Aggregation induced delayed green fluorescence from assembly of gold nanoclusters: An advanced probe for “background free” pyrophosphate recognition

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Electronic Supplementary Information

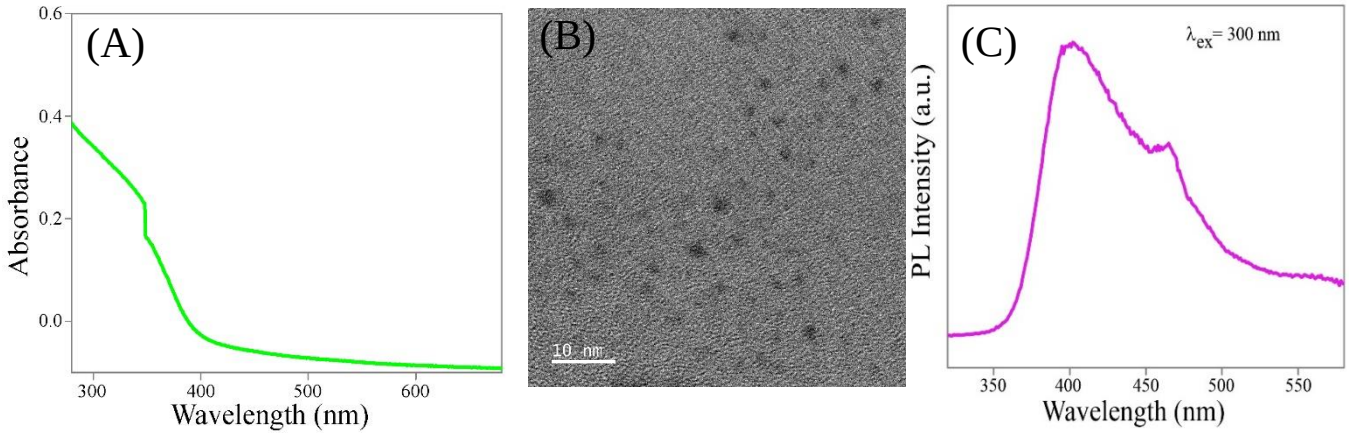

Fig. S1. (A) UV- vis absorbance spectra of Au NCs. (B) Transmission electron microscopic (TEM) images of Au NCs. (C) Luminescence emission spectrum of Au NCs upon excitation at 300 nm (without delay).

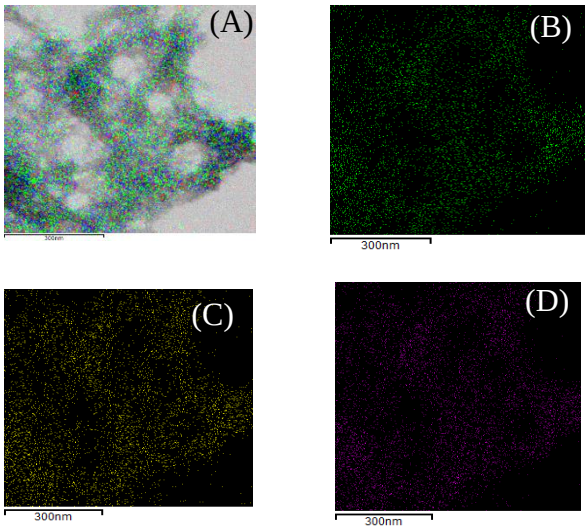

Fig. S2. (A) STEM image of Zn Au NCs superimposed by the elemental mapping (B) of that of Zn, (C) of that of Au and (D) of that of S in a sample of Zn Au NCs.

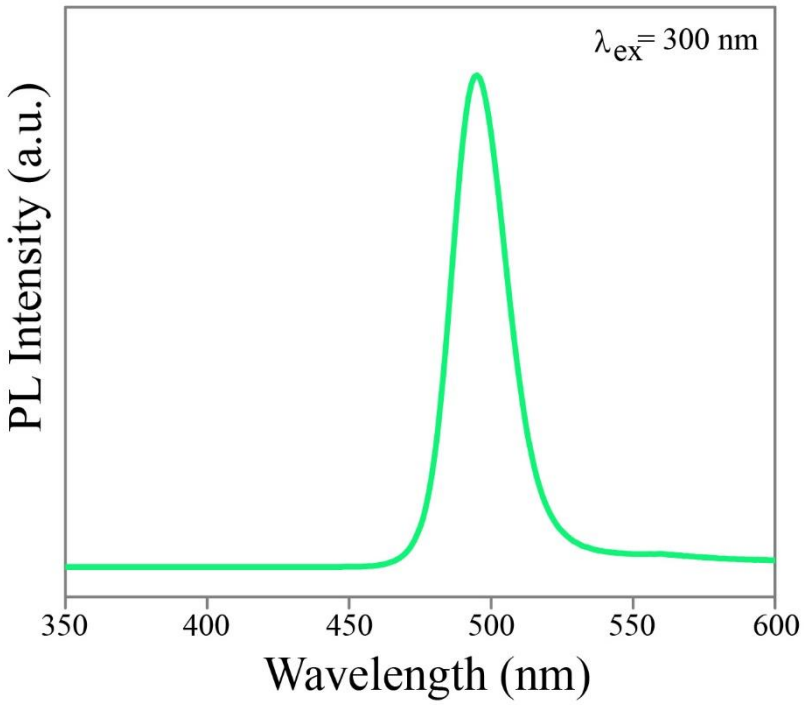

Fig. S3. Delayed luminescence emission spectrum of Zn Au NCs.

Table S1. Time resolved ***delayed*** fluorescence decay parameters of Zn Au NCs.

Sample	A_1	τ_1 (μs)	A_2	τ_2 (μs)
Zn Au NCs	0.909	9.8557	0.091	95.7553
Zn Au NCs + $P_4O_7^{2-}$	1.0	9.336	…..	…..

Table S2. Time resolved photoluminescence (TRPL) decay parameters of Zn Au NCs

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)
Zn Au NCs	0.33	5.823	0.25	0.913	0.42	19.53
Zn Au NCs + $P_4O_7^{2}$	0.53	13.53	0.32	4.12	0.15	38.43

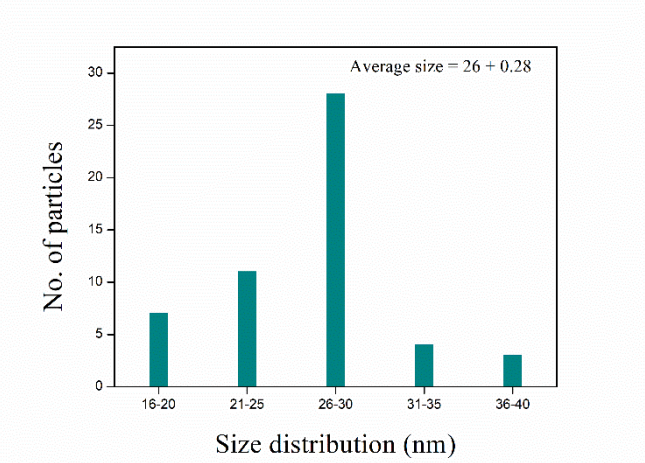

Fig. S4: Bar diagram showing size distribution of Zn Au NCs

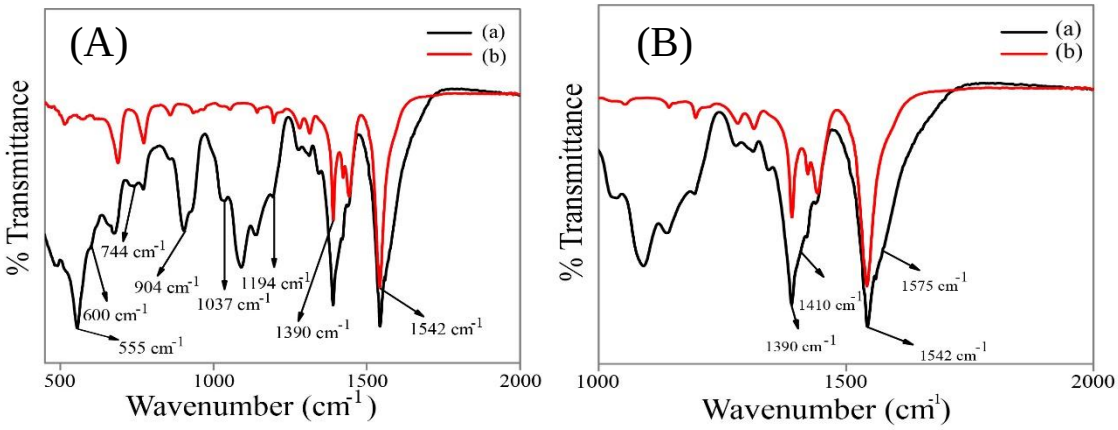

Fig. S5. FTIR spectra of Zn Au NCs (red) and that of Zn Au NCs upon treatment with sodium pyrophosphate (black).

Table S3. FTIR spectra peak assignments of Zn Au NCs and Zn Au NCs upon addition of pyrophosphate.

Zn Au NCs			Zn Au NCs + $P_2O_7^{2-}$		
Peak (cm^{-1})	Assignment	Reference	Peak (cm^{-1})	Assignment	Reference
555	$\upsilon_s(PO_3)$	A Simple Synthesis, Characterization, Kinetics and Thermodynamics of Zinc Ammonium Phosphate, $ZnNH_4PO_4$			Visible Light Excitation – Induced Luminescence from Gold Nanoclusters Following Surface Lgand Complexation with Zn2+ for Daylight Sensing and Cellular Imaging Chirantan Gayen, Srestha Basu, Upashi Goswami and Anumita Paul *Langmuir* 2019 **35(27)** 9037-9043
600	$\upsilon_{as}(PO_3)$	Rattanai Baitahe & Banjong Boonchom			
744	$\upsilon_s(POP)$	*International Journal of Thermophysics* 2020 **41** Article number: 33			
904	$\upsilon_{as}(POP)$				
1037, 1194	$\upsilon_s(PO_3)$				
1390	$\upsilon_s(COO^-)$		1390, 1410	$\upsilon_s(COO^-)$	
1542	$\upsilon_{as}(COO^-)$		1542, 1575	$\upsilon_{as}(COO^-)$	

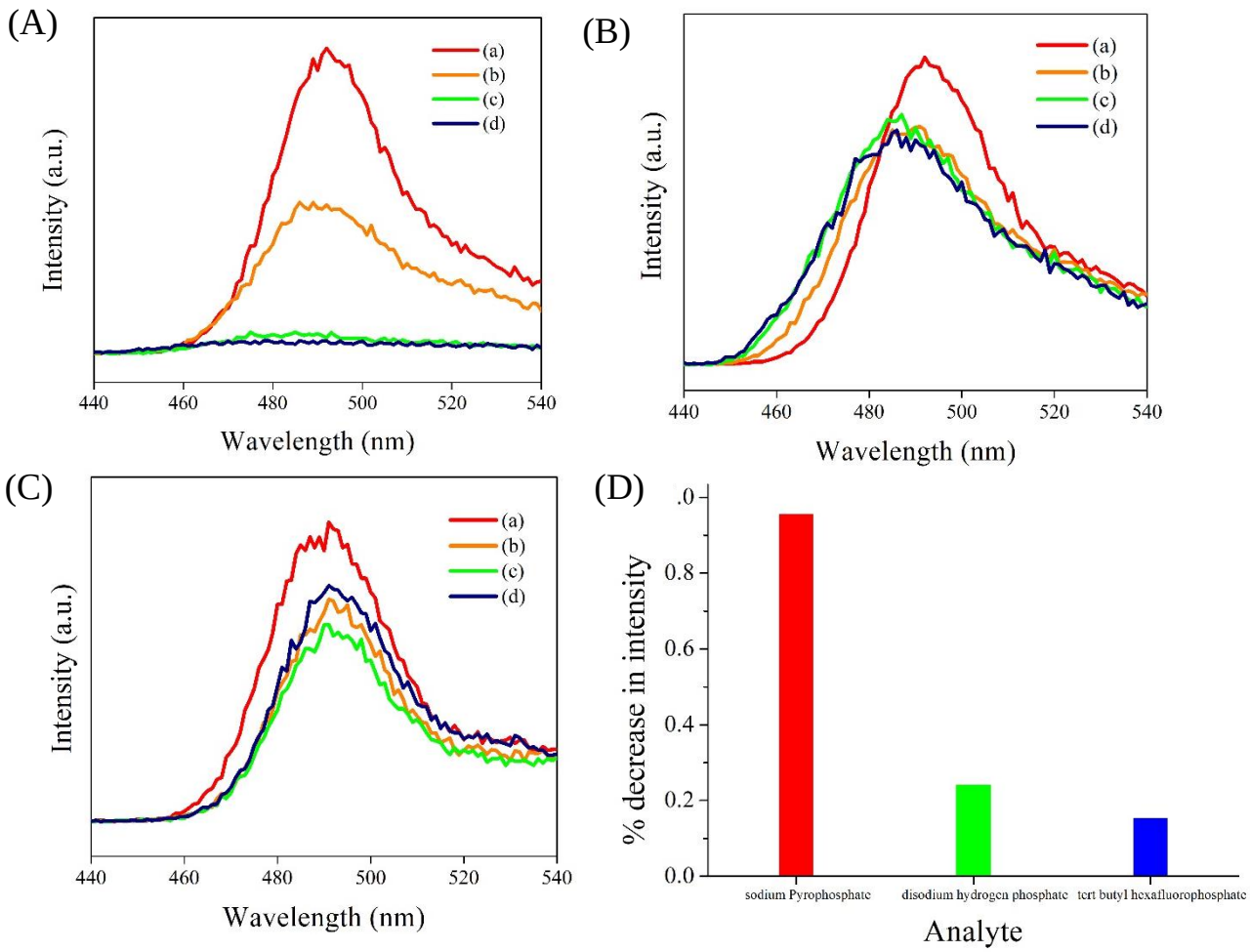

Fig S6. (A): Delayed fluorescence emission spectrum of (a) Zn Au NCs and that following addition of (b) 20 µL, (b) 30 µL and (c) 40 µL of sodium pyrophosphate (100mM). **(B)** Delayed fluorescence emission spectrum of (a) Zn Au NCs and that following addition of (b) 20 µL, (b) 30 µL and (c) 40 µL of di-sodium hydrogen phosphate (100mM). **(C)** Delayed fluorescence emission spectrum of (a) Zn Au NCs and that following addition of (b) 20 µL, (b) 30 µL and (c) 40 µL of tetra butylammonium hexafluoro phosphate (100mM).

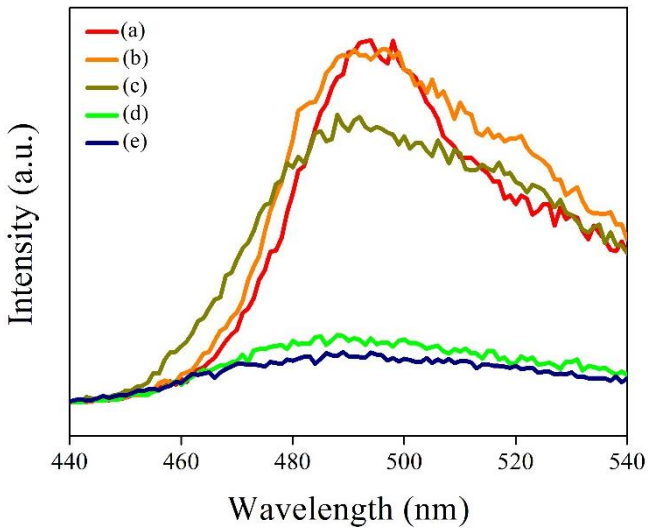

Fig. S7: Delayed emission spectrum of (a) Zn Au NCs and that following addition of (b) 20 µL of tetrabutylammonium hexafluorophosphate and 20 µL disodium hydrogen phosphate, (c) 40 µL of tetrabutylammonium hexafluorophosphate and 40 µL disodium hydrogen phosphate, (d) 20 µL of sodium pyrophosphate and (e) 40 µL of sodium pyrophosphate to the aqueous dispersion of Zn Au NCs previously added with (b) and (c).

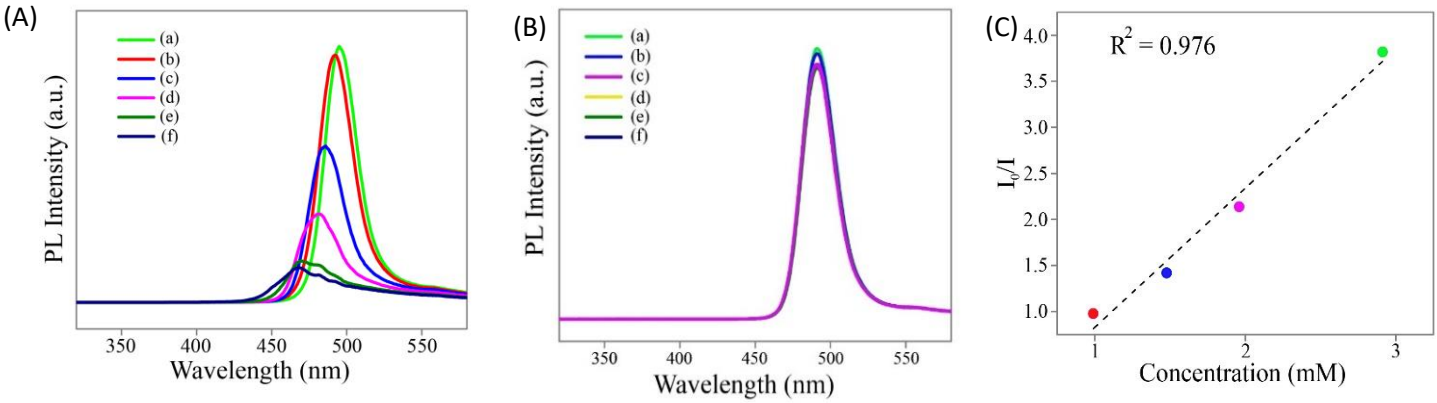

Fig. S8. Normal luminescence spectrum of (A) Zn Au NCs upon addition of indicated amount of pyrophosphate ion and of (B) (a) Zn Au NCs & of following addition of (b) 20 µL (c) 30 µL (d) 40 µL (e) 50 µL (f) 60 µL of 100 mM of sodium nitrate. The excitation wavelength was set at 300 nm. (C) Corresponding Stern Volmer plot.

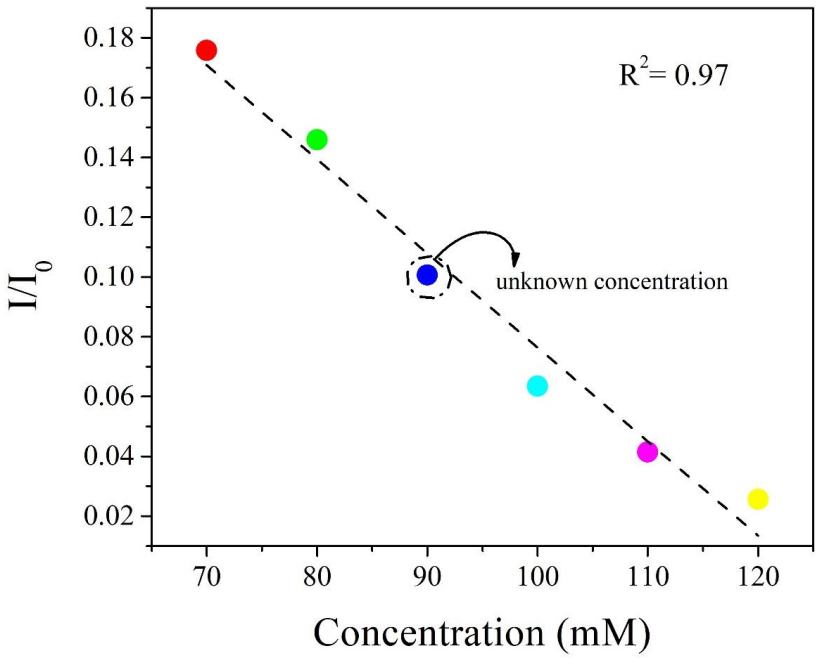

Fig. S9: Plot of "extent of decrease in delayed luminescence intensity" of Zn Au NCs as function of concentration of pyrophosphate in human blood serum.

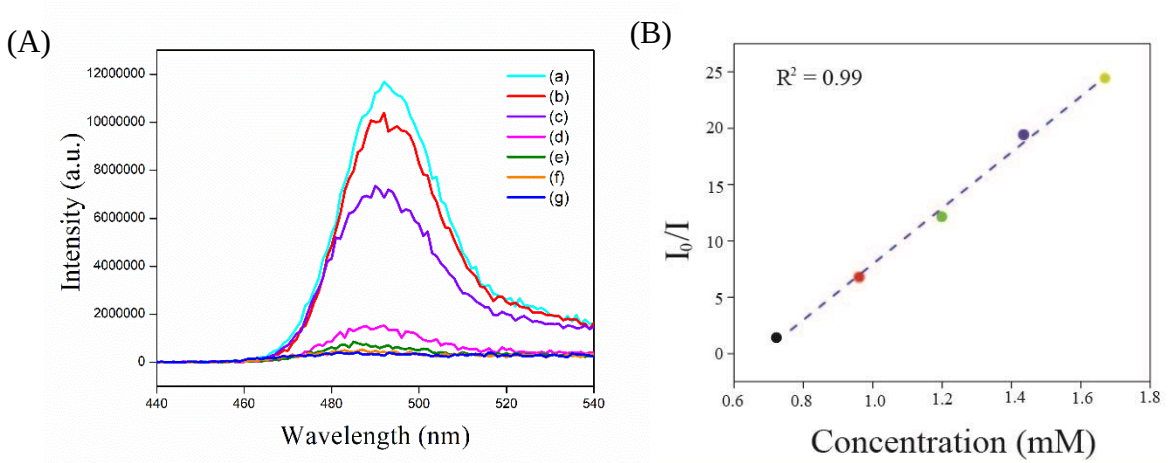

Fig. S10 (A): (a) Delayed fluorescence emission spectrum of Zn Au NCs and that following addition of (b) a mixture of 20 µL of sodium nitrate (100mM), 20 µL of sodium sulphate (100mM) & 20 µL of sodium thiosulphate (100mM). Followed by addition of (c) 15 µL, (d) 20 µL, (e) 25 µL, (f) 30 µL, (g) 35 µL of sodium pyrophosphate solution (100mM). **(B)** Corresponding Stern-Volmer plot.

Additional tables and figures:

Table S4: Comparative study of sensors for recognition of pyrophosphate

SL no.	Reference	Nature of Materials	Advantages	Disadvantages
1.	D. H. Lee, S. Y. Lim, J. I-Hong, *Angew. Chem.* **2004**, *43*, 4777-80	Naphthalene- bis(2-pyrimidyl) amine system	1. High selectivity 2. High sensitivity	1. Based on prompt fluorescence i.e. without delay. This leads to background interference. 2. Complicated methodology involved in fabrication of the sensor.
2.	W-H. Chen, Y. Xing, Y. Pang, *Org lett.* **2011**, *13*, 1362-1365	Binuclear zinc complex	1. Ratiometric sensing 2 Turn on sensor	1. Based on prompt fluorescence i.e. without delay. This leads to background interference.
1.	Y. Li, Z-Z. Huang, Y. Weng, H. Tan, *Chem Commun*, **2019**, *55*, 11450-11453	Alginate hydrogel comprising of copper ions and carbon dots	1. High selectivity owing to interaction between copper ions and pyrophosphate ions	1. Based on prompt fluorescence i.e. without any delay. This leads to background interference.
2.	Current work	Assembly of nanoclusters	1. High selectivity owing to interaction between zinc ions and pyrophosphate ions. 2. Based on delayed fluorescence. Thus any interference from background is eliminated. 3. Simple methodology for fabrication of sensor 4. Long luminescence lifetime enabling elimination of interference of allied analytes 5. Effective in biological media	----------

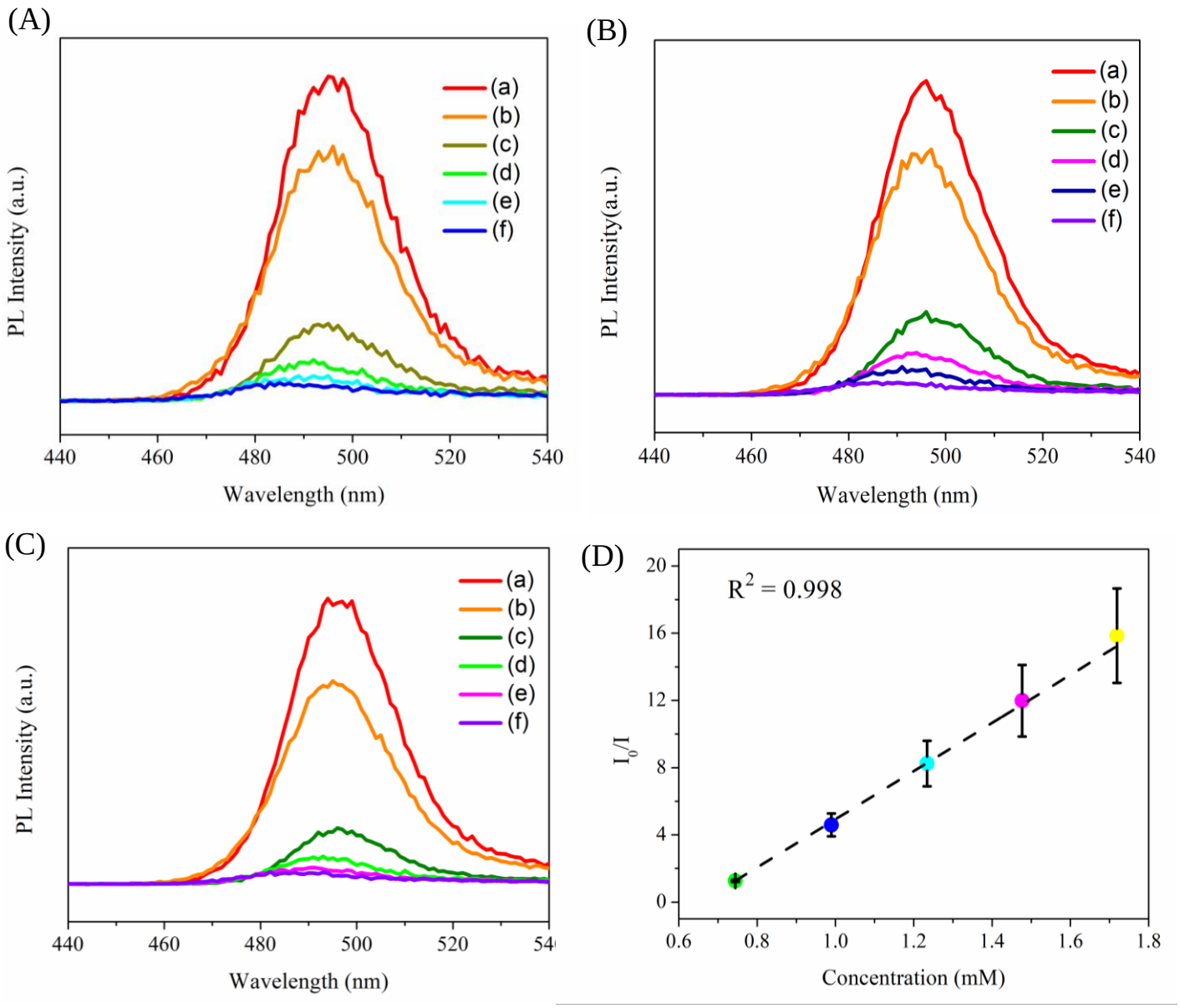

Fig. S11 (A) Delayed emission spectrum of (a) Zn Au NCs and of that following addition of (b) 15 µL, (c) 20 µL, (d) 25 µL, (e) 30 µL and (f) 35 µL of 100 mM of sodium pyrophosphate. (B) Delayed emission spectrum of (a) Zn Au NCs and of that following addition of (b) 15 µL, (c) 20 µL, (d) 25 µL, (e) 30 µL and (f) 35 µL of 100 mM of sodium pyrophosphate. (C) Delayed emission spectrum of (a) Zn Au NCs and of that following addition of (b) 15 µL, (c) 20 µL, (d) 25 µL, (e) 30 µL and (f) 35 µL of 100 mM of sodium pyrophosphate. *The three sets of data were collected in three different batches*. (D) Corresponding Stern Volmer plot.

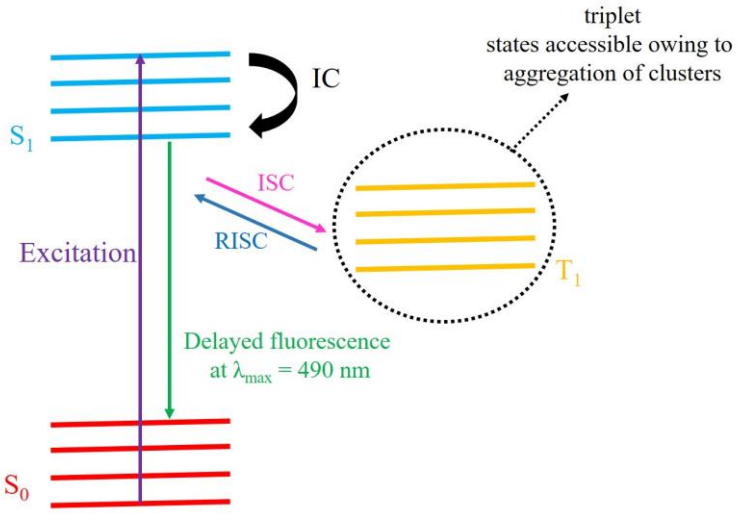

Fig. S12: Schematic representation of the possible energy diagram of the aggregates of Au NCs exhibiting delayed fluorescence

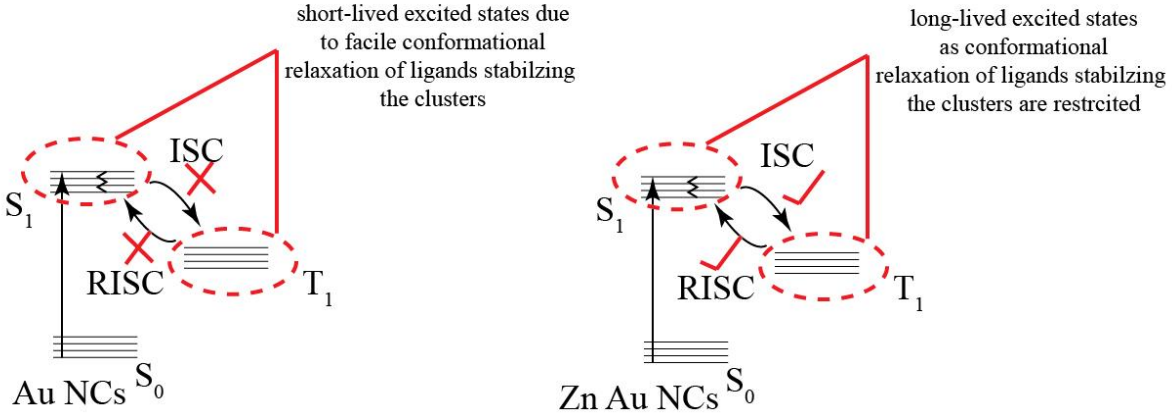

Fig. S10: Schematic representation of the possible energy diagram of Au NCs prior to and following aggregation with zinc ions.

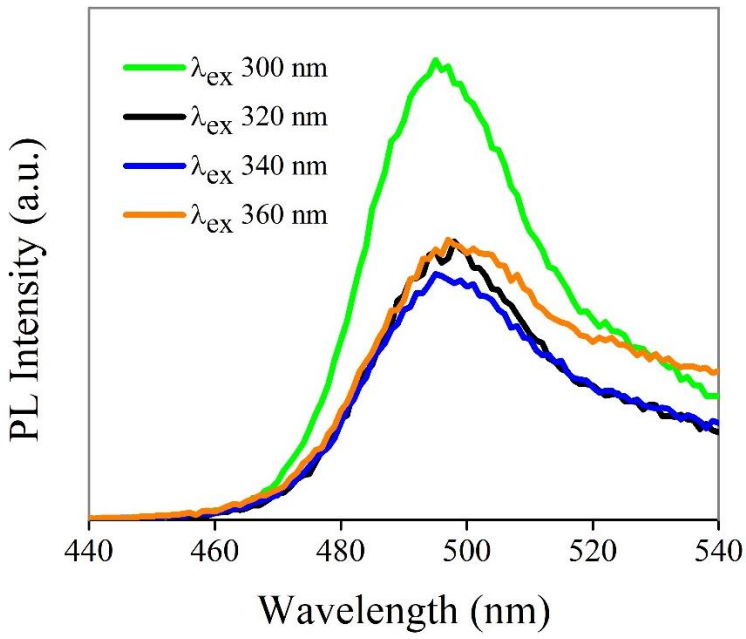

Fig. S13: Excitation dependent delayed emission spectra of Zn Au NCs

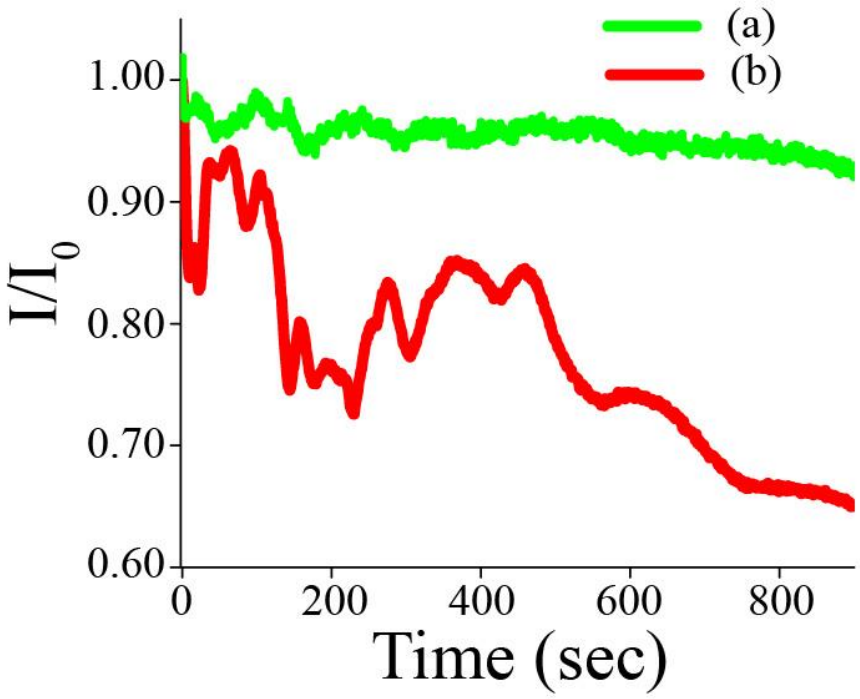

Fig. S14: Effect of photo irradiation on the luminescence intensity of (a) Zn Au NCs and (b) rhodamine 6G, over 15 min. The excitation wavelength was set at 300 nm.

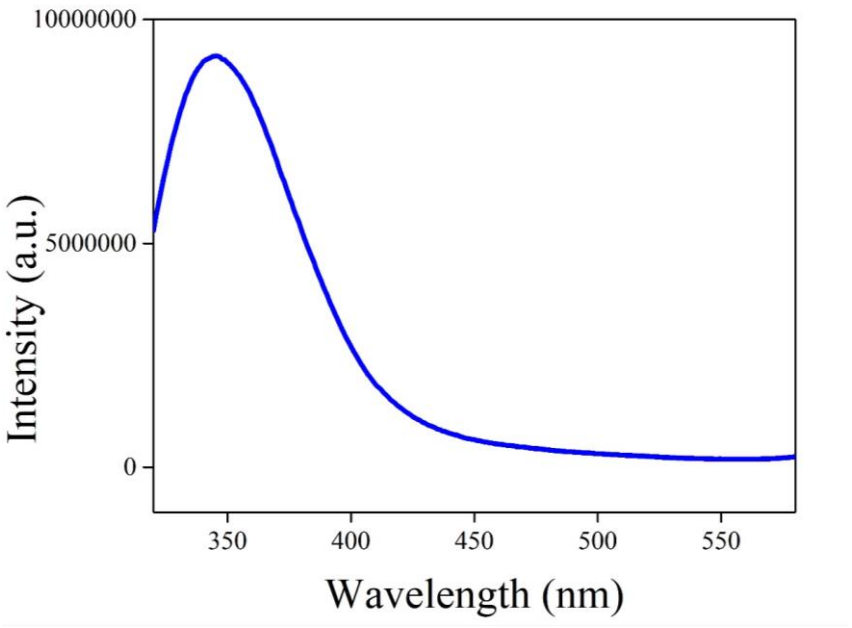

Fig. S15: Luminescence spectrum of human blood serum.

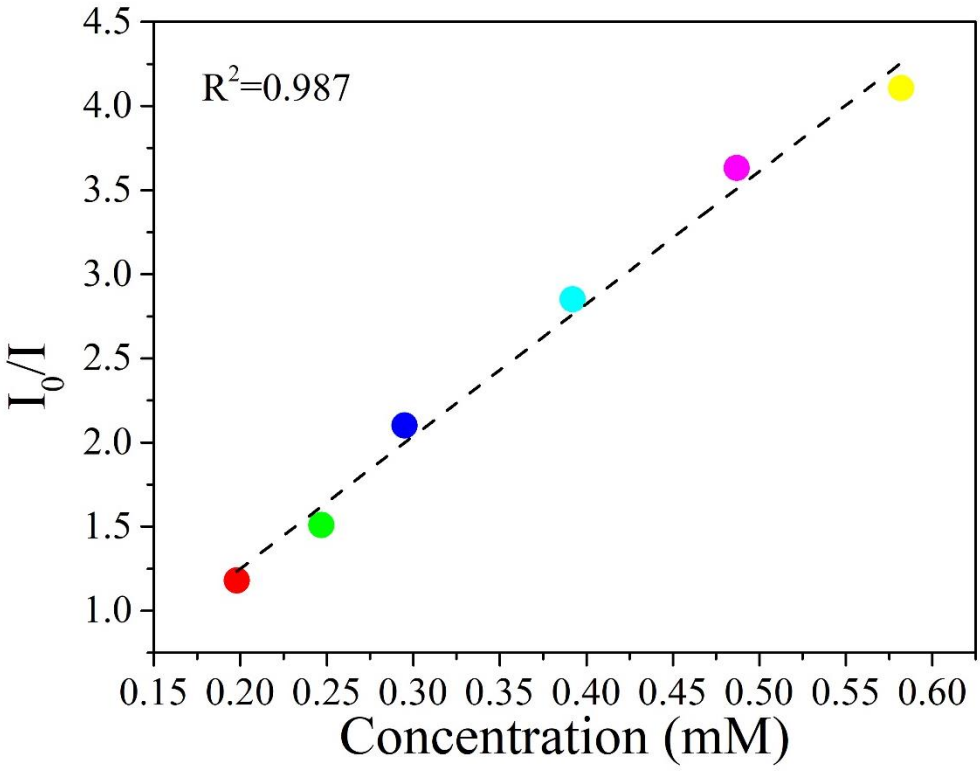

Fig. S16: Calibration curve for determination of limit of detection of pyrophosphate by Zn Au NCs