

Supporting Information

Ultrafast static and diffusion-controlled electron transfer at Ag₂₉ nanocluster/molecular acceptor interfaces

Shawkat M. Aly,[‡] Lina G. AbdulHalim,[‡] Tabot M.D. Besong,[‡] Giada S. Soldan, Osman M. Bakr* and Omar F. Mohammed*

Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

Experimental Section

Instrumentation

Steady-State Measurements. Steady state absorption, fluorescence, and Raman spectroscopies were carried out in freshly prepared solutions in deaerated acetonitrile solution (CH_3CN). A Cary 5000 UV-Vis-NIR spectrometer (Varian Inc.) was used for absorption measurements. A Fluoromax-4 spectrofluorometer (Horiba Scientific) was used to record fluorescence spectra from 550 to 850 nm after excitation at 450 nm.

Electrospray mass spectrometry (ESI-MS) were performed using a Bruker MicroTOF-II. Dilute solution of Ag_{29}NC in acetonitrile (HPLC grade) was electro sprayed at 300 $\mu\text{L}/\text{min}$ flow rate in negative mode. The instrument parameters were maintained as follows: mass range from 100 to 5000 Da, capillary voltage at 2.5 kV, nublizer at 0.4 bar, dry gas 0.1-0.5 l/min at 50°C.

X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Kratos Axis Ultra DLD spectrometer equipped with Al $\text{K}\alpha$ X-ray source.

Sedimentation velocity-analytical ultracentrifugation (SV-AUC) experiments were acquired using an Optima XL-A analytical ultracentrifuge from Beckman Coulter with an absorbance optical detection system and an An-60 Ti rotor. The sedimentation coefficient distributions were calculated using Ultrascan III. ¹ Details about the method can be found in the work reported by Carney *et. al.*²

Nuclear magnetic resonance (NMR) spectra were measured at 298K on a Bruker 600 AVANAC III spectrometer equipped with Bruker BBO multinuclear probe.

FTIR measurements were performed on Cary 680 spectrometer from Varian Inc.

Transient Measurements: Femtosecond transient absorption was collected using an ultrafast Systems Helios UV-NIR femtosecond transient absorption spectroscopy system. Nanosecond transient absorption recorded using EOS-sub-nanosecond transient absorption spectrometer from Ultrafast systems. Samples were measured in deaerated CH_3CN solutions at room temperature using photoexcitation at 350 nm. Helios and EOS detection systems, from Ultrafast systems, with time resolutions of 120 fs and 200 ps and detection limits of 5.5 ns and 400 μs , respectively. The probe beam white-light-continuum probe pulse generated in a 2-mm-thick Calcium Fluoride (CaF_2) plate in an Ultrafast System LLC spectrometer using a few μJ pulse energy of the fundamental output of a Ti:Sapphire femtosecond regenerative amplifier operating at 800 nm with 35 fs pulses and a repetition rate of 1 kHz. For both Helios and EOS a two-channel probe (probe-reference) method is used. In this method the probe beam is split into two before passing through the sample. While one arm travels through the sample, the other is sent directly to the reference spectrometer that monitors the fluctuations in the probe beam intensity. The main advantage of this technique is that it allows the user to achieve the specified signal-to-noise ratio with a lower number of averaged laser pulses. The pump pulses at 650 nm were created from spectrally tunable (240-2600 nm) femtosecond pulses generated in the Optical Parametric Amplifier (Newport Spectra-Physics). The pump and probe beams were focused

on the sample solution, and the transmitted probe light from the samples was collected and focused on the broadband UV-Vis detector to record the time-resolved transient absorption spectra. A setup of the experiment is given in Figure S1.

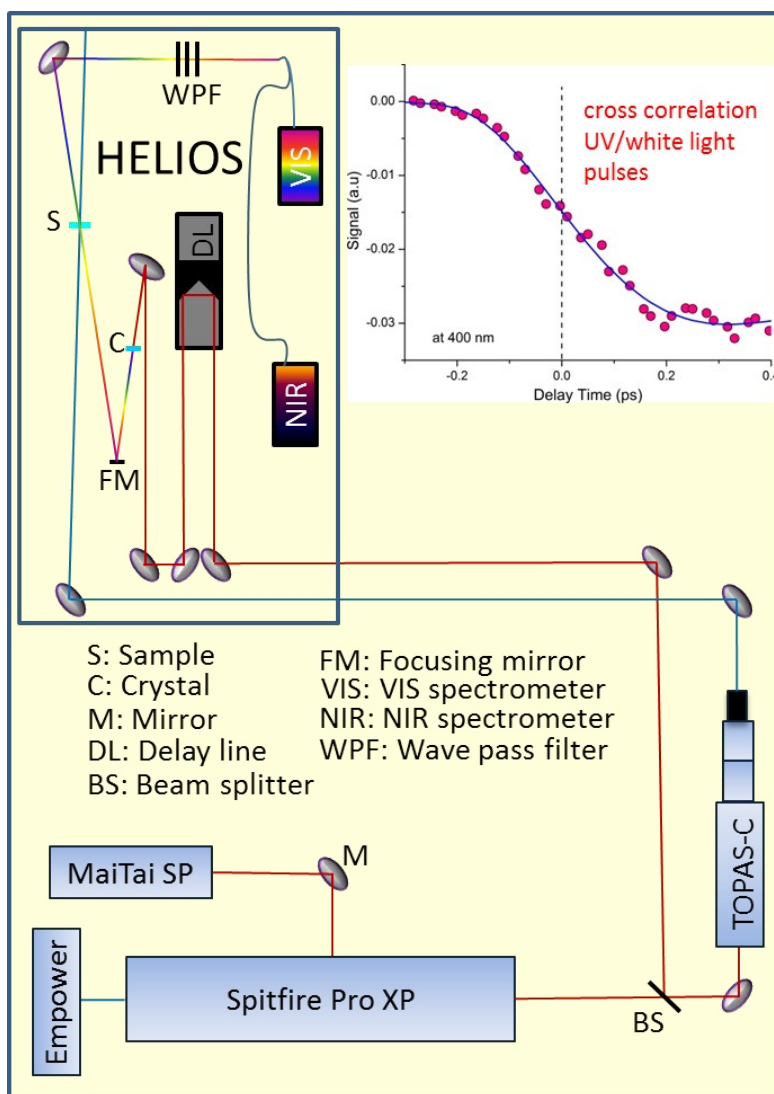


Figure S1: Experimental setup of the femtosecond laser system and the broadband-transient absorption spectroscopy.

Time-correlated single photon counting (TCSPC) measurements were done using a Halcyone ultrafast spectrometer (Ultrafast System). Halcyone is an all-in-one box that uses a PMT detector with a spectral range of 200-700 nm where the instrument response function (IRF) is approximately ~250 ps and a time window up to 200 μ s. This unit is integrated in our existing laser system described above. The samples were measured in 2-mm cuvettes, and a magnetic stirrer was used to ensure that experiments were constantly performed on fresh portions of the sample.

Time constants given in the paper are extracted from kinetic profile using global fit. The Global fit is the Surface Explorer (SX) global fit. It is a commercial software (Ultrafast Systems LLC, Sarasota, FL 34234, USA). In this type of analysis, (wavelength, time) data matrix is corrected for the chirp of the super-continuum probe pulse and the time zero is adjusted for the real time zero using the coherent signal from the solvent. First step of global fit is singular value decomposition (SVD) of data matrix into principal components. Then, during global fit itself SX uses exponential decay kinetics as fit functions for the Principal kinetics. These fit functions are the same as in single kinetics resonant fit (Fit kinetic item in kinetics menu). This step gives us times: t_0 , t_{IRF} and component lifetimes, optimal to fit all principal kinetics. Then SX determines the amplitudes of the components that best fit the 2D surface in all points. For each wavelength these amplitudes are different, but lifetimes are the same. For more information, please see SX manual (sections 7 Fitting Kinetics, 8 Principal components via SVD, 9 Global Fit).

Chemicals and Reagents

All chemicals including silver nitrate (AgNO_3 , 99%), Benzene-1,3-dithiol (BDT, 99%), sodium borohydride (NaBH_4 , 99.99% metals basis), and triphenylphosphine (TPP, 97%) were purchased from Sigma Aldrich and used without further purifications, while methyl viologen dichloride purchased from Acros Organics. Solvents including methanol, dichloromethane and acetonitrile were used from Sigma as received. Distilled water (H_2O) is obtained from Milli-Q (Millipore apparatus).

Synthesis and purification of Ag_{29} NC

In a 20 mL amber glass scintillation vial, 13.5 μL of 1,3-benzenedithiol (BDT) was added to 10 mL dichloromethane. A solution of 20 mg silver nitrate in 5 mL methanol was then added to the reaction vial whereby the color of the solution turned turbid yellow indicating the formation of the insoluble Ag-S complex. Shortly after that, a solution of 200 mg triphenylphosphine in 1 mL dichloromethane was added, and the solution turned colorless indicating the complex formation of Ag-S-P, which completely dissolves in the methanol/DCM mixture. The complex was allowed to stir for ten minutes before the addition of a fresh solution of 10.5 mg NaBH_4 in 500 μL water. The color of the solution turns dark brown immediately, which gradually changed (over the course of 10-12 hours) to orange indicating the formation of NC. The floating NC were centrifuged at high speed (8000 rpm) for 2 min and collected at the bottom of the centrifuge tube. The clear supernatant was discarded, and the dark orange NC was washed several times by ethanol to ensure the removal of all unreacted compounds. The purified Ag_{29} were left to dry overnight under vacuum. **ESI MS** spectrum was recorded using a Bruker MicroTOF-II, see Figure S3. The nanoclusters were dissolved in acetone (HPLC grade) and the solution was electrosprayed at 300 $\mu\text{L}/\text{min}$ flow rate in negative mode. The instrument parameters were maintained as follows: mass range: 100-5000 Da, capillary voltage: 2.5 kV, nebulizer: 0.4 bar, dry gas: 0.1-0.5 l/min at 50 $^\circ\text{C}$.

Sample preparation for steady-state measurements

Two patches of solutions are prepared where the NC concentration is the same as confirmed by steady-state absorption. A stock of the quencher is prepared in one of the two NC patches without changing the concentration of

the Ag₂₉ NC. The desired quenching is then induced in the free Ag₂₉ NC by adding MV2+ dissolved in Ag₂₉ NC thus NC concentration maintained constant during the measurements.

Characterization of Ag Ag₂₉ NC

Sedimentation velocity data was acquired on a Beckman XLA analytical ultracentrifuge at 20.0°C, 440nm and 40000 rpm and data was collected for 5-6 hours. Data analysis was carried out with Ultrascan 3.0^[1] version 1996 using 2-Dimensional Spectrum Analysis (2DSA) with 80 Monte Carlo iterations. A Varian 730-ES Spectrometer (Varian Inc., The Netherlands) was used for ICP-OES (inductively coupled plasma – optical emission spectroscopy) analysis with the solutions presented to the spectrometer using the Varian SPS3 (Sample Preparation System). Three standard solutions was used for calibration and, in addition, two quality controls (continuous calibration verification) was employed to verify the calibration, for all elements of interest (Ag, Na, P and S). The thermo-microbalance TG 209 F1 Iris (Netsch, Germany) was employed for thermogravimetric analysis with decomposition monitored between 0 – 1000°C. Elemental analysis was conducted on the Organic Elemental Analyzers FLASH 200 series (Thermo Fisher Scientific). Four calibration standards and two quality controls (commercially available) were used to prepare the instrument. This was followed by the analysis of 3 samples (2mg each) of Ag₂₉ NC and oxidation was carried out at a temperature of 900°C.

In order to assess the purity and composition of the Ag₂₉ nanocluster, it was analyzed with analytical ultracentrifugation, ICP-OES, thermogravimetric and elemental analyses. Four batches of the Ag₂₉ NC were synthesized in acetone (with one batched dissolved in DMF) and subjected to sedimentation velocity in the analytical ultracentrifuge (SV-AUC – see Figure S5 and Table S1). In all cases, a high degree of purity and monodispersity was observed as evidenced from a major sedimenting component (98 ± 2 %) in the presence of minute amounts of minor components (Table 1). The sedimentation coefficient of the major component is consistent with the monomeric species of the Ag₂₉ NC. This component is observed to sediment with a sedimentation coefficient of 3.65±0.06 (Table S1; Figure S5). Figure S10 shows the decomposition profile of the Ag₂₉ clusters under a controlled temperature environment (0-1000°C). The profile is typical for samples consisting of organic and inorganic components and the initial mass loss (~11.7%) from 40-250°C is attributed to residual moisture in the sample following synthesis and drying. A recalculation of the final residual mass to exclude the moisture content after thermal decomposition of the organic components results in an inorganic composition of 53.9%, which is in line with theoretical calculations of 53.4%. The residual mass is made almost entirely of Ag given the very low levels of sodium detected via ICP-OES (Table S2). The detected sodium comes from residual NaBH₄ that was used as a reductant during synthesis, most of which was removed following synthesis. For ICP-OES analysis, it is often useful to determine the ratio of the detected elements in a given sample. The experimental results compare well with the expected theoretical ratios of the detected elements (Table S2). Elemental analysis in the Flash 2000 Combustion CHNS Analyzer (Thermo Fisher Scientific) detected 29.7 (± 1.5) % of carbon, 2.2 (± 0.1) % of hydrogen and 12.5 (± 0.6) % of sulphur and these are in line with theoretical calculations (29.5%, 1.8% and 13.2 %, respectively) (Table S3). Taken together, these results show that the Ag₂₉ NC used in these experiments displayed high levels of purity (~96%) and monodispersity.

Table S1 Summary of Sedimentation velocity analysis of Ag₂₉ NC in acetone following synthesis and characterization of 3 separate batches.

Solution components	Sedimentation coefficient (S)	Diffusion coefficient (cm ² /s)	%	
1	3.65 ± 0.06	2.64 ± 0.21	95.96	± 1.99
2	4.38 ± 1.02	1.95 ± 0.35	1.80	± 1.41
3	5.01 ± 0.49	2.34 ± 0.12	1.39	± 0.81
others			0.84	- -

Table S2 ICP-OES Elemental analysis of Ag₂₉ NC

	Ag	S	P	Na
Concentration (µg L⁻¹)	40.77 ± 1.68	10.07 ± 1.25	1.69 ± 0.82	0.20 ± 0.04
Experimental ratio of elements (Ag : S : P)	1.000	0.247	0.041	-
Theoretical ratio of elements (Ag : S : P)	1.000	0.246	0.040	-

Table S3 Elemental analysis of Ag₂₉ NC (C/H/O/S)

Theoretical						Experimental
Elements	# of atoms	M _w (g/mol)	Atomic masses	Weight fraction	Weight %	Weight %
Ag	29	107.8	3126.2	0.53	53.4	53.9 ± 2.8*
C	144	12	1728	0.3	29.5	29.7 ± 1.5
H	108	1	108	0.02	1.8	2.2 ± 0.1
P	4	31	124	0.02	2.1	-
S	24	32.1	770.4	0.13	13.2	12.5 ± 0.6
Total	-	-	5856.6	1	100	-
*From Thermogravimetric analysis						

UV-Vis and Emission of Ag₂₉ NC

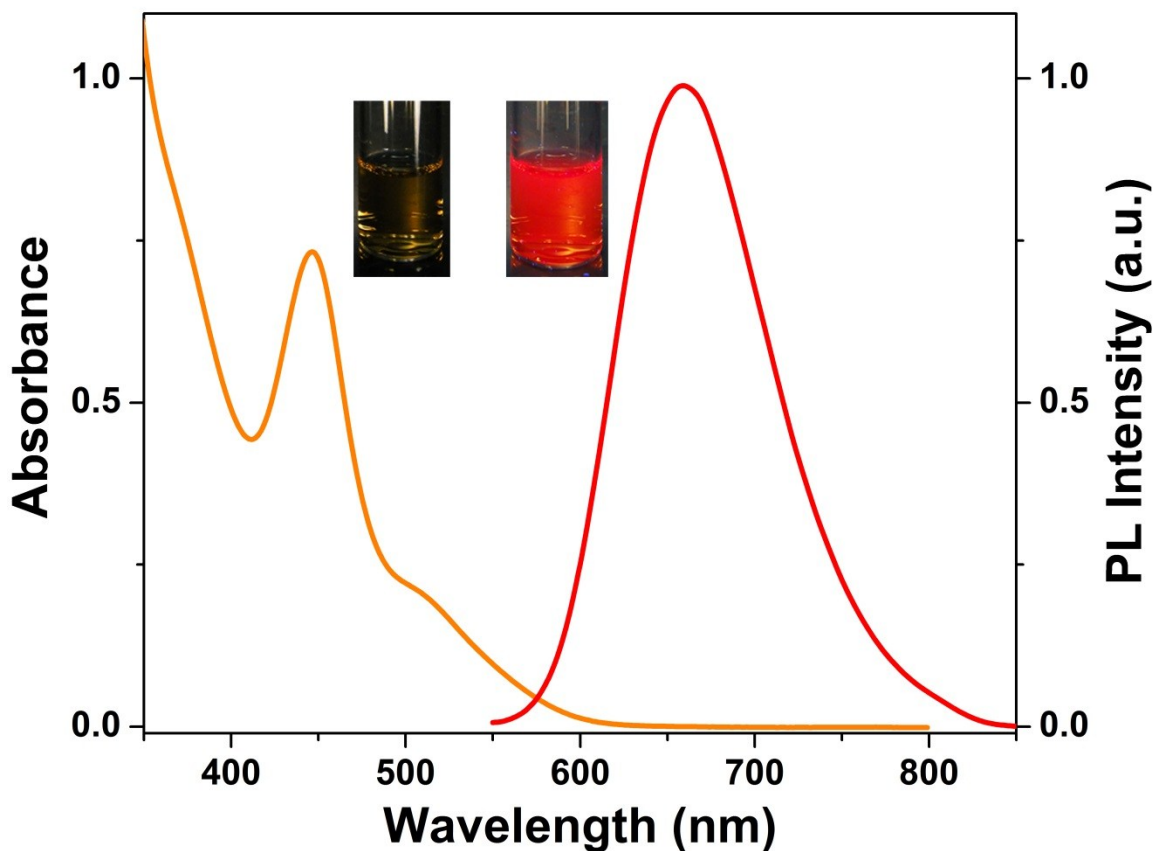


Figure S2. UV-Vis absorbance (orange) and emission (red) using λ_{ex} at 450 nm of Ag_{29} NC in CH_3CN . Inset shows photographs of Ag_{29} under normal (left) and UV light (right).

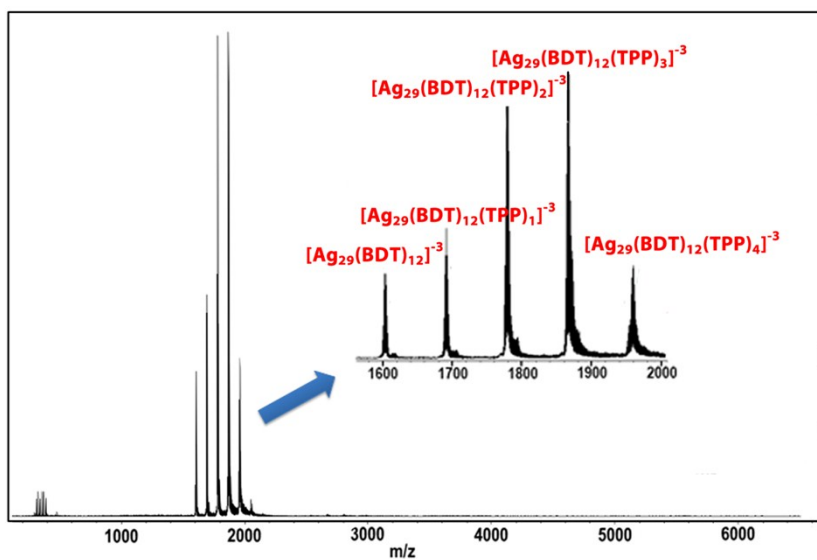


Figure S3. Negative ion mode ESI MS of $[\text{Ag}_{29}(\text{BDT})_{12}\text{TPP}_4]^{-3}$ indicating the presence of one species only with a charged state of -3. Phosphines are lost during ionization.

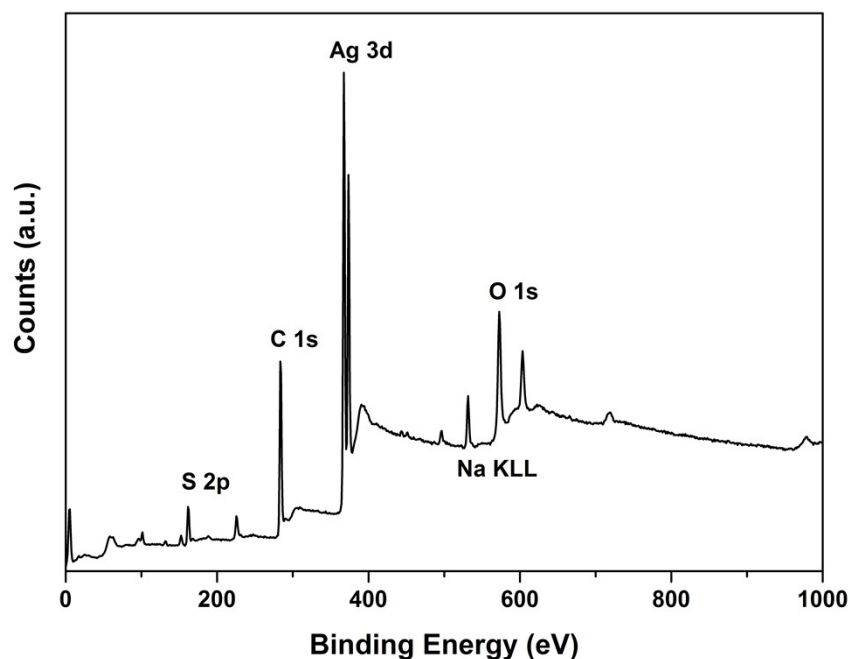


Figure S4. XPS survey spectrum of Ag₂₉ NCs drop-casted on glass/ITO substrate confirming the presence of Ag, S, C, O and residual amount of Na; no other elements were detected indicating the high purity of the sample.

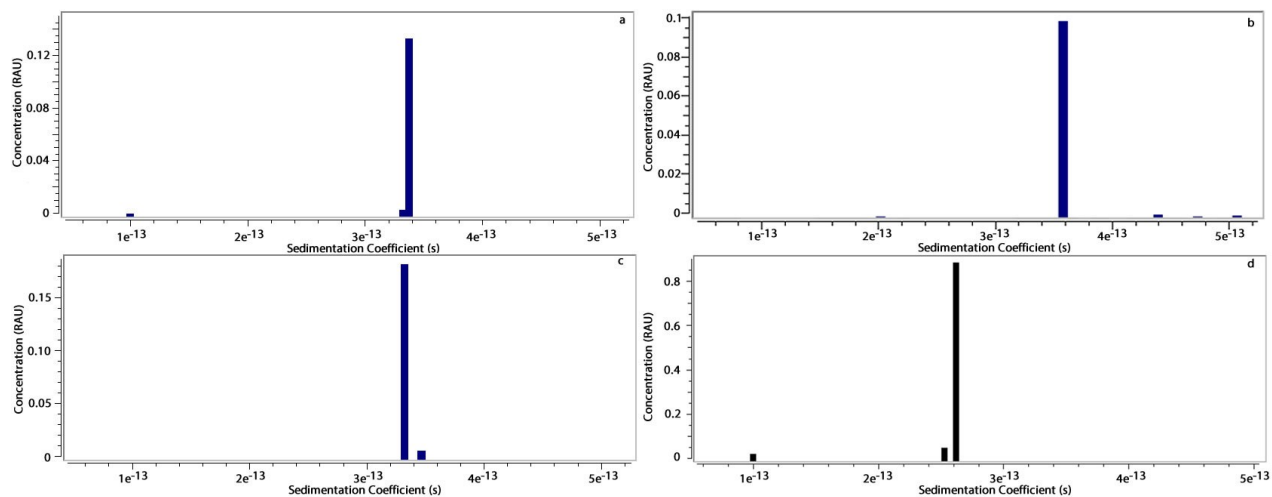


Figure S5 Sedimentation Velocity analysis plot of sedimentation coefficient against relative particle concentration for Ag₂₉ NC in acetone. Analysis of 3 separate batches in acetone (a, b, c) and DMF (d) indicating high level of purity and monodispersity. A major component (~93-96%) can be seen sedimenting with a sedimentation coefficient of 3.65 ± 0.06 S in the presence small amounts of a few minor components (~2-4%).

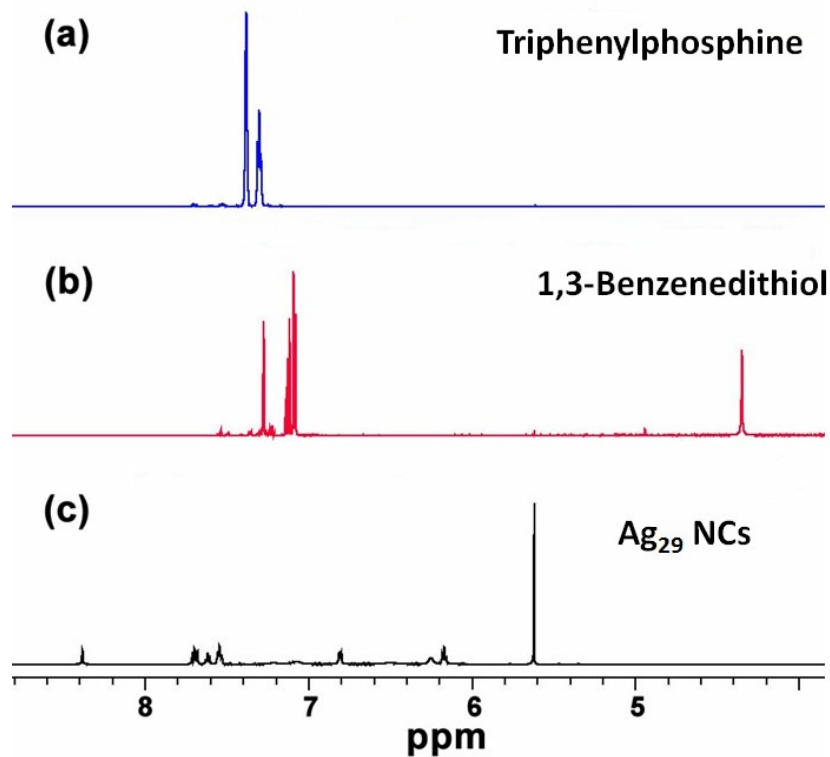


Figure S6. Aromatic region of ^1H NMR spectra of (a) free triphenylphosphine; (b) free 1,3-benzenedithiol ligands and (c) Ag_{29} NCs dispersed in deuterated acetone. Exact assignment of peaks is difficult in the case of the Ag_{29} NCs, but the apparent shift and broadening of the peaks indicate the formation of the NCs and the absence of any starting materials.

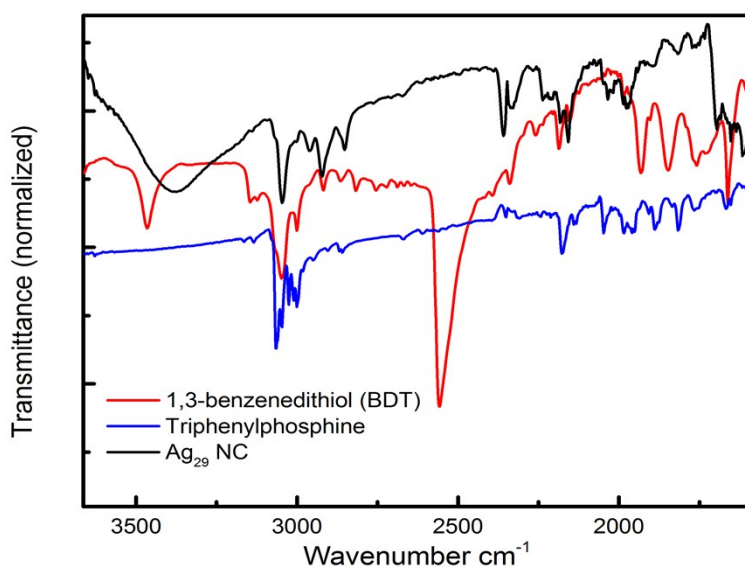


Figure S7. FTIR of 1,3-benzenedithiol (red), triphenylphosphine (blue) and Ag_{29} NC (black). The $-\text{SH}$ stretching of BDT disappeared in Ag_{29} NC confirming complexation.

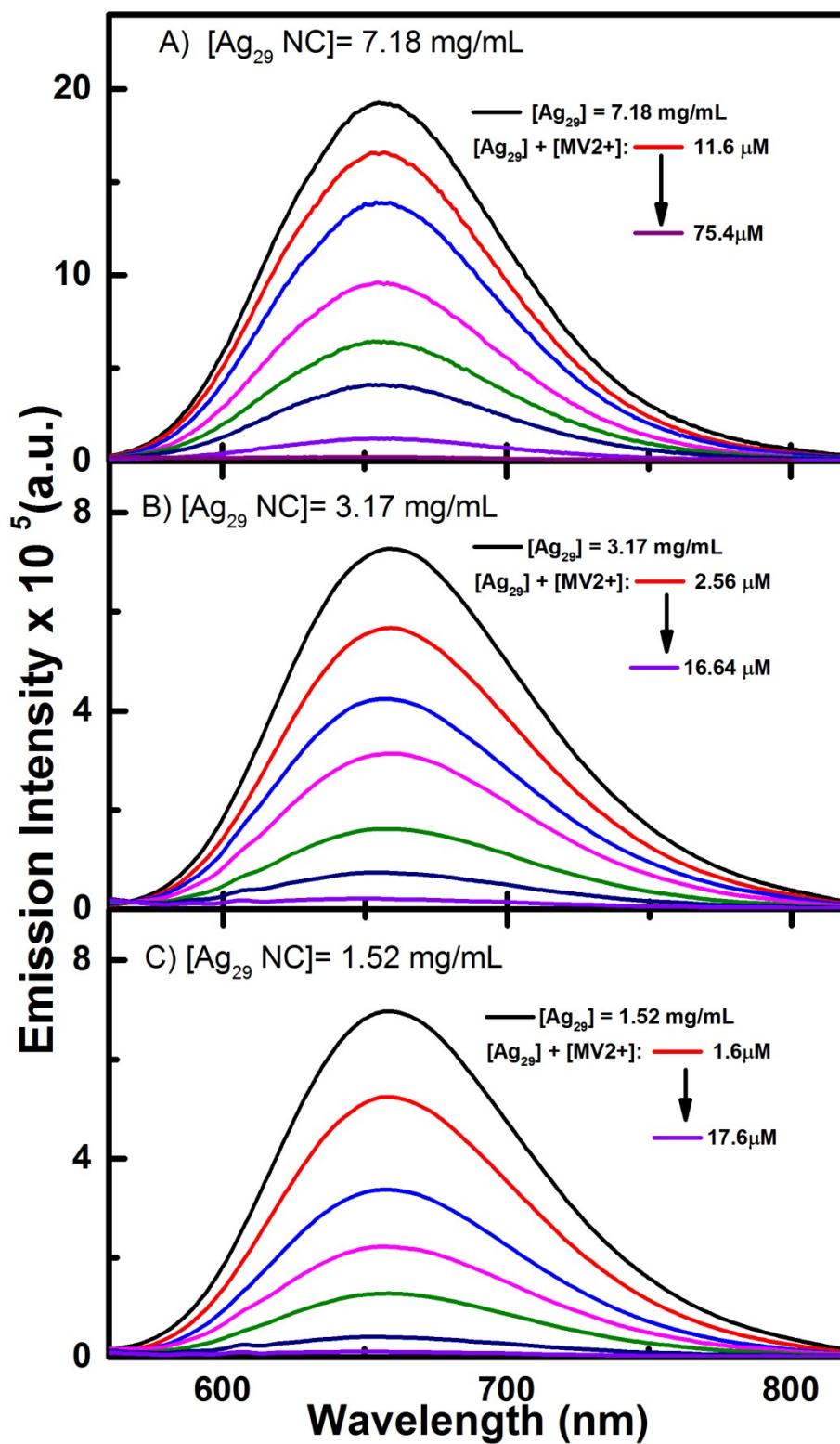


Figure S8. Luminescence quenching of three different concentrations of a deaerated CH_3CN solution of Ag_{29} NCs (concentrations are given on the graph) upon the addition of MV^{2+} .

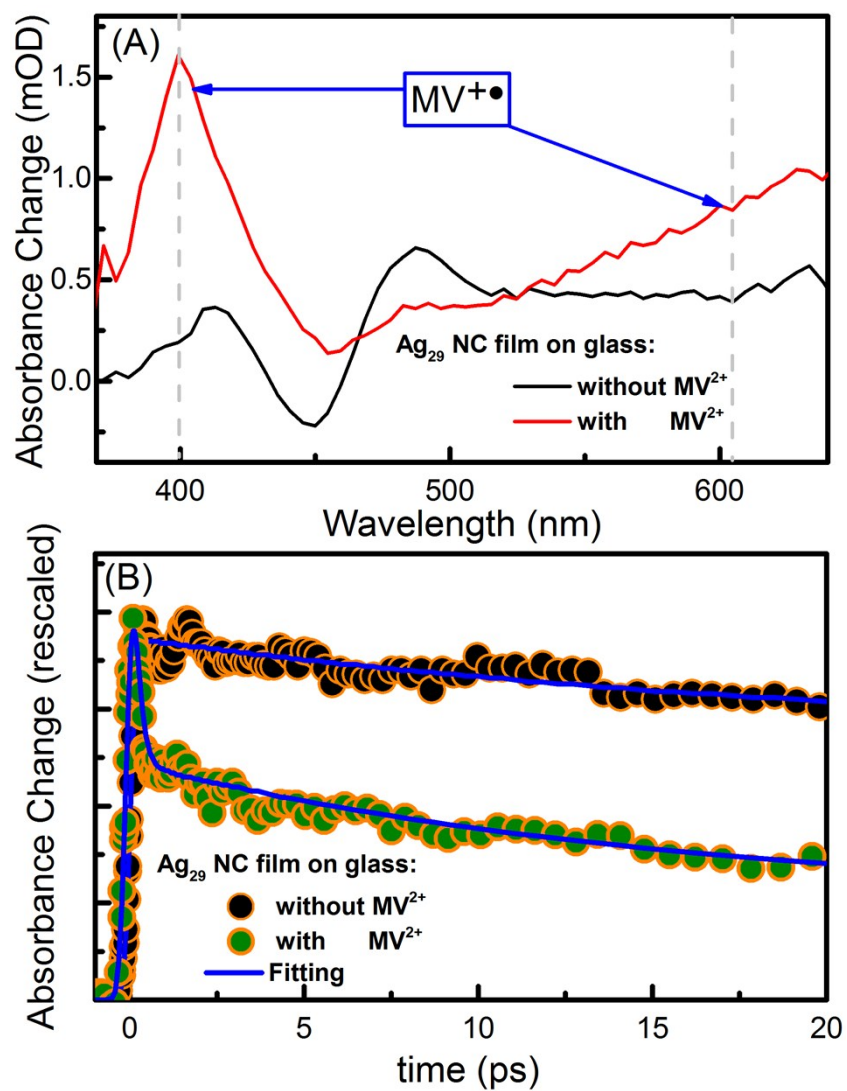


Figure S9. Femtosecond transient absorption of Ag_{29} NCs film on glass in the presence (red) and absence (black) of MV^{2+} collected at 1.5 ps delay time and excited state dynamic at 480 nm after laser excitation at 350 nm.

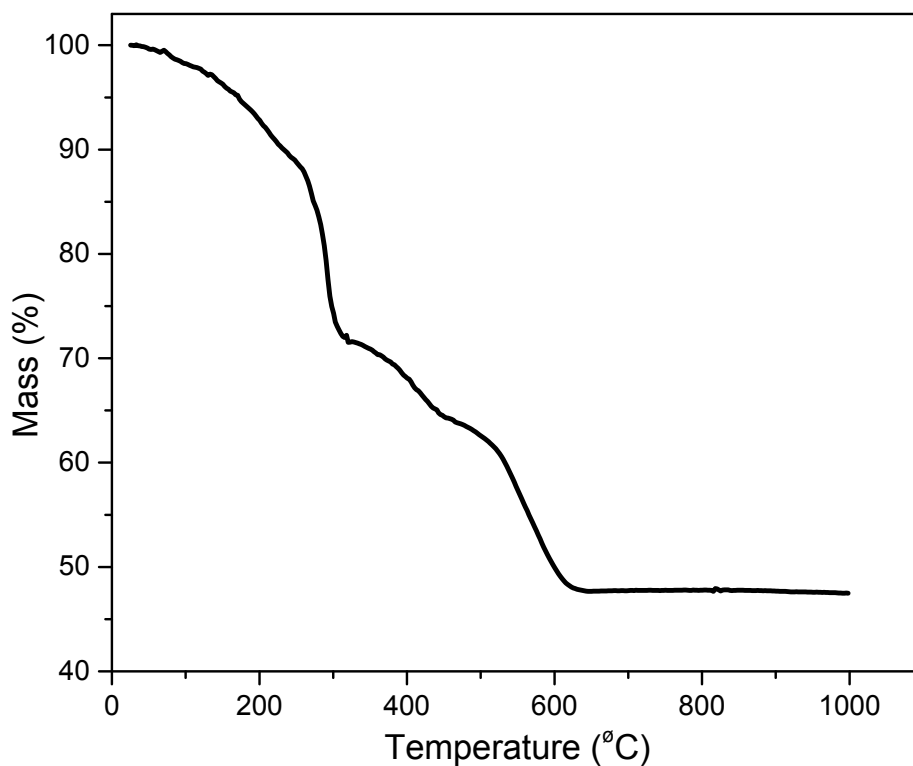


Figure S10 Decomposition profile of Ag₂₉ NC as a function of temperature in Thermogravimetric analysis. The initial 11.7% loss of mass is attributed to residual water in the sample. A recalculation of the final residual mass gives a value of 53.9% and is in agreement with theoretical calculations (53.4%).

References:

1. B. Demeler, in *UltraScan-III version 2.0, a Comprehensive Data Analysis Software Package for Analytical Ultracentrifugation Experiments*. The University of Texas Health Science Center at San Antonio, Department of Biochemistry.
2. R. P. Carney, J. Y. Kim, H. Qian, R. Jin, H. Mehenni, F. Stellacci and O. M. Bakr, *Nat. Commun.*, 2011, **2**, 335.