Supplementary Material (ESI) for Chemical Communications

Potassium ion recognition by facile dithiocarbamate assembly of benzo 15-crown-5 gold-nanoparticles

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Supporting Information:

Synthetic procedure:

Spectrophotometric grade CS_2 (Aldrich) was freshly distilled from CaH_2 just prior to use. **Caution: Carbon disulfide is highly toxic and has to be handled under a fume hood.** 4 amino benzo 15 crown 5 was purchased from Sigma-Aldrich and used without further purification. For the formation of secondary amine of crown ether, sodium bicarbonate was used as base catalyst with benzyl chloride reaction.

Synthesis of Gold nanoparticles

The procedures were essentially the same as those developed by Turkevich-Frens.[1] with difference only in the molar ratio of $HAuCl_4$ to sodium citrate, where higher $HAuCl_4$ concentration resulted in larger particles. All glassware was thoroughly cleaned with freshly prepared 3:1 HCl/HNO_3 (aqua regia) and rinsed thoroughly with Millipore-Q water prior to use. The 18 M Ω cm^{-1} water was used to prepare all solutions in this study. To synthesize 18-nm-diameter colloids, in a round bottom flask equipped with a condenser, 180 mL of 0.8 mM $HAuCl_4$ was brought to a boil with vigorous stirring, and 10 mL of 19.4 mM sodium citrate was rapidly added to the vortex of the solution. The solution changed from pale yellow to burgundy. The solution was boiled for additional 10 min and then cooled with stirring for another 15 min. After the solution reached room temperature, it was filtered through a 0.45μ filter (Millipore, Nylon membrane).

[1] Enustun B V, Turkevich J, J. Am. Chem. Soc, 1963, 85: 3317

Synthesis of N benzyl 4 amino benzo 15-crown-5

4-Aminobenzo 15 crown 5 (1.00 g) was dissolved in DMF. 0.4 g sodium bicarbonate was added and subsequently benzyl chloride (2.5 mL) was added, and the mixture was heated at reflux temperature for 3 hrs. In the next step, the reaction mixture was washed with a saturated solution of 0.1 M HCl and then with water. The organic layer was concentrated, and the product was recrystallized in THF. The product was purified by column chromatography (SiO2, hexane/EtOAC) 1:3) to give as a brown color 0.8 g product (84% yield): ^{1}H NMR (400 MHz BRUKER) δ 10.5 (s, 1H); , 6.4- 7.2 (m, 8H); Ar-H, 3.1-4.1(m, 16H); crown moiety

Synthesis of benzo 15-crown-5 modified gold nanoparticles

1 mM solution of N benzyl 4- amino benzo 15-crown-5 in ethanol was treated with an equimolar concentration of CS_2 in same solvent. The reaction was continued for one hour to generate the dithiocarbamate ligand. Gold nanoparticles was then added to the above mixture and kept shaking for 1 hour.

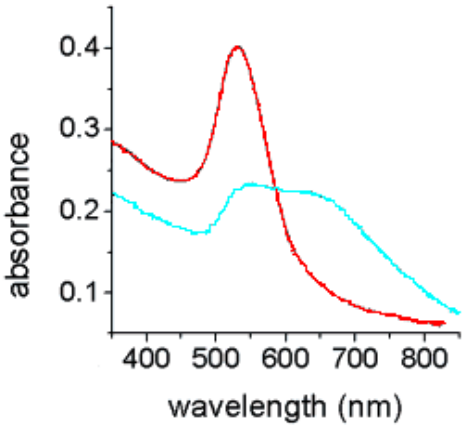

Figure S1 shows the UV spectrum of 26.6 mM crown modified colloidal solution containing interferences of the aforementioned cations (0.5 mM each). UV-visible spectra of crown capped colloidal gold containing (red) Na^{+}, Li^{+}, Cs^{+}, NH_4^{+}, Mg^{2+}, and Ca^{2+} (0.5 mM each) and (blue) the above species and 0.1 mM K^{+}.

Table S1.

Solution pH	2	4	6	8	10
Stability of Au Np-DTC-CE	1 h	2 h	Week	Months	Months

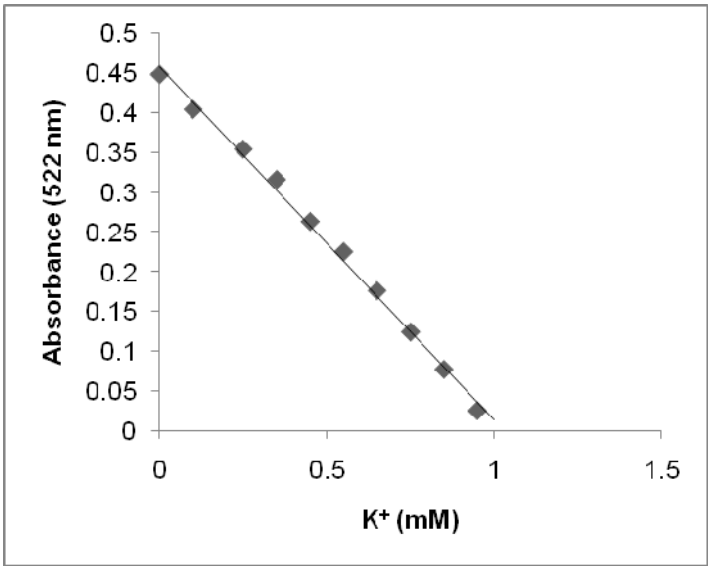

Figure S2. Calibration curves for quantitative measurements of K^+. The calibration curves was obtained 15−20 min after introducing the samples in 0.26 mM of Crown modified Au Nps

The serum sample was collected from one of the co author Gaurang. Immediately after blood sample collection, the samples were stored in a 0 °C refrigerator and centrifuged at 3000 rpm for 20 min. The supernatant serum sample was 10-fold diluted by deionized water.

Table S2. Parallel comparison of K^+ in serum sample measured by Crown capped Au Nps and atomic absorption spectrometer (AAS)

Sample No.	Crown capped Au Nps mM (Absorbance)	AAS (mM)
1.	0.45 (0.263)	0.45
2.	0.45 (0.262)	0.44
3.	0.45 (0.263)	0.45
S.D	**0 (0.006)**	**0.006**