Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Tailoring the luminescence of atomic clusters via Ligand Exchange Reaction Mediated post synthetic modification

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Electronic Supplementary Information

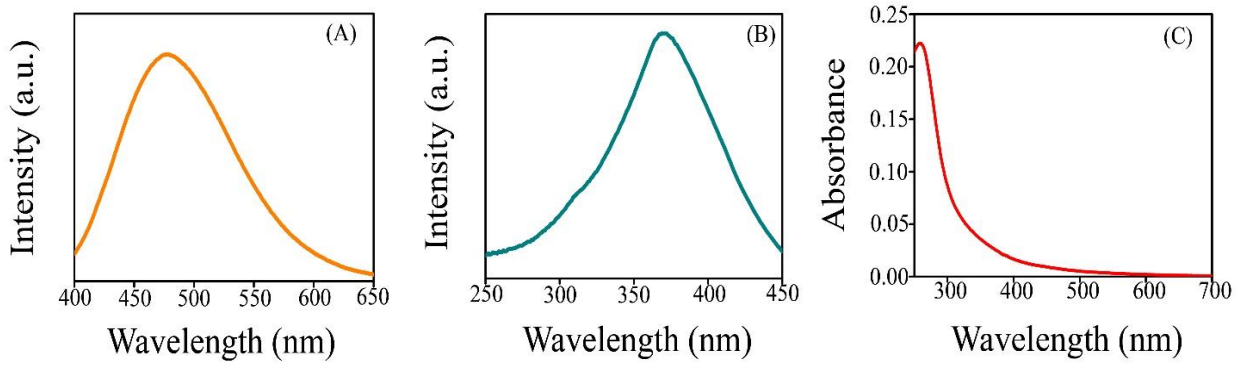

Fig. S1 (A) Emission spectrum of His Au NCs. Excitation wavelength was set at 370 nm (B) Excitation spectrum of His Au NCs. Emission wavelength was set at 475 nm (C) UV-visible absorbance spectrum of His Au NCs.

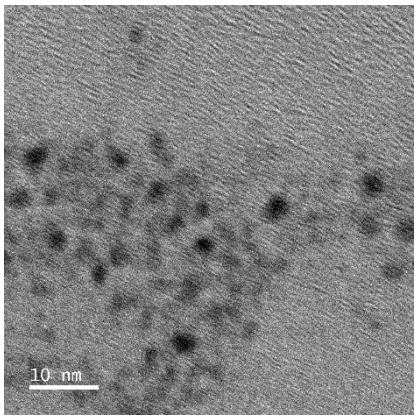

Fig. S2 TEM image of His Au NCs.

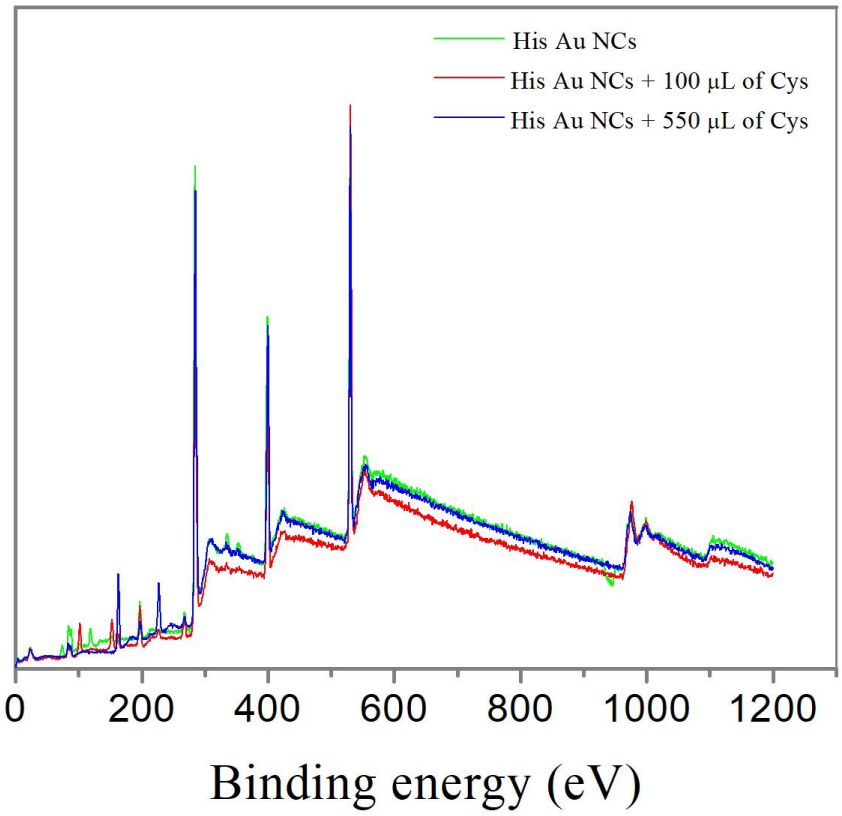

Fig. S3 Survey spectra of His Au NCs, His Au NCs + 100 µL cysteine and His Au NCs + 550 µL cysteine

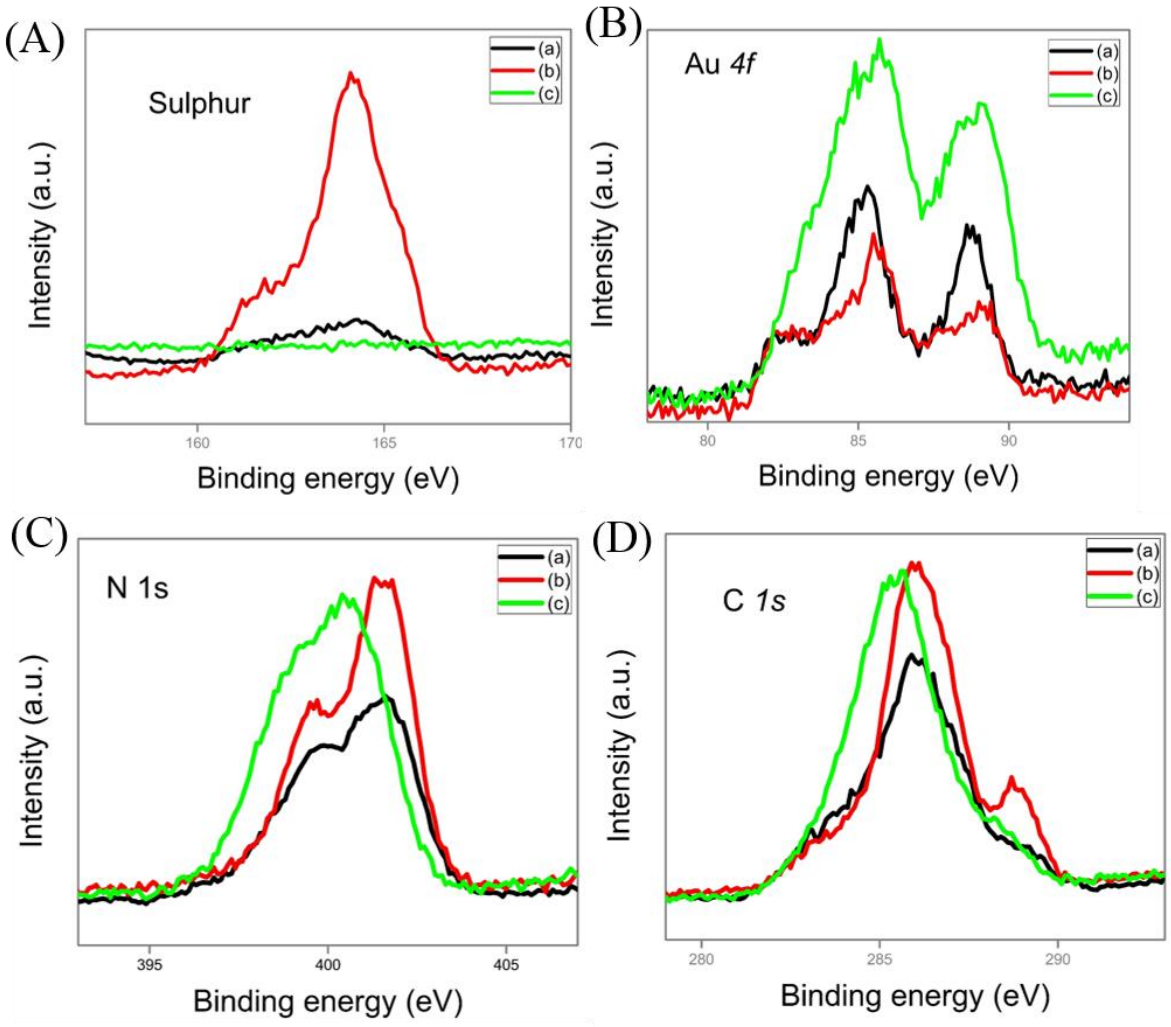

Fig. S4 XPS spectrum of (A) sulphur 2p, (B) Au 4f, (C) N 1s and (D) C 1s. (a) Black lines denote His Au NCs following addition of 100 μL cysteine, green lines denote only His Au NCs and red lines denote His Au NCs following addition of 500 μL cysteine.

Table S1: pH variation of dispersions of His Au NCs upon addition of varying amounts of cysteine.

Solution	pH of the solution
His Au NCs	6.85
His Au NCs +10 µL of 100 mM cysteine	6.86
His Au NCs +20 µL of 100 mM cysteine	6.85
His Au NCs +30 µL of 100 mM cysteine	6.80
His Au NCs +40 µL of 100 mM cysteine	6.78
His Au NCs +50 µL of 100 mMm cysteine	6.76
His Au NCs +60 µL of 100 mM cysteine	6.80
His Au NCs +70 µL of 100 mM cysteine	6.79
His Au NCs +80 µL of 100 mM cysteine	6.79
His Au NCs +90 µL of 100 mM cysteine	6.78
His Au NCs +100 µL of 100 mM cysteine	6.82
His Au NCs +110 µL of 100 mM cysteine	6.75
His Au NCs +120 µL of 100 mM cysteine	6.76
His Au NCs +130 µL of 100 mM cysteine	6.76
His Au NCs +140 µL of 100 mM cysteine	6.76
His Au NCs +150 µL of 100 mM cysteine	6.77
His Au NCs +200 µL of 100 mM cysteine	6.8
His Au NCs +400 µL of 100 mM cysteine	6.79

Table S2: Variation in luminescence lifetime of His Au NCs upon addition of cysteine

Sample	T_1		T_2		T_3		Average lifetime (ns)
	Lifetime (ns)	**Contribution (%)**	**Lifetime (ns)**	**Contribution (%)**	**Lifetime (ns)**	**Contribution (%)**	
His Au NCs	1.24	37.45	5.45	53.99	0.15	8.56	4.86
His Au NCs +40 µL of 100 mM cysteine	0.97	24.65	5.37	65.81	0.04	9.55	5.08
His Au NCs +440 µL of 100 mM cysteine	1.48	30.64	6.54	62.71	0.07	6.65	6.03

Table S3: Details of XPS analysis of His Au NCs and of that following addition of a cysteine

Element	BE@0 (width)	%	BE@100 (width)	%	BE@500 (width)	%	Peak assignment	Reference & notes
Au $4f_{5/2}$	88 (0.9) 89.2 (1.6)	6 29	87.4 (0.9) 88.8 (1.1)	4 31	88 (1.9) 89.3 (1)	23 11	Au(0) Au(δ+)	**Nanoscale**, 2015,**7**, 16372-16380 **Nanoscale**, 2017,9, 15033-15043
Au $4f_{7/2}$	83.2 (1.5) 85.5 (2.5)	8 57	82.6 (1.4) 85.1 (1.6)	12 53	82.4 (1.0) 84.6 (2.5) 85.6 (1.8)	11 38 17	Au(0) Au(δ+)	**Nanoscale**, 2018,10, 3792-3798 **J. Am. Chem**. Soc., 2005, 127, 5261–5270 **Nanoscale**, 2012, 4, 7727–7734 Peak sharpens: Au-S bond formation δ+ assignment means oxidation state close to +1
Sulphur $2p_{3/2}$-$2p_{1/2}$=1.18eV, (2:1)	-	-	161.9 (1.8) 164.3 (2.1)	27 73	161.5 (1.2) 162.8 (1.2) 164.2 (1.3) 165.5 (1)	12 14 58 16	Au-SR Au-SR RS-H	**Journal of Nanobiotechnology** volume 9, article number: 26 (2011) **Nanoscale**, 2014, 6, 8091-8099 **Langmuir** 2004, 20, 10223-10230 **Nanoscale**, 2012, 4, 7727–7734 **Colloids and Surfaces A: Physicochem. Eng. Aspects** 2000, 175, 121 – 128 $S_{3/2}$ and $S_{5/2}$ peaks: unresolved in fig3 due to poor signal to noise ratio. Incomplete resolution in fig 3F due to close overlapping shoulder peaks

Nitrogen 1s			396.7 (1.3)	3				**J. Phys. Chem. B**, 2005, 109, 884-891 **J. Phys. Chem. B** 2008, 112, 13655–13660
	398.9 (2.1)	45	398.1 (1.1)	7			imine (-N=C-NH)	**Langmuir** 2010, 26(11), 8606–8613 **Nanoscale**, 2012, 4, 7727–7734
			399.5 (1.6)	32	399.5 (1.6)	33	-NH_2 (cys)	**Langmuir** 2004, 20, 10223-10230
	400.9 (1.9)	55					amine(N=C-NH-) –NH_2 (his)	**J. Phys. Chem. C** 2014, 118, 10481−10487
			401.6 (1.8)	58	401.6 (1.6)	67	-NH_3^+	Deconvolution and assignment is complicated by zwitterionic and protonated forms of histidine & cysteine
Carbon 1s			283.1 (1.5)	8	284.2 (2.4)	17	C-SAu (cys)	**J. Phys. Chem. B**, 2005, 109, 884-891 **J. Phys. Chem. B** 2008, 112, 13655–13660
	285.5 (2.5)	92	285.5 (2.4)	52			imidazole C, -CH_2- -$C(NH_2)HCOO^-$	**Langmuir** 2004, 20, 10223-10230 **Applied Surface Science** 2018, 435, 870–879
			286 (1)	13	285.8 (1.2)	38	C-SH (cys)	
	288 (1.4)	8	287.2 (1.3)	17	286.9 (1.3)	30	-C-NH_2 (cys) COO^-	
			288.9 (1.4)	10	288.8 (1.2)	15	COOH	

Additional figures:

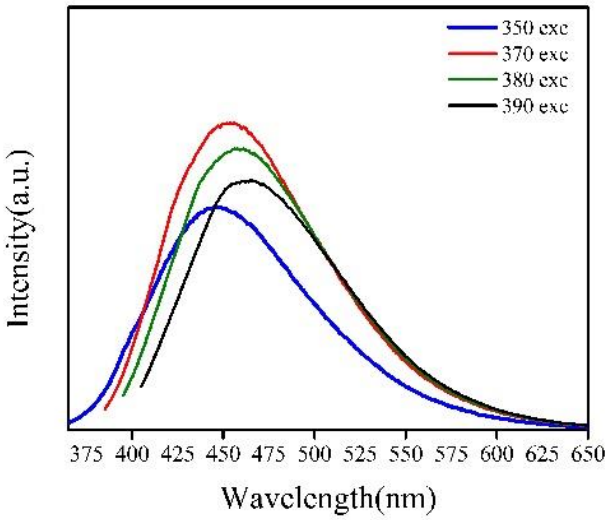

Fig. S5 Excitation dependent (as mentioned in figure legends) emission spectra of His Au NCs

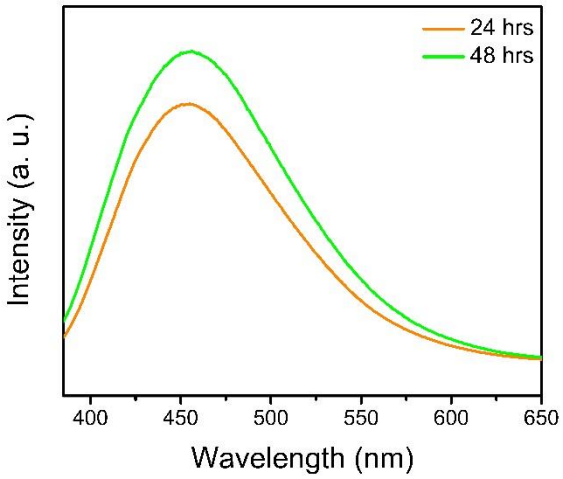

Fig. S6 Emission spectra of His Au NCs recorded after 24 h and 48 h of preparation.