Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Materials

Tuning of Morphology of Riboflavin –Melamine Equimolar Supramolecular Assembly by In-situ Silver Nanoparticle Formation

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Experimental:

A. Materials and Methods:

(-)- Riboflavin (R), Melamine (M) and silver nitrate ($AgNO_3$) were purchased from Aldrich Chemical Co., USA. A mixture of riboflavin and melamine in a 1:1 mole ratio was taken in a sealed glass tube and 2 ml of water was added to make the total complex concentration 0.2% (w/v). In it 0.02, 0.2 and 2 mg of finely powdered $AgNO_3$ is added very carefully. It was homogenized at 90^0C and quenched to room temperature to have a yellow, orange and red colored supramolecular complex. This was then was frozen dried to get dry RMAg0.02, RMAg0.2 and RMAg2 complexes. Freeze dried samples are taken for use in several experiments.

B. Microscopy:

(i) ***Field Emission Scanning Electron Microscopy (FESEM)*****:** To understand the network morphology of the gel small portions of the complexes of different concentrations, produced at 30^0C, were placed on glass cover slip and after drying in air and finally in vacuum at room temperature. The samples were platinum coated and observed through a FESEM instrument (JEOL, JSM 6700F) operating at 5 KV.

(ii) ***Transmission Electron Microscopy (TEM)*****:** TEM study of the sample was done by taking a dilute solution of a small portion of the complex on a carbon coated copper grid (200 mesh) and after drying in air at room temperature it was observed through a TEM instrument (JEOL, Model- 2010EX) directly under a voltage of 200 KV. The TEM picture was taken with the help of a CCD camera attached to the instrument.

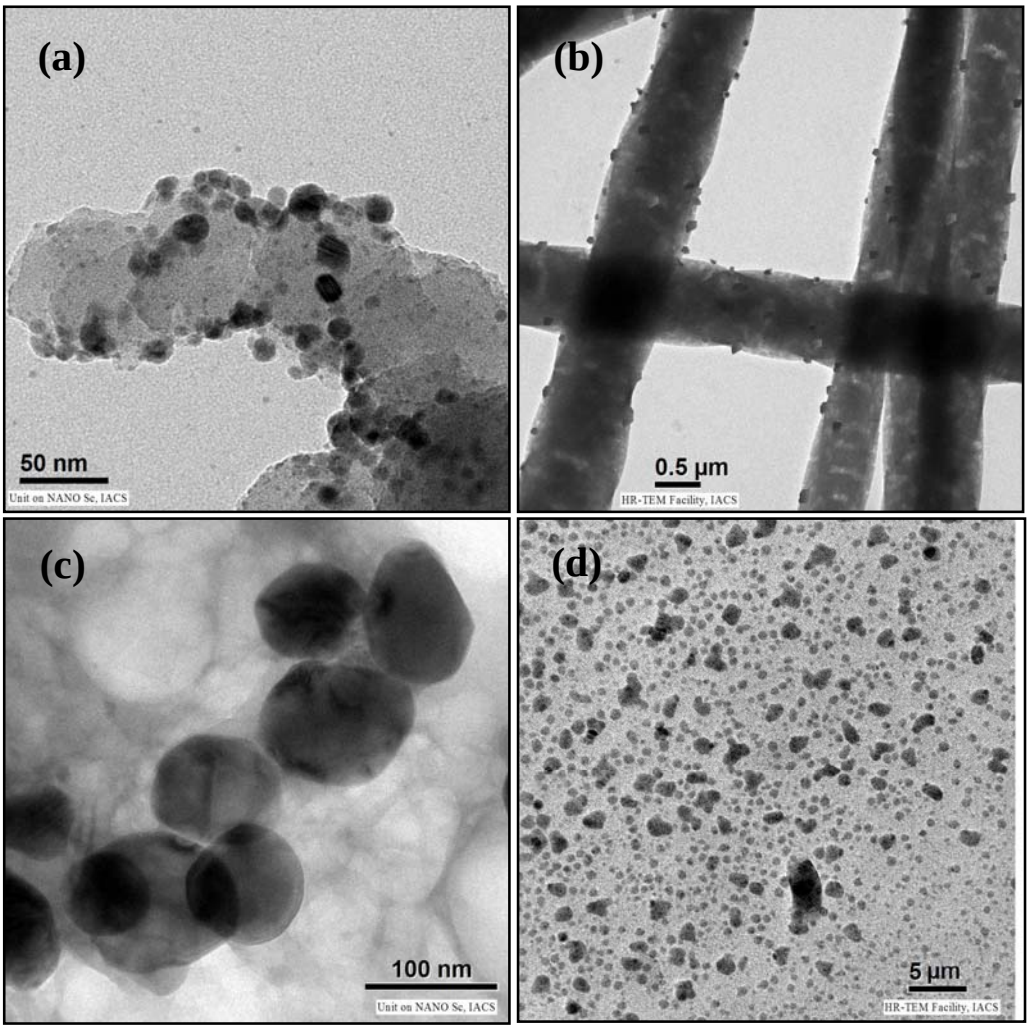
C. Spectroscopy:

(i) ***UV-Vis Spectroscopy*****:** UV-Vis spectra of the sample solutions were taken by using Hewlett-Packard UV-Vis Spectrophotometer (Model-8453). The concentration was 0.055%.

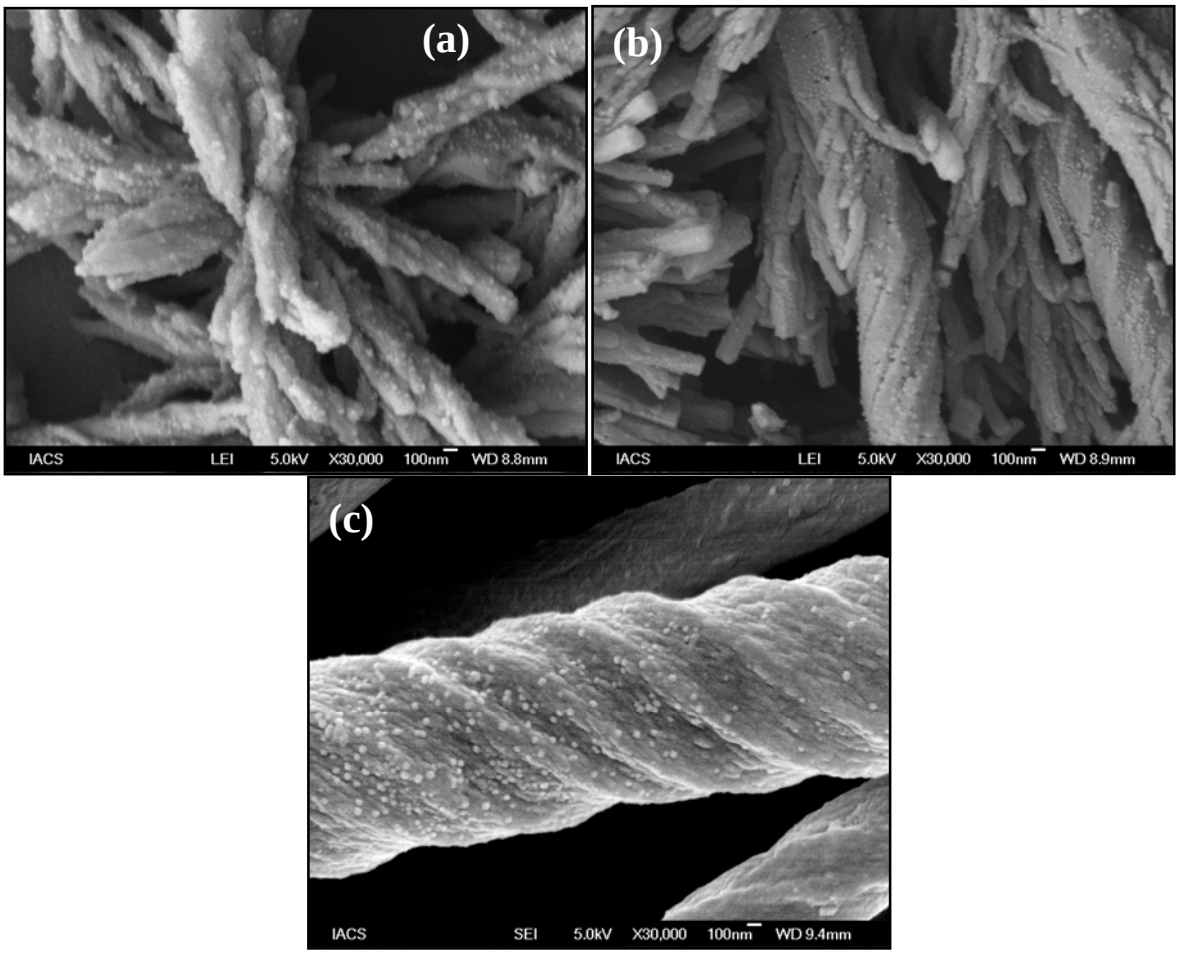
(ii) ***FTIR Spectroscopy:*** FTIR spectra of three freeze dried samples were taken by making a KBr pallet in a Perkin-Elmer spectrophotometer (Spectrum100).

(ii) ***Photoluminescence Spectroscopy*****:** Fluorescence studies of RMAg samples prepared in a sealed cuvette were made in a Horiba Jobin Yvon Fluoromax 3 instrument. The samples were taken in a Quartz cell of path length one cm and were excited at 365 nm. The emission scans were taken from 400 nm to 800 nm using slit width 2 nm both for excitation and emission with an increment of wavelength 1 nm having integration time 0.5 second. The spectra were normalized with respect to concentration of riboflavin. For temperature dependent PL study the eqilibriation time was 30 minutes for each temperature.

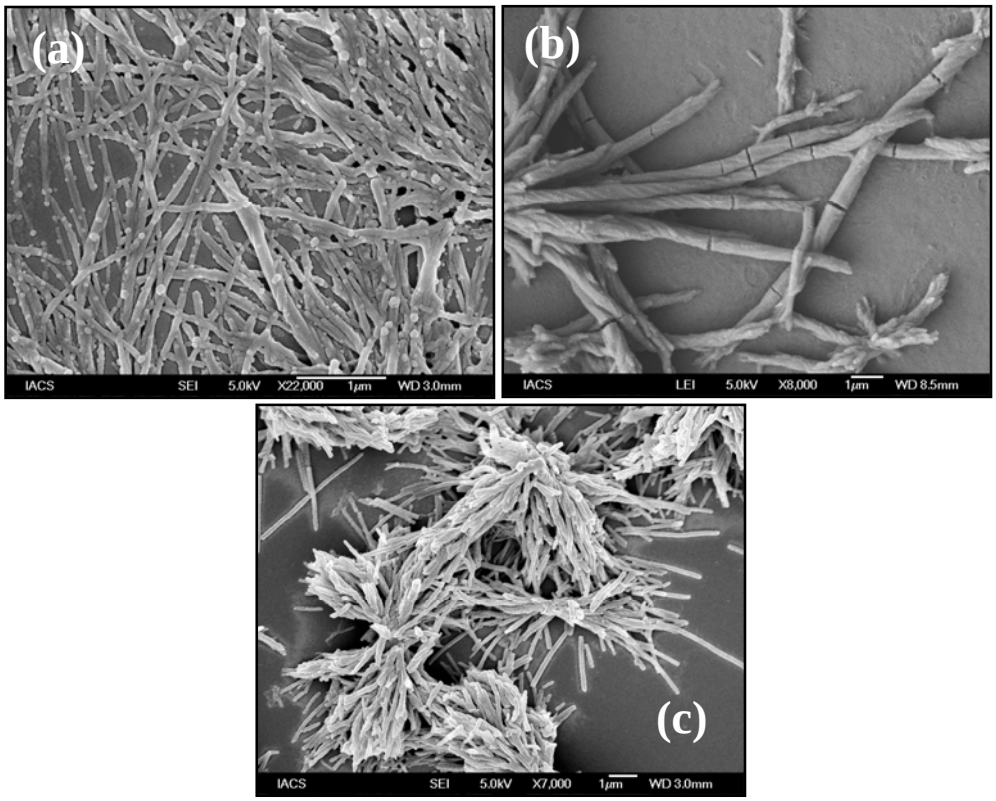
(iii) ***Circular Dichroism Spectroscopy*****:** All the CD spectra were taken in a JASCO CD Spectrophotometer (Model J-815) in a one mm cuvette. The scan range was 600 nm to 200 nm at the rate of 500 nm/minute.



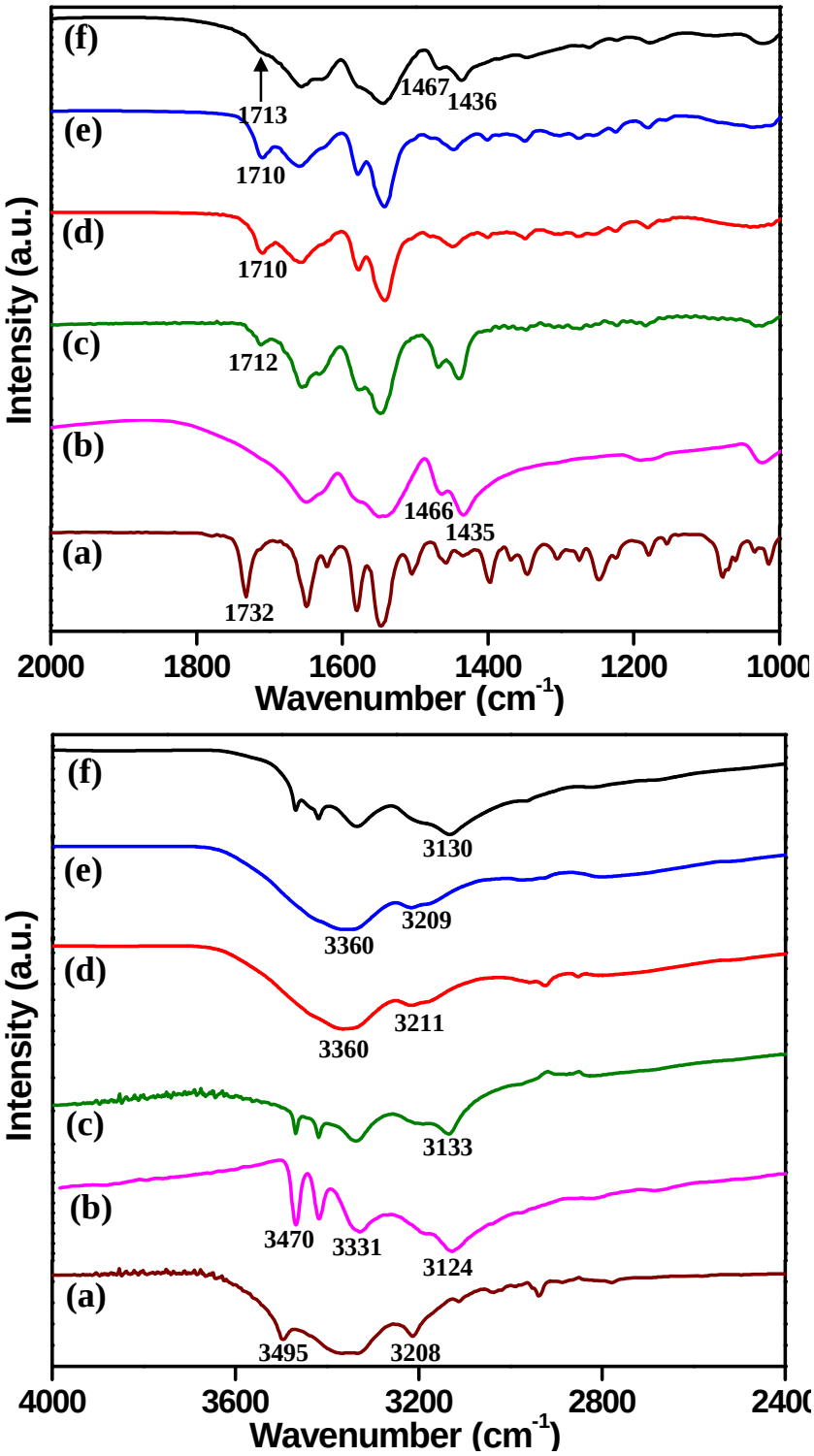
Suppl.Fig.1. HRTEM images of (a) RMAg0.02 (b,c) RMAg0.2 (d) RMAg2



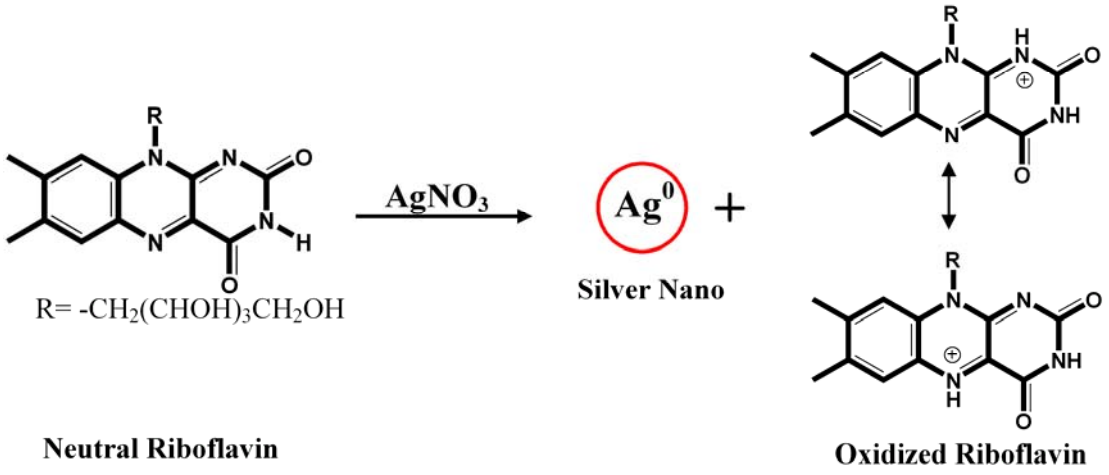
Suppl.Fig.2. Time evolution FESEM images of RMAg0.2 supramolecular self assembled complex (a) after 1 hr. (b) after 3 hr. and (c) after 12 hr. The SEM picture indicates how helical fibers are formed from combination of AgNP decorated helical fibrils.



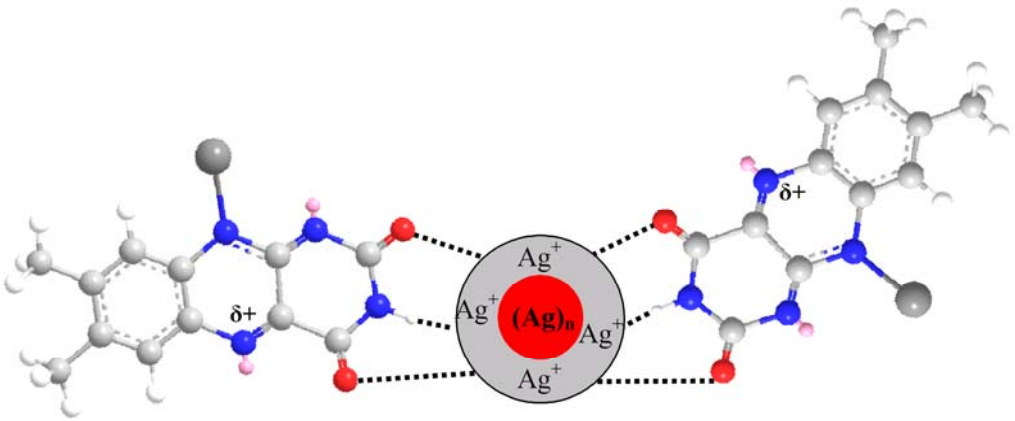
Suppl. Fig.3. FESEM images of (a) RM31Ag0.2 (b) RM12Ag0.2 and (c) RM13Ag0.2 supramolecular complexes.



Suppl. Fig.4. FTIR spectra of (a) R (b) M (c) RM11 gel (d) RMAg0.02 (e) RMAg0.2 and (f) RMAg2 for two different wave number regions.

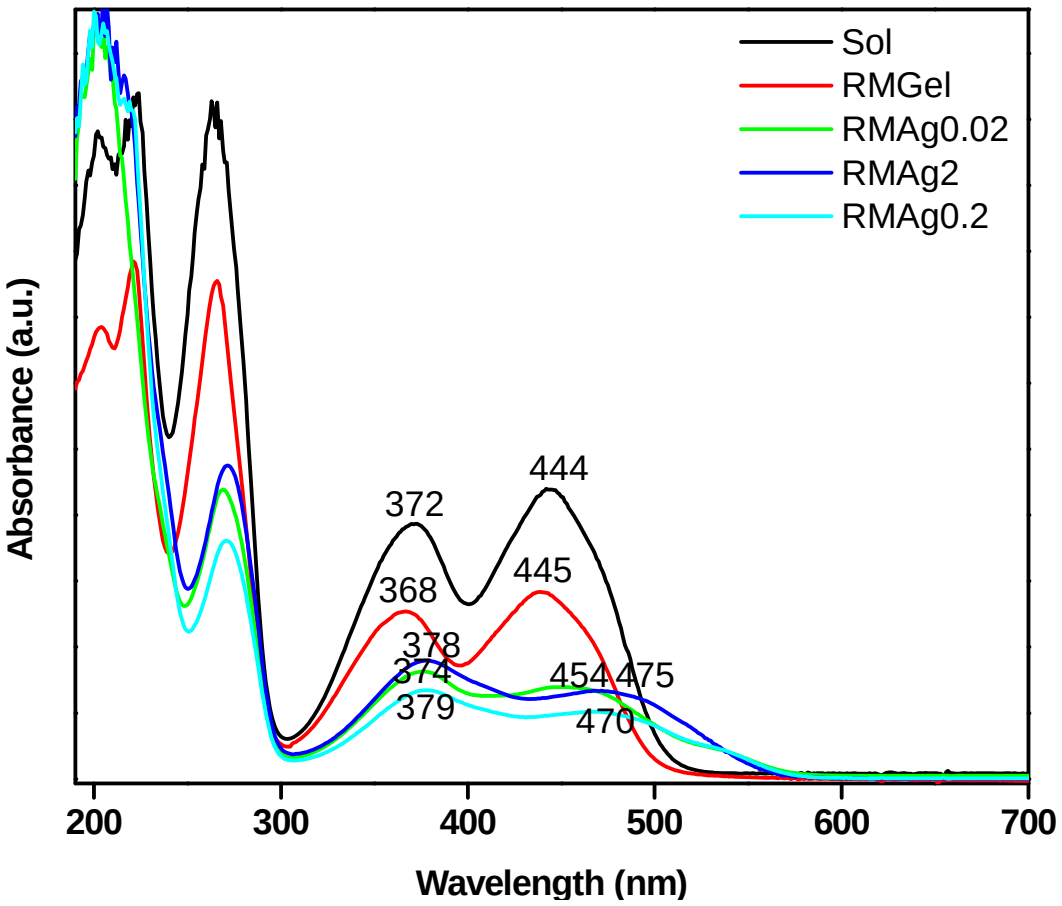


(a)

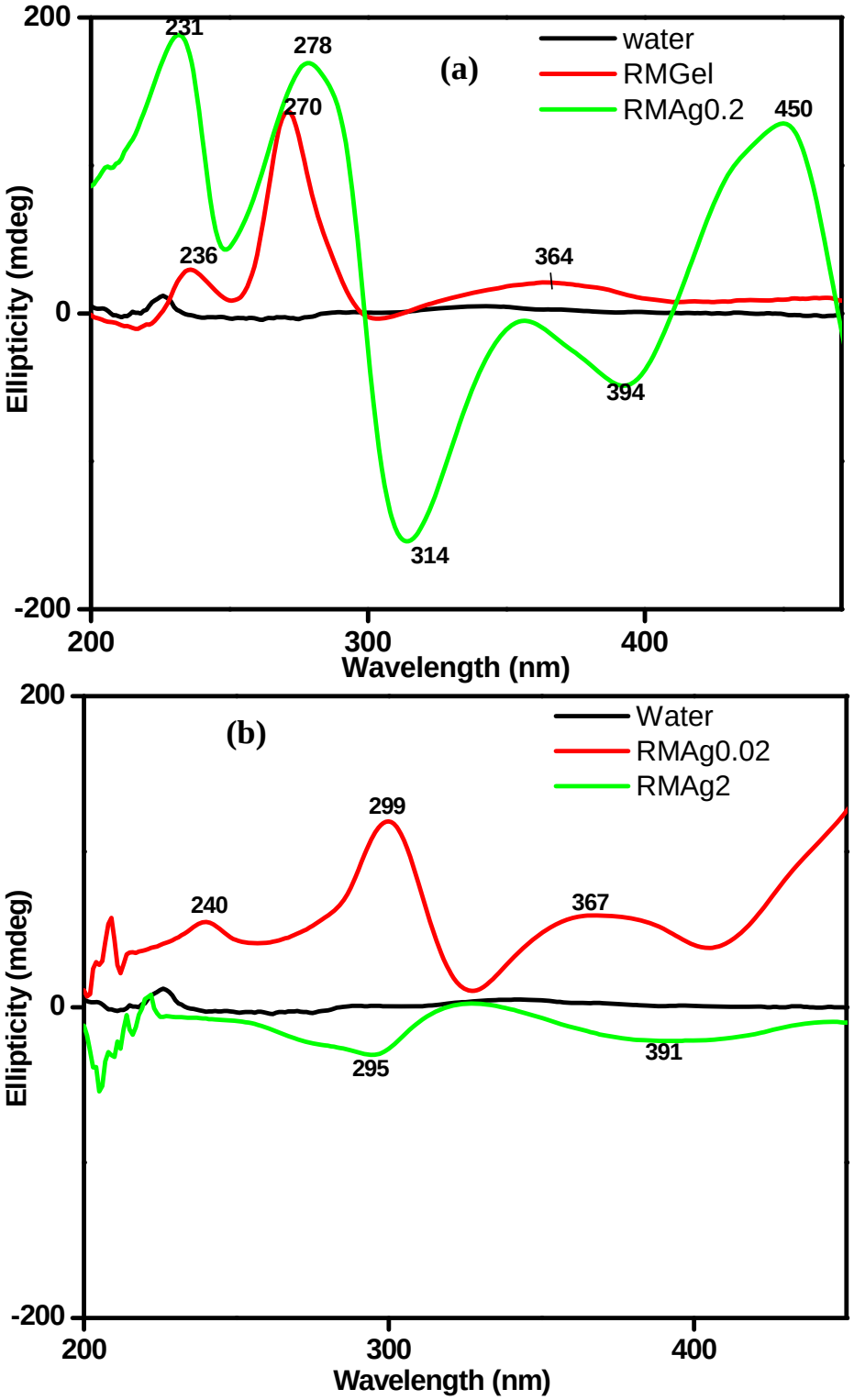


(b)

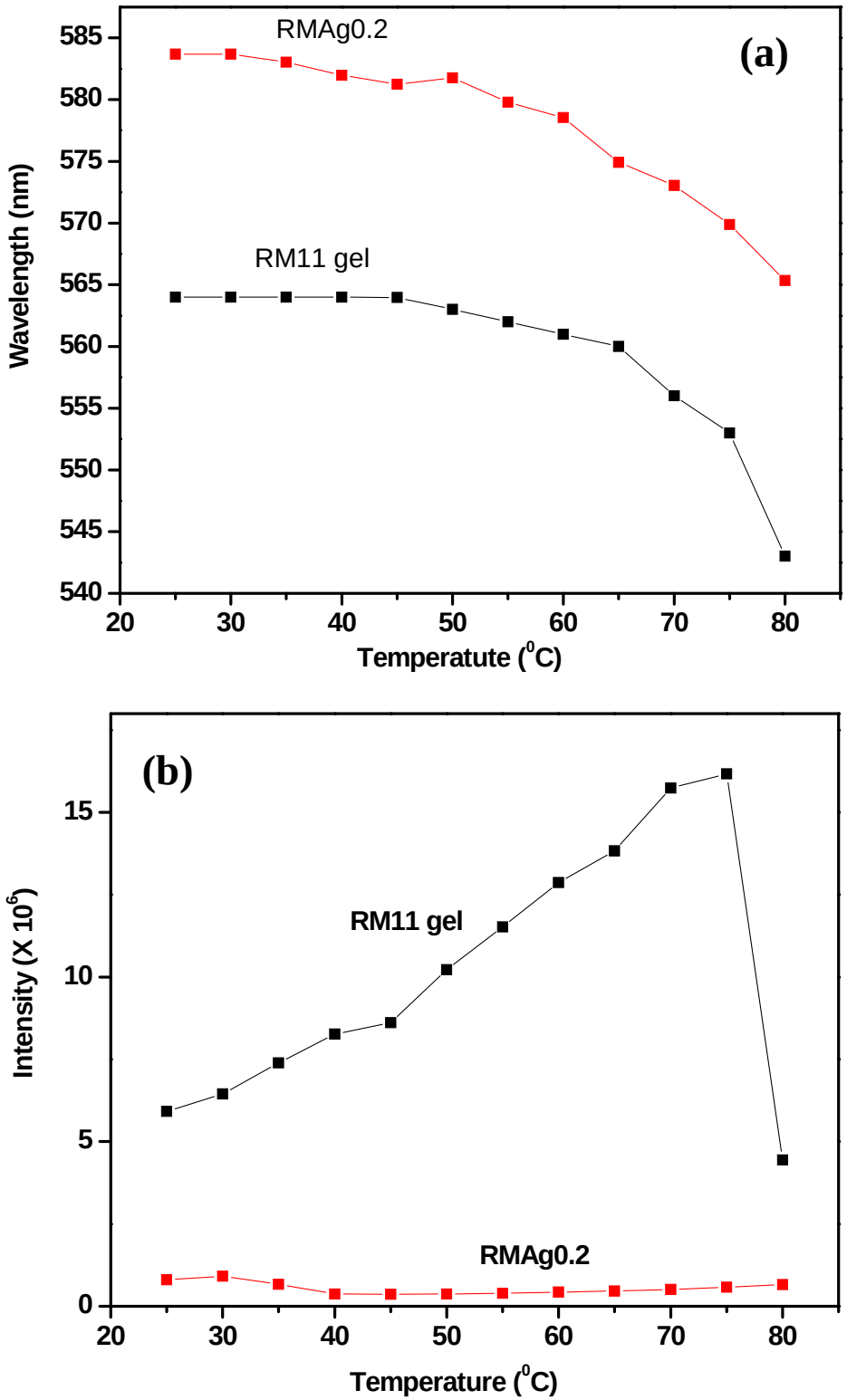
Suppl. Fig.5. (a) Formation mechanism of silver nano after reduction by riboflavin. (b) Schematic presentation of the stabilization of Ag nanoparticles (big red sphere) by complexation of adsorbed silver ion with oxidized riboflavin (R), Oxygen atom = small red sphere, Nitrogen atom = small blue sphere.



Suppl. Fig.6. UV-vis spectra of pure R, RM11 gel, RMAg0.02, RMAg0.2 and RMAg2 supramolecular complex.



Suppl.Fig.7. (a) CD spectra of RM11gel and RMAg0.02 supramolecular complex (b) CD spectra for RMAg0.02 and RMAg2 systems.



Suppl. Fig.8. (a) Comparison of λ_{max} of PL-spectra with. temperature of RM11 gel and RMAg0.2 system (b) Comparison of PL- intensity with temperature of RM11 gel and RMAg0.2 system.