Supporting Information

Solvent Polarity Dependent Behavior of Aliphatic Thiols and Amines towards Intriguingly Fluorescent AuAgGSH Assembly

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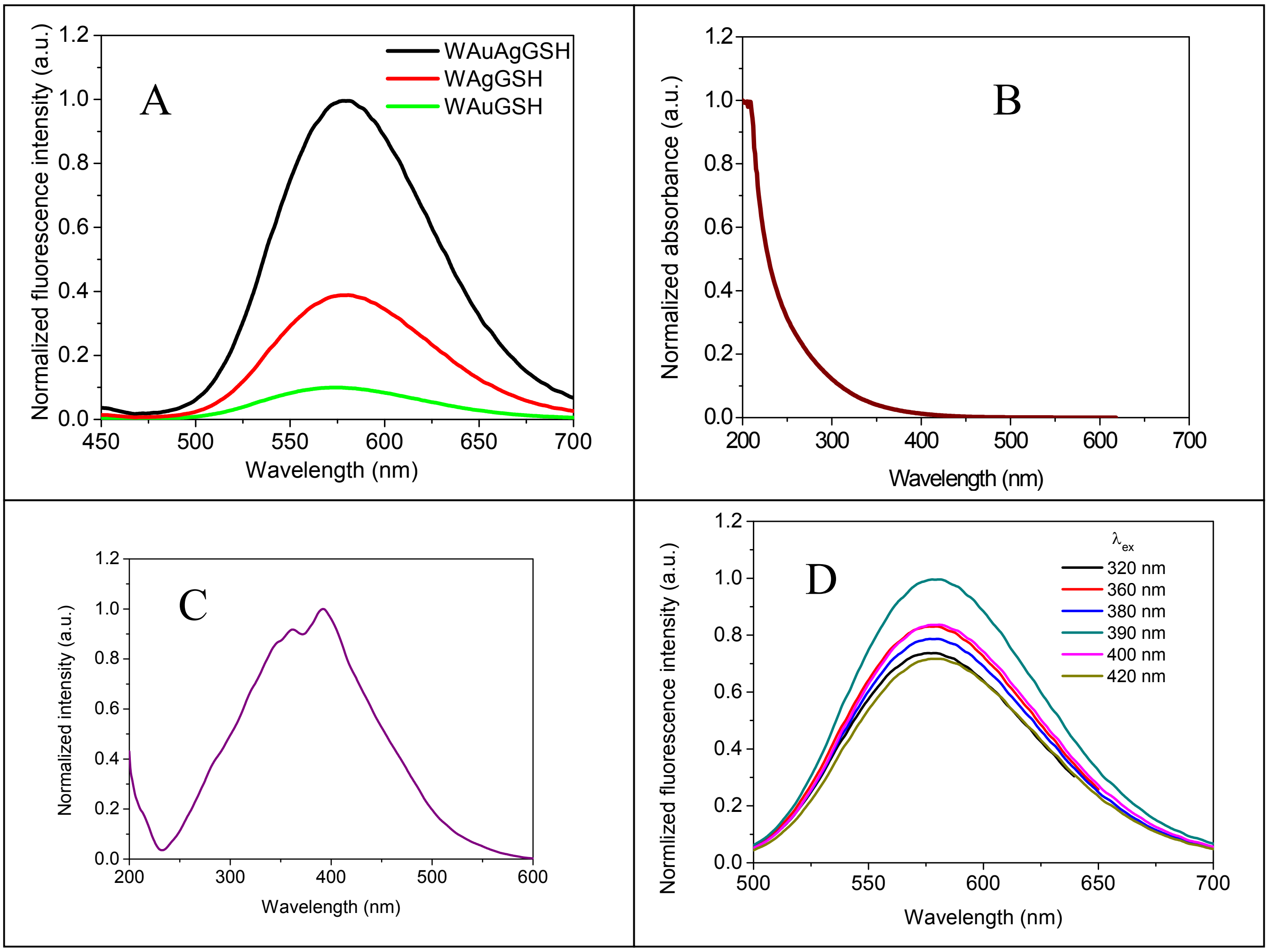


Figure S1: (A) Fluorescence spectral profile of WAuAgGSH, WAgGSH and WAuGSH. λ_{ex} = 390 nm. (B) Absorption spectrum and (C) Excitation spectrum with emission maxima at 580 nm of WAuAgGSH. (D) Fluorescence spectra of WAuAgGSH at different wavelengths.

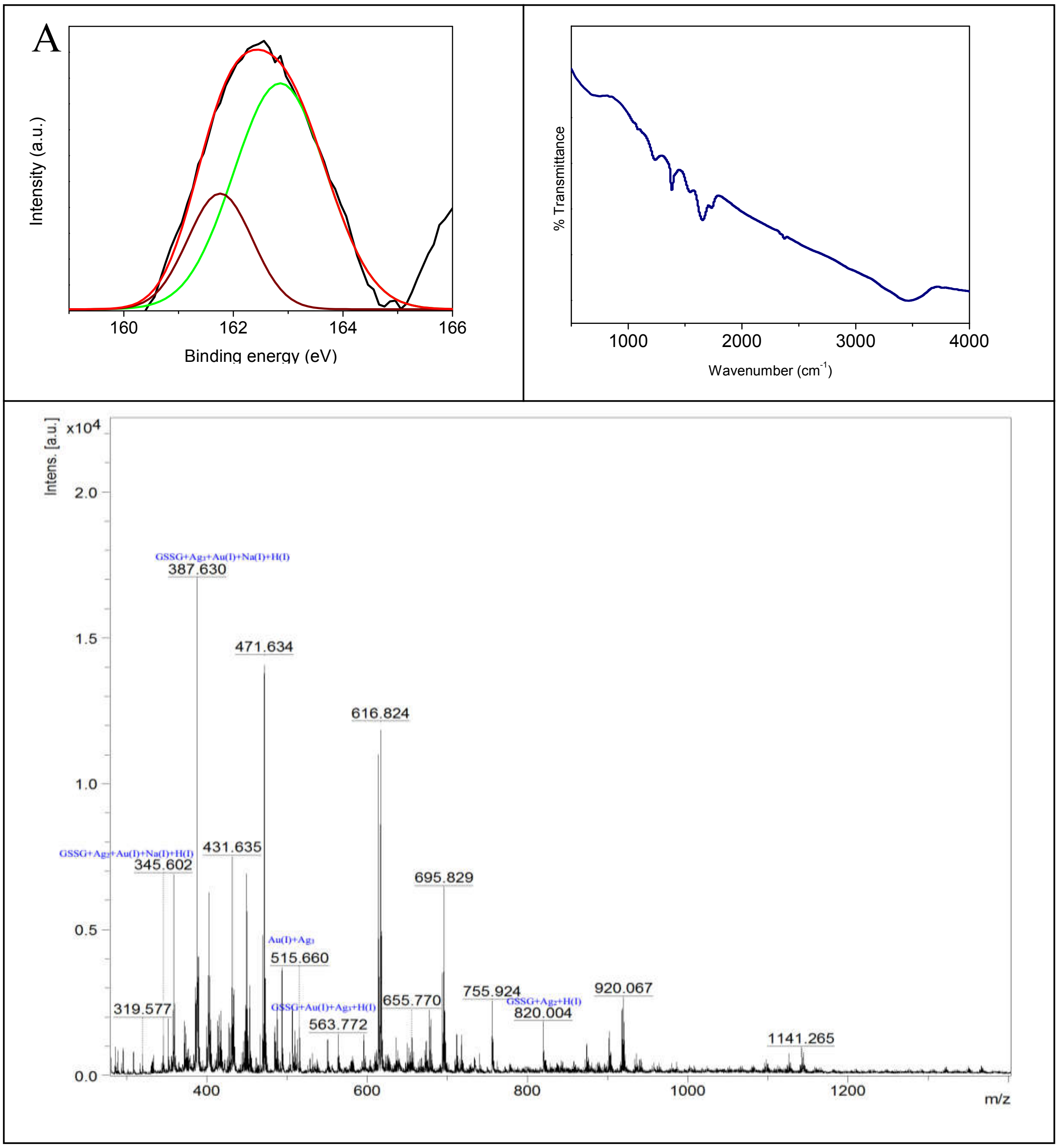


Figure S2: (A) Narrow range XPS spectrum of S2p of WAuAgGSH. (B) FTIR spectrum of WAUAgGSH. (C) MALDI-TOF Mass spectra of fluorescent AuAgGSH assembly.

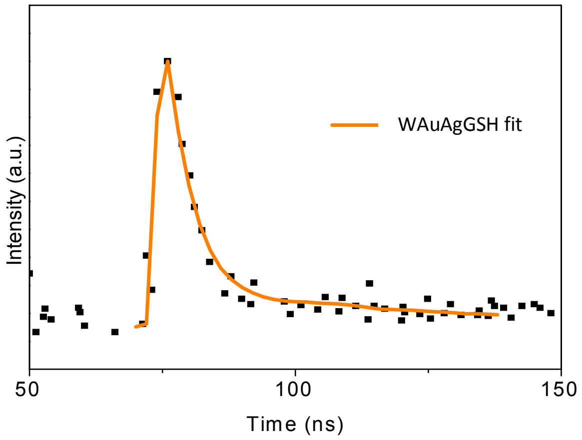


Figure S3: Fluorescence decay profile of WAuAgGSH. λ_{ex} = 390 nm.

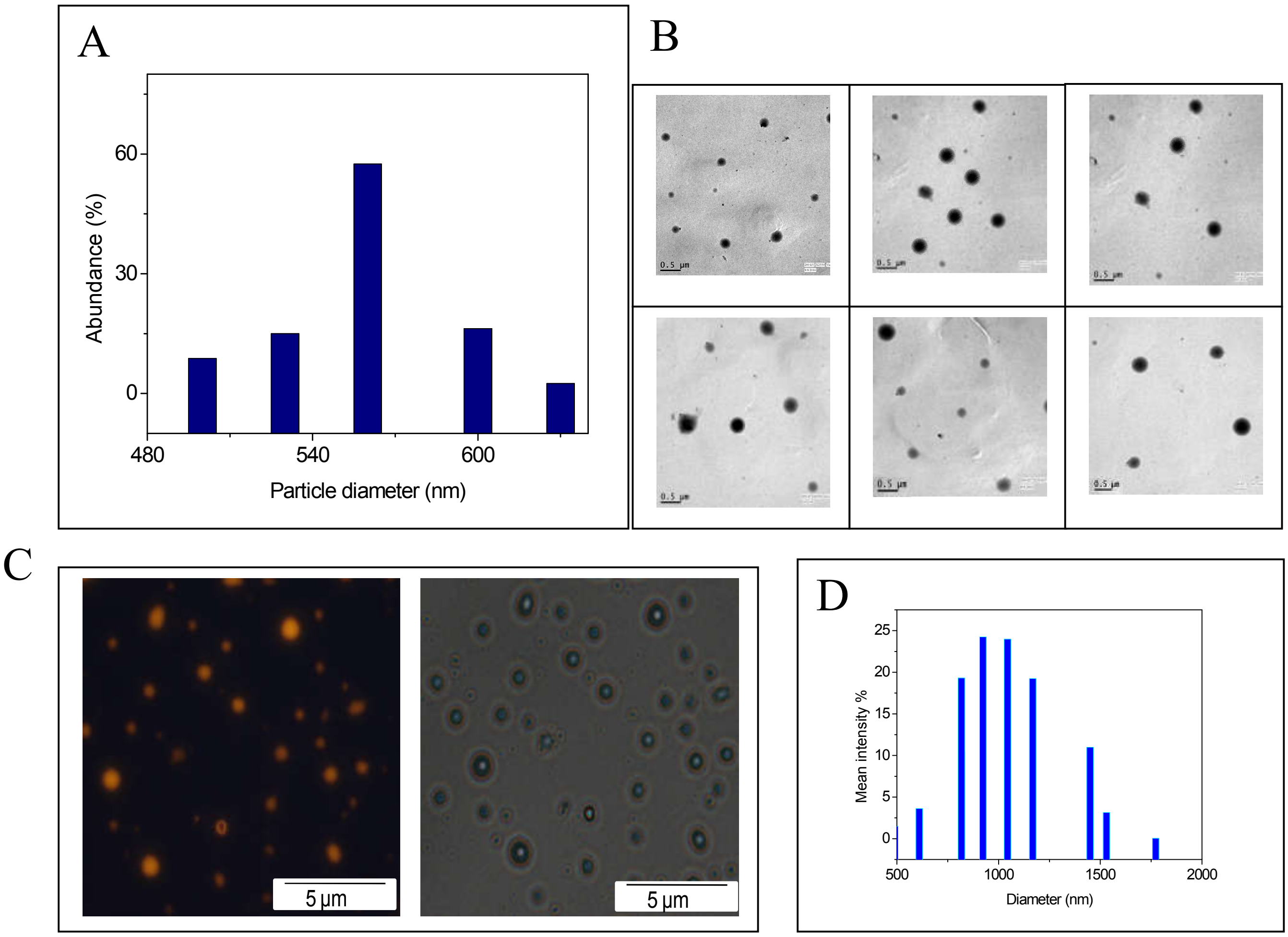


Figure S4: (A) Particle size distribution WAuAgGSH particles. (B) TEM and (C) Fluorescence microscopic of WAuAgGSH at different scan window. (D) DLS studies of WAuAgGSH.

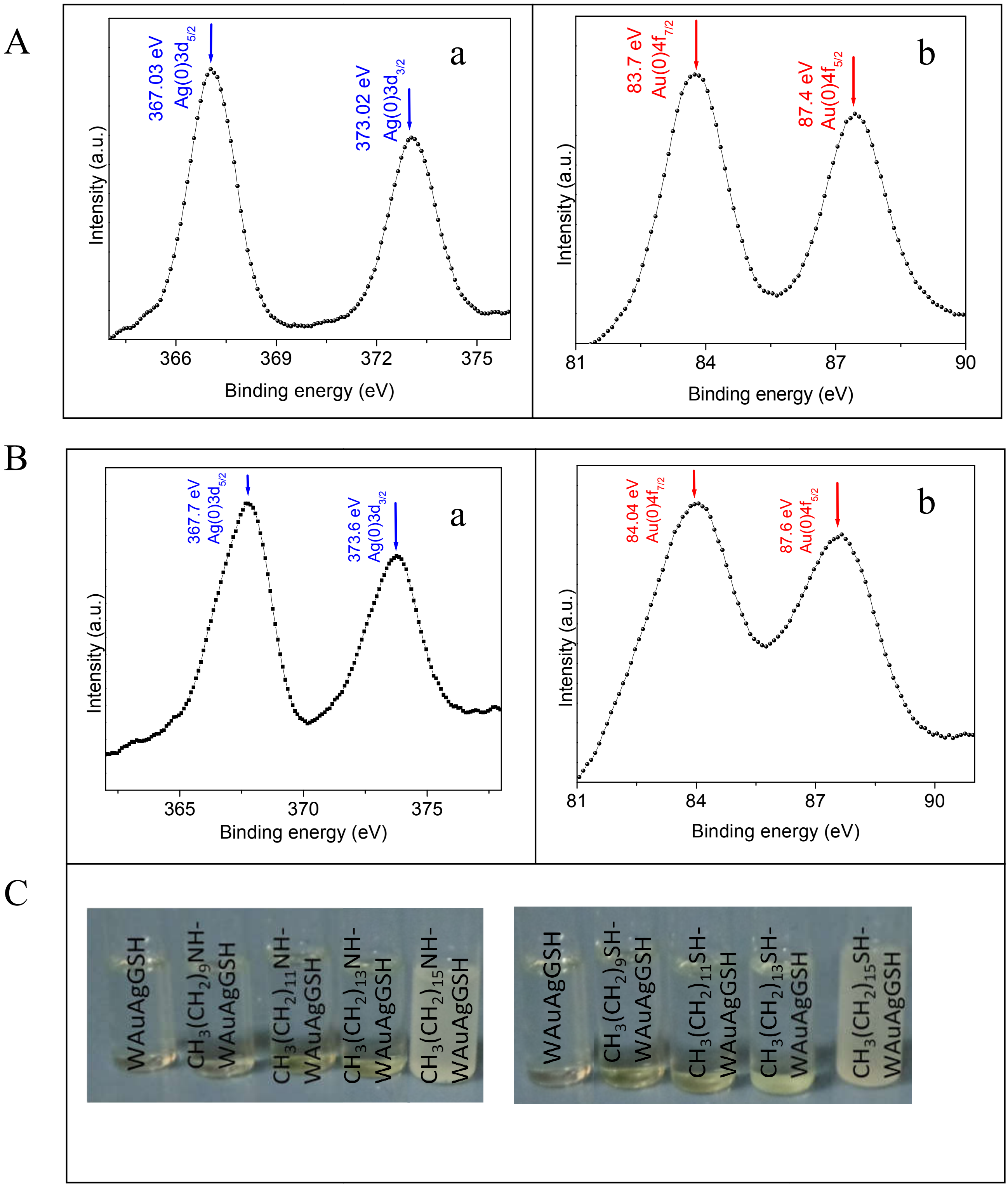


Figure S5: (A) Narrow range XPS spectra of elemental (a) Ag and (b) Au of $CH_3(CH_2)_9SH$-WAuAgGSH. (B) Narrow range XPS spectra of elemental (a) Ag and (b) Au of $CH_3(CH_2)_9NH$-WAuAgGSH under fridge drying condition. (C) Image of WAuAgGSH with and without thiols and amines.

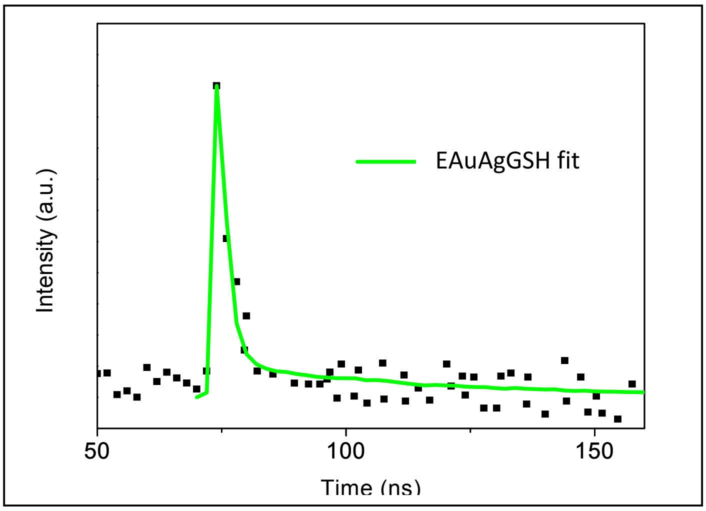


Figure S6: Fluorescence decay profile of EAuAgGSH. λ_{ex} = 390 nm.

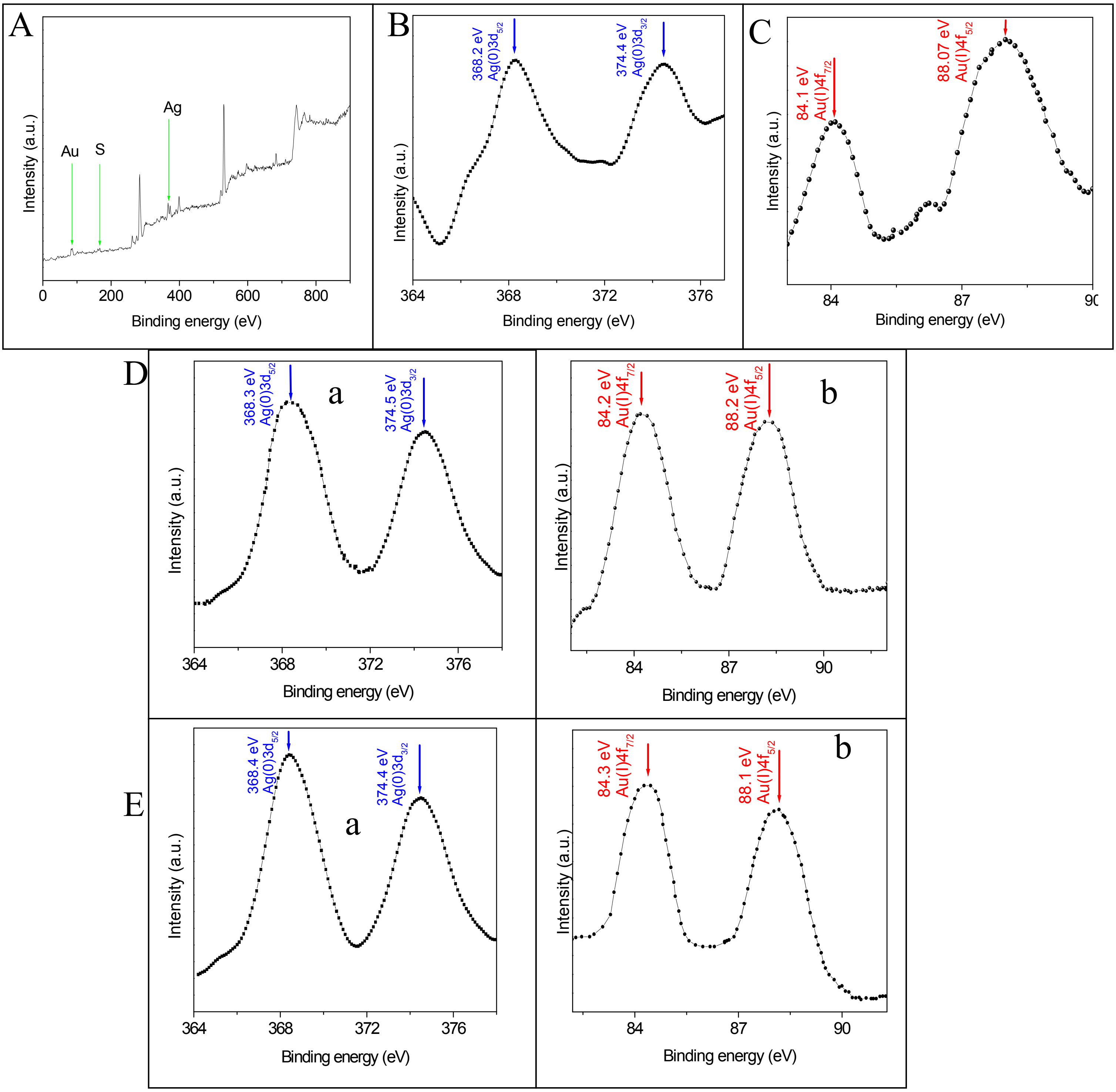


Figure S7: (A) Broad range XPS spectrum of EAuAgGSH. Narrow range XPS spectra of elemental (B) Ag and (C) Au of EAuAgGSH. (D) Narrow range XPS spectra of elemental (a) Ag and (b) Au of $CH_3(CH_2)_9SH$-EAuAgGSH. (E) Narrow range XPS spectra of elemental (a) Ag and (b) Au of $CH_3(CH_2)_9NH$-EAuAgGSH. Measurements are under fridge drying condition.

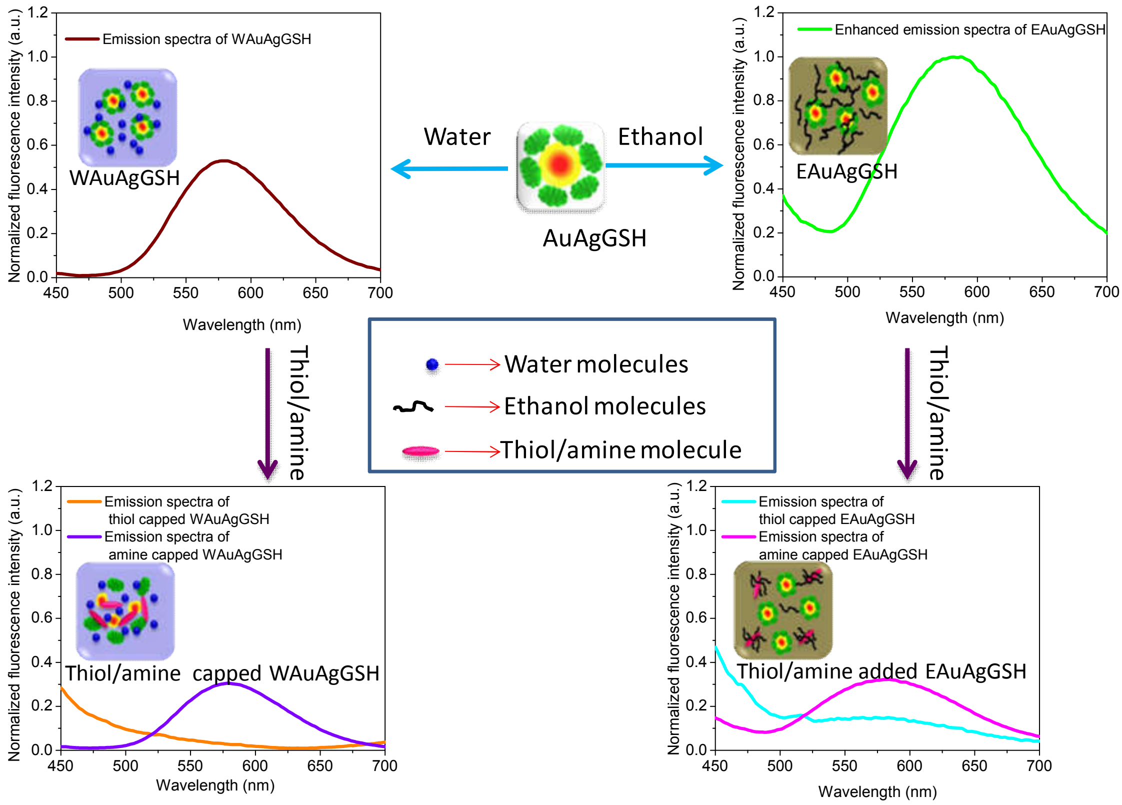


Figure S8: Schematic representation of emission peaks related to the AuAgGSH in different solvents with and without addition of aliphatic thiol or amine.

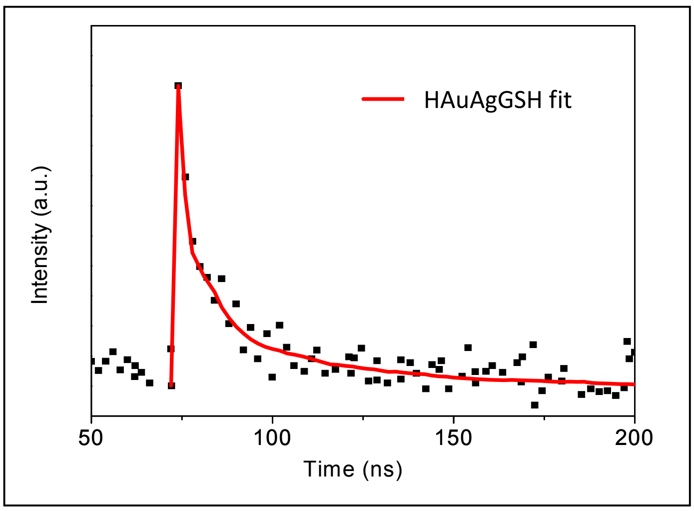


Figure S9: Fluorescence decay profile of HAuAgGSH. λ_{ex} = 390 nm.

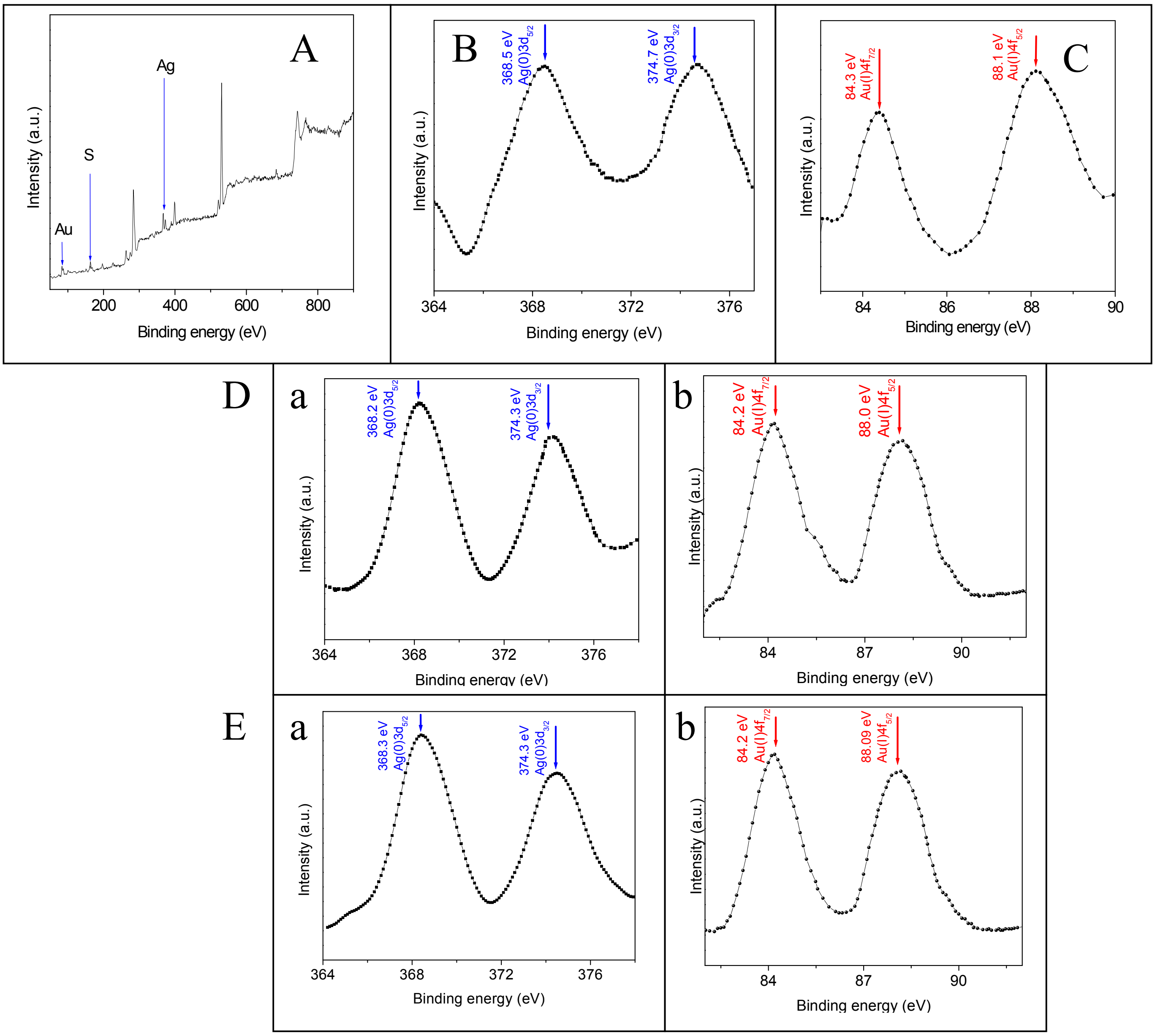


Figure S10: (A) Broad range XPS spectrum of HAuAgGSH. Narrow range XPS spectra of elemental (B) Ag and (C) Au of HAuAgGSH. (D) Narrow range XPS spectra of elemental (a) Ag and (b) Au of $CH_3(CH_2)_9SH$-HAuAgGSH. (E) Narrow range XPS spectra of elemental (a) Ag and (b) Au of $CH_3(CH_2)_9NH$-HAuAgGSH. Measurements are under fridge drying condition.

Construction of molecular logic gate in aqueous as well as non-aqueous medium

Molecular logic gates are used in sensing technology, different molecular interaction studies, biofuel powered sensors etc. fields.[1] The operation of molecular logic gates based on phosphorescence technique depends on the "turn off/turn on" response of the fluorophore.

Different quenching processes like fluorescence resonance energy transfer (FRET), proton energy transfer (PET) etc. are important in this respect. In the present study the molecular logic gate has been constructed in non-aqueous medium. Non-aqueous solvents are important for laboratory usages. The logic operation on the as-synthesized fluorescent assembly is dependent on the mechanism of the interaction between assembly and ligand.

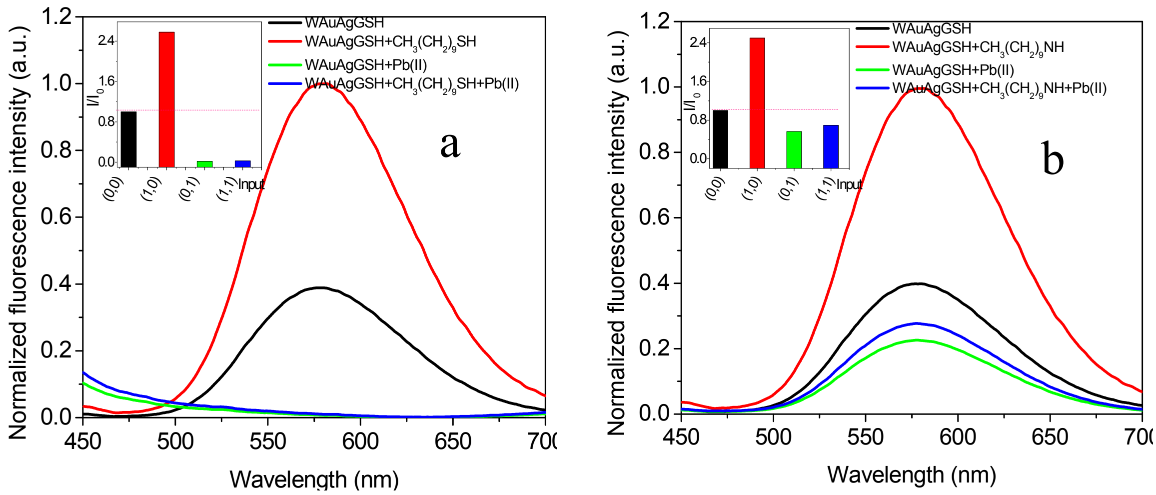
EAuAgGSH alone (input = 0,0) is fluorescent (output = 1), the addition of long chain aliphatic thiol or amine only (input = 1,0) triggered the fluorescence turn-off response of EAuAgGSH (output = 1). Pb(II) alone (input = 0,1) triggered the fluorescence turn-on response of EAuAgGSH (output = 1). Also in the simultaneous presence of both thiol or amine and Pb(II) (input = 1,1), the solution remains fluorescent (output = 1). These results correlate well with the proper execution of IMPLICATION logic operation. The same operation can be done using HAuAgGSH.

However for WAuAgGSH this case does not occur. On addition of Pb(II), the fluorescence of thiol or amine capped WAuAgGSH cannot be recovered. This is schematically shown in Figure 10. Even addition of other cations cannot bring back the lost fluorescence of WAuAgGSH. Although addition of Pb(II) to WAuAgGSH causes fluorescence enhancement. This indicates that the fluorescent system is completely disturbed upon the addition of thiol or amines. If we consider thiol or amine as first input and Pb(II) as second input then we find that WAuAgGSH, without any thiol or amine and Pb(II) (input =0,0), is fluorescent (output = 1). Addition of only thiol or amine (input = 1, 0) causes fluorescence quenching (output = 0) but addition of only Pb(II) (input = 0, 1) causes fluorescent system (output = 1). Again addition of both thiol or amine and Pb(II) (input = 1,1) causes quenching (output = 0) of fluorescence. The output style (1,0,1,0) indicates that this gate can be built with an inverter on the second input, and with the first input hanging. Thus HAuAgGSH cannot initiate the design of any useful logic gate (Figure S11, Supporting Information). In the constructed logic gates the inputs, namely thiol or amine and Pb(II) are labelled as input 1 and input 2 according to the sequence of use. The experimental concentrations of both the inputs are same i.e. 1.6×10^{-4} M.

Reference:

1. Lai, Y.-H.; Sun, S.-C.; Chuang, M. –C. Biosensors with Built-In Biomolecular Logic Gates for Practical Applications. *Biosensors* **2014**, *4*, 273-300.

A



B

System	Input 1 Thiol/amine	Input 2 Pb(II)	Output
WAuAgGSH	0	0	1
	1	0	0
	0	1	1
	1	1	0

Figure S11: Fluorescence spectral profile for logic operation on (A) WAuAgGSH using (a) $CH_3(CH_2)_9SH$ and Pb(II) as inputs and (b) $CH_3(CH_2)_9NH$ and Pb(II) as inputs. (B) Truth table for logic operations on WAuAgGSH.

Compound	τ_1(ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{avg} (ns) [upto two decimal]
WAuAgGSH	0.079	4.66	6.213	8.82	67	24.18	0.85	4.67
$CH_3(CH_2)_9NH$-WAuAgGSH	0.43	3.56	0.98	14.36	28.94	56.7	1.012	1.65
$CH_3(CH_2)_9SH$-WAuAgGSH	0.99	1.97	1.66	64.9	11.7	23.4	0.99	1.26
EAuAgGSH	5.67	4.26	6.71	20.2	46.5	33.3	0.95	5.36
$CH_3(CH_2)_{15}NH$-EAuAgGSH	4.98	2.03	0.59	38.1	29.7	32.2	0.86	2.96
$CH_3(CH_2)_{15}SH$-EAuAgGSH	1.72	3.44	0.35	49.3	28.7	22.0	0.99	1.91
HAuAgGSH	0.077	2.516	9.214	33.33	33.32	33.36	0.96	3.93
$CH_3(CH_2)_{15}NH$-HAuAgGSH	0.9	1.07	2.02	30.9	37.3	31.8	0.89	1.32
$CH_3(CH_2)_{15}SH$-HAuAgGSH	1.51	1.52	1.51	33.3	33.3	33.3	1.1	1.51

Table S1: Fluorescence lifetime values of different compounds.