Supporting Information

Chiral Ionic Liquid Monolayer–Stabilized Gold Nanoparticles: Synthesis, Self–assembly and Application to SERS

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Synthesis [S1]

***S*-2-(imidazol-1-yl)-propionic acid ethyl ester**:[S2] Formaldehyde aqueous solution (36 %, 24.4 g) and glyoxal aqueous solution (32 %, 52.9 g) were added to a 250 mL flask. While the mixture was heated to 50 °C with stirring, a mixture of L-alanine (26.0 g) and ammonia solution (28 %, 17.7 g) was added to the flask; sodium hydroxide solution (10%, 116 g) was then added in small portions over 0.5 h. The mixture was stirred for an additional 4 h at 50 °C, and the water was removed under reduced pressure. The residue was dried in a vacuum desiccator with P_2O_5. The crude product, sodium *S*-2-(imidazol-1-yl)-propionate, was obtained as a white solid. ***S*-2-(imidazol-1-yl)-propionic acid ethyl ester** was prepared by refluxing sodium *S*-2-(imidazol-1-yl)-propionate in anhydrous ethyl alcohol saturated with dry hydrogen chloride. After the reaction was complete, excess hydrogen chloride and alcohol were removed under reduced pressure. The pH of the residue was adjusted to ~ 8.5 with saturated sodium carbonate solution. The resulting product was extracted with ethyl acetate and dried with Na_2SO_4. The product was further purified by column chromatography (1:6 petroleum ether/ethyl acetate).

***S*-2-(imidazol-1-yl)propan-1-ol:**[S3] Lithium aluminum hydride (LAH) (8.6 g) in 250 mL of anhydrous ether was added to a 500 mL flask. With stirring, 25.3 g of

***S*-2-(imidazol-1-yl)-propionic acid ethyl ester** was added in small portions over 1 h. After the mixture was stirred for 1 h at room temperature, more LAH (11.4 g) was added. The mixture was stirred for an additional 2 h, and then 50 mL of water was very carefully added dropwise. The resulting suspension of a white granular solid in ether was filtered. The solid was suspended in methanol under reflux for 1 h and then filtered. The combined ether and methanol filtrates were evaporated to dryness, and the resultant product was further purified by column chromatography (1:10, methanol/ethyl acetate).

***S*-3-Hexadecyl-1-(2-hydroxy-1-methyl-ethyl)-imidazolium bromide** ([C_{16}hmim]Br)**:** Under vigorous stirring, 78 g of cetyl bromide was added dropwise to a solution of 12.0 g of *S*-2-(imidazol-1-yl)propan-1-ol in 100 mL of 1,2-dichlorethane over 0.5 h. The mixture was stirred for an additional 6 h under reflux and evaporated to dryness. The resulting product was further purified by recrystallization from ethyl acetate 5 times and dried under vacuum for 48 h.

The calculation of EF is followed:[S4]

In order to determine the enhancement effect of R6G on the assembling film, the enhancement factor (EF) values of R6G in the assembling film are determined using the following expression:

$$EF = (I_{SERS}/N_{ads}) / (I_{bulk}/N_{bulk})$$

where I_{SERS} is the intensity of a vibrational mode in the surface-enhanced spectrum, I_{bulk} is the intensity of the same mode in the Raman spectrum, N_{ads} is the number of molecules adsorbed and sampled on the SERS-active substrate, and N_{bulk} is the number of molecules sampled in the bulk. N_{abs} can be obtained according to the method proposed by Orendorff et al. [S5] which is

$$N_{ads} = N_d A_{laser} A_N/\sigma$$

where N_d is the number density of the gold nanoparticles, A_{laser} is the area of the focal spot of laser, A_N is the footprint area of the gold nanoparticles, and σ is the surface area occupied by an adsorbed R6G molecule. In order to simplify the model, we assume that patterns of gold nanoparticles are densely packed and then N_d can be obtained. From the TEM we find that the

mean diameter of the gold nanoparticles is 6.0 ± 1.4 nm and then A_N can be obtained. A_{laser} can be obtained from the diameter of the laser spot (~1 μm). The long-axis length of an R6G molecule is ca. 1.4 nm.[S6] Therefore, one can assume that in the densely packed R6G monolayer a single R6G molecule should take no more than 4 nm^2 in area, indicating that σ can be adopted as ~ 4 nm^2/molecule.[S7] Then the total number of surface adsorbed molecules (N_{ads}) within the illuminated laser spot can be obtained at 6.16×10^5. N_{bulk} is the molecule number of the solid R6G in the laser illumination volume. In our experiment, the laser spot is about 1 μm in diameter and the penetration depth is about 2 μm. Taking the density of the solid R6G (1.26 g/cm^3) into account, N_{bulk} was calculated to be about 2.49×10^9 within the illuminated laser light. The intensity of the measured light at 1366 cm^{-1} was about 18000 and 1000 for SERS and ordinary Raman, respectively. Finally, the EF at the assembled film for the band located at 1366 cm^{-1} can be calculated to be about 7.28×10^4.

References

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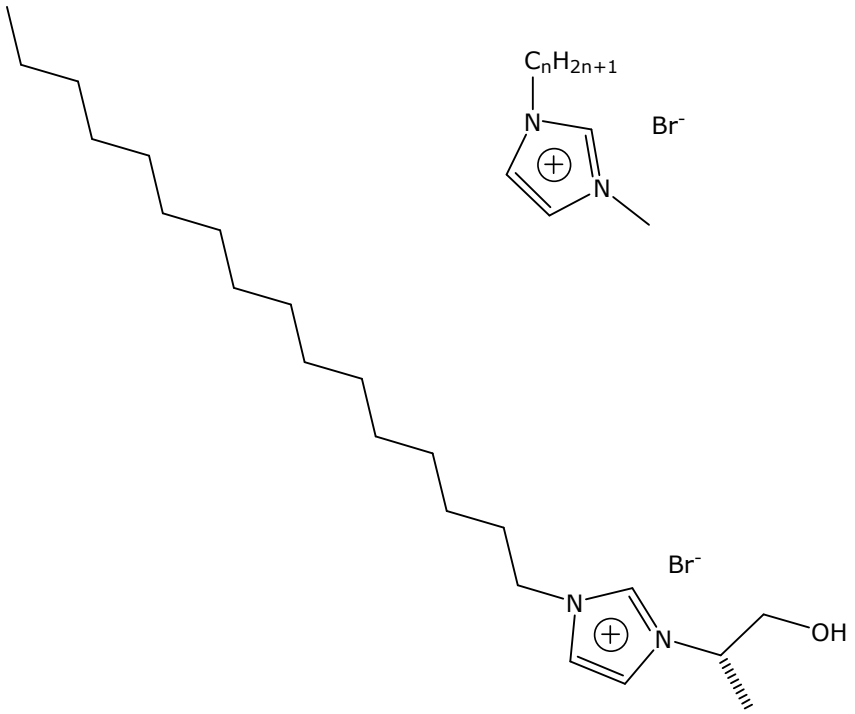
Figures



S-3-Hexadecyl-1-(2-hydroxy-1-methyl-ethyl)-3*H*-imidazol-1-ium bromide

Figure S1. Molecular structures of [$C_n$mim]Br (n = 12 or 16) and [C_{16}hmim]Br.

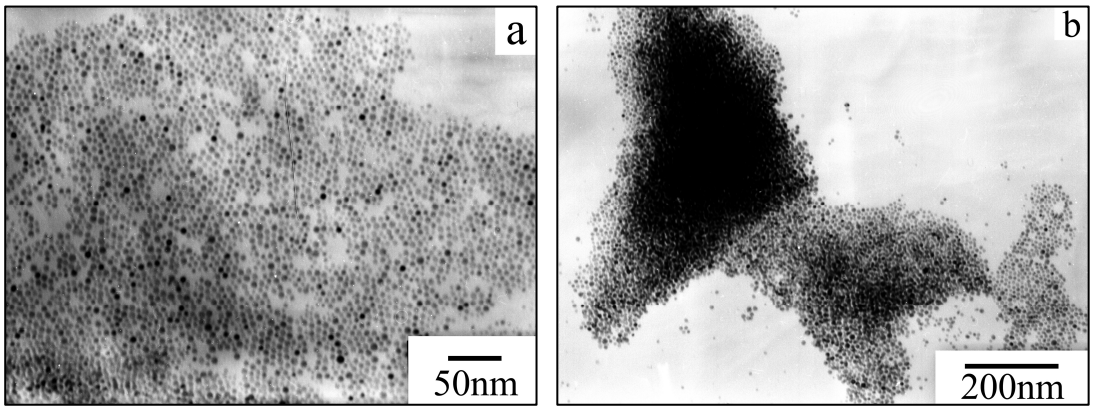


Figure S2. Ionic liquid nanoparticle morphologies of C_{12}-Au (a) and C_{16}-Au (b) mixtures at the air/water interface.