Supplementary Information

Functional Dialkylimidazolium-Mediated Synthesis of Silver Nano-crystals with Sensitive Hg$^{2+}$-Sensing and Efficient Catalysis

Hucheng Zhang,* Lu Ye, Xingang Wang, Fangfang Li, Jianji Wang*

Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, P. R. China.
**Chemicals.** 1-methylimidazole (99%), 1, 10- dibromodecane (98%), potassium thioacetate (98%), p-nitrophenol (>99%), Hg(NO$_3$)$_2$·H$_2$O (99.99%), and rhodamine 6G (99%) were obtained from Sigma-Aldrich Co.; chloroform (99%), acetonitrile (99.5%), NaOH (≥96%), HBr (40%, AR), CH$_2$Cl$_2$ (99.5%), hexane (98%), NaBH$_4$ (≥99%), AgNO$_3$ (99.8%), ethanol (99.5%), KNO$_3$ (99%), NaNO$_3$ (99%), Pb(NO$_3$)$_2$ (99%), Mg(NO$_3$)$_2$·6H$_2$O (99%), Ba(NO$_3$)$_2$ (99.5%), Zn(NO$_3$)$_2$·6H$_2$O (99%), Co(NO$_3$)$_2$·6H$_2$O (99%), Cu(NO$_3$)$_2$·3H$_2$O (99%), Fe(NO$_3$)$_3$·9H$_2$O (99%), Ca(NO$_3$)$_2$·4H$_2$O (99%), Cd(NO$_3$)$_2$·4H$_2$O (99%), and Ni(NO$_3$)$_2$·6H$_2$O (99%) were purchased from Aladdin-Reagent Co., Shanghai. All reagents were used as received without any further purification.

**Measurements:** $^1$H and $^{13}$C NMR spectra were collected on a Bruker AV 400 MHz, and referenced to tetramethylsilane in D$_2$O. The sample for transmission electron microscope (TEM) measurement was prepared by placing a drop of the suspension onto a carbon-coated copper grid, and TEM experiments were conducted on a JEM-2100 high-resolution transmission electron microscope operated at 200kV. The UV-vis absorption spectrum measurements were performed on a TU-1810 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd), using a matched pair of quartz cuvettes with a path length of 1 cm. The fluorescence spectra of the samples were measured on FLS980 spectrophotometer with a 450W xenon lamp (Edinburgh Instruments) at room temperature, and recorded under the same instrumental conditions using the excitation wavelength of 425 nm. The silver content
was determined using a PE700 atomic absorption spectrometer (PerkinElmer). After samples were filled into the disposable plastic cuvettes, the data of dynamic light scattering and zeta potentials were collected using Zetasizer Nano-ZS90 (Malvern instruments) with a 633 nm He-Ne laser, and were analyzed by standard procedures provided with instrument software.

**Synthesis of thiol-functionalized ligands:** In a typical process, 1-methylimidazole (2.0180g) was fully mixed with 1, 10-dibromodecane (22.1460g) in chloroform (30 mL) at room temperature. After reflux for 15 h, chloroform was removed by rotary evaporator, and the reaction mixture was washed with hexane. The residue was dissolved in water, and hexane was employed to extract repeatedly unreacted 1, 10-dibromodecane. After evaporation of water, 1-(10-bromodecyl)-3-methylimidazolium bromide in 89% yield was dried in vacuum at 60 °C for 48 h. Then, potassium thioacetate (2.4701g) was mixed with the acetonitrile solution (30 mL) of 1-(10-bromodecyl)-3- methylimidazolium bromide (8.2658g). The reaction mixture was refluxed for 8 h, and cooled to room temperature. After filtering out the precipitate, 1-(10-(S-acetyl)mercaptodecyl)-3- methylimidazolium bromide in 91% yield was obtained using rotary evaporator to remove acetonitrile in the filtrate, and finally was vacuum-dried at 60 °C for 48 h. Finally, aqueous solution (8 ml) of NaOH (0.07872g) was added to the solution of 1-(10-(S-acetyl) mercaptodecyl)-3- methylimidazolium bromide (7.4280g) in ethanol (24 ml). The reaction mixture was stirred at 0 °C for 6 h, and subsequently the acidification with HBr was carried out the mixture until pH = 2. [HS-C_{10}mim]Br was collected by extraction with CH$_2$Cl$_2$, and dried with MgSO$_4$. After evaporation of CH$_2$Cl$_2$, the resulting product in 92% yield
was vacuum-dried at 60 °C for 48 h. The desired compounds are confirmed from $^1$H and $^{13}$C NMR spectra as shown in Figures S4-S9.

**Preparation of Ag Nanocrystals:** In a typical experiment, 12 mL of freshly-prepared AgNO$_3$ solution (1.5 mM) was kept away from the light, and was deaerated by bubbling with N$_2$ for at least 20 min. Then, 1 mL of [HS-C$_{10}$mim]Br solution (18 mM) was slowly injected into AgNO$_3$ solution under magnetic stirring to obtain a clear solution. After 30 min incubation, 10 mL of NaBH$_4$ solution (7.2 mM) was added dropwise to the reaction mixture, and silver nanocrystals were grown at room temperature. The stirring was continued for 2 h. The solution developed from colourless to light yellow, and finally represents a bright wine red of Ag nanocrystals.

**Hg$^{2+}$ Ion Sensing Studies:** The as-synthesized Ag NCs were used for the Hg$^{2+}$ detection. The composite sensors were formed by mixing rhodamine 6G (1.0×10$^{-6}$ M) solution with equal volume solution of Ag nanocrystal (2.0×10$^{-7}$ M) with magnetic stirring for 30 min. The standard stock solution of Hg$^{2+}$ (1.0×10$^{-3}$ M) was prepared by dissolving Hg(NO$_3$)$_2$ in deionized water, and serially diluted to get solutions of Hg$^{2+}$ with different concentration. These solutions were respectively introduced into the composite sensor, and fluorescence spectrum was measured after the sample was stood for 45 min. To evaluate the selectivity of composite sensor to Hg$^{2+}$, different nitrate salts of K$^+$, Na$^+$, Pb$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Ca$^{2+}$, Cd$^{2+}$, and Ni$^{2+}$ were respectively used as a substitute for Hg(NO$_3$)$_2$, and the exactly similar procedures were carried out as done for the detection of Hg$^{2+}$.
Catalytic Reduction Studies: The solution of as-synthesized Ag NCs was centrifuged to remove the excess ligands at 17,000 rpm for 1 h. The sediment was redispersed in deionized water, and the resulting solution was used as the catalyst. A 5 mL solution of the purified colloidal nanocrystal sample was dried, and the obtained solid residue was completely digested by aqua regia. The digested sample was used to prepare an aqueous solution, and the silver content in the purified sample was determined to be $4.41 \times 10^{-5} \text{ g/mL}$ by atomic absorption measurements. In the catalytic reduction experiment, the freshly prepared solutions of p-nitrophenol (16 μL, 5mM) and NaBH$_4$ (75μL, 0.2M) were mixed in a standard quartz cell with a 0.5 cm path length, and 0.81 mL of deionized water was introduced to adjust the volume to 0.90 mL. Thereafter, 0.1 mL of the purified Ag nanocrystal was added to induce the reduction, and immediately the reaction kinetics at 298K was monitored by the measurement of UV-Vis absorption spectrum over the range of 250–550 nm.
Figure S1. The hydrodynamic diameter distribution histograms of Ag NCs in water obtained from the measurements of dynamic light scattering.
Figure S2. The energy-dispersive X-ray spectra obtained respectively from the as-synthesized Ag NC coated on the copper grid (A) and the employed carbon-coated copper grid (B). Besides background peaks from the copper grid, evidently, the presence of Ag, Br, S, N elements in the as-synthesized Ag NCs can be confirmed by the energy-dispersive X-ray spectrum (A), and is consistent with the expected those.
Figure S3. UV-vis absorption spectrum of the aqueous solutions for Ag nanocrystals (a), Rh6G-Ag nanocomposite (b), and Rh6G-Ag nanocomposite with Hg$^{2+}$ concentration (mol•L$^{-1}$) at 1.0×10$^{-4}$ (c) and 1.0×10$^{-3}$ (d), respectively.
Figure S4. $^1$H NMR spectrum of 1-(10-bromodecyl)-3- methylimidazolium bromide.
**Figure S5.** $^{13}$C NMR spectrum of 1-(10-bromodecyl)-3- methylimidazolium bromide.
Figure S6. $^1$H NMR spectrum of 1-\((10\text{-}(S\text{-acetyl})\text{mercaptodecyl})\text{-}3\)\text{-methylimidazolium bromide.}
Figure S7. $^{13}$C NMR spectrum of 1-(10-(S-acetyl)mercaptodecyl)-3-methylimidazolium bromide.
Figure S8. $^1$H NMR spectrum of 1-(10-mercaptopdecy1)-3-methylimidazolium bromide
Figure S9. $^{13}$C NMR spectrum of 1-(10-mercaptodecyl)-3-methylimidazolium bromide