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Enhanced birghtness of ultra-small gold nanoparticles in the second biological window through thiol ligand shell control

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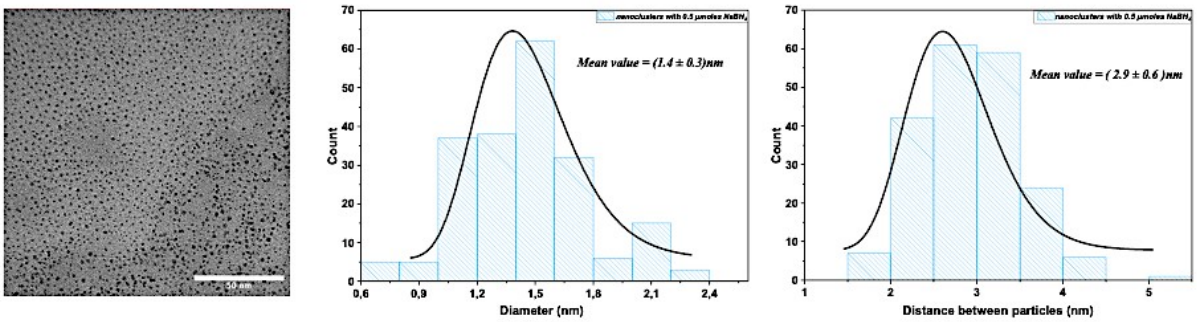

Figure S1. TEM micrograph of AuMHA/HDT prepared with 0.5 µmol of $NaBH_4$ and distribution of core size and distance between particles. Distributions were estimated on 200 measurements.

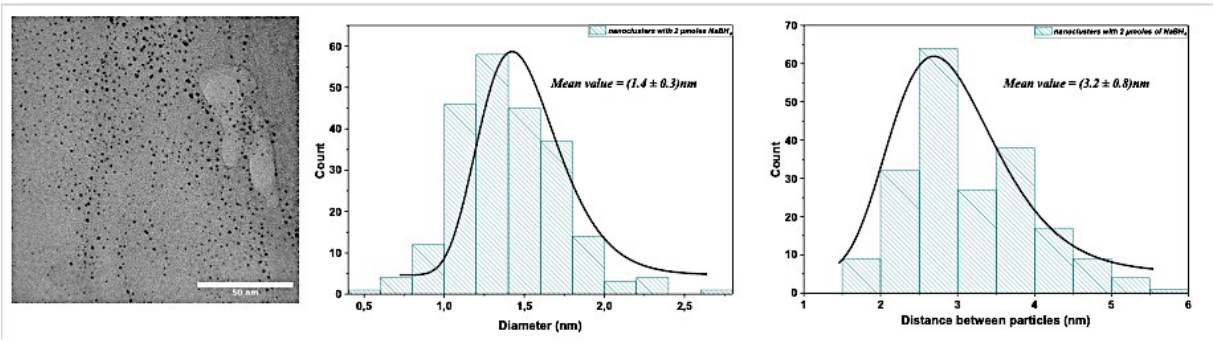

Figure S2. TEM micrograph of AuMHA/HDT prepared with 2 μmol of $NaBH_4$ and distribution of core size and distance between particles. Distributions were estimated on 200 measurements.

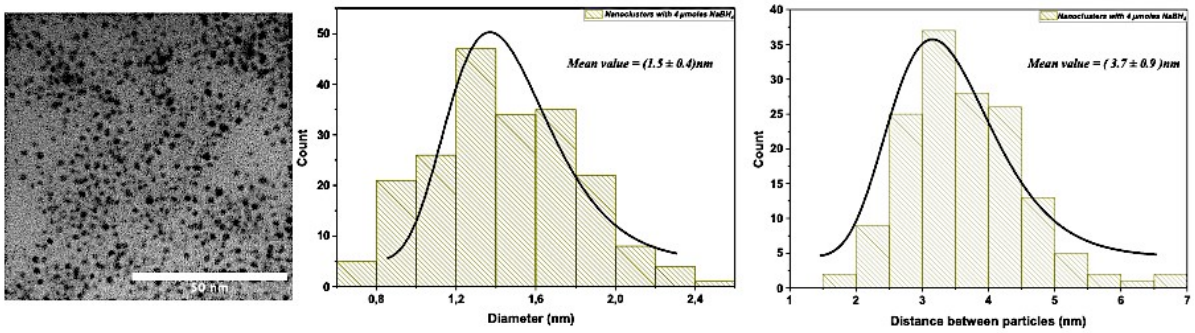

Figure S3. TEM micrograph of AuMHA/HDT prepared with 4 μmol of $NaBH_4$ and distribution of core size and distance between particles. Distributions were estimated on 200 measurements.

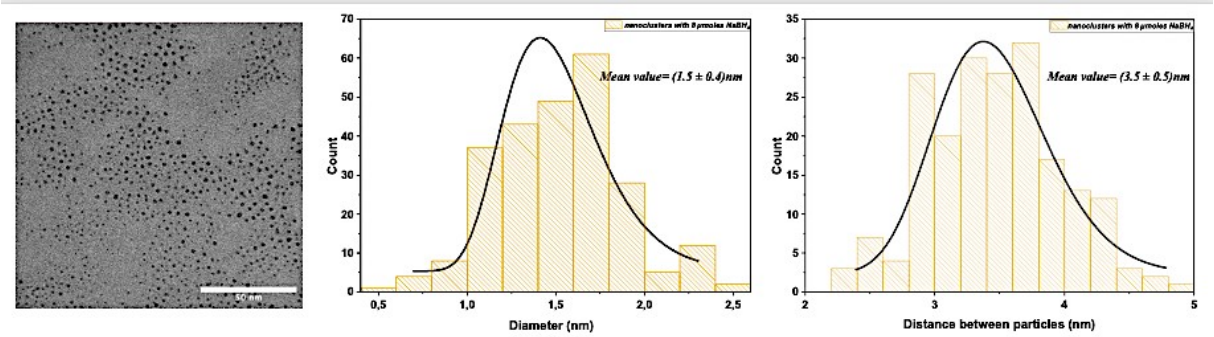

Figure S4. TEM micrograph of AuMHA/HDT prepared with 6 μmol of $NaBH_4$ and distribution of core size and distance between particles. Distributions were estimated on 200 measurements.

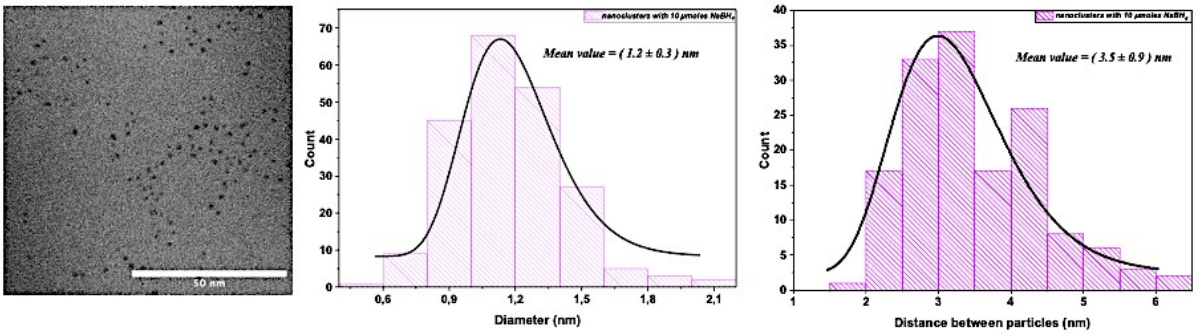

Figure S5. TEM micrograph of AuMHA/HDT prepared with 10 µmol of $NaBH_4$ and distribution of core size and distance between particles. Distributions were estimated on 200 measurements.

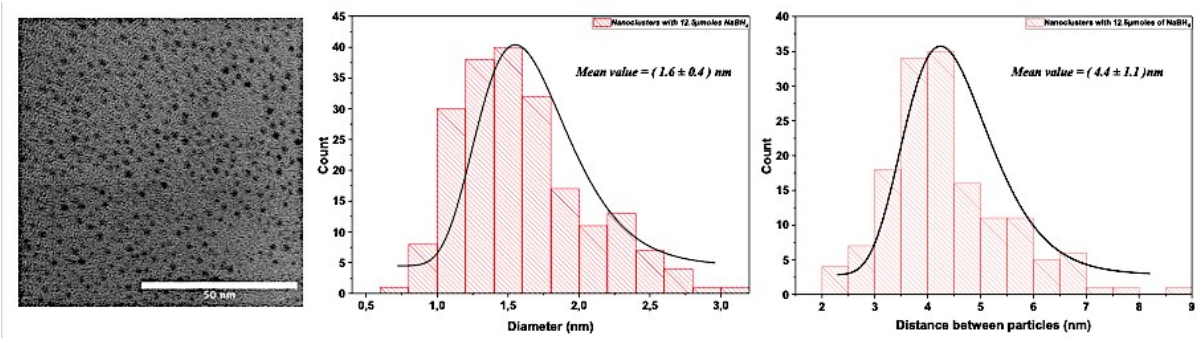

Figure S6. TEM micrograph of AuMHA/HDT prepared with 12.5 µmol of $NaBH_4$ and distribution of core size and distance between particles. Distributions were estimated on 200 measurements.

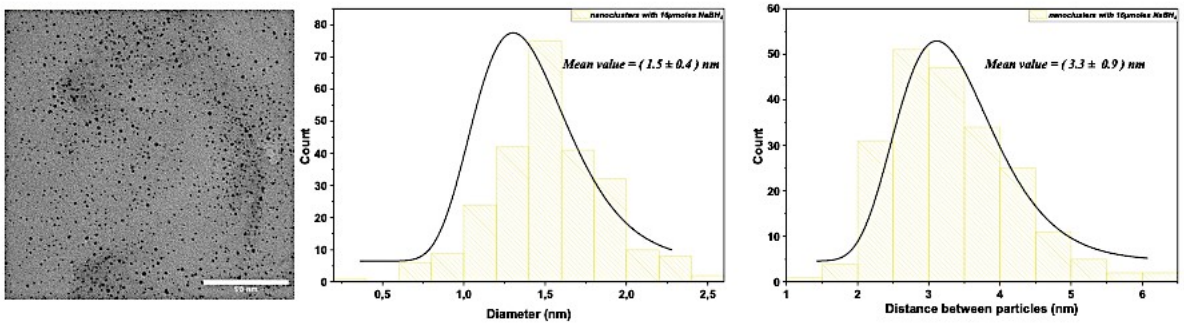

Figure S7. TEM micrograph of AuMHA/HDT prepared with 16 µmol of $NaBH_4$ and distribution of core size and distance between particles. Distributions were estimated on 200 measurements.

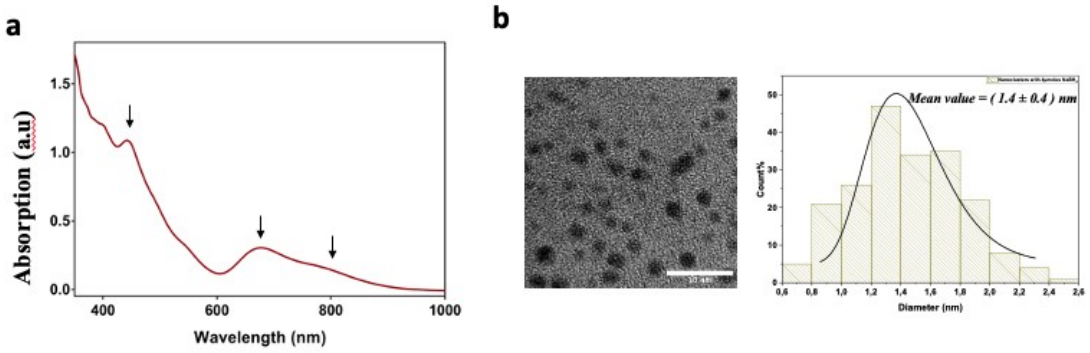

Figure S8. **a**. Absorbance spectra of AuMHA dispersed in water showing the specific bands at 420 nm, 670 nm and 780 nm. **b**. TEM micrograph of AuMHA and distribution of particle size. Distributions were estimated on 200 measurements.

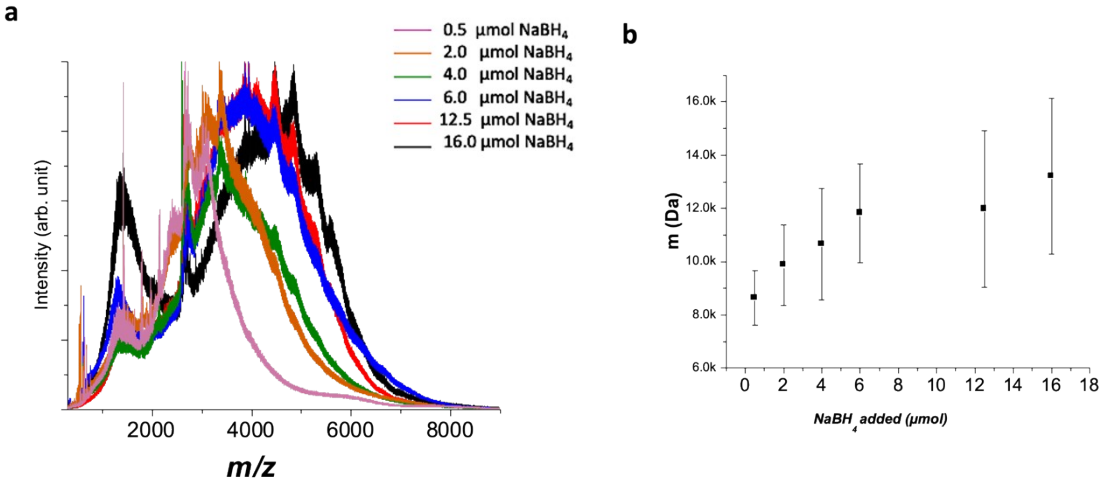

Figure S9. **a**. ESI-MS spectra of us-Au NPs samples as a function of $NaBH_4$ used during the synthesis. **b**. Estimation of average molecular weight of us-Au NPs, determined from the deconvolution of the broad envelope in the m/z spectra and assuming the same average charge state for all us-Au NPs (e.g. +3). The error bar corresponds the standard deviation.

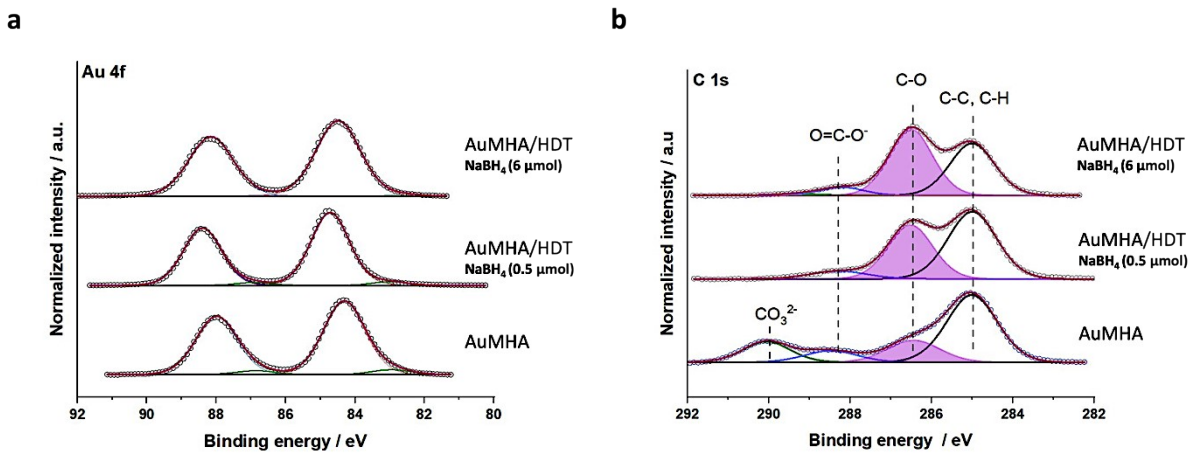

Figure S10. **a**. XPS spectra for gold Au4f. **b**. XPS spectra of C1s of AuMHA, AuMHA/HDT samples .

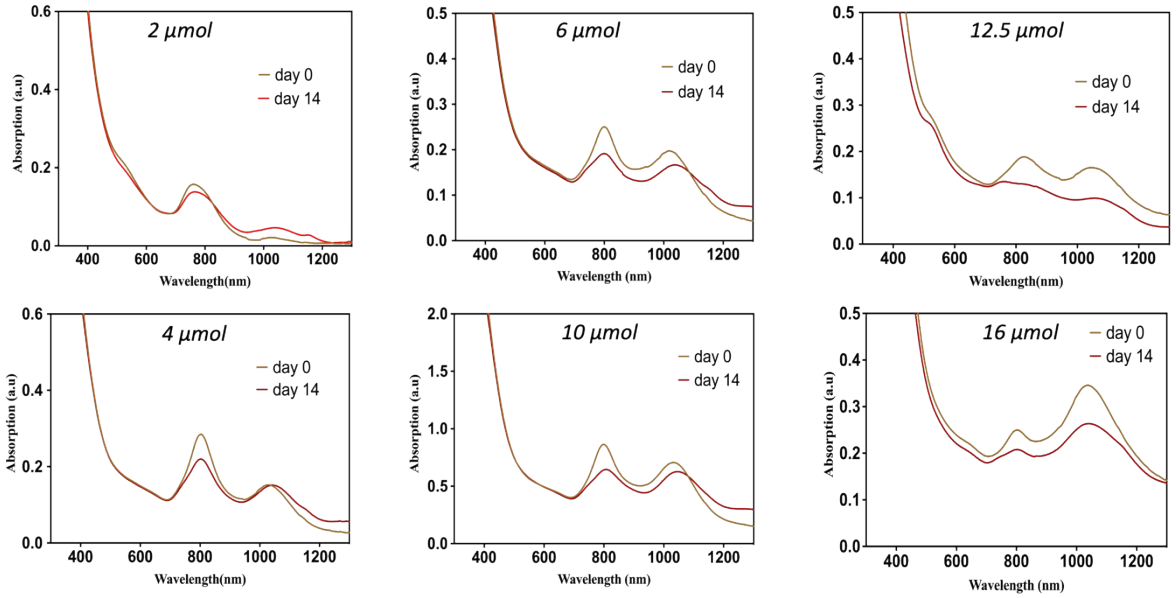

Figure S11. Absorbance spectra of AuMHA/HDT samples in PBS (pH 7.4) prepared with different amount of $NaBH_4$ at day 0 and day 14.

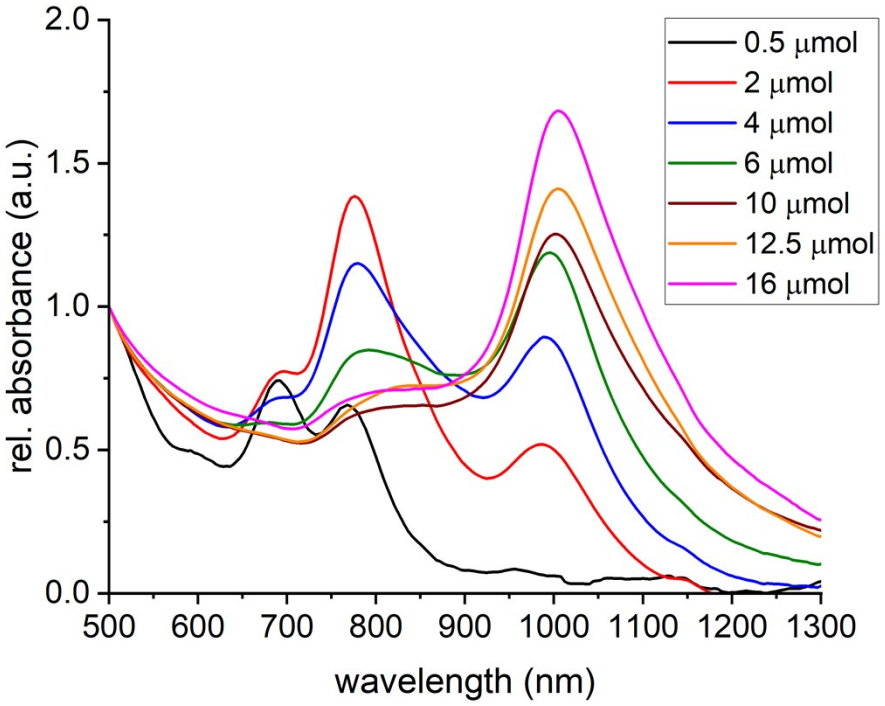

Figure S12. Absorbance spectra of AuMHA/HDT samples prepared with different amount of $NaBH_4$ and normalized at $\lambda_{exc.}$ 500 nm.

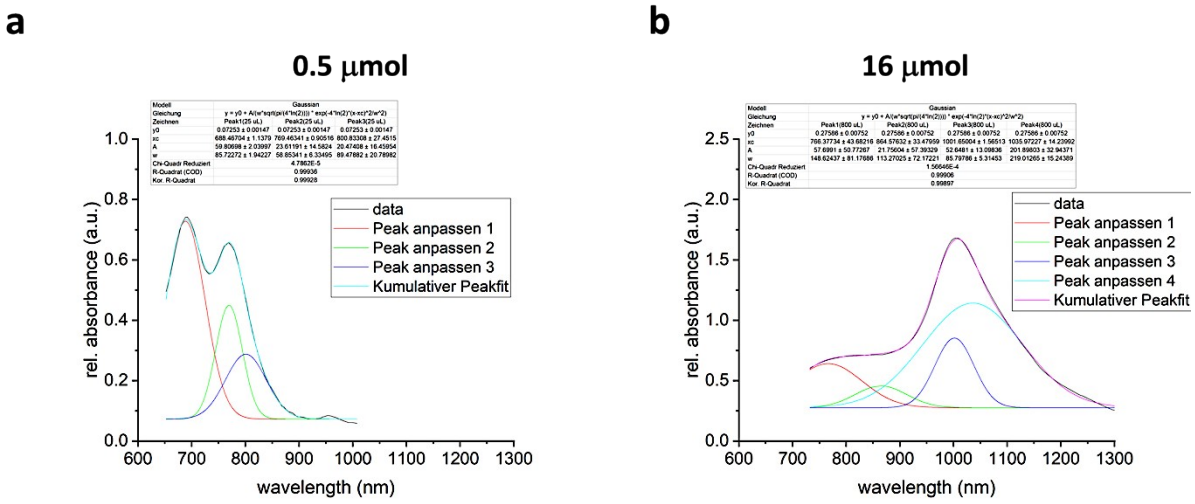

Figure S13. Deconvolution of the absorbance spectra normalized at $\lambda_{exc.}$ 500 nm of AuMHA/HDT samples prepared with 0.5 µmol (a) and 16 µmol (b) of $NaBH_4$.

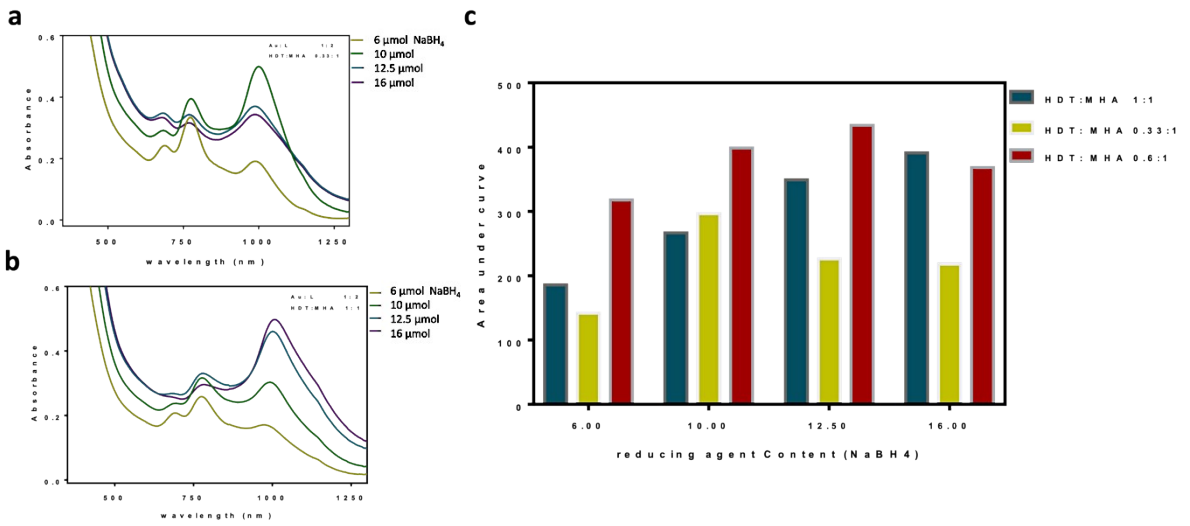

Figure S14. Absorbance spectra of AuMHA/HDT prepared at the ratio MHA:HDT = 0.33:1 (**a**) and 1:1 (**b**) as a function of $NaBH_4$ amount. (**c**) Area under the absorbance band at 990 nm at the different ratio AuMHA/HDT and controlling the amount of $NaBH_4$.

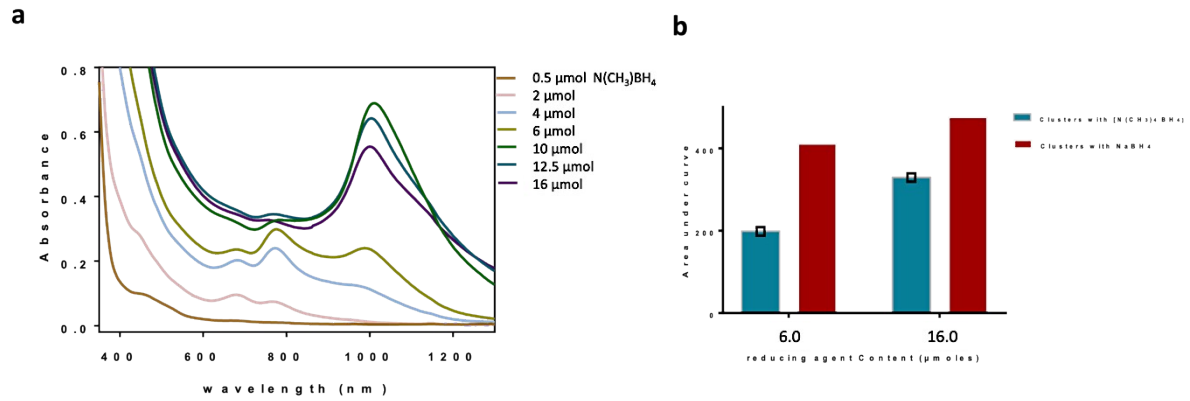

Figure S15. **a**. Absorbance spectra of AuMHA/HDT prepared with different amount of $TMABH_4$. **b**. Area under the absorbance band at 990 nm for AuMHA/HDT prepared using 6 or 16 µmol of $NaBH_4$ or $TMABH_4$.

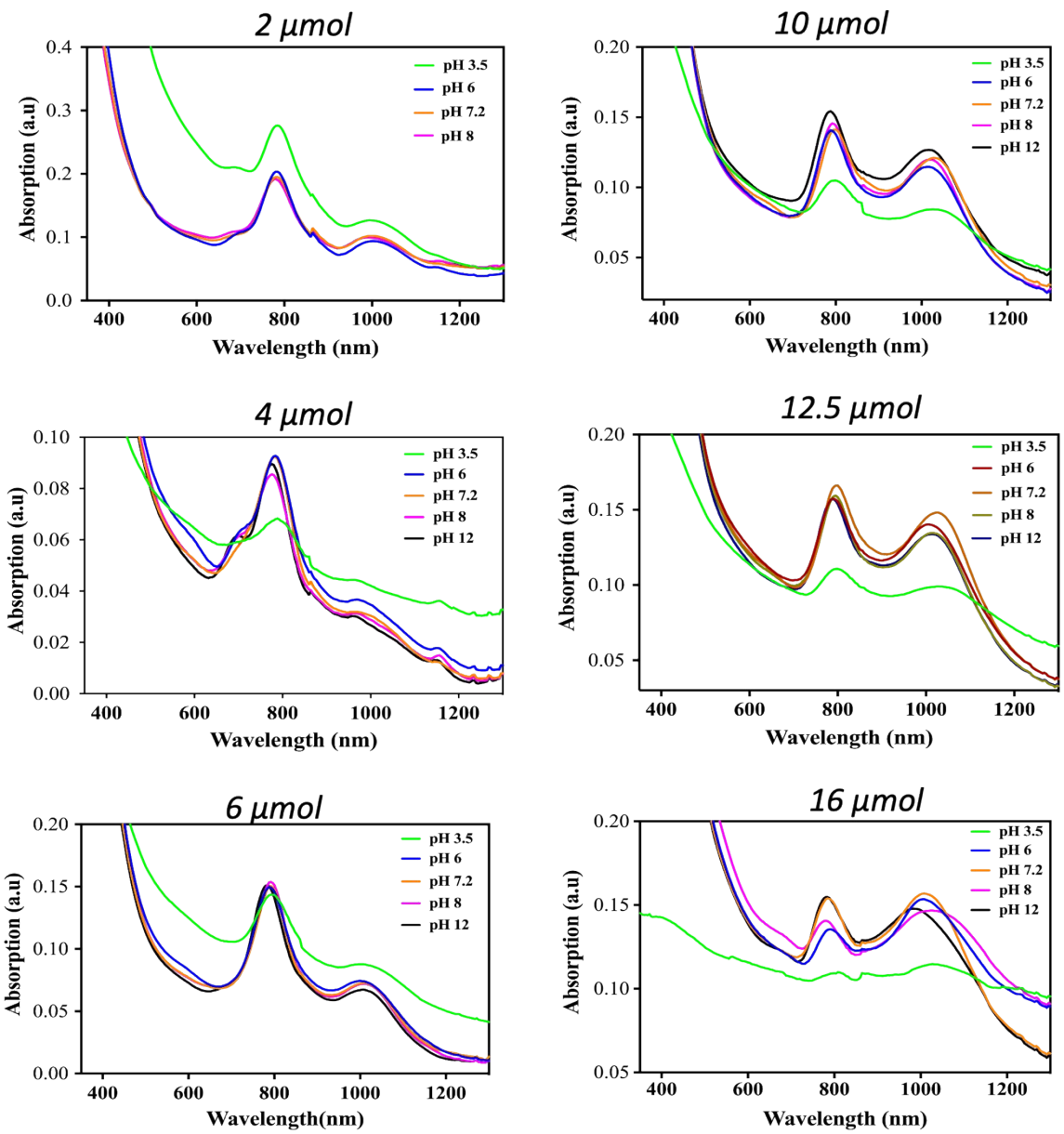

Figure S16. Absorbance spectra of AuMHA/HDT samples prepared with different amount of $NaBH_4$ and diluted in solutions at different pH.

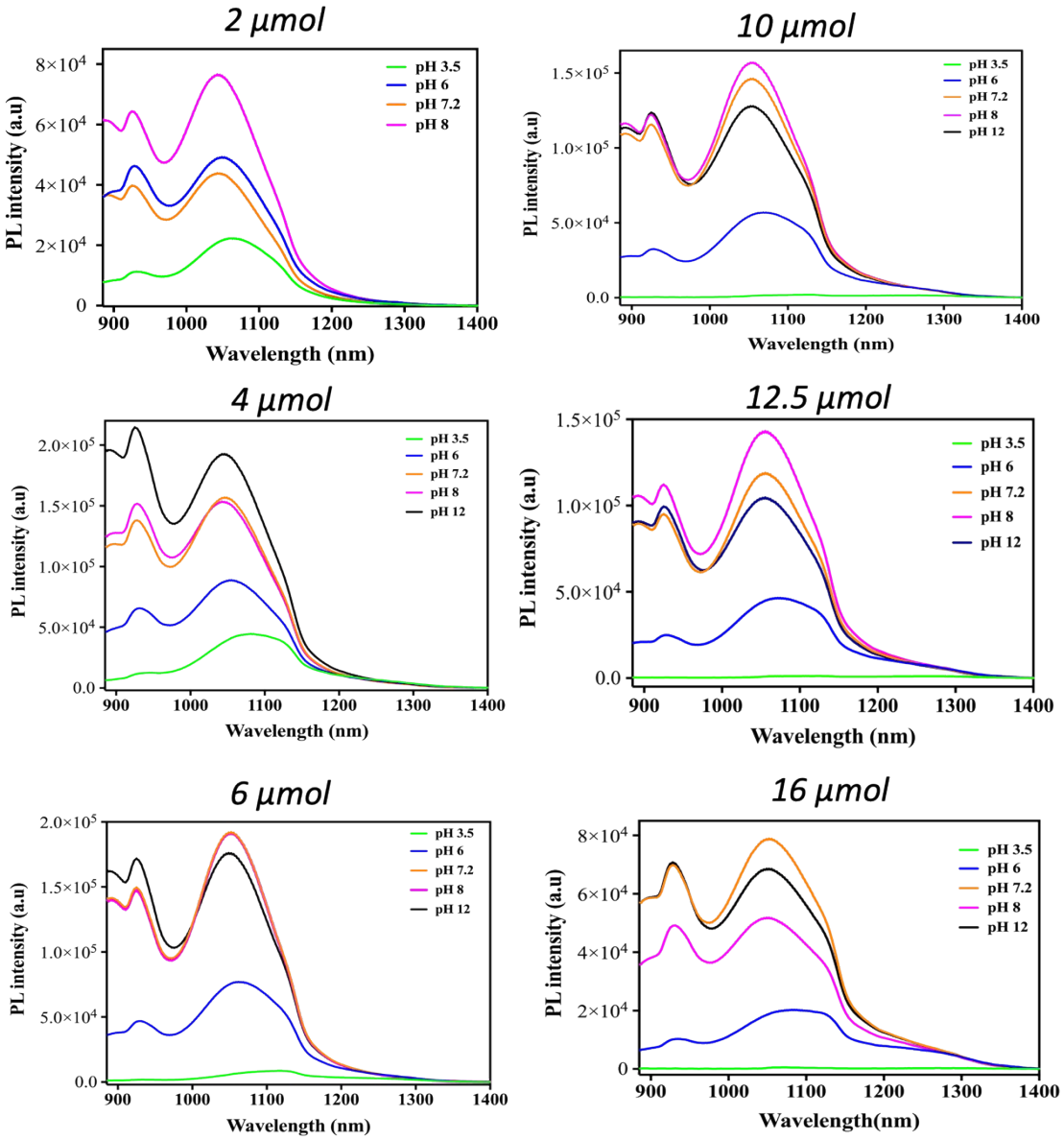

Figure S17. PL spectra ($\lambda_{exc.}$808 nm) of AuMHA/HDT samples prepared with different amount of $NaBH_4$ and diluted in solutions at different pH.

a

450.8 nm Excitation	τ_1 (ns)	A_1(%)	τ_2(ns)	A_2(%)	τ_3(ns)	A_3(%)	R^2
S1 (2 µmol $NaBH_4$)	1.057 ± 0.003	2.0	86.3 ± 0.5	16.9	729± 3	81.1	0.99674
S2 (6 µmol $NaBH_4$)	1.0198 ± 0.0008	8.8	77.0± 0.5	23.9	523 ± 3	67.4	0.99957
S3 (16 µmol $NaBH_4$)	0.8489 ± 0.0006	12.3	41.1 ± 0.2	30.6	250± 2	57.0	0.99975

b

634.3 nm Excitation	τ_1(ns)	A_1(%)	τ_2(ns)	A_2(%)	τ_3(ns)	A_3(%)	R^2
S1 (2 µmol $NaBH_4$)	0.782 ± 0.005	1.2	115.7 ± 1.7	17.8	680 ± 7	81.0	0.99279
S2 (6 µmol $NaBH_4$)	0.784 ± 0.002	3.7	66.2 ± 0.5	22.6	459± 3	73.7	0.99864
S3 (16 µmol $NaBH_4$)	0.750 ± 0.002	5.8	38.4 ± 0.3	30.3	230 ± 2	63.8	0.99875

Figure S18. a. PL lifetime components for AuMHA/HDT samples dispersed in PBS (pH 7.4) using 450.8 nm excitation (a) and 634.3 nm excitation (b). Lifetimes measured at 20 ºC.