Supplemental Information

Highly Selective Arsenite Sensor Based on Gold Nanoparticles and Ionic Liquids

Xuan Hao Lin[1], Mann Joe Wong [1] and Sam Fong Yau Li[1,2]*

[1] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

[2] NUS Environmental Research Institute (NERI), #02-01, T-Lab Building (TL), 5A Engineering Drive 1, Singapore 117411, Singapore

* Correspondence: Tel.: +65 6515 2681; fax: +65 6779 1691. Email address: chmlifys@nus.edu.sg (Sam F. Y. Li).

Chemicals and apparatus

HAuCI$_4$ •3H$_2$O (AR, > 99.8%), 3-(N-morpholino) propane-sulfonic acid (MOPS) (AR, > 99.5%, CPMI (99%), cetylpyridinium chloride monohydrate (98%) (CP), BMP (50% in 7:3 water/methanol) and TBMP (50% in 3:2 water/methanol) trisodium citrate dihydrate (AR, >99.5%), and sodium metaarsenite (AR, >99.5%) were purchased from Sigma (St Louis, MO). CPP (Technical grade, 98.5%) was purchased from Fluka. TDDBA was procured from Tokyo Kasei. Chemical structures of the 6 ILs are shown in Figure 1.

Hach DR 5000 UV-Vis spectrometer (Hach Co., Loveland, USA) was used to record visible spectrum with scanning wavelength from 400 to 800 nm. The morphology of AuNPs was studied with a Transmission Electron Microscope (JEOL JEM-3011F, Tokyo, Japan). Hydrodynamic particle size and zeta potential of AuNPs were measured at 25 ℃ using a Zetasizer Nano ZS90 (Malvern Instruments Ltd., Malvern, Worcester, U.K.).

Synthesis of AuNPs

AuNPs was synthesized according to Turkevich method [29]. Briefly, 95 mL of 267 μM HAuCI$_4$•3H$_2$O (25.365 μmole) solution was heated to reflux with agitation. Subsequently, 5 mL of 17 mM trisodium citrate dihydrate solution (85 μmole) was added to it. The reaction was heated and refluxed for 10 min with stirring. After reaction, the synthesized AuNPs was cooled down to room temperature and then transferred into a light-proof bottle for storage in a 4 ℃ refrigerator. AuNPs suspension were well dispersed, its concentration was determined to be 0.1439 nM, individual particle sizes were around 15 nm, as shown in Fig. 1C. The excess 89.1 μM of citrate ions was kept in the solution for better stability.
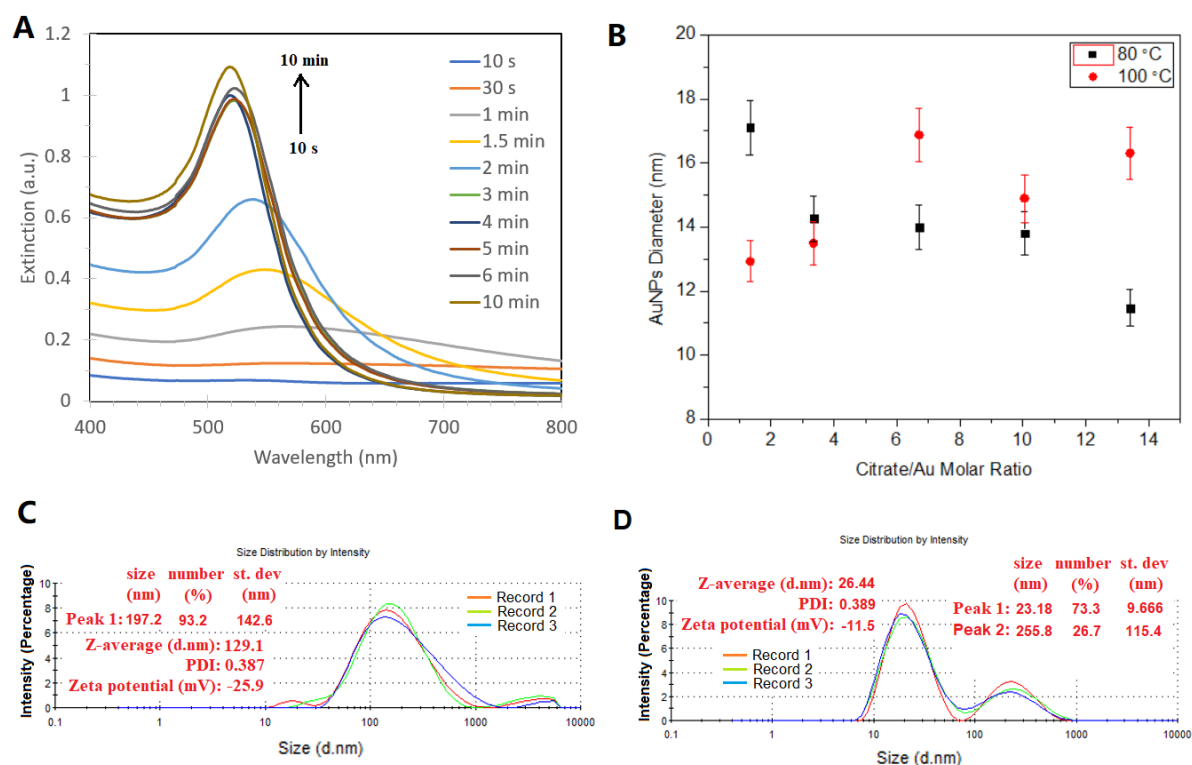
Discussion of AuNPs synthesis and characterization

When gold chloride was reduced to intermediate gold ions Au^+ and further to gold atoms by sodium citrate, citrate ions was oxidized to form dicarboxy acetone and carbon dioxide (eq. S1). The reaction stoicheometric citrate/Au molar ratio was 3:1. Gold atoms gradually aggregated to form AuNPs with surface preferentially capped by citrate anions (Fig. 2B) [19], whose negative electrostatic repulsion formed steric barrier to inhibit particles growth and prevent aggregation [1], imparting stability to AuNPs suspension. At a reaction temperature 100 °C with a starting citrate/Au molar ratio 3.35 – slightly higher than stoicheometric ratio 3, the reaction mixture was light grey initially, which turned bluish grey (<1 min), purple (1-2 mins), and final red (3 mins and onwards). It is well established that the surface plasmonic resonance (SPR) extinction peak redshifts when the nanoparticles size increases [18]. SPR wavelength shift is attributed to the coupling difference of light wave and plasmons at the surface of AuNPs. *The* bluish grey suspension (< 1 min) was in seed and nucleation period and had little or very slight extinction (absorbance) in 400-800 nm wavelength indicating formation of few AuNPs (Fig. 2A). The purple suspension (1-2 mins) showed medium extinction band in a range of 500-600 nm peaked at 538-548 nm owing to increased concentration of AuNPs and their aggregation [30]. Individual particles in the aggregation further coalescenced into larger single particles such that the aggregation gradually dissappeared, denoted by red suspention (3 mins) and peak wavelength blue shift to 522 nm which was mainly attributed to the SPR of single AuNPs instead of aggregate. With a longer reaction time (3-10 mins) the extinction band changed little, which affirmed that the reaction has almost completed within 3 mins.

$$HAu(III)Cl_4 + 3\ Na_3C_6H_5O_7 \rightarrow Au + 3\ NaCl + 3\ CO_2 + HCl + 3\ Na_2C_5H_5O_5 \qquad (S1)$$

The stability of AuNPs depends not only on liquid media, but also on size and shape [18]. It was reported that the ratio of gold ion and citrate concentrations was a crucial factor for controlling the size of AuNPs, recently more factors, including solution pH and chloride ion concentrations, were found to govern the size tunability [31, 32]. To get stable AuNPs suspension, their size dependence was investigated with two reaction temperatures 80 and 100 °C, and five different molar ratios of citrate/Au. SPR wavelength and extinction at SPR (~ 517 nm) and 450 nm were recorded for the size calculation. The mean size (diameter, d) of dry AuNPs was calculated according to Haiss equation (eq. S2) [33].

$$d = \text{Exp}\ (B_1 \frac{A_{spr}}{A_{450}} - B_2) \qquad\qquad (S2)$$

Here A_{spr} - SPR extinction, A_{450} – extinction at 450 nm, B_1 and B_2 are constants, $B_1 = 3.00$ and $B_2 = 2.20$. The calculated d values are summarized in Table S1. Results show that at a reaction temperature 80 °C, AuNPs particle size decreased with increased citrate/Au molar ratio (Fig. S1B) while at 100 °C no such trend existed. At a low citrate/Au molar ratio, there was less surface coverage of AuNPs with citrate ions which served as steric barrier to prevent coalescence of two single AuNPs into one single larger particle, therefore AuNPs grew in an easier manner to larger sizes. The higher citrate/Au molar ratio decreased the rate of particle coalescence, resulting in smaller particle sizes. For the AuNPs synthesied at 100 °C with a citrate/Au ratio of 3.35/1, the calculated particle size 13.5 nm was 10% smaller than the experimental average size ~ 15 nm estimated from the high resolution SEM investigation. This is expected because calculated sizes from the Haiss equation do have an average deviation of ~ 11% from experimental sizes measured by TEM [33].
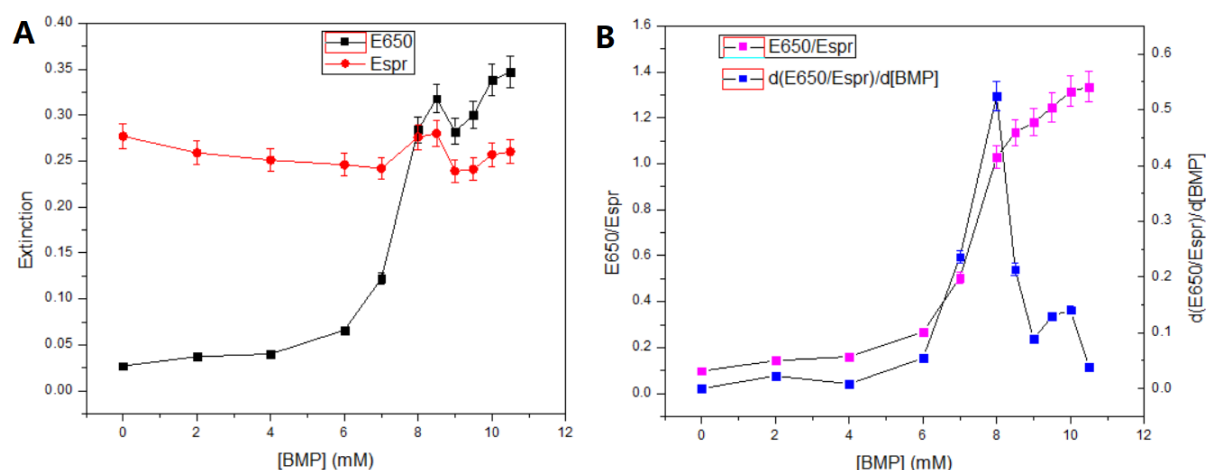
Figure S1 (A) Extinction spectra and (B) Calculated AuNPs' size in dependence of the starting citrate/Au molar ratio at 80 and 100 °C; (C) Particle size distribution and zeta potential of a BMP-induced AuNPs aggregate sample (D) Particle size distribution and zeta potential of the same sample of (C) but with addition of 1 ppm arsenite

Table S1 SPR wavelength, extinction and size of AuNPs in dependence of the starting citrate/Au molar ratio

Citrate/Au molar ratio	SPR wavelength (nm)		SPR extinction (absorbance)		Extinction (absorbance) at 450 nm		Mean size of AuNPs (nm)	
	80 ℃	100 ℃	80 ℃	100 ℃	80 ℃	100 ℃	80 ℃	100 ℃
1.34	527	525	1.364	0.844	0.812	0.532	17.1	12.9
3.35	519.5	517.5	1.004	1.303	0.62	0.814	14.3	13.5
6.70	519	519.5	1.074	1.037	0.666	0.619	14.0	16.9
10.05	519.5	520	1.018	1.717	0.633	1.051	13.8	14.9
13.40	521.5	520	0.948	1.401	0.613	0.842	11.5	16.3

The experimental particle size measured from TEM or SEM images represents dry size due to the high vacuum experimental conditions. However, in the sensor experimental conditions, AuNPs were suspended in aqueous media. AuNPs suspended in liquid may have larger hydrodynamic diameter (wet size) due to surface solvation, adsorbed molecules or immobilized functional molecules. Dynamic light scattering (DLS) measurements of AuNPs solution, before and after aggregation by BMP, were conducted to get their hydrodynamic sizes. As synthesized under 100 °C with a citrate/Au ratio 3.35, AuNPs had hydrodynamic size 22.5 nm (Fig. 2D) which was ~7.5 nm larger than the dry size measured by TEM. The particle size distribution from three duplicates were very close to each other, which also indicates stable AuNPs suspension. The size discrepancy ~7.5 nm was largely attributed to the water molecules and citrate anions adsorbed on AuNPs surface. Together with DSL, zeta potential (ZP) was also measured which represents the electrical potential at the slipping plane of AuNPs, where mobile fluids are separated from the fluid remaining attached to the surface. The AuNPs suspension sample had a ZP -14.5 mV, a bit lower than expected due to unknown reasons, indicating somehow incipient stability [20]. However, in fact the prepared AuNPs suspension have been used in this study for longer than a month without any stability issue observed or

any wavelength shift in the SPR extinction peak. Particle size distribution and zeta potential of a BMP-induced AuNPs aggregate sample is shown in Fig. S1C, where it's average dynamic particle size is 197.2 nm, much larger than that (22.5 nm) of the pristine AuNPs, its zeta-potential is -25.9 mV, near to stable state since the particles have aggregated. A sample similar to Fig. S1C but with the addition of 1 ppm arsenite (Fig. S1D) shows a similar dynamic particle size and zeta-potential values (26.44 nm, -11.5 mV) as the pristine AuNPs (22.5 nm, -14.5 mV), indicating that formation of the probes could also be confirmed by zeta-potential changes.
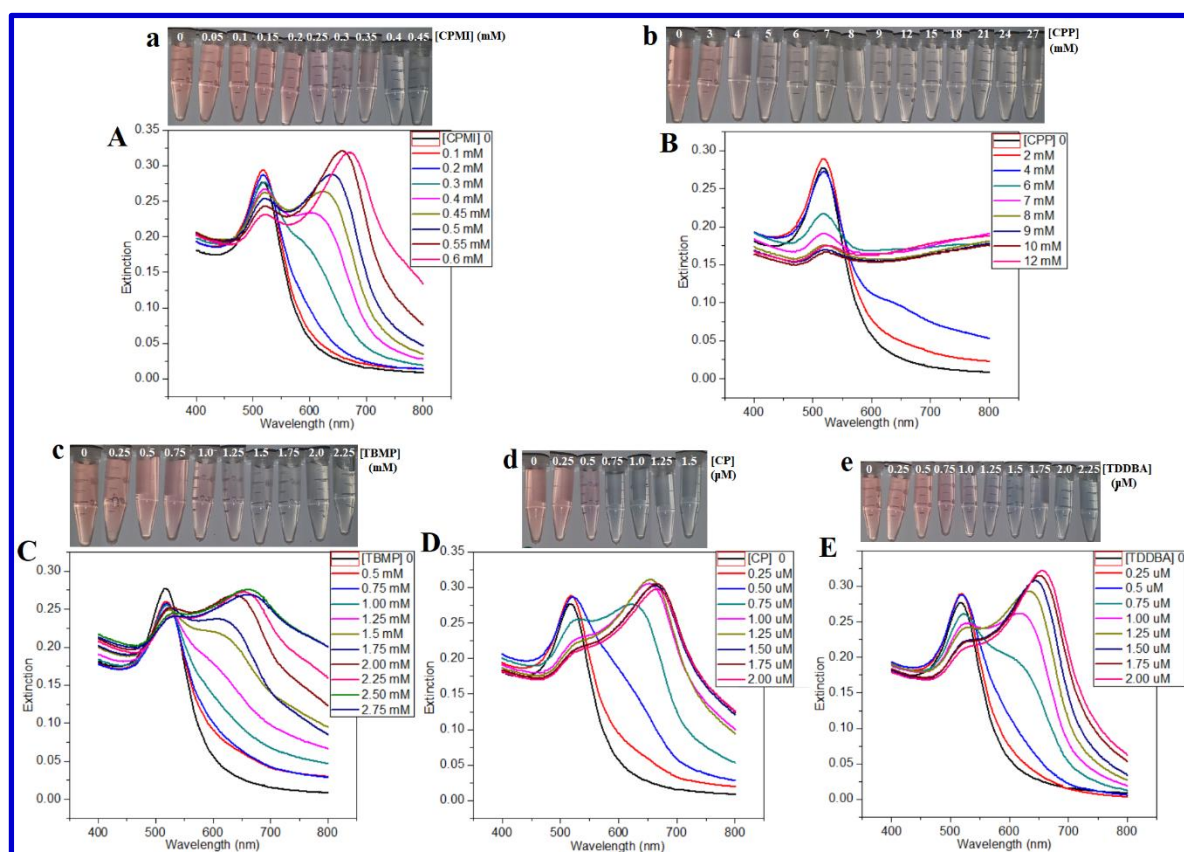

Figure S2 (A) E_{spr}, E_{650}, and (**B**) E_{650}/E_{spr}, $d(E_{650}/E_{spr})/d[BMP]$ of AuNPs in dependence of BMP concentration
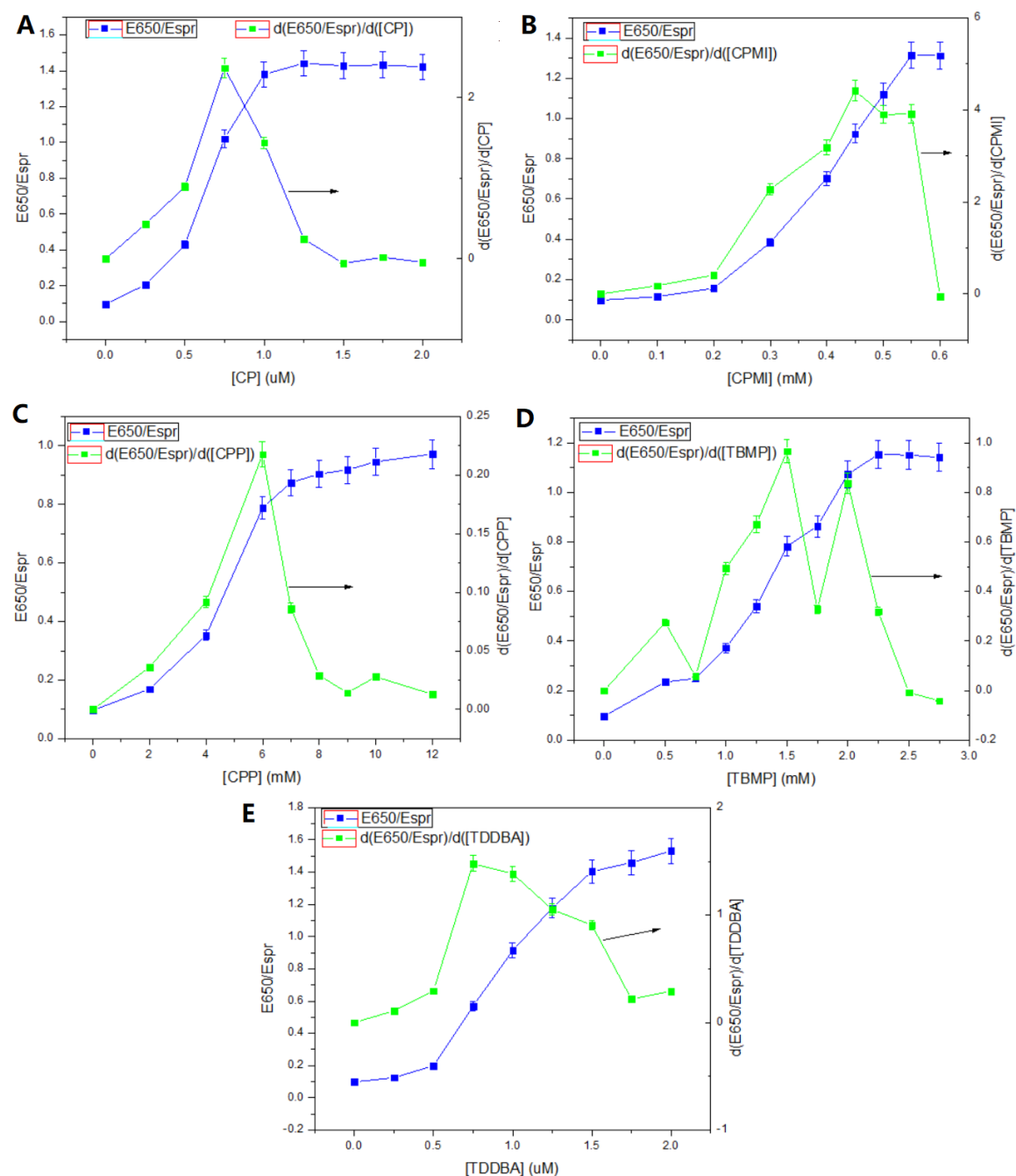
Optimizing IL Concentration

AuNPs capped with citrate anions repel each other owing to the negatively charged steric barrier on the surface, preventing them from aggregation. Therefore, in the absence of IL, AuNPs suspension were well-dispersed. A single SPR extinction peak of AuNPs was observed at 517 nm wavelength in the UV-Vis spectrum (Fig 2E). In the presence of BMP, the pink AuNPs suspension gradually turned blue with increased BMP concentration (Fig 2C). Along

with color change, the SPR peak height decreased, and a broad shoulder band emerged at 600 – 700 nm centered at around 650 nm. The other 5 ILs also had similar effect on color (Fig. S3a-e) and spectra (Fig. S3A-E) changes as BMP, with an unexpected exception of CPP whose spectra did not have apparent band at 650 nm. The surface negative charges of AuNPs were shielded by ILs at enough concentration, resulting in shortened inter-particle distance and subsequent aggregation, which explained the SPR peak diminishing/dismissing and the band at 650 nm emerging. Therefore, the ratio E_{650}/E_{spr} at 650 nm and SPR wavelength (517 nm in our case) is commonly used to indicate AuNPs aggregation [11]. In addition, here we also plotted the differential function $d(E650/Espr)/d[ILs]$ against [ILs] to better visualize the minimum [ILs] required (Fig. S2B,). The dry size of one precipitated aggregate of AuNPs was estimated to be around 1-2 μm from the TEM photo (Fig. 1C) while those suspended aggregate had a measured average wet size of 129 nm (Fig. S1C). The minimum concentrations and working concentrations of ILs for AuNPs aggregation are listed in Table 1.
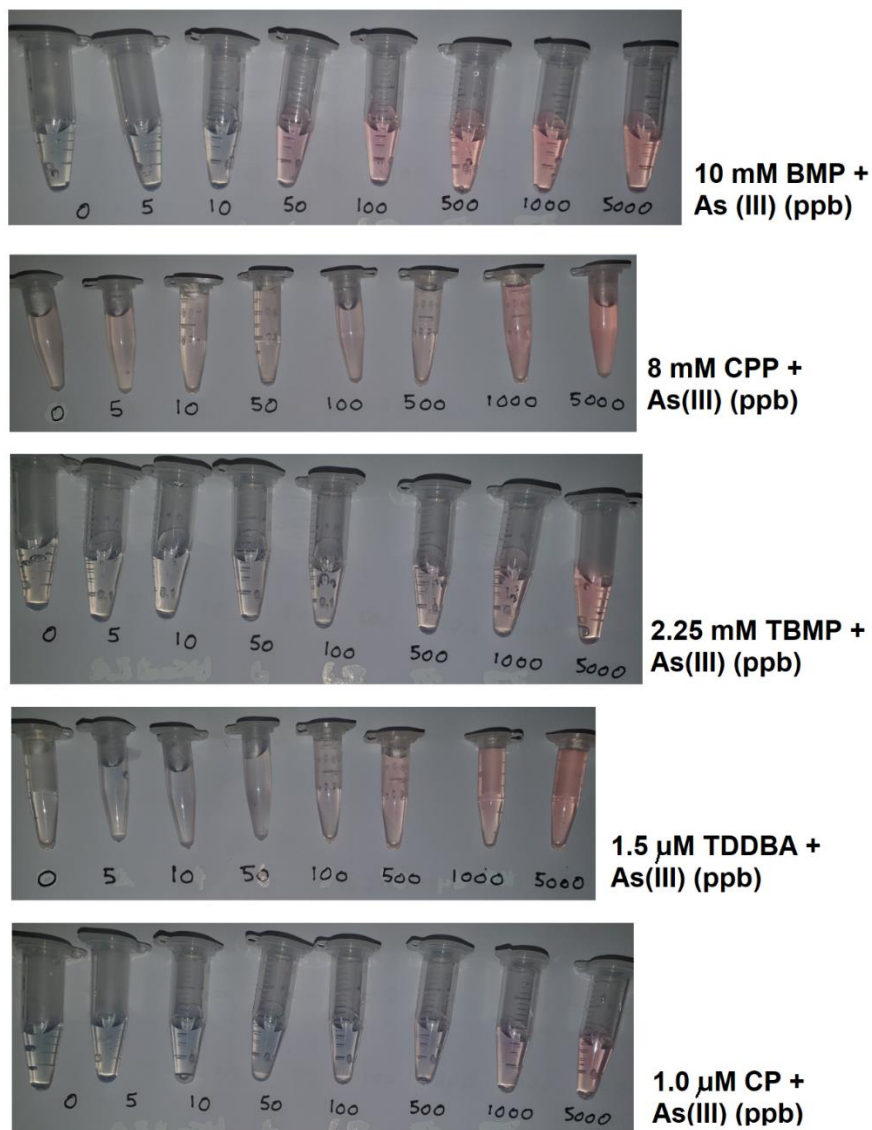
Fig. S3 UV-Vis spectra and photographs of AuNPs in the presence of different concentration of (A) CPMI, (B) CPP, (C) TBMP, (D) CP and (E) TDDBA

Fig. S4 E_{650}/E_{spr} and $d(E_{650}/E_{spr})/d[IL]$ of AuNPs in dependence of ILs concentration, (A) CP, (B) CPMI, (C) CPP, (D) TBMP, and (E) TDDBA

The ratio E_{650}/E_{spr} at 650 nm and 517 nm is commonly used to indicate AuNPs aggregation [10]. In addition, here we also plotted the differential function $d(E_{650}/E_{spr})/d[ILs]$ against [ILs] to better visualize the minimum [ILs] required (Fig. S4).

$$\text{Normalized Relative Selectivity (NRS) (\%)} = \left(1 - \frac{\left(\frac{E_{650}}{E_{spr}}\right)_{ion} - \left(\frac{E_{650}}{E_{spr}}\right)_{lowest}}{\left(\frac{E_{650}}{E_{spr}}\right)_{highest} - \left(\frac{E_{650}}{E_{spr}}\right)_{lowest}}\right) \times 100\ \% \qquad \text{(eq. S3)}$$

Fig. S5 Color change of the AuNPs suspension in dependence of As(III) concentration with optimized concentrations of ILs: (A) BMP, (B) CPP, (C) TBMP, (D) TDDBA, and (E) CP