Supporting Information

Tuning Optical Limiting of Heterosized AuNPs and Fullerene by Countable Electrochemical Assembly

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**Figure. S1** Mass spectrum of 1 nm carbazolyl thiol capped AuNPs (A); TEM images of carbazolyl thiol capped 5 (B) and 10 nm (C) AuNPs. Scale bar: 100 nm. Electrospray mass spectrometry was used to characterize 1 nm AuNPs carrying 25 gold atoms and 18 ligands. The molecular ion peak of 10007.4 is exactly corresponding to the molecular mass of 1 nm AuNPs, indicating that the 1 nm AuNPs was successfully synthesized.

**Figure S2.** Profilometer thickness analysis of (A) 1, (B) 5, and (C) 10 nm AuNPs films.
Figure S3. AFM images of 1 (A), 5 (B) and 10 nm (C) AuNPs films with thickness of 200 nm on ITO electrodes. Scale bar: 5 μm.

Figure S4. XRD patterns of bare ITO (A) and FTO (B), and AuNPs films on ITO (C) and FTO (D), respectively.
Figure S5. (A) Last CVs of AuNPs films after each assembly of 10 nm AuNPs (20 cycles, pink), 5 nm AuNPs (10 cycles, purple) and 1 nm AuNPs (6 cycles, black); (B) Profilometer thickness analysis of heterosized AuNPs trilayer.

In Figure S5, all cycles were studied from same ITO. Each kind of AuNPs was fabricated via successive CV mode in different AuNPs solutions. This figure showed last CV cycle for preparation of each layer on identical ITO electrode. First cycle (pink) is relative to last CV of 10 nm AuNPs layer. Second cycle (purple) is relative to last CV of 5 nm AuNPs/10 nm AuNPs. Third cycle (black) is relative to last CV of 1nm AuNPs/5nm AuNPs/10 nm AuNPs
Figure S6. FT-IR spectra of 5 (A) and 10 nm (B) AuNPs before (red) and after (black) ligand exchange. The bands of oleylamine disappear after the ligand exchange of AuNPs, two new bands appear and belong to the benzen ring vibration of carbazoles.

Figure S7. CVs with different scan rates of 10 (A, B), 5 (C, D) and 1 nm (E, F) AuNPs films in AuNPs free solutions. The shapes of CV do not change obviously, that can be considered that most of carbazoles have reacted.
Figure S8. (A) Absorption spectra of AuNPs films; (B) Profilometer thickness analysis of 10 nm and 1 nm heterosized AuNPs bilayer.

Figure S9. Optical limiting of films at 532 nm in reverse position of mono-sized AuNPs films and heterosized AuNPs trilayer film.

Figure S10. Optical limiting at 532 nm of ITO coated glass.
**Figure S11.** Absorption spectra of 10 and 1 nm heterosized AuNPs films with periodic numbers of 5 (A) and 10 (B), and their absorbance values at 550 nm as a function of number of layers (insert), and profilometer thickness analysis of 10 nm and 1 nm AuNPs films with the assembly periods of 5 (C) and 10 (D). The film assembly of 5 periods began with 10 cycles of 10 nm AuNPs and 2 cycles of 1 nm AuNPs, and this process was repeated for 5 times. The film assembly of 10 periods began with 9 cycles of 10 nm AuNPs and 1 cycle of 1 nm AuNPs, and the process was repeated for 10 times.
Figure S12. Optical limiting of films at 532 nm in reverse position for 10 and 1 nm heterosized AuNPs films with bilayer periods of 1 (A), 5 (B) and 10 (C). All films have same thickness of ~200 nm.

Figure S13. Absorption spectra of 10 and 1 nm heterosized AuNPs films with periodic numbers of 5 (A) and 10 (B), and their absorbance values at 550 nm as a function of number of layers (insert), and profilometer thickness analysis of 10 and 1 nm AuNPs films with the assembly periods of 5 (C) and 10 (D). The film assembly of 8 periods began with 12 cycles of 10 nm
AuNPs and 2 cycles of 1 nm AuNPs, and this process was repeated for 5 times. The film assembly of 10 periods began with 12 cycles of 10 nm AuNPs and 3 cycle of 1 nm AuNPs, and the process was repeated for 10 times.

**Figure S14.** Optical limiting at 532 nm of 10 and 1 nm heterosized AuNPs films (A, B); Optical limiting at 532 nm of 10 and 1 nm heterosized AuNPs films in reverse position (C, D). All films have same thickness of ~300 nm.
Figure S15. No. of AuNPs as a function of the No. of bilayer periods, the film thicknesses are 200 nm (A, B) and 300 nm (C, D).
Figure S16. CVs of AuNPs(1 nm)/C_{70} electrochemical copolymerizations with different ratios and photos of films of 10:1 (A), 5:1 (B), 1:1 (C), 1:5 (D), and 1:10 (E). In the process of electrochemical copolymerization, 15 mL CH_{2}Cl_{2} was selected as solvent, 495 mg TBABF_{4} (0.1 M) was selected as supporting electrolyte, the concentration of 1 nm AuNPs and C_{70} is 1 mg mL^{-1} and the specific ratios are as follows:

a. n_{1 nm AuNPs} : n_{C_{70}} = 10 : 1, n_{1 nm AuNPs} = 1.5E-3 mM, n_{C_{70}} = 1.5E-4 mM, m_{1 nm AuNPs} = 14.71 mg, m_{C_{70}} = 0.29 mg;

b. n_{1 nm AuNPs} : n_{C_{70}} = 5 : 1, n_{1 nm AuNPs} = 1.455E-3 mM, n_{C_{70}} = 2.91E-4 mM, m_{1 nm AuNPs} = 14.56 mg, m_{C_{70}} = 0.44 mg

c. n_{1 nm AuNPs} : n_{C_{70}} = 1 : 1, n_{1 nm AuNPs} = 1.3E-3 mM, n_{C_{70}} = 1.3E-3 mM, m_{1 nm AuNPs} = 13 mg, m_{C_{70}} = 2 mg

d. n_{1 nm AuNPs} : n_{C_{70}} = 1 : 5, n_{1 nm AuNPs} = 8.68E-4 mM, n_{C_{70}} = 4.34E-3 mM, m_{1 nm AuNPs} = 8.68 mg, m_{C_{70}} = 6.32 mg

e. n_{1 nm AuNPs} : n_{C_{70}} = 1 : 10, n_{1 nm AuNPs} = 6.11E-4 mM, n_{C_{70}} = 6.11E-3 mM, m_{1 nm AuNPs} = 6.11 mg, m_{C_{70}} = 8.89 mg.
Figure S17. AFM images of 1 nm AuNPs/C$_{70}$ hybrid films, the assembly periods are 1 (A) and 5 (B), respectively. Scale bar: 1 $\mu$m.

Figure S18. AFM images of 1 nm AuNPs/C$_{70}$ hybrid films, the ratios of 1 nm AuNPs to C$_{70}$ are 10: 1 (A), 5: 1 (B), 1: 1 (C), 1: 5 (D) and 1: 10 (E), respectively. Scale bar: 1 $\mu$m.

Figure S19. Optical limiting at 532 nm of 1 nm AuNPs/C$_{70}$ hybrid films with same thickness of ~200 nm and with differently nanostructures of 1 (A) and 5 (B) periods.
Figure S20. Optical limiting at 532 nm of 1 nm AuNPs/C$_{70}$ with different ratios and photos of films of 10:1 (A), 5:1 (B), 1:1 (C), 1:5 (D), and 1:10 (E) electrochemically copolymerized hybrid films with same thickness of ~200 nm.

2. Gold Nanoparticles (AuNPs) Preparation

a) Synthesis of carbazoyl thiol capped 1 nm AuNPs

Figure S21. Synthesis route of 1 nm AuNPs.

1 nm AuNPs were prepared according to previous method.$^{51}$ HAuCl$_4$:3H$_2$O (0.16 g, 0.41 mM) dissolved in 5 mL water, and TOAB (0.26 g, 0.47 mM) dissolved in 10 mL toluene, were combined in a 25 mL tri-neck round bottom flask. The solution was vigorously stirred (~1100
r.p.m.) with a magnetic stir bar to facilitate phase transfer of Au(III) salt into toluene phase. After 15 min, phase transfer was completed, leaving a clear aqueous phase at the bottom of flask. The aqueous was then removed using a syringe of 10 mL. The toluene solution of Au(III) was purged with N₂ and cooled down to 0°C in ice bath over 30 min under magnetic stirring. Cbz(CH₂)₆SH (0.21 g, ~3 equivalents of the moles of gold) was added, and stirring speed was reduced to a very low speed (~30 r.p.m.). Notely, the fast stirring significantly reduces the final Au₂₅ yield. The deep red solution turned to faint yellow over 5 min, and finally to colorless after 1 h, and then the stirring speed was immediately tuned to fast (~1100 r.p.m.). The aqueous solution of NaBH₄ (0.16 g, 4 mM, 10 equivalents versus the moles of gold, freshly made in 7 mL ice-cold water) was quickly added all at once. The mixture was allowed to react overnight under N₂ atmosphere. The solution mixed with ethanol was centrifuged at 8000 r.p.m. for 5 min to remove any large aggregates of nanoparticles and excess Cbz(CH₂)₆SH. The supernatant was removed and the precipitate was taken and dissolved in the mixed solution again for further centrifugal process with same processes for twice. In the end, a drop of the centrifuged solution was dipped onto a copper grid for TEM measurement.

b) Synthesis of 5 nm and 10 nm carbazolyl thiol capped AuNPs

HAuCl₄·3H₂O (0.08 g) dissolved in 20 mL oleylamine (OLA) at room temperature and the resulting solution was heated to 150°C with a heating rate of 5°C per minute and then kept at 150°C for 1h, resulting in a wine red solution. The ethanol was added to precipitate AuNPs, and then the centrifugation was performed to purify the NPs to give sepia solid. To complete the ligand exchange, Cbz(CH₂)₁₂SH rather than Cbz(CH₂)₆SH was used to reduce the steric hindrance. A mixture of AuNPs in toluene and electroactive ligand Cbz(CH₂)₁₂SH in chloroform was stirred for overnight at room temperature. The resulting solution was precipitated with
ethanol and centrifuged to purify the NPs. The resulting solid was dried with Argon flow, and dissolved in refined CH$_2$Cl$_2$ for electrochemical assembly. As for 10 nm carbazolyl thiol capped AuNPs, except that HAuCl$_4$·3H$_2$O (0.08 g) dissolved in 10 mL oleylamine (OLA) in the synthetic process of AuNPs, the other processes were unchanged.

c) Synthesis and characterization of organic electroactive ligand

6-(9H-carbazol-9-yl)hexane-1-thiol

![Synthesis route of 6-(9H-carbazol-9-yl)hexane-1-thiol.](image)

**Figure S22.** Synthesis route of 6-(9H-carbazol-9-yl)hexane-1-thiol.

9-(6-Bromohexyl)-9H-carbazole

Organic electroactive ligands were synthesized according to previous method.$^{52}$ NaH (0.96 g, 39.9 mM) was slowly added to a mixture of carbazole (3.3 g, 19.9 mM) in 60mL THF. The mixture was stirred for 1 h and slowly (10 min) added into a solution of 1,6-dibromohexane (4.3 g, 19.9 mM) in a dropping funnel under nitrogen. This solution was stirred for 12 h at 90°C, quenched with water, extracted with dichloromethane (3×50 mL). The organic phases were collected and combined, dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was purified by chromatography (from hexane: CH$_2$Cl$_2$ 20:1). Yield: 3.3 g, 50%. $^1$H NMR (ppm, CDCl$_3$, 300 MHz): $\delta = 8.09$ (d, 2H, Ar-H), 7.50-7.41 (m, 4H, Ar-H), 7.25-7.18 (m, 2H, Ar-H), 4.32 (t, 2H, NCH$_2$), 3.16 (t, 2H, CH$_2$Br), 1.94-1.72 (m, 4H, CH$_2$), 1.49-1.35 (m, 4H, CH$_3$).
6-(9H-carbazol-9-yl) hexyl ethanethioate

9-(6-bromoethyl)-9H-carbazole (3.0 g, 9.1 mM) was dissolved in DMF (60 mL), and then potassium thioacetate (1.5 g, 13.3 mM) was added. The mixture was stirred at room temperature for overnight. The solution was quenched with dichloromethane/acidic water (0.5 M HCl) and washed with acidic water for twice. The organic phases were collected and combined, dried with Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was purified by chromatography (from hexane: CH$_2$Cl$_2$ 1:1). Yield: 2.8 g, 95%. $^1$H NMR (ppm, CDCl$_3$, 300 MHz): δ = 8.11-8.07 (d, 2H, Ar-H), 7.50-7.40 (m, 4H, Ar-H), 7.25-7.18 (m, 2H, Ar-H), 4.31 (t, 2H, NCH$_2$), 2.82 (t, 2H, CH$_2$S), 2.29 (s, 3H, CH$_3$), 1.94-1.80 (m, 2H, CH$_2$), 1.57-1.48 (m, 2H, CH$_2$), 1.47-1.33 (m, 4H, CH$_2$).

6-(9H-carbazol-9-yl) hexane-1-thiol

6-(9H-carbazol-9-yl) hexyl ethanethioate (2.5 g, 7.7 mM) was dissolved in isopropyl alcohol/THF/H$_2$O 2.5:6:1.5, and subsequently the mixture was carefully degassed through a freeze/thaw cycle. Solid KOH (4.3 g, 76.9 mM) was added and stirred at 60°C for 5 h. The resulting solution was quenched with 0.5 M HCl (pH = 7). The mixture was extracted with dichloromethane (3×50 mL), and the organic phases were collected and combined, dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was washed with water and purified by chromatography (from hexane: dichloromethane 2:1). Yield: 1.7 g, 80%. $^1$H NMR (ppm, CDCl$_3$, 300 MHz): δ = 8.10 (d, 2H, Ar-H), 7.51-7.40 (m, 4H, Ar-H), 7.26-7.18 (m, 2H, Ar-H), 4.32 (t, 2H, NCH$_2$), 2.47 (t, 2H, CH$_2$), 1.95-1.82 (m, 2H,CH$_2$), 1.63-1.50 (m, 2H, CH$_2$), 1.49-1.29 (m, 4H, CH$_2$).
**Figure S23.** $^1$H NMR spectrum of 9-(6-bromohexyl)-9H-carbazole.

**Figure S24.** $^1$H NMR spectrum of 6-(9H-carbazol-9-yl)hexyl ethanethioate.
Figure S25. $^1$H NMR spectrum of 6-(9H-carbazol-9-yl)hexane-1-thiol.

Figure S26. Synthesis route of 12-(9H-carbazol-9-yl) hexane-1-thiol.

9-(12-Bromohexyl)-9H-carbazole

Carbazole (6.7 g, 39.9 mM) was dissolved in 80 mL THF, and then NaH (1.9 g, 79.9 mM) was slowly added and stirred for 1 h. The resulting solution was introduced under nitrogen in a dropping funnel and slowly added in 10 min to a solution of 1,12-dibromohexane (13.1 g, 39.9 mM). The reaction mixture was stirred at 90°C for 12 h, and quenched with water. The mixture was extracted with dichloromethane (3×50 mL) and the organic phases were collected and combined, dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was
purified by chromatography (from hexane: CH\textsubscript{2}Cl\textsubscript{2} 10:1). Yield: 9.1 g, 55%. \textsuperscript{1}H NMR (ppm, CDCl\textsubscript{3}, 300 MHz): \(\delta = 8.09\) (d, 2H, Ar-H), 7.48-7.37 (m, 4H, Ar-H), 7.25-7.18 (m, 2H, Ar-H), 4.26 (t, 2H, NCH\textsubscript{2}), 3.38 (t, 2H, CH\textsubscript{2}Br), 1.91-1.79 (m, 4H, CH\textsubscript{2}), 1.37-1.19 (m, 16H, CH\textsubscript{2}).

\textit{12-(9H-carbazol-9-yl) hexyl ethanethioate}

9-(12-bromohexyl)-9H-carbazole (6.9 g, 16.7 mM) was dissolved in DMF (100 mL), and then potassium thioacetate (2.2 g, 13.3 mM) was added. The mixture was stirred at room temperature for overnight. The reaction was quenched by adding dichloromethane/acidic water (0.5 M HCl), and washed with acidic water for twice. The organic phases were then dried over Na\textsubscript{2}SO\textsubscript{4} and evaporated under reduced pressure. The crude product was purified by chromatography (from hexane: CH\textsubscript{2}Cl\textsubscript{2} 1:1). Yield: 6.2 g, 90%. \textsuperscript{1}H NMR (ppm, CDCl\textsubscript{3}, 300 MHz): \(\delta = 8.11-8.07\) (d, 2H, Ar-H), 7.37-7.24 (m, 4H, Ar-H), 7.14-7.08 (m, 2H, Ar-H), 4.13 (t, 2H, NCH\textsubscript{2}), 2.74 (t, 2H, CH\textsubscript{2}S), 2.18 (s, 3H, CH\textsubscript{3}), 1.76-1.65 (m, 2H, CH\textsubscript{2}), 1.51-1.39 (m, 2H, CH\textsubscript{2}), 1.25-1.09 (m, 16H, CH\textsubscript{2}).

\textit{12-(9H-carbazol-9-yl) hexane-1-thiol}

12-(9H-carbazol-9-yl)hexylethanethioate (4.9 g, 12.0 mM) was dissolved in isopropyl alcohol/THF/H\textsubscript{2}O 2.5:6:1.5, and the mixture was subsequently and carefully degassed through a freeze/thaw cycle. Solid KOH (6.7 g, 119.7 mM) was then added and the mixture was stirred at 60°C for 5 h. The resulting solution was quenched with 0.5 M HCl (pH =7). The mixture was extracted with dichloromethane (3×50 mL), and the organic phases were collected and combined, dried over Na\textsubscript{2}SO\textsubscript{4} and evaporated under reduced pressure. The crude product was washed with water and purified by chromatography (from hexane: dichloromethane 2:1). Yield: 3.5 g, 80%. \textsuperscript{1}H NMR (ppm, CDCl\textsubscript{3}, 300 MHz): \(\delta = 8.10\) (d, 2H, Ar-H), 7.48-7.36 (m, 4H, Ar-H), 7.24-7.18 (m, 2H, Ar-H), 4.28 (t, 2H, NCH\textsubscript{2}), 2.81 (t, 2H, CH\textsubscript{2}), 1.98-1.82 (m, 2H, CH\textsubscript{2}), 1.63-1.50 (m, 2H, CH\textsubscript{2}), 1.49-1.29 (m, 16H, CH\textsubscript{2}).
Figure S27. $^1$H NMR spectrum of 9-(12-bromohexyl)-9H-carbazole.

Figure S28. $^1$H NMR spectrum of 6-(9H-carbazol-9-yl)hexyl ethanethioate.
Figure S29. $^1$H NMR spectrum of 12-(9H-carbazol-9-yl)hexane-1-thiol.

3. References

(S1) Zhu, M. Z.; Lanni, E.; Garg, N. Kinetically Controlled, High-Yield Synthesis of Au$_{25}$ Clusters. *J. Am. Chem. Soc.* **2008**, 130, 1138-1139.

(S2) Gao, Y. X.; Qi, J.; Zhang, J. Li, M. Fabrication of both the photoactive layer and the electrode by electrochemical assembly: towards a fully solution-processable device. *Chem. Commun.* **2014**, 50, 10448-10451.