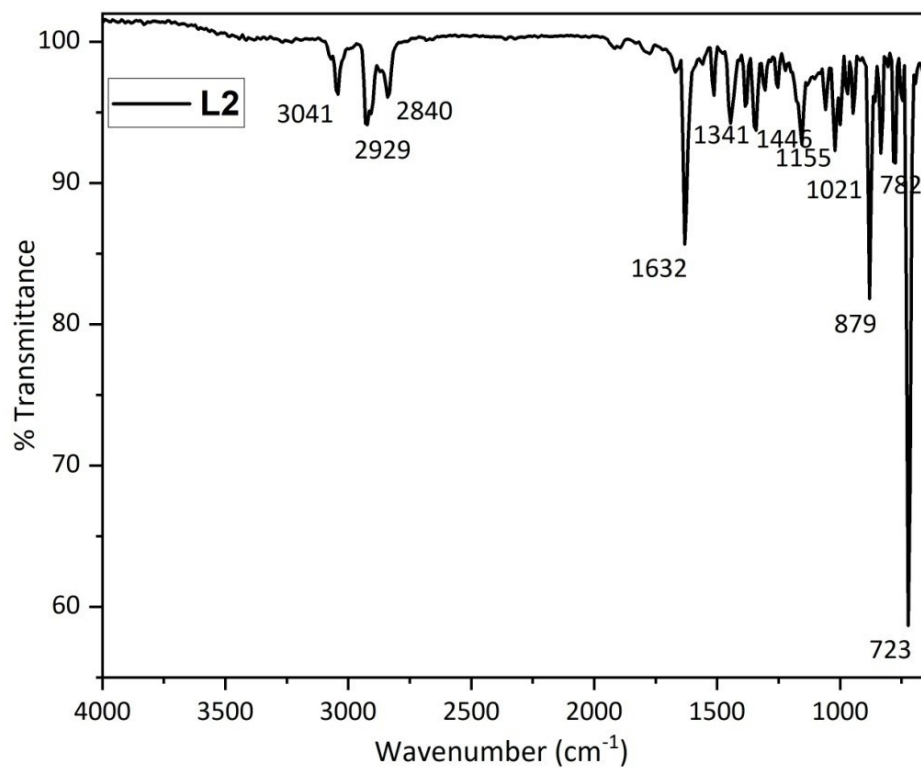


Figure S10. Infrared spectra of L2

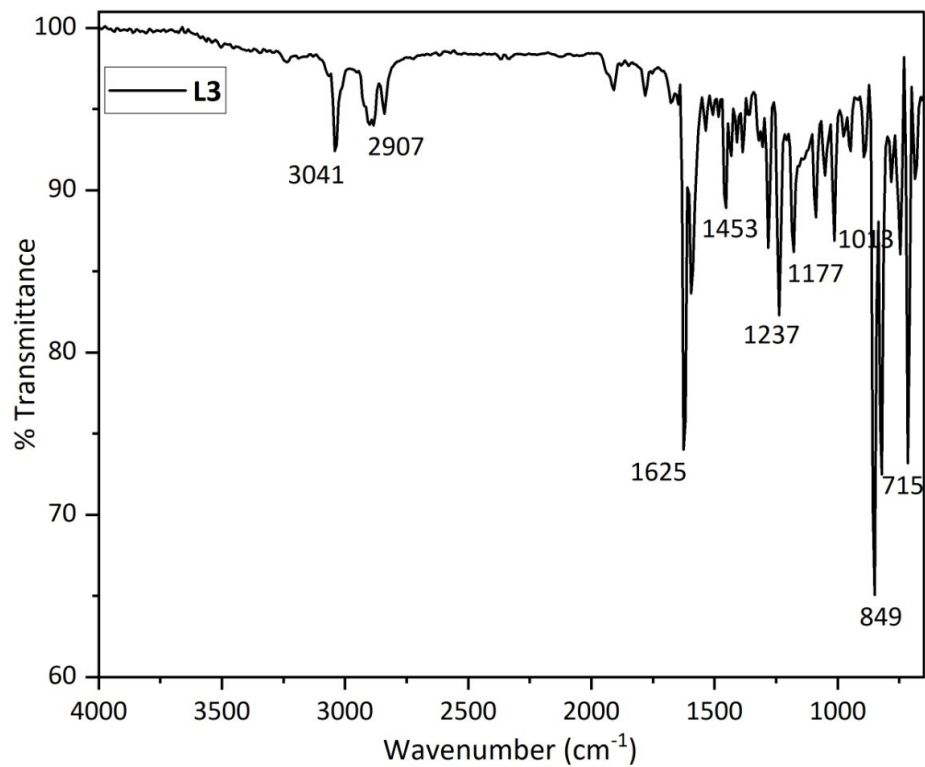


Figure S11. Infrared spectra of L3

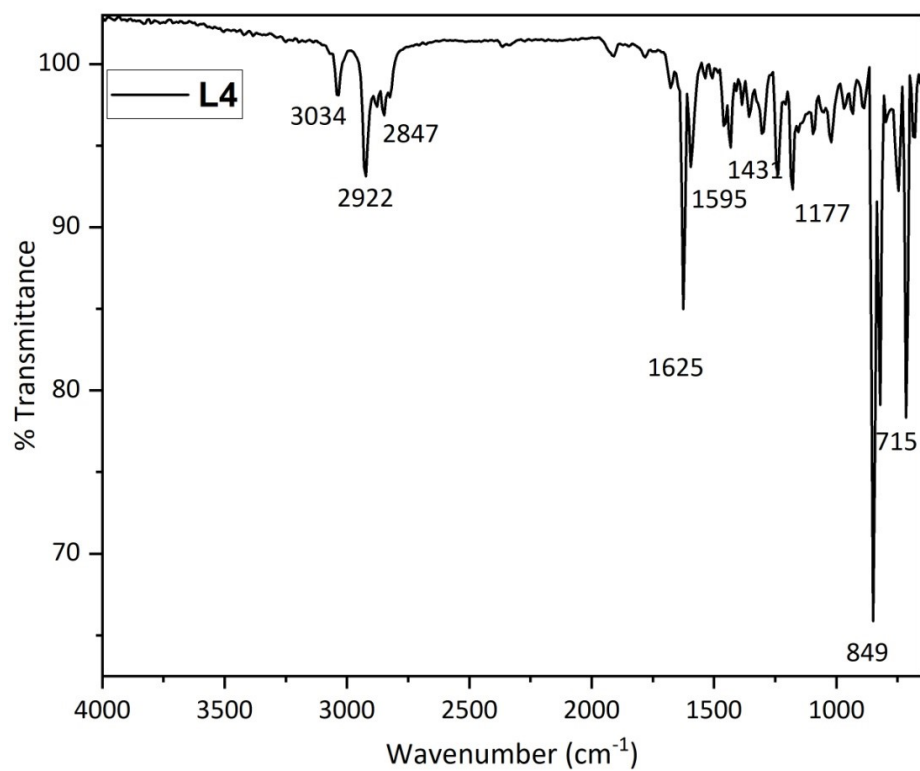


Figure S12. Infrared spectra of L4

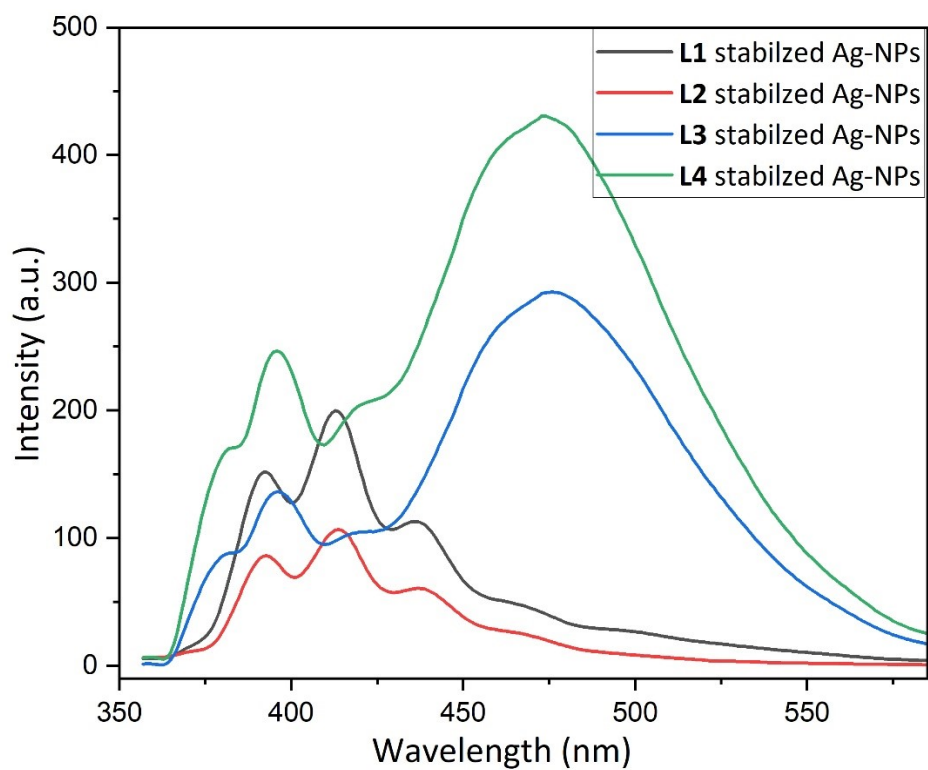


Figure S13. Fluorescence spectra of **L1–L4** stabilized silver nanoparticles

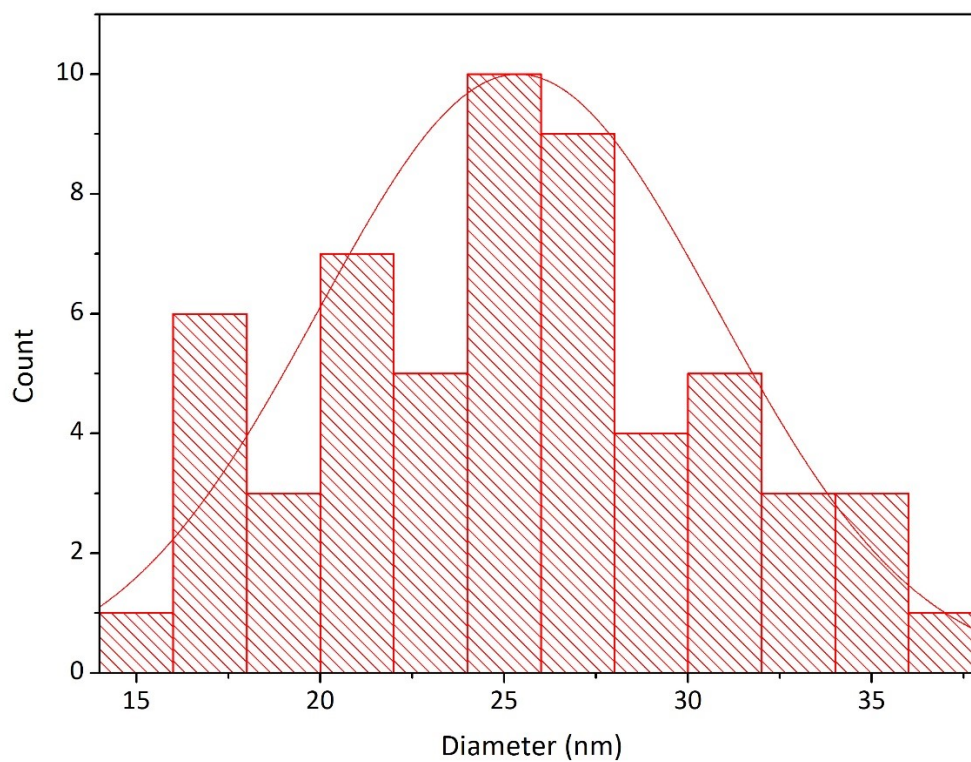


Figure S14. Particle size distribution in the case of **L1** stabilized silver nanoparticles

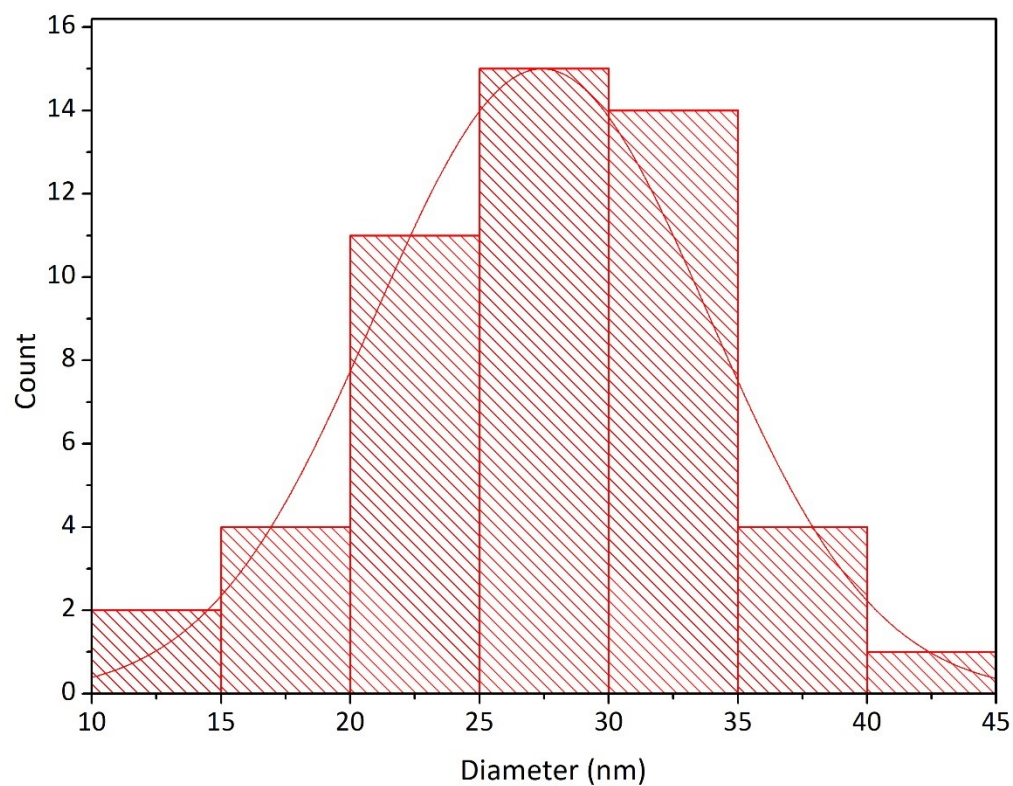


Figure S15. Particle size distribution in the case of **L2** stabilized silver nanoparticles

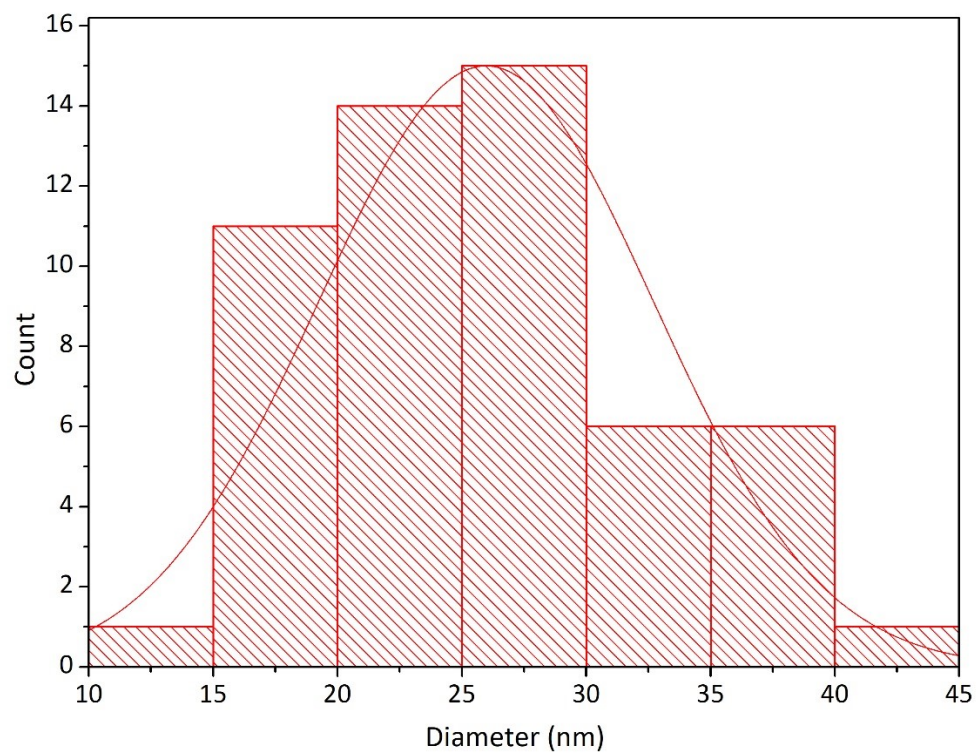


Figure S16. Particle size distribution in the case of **L3** stabilized silver nanoparticles

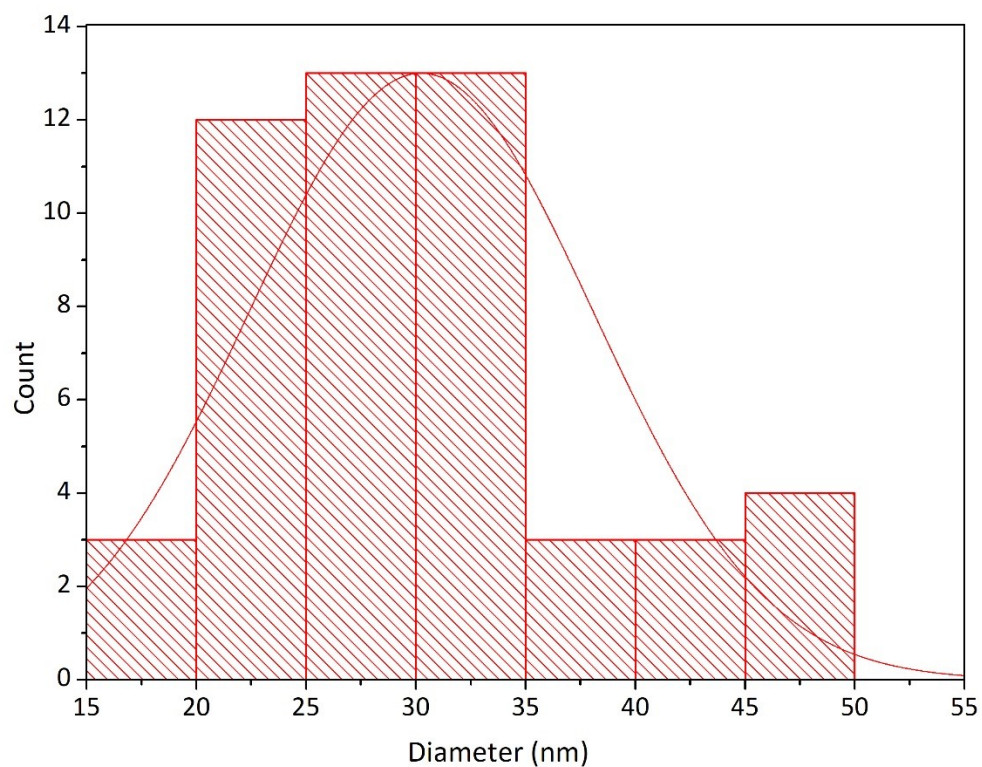


Figure S17. Particle size distribution in the case of **L4** stabilized silver nanoparticles

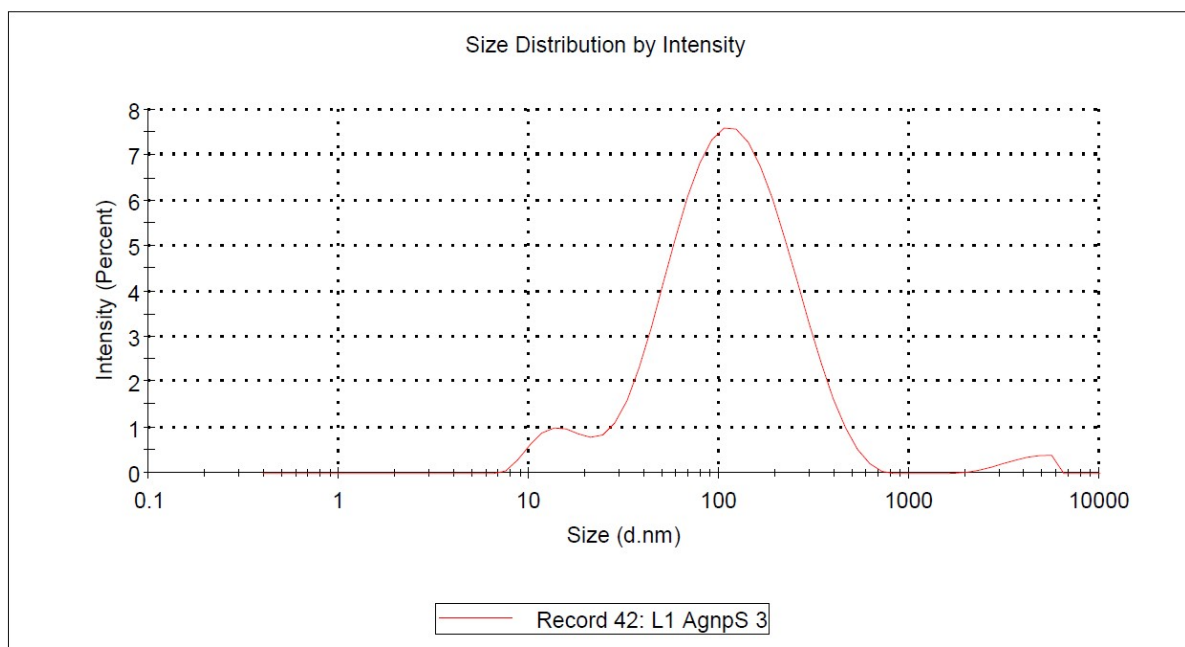


Figure S18. DLS data of **L1** stabilized silver nanoparticles (freshly synthesized)

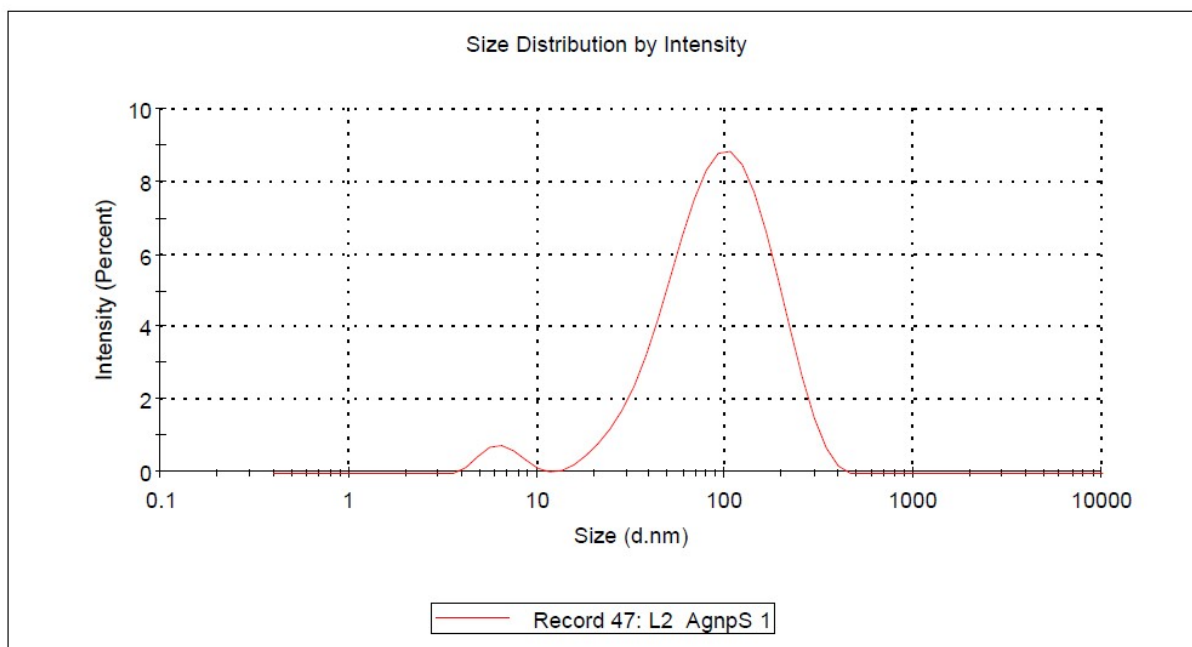


Figure S19. DLS data of **L2** stabilized silver nanoparticles (freshly synthesized)

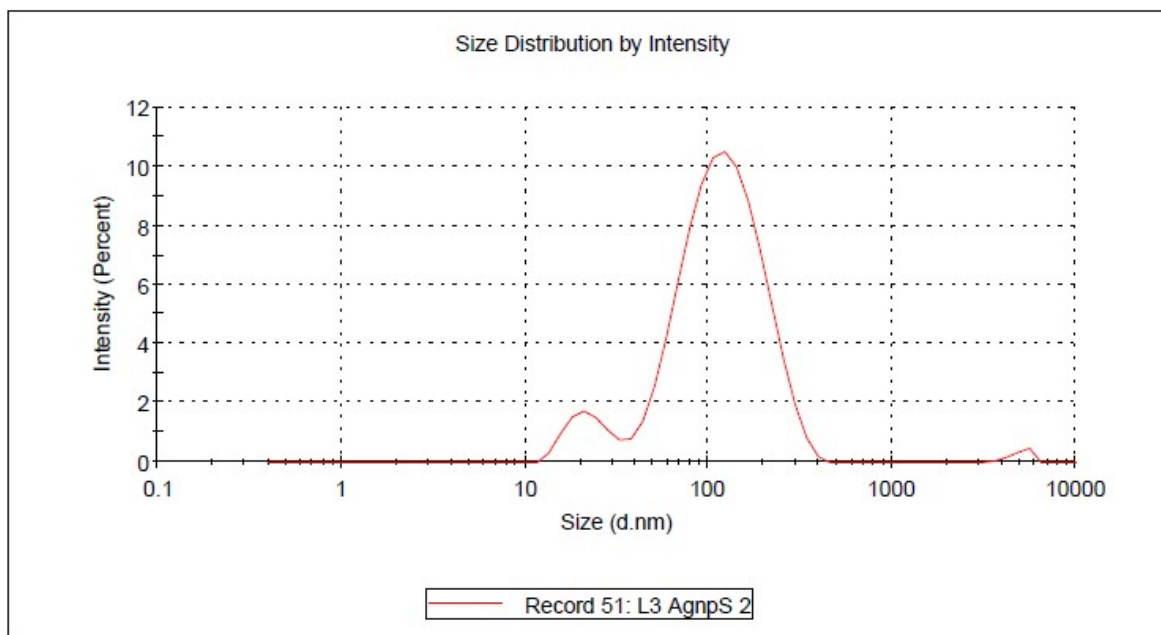


Figure S20. DLS data of **L3** stabilized silver nanoparticles (freshly synthesized)

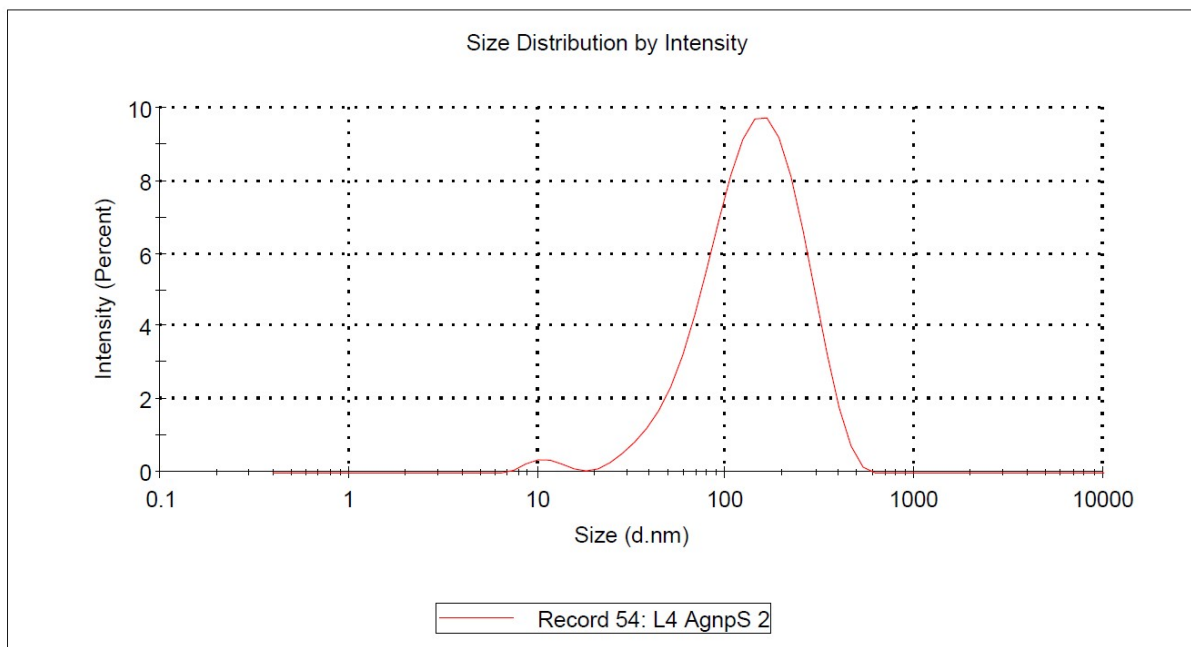


Figure S21. DLS data of **L4** stabilized silver nanoparticles (freshly synthesized)

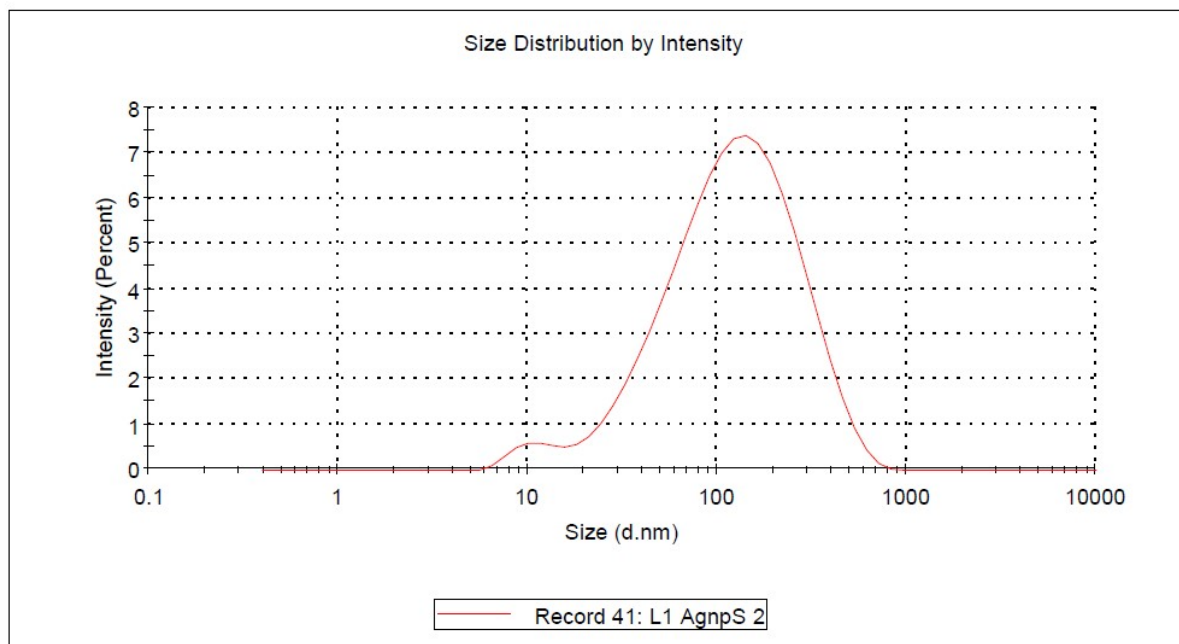


Figure S22. DLS data of **L1** stabilized silver nanoparticles (at 15th day)

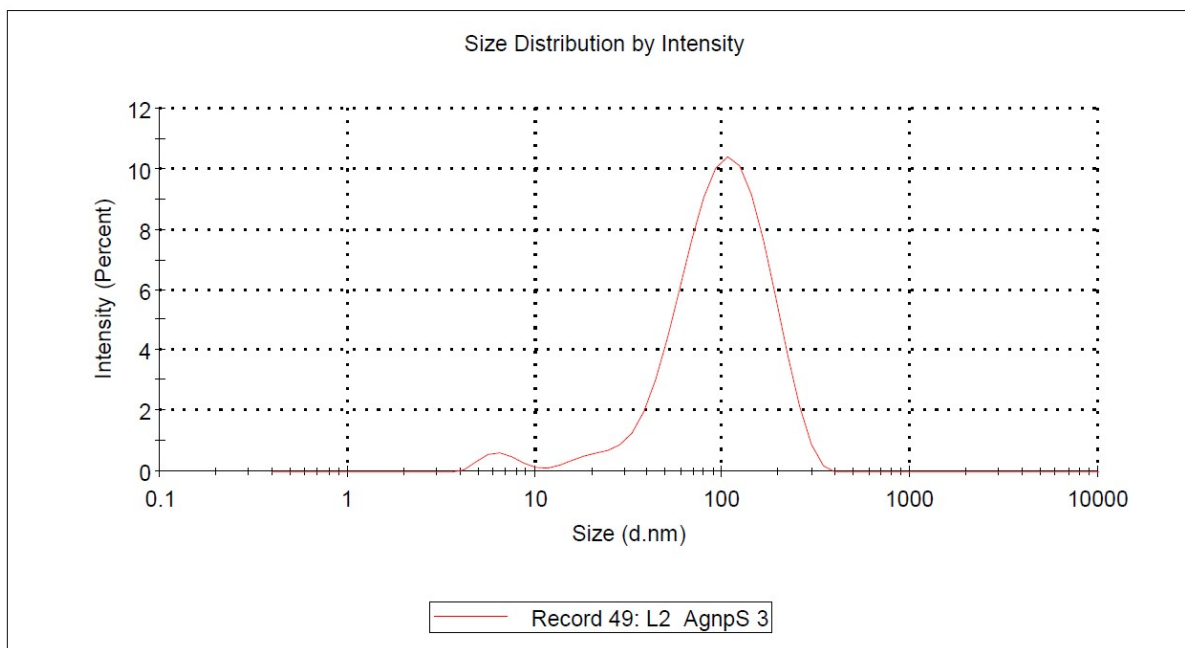


Figure S23. DLS data of **L2** stabilized silver nanoparticles (at 15th day)

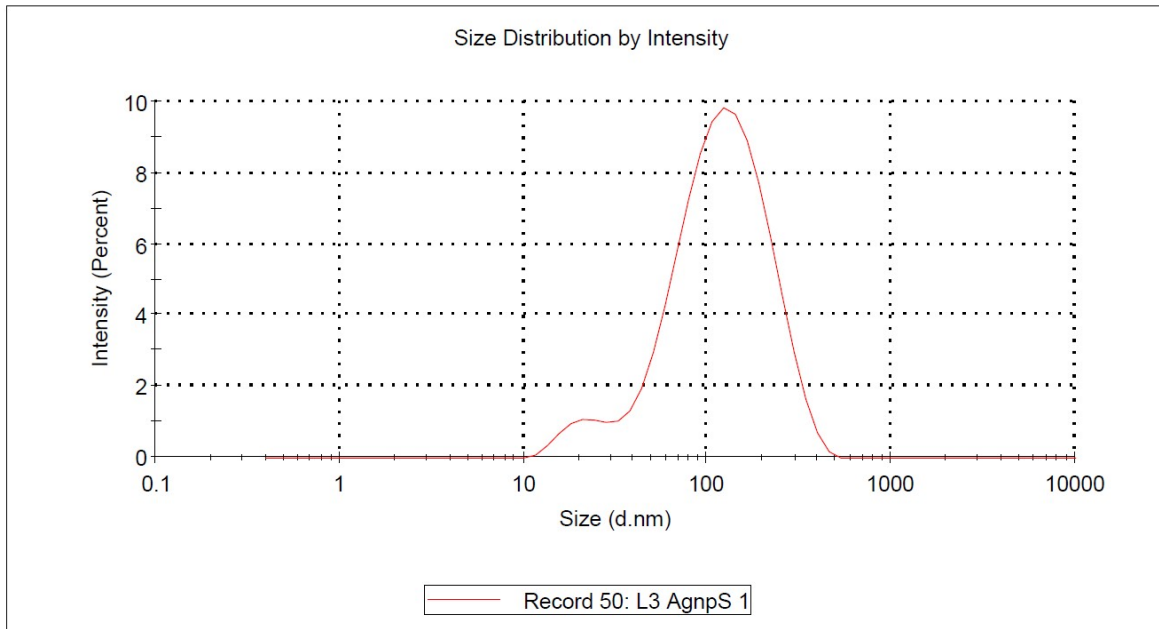


Figure S24. DLS data of **L3** stabilized silver nanoparticles (at 15th day)

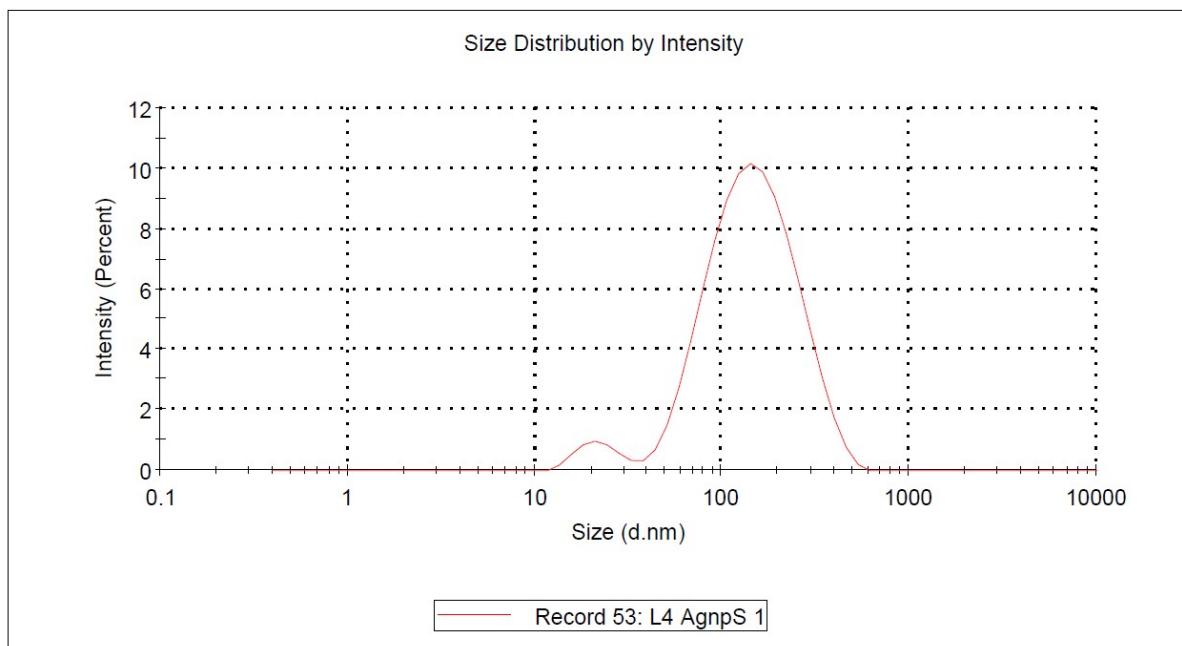


Figure S25. DLS data of **L4** stabilized silver nanoparticles (at 15th day)

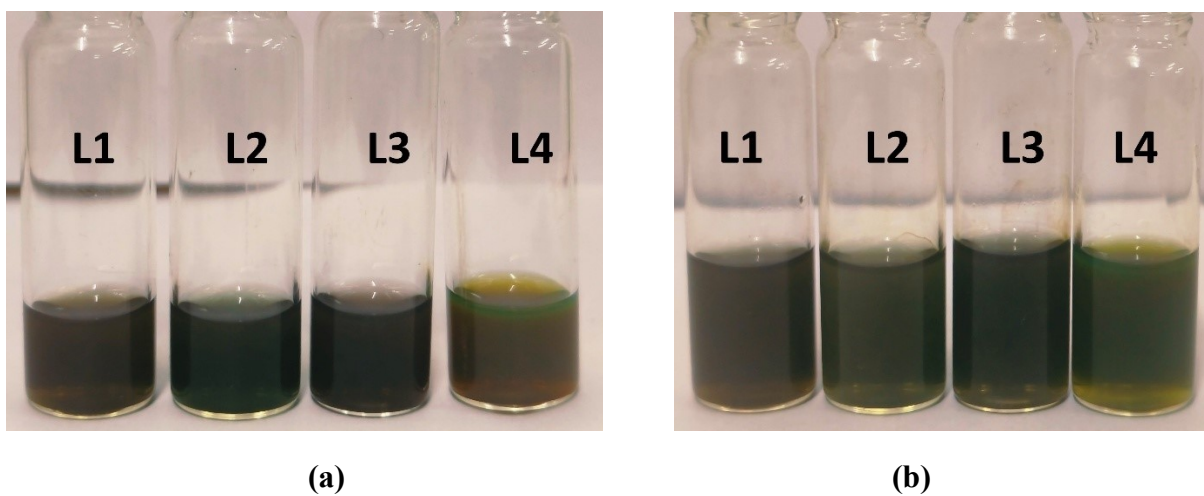
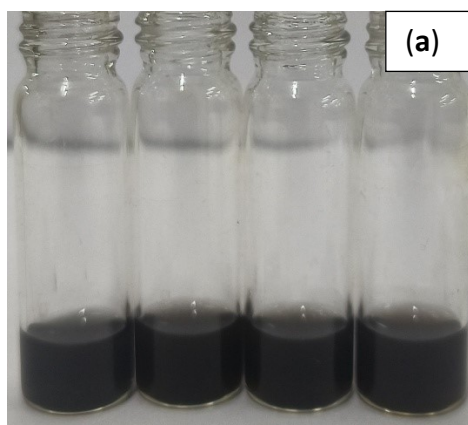
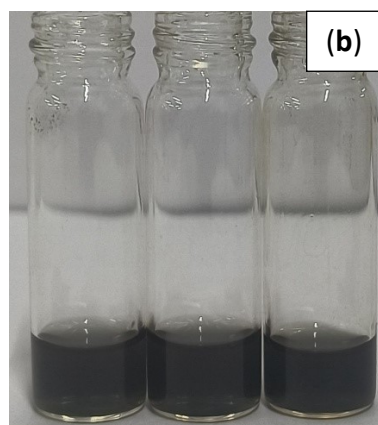


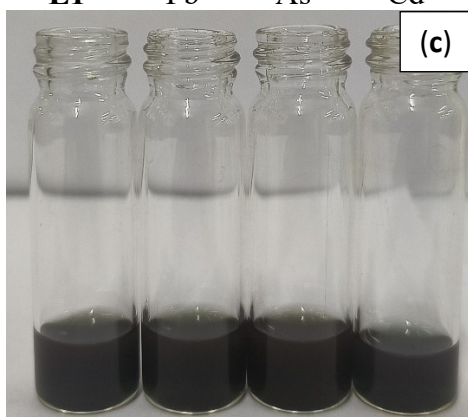
Figure S26. Photographs of; (a) as-synthesized colloidal Ag-NPs and (b) colloidal Ag-NPs at 60th day



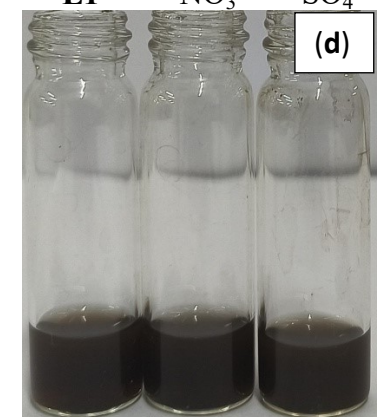
L1 **Pb²⁺** **As³⁺** **Cd²⁺**



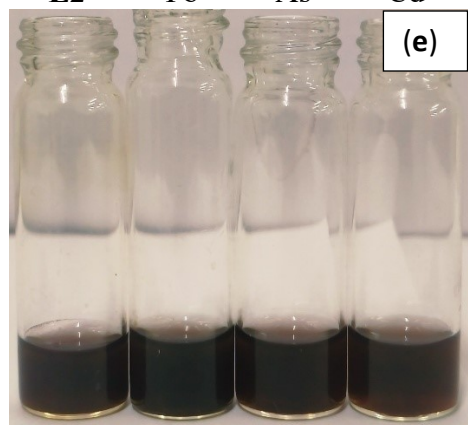
L1 **NO₃⁻** **SO₄²⁻**



L2 **Pb²⁺** **As³⁺** **Cd²⁺**



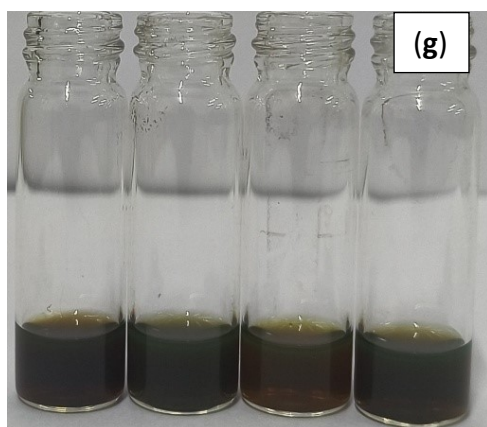
L2 **NO₃⁻** **SO₄²⁻**



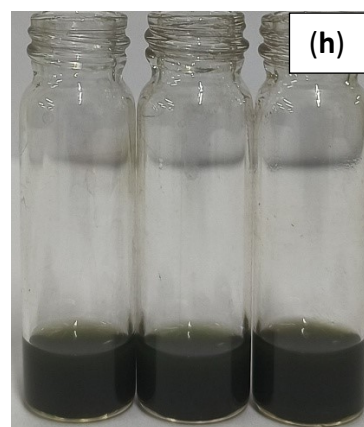
L3 **Pb²⁺** **As³⁺** **Cd²⁺**



L3 **NO₃⁻** **SO₄²⁻**



L4 Pb^{2+} As^{3+} Cd^{2+}



L4 NO_3^- SO_4^{2-}

Figure S27. Colorimetric sensing of metal ions with added metal salt $\{\text{Pb}^{2+}, \text{As}^{3+}, \text{Cd}^{2+}$ (10 μL of 50 mM) $\}$ in the colloidal solution of (a) **L1** capped Ag-NPs; (c) **L2** capped Ag-NPs; (e) **L3** capped Ag-NPs; (g) **L4** capped Ag-NPs; and with added anions $\{\text{NO}_3^-, \text{SO}_4^{2-}$ (10 μL of 10 mM) $\}$ in the colloidal solution of (b) **L1** capped Ag-NPs; (d) **L2** capped Ag-NPs; (f) **L3** capped Ag-NPs; (h) **L4** capped Ag-NPs.

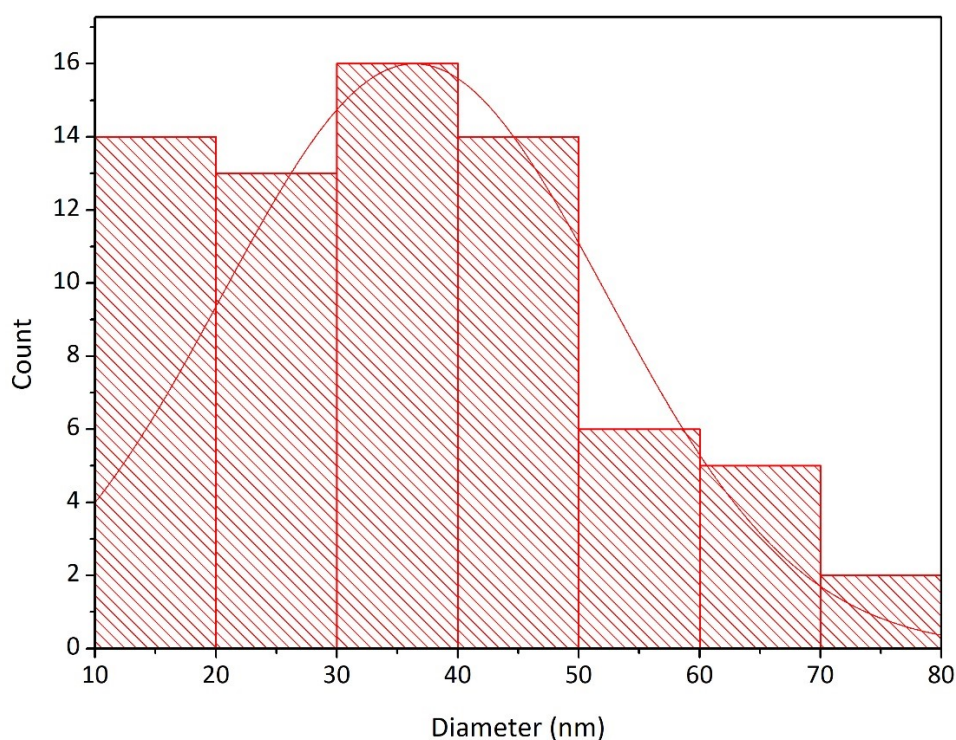


Figure S28. Particle size distribution in the case of **L1** stabilized silver nanoparticles after the addition of Hg^{2+} ions

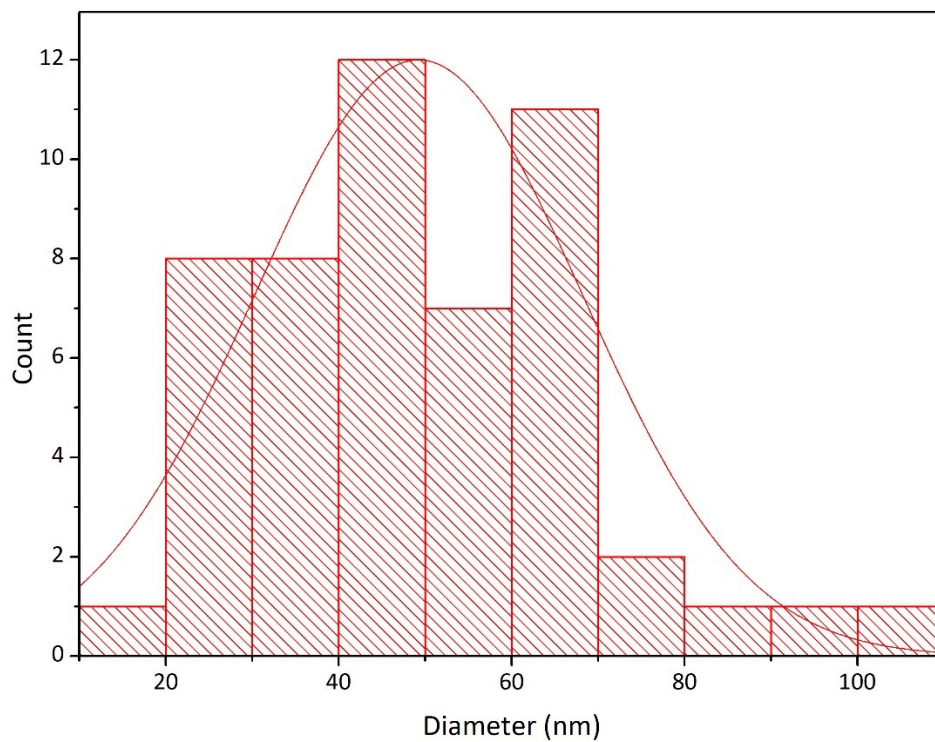


Figure S29. Particle size distribution in the case of **L1** stabilized silver nanoparticles after the addition of Cl^- ions

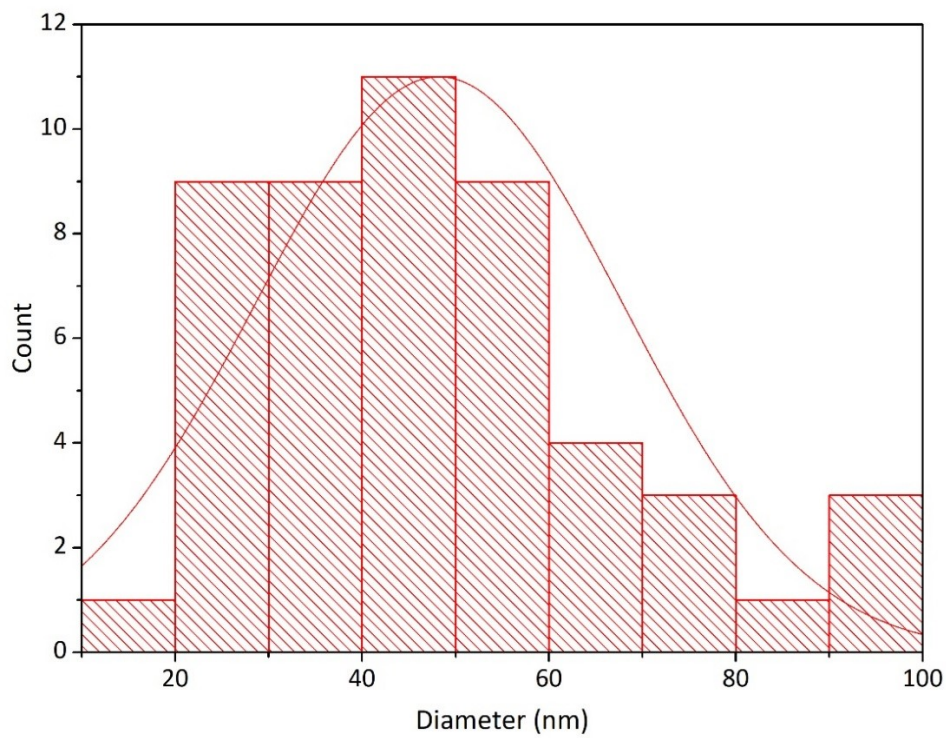


Figure S30. Particle size distribution in the case of **L2** stabilized silver nanoparticles after the addition of Hg^{2+} ions

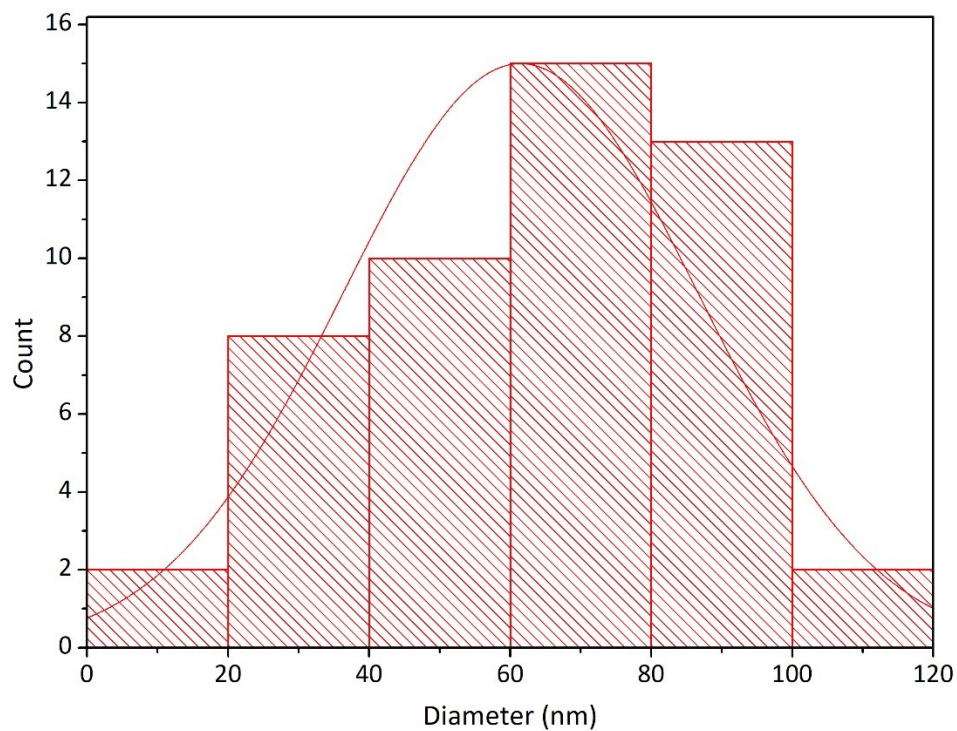


Figure S31. Particle size distribution in the case of **L2** stabilized silver nanoparticles after the addition of Bi^{3+} ions

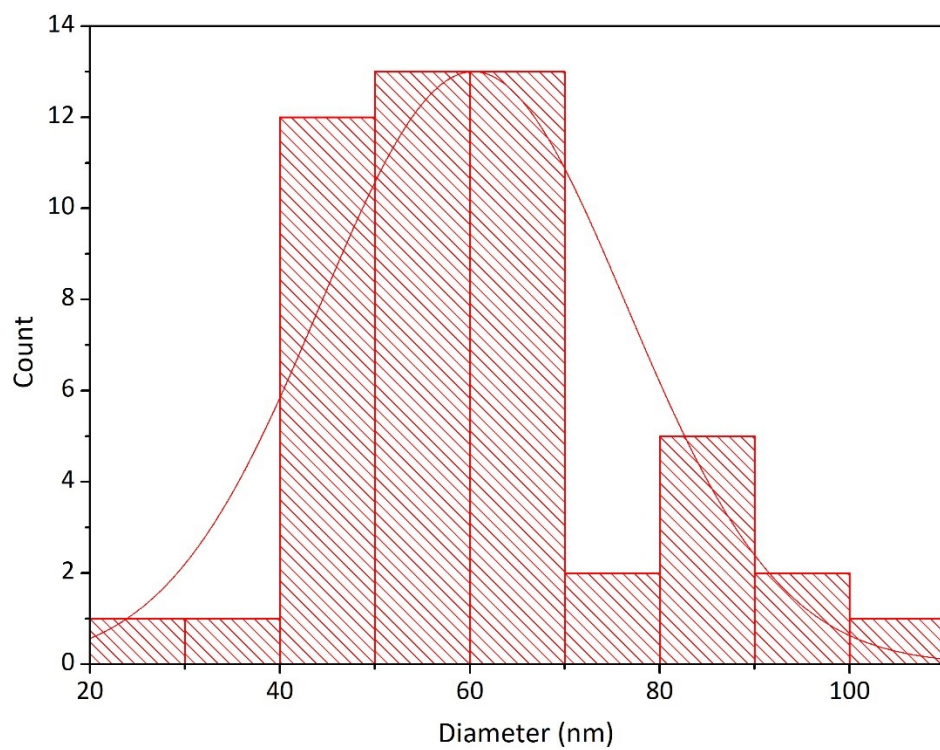


Figure S32. Particle size distribution in the case of **L2** stabilized silver nanoparticles after the addition of I^- ions

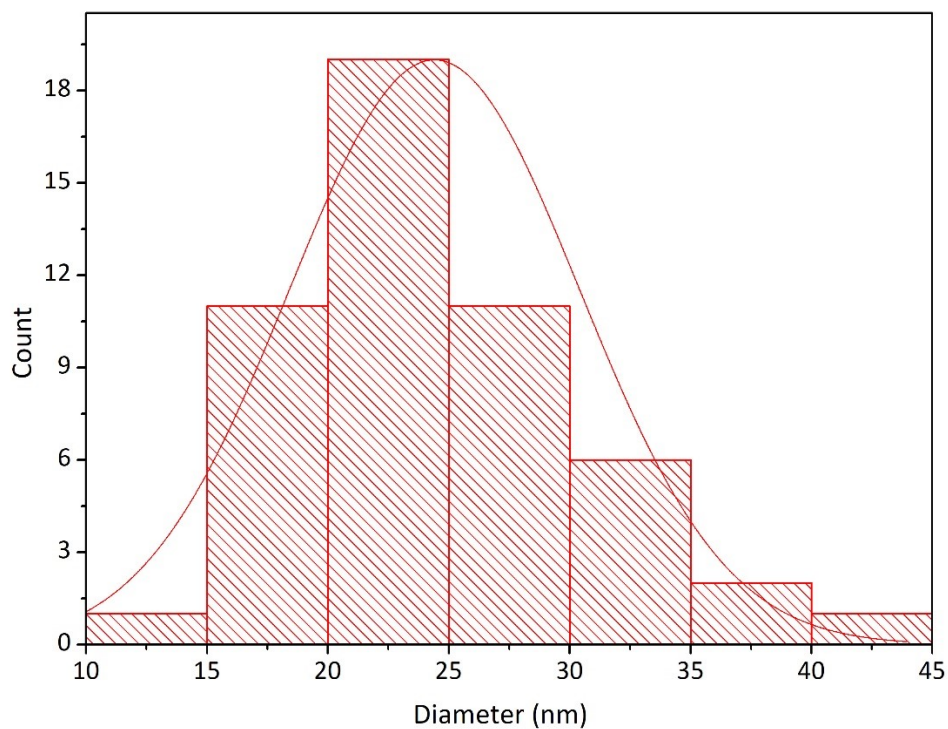


Figure S33. Particle size distribution in the case of **L3** stabilized silver nanoparticles after the addition of Hg^{2+} ions

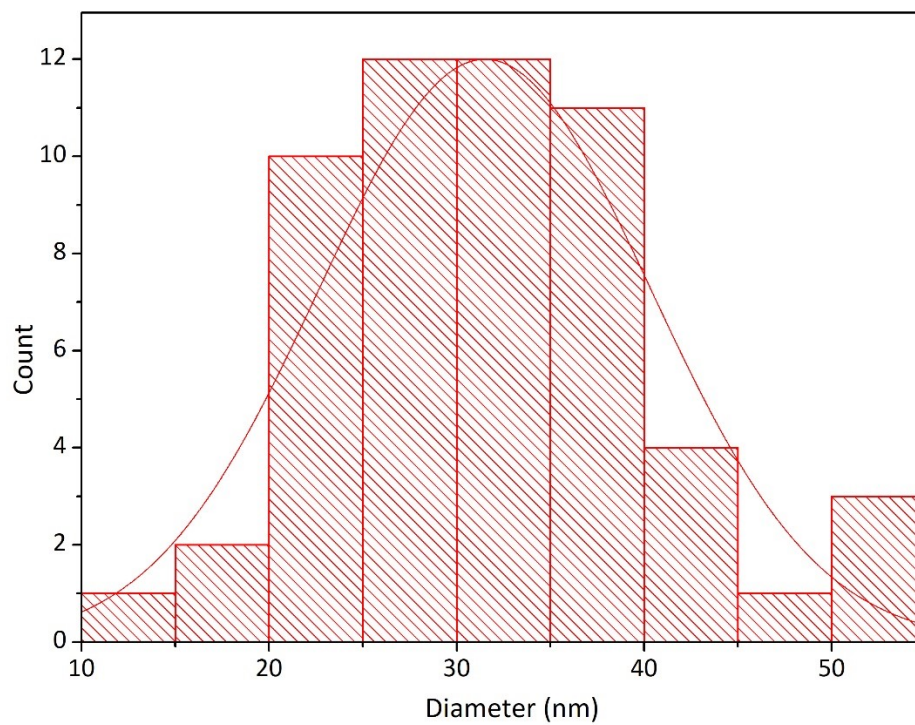


Figure S34. Particle size distribution in the case of **L3** stabilized silver nanoparticles after the addition of HSO_4^- ions

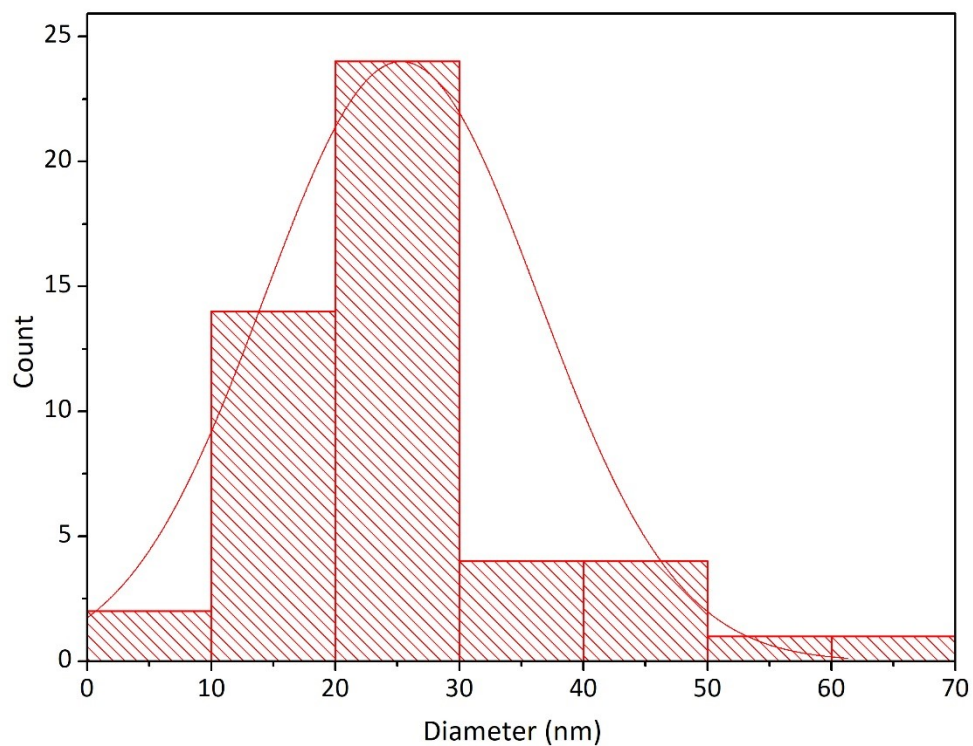


Figure S35. Particle size distribution in the case of **L4** stabilized silver nanoparticles after the addition of Hg^{2+} ions

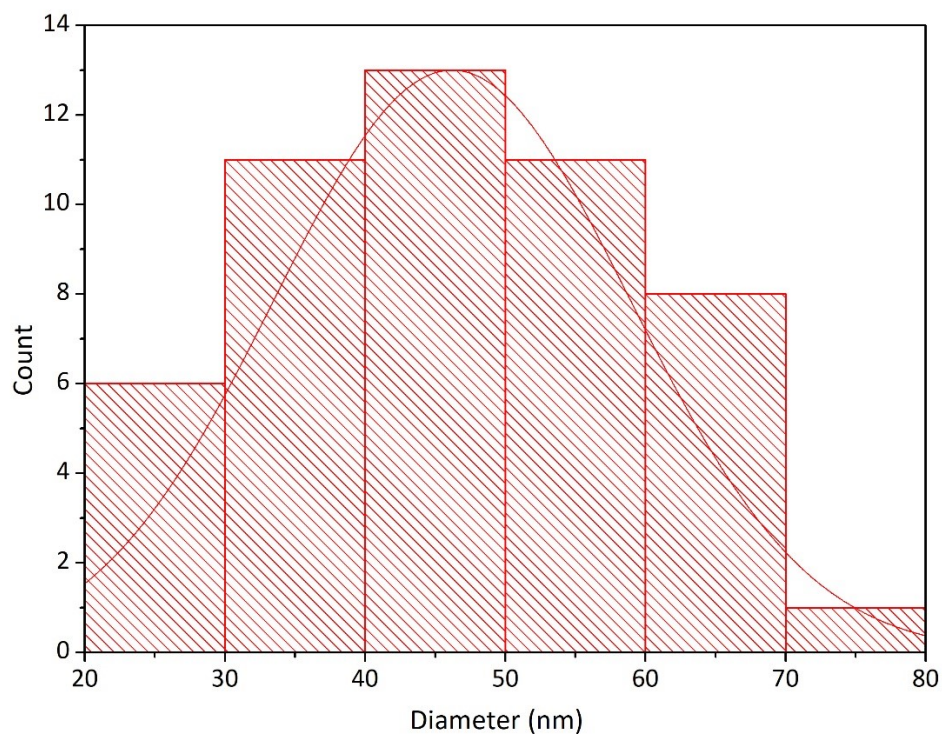


Figure S36. Particle size distribution in the case of **L4** stabilized silver nanoparticles after the addition of Cr^{3+} ions

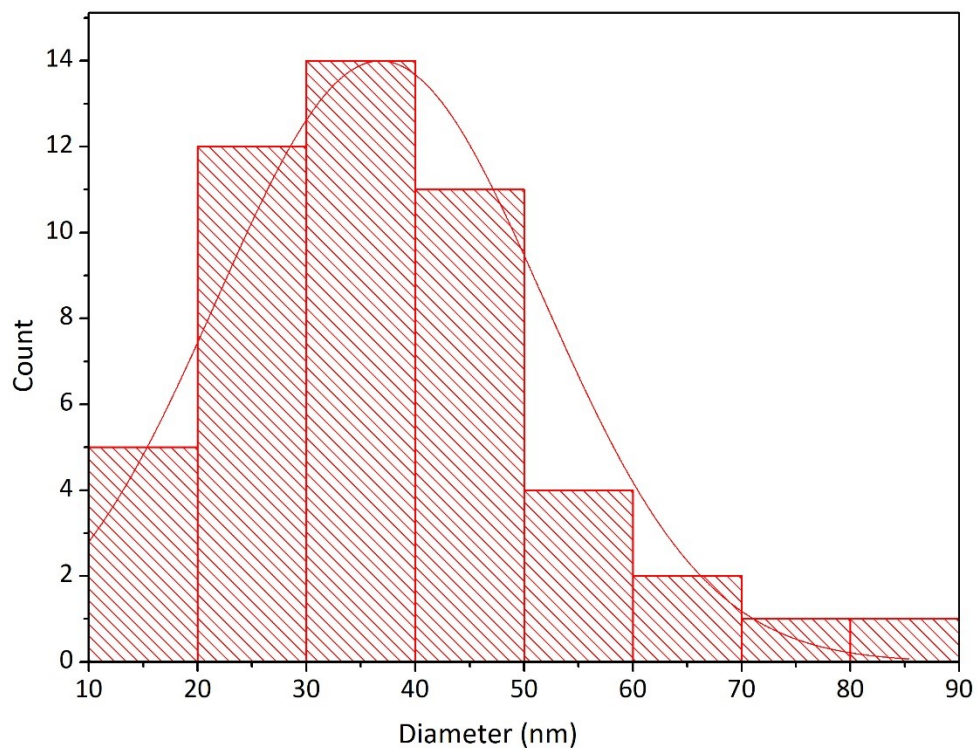


Figure S37. Particle size distribution in the case of **L4** stabilized silver nanoparticles after the addition of Bi^{3+} ions

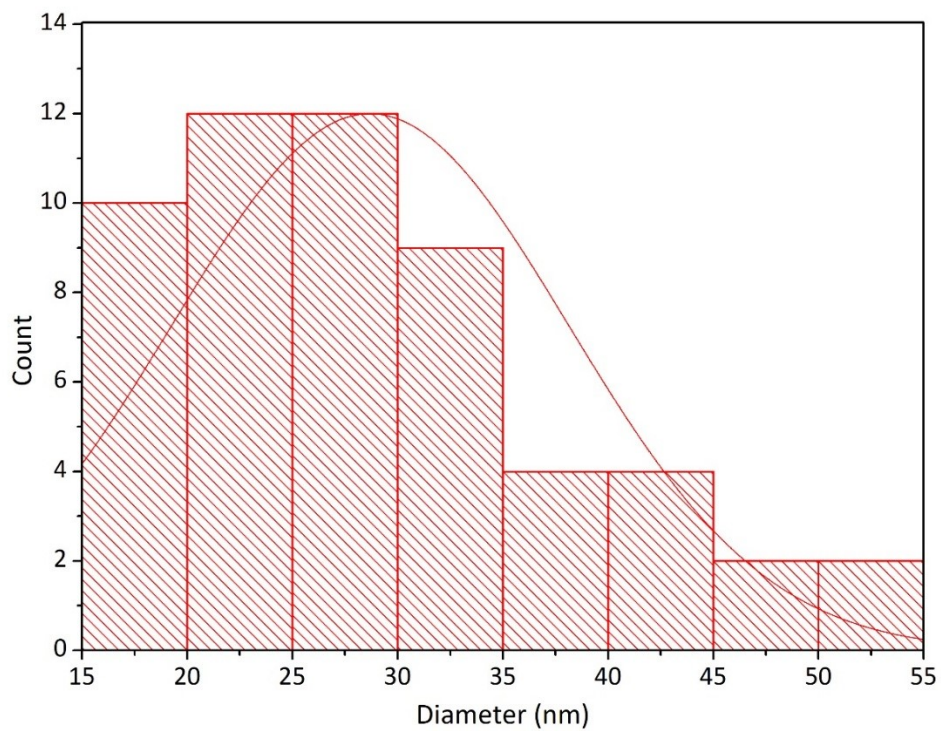


Figure S38. Particle size distribution in the case of **L4** stabilized silver nanoparticles after the addition of HSO_4^- ions

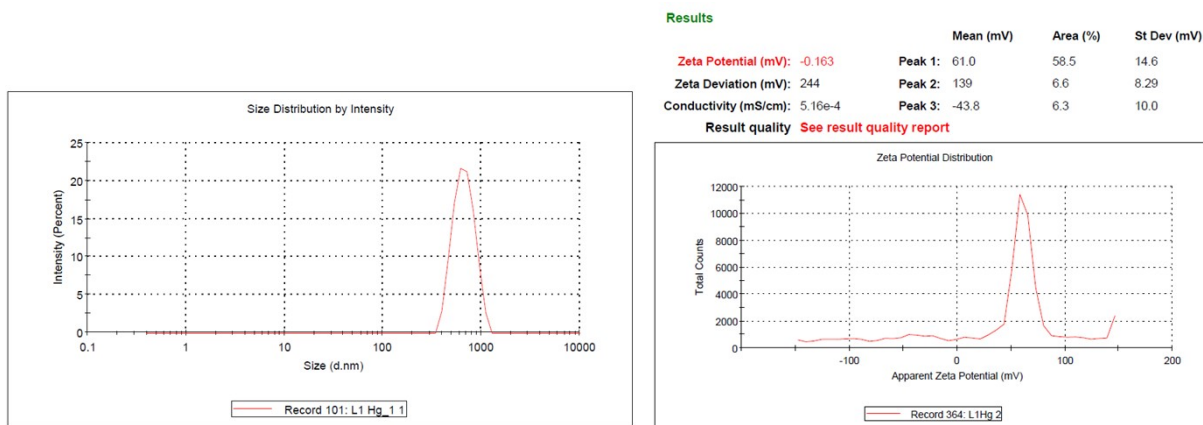


Figure S39. DLS data and zeta potential in the case of **L1** stabilized silver nanoparticles after the addition of Hg^{2+} ions

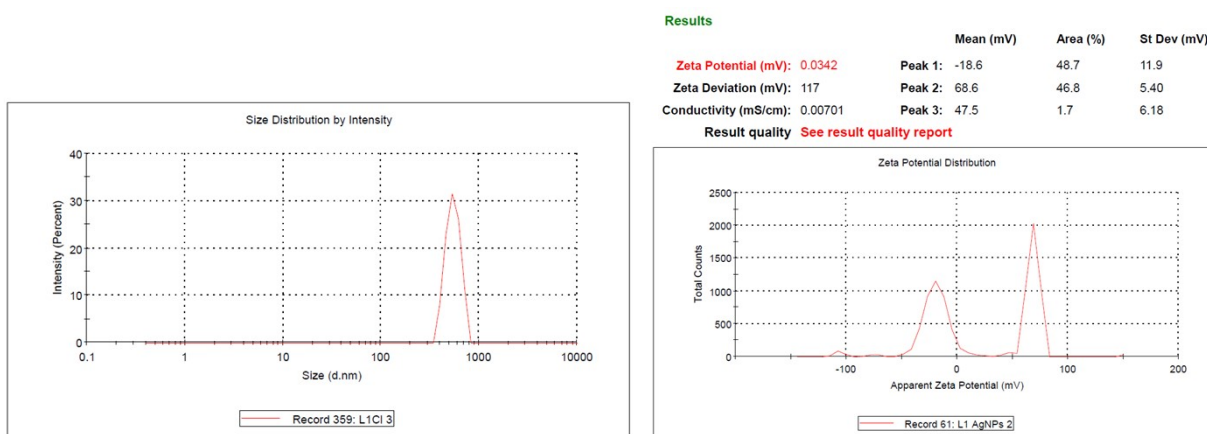


Figure S40. DLS data and zeta potential in the case of **L1** stabilized silver nanoparticles after the addition of Cl^- ions

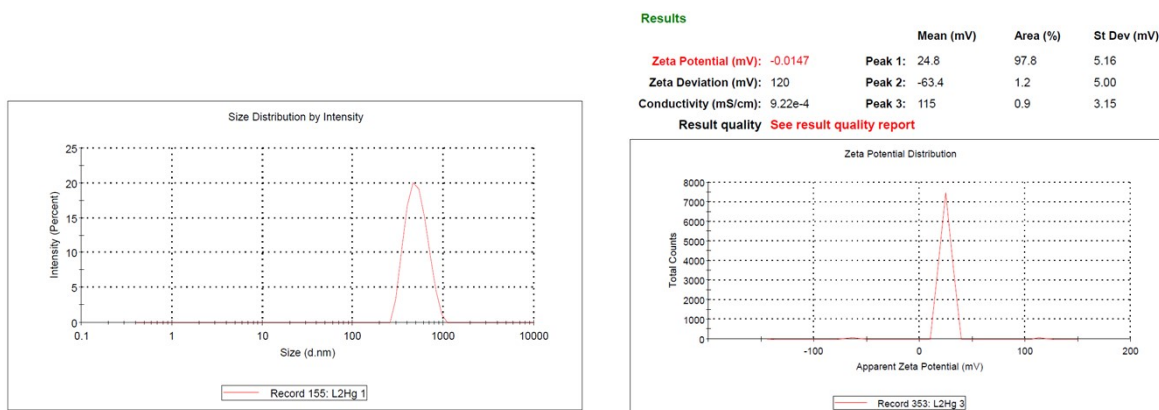
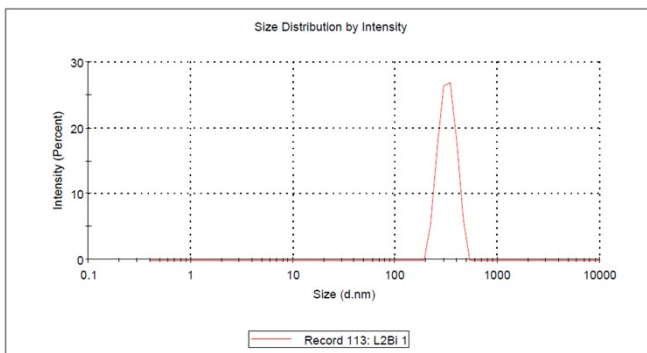


Figure S41. DLS data and zeta potential in the case of **L2** stabilized silver nanoparticles after the addition of Hg^{2+} ions



Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -0.693	Peak 1: 23.0	48.8	26.2
Zeta Deviation (mV): 242	Peak 2: -55.9	18.8	20.1
Conductivity (mS/cm): 0.00719	Peak 3: 100	14.7	16.3

Result quality See result quality report

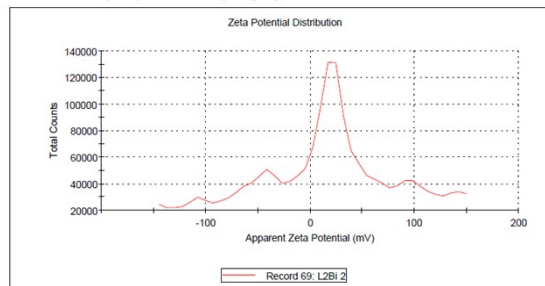
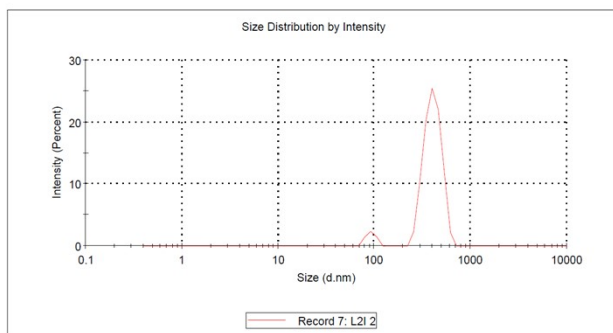


Figure S42. DLS data and zeta potential in the case of **L2** stabilized silver nanoparticles after the addition of Bi^{3+} ions



Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -0.730	Peak 1: -1.61	99.0	9.29
Zeta Deviation (mV): 12.8	Peak 2: 88.4	1.0	0.00
Conductivity (mS/cm): 2.29e-4	Peak 3: 0.00	0.0	0.00

Result quality See result quality report

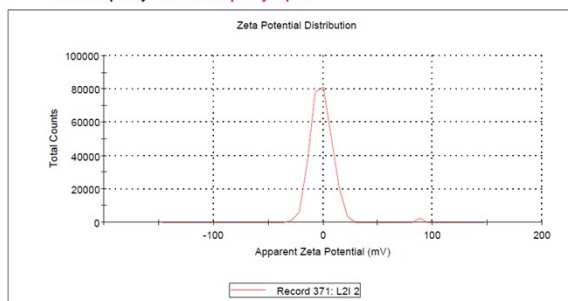
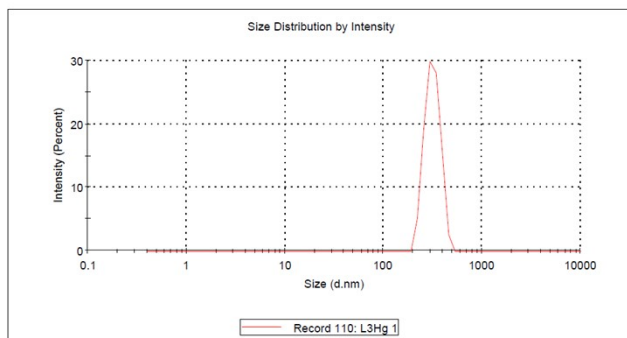


Figure S43. DLS data and zeta potential in the case of **L2** stabilized silver nanoparticles after the addition of I^- ions



Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -0.0314	Peak 1: 102	79.6	5.15
Zeta Deviation (mV): 245	Peak 2: 20.6	9.8	9.71
Conductivity (mS/cm): 8.53e-4	Peak 3: -6.03	7.1	8.24

Result quality See result quality report

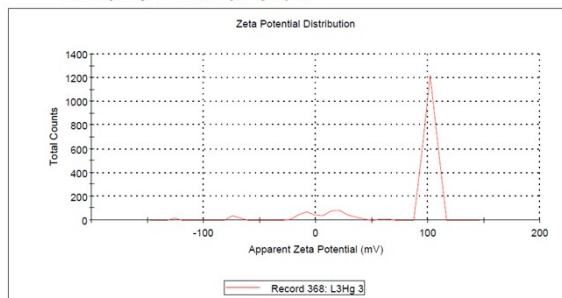
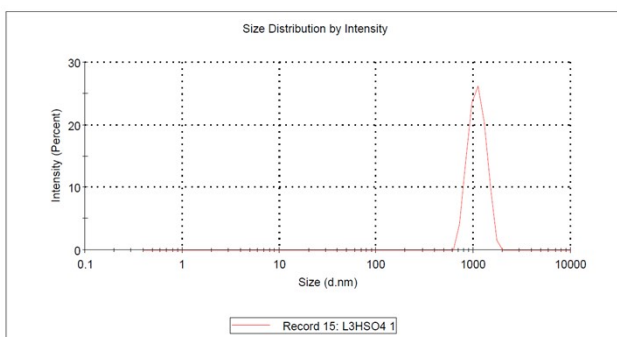


Figure S44. DLS data and zeta potential in the case of **L3** stabilized silver nanoparticles after the addition of Hg^{2+} ions



Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -0.0836	Peak 1: -4.07	95.4	9.76
Zeta Deviation (mV): 20.6	Peak 2: 83.1	4.6	4.88
Conductivity (mS/cm): 0.00217	Peak 3: 0.00	0.0	0.00

Result quality [See result quality report](#)

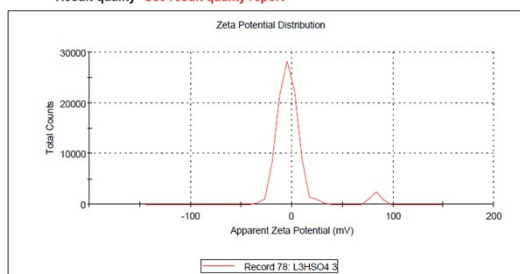
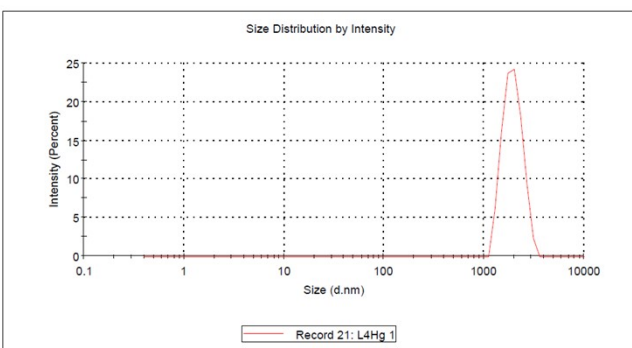


Figure S45. DLS data and zeta potential in the case of **L3** stabilized silver nanoparticles after the addition of HSO_4^- ions



Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): 0.634	Peak 1: 0.634	100.0	8.82
Zeta Deviation (mV): 8.82	Peak 2: 0.00	0.0	0.00
Conductivity (mS/cm): 0.00616	Peak 3: 0.00	0.0	0.00

Result quality [See result quality report](#)

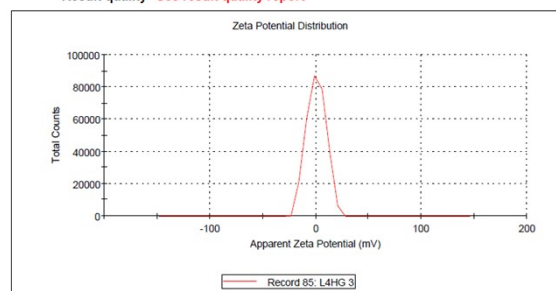
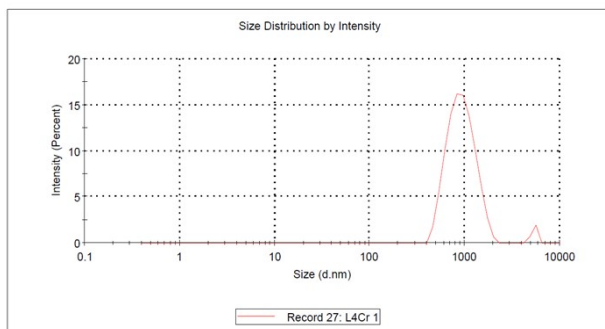


Figure S46. DLS data and zeta potential in the case of **L4** stabilized silver nanoparticles after the addition of Hg^{2+} ions



Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -0.0677	Peak 1: -20.1	76.9	8.89
Zeta Deviation (mV): 38.9	Peak 2: 67.8	23.1	5.10
Conductivity (mS/cm): 0.00595	Peak 3: -108	0.0	0.00

Result quality [See result quality report](#)

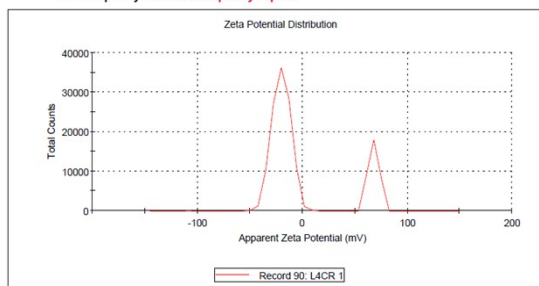


Figure S47. DLS data and zeta potential in the case of **L4** stabilized silver nanoparticles after the addition of Cr^{3+} ions

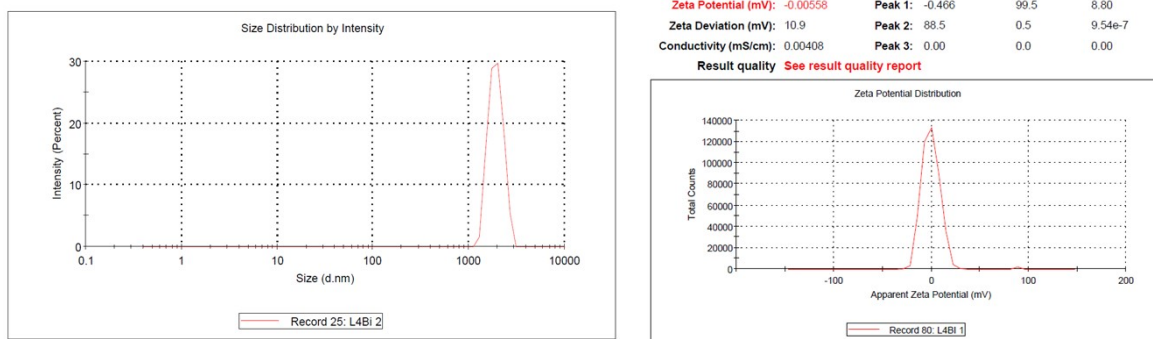


Figure S48. DLS data and zeta potential in the case of **L4** stabilized silver nanoparticles after the addition of Bi^{3+} ions

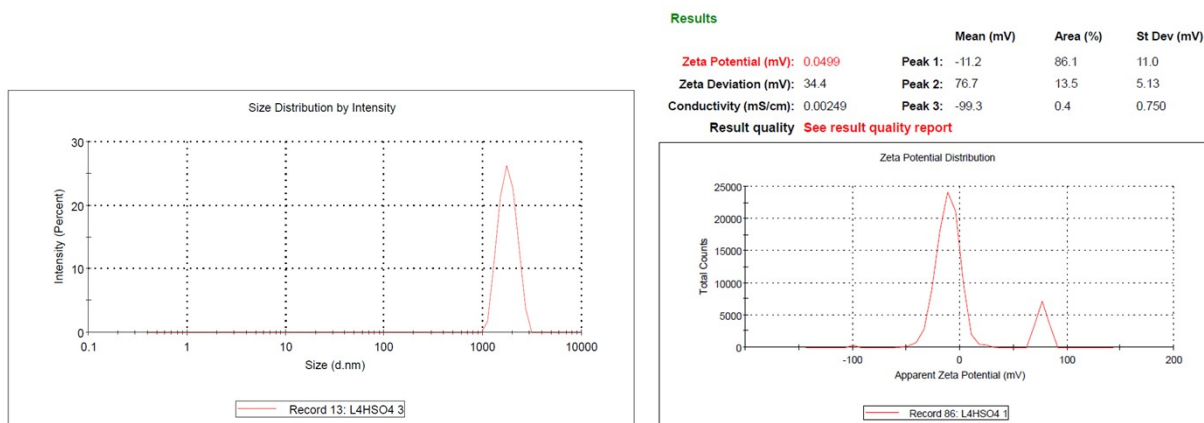


Figure S49. DLS data and zeta potential in the case of **L4** stabilized silver nanoparticles after the addition of HSO_4^- ions

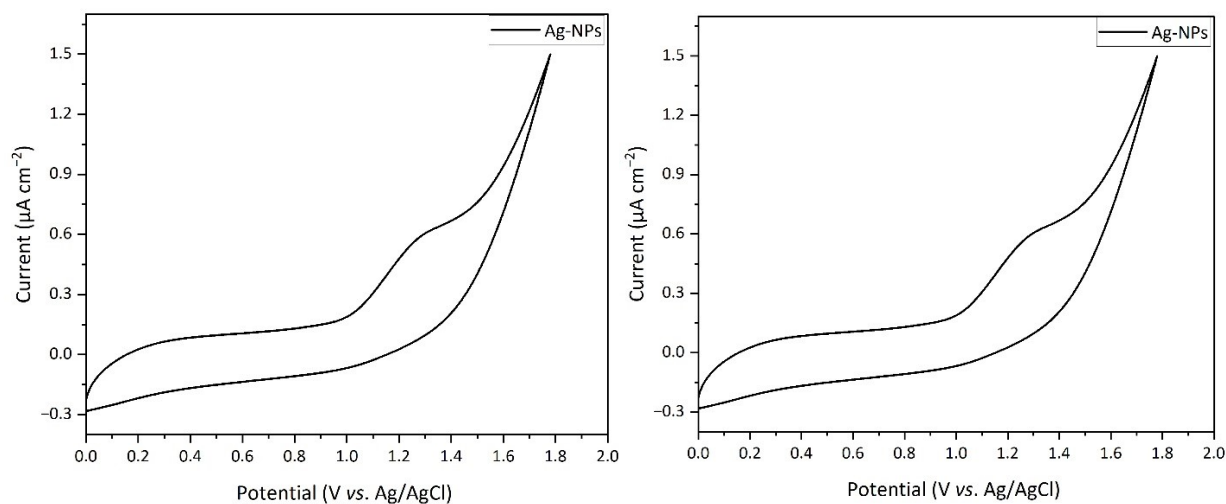


Figure S50. (a) Cyclic voltammogram of **L3** stabilized silver nanoparticles; (b) Differential pulse voltammogram of **L3** stabilized silver nanoparticles and with the addition of I^- ions

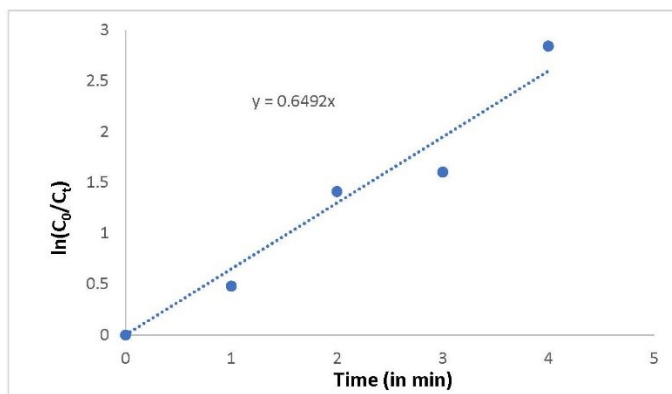
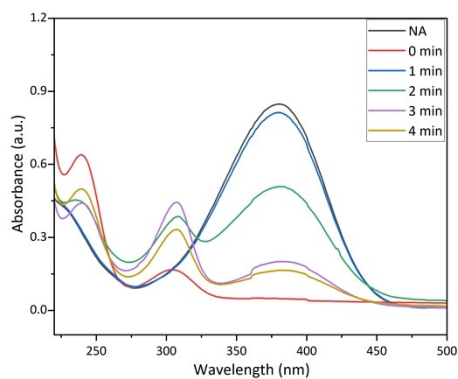


Figure S51. UV spectra of reduction of Nitroaniline and rate constant $\ln C_0/C_t$ Vs time

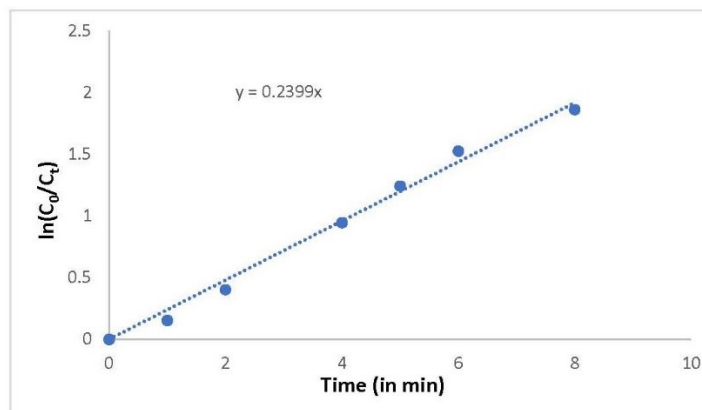
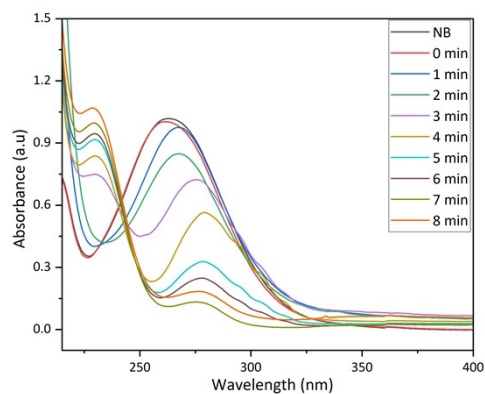


Figure S52. UV spectra of reduction of Nitrobenzene and rate constant $\ln C_0/C_t$ Vs time

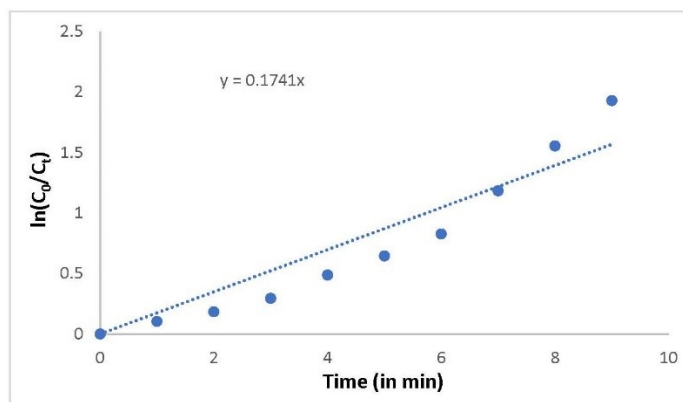
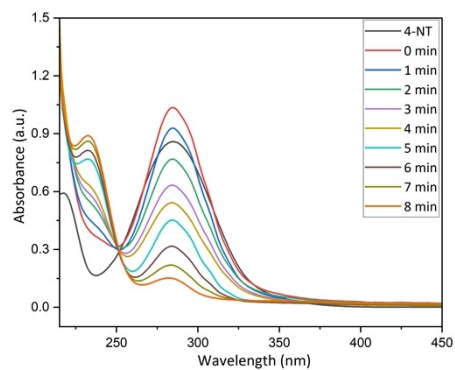


Figure S53. UV spectra of reduction of 4-Nitrotoulene and rate constant $\ln C_0/C_t$ Vs time

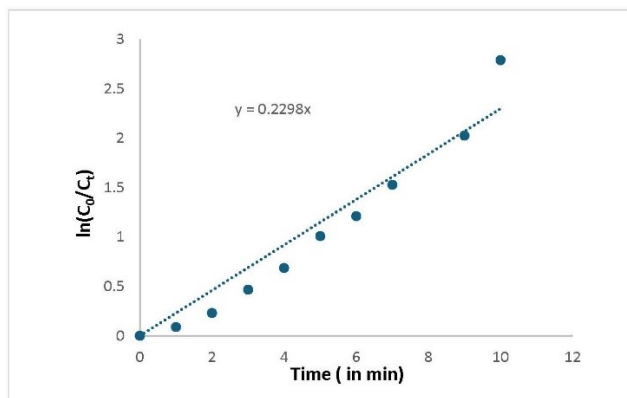
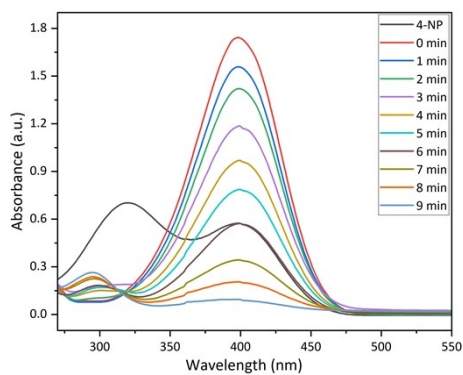


Figure S54. UV spectra of reduction of 4-Nitrophenol and rate constant $\ln C_0/C_t$ Vs time

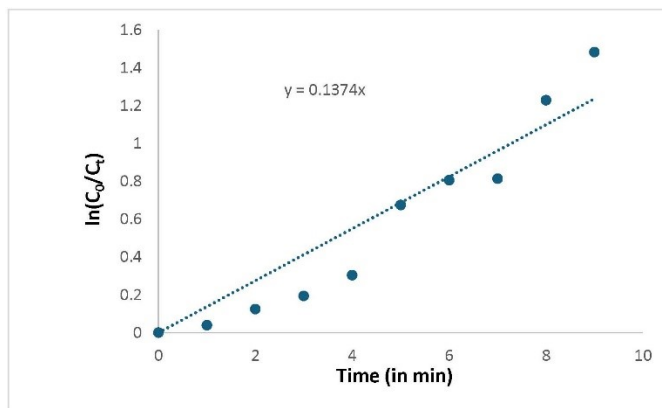
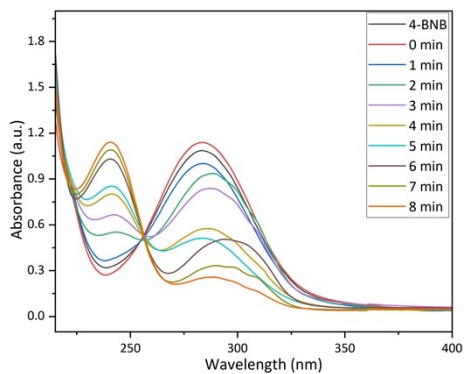


Figure S55. UV spectra of reduction of 1-bromo-4-nitrobenzene and rate constant $\ln C_0/C_t$ Vs time

Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -26.1	Peak 1: -26.1	100.0	5.64
Zeta Deviation (mV): 5.64	Peak 2: 0.00	0.0	0.00
Conductivity (mS/cm): 0.0121	Peak 3: 0.00	0.0	0.00
Result quality Good			

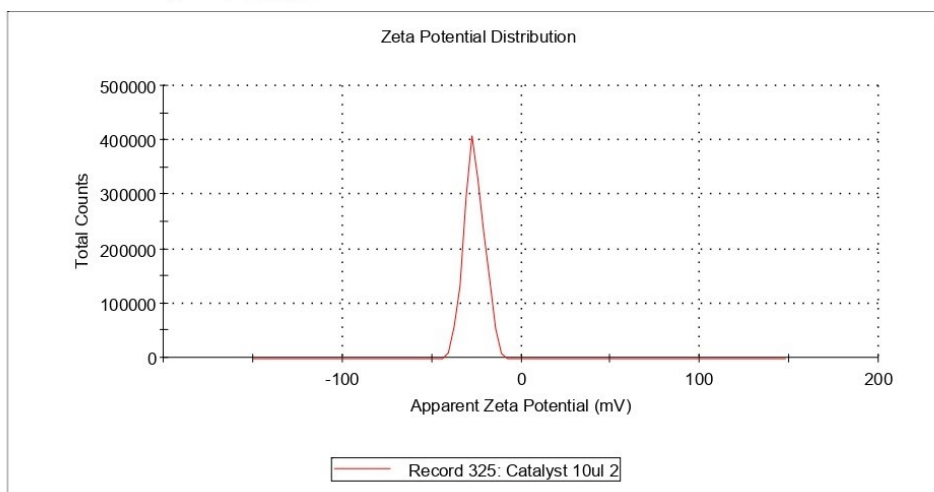


Figure S56. Surface charge on the catalyst

Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -43.5	Peak 1: -43.5	100.0	10.2
Zeta Deviation (mV): 10.2	Peak 2: 0.00	0.0	0.00
Conductivity (mS/cm): 0.329	Peak 3: 0.00	0.0	0.00
Result quality Good			

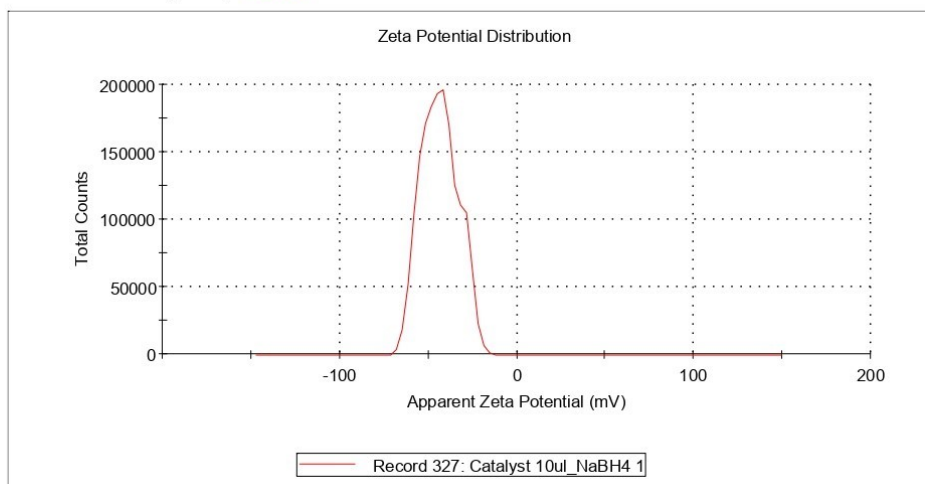


Figure S57. Surface charge after the addition of NaBH₄ and 4-nitrophenol in the catalyst solution

Results

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -28.2	Peak 1: -28.2	100.0	6.29
Zeta Deviation (mV): 6.29	Peak 2: 0.00	0.0	0.00
Conductivity (mS/cm): 0.206	Peak 3: 0.00	0.0	0.00
Result quality Good			

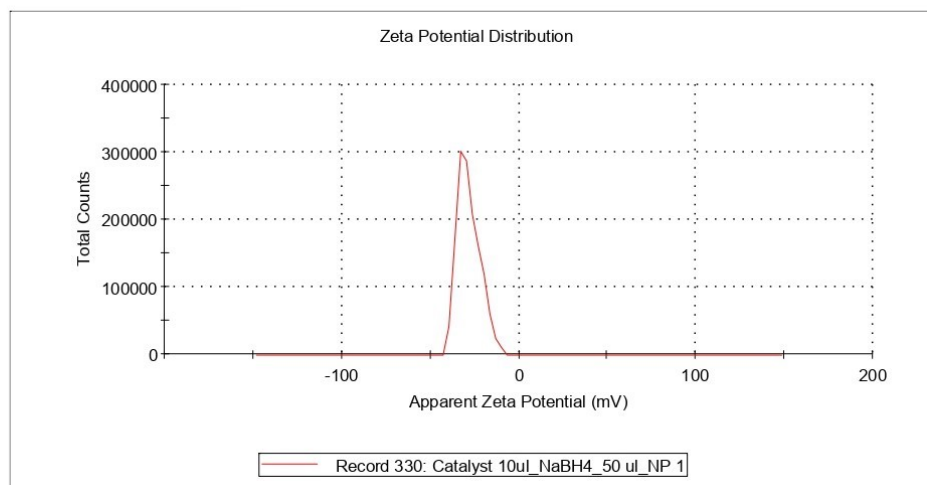
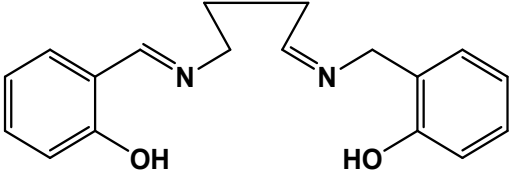
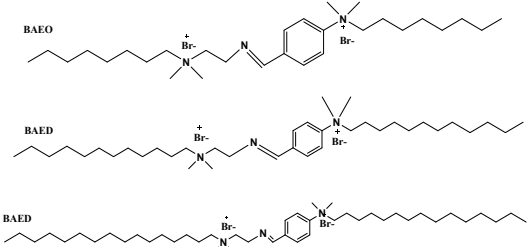
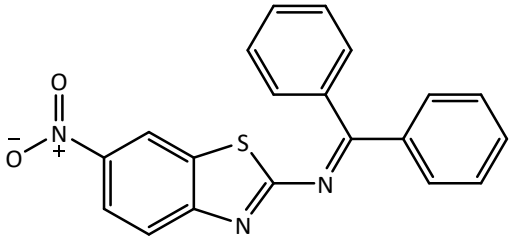
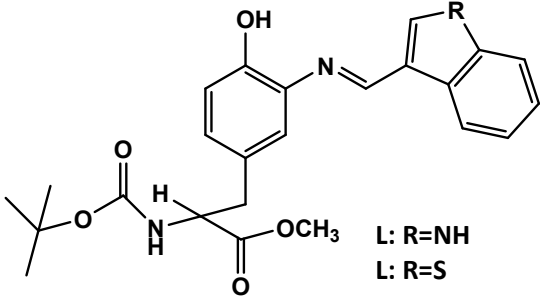
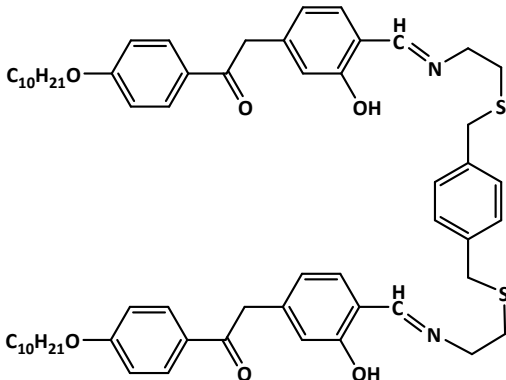


Figure S58. Surface charge after completion of reaction

Table S1. Ag-NPs synthesized using imine containing small molecules for various applications

S. No.	Metal precursor and reducing agent	Imine containing small molecule	Size of NPs	Application	Reference
1.	AgNO ₃ , NaBH ₄		29.93 nm	Detection of toxic metal (Hg ²⁺) and catalytic application of dye degradation.	1
2.	AgNO ₃ , NaBH ₄		10 ± 25 nm	Catalyst to reduce nitroaromatic compounds	2
3.	AgNO ₃ , NaBH ₄		72 nm	Good antibacterial activity against pathogenic propionic bacteria with comparative studies	3
4.	AgNO ₃ , Hydrazine		12 ± 3.5 nm	Detection of Cu ²⁺ ions in the absolute ethanol solution	4

5.	AgNO ₃ , NaBH ₄		5 nm	Colorimetric detection of Hg ²⁺ and Cu ²⁺ ions and catalytic reduction of nitroaromatics.	5
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References:

1. A. Minhaz, N. Khan and N. Jamila, *Arab J. Chem.*, 2020, **13**, 8898–8908.
2. E. Badr, S. Shafek, H. Hefni, A. Elsharif, A. Alanezi, S. Shaban and D. Kim, *J. Mol. Liq.*, 2021, **326**, 115342.
3. K. Kumar, S. Anand, M. Kori, N. Mishra and S.P. Shrivastava, *J. Indian Chem Soc.*, 2023, **100**, 100965.
4. E. Oliveira, J. Miranda and H. Santos, *Inorganica Chim Acta.*, 2012, **380**, 22-30.
5. N. Yadav, S. Shiva, P. Oswal, A. Kumar, A.K. Singh, B. Singh, B. Pandit, J. Ahmed and G. K. Rao, *J. Mol. Liq.*, 2023, **377**, 121531.