Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Polydentate Disulfide for Enhanced Stability of AuNPs and Facile Nanocavity Formation

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Supporting Information

1.1 Synthesis of Bis (methacryloyl hydroxyethyl) disulfide (DSDMA)

Synthesis procedure

The procedure reported by Li and Armes[1] was slightly modified. Bis (2-hydroxy ethyl) disulfide 5 g (1equivalent) and triethyl amine (35 ml, 8 equivalents) were dissolved in 100 ml DCM. The flask containing the solution was then immersed in ice bath, and methacryloyl chloride (13 ml, 4 equivalents) was added drop wise to DCM solution and stirred for 24 h. The reaction mixture was then filtered to remove triethylamine salt precipitated. The product was purified by column chromatography (yield 80%)

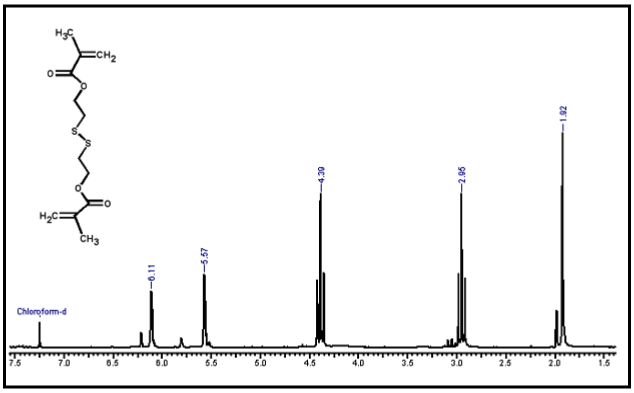


Figure S1 ^{1}H NMR of DSDMA

^{1}H NMR (200 MHz, $CHCl_3$): 5.57 δ and 6.11 δ (4H, singlet, terminal olefin proton) 4.30 δ (4H, $-OCH_2-$), 2.96 δ (4H, $-SCH_2-$) and 1.92 δ (6H, 2-CH_3 of DSDMA)

1.2 UV-Vis spectra of DSDMA stabilized AuNPs

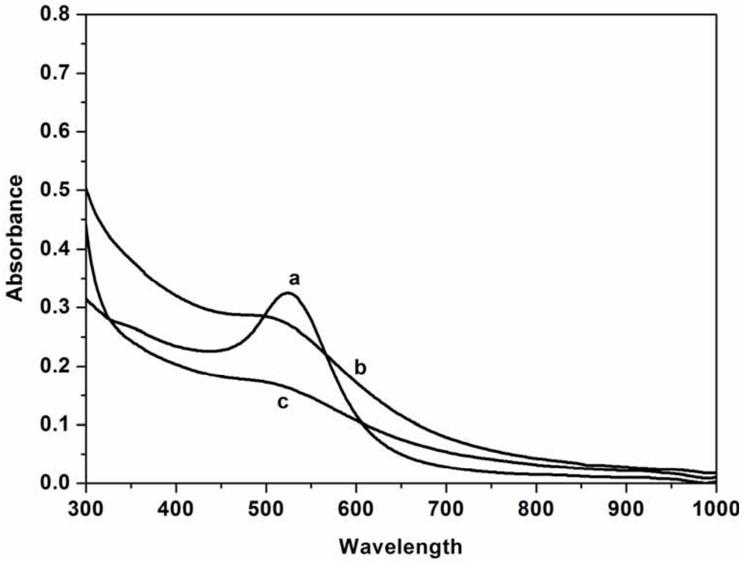


Figure S2 UV-Vis spectra of DSDMA AuNPs. Disulfide to gold ratio a) 1:1 b) 10:1 c) 25:1

DSDMA stabilized AuNPs show peak at 516 nm for 1:1 disulfide: Au ratio. Further increase in disulfide: Au ratio, 10:1 and 25:1 results in broad peak indicating decrease in particle size.

1.3 TEM analysis of DSDMA stabilized AuNPs

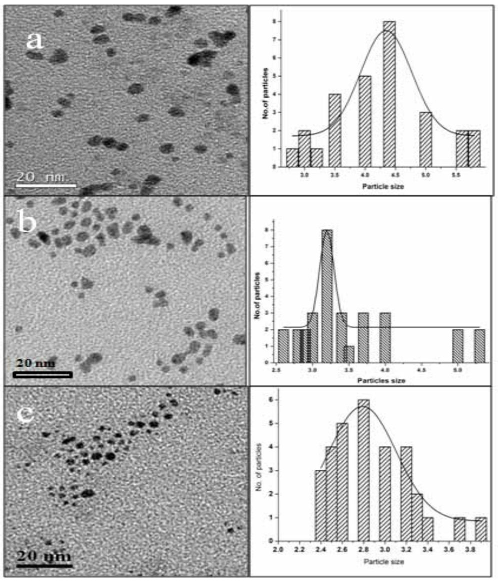


Figure S3 TEM of DSDMA stabilized AuNPs. Disulfide: Au a) 1:1 b) 10:1 c) 25:1

TEM analysis shows particle sizes 4.4, 3.2 and 2.8 nm at disulfide: Au a) 1:1 b) 10:1 c) 25:1.

1.4 FT-IR spectrum of DSDMA stabilized AuNPs

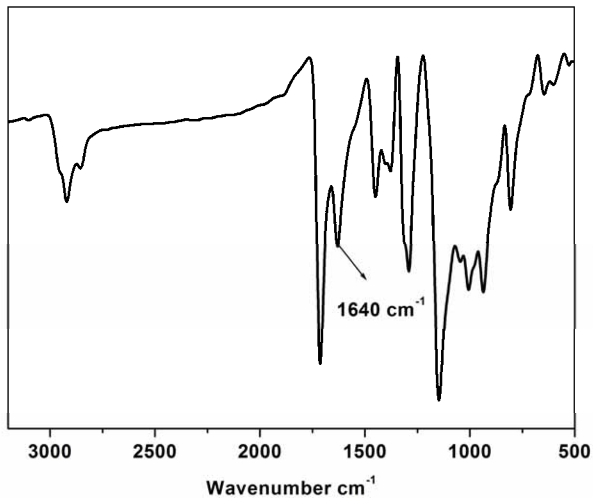


Figure S4 IR spectrum of DSDMA stabilized AuNPs

DSDMA stabilized AuNPs show presence of unsaturation (1640 cm^{-1})

1.5 Solvent stability

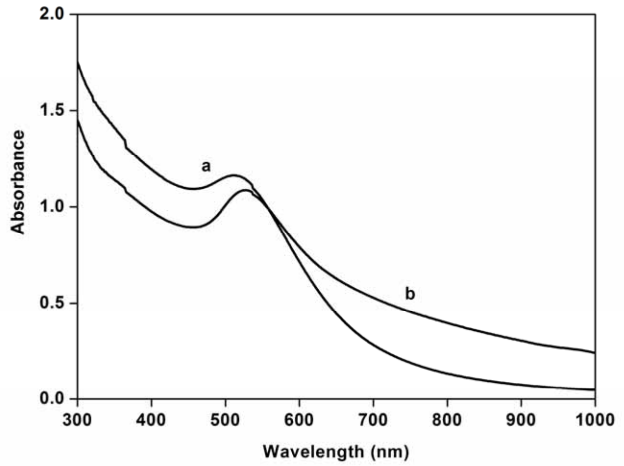


Figure S5 UV-Visible spectra of DSDMA AuNPs after a) 1 day b) 15 days.

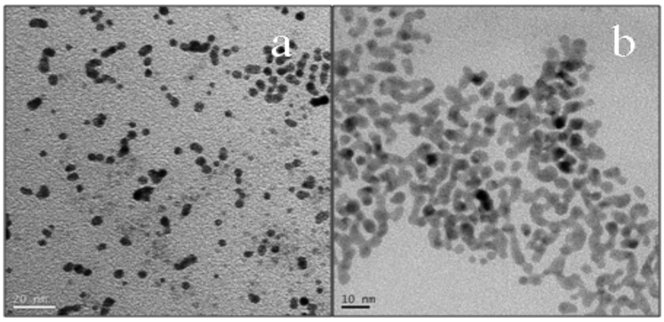


Figure S6 TEM image of DSDMA stabilised AuNPs at 1:1 ratio after a) 1 day b) 15 days.

1.6 Stability against DTT

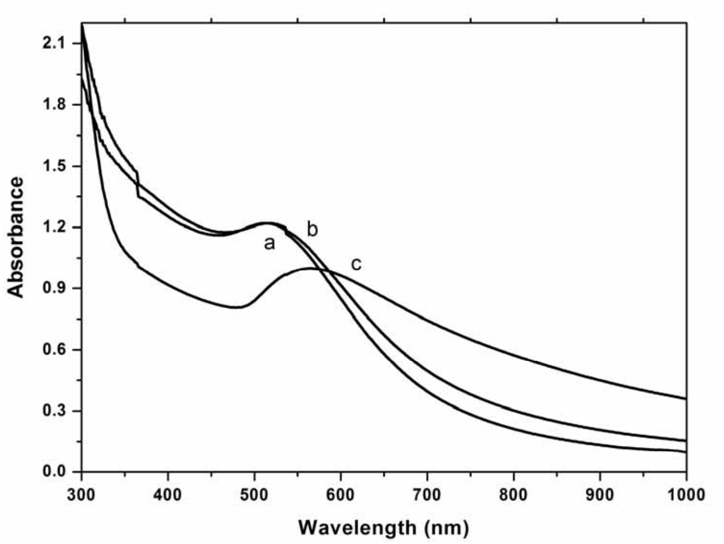


Figure S7 UV-Vis spectra of 4.4 nm AuNPs stabilized on DSDMA and after DTT addition a) before b) at 24 h c) 24.5 h

1.7 Thermal stability of DSDMA stabilized AuNPs

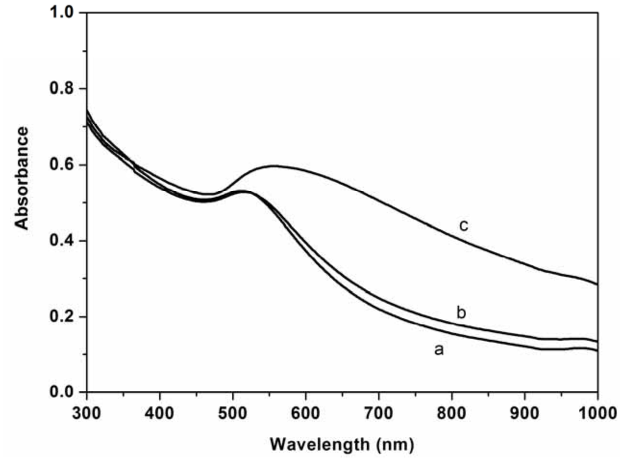


Figure S8 UV-Vis spectra of DSDMA stabilized AuNPs at a) 30 ^{0}C b) 90 ^{0}C c) 100 ^{0}C

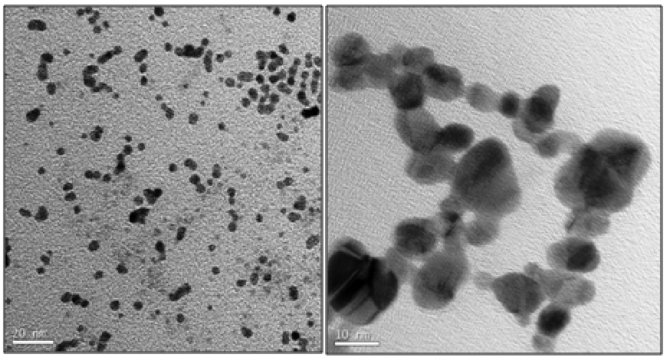
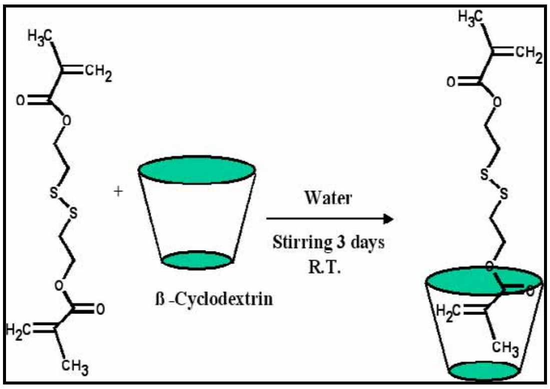


Figure S9 TEM analysis of DSDMA stabilized AuNPs at a) 30 ^{0}C b) 100 ^{0}C

AuNPs stabilized on DSDMA are thermally stable up to 90 ^{0}C. Above this temperature SPR peak shifted from 516 to 540 nm as shown in Figure S8, which results in color change from dark brown to pink and was followed by aggregation, as confirmed by TEM Figure S9.

2.1. Synthesis of DSDMA -β CD inclusion complex



Scheme 1 DSDMA inclusion complex synthesis

The 1:1inclusion complex of DSDMA was synthesized by the precipitation method reported by Satav et al[2], DSDMA and cyclodextrin mixture was stirred for 72 h.

2.2 Poly (DSDMA) stabilized AuNPs

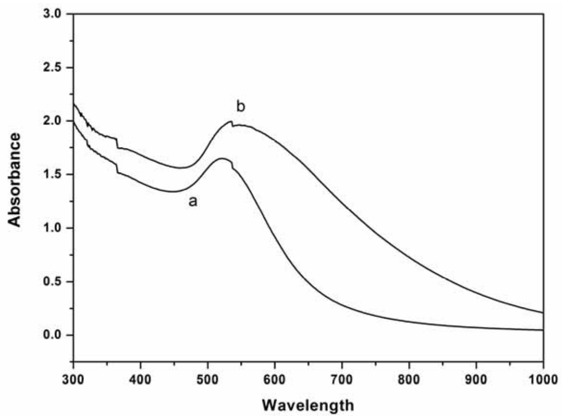


Figure S10 UV-Vis spectra of Poly (DSDMA) stabilized AuNPs at disulfide : Au a) 1:5 b) 1:10

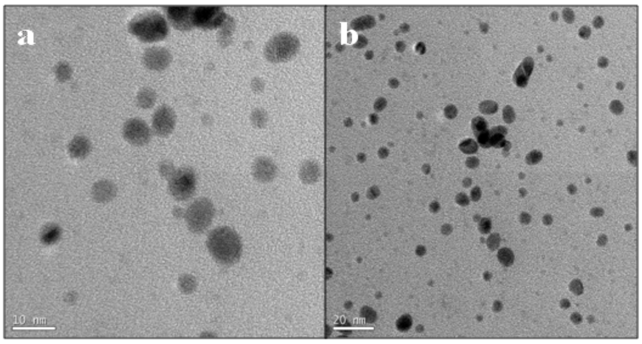


Figure S11 TEM analysis of Poly (DSDMA) stabilized AuNPs at disulfide: Au a) 1:5 b) 1:10

2.3 X-ray photoelectron spectroscopy of Poly (DSDMA) stabilized AuNPs

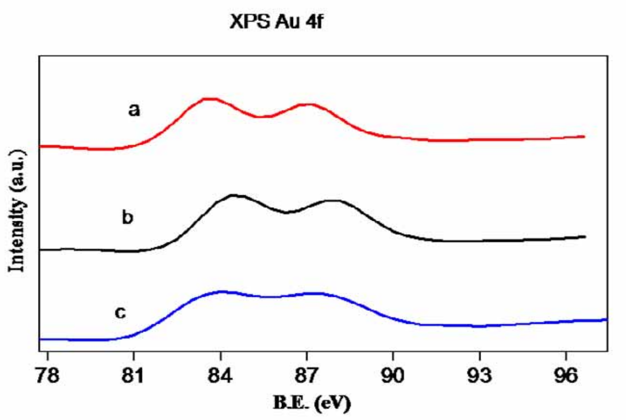


Figure S12 Binding energy of AuNPs of particle size a) 2.2 nm b) 2.8 nm c) 3.2 nm

2.4 Dynamic light scattering (DLS)

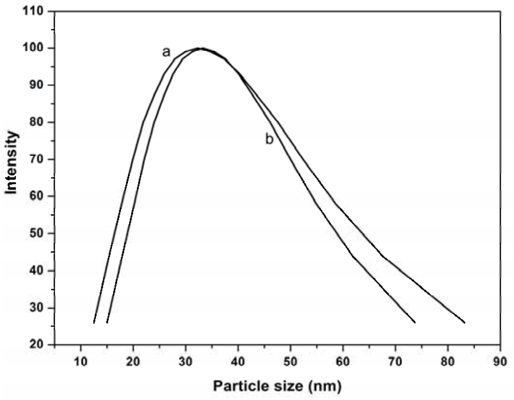


Figure 13 DLS of Poly (DSDMA) stabilized AuNPs a) before b) after etching

2.5 Estimation of number of disulfide units for 3.2 nm DSDMA stabilized AuNPs

1) Volume of a spherical particle = $\frac{4}{3}\Pi r^3$

r = 1.6 nm for DSDMA stabilized 3.2 nm AuNPs

Volume of particle = $\frac{4}{3}$ x3.142 x $(1.6)^3$ nm^3

Volume of particle = 17.15 x 10^{-21} cc

2) Mass of gold particle = Volume x Density

= 17.15 x 10^{-21} cc x 19.32 g/cc

Mass of gold particle = 3.31 x 10^{-19} g

From TGA, wt % of DSDMA = 29.2

wt % of Au = 66.25

3) Mass of DSDMA = $\frac{29.2}{66.25}$ x 3.31 x 10^{-19} g

Mass of DSDMA = 1.458 x 10^{-19} g

4) 290 g DSDMA contain 6.023 x 10^{23} molecules

1.458 x10^{-19} g DSDMA contain 302 DSDMA molecules

5) Area of AuNPs of diameter 3.2 nm = 32.15 nm^2

Number of DSDMA units per unit area of AuNPs = $\frac{302}{32.15}$

Number of DSDMA units per unit area of AuNPs = 9.39 DSDMA unit / nm^2

Estimation of number of disulfides for 2.8 nm Poly (DSDMA) stabilized AuNPs

1) Volume of a spherical particle = $\frac{4}{3}\Pi r^3$

r = 1.4 nm for Poly DSDMA stabilized 2.8 nm AuNPs

Volume of particle = $\frac{4}{3}$ x 3.142 x $(1.4)^3$ nm^3

Volume of particle = 11.48 x 10^{-21} cc

2) Mass of Particle = Volume x Density

$= 11.48 \times 10^{-21}$ cc x 19.32 g/cc

Mass of particle $= 2.21489 \times 10^{-19}$ g

From TGA, wt % of Au = 32.74

wt % of Polymer = 65.44

3) Mass of Poly (DSDMA) $= \frac{65.44}{32.74} \times (2.21489 \times 10^{-19})$ g

Mass of Poly (DSDMA) $= 4.4428 \times 10^{-19}$ g

4) 290 g of DSDMA contain 6.023×10^{23} molecules

$4.4428 * 10^{-19}$ DSDMA will have 922 molecules

5) Area of AuNPs of diameter 2.8 nm = 24.6 nm^2

Number of DSDMA units per unit area of AuNPs $= \frac{922}{24.6}$

Number of DSDMA units per unit area of AuNPs = 37.47 DSDMA unit / nm^2

6) DP of Poly (DSDMA) is 20 , therefore graft density will be 1.8 chains / nm^2

Reference

1) Y. Li and Armes, S.P. Macromolecules 2005, **38**, 8155-8162.

2) Satav, S.S.; Karmalkar, R.N.; Kulkarni, M.G.; Mulpuri, N. Sastry, G.N. J. Am. Chem. Soc., 2006, **128**, 7752-7753.