

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

Nisha Yadav,^a Annu Rathee,^a Shreya Sachdeva,^a Bharat Kumar,^b Jahangeer Ahmed,^c Monu Verma,^d Gyandshwar Kumar Rao*^a

^aDepartment of Chemistry, Biochemistry and Forensic Science, Amity School of Applied Sciences, Amity University Haryana, Manesar, Gurgaon-122413, Haryana, India.

^bDepartment of Chemistry, M V College Buxar, (A constituent unit of Veer Kunwar Singh University Arrah) Bihar-802101, India.

^cDepartment of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia.
Water-Energy Nexus Laboratory, Department of Environmental Engineering, University of Seoul, Seoul, 02504, South Korea.

*gyan23iitd@gmail.com, gkrao@ggn.amity.edu

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). ($^{13}\text{C}\{\text{H}\}$, 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.

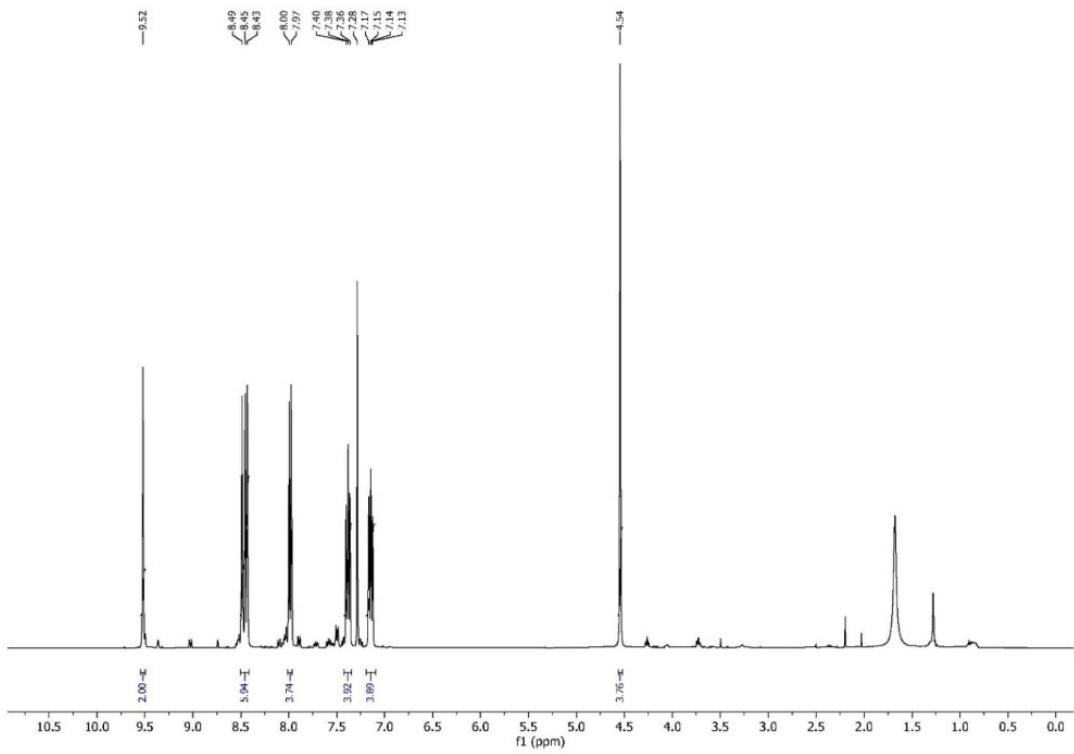


Figure S1. ^1H NMR spectra of **L1**

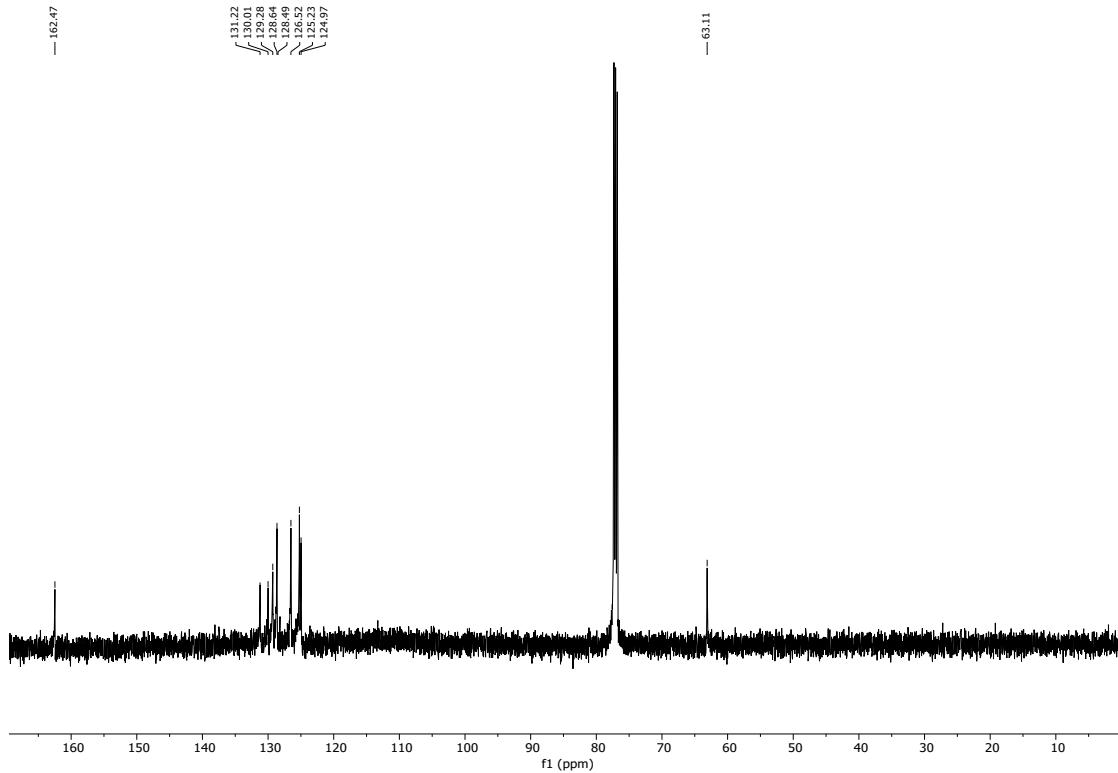


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **L1**

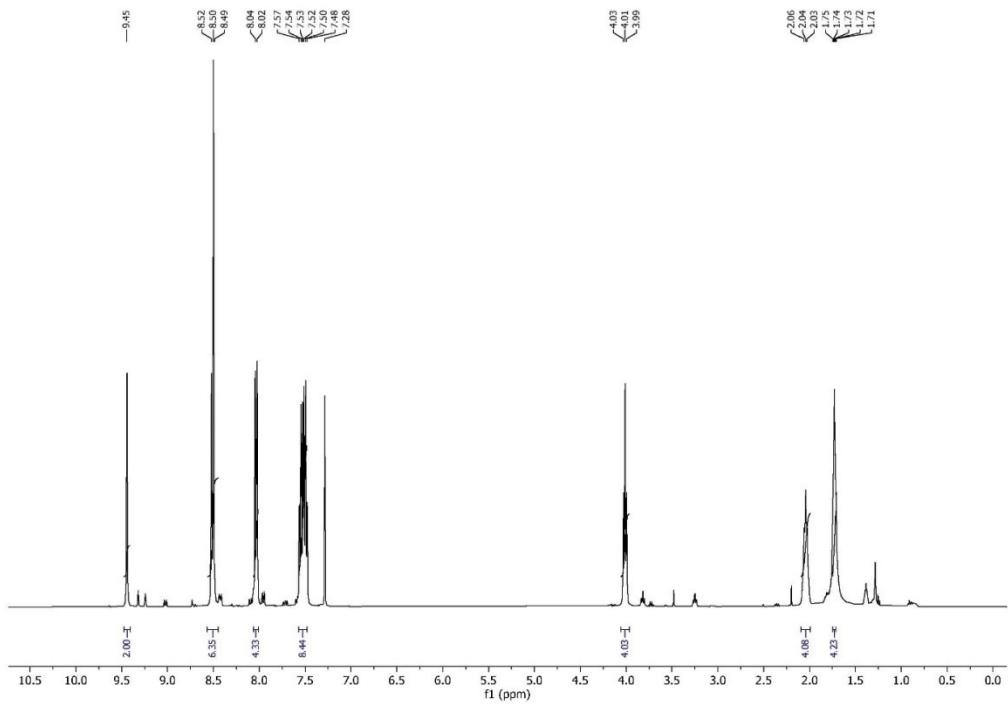


Figure S3. ^1H NMR spectra of **L2**

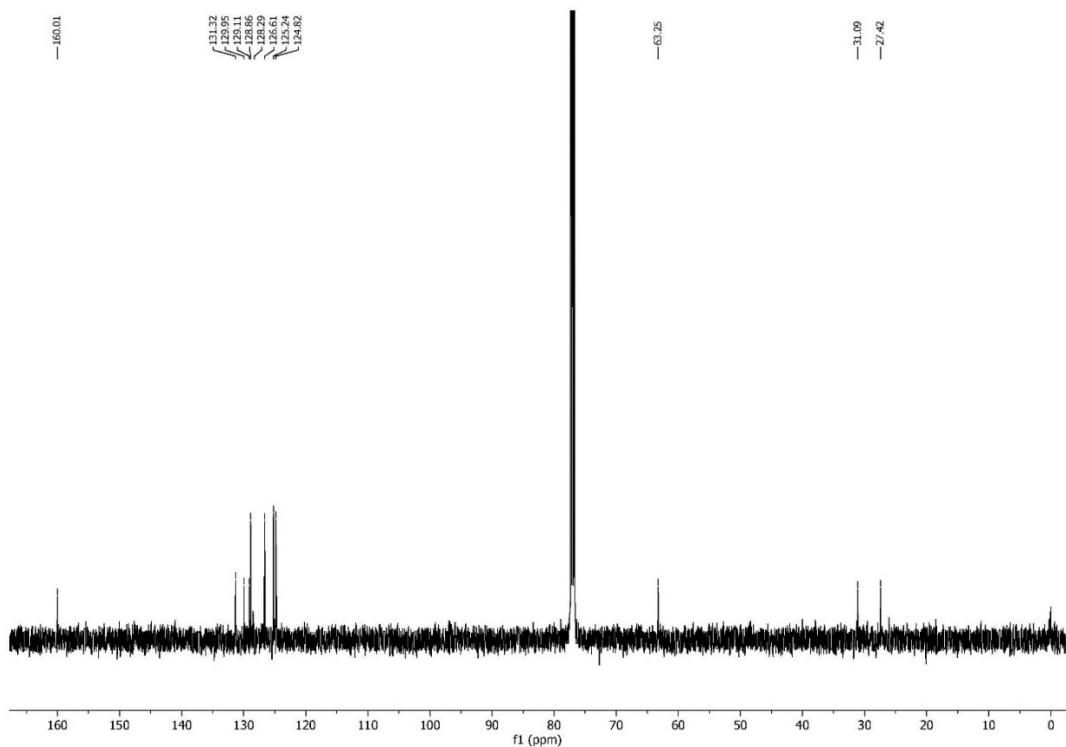


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **L2**

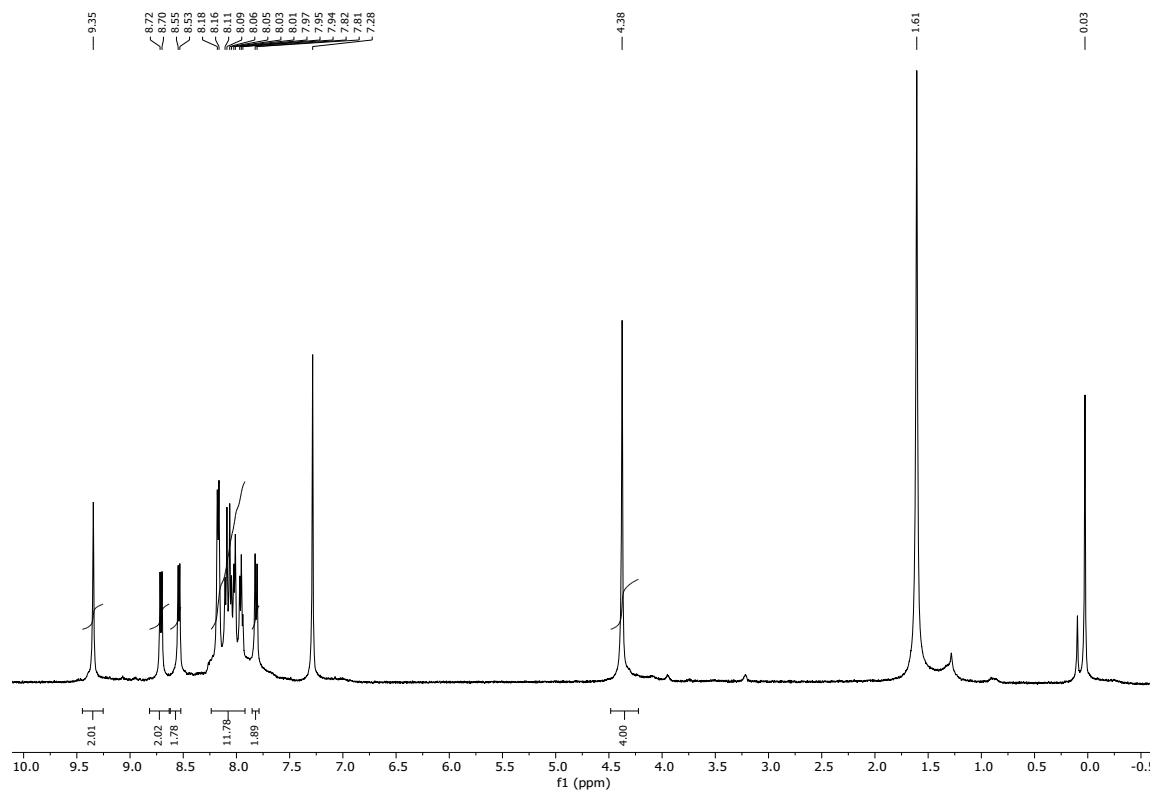


Figure S5. ^1H NMR spectra of **L3**

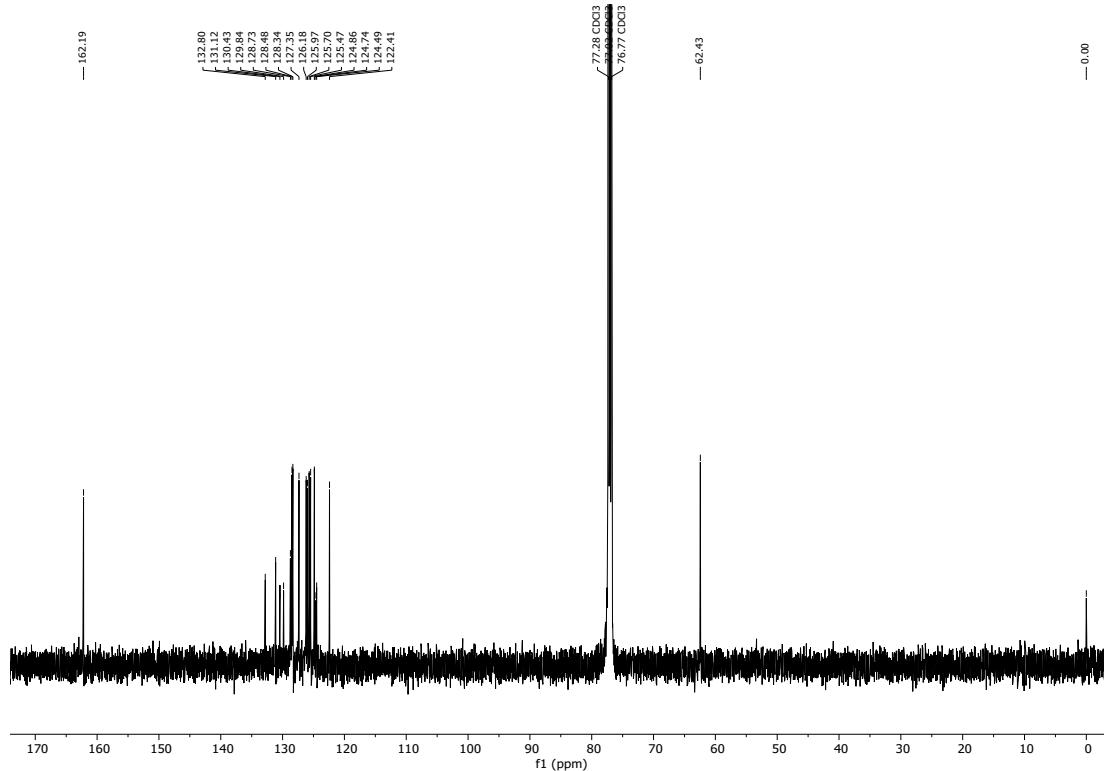


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **L3**

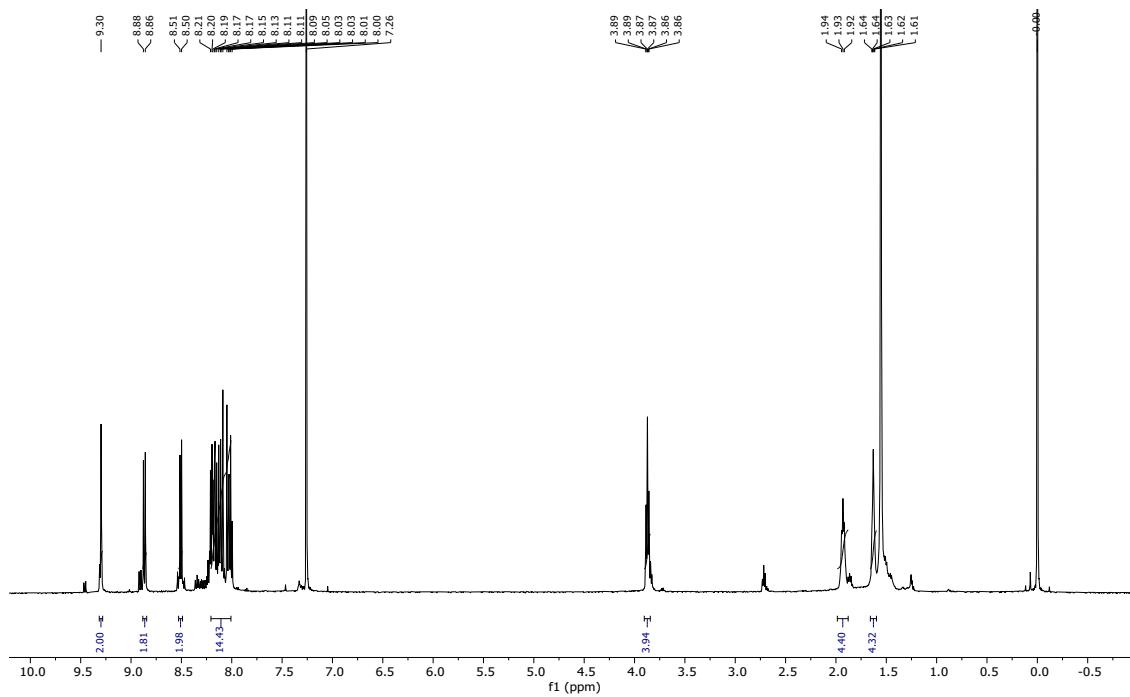


Figure S7. ^1H NMR spectra of **L4**

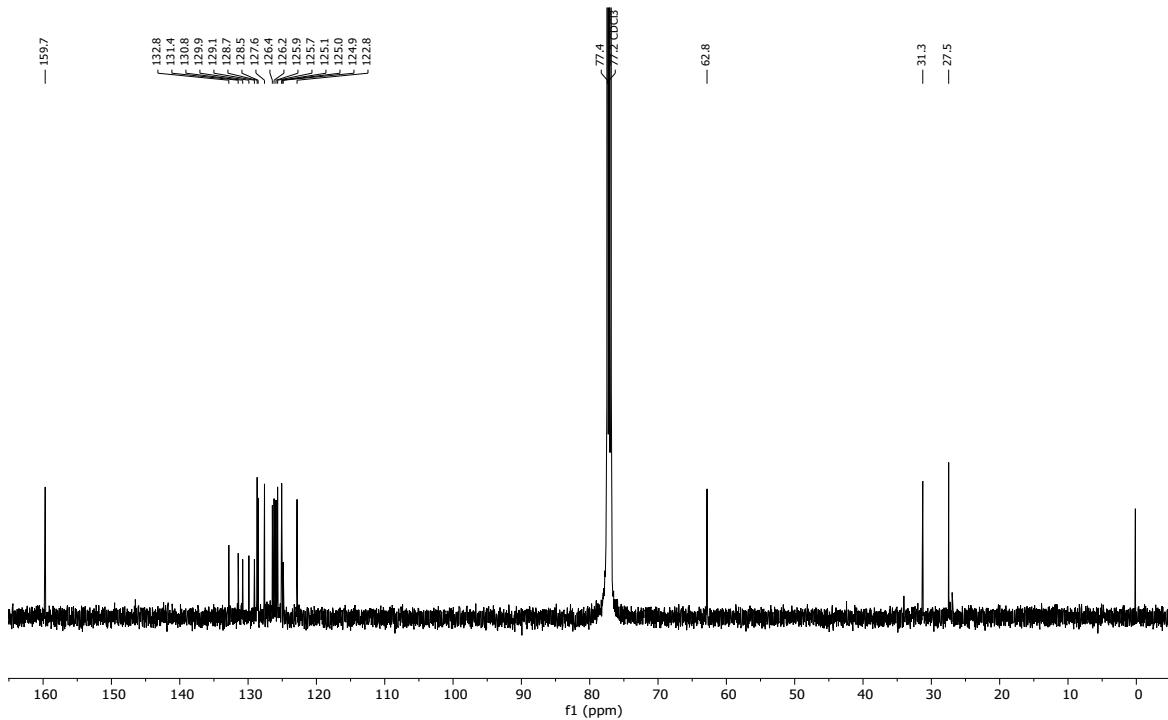


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **L4**

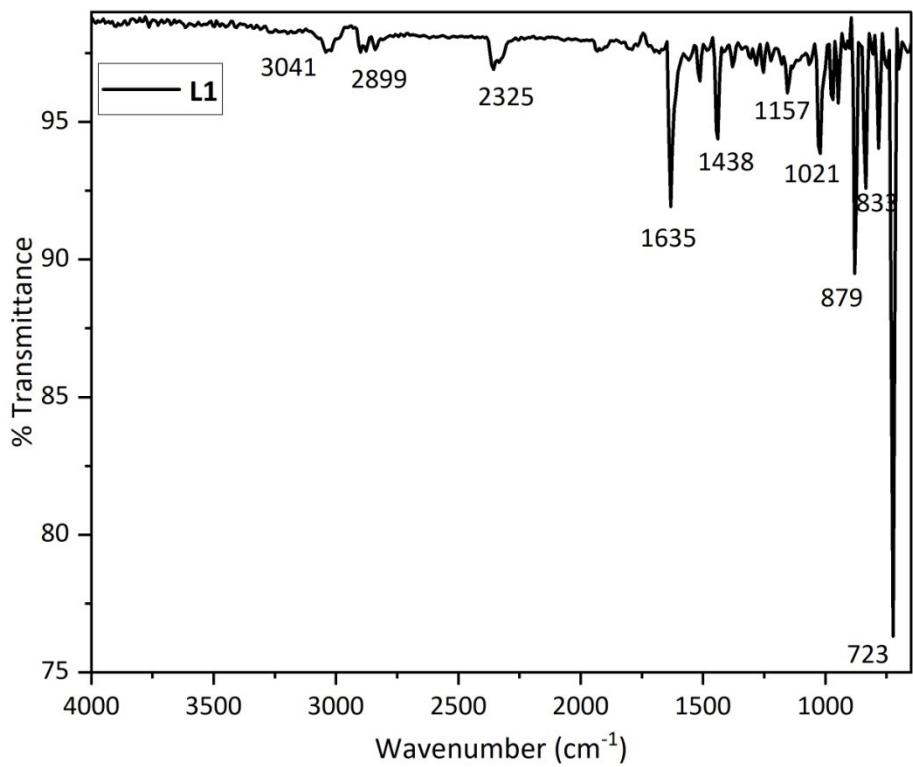


Figure S9. Infrared spectra of L1

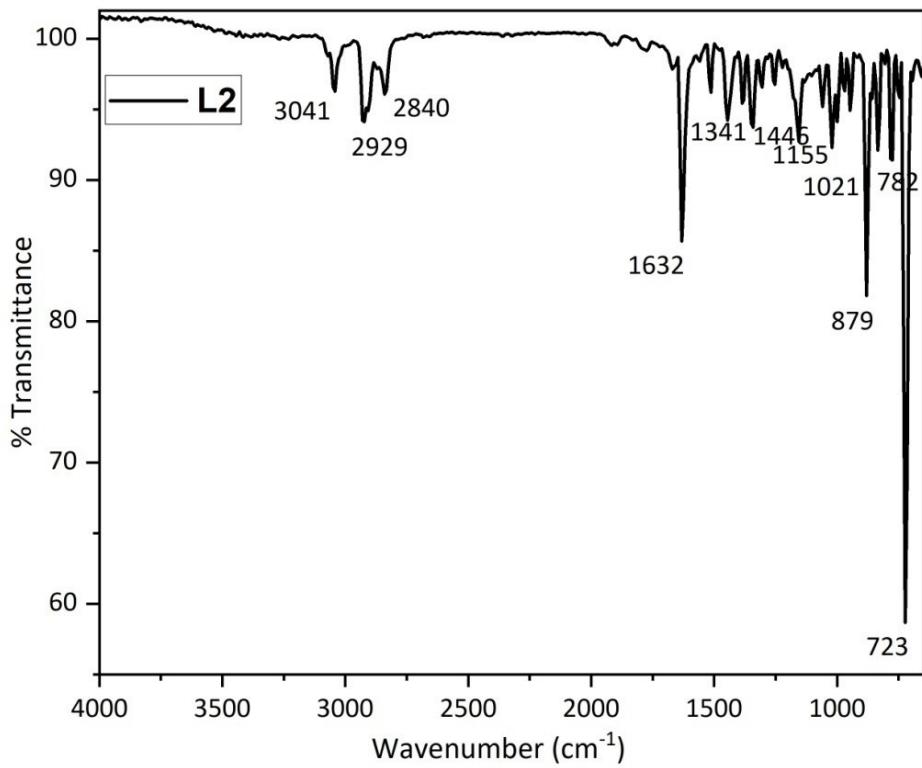


Figure S10. Infrared spectra of L2

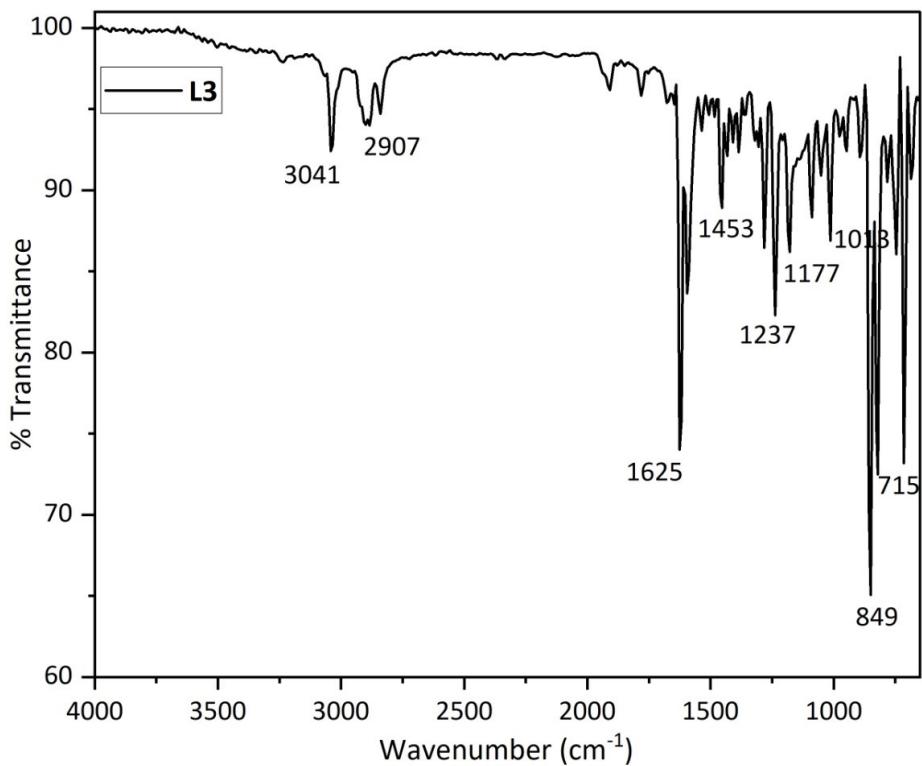


Figure S11. Infrared spectra of L3

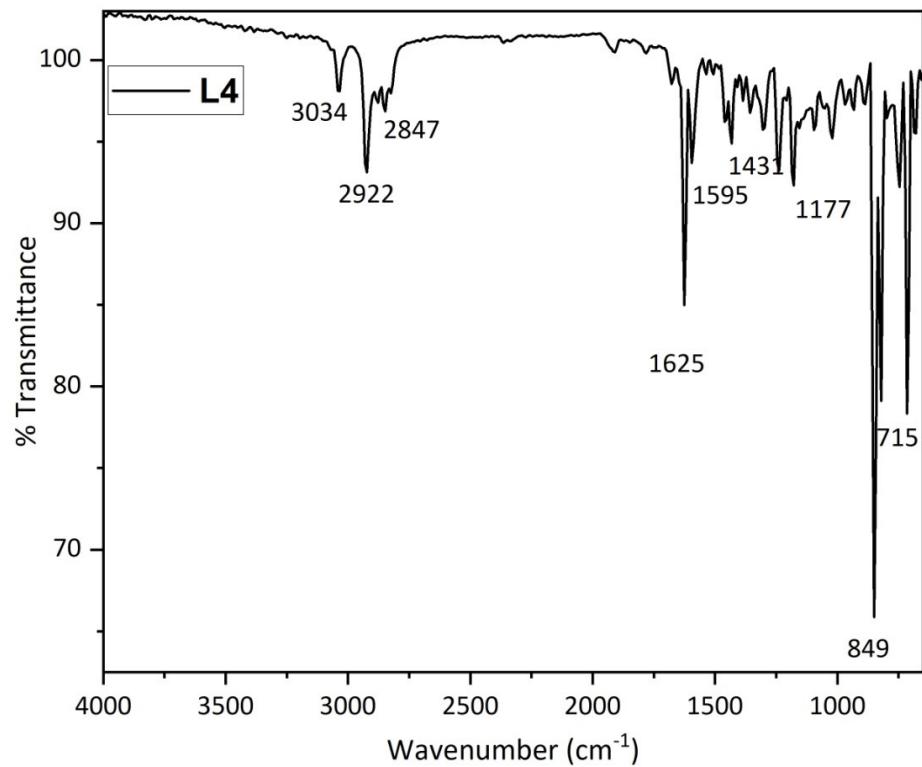


Figure S12. Infrared spectra of L4

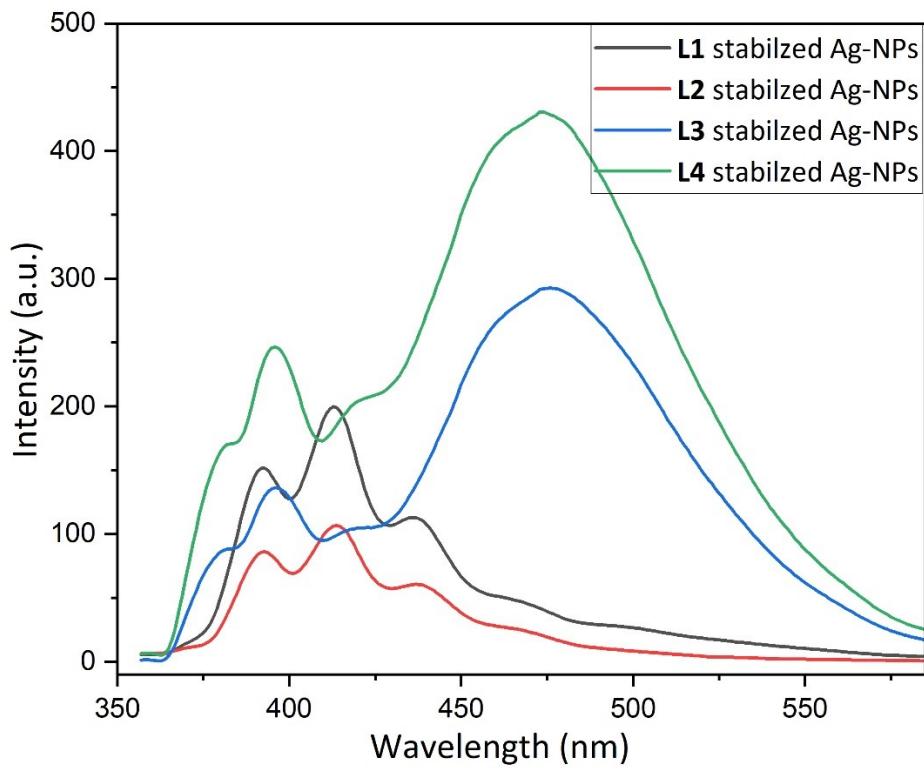


Figure S13. Fluorescence spectra of **L1–L4** stabilized silver nanoparticles

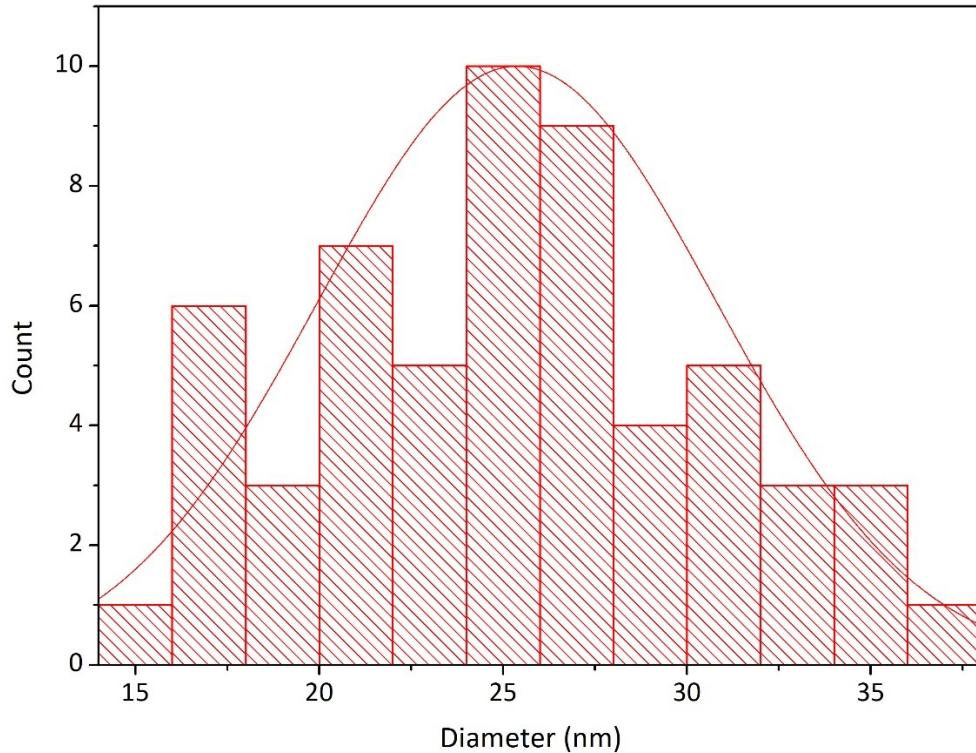


Figure S14. Particle size distribution in the case of **L1** stabilized silver nanoparticles

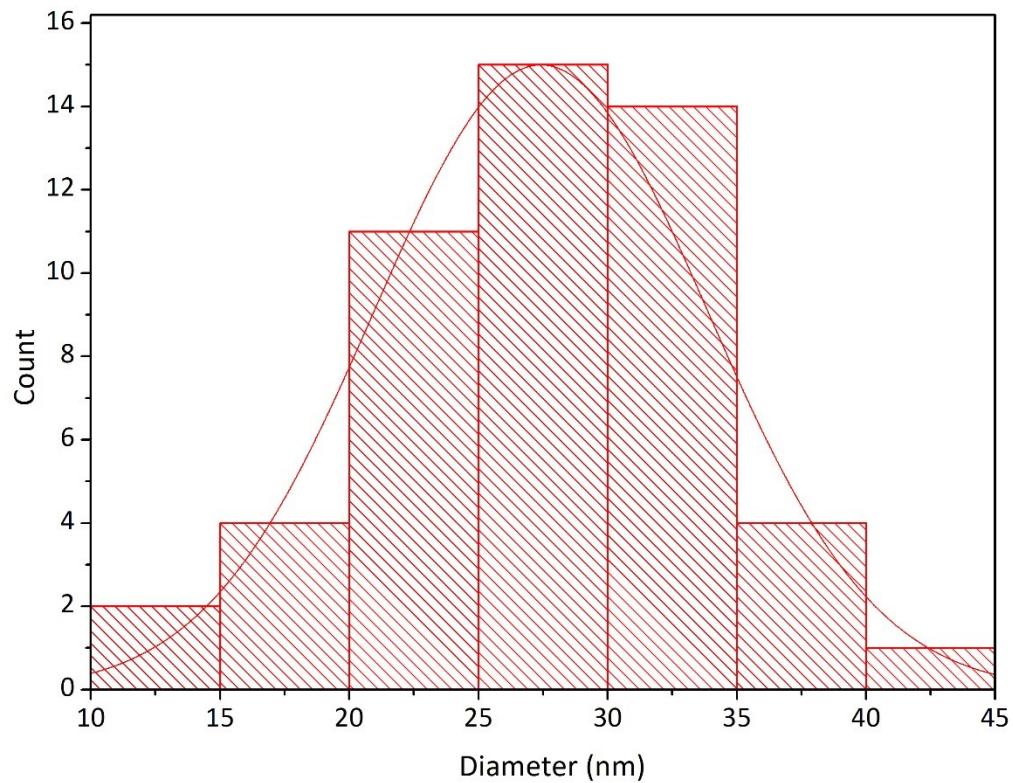


Figure S15. Particle size distribution in the case of L2 stabilized silver nanoparticles

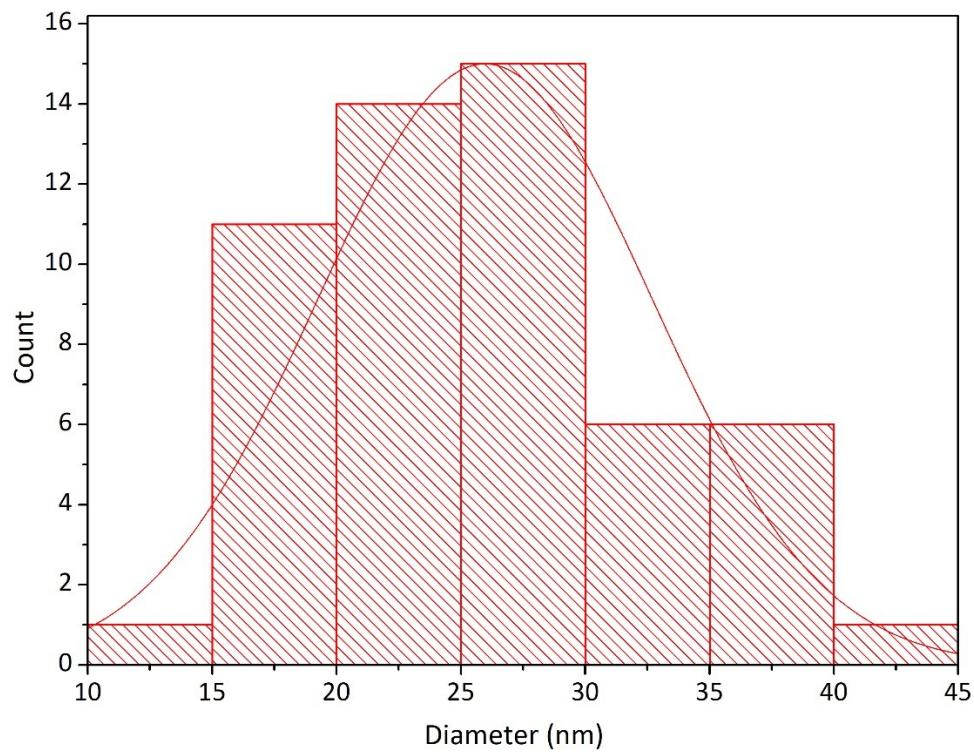


Figure S16. Particle size distribution in the case of L3 stabilized silver nanoparticles

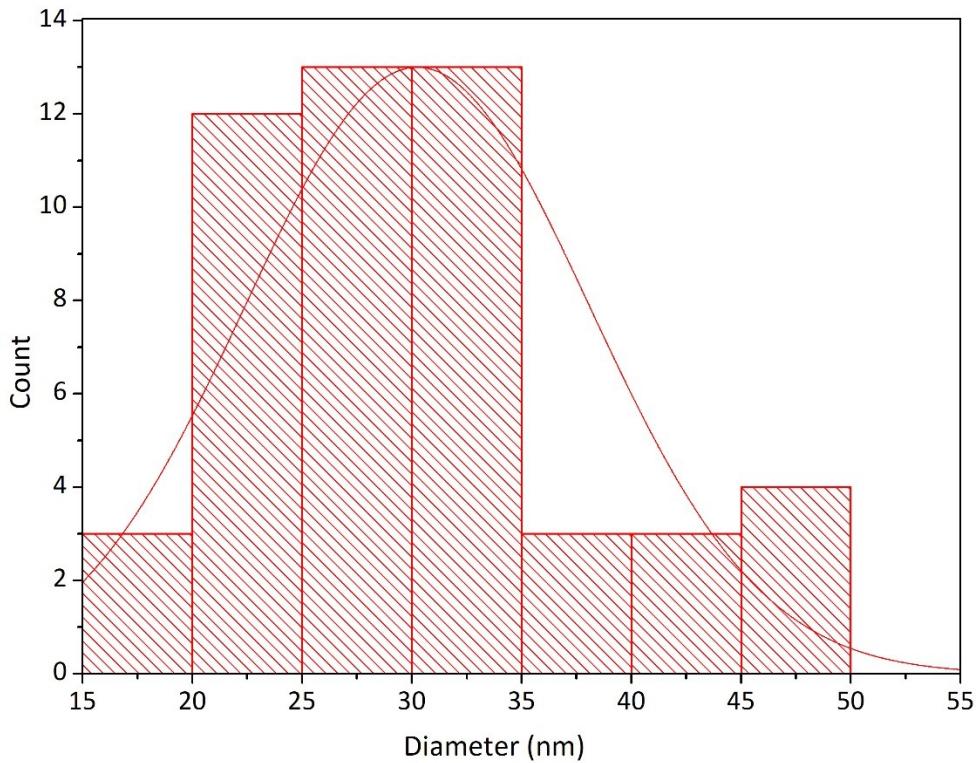


Figure S17. Particle size distribution in the case of **L4** stabilized silver nanoparticles

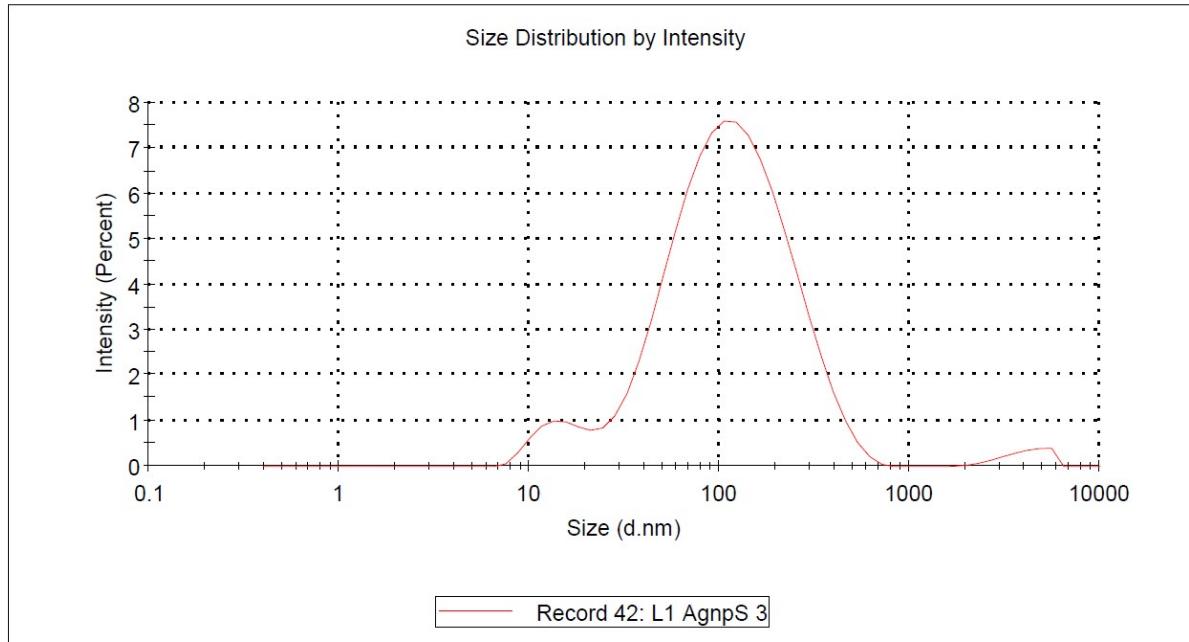


Figure S18. DLS data of **L1** stabilized silver nanoparticles (freshly synthesized)

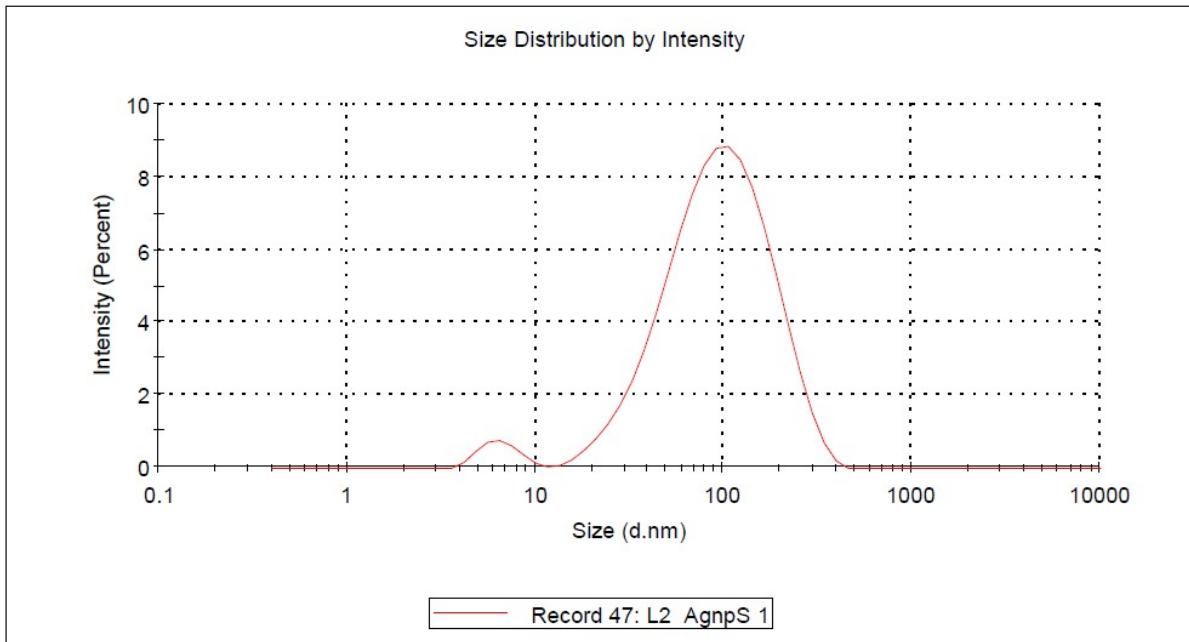


Figure S19. DLS data of **L2** stabilized silver nanoparticles (freshly synthesized)

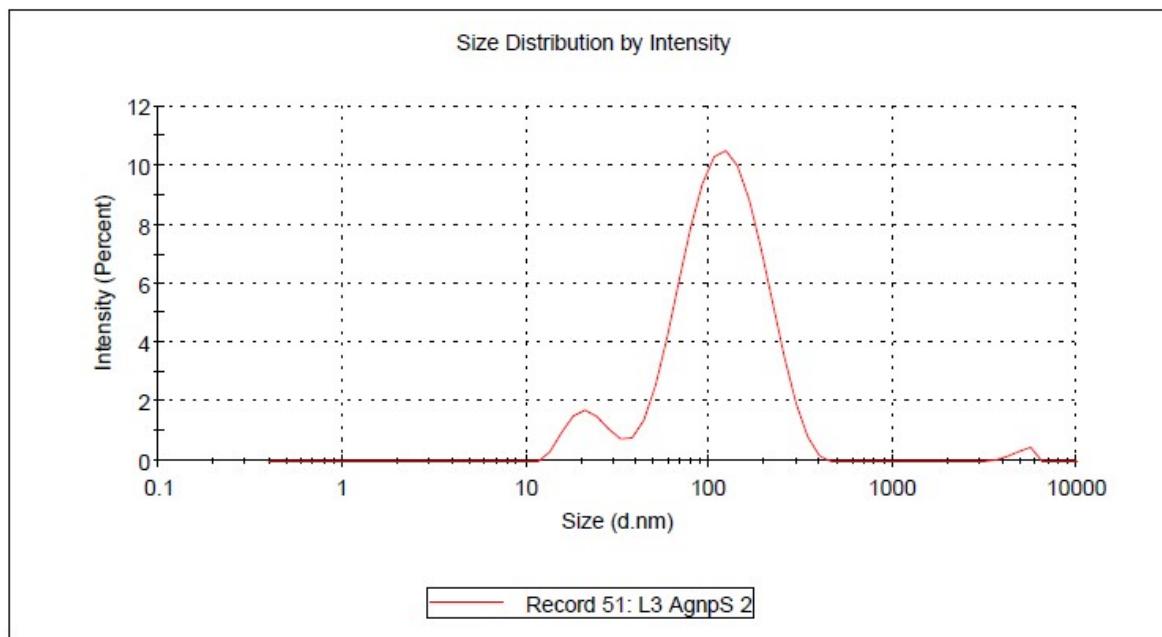


Figure S20. DLS data of **L3** stabilized silver nanoparticles (freshly synthesized)

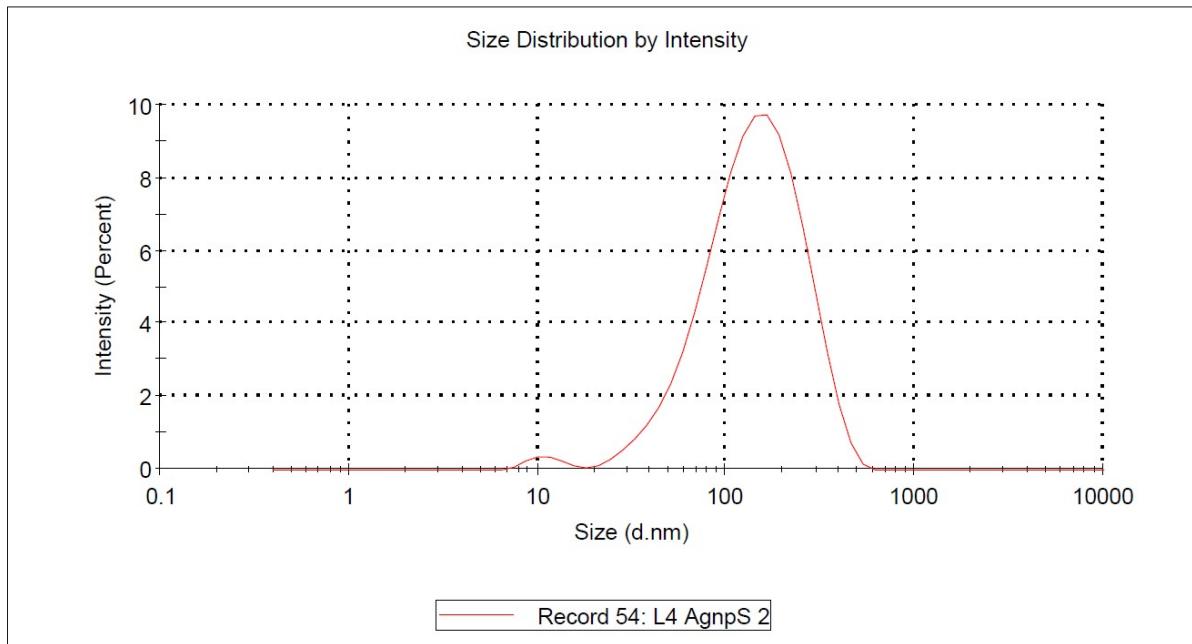


Figure S21. DLS data of **L4** stabilized silver nanoparticles (freshly synthesized)

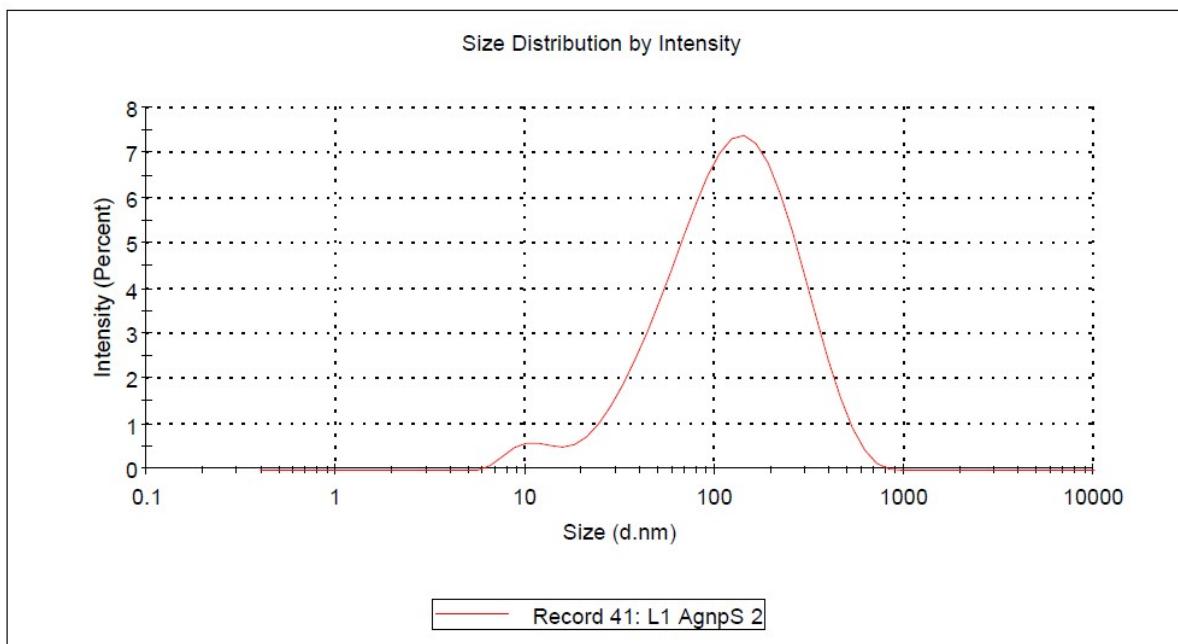


Figure S22. DLS data of **L1** stabilized silver nanoparticles (at 15th day)

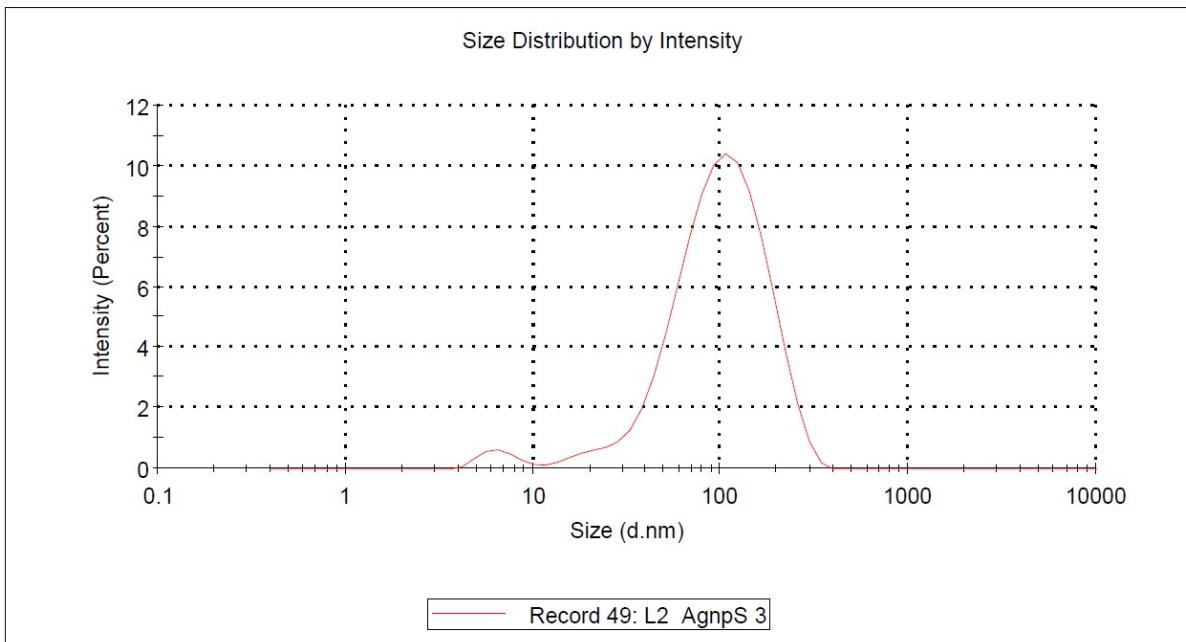


Figure S23. DLS data of **L2** stabilized silver nanoparticles (at 15th day)

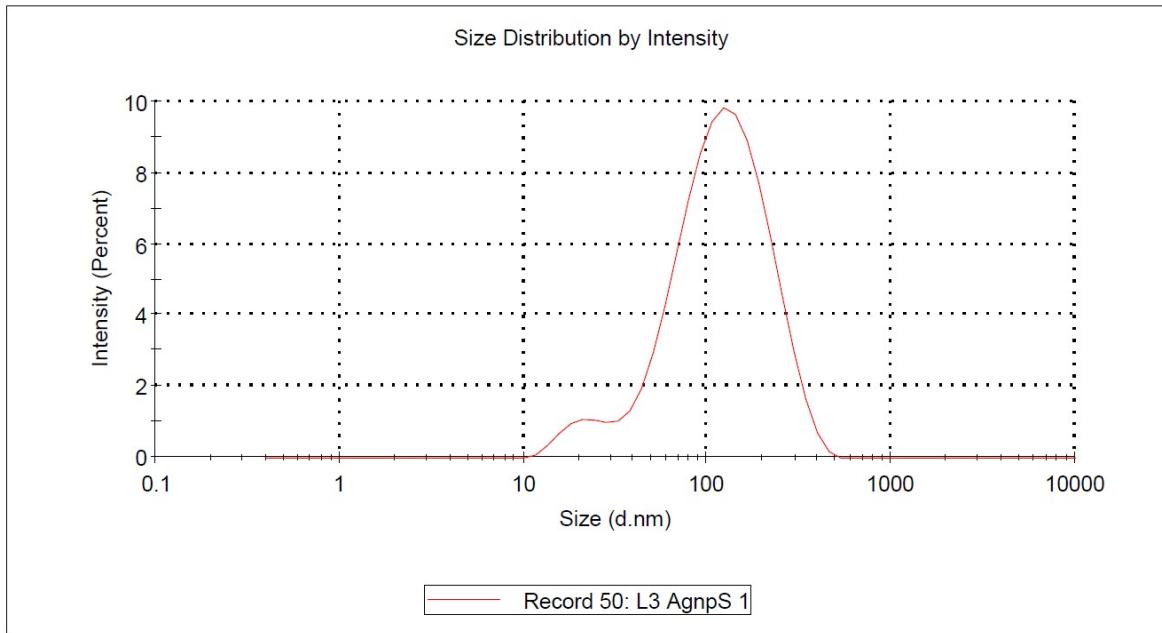


Figure S24. DLS data of **L3** stabilized silver nanoparticles (at 15th day)

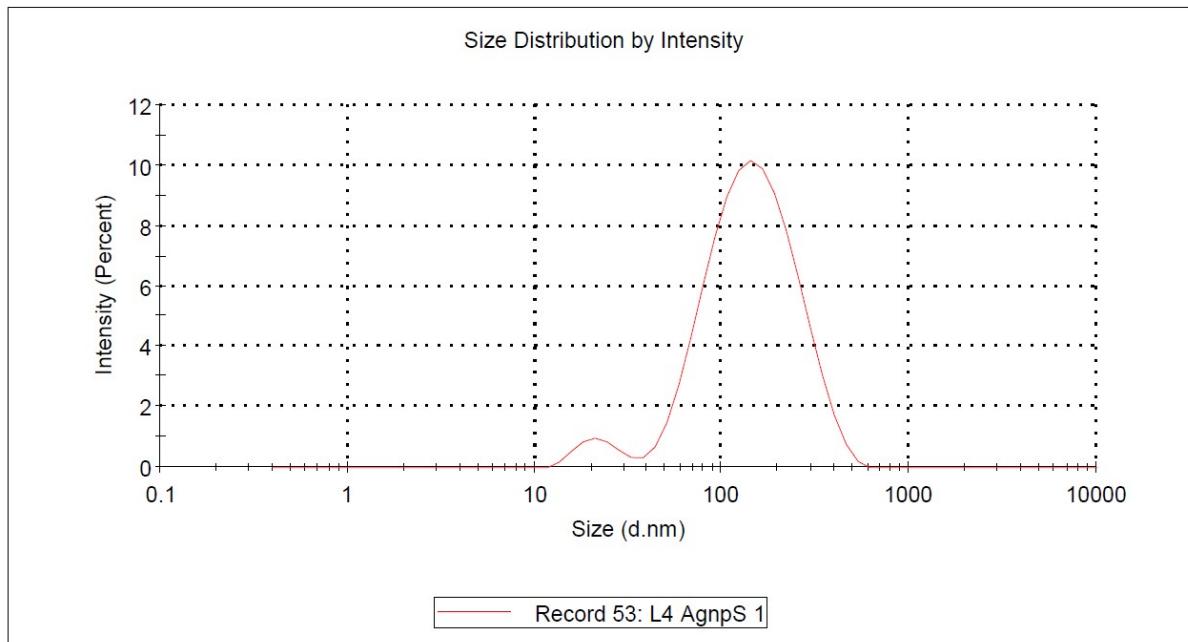


Figure S25. DLS data of **L4** stabilized silver nanoparticles (at 15th day)

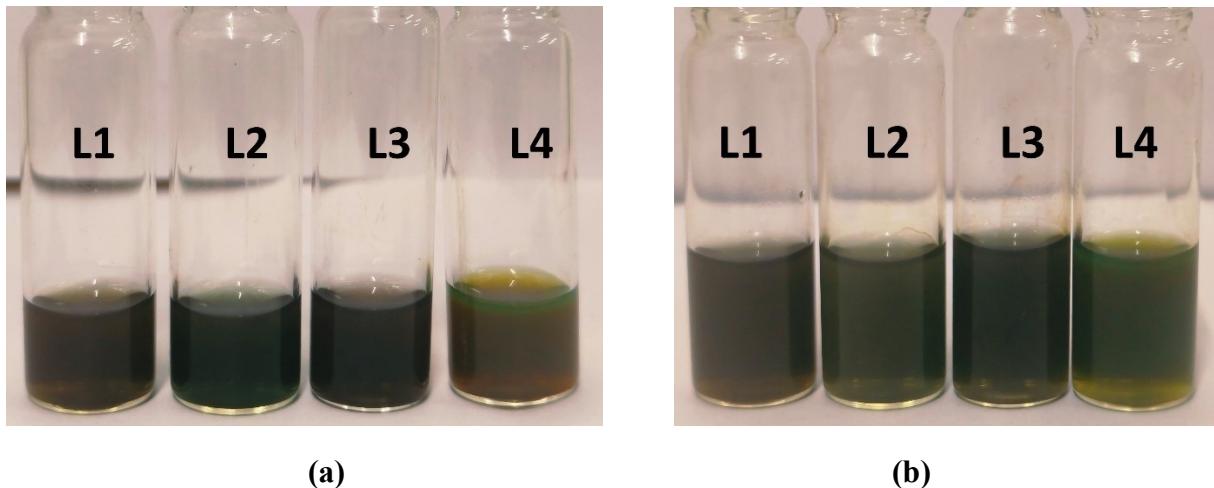
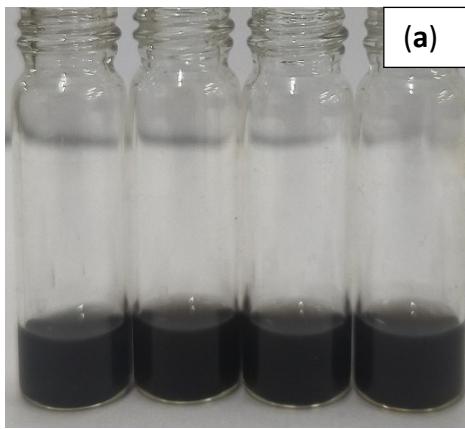
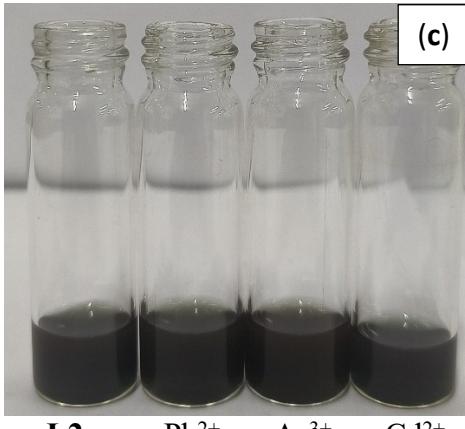


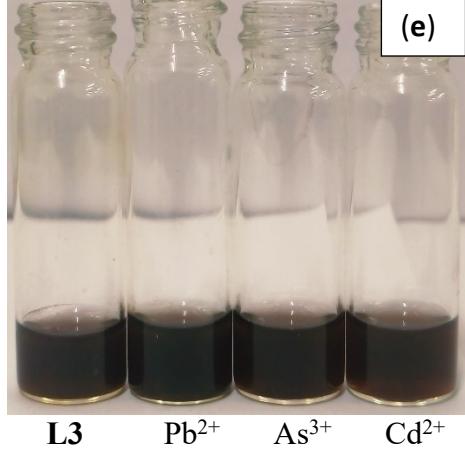
Figure S26. Photographs of; (a) as-synthesized colloidal Ag-NPs and (b) colloidal Ag-NPs at 60th day



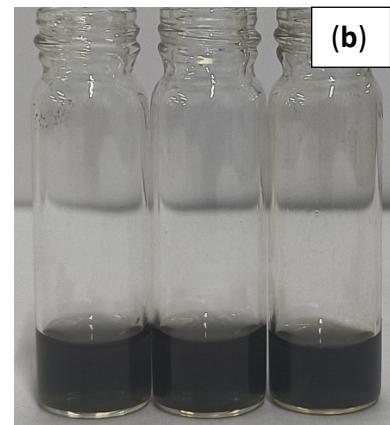
L1 Pb²⁺ As³⁺ Cd²⁺



L2 Pb²⁺ As³⁺ Cd²⁺



L3 Pb²⁺ As³⁺ Cd²⁺



L1 NO₃⁻ SO₄²⁻



L2 NO₃⁻ SO₄²⁻



L3 NO₃⁻ SO₄²⁻

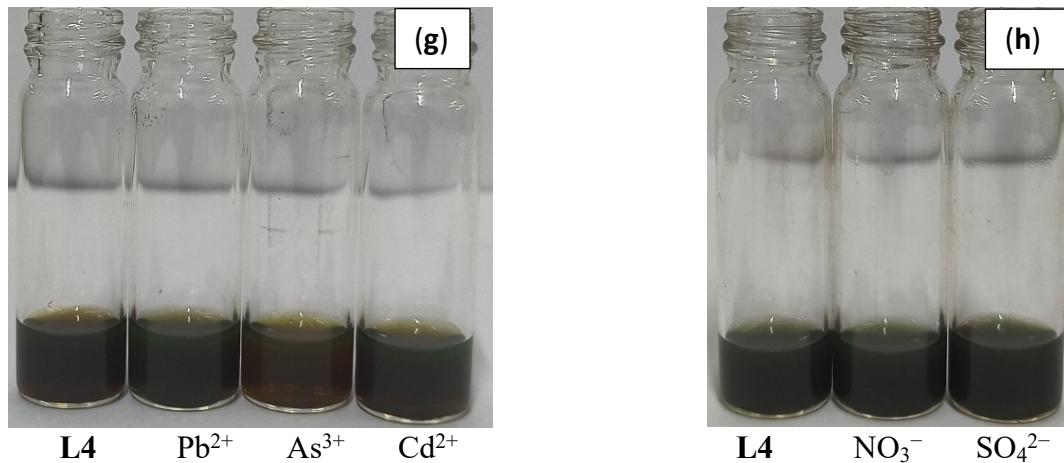


Figure S27. Colorimetric sensing of metal ions with added metal salt $\{\text{Pb}^{2+}, \text{As}^{3+}, \text{Cd}^{2+}$ (10 μL of 50 mM) in the colloidal solution of (a) L1 capped Ag-NPs; (c) L2 capped Ag-NPs; (e) L3 capped Ag-NPs; (g) L4 capped Ag-NPs; and with added anions $\{\text{NO}_3^-, \text{SO}_4^{2-}$;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

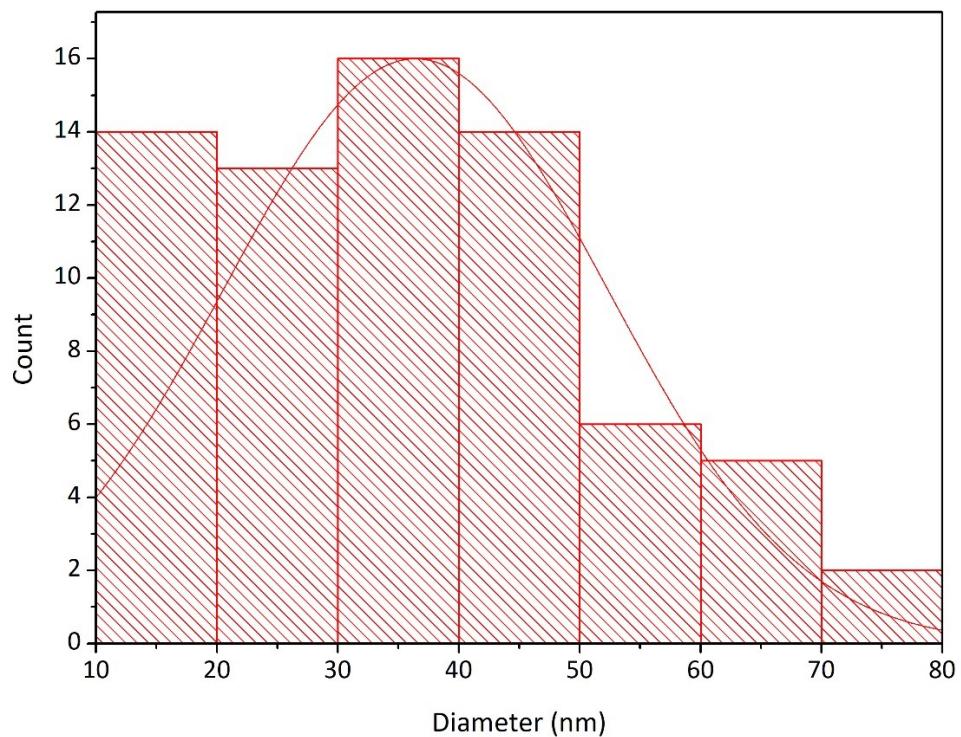


Figure S28. Particle size distribution in the case of L1 stabilized silver nanoparticles after the addition of Hg^{2+} ions

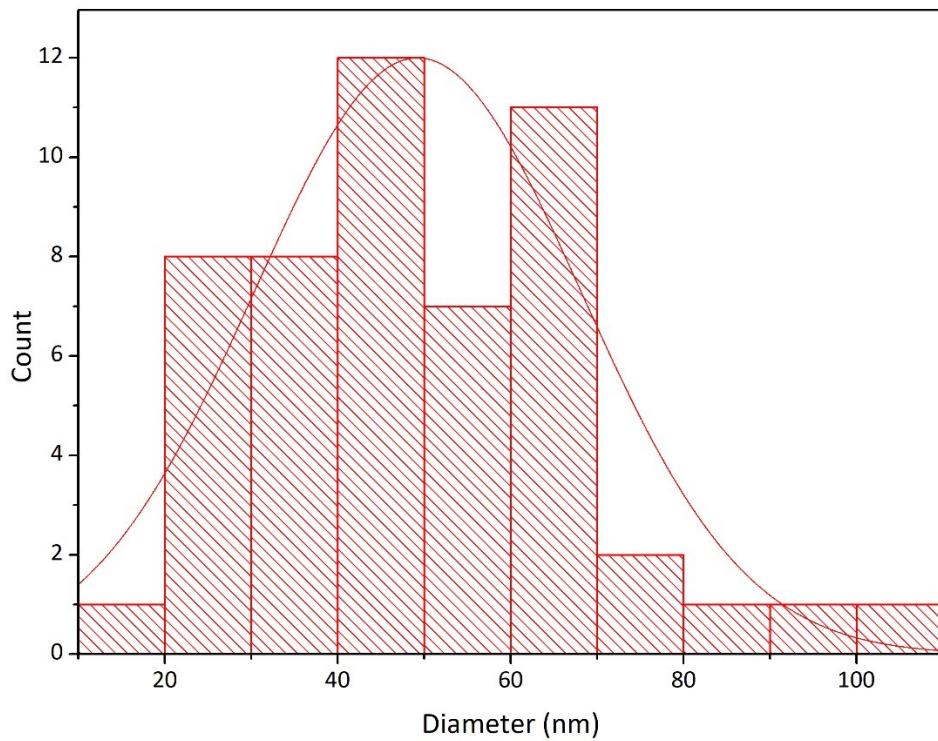


Figure S29. Particle size distribution in the case of **L1** stabilized silver nanoparticles after the addition of Cl^- ions

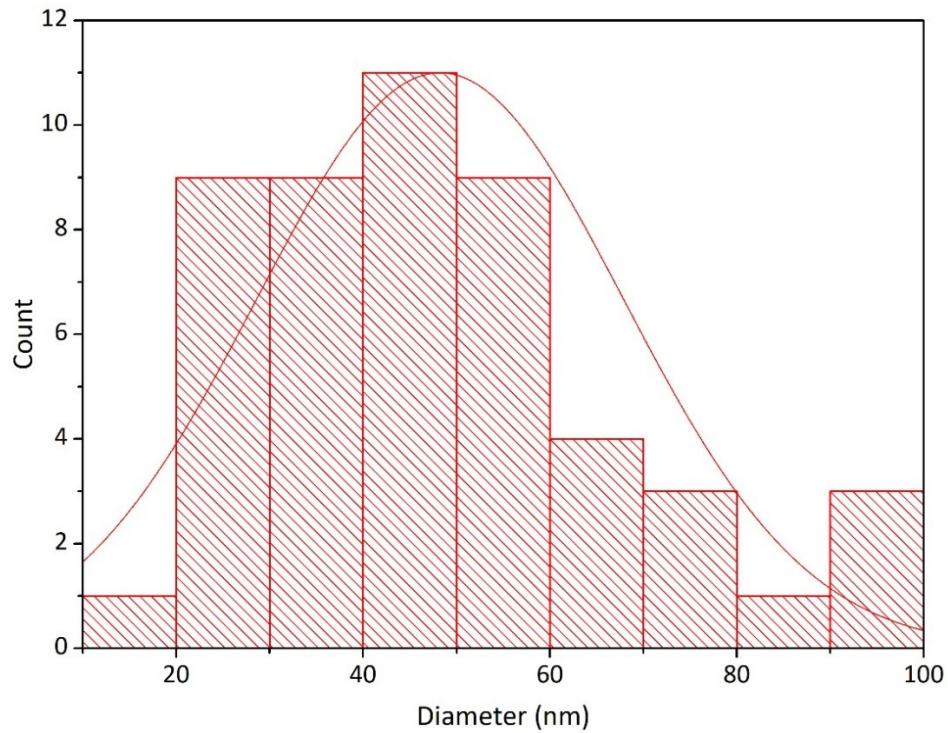


Figure S30. Particle size distribution in the case of **L2** stabilized silver nanoparticles after the addition of Hg^{2+} ions

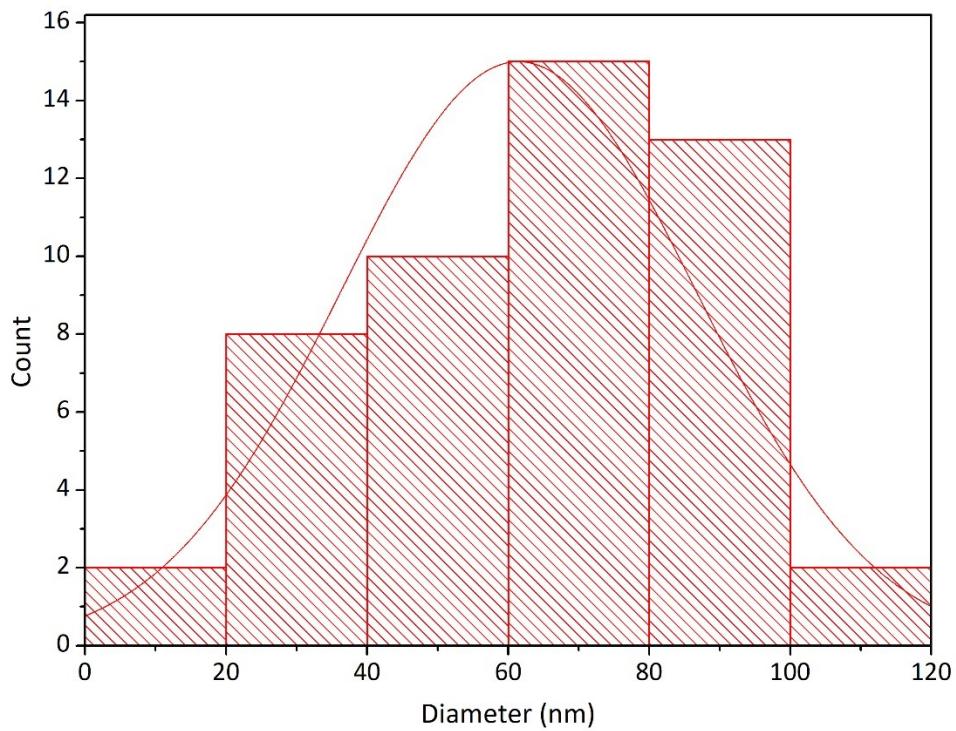


Figure S31. Particle size distribution in the case of **L2** stabilized silver nanoparticles after the addition of Bi^{3+} ions

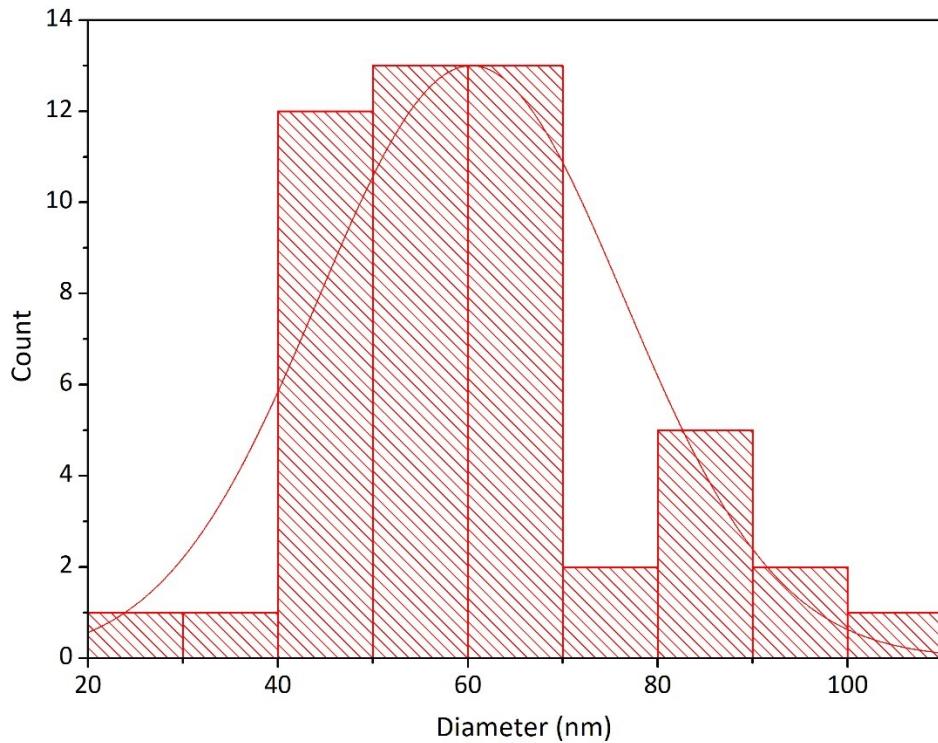


Figure S32. Particle size distribution in the case of **L2** stabilized silver nanoparticles after the addition of I^- ions

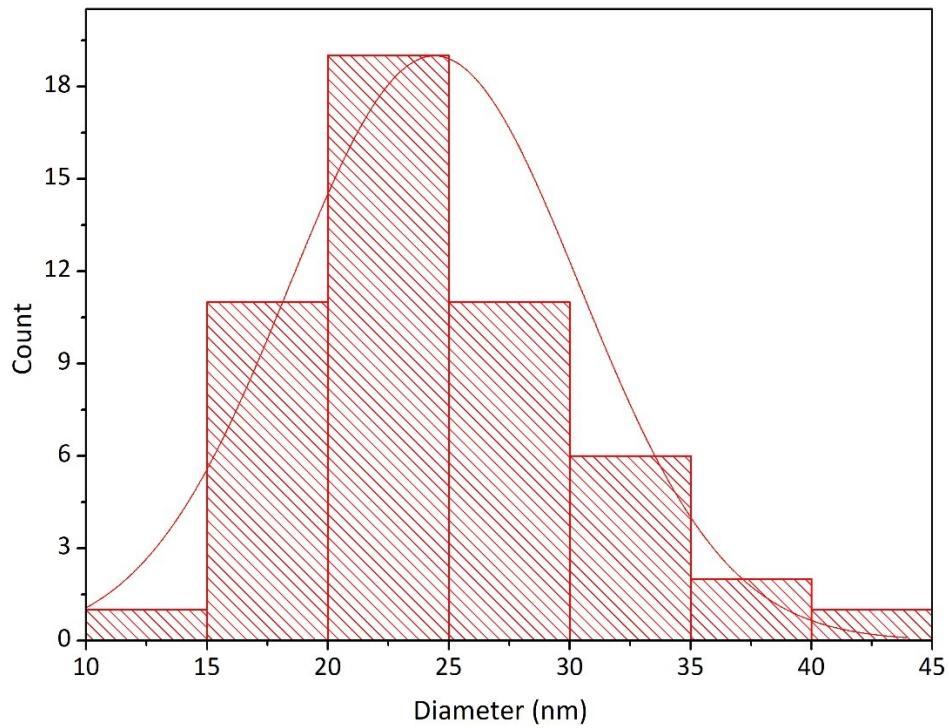


Figure S33. Particle size distribution in the case of **L3** stabilized silver nanoparticles after the addition of Hg^{2+} ions

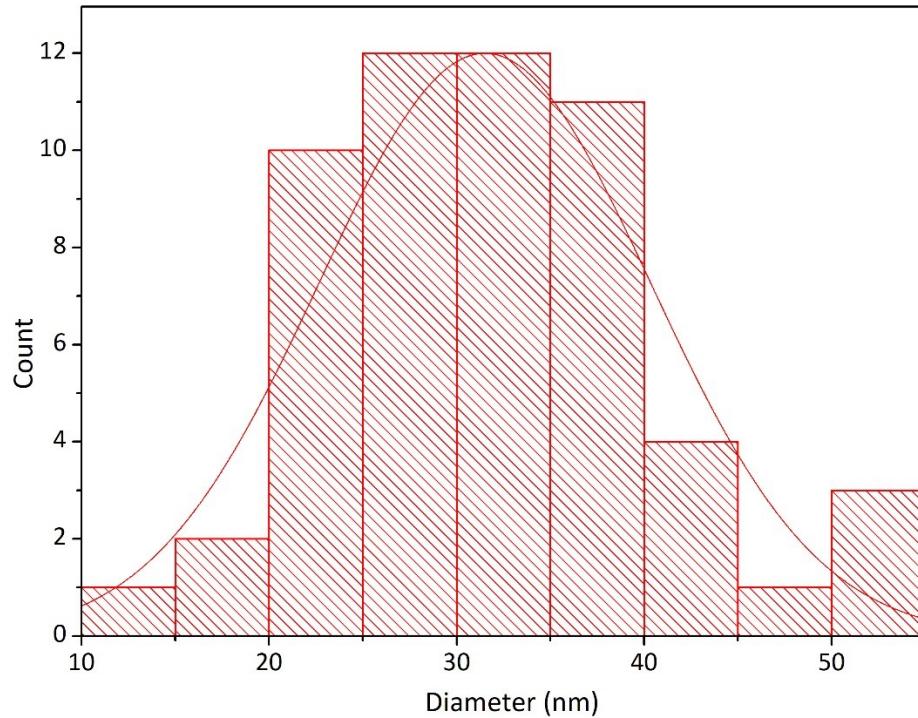


Figure S34. Particle size distribution in the case of **L3** stabilized silver nanoparticles after the addition of HSO_4^- ions

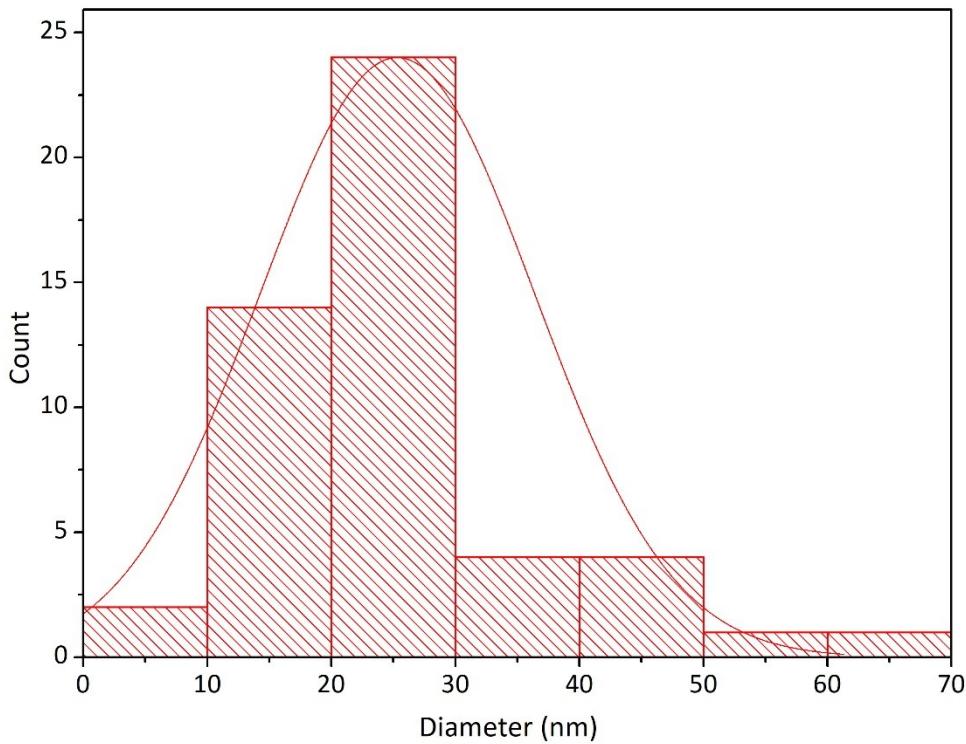


Figure S35. Particle size distribution in the case of L4 stabilized silver nanoparticles after the addition of Hg^{2+} ions

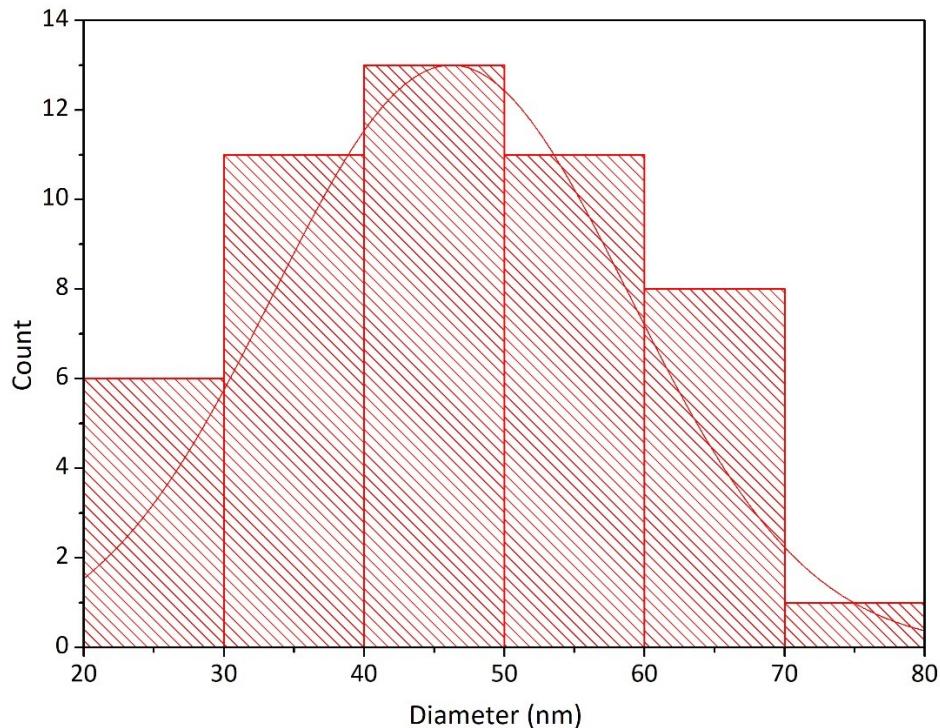


Figure S36. Particle size distribution in the case of L4 stabilized silver nanoparticles after the addition of Cr^{3+} ions

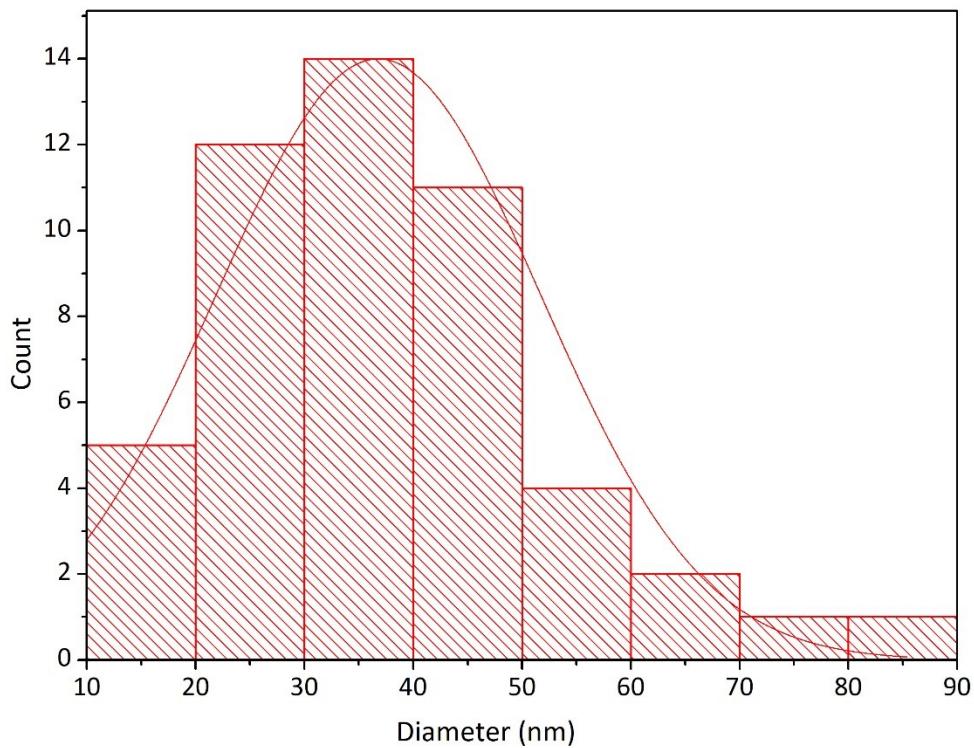


Figure S37. Particle size distribution in the case of L4 stabilized silver nanoparticles after the addition of Bi^{3+} ions

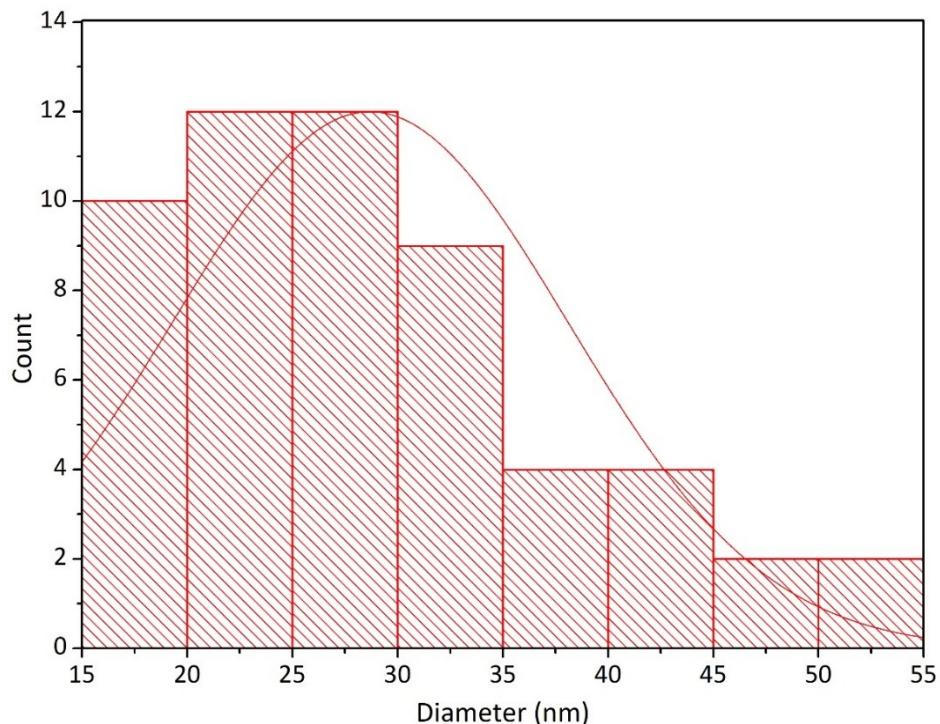


Figure S38. Particle size distribution in the case of L4 stabilized silver nanoparticles after the addition of HSO_4^- ions

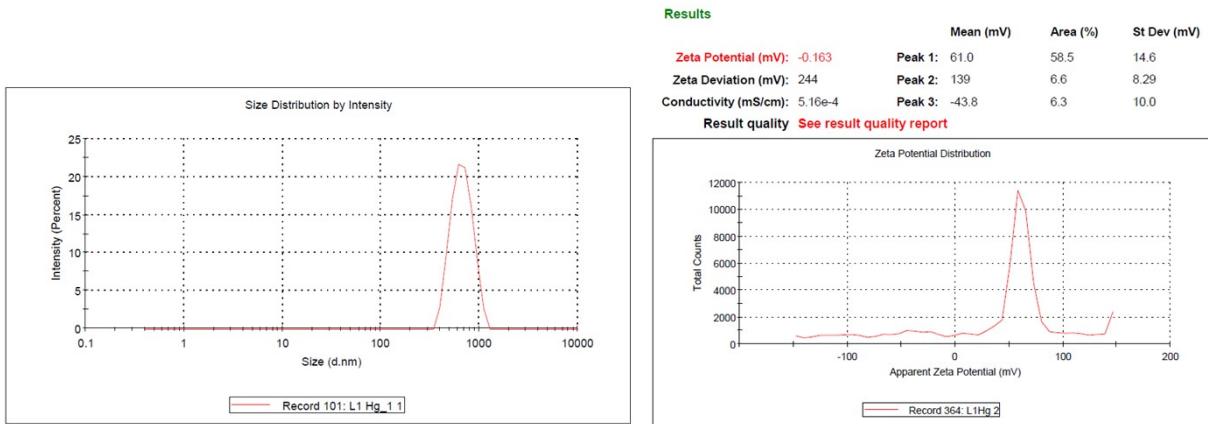


Figure S39. DLS data and zeta potential in the case of **L1** stabilized silver nanoparticles after the addition of Hg^{2+} ions

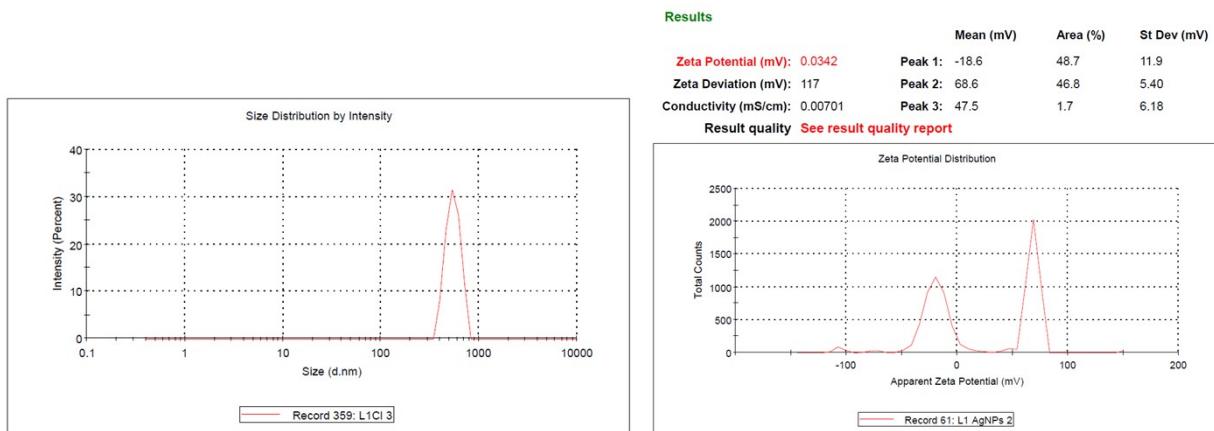


Figure S40. DLS data and zeta potential in the case of **L1** stabilized silver nanoparticles after the addition of Cl^- ions

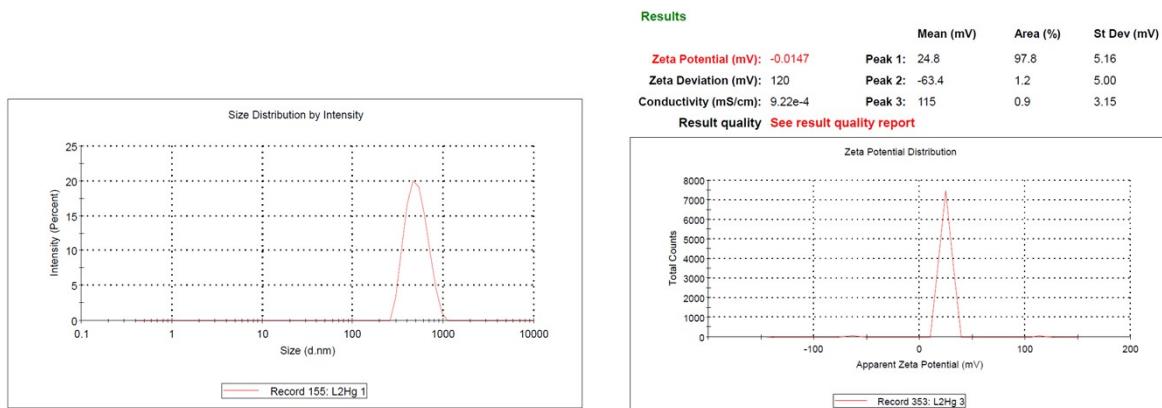


Figure S41. DLS data and zeta potential in the case of **L2** stabilized silver nanoparticles after the addition of Hg^{2+} ions

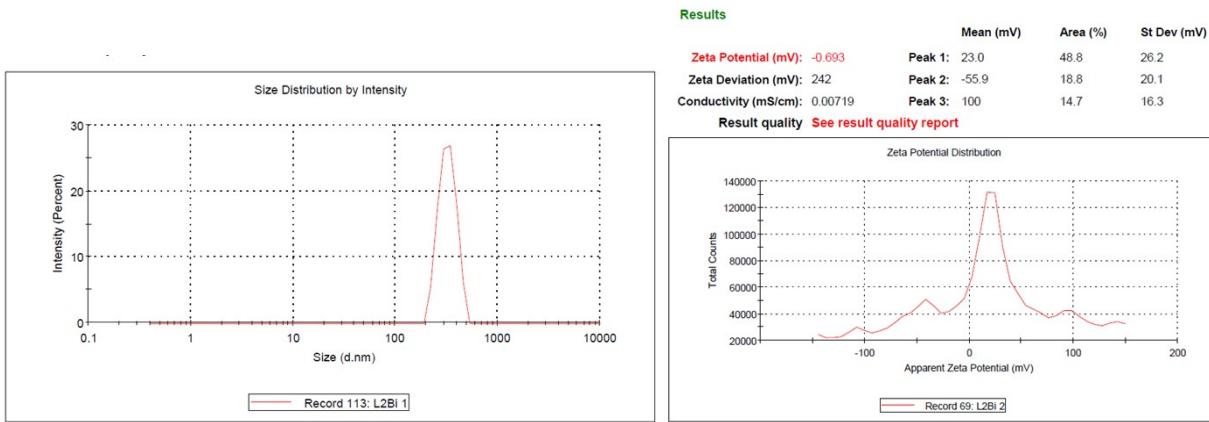


Figure S42. DLS data and zeta potential in the case of L2 stabilized silver nanoparticles after the addition of Bi^{3+} ions

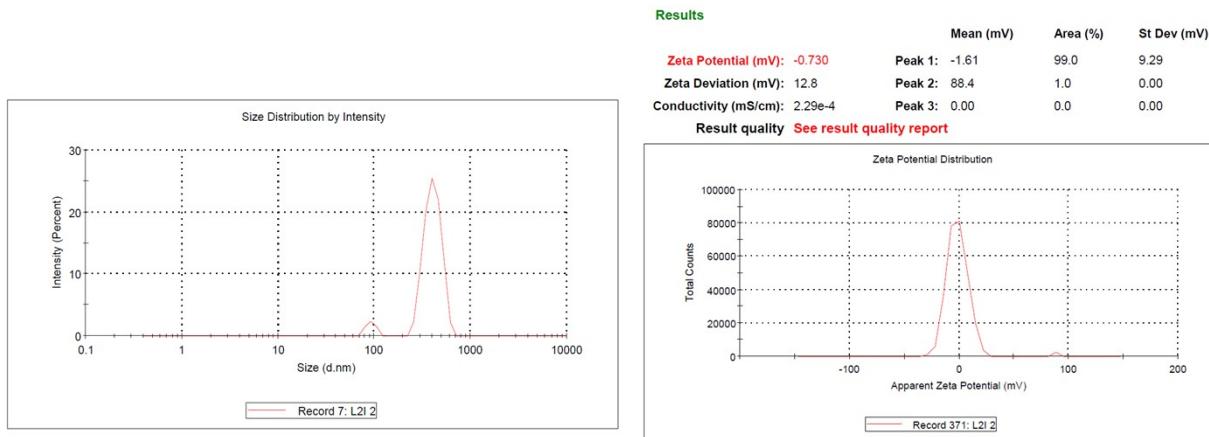


Figure S43. DLS data and zeta potential in the case of L2 stabilized silver nanoparticles after the addition of I^- ions

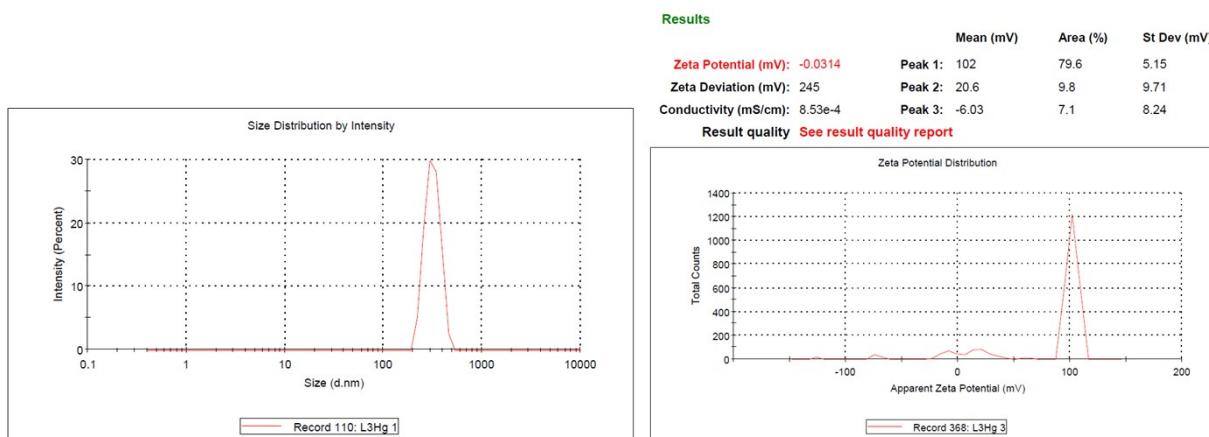


Figure S44. DLS data and zeta potential in the case of L3 stabilized silver nanoparticles after the addition of Hg^{2+} ions

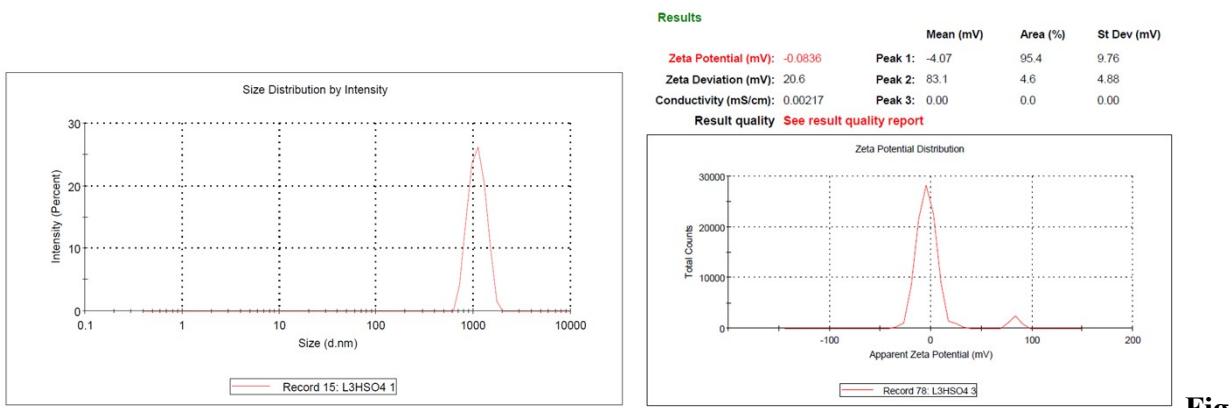


Figure S45. DLS data and zeta potential in the case of L3 stabilized silver nanoparticles after the addition of HSO_4^- ions

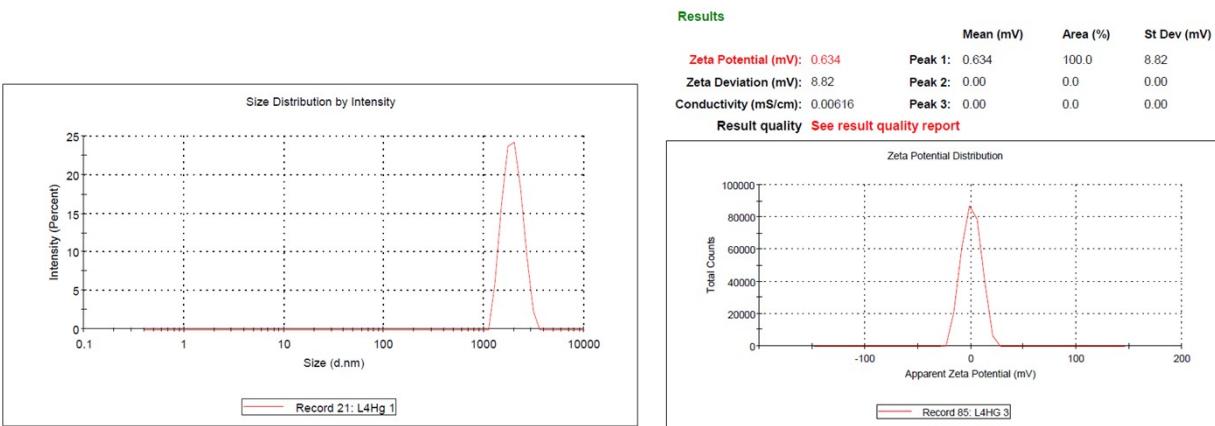


Figure S46. DLS data and zeta potential in the case of L4 stabilized silver nanoparticles after the addition of Hg^{2+} ions

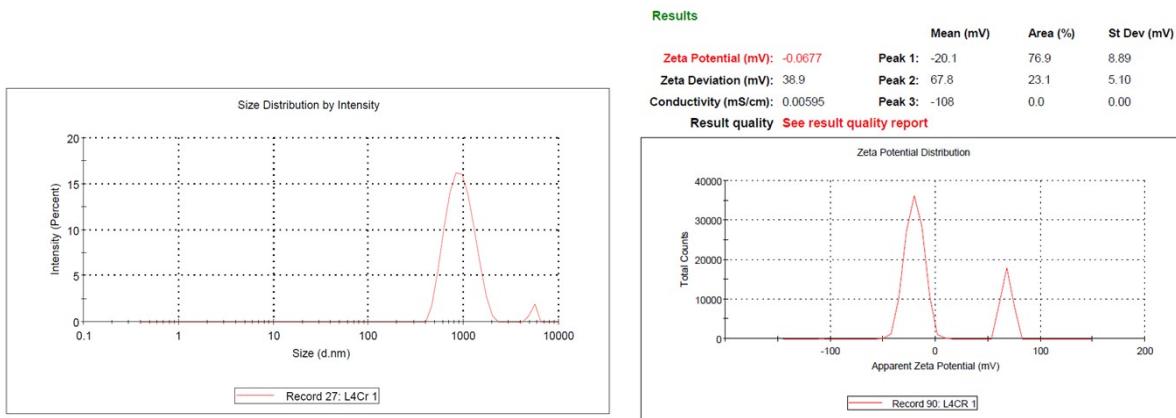


Figure S47. DLS data and zeta potential in the case of L4 stabilized silver nanoparticles after the addition of Cr^{3+} ions

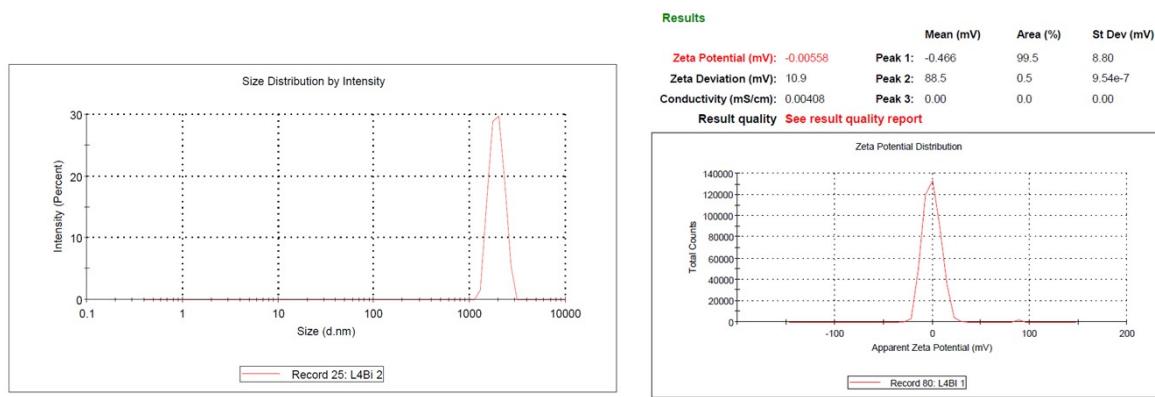


Figure S48. DLS data and zeta potential in the case of **L4** stabilized silver nanoparticles after the addition of Bi^{3+} ions

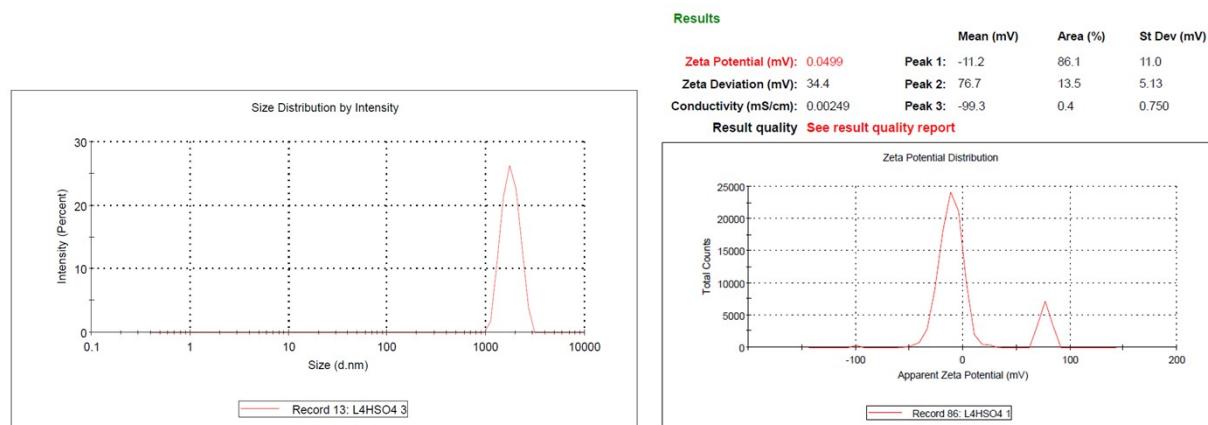


Figure S49. DLS data and zeta potential in the case of **L4** stabilized silver nanoparticles after the addition of HSO_4^- ions

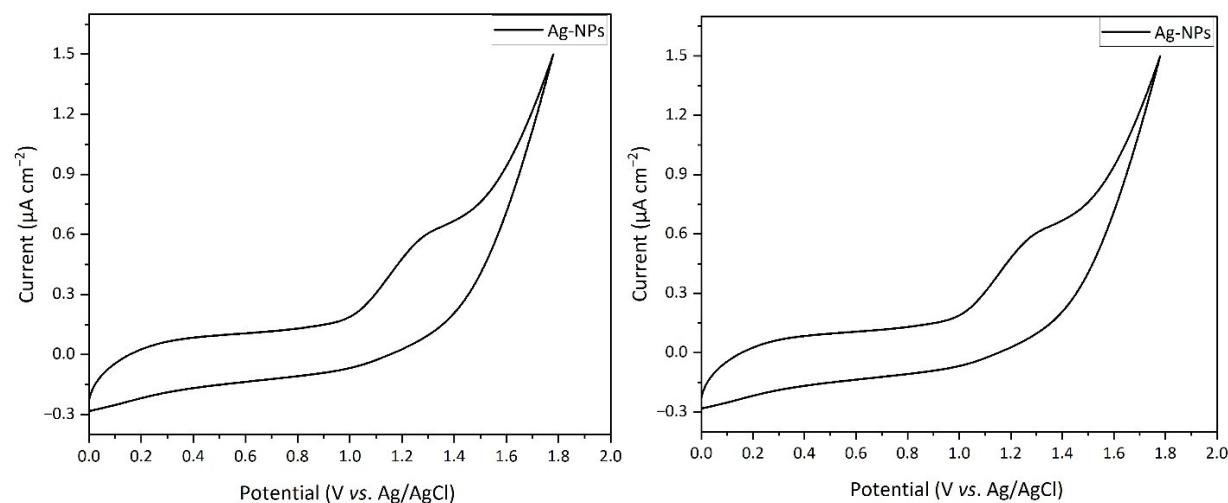


Figure S50. (a) Cyclic voltammogram of **L3** stabilized silver nanoparticles; (b) Differential pulse voltammogram of **L3** stabilized silver nanoparticles and with the addition of I^- ions

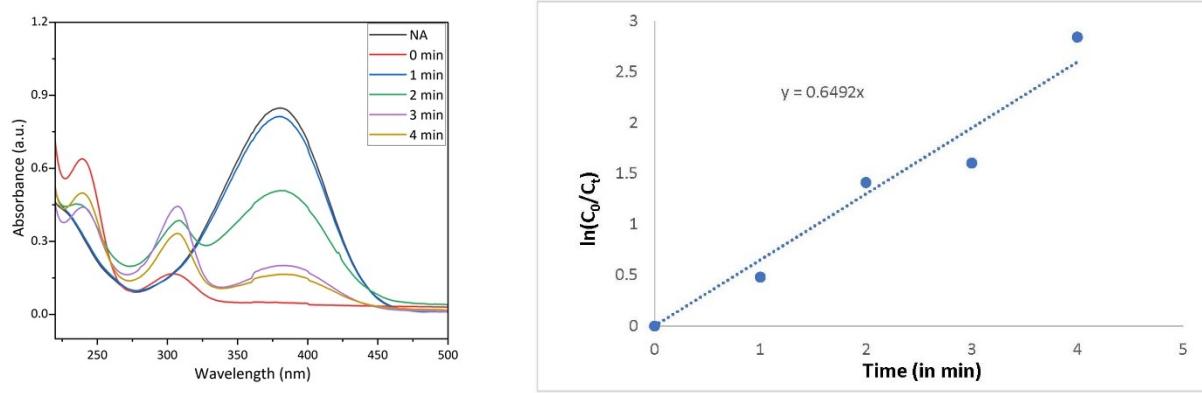


Figure S51. UV spectra of reduction of Nitroaniline and rate constant $\ln C_0/C_t$ Vs time

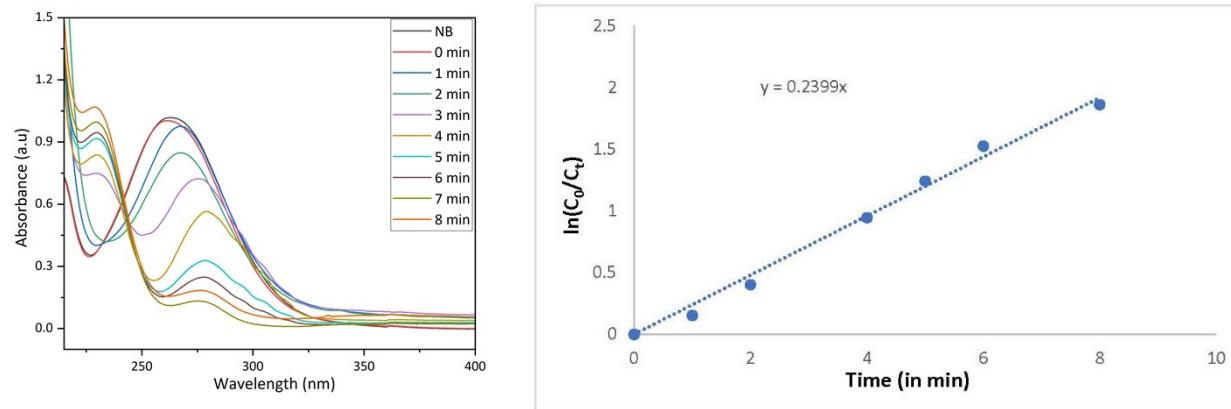


Figure S52. UV spectra of reduction of Nitrobenzene and rate constant $\ln C_0/C_t$ Vs time

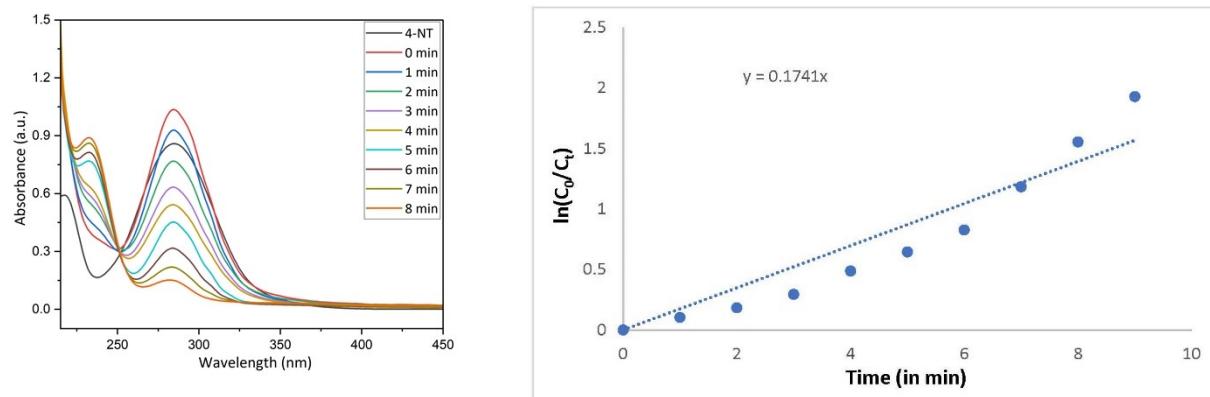


Figure S53. UV spectra of reduction of 4-Nitrotoulene and rate constant $\ln C_0/C_t$ Vs time

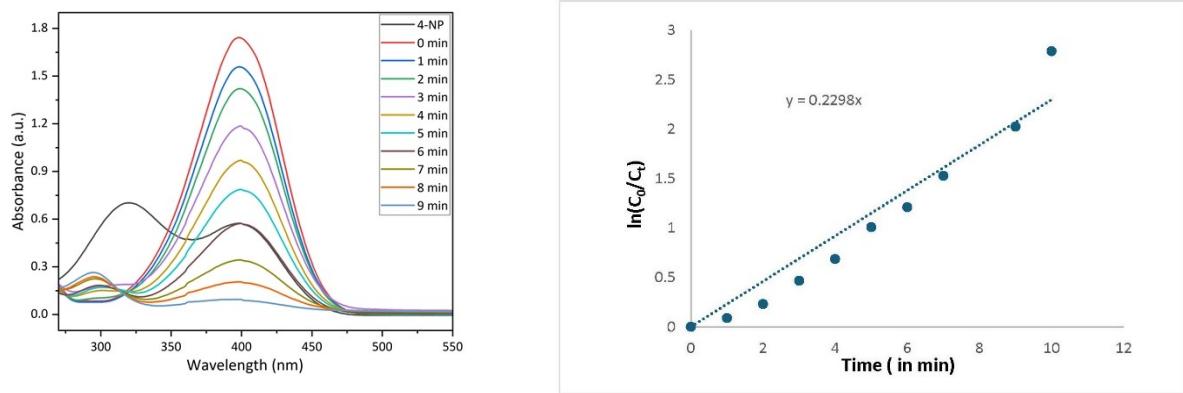


Figure S54. UV spectra of reduction of 4-Nitrophenol and rate constant $\ln C_0/C_t$ Vs time

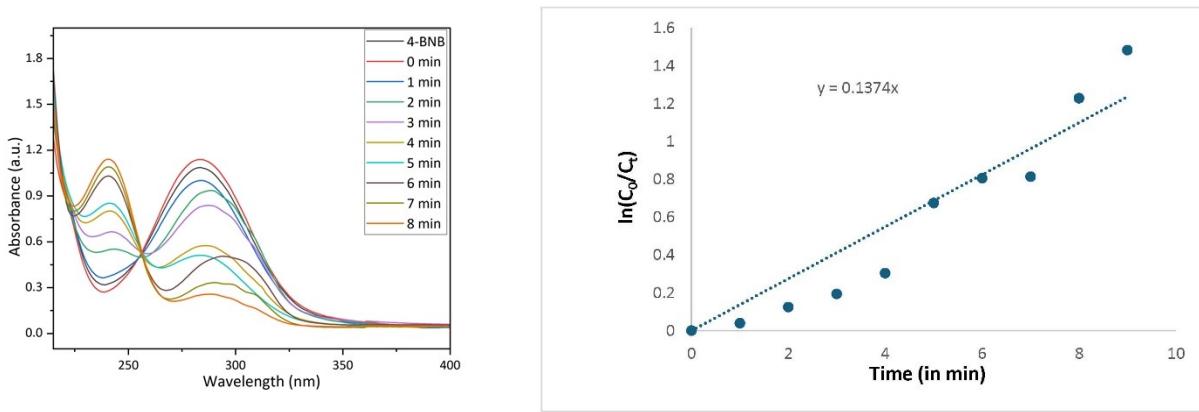


Figure S55. UV spectra of reduction of 1-bromo-4-nitrobenzene and rate constant $\ln C_0/C_t$ Vs time

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**

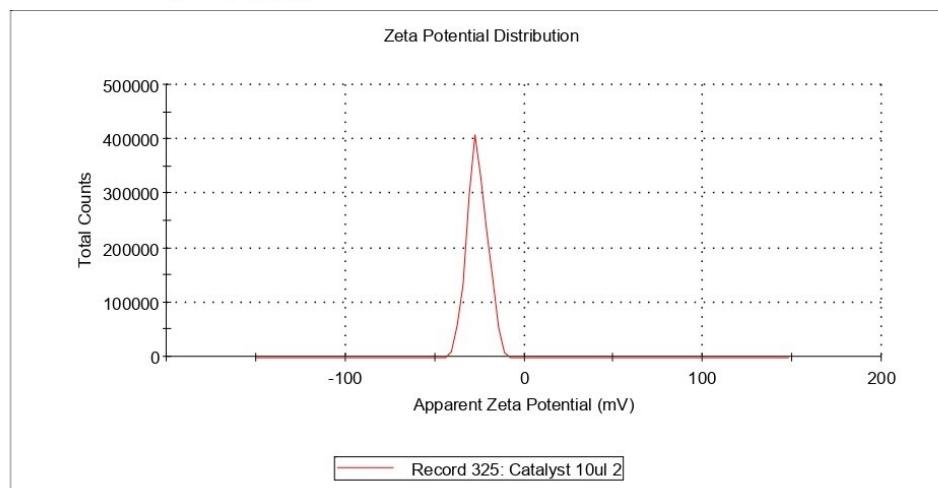


Figure S56. Surface charge on the catalyst

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**

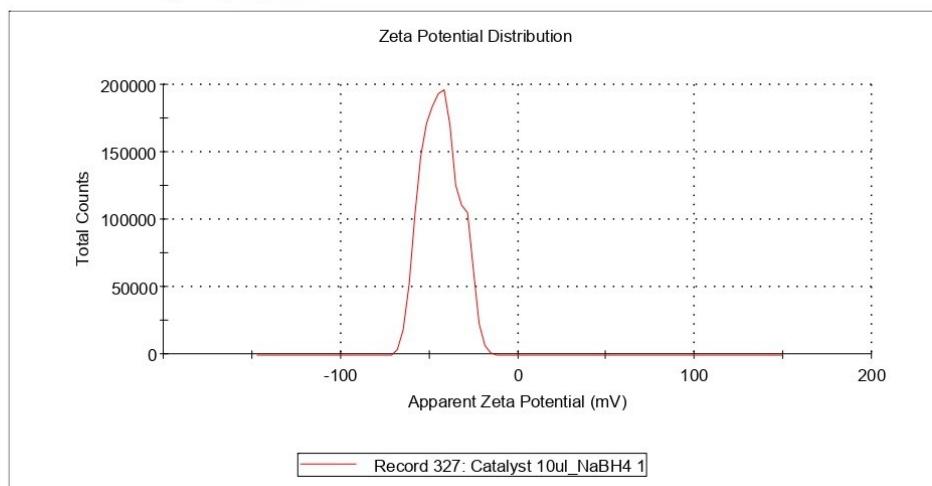


Figure S57. Surface charge after the addition of NaBH₄ and 4-nitrophenol in the catalyst solution

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**

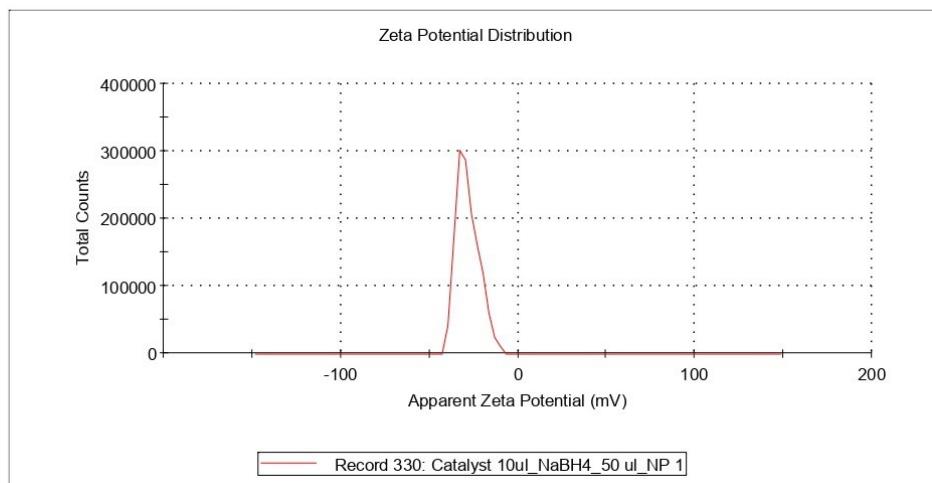
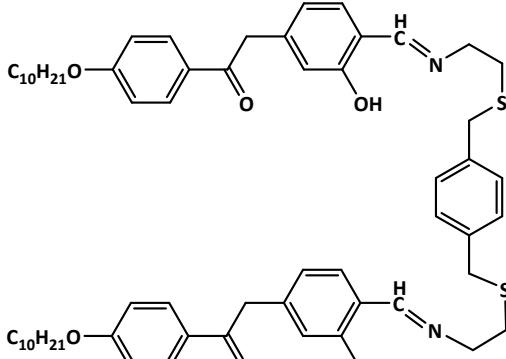
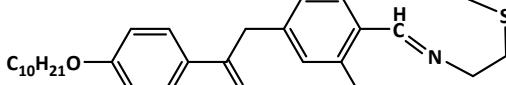


Figure S58. Surface charge after completion of reaction

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
----	--	--	------	---	---

References:

1. A. Minhaz, N. Khan and N. Jamila, *Arab J. Chem.*, 2020, **13**, 8898–8908.
2. E. Badr, S. Shafeek, 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. Srivastava, *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.