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Synthesis of Fluorescence emitting Ag-nanoparticles via Chemical reduction method

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Abstract : In the present work, the formation, morphology, and photophysical activity of Dithizone-capped Ag-nanoparticles (Ag-NP's) were carried. The Ag-NP's with uniform shapes and sizes are often obtained by the tactic proposed during this work. the tactic utilizes an easy reaction of iodide and Sodiumborohydride. The benefits of the tactic are the convenience of preparation, convenience in use, and particularly, that the obtained Ag-NP's are uniform in their shapes and sizes. The last point is vital for fluorescence measurements because the shapes and sizes of the metal nanoparticles are significant parameters.

Keywords: Fluorescence, Ag-nanoparticles, Chemical reduction method.

Introduction:

Recently, fluorescent nanoparticles, have attracted much attention for a spread of purposes and applications in biology and medicine, for instance, in immuno-labeling,¹ as cell markers,² in cell motility assays,³ in biological assembly,⁴ and particularly in optical imaging agents,⁵ thanks to their photostability and other excellent optical properties. Thanks to the urgent need of environmentally-friendly fluorescent nanoparticles, the emerging carbon dots (CDs) appear to be a promising alternative to semiconductor QDs in many applications like bioimaging, disease detection, and drug delivery⁶⁻⁸ due to their superiority in chemical inertness, biocompatibility, low toxicity, cheaper cost and promising up-conversion property.^{9,10} However, the fluorescent intensity of Carbon Dots is comparatively low in most reports,¹¹ but metal (such as gold or silver) has an enhanced effect on the fluorophore, as referred to as metal-enhanced fluorescence (MEF).^{12,13}

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It's well established that the interactions of fluorophores with silver nano particles leads to an increased photostability, fluorescence enhancement, and a decreased lifetime thanks to increased rates of system decay.¹⁴ The fluorescence enhancement noted in these studies can stem from a mechanism of Surface Plasmon Resonance.¹⁵

Excellent overlap of the CDs absorption/emission spectrum with the scattering spectrum of the silver surface is required for effective surface plasmon resonance, while CDs show a broad absorption and spectrum, which provides an honest overlap with the silver scattering spectrum.¹⁶ The spontaneous emission of sunshine by molecules and atoms at nano structured metallic surfaces is remarkably modified thanks to a posh interplay of enhancing and quenching physicochemical processes. Fluorescence enhancement are often promoted by surface plasmons excited in metal and by a modified density of photon states during a nano structured surface,¹⁷ while quenching processes include chemical bonding and non radiative energy transfer from the luminescent species to the metal. Importantly, the degree of metal-fluorophore interactions strongly depends on the space between the fluorophore and therefore the metal surface.

Synthesis of the Silver Nanoparticle Assembly:

Dithizone-Capped Ag-NP's:

A total of 2.5 mL of 10^{-2} M AgNO_3 was added to 75 mL of triply distilled water. After 10 min 2.5 mL of 10^{-2} M NaI was dropped into the solution slowly, yielding a green yellow AgI colloid. A total of 20 mg of NaBH_4 was added to the AgI colloidal solution, and the reaction mixture was continually stirred. Immediately after addition of NaBH_4 , a total of 5 mL of 10^{-2} M Dithizone (dissolved in hot water) was added as stabilizer to the solution with stirring. The silver colloid was finally obtained. During the whole reaction, the color of the colloidal solution changed from green-yellow to nut-brown, and then to black.

Results and discussion:

Evolution and Characterization of Ag-NP's Aggregates:

Scanning electron microscopy study:

The SEM images obtained for colloid is shown in figure 1. It is clear from the SEM images in figures 1 that the particles are nearly crystalline, rod-like and spherical particles respectively.

The Scherrer rings, characteristic of fcc silver is clearly observed, showing that the structure seen in the SEM image are nano crystalline in nature. It is observed that the silver nanoparticles are scattered over the surface and no aggregates are noticed under SEM. The difference in size is possibly due to the fact that the nanoparticles are being formed at different times. Scanning electron microscopic (SEM) measurement of the synthesized nanoparticles showed the particles have rod like shape.

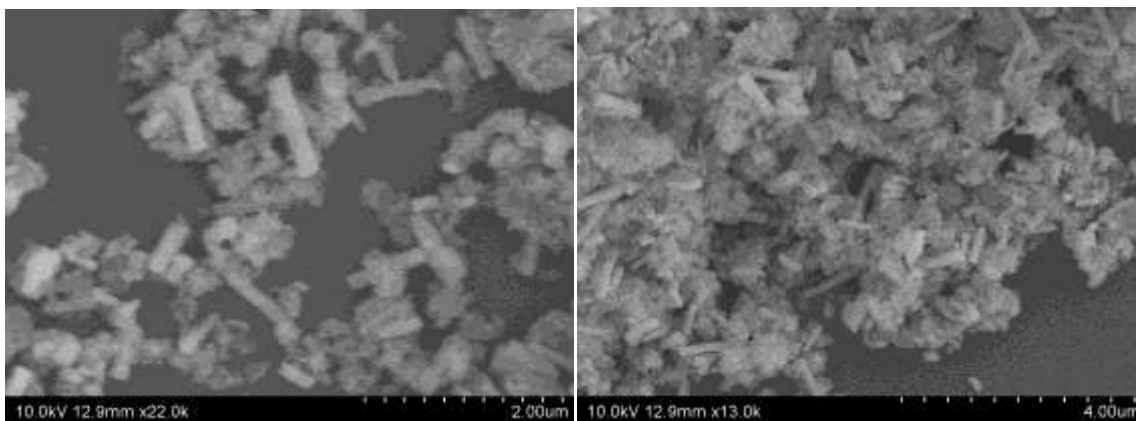


Figure 1: SEM images of synthesized Dithizone capped silver nanoparticles

X-ray diffraction study:

XRD spectra of Ag-NPs measured in the small and wide angle region are shown in Fig. 2. The XRD spectrum confirms the tendency of nano particles to form the organized structures, as seen from the peaks in the small angle XRD spectrum in Fig. 2. The wide angle XRD pattern of Ag nano particles is shown in Fig. 2. The peaks are broadened because of the nano crystalline nature of silver nanoparticles. By comparing with standard database values, all the peaks can be indexed to face-centered cubic (fcc) silver crystal structure. Fig. 2, shows four peaks at 2θ values of 38.166, 44.346, 64.549 and 77.508 corresponds to the planes (111), (200), (220) and (311), respectively.

The XRD of different particle sizes of Ag-NPs capped with dithizone prepared in water as solvent. From this figure, it can be noticed that the particles appeared basically amorphous and abroad. Size-dependent and structure-specific features in diffraction patterns can be quite striking in nano meter-sized particles. Small particles have fairly distinct diffraction patterns, both as a function of size and as a function of structure type.

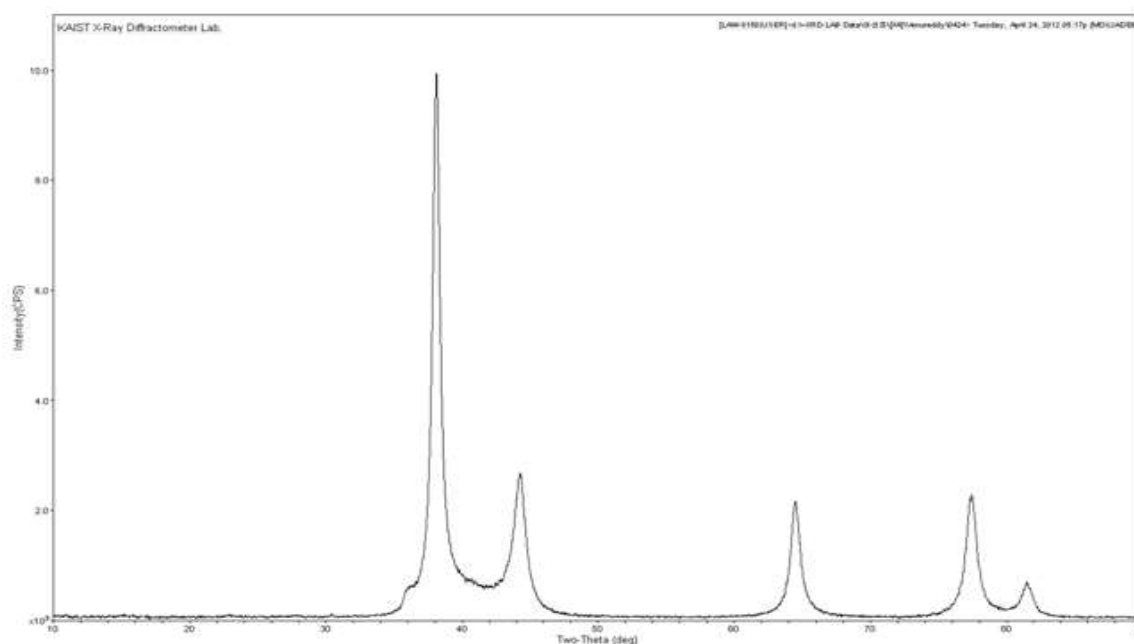


Figure 2: XRD patterns Dithizone capped silver nanoparticles

FT-IR analysis:

The IR spectra of the free dithizone and the particles capped by dithizone are given in Fig. 3. The IR spectra of the nano particles and the free dithizone molecule are similar to one another, indicating that the organic molecules have indeed become a part of the nano particles. However, are markable difference in the peak intensity is found between the peaks of IR spectra of free dithizone and dithizone capped Ag-NP in Fig. 3. The reason for the intensity difference between the spectra is believed to be the thiolate molecules on the nano particle forming a relatively closely packed thiol layer and molecular motion beingconstrained. Thus, this steric constraining effect on the transverse mode (rocking mode, wagging mode, etc.) is stronger than that on the longitudinal mode (stretching mode, etc). Therefore, the change of the peak intensity of the longitudinal modes is smaller than that of the transverse mode. The C–S stretching mode is due to the position of the C–S bond nearest to the surface of the silver particle, and a chemical bond can form between S and Ag atoms.

The FTIR spectrum of the nano crystals provides additional information about the local molecular environment of dithizone. The FTIR spectra of the free dithizone and Ag nanoparticle capped by dithizonethiol are represented in Fig. 4. From the spectrum of free dithizonethiol, it can be noticed that the azo group appeared at 1580 – 1650 cm^{-1} , respectively. The weak band appeared at 2360 cm^{-1} is attributed to the S–H stretching vibration mode. The two bands appeared between 1380and 1240 cm^{-1} are assigned to the stretching vibration of C–N group. The band appeared at 1627 - 1690 cm^{-1} is attributed to the N–H primary stretching group. The band

appeared at 756cm^{-1} is assigned to C–S stretching mode. Generally, the vibrational spectrum of Ag-NPs capped with dithizonethiol molecule is similar to the spectrum of dithizonethiol indicating that, the organic molecules have indeed become a part of the nanoparticles.

However, there is a remarkable difference in the peak intensity found between the peaks of the transverse mode (rocking mode, bending mode, etc.) in dithizone and Ag nanoparticles capped by dithizone. The reason for the intensity difference between the spectras is believed to be that the thiolate molecules on the nanoparticle form are relatively close packed thiol layer and molecular motion is constrained. Thus, this steric constraining effect on the transverse mode is stronger than that on the longitudinal mode. Therefore, the change of the peak intensity of the longitudinal modes is smaller than that of the transverse mode. The small peak at 2360 cm^{-1} which corresponds to the S–H stretching vibration mode, disappears when the dithizone molecules adsorb on the silver particle surface (comparing spectra of free dithizone(3a) and Ag-NP capped by dithizone, giving strong evidence that dithizone anchors on the silver surface through the sulfur atom in the mercapto group.

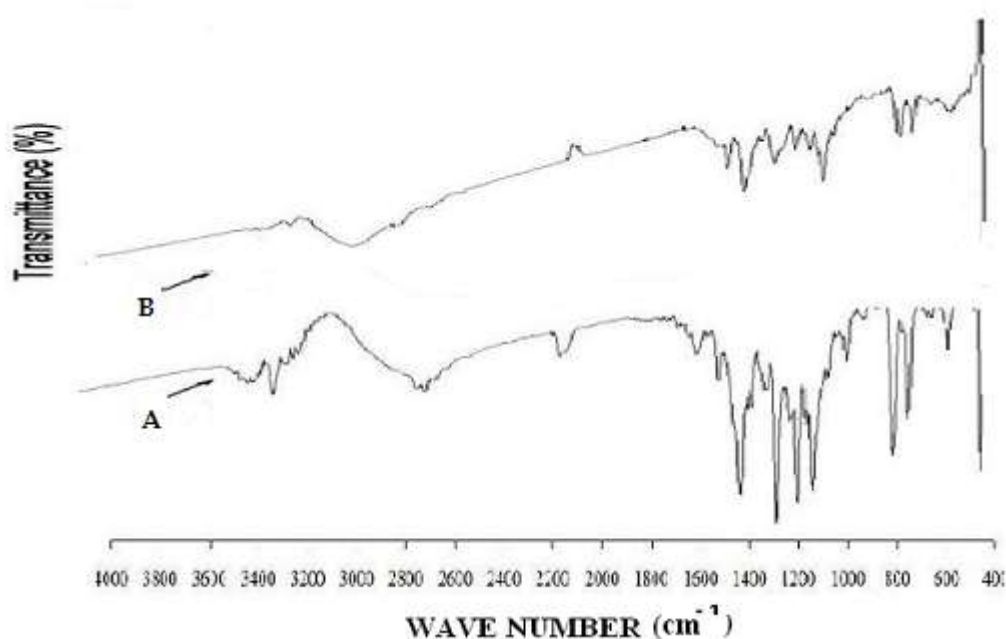


Fig. 3: FT-IR spectra of (A) Dithizone; (B) Dithizone capped AgNP.

Photophysical properties of the new Dithizone capped AgNPs:

Chemicals & Spectroscopic measurements:

Dithizone was purchased from Sigma and was used without further purification. Fluorescence spectra were measured on a Shimadzu spectrofluorometer. The optical path was 1 cm and spectra were collected at a resolution of five data points per nanometer. When recording fluorescence spectra the total absorption in no case exceeded 0.06, making the necessary correction for the inner filter effect small.

Results & Discussion:

The above synthesized Dithizone capped Ag-NP (0.1mmoles) were dissolved in three different solvents (DMSO, THF & CHCl_3) to study their photoluminescence activity. Figure 4 shows the luminescence of Dithizone (Left) & Ag-NP (Right) in DMSO at (a) daylight and (b) UV-lamp of 254 nm excitations respectively. Basing on this reference, the fluorescence studies were carried to our synthesized silver nanomaterials. Figures 5 and 6 shows the fluorescence emission spectra for synthesized silver nanoparticles

&Dithizone in THF & CHCl₃ respectively. The emission spectra were recorded for these systems, in which fluorescence excitation wavelength was fixed.

Silver nanoparticles in DMSO showed fluorescence emissions at 479nm. Whereas dithizone in DMSO showed 522nm emission which is little bit more than the synthesized nanoparticles. From absorption and emission spectra's the stokes shifts observed as 58nm. The detailed description with Stokes shifts were presented in table-1.

Silver nanoparticles in THF showed fluorescence emissions at 466nm. Whereas dithizone in THF showed 467nm emission. From absorption and emission spectra, stokes shifts observed as 56nm. The detailed description with Stokes shifts were presented in table-1.

Silver nanoparticles in CHCl₃ showed fluorescence emissions at 507nm. Whereas dithizone in CHCl₃ showed 499nm emission. From absorption and emission spectra, stokes shifts observed as 39nm. The detailed description with Stokes shifts were presented in table-1.

Hence, it is clearly evident that these Ag-NPs are suitable biomarkers and further studies regarding the biomasking will be produced later.

Fluorescence Data

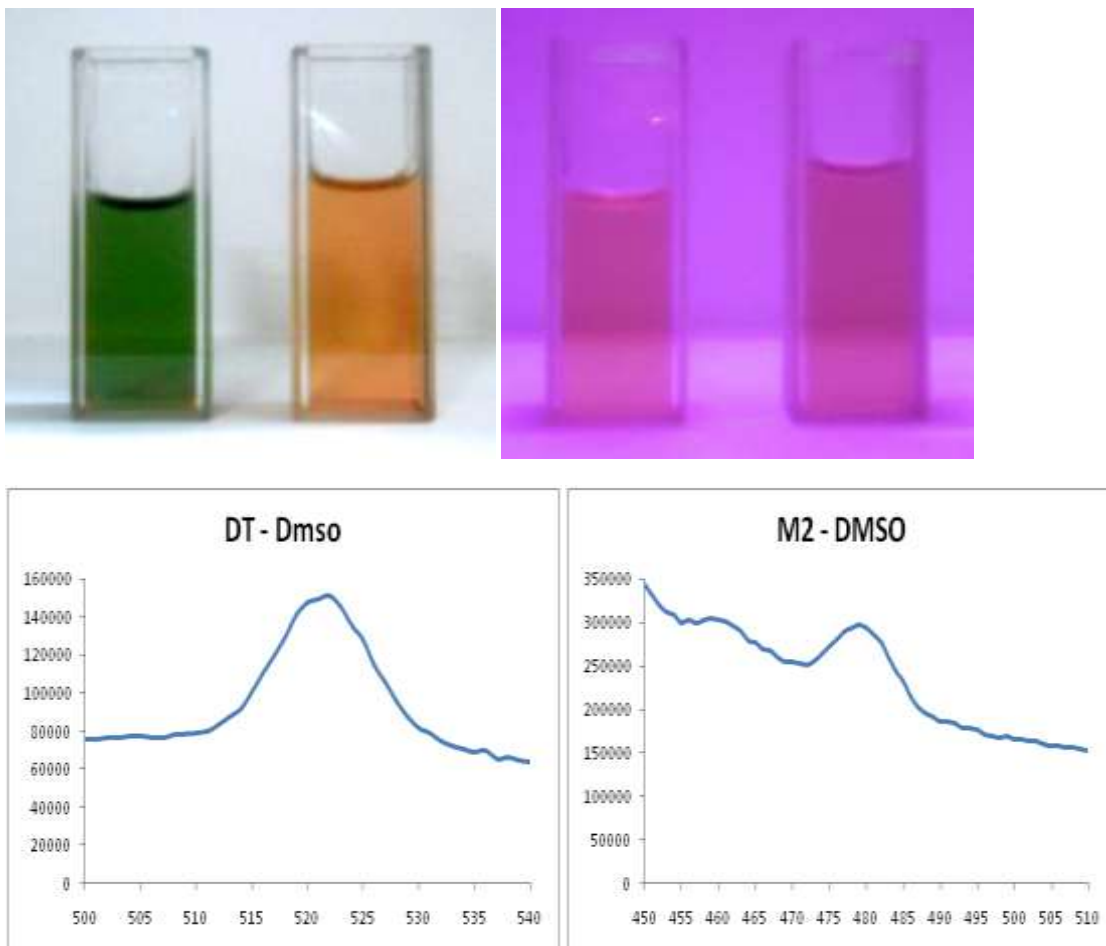


Figure 4. Emission colors of fluorescent Dithizone capped AgNPnanoclusters excited with a UV lamp (Left - In day light; Right – In UV lamp@254 nm) in DMSO solvent. Lower figures: Fluorescence spectra's exhibited by Dithizone& synthesized AgNP's in DMSO solvent.

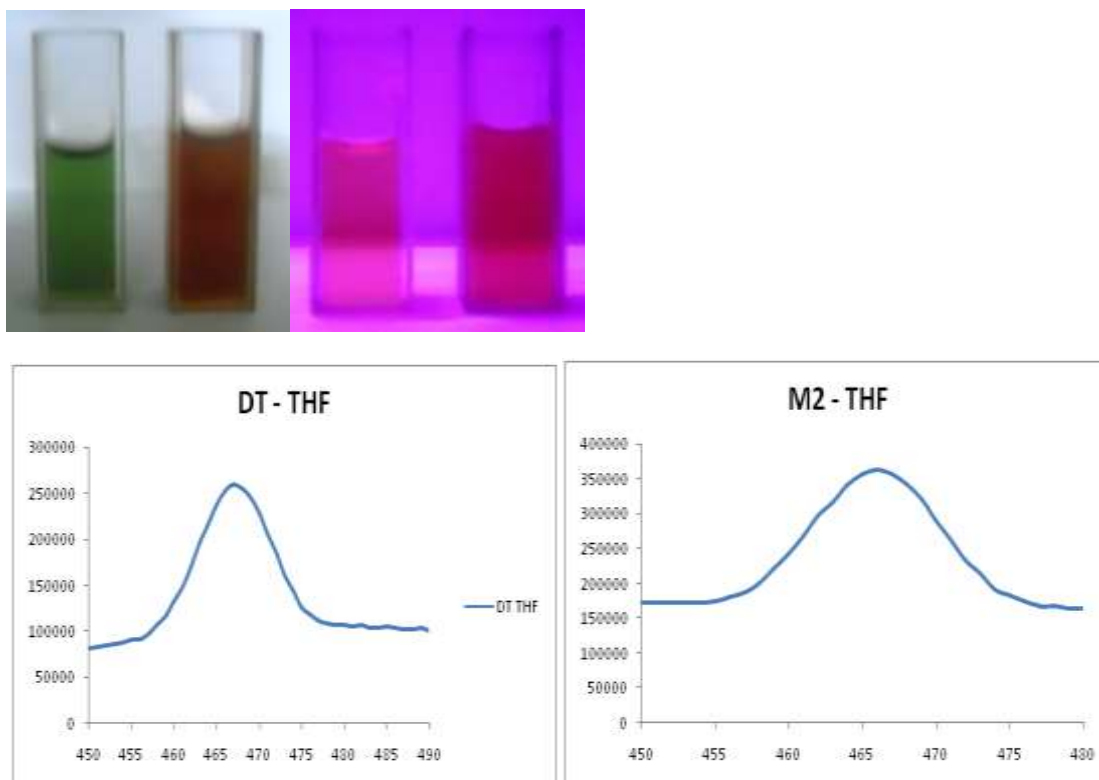


Figure 5. Emission colors of fluorescent Dithizone capped AgNPnanoclusters excited with a UV lamp (Left - In day light; Right – In UV lamp@254 nm) in THF solvent. Lower figures: Fluorescence spectra's exhibited by Dithizone& synthesized AgNP's in THF solvent.

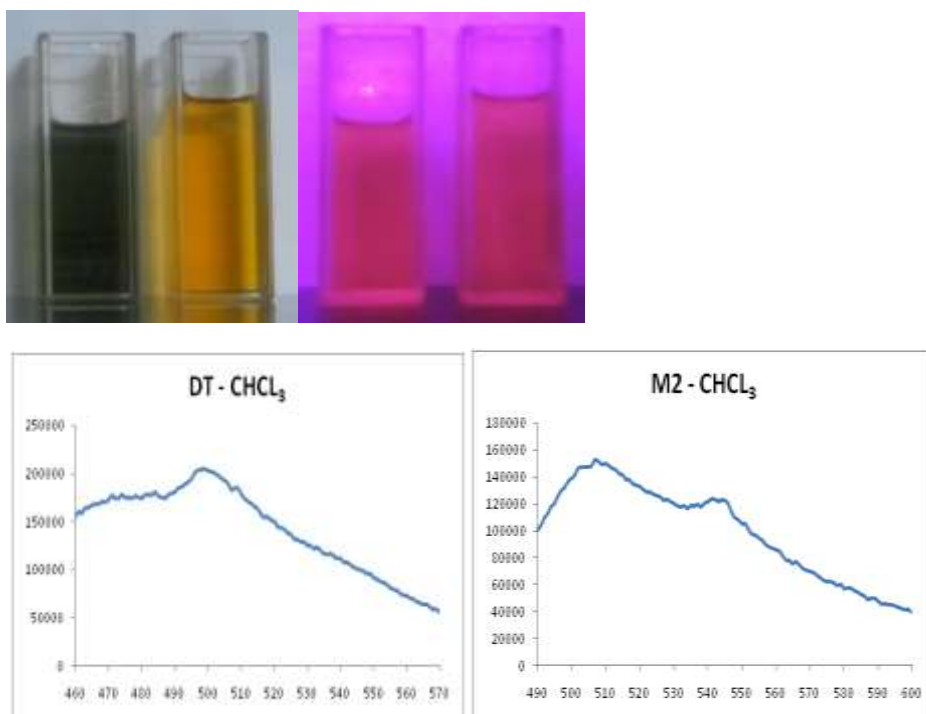


Figure 6. Emission colors of fluorescent Dithizone capped AgNPnanoclusters excited with a UV lamp (Left - In day light; Right – In UV lamp@254 nm) in CHCl₃ solvent. Lower figures: Fluorescence spectra's exhibited by Dithizone& synthesized AgNP's in CHCl₃ solvent.

Table 1: Photophysical Data of Dithizone Capped AgNP's:

Sl.no	Sample	Excitationwavelength(nm)			Emission wavelength(nm)			Stocks shift (nm)		
		DMSO	THF	CHCl ₃	DMSO	THF	CHCl ₃	DMSO	THF	CHCl ₃
1	Dithizone	452	412	434	522	467	499	50	55	65
2	Dithizone capped Ag-NP's	421	410	468	479	466	507	58	56	39

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