

**Supporting Information**

**Exploration of carboxymethyl guar gum grafted hyperbranched poly (acrylic acid) as a scaffold for silver nanoparticles for ultrafast and selective sensing of Hg (II)**

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## Materials

Branched carboxymethyl guar gum (bCMGG; average molecular weight; M.W  $4.1 \times 10^5$   $\text{g mol}^{-1}$  and degree of substitution; D.S 0.6; Hindustan Gums and Chemicals Ltd., Haryana, India) was purified from the natural impurities through soxhlet extraction using ethanol (98%; Merck, India); according to a method adopted by Whitcomb et al<sup>1</sup> and oven dried prior to use. Acrylic acid (AA; 99%; Merck) and divinyl benzene (DVB; technical grade: 80 % contained 1000 ppm of p-tert-butylcatechol as an inhibitor; Sigma Aldrich, India) were passed through cold basic alumina columns to remove inhibitors. Potassium persulphate (KPS;  $\geq 98\%$ ; Merck) was purified by re-crystallization from methanol (98%; Merck). Dodecane thiol (DDT;  $\geq 98\%$ ; Aldrich), sodium dodecyl sulphate (SDS; Merck), sodium hydroxide pellets (NaOH; Merck), silver nitrate ( $\text{AgNO}_3$ ; 99.9%; Merck), sodium borohydride ( $\text{NaBH}_4$ ; 97%; Merck), sodium chloride (NaCl, 97%, Merck), ethanol (EtOH, 98%, Merck) and diethyl ether (99.8%; Merck) were used as received. Milli Q was used for the suspension of bCMGG, dialysis and in the synthesis of silver nanoparticles. Analytical grade of mercury (II) nitrate ( $\text{HgNO}_3$ ; 99.8%; Aldrich) was dissolved in Milli Q to prepare an analyte solution of 1000 ppm; subsequently this was diluted to different levels of ppm for further analysis. All other solvents and metal salts were of analytical grades and were used as received.

### Synthesis of bCMGG-g-PAA 1 and bCMGG-g-XPAA 5

Typically, for the synthesis of bCMGG-g-PAA 1, bCMGG (2 w/v aqueous suspension, 20 ml maintained at pH 7), SDS (0.15 g), AA (10 m.mol) and KPS (0.05 m.mol) were homogenized for 30 mins under a constant blanket of  $\text{N}_2$ . Then the resultant mixture was allowed to react at a constant temperature of  $70^\circ\text{C}$  for 24 hrs. Finally bCMGG-g-PAA 1 was purified

from the water soluble un-reacted components and SDS by incessant dialysis against Milli Q for 48 hrs at 60°C and was subsequently freeze dried.

**IR (KBr, cm<sup>-1</sup>);** Fig. S1A: 3403 (broad),  $\nu_{\text{O-H}}$  str; 2925/ 2845,  $\nu_{\text{C-CH}_2}$  asym/ sym str; 1720,  $\nu_{\text{CHO}}$  str; 1635,  $\nu_{\text{COOH}}$  str; 1440/ 1380,  $\nu_{\text{O-H}}$  bend; 1161,  $\nu_{\text{C-O-C}}$  str.

**<sup>1</sup>H NMR (D<sub>2</sub>O, 60°C, 300 MHz,  $\delta$  ppm);** Fig. 1A (main text): 10.822 (d, 1H, -O-CH<sub>2</sub>-COOH of bCMGG); 11.22, 10.736 (d, 1H, -COOH of poly AA chains); 10.045 (d, 1H, -CHO introduced after grafting); 4.700 (D<sub>2</sub>O); 4.280 (m, 2H, -CH<sub>2</sub> of polymer backbone); 3.701 (s, 10H, ring protons); 2.506 (s, 4H, -CH<sub>2</sub> at C-6 of  $\alpha$ -D glucose and C-3 of  $\beta$ -D mannose).

**<sup>13</sup>C NMR (D<sub>2</sub>O, 60°C, 500 MHz,  $\delta$  ppm);** Fig. 1C (main text): 181.2 (-O-CH<sub>2</sub>-COOH of bCMGG); 180.31 (-CHO introduced after grafting); 148.9-148.5 (-COOH of poly AA chains); 110 (anomeric -C-O-C-); 60.56 (-CH<sub>2</sub>-O-CH<sub>2</sub>-COOH of bCMGG); 61.23 (-CH(COOH) of AA chains); 57.14 (-CH(OH) of sugar rings), 41.77 (-CH<sub>2</sub> of polymer backbone).

**<sup>13</sup>C-DEPT-135° (D<sub>2</sub>O, 60°C, 500 MHz);** Fig. 1C inset (main text): 180.21 (+ve), 110.3 (+ve), 62.33 (+ve), 56.14 (+ve), 43.8 (-ve), 13.01 (+ve).

Typically, for the synthesis of bCMGG-g-XPAA 5, bCMGG (2 w/v aqueous suspension, 20 ml maintained at pH 7), SDS (0.3 g), AA (20 m.mol), DVB (1 m.mol) and KPS (0.1 m.mol) for 20 mins under a constant blanket of N<sub>2</sub>. The resultant mixture was allowed to react at a constant temperature of 70°C until a gel was formed. Finally bCMGG-g-XPAA 5 was purified from the water soluble un-reacted components and SDS by incessant dialysis against a mixture of Milli Q and ethanol for 48 hrs at 60°C. The purified aqueous suspension of bCMGG-g-XPAA 5 was further precipitated from diethyl ether, dried under vacuum at 60°C for an overnight.

**IR (KBr, cm<sup>-1</sup>);** Fig. S1E: 3443 (broad),  $\nu_{\text{O-H}}$  str; 2925/ 2845,  $\nu_{\text{C-CH}_2}$  asym/ sym str; 1730,  $\nu_{\text{CHO}}$  str; 1630,  $\nu_{\text{COOH}}$  str; 1460/ 1390,  $\nu_{\text{O-H}}$  bend; 1178,  $\nu_{\text{C-O-C}}$  str; 812,  $\nu_{\text{Ar-CH}}$  oop bend.

## **Procedure for the determination of specific gravity of bCMGG-g-PAA 1/ bCMGG-g-HBPAA 2/3/4**

Before proceeding to the determination of sp. gravity, a swelling study was performed on each sample in H<sub>2</sub>O as well as in a mixture of H<sub>2</sub>O + EtOH. bCMGG- polymer conjugates (both linear and hyperbranched) being highly hydrophilic have a tendency to swell in the aqueous media (Table S1). However, after the addition of minimal quantity of EtOH (say 20  $\mu$ l i.e. each drop), the swelling ratio of each samples decreased dramatically (Table S2). This happened due to the de-swelling tendency of any swollen hydrophilic polymer in EtOH.<sup>2, 3</sup> EtOH forms extensive hydrogen bonds with water for which EtOH molecules and H<sub>2</sub>O molecules prefer to stay in the solution. This phenomenon in turn reduces the gel swelling. In our case, even a minimal quantity of EtOH significantly reduced the swelling of bCMGG-g-HBPAA samples in H<sub>2</sub>O. Thus, specific gravity (sp.gravity) of the samples could be determined with minimum error. For the determination of sp.gravity, all the samples (~ 0.5 g each) were pressed into pellet forms using a pelletizer under a pressure of 7 tons. Typically, each of the sample pellets was immersed in 50 ml H<sub>2</sub>O contained in a graduated cylinder; being heavier they all sank in H<sub>2</sub>O. At this moment, a liquid having a density lower than H<sub>2</sub>O (e.g.; EtOH) was added dropwise to the sample pellet/ H<sub>2</sub>O system, stirred well and the addition was continued until the sample pellet just floated over. Care was taken that EtOH was added to the system within 2 mins of the immersion of the samples in H<sub>2</sub>O in order to avoid undue gain in weight of the samples through swelling. Swelling study has shown that each of the sample swelled in insignificant amount within 2 mins of immersion and thus were ignored during the measurement of sp.gravity. Apparent sp.g<sub>sample</sub> was determined from Equation S1.

$$\text{Apparent sp.g}_{\text{sample}} = \left\{ \frac{(W_3 - W_1)}{W_2 - W_1} \right\} \quad (\text{S1})$$

where  $\text{apparent sp.g}_{\text{sample}}$  is the sp. gravity of the sample pellet at a particular instance,  $W_1$  is the weight of empty sp. gravity bottle,  $W_2$  is the weight of (sp. gravity bottle +  $\text{H}_2\text{O}$ ) and  $W_3$  is the weight of (sp. gravity bottle + final liquid mixture).

**P.S:** Apparent  $\text{sp.g}_{\text{sample}}$  of all the samples was determined at  $30^\circ\text{C}$  and  $\text{pH} \sim 6$ , when the respective samples were insoluble in  $\text{H}_2\text{O}$ .

### **Instrumentation and sample preparation for various tests**

**NMR study.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the synthesized bCMGG-g-PAA 1 and bCMGG-g-HBPAA 3 samples were recorded at  $60^\circ\text{C}$  on Bruker 300 and 500 MHz spectrometers respectively, using  $\text{D}_2\text{O}$  as the solvent and TMS as the internal reference ( $\delta \text{H}$  0.00 and  $\delta \text{C}$  0.00). The respective DEPT sequences for the samples were acquired using a selection pulse of  $135^\circ$ .

**FTIR spectroscopic study.** The FTIR characterization of bCMGG-g-PAA 1, bCMGG-g-HBPAA 2/3/4 were performed in transmission mode on a Shimadzu IR affinity- 18000 FTIR spectrometer. All the samples were thoroughly dried and immediately mixed to fine powder with spectroscopic grade KBr in a ratio of 1:120 (w/w) and pressed to pellets prior to characterization.

**Turbidity analysis.** Turbidity of the aqueous suspensions of bCMGG-g-PAA 1, bCMGG-g-HBPAA 2/3/4, AgNPs 1, AgNPs-HB 2/3/4 were recorded on Systronics Digital Nepheloturbidity meter, Model 132 at  $30^\circ\text{C}$ .

**Viscosity measurements.** Intrinsic viscosities of bCMGG-g-PAA 1, bCMGG-g-HBPAA 2/3/4 were determined from the respective flow times in double distilled water (maintained at  $\text{pH}$  8), recorded in an Ubbelohde viscometer (size 1, number 424 and calibrated as per ASTM D 445) at  $30^\circ\text{C}$ .

**Rheology study.** The linear viscoelastic behavior of bCMGG-g-PAA1, bCMGG-g-HB 2/3/4 was studied in a small amplitude oscillatory shear mode, on an Anton Paar Rheometer, Physica (MCR-102). Rheologies of the samples were determined at a constant temperature of 30°C using parallel plate (diameter- 25 mm) and CTD attachment. Samples having 1 cm<sup>2</sup> cross sectional area each were subjected to angular frequency ramp from 100 to 0.1 rad s<sup>-1</sup>, under a constant temperature (30°C), strain (0.001 %) and normal force (1 N).

**DLS studies.** The hydrodynamic diameters of AgNPs 1/ AgNPs-HB 2/3/4 at different time were obtained from Zeta Sizer Nano Series, Malvern, USA. All samples were ultra sonicated for 1 hr at 20°C prior to acquiring of results.

**UV-Vis characterization.** The UV-Vis spectra of AgNPs 1/ AgNPs-HB 2/3/4, AgNPs-HB 3 (in the presence of Hg<sup>2+</sup> and Hg<sup>2+</sup> + NaCl) were recorded against air at 25°C on a UV-Vis spectrophotometer (CECIL CE7200, 7000 series, UK) from 200 nm to 600 nm, using a quartz cuvette of 1 cm optical path length. Milli Q was used as the blank.

**XRD characterization.** The diffractograms of properly dried AgNPs-HB 3/ AgNPs-HB 3 + Hg<sup>2+</sup>/ AgNPs-HB 3 + NaCl + Hg<sup>2+</sup> casts were recorded by using wide angle X- PERT- PRO Panalytical diffractometer at an accelerating voltage of 40 kV and in reflection mode, employing Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) as the X-ray source.

**HRTEM & EDX studies.** HRTEM images of AgNPs 1/ AgNPs-HB 3/ AgNPs-HB 3 + Hg<sup>2+</sup>/ AgNPs-HB 3 + NaCl + Hg<sup>2+</sup> were acquired on a model JEM, 2010 EM, fitted with a CCD camera at an accelerating voltage of 50 kV. For HRTEM study, all the samples were drop casted on a carbon coated copper grid of 300 mesh size and vacuum dried for 48 hrs prior to capturing of images.

The EDX spectra of AgNPs-HB 3/ AgNPs-HB 3 + Hg<sup>2+</sup>/ AgNPs-HB 3 + NaCl + Hg<sup>2+</sup> were obtained from the EDX attachment to HRTEM.

**Cyclic Voltammetry.** CVs of AgNPs-HB 3 + Hg<sup>2+</sup>/ AgNPs-HB 3 + KCl + Hg<sup>2+</sup>/ AgNPs-HB 3 + NaCl + Hg<sup>2+</sup> were obtained from an AUTOLAB, PGSTAT 30 with GPES software (version 4.9), using the conventional 3 electrode system of a bare or modified working platinum electrode (surface area 0.64cm<sup>2</sup>), a platinum wire counter electrode and Ag-AgCl reference electrode. Data were acquired at a scan rate of 20 mV s<sup>-1</sup> and 80 mV s<sup>-1</sup> for AgNPs-HB 3 + Hg<sup>2+</sup>/ AgNPs-HB 3 + KCl + Hg<sup>2+</sup> system and AgNPs-HB 3 + NaCl + Hg<sup>2+</sup> system respectively.

### Additional results

**Table S1.** Swelling study of bCMGG-g-PAA and bCMGG-g-HBPAA in H<sub>2</sub>O with time

Sample	Swelling ratio after 2 mins of swelling	Swelling ratio after 4 mins of swelling	Swelling ratio after 6 mins of swelling	Swelling ratio after 8 mins of swelling	Swelling ratio after 10 mins of swelling
bCMGG-g-PAA 1	0.68	0.89	1.33	1.56	1.93
bCMGG-g-HBPAA 2	0.72	1.43	1.93	2.62	3.01
bCMGG-g-HBPAA 3	0.93	1.82	2.89	3.15	4.64
bCMGG-g-HBPAA 4	0.96	1.91	2.93	3.56	4.63

Swelling ratio = weight of swollen polymer pellet/ weight of dry polymer pellet. All the experiments were carried out at 30°C and in aqueous media maintained at pH ~ 6. To be precise, these conditions were maintained during the study of sp.gravity. Data were collected for a period of 10 mins (and not up to the point of equilibrium) as during the measurement of sp. gravity of the grafted polymers, EtOH was added dropwise just within 2 mins of immersion of the samples in H<sub>2</sub>O.

**Table S2.** Swelling study of bCMGG-g-PAA and bCMGG-g-HBPAAAs in a mixture of H<sub>2</sub>O and EtOH

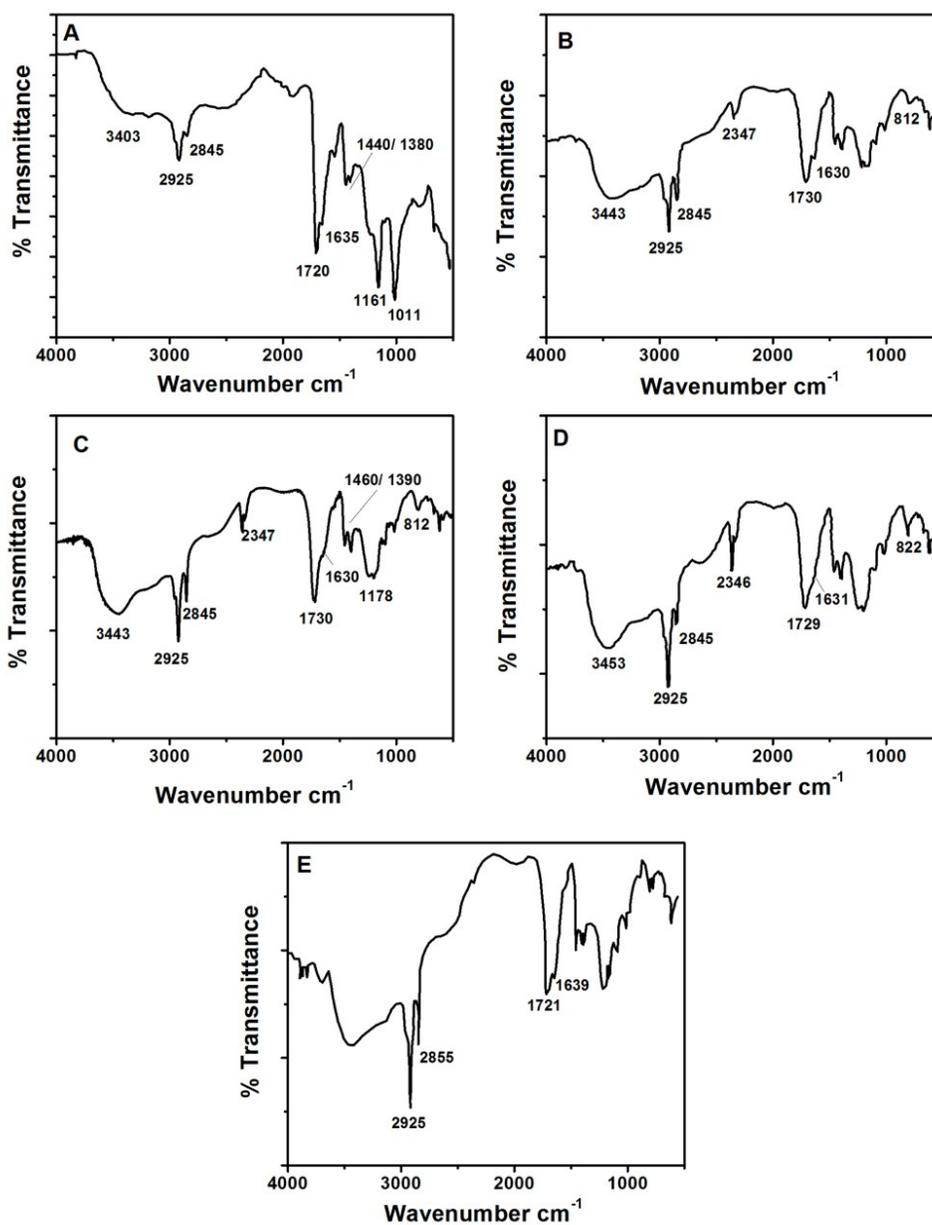
Sample	Swelling ratio after 2 mins of swelling in H <sub>2</sub> O	After	After	After	After	After
		addition of 20 µl of EtOH	addition of 40 µl of EtOH	addition of 60 µl of EtOH	addition of 80 µl of EtOH	addition of 100 µl of EtOH
bCMGG-g-PAA 1	0.68	0.71	0.72	0.72	0.72	0.72
bCMGG-g-HBPAA 2	0.72	0.74	0.76	0.76	0.76	0.76
bCMGG-g-HBPAA 3	0.93	0.96	0.97	0.98	0.98	0.99
bCMGG-g-HBPAA 4	0.96	0.99	0.30	1.56	2.06	2.11

EtOH was added to the respective system of bCMGG-g-HBPAAAs pellets already immersed in H<sub>2</sub>O (just within 2 mins of immersion). All the experiments were carried out at 30°C and in the aqueous media of pH around 6, at the start of the experiment.

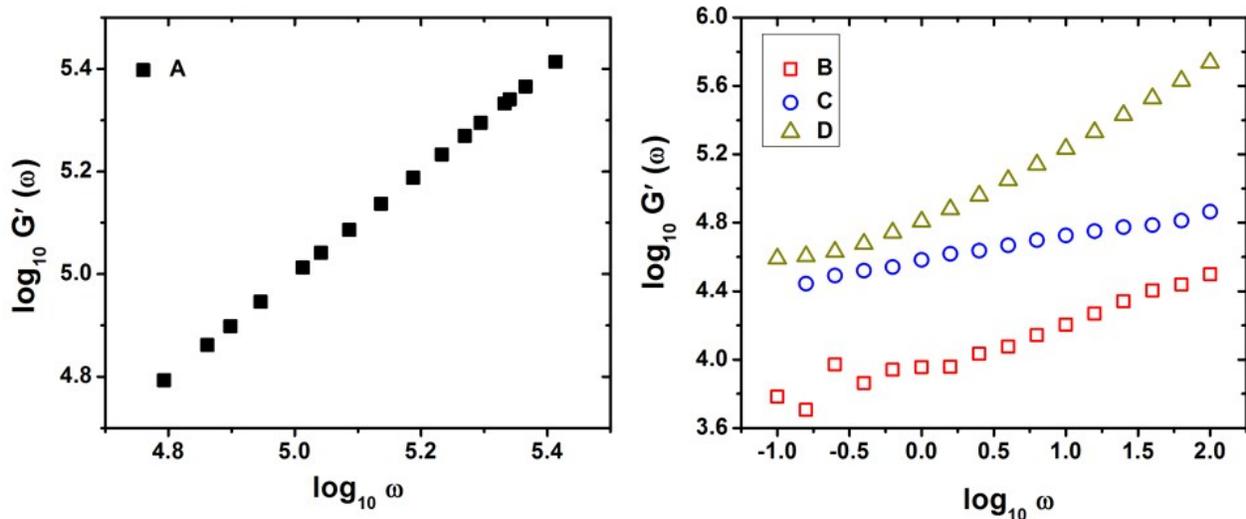
**Table S3.** Record of stability & turbidity of AgNPs-HB 3 with time

Sample	Time of recording after formation of AgNPs	D <sub>h</sub> (nm)	Turbidity of AgNPs dispersions (NTU)
AgNPs-HB 3	1 hr	27.46	10.1
AgNPs-HB 3	24 hrs	27.8	10.4
AgNPs-HB 3	48 hrs	28	10.5
AgNPs-HB 3	72 hrs	28.2	12
AgNPs-HB 3	7 days	33	16.5
AgNPs-HB 3	14 days	54	18.2

Each test samples were ultra sonicated for 1 hr at 20°C prior to acquiring of data.

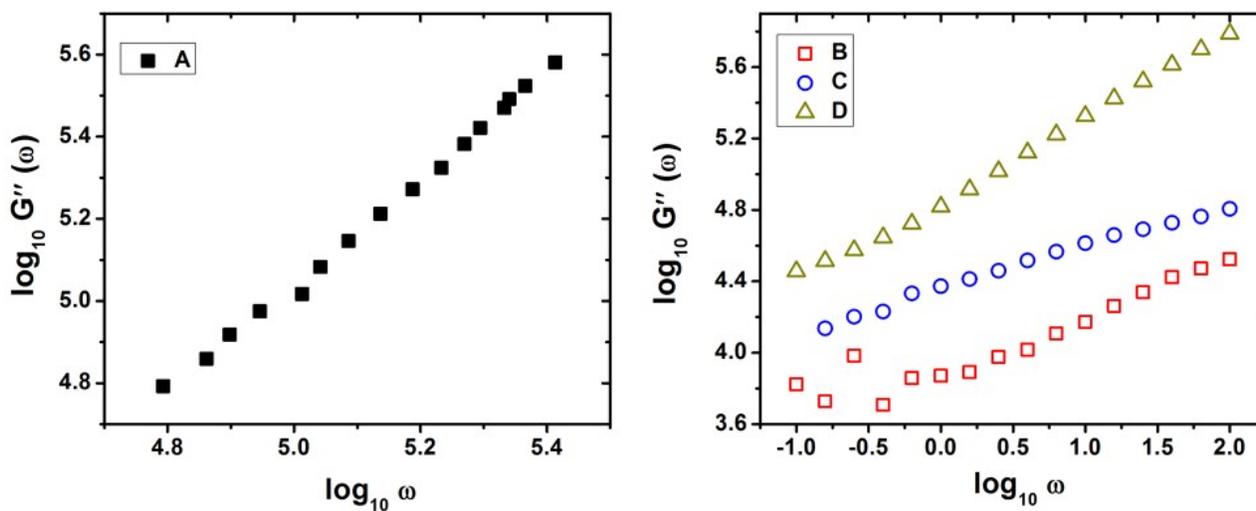


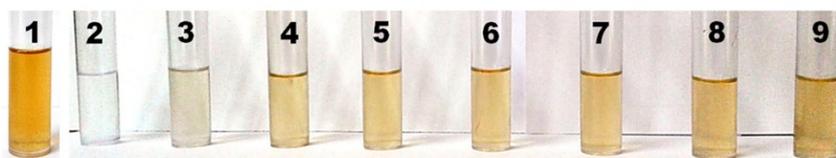
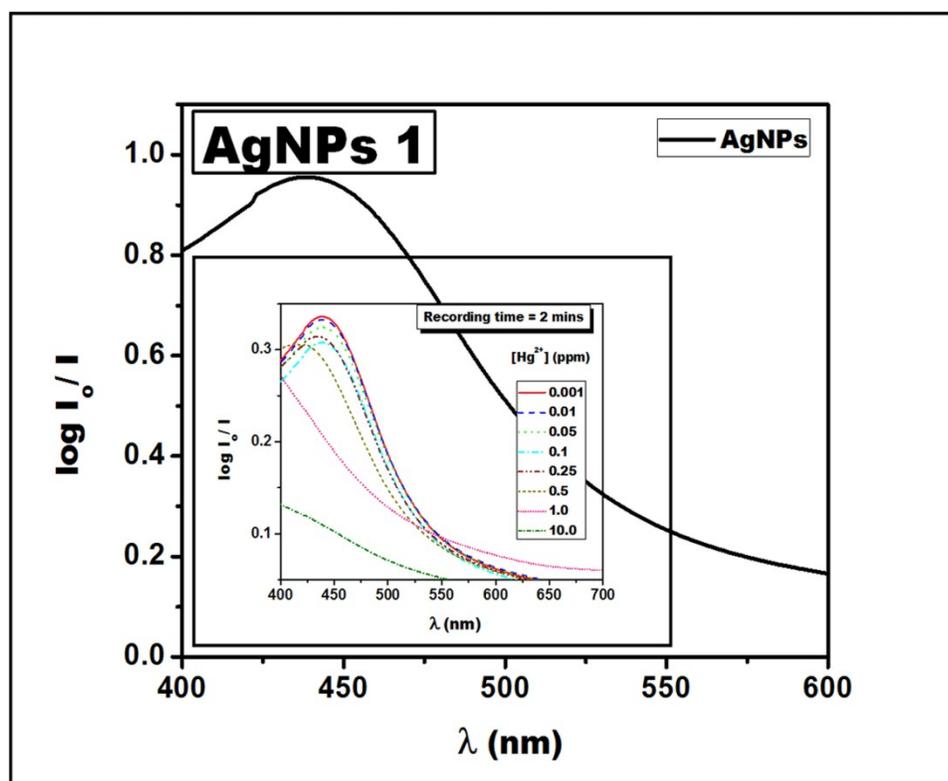
**Figure S1.** The FTIR spectra of A) bCMGG-g-PAA 1/ B) bCMGG-g-HBPAA 2/ C) bCMGG-g-HBPAA 3/ D) bCMGG-g-HBPAA 4/ E) bCMGG-g-XPAA 5



**Figure S2.**  $\log G'$  vs  $\log \omega$  plots for A) bCMGG-g-PAA 1/ B) bCMGG-g-HBPAA 2/ C) bCMGG-g-HBPAA 3/ D) bCMGG-g-HBPAA 4, obtained from dynamic oscillation measurements at 30°C

**Figure S3.**  $\log G''$  vs  $\log \omega$  plots for A) bCMGG-g-PAA 1/ B) bCMGG-g-HBPAA 2/ C) bCMGG-g-HBPAA 3/ D) bCMGG-g-HBPAA 4, obtained from dynamic oscillation measurements at 30°C

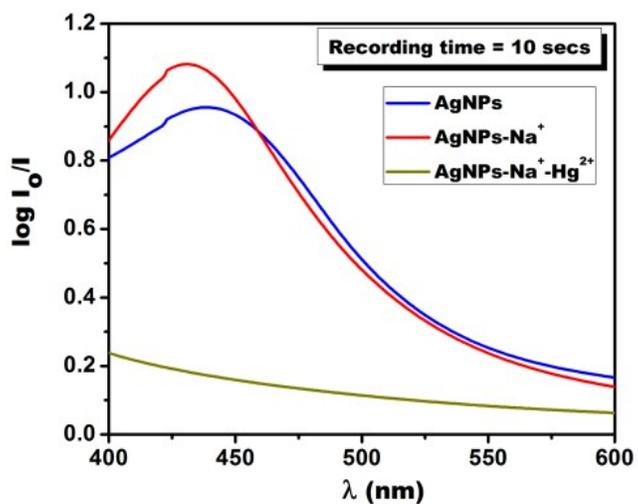




**Figure**

**S4.** UV-

Vis spectra for (I) AgNPs 1 in the presence of different  $[Hg^{2+}]$ ; all data were recorded after reaching equilibrium i.e.; 2 mins; outset displays the photographs of the change in color of AgNPs 1 in the presence of  $[Hg^{2+}]$  where 1- 0 ppm, 2- 10 ppm, 3- 1 ppm, 4- 0.5 ppm, 5- 0.25 ppm, 6- 0.1 ppm, 7- 0.05 ppm, 8- 0.01 ppm, 9- 0.001 ppm. All tests were performed in aqueous media maintained at around pH 6.



**Figure S5.** UV-

AgNPs-HB 3/

the presence of NaCl (10 mM)/ AgNPs-HB 3 in the presence of NaCl (10 mM) and Hg<sup>2+</sup> (1 ppm)

Vis spectra of

AgNPs-HB 3 in

### References

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