Supplementary Information

REVISED

N-Heterocyclic Carbene-Stabilized Gold Nanoparticles and their Assembly into 3D Superlattices

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General considerations

All manipulations were performed under an atmosphere of dry nitrogen using Schlenk techniques and/or a M. Braun glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses (C, H, N) were performed by the microanalytical laboratory at the University of California, Berkeley. Elemental analyses (Cl^-) were performed by Galbraith Laboratories. UV-vis spectra were collected on an HP 89531A diode array spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 MHz NMR spectrometer and are reported with reference to solvent resonances (C_6D_6, δ 7.16 and δ 128.0). Nanocrystal size, morphology, structure, and superstructures were probed by TEM at the Electron Microscope Lab at the University of California, Berkeley, using a Tecnai 12 TEM (100kV). All TEM samples were prepared by placing a drop of the nanocrystal solution onto a carbon-coated copper grid at room temperature. The crystal structure of the samples was measured using powder X-ray diffraction with CoKα radiation (1.790 Å) and a general area detector (GADDS, Bruker). XRD samples were prepared by evaporating a nanocrystal solution onto a quartz plate. Particle sizes were determined on the basis of the Scherrer correlation of particle diameter (D) with peak width (Δs, full width at half-maximum) for Bragg diffraction from ideal single domain crystallites ($\Delta s = 0.9/D$, where $s = 2\sin\theta/\lambda$). SAXS data were collected with a Bruker Nanostar instrument. The illumination source was a copper tube ($\lambda = 1.54$ Å). The scattered photons were collected up to $2\theta = 3°$ with a two-dimensional gas-filled detector (Bruker HiStar) positioned at 105 cm, calibrated with silver behenate. The lowest scattering angles are occluded by a beam stop ($\theta < 0.5°$).

Silver(I)oxide (99%) and chloro(dimethylsuldide)gold(I) were purchased from Aldrich and used as received. $Ag((C_{14}H_{29})_2\text{-imy})Br$[1] (imy = N,N-disubstituted imidazol-2-ylidene) and $(^iPr_2Im)AuCl$[2] were synthesized according to litterature procedures.

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[1] C. K. Lee, K. M. Lee and I. J. B. Lin, *Organometallics,* 2002, **21**, 10.

Complex **1** :

To a 1/1 mixture (15.6 mmol) of Ag(($C_{14}H_{29}$)$_2$-imy)Br (imy = N,N-disubstituted imidazol-2-ylidene) and 4.6 g of Au(SMe_2)Cl in a 250 mL round bottom flask, 120 mL of CH_2Cl_2 were added at room temperature. After stirring 4h at room temperature, the solution was filtered thru a silica plug. All the volatiles were removed and the crude complex was dissolved in the minimum of CH_2Cl_2 and filtered slowly thru silica. After washing the silica with small amount of CH_2Cl_2, the solvent was removed under reduced pressure, yielding 7.9 g of **1** as a white solid (72%). ^{1}H NMR (400 MHz, C_6D_6, 25°C) : δ=0.91 (t, ^3J(H,H) = 7.2 Hz, 6 H; CH_3), 1.02 (m, 4 H; CH_2), 1.15 (m, 8 H; CH_2), 1.25-1.35 (m, 32 H; CH_2), 1.45 (m, 4 H; CH_2), 3.65 (t, ^3J(H,H) = 7.2 Hz, 4 H; CH_2N), 6.20 (s, 2 H; CH); ^{13}C NMR (100 MHz, C_6D_6, 25°C): δ=14.4 (s, CH$_3$), 23.1 (s, CH$_2$), 26.5 (s, CH$_2$), 29.5 (s, CH$_2$), 29.9 (s, CH$_2$), 30.0 (s, CH$_2$), 30.1 (s, CH$_2$), 30.2 (s, CH$_2$), 30.3 (s, CH$_2$), 30.4 (s, CH$_2$), 31.1 (s, CH$_2$), 32.4 (s, CH$_2$), 51.0 (s, CH$_2$N), 51.1 (s, CH$_2$N), 120.1 (s, CH), 120.2 (s, CH), 171.7 (s, C_{carbene}); LSIMS: *m/z* (%):1118 (100) [Au(($C_{14}H_{29}$)$_2$-imy)$_2^+$], 655 (50) [Au(($C_{14}H_{29}$)$_2$-imy)$^+$]; Anal. Calcd. For $C_{31}H_{60}AuClN_2$: C, 53.71; H, 8.72; N, 4.04. Found: C, 53.47; H, 8.73; N, 3.78.

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[2] M. V. Baker, P. J. Barnard, S. J. Berners-Price, S. K. Brayshaw, J. L. Hickey, B. W. Skelton and A. H. White, *J. Organomet. Chem.,* 2005, 5625.

Synthesis of AuNP(A) by reduction of ($^{i}Pr_2Im$)AuCl with $KBEt_3H$

1.2 equiv. of Potassium Triethylborohydride (1.56 mmol, 1M in THF) was added in one portion, at room temperature, to a stirred solution of 500 mg of ($^{i}Pr_2Im$)AuCl (1.30 mmol) in 20 mL of THF. After 40 min of stirring at room temperature, the resulting brown solution was quenched with 0.3 mL of EtOH. An aliquot of that solution was drop-casted on a TEM grid to reveal the presence of small nanoparticles (2.19 ± 0.47 nm).

Synthesis of AuNP(B) by reduction of **1** with $KBEt_3H$

1.2 eq. of Potassium Triethylborohydride (0.87 mmol, 1M in THF) was added in one portion, at room temperature, to a stirred solution of 500 mg of **1** (0.72 mmol) in 20 mL of THF. After 40 min of stirring at room temperature, the resulting ruby red solution was quenched with 0.3 mL of EtOH. The gold NP were isolated by adding 60 mL of acetone followed by centrifugation at 7000 rpm for 10 min. The resulting golden residu was dissolved in 8 mL of THF and filtered thru a silica plug. The gold NP were purified by precipitation with 8 mL of acetone. Redispersion of the NP in THF (8 mL) followed by precipitation with acetone 8 mL (2 times) lead to 31 mg (22%) of a golden powder after drying under vaccum overnight. These NP are redispersable in hexanes, toluene, THF but not in EtOH or acetone. UV/Vis (THF) : λ_{max} = 525 nm; ^{1}H NMR (C_6D_6, 25°C) : –1.20-4.10 (br, 58 H; CH_2 and CH_3); LSIMS: *m/z* (%): 1118 (100) $[Au((C_{14}H_{29})_2\text{-imy})_2^+]$; Anal. Found: C, 4.72; H, 0.66; N, 0.26; Cl^- Analysis: 878 ppm. Given the average particle size (6.8 nm), the number of gold atoms in the metal core is estimated to be ~ 9713 by the method of Whetten et al.[3] and leads to an estimated formula of $Au_{9713}C_{7897}H_{13126}N_{404}$ *i.e.* $Au_{9713}((C_{14}H_{29})_2\text{-imy})_{202}$.

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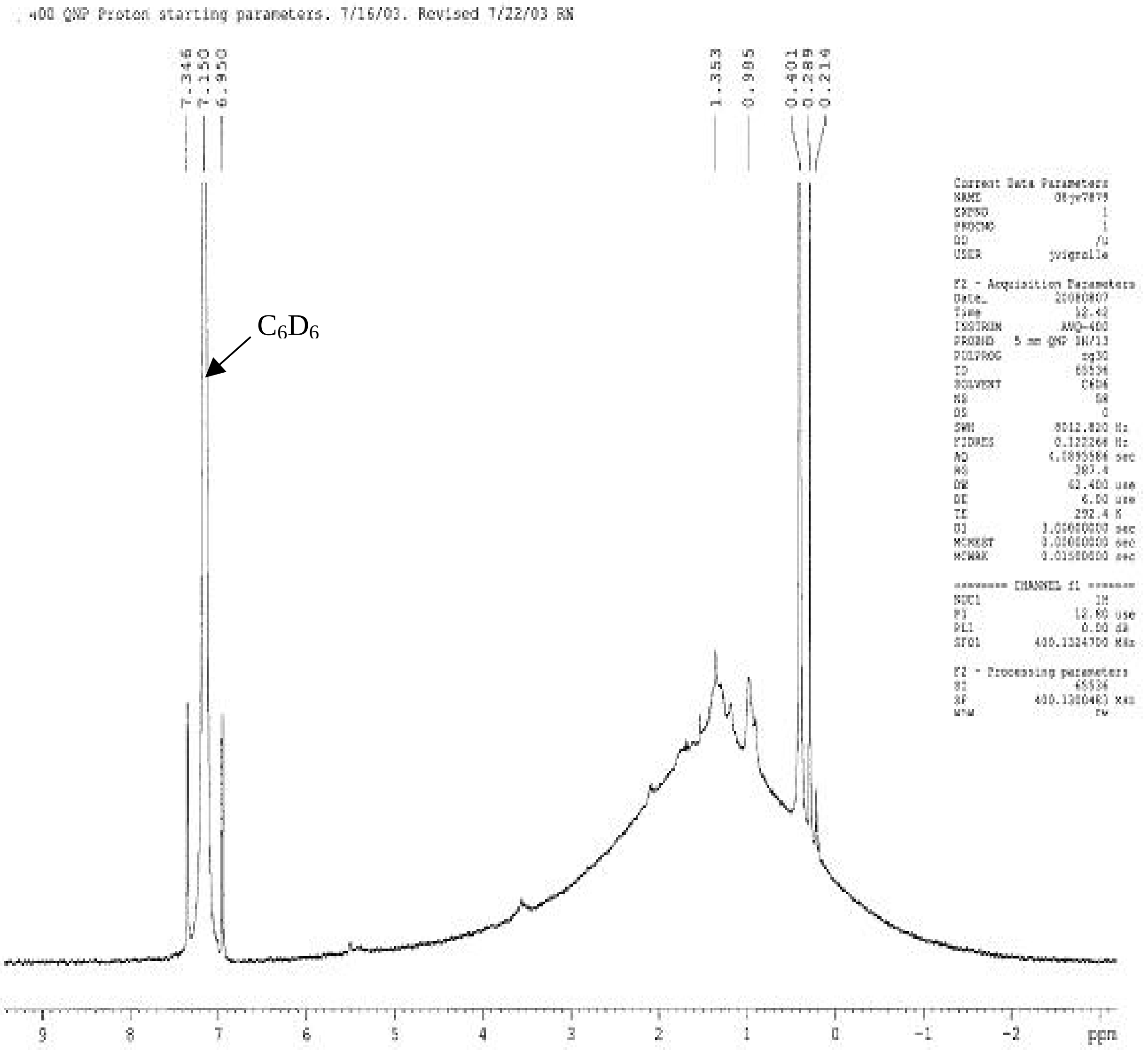
[3] M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. N. Shafigullin, I. Vezmar and R. L. Whetten, *J. Phys. Chem. B,* 1997, **101**, 3706.

Synthesis of AuNP(C) by reduction of **1** with 9-BBN

3.6 eq. of 9-BBN (2.08 mmol, 0.5M in THF) was added in one portion, at room temperature, to a stirred solution of 400 mg **1** (0.58 mmol) in 32 mL of Et_2O. After 40 min of stirring at room temperature, 0.5 mL of EtOH was added to the resulting ruby red solution. The gold NP were isolated by adding 60 mL of acetone followed by centrifugation at 7000 rpm for 10 min. The resulting golden residu was dissolved in 5 mL and purified by precipitation with 20 mL of acetone, followed by centrifugation at 7000 rpm for 10 min. 28 mg (25%) of a golden powder are obtained upon drying overnight under vaccum. These NP are redispersable in hexanes, toluene, THF but not in EtOH or acetone. UV/Vis (THF): λ_{max} = 535 nm; LSIMS: *m/z* (%): 1118 (100) [$Au((C_{14}H_{29})_2\text{-imy})_2^+$]; Anal. Found: C, 4.83; H, 0.71; N, 0.39. Given the average particle size (5.75 nm), the number of gold atoms in the metal core is estimated to be ~ 5873 by the method of Whetten et al. and leads to an estimated formula of $Au_{5873}C_{4894}H_{8512}N_{367}$ *i.e.* $Au_{5873}((C_{14}H_{29})_2\text{-imy})_{184}$.

Figure S7. ^{1}H NMR spectrum of AuNP(B)



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EXPNO 1
PROCNO 1
CURD /u
USER jvignolle

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PULPROG zg30
TD 65536
SOLVENT C6D6
NS 58
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0895584 sec
RG 287.4
DW 62.400 use
DE 6.00 use
TE 292.4 K
D1 3.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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NUC1 1H
P1 12.60 use
PL1 0.00 dB
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F2 - Processing parameters
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SF 400.1300463 MHz
WDW EM

Figure S8. UV/Vis Absorption spectrum of AuNP(B) in THF

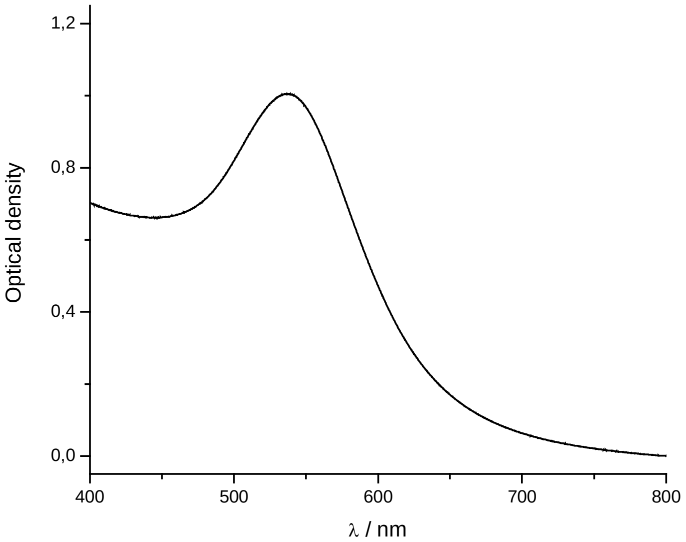


Figure S9. UV/Vis Absorption spectrum of AuNP(C) in THF

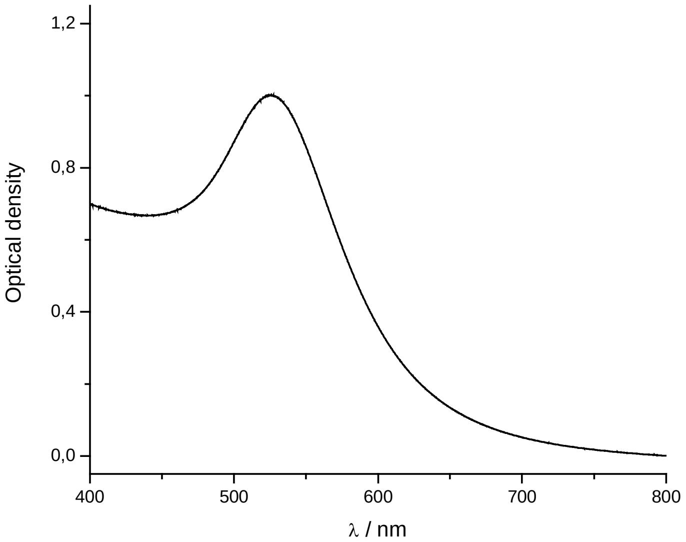


Figure S10. X-ray diffraction of powder sample AuNP(B)

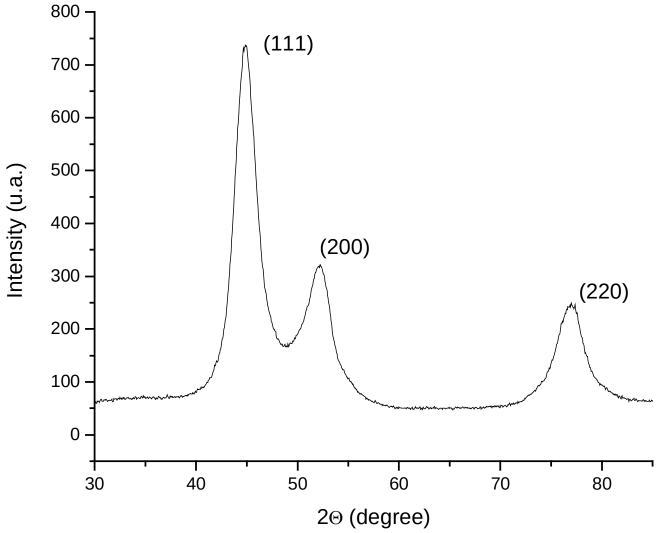


Figure S11. X-ray diffraction of powder sample AuNP(C)

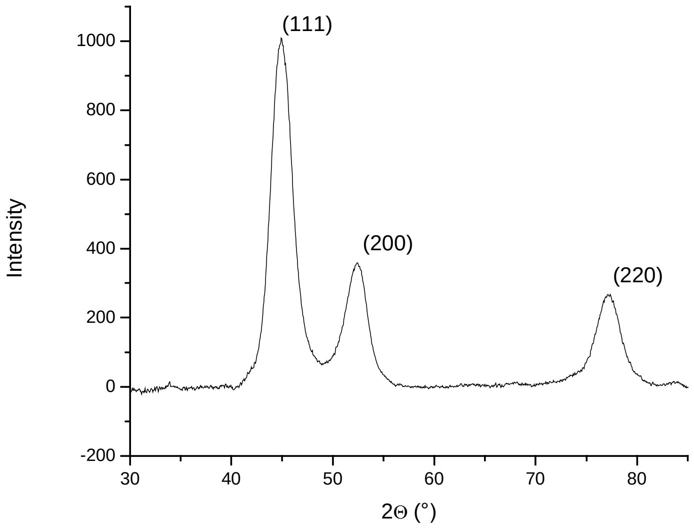


Figure S12. SAXS data of AuNP(C): experimental data (blue line) and fitted data (pink line).

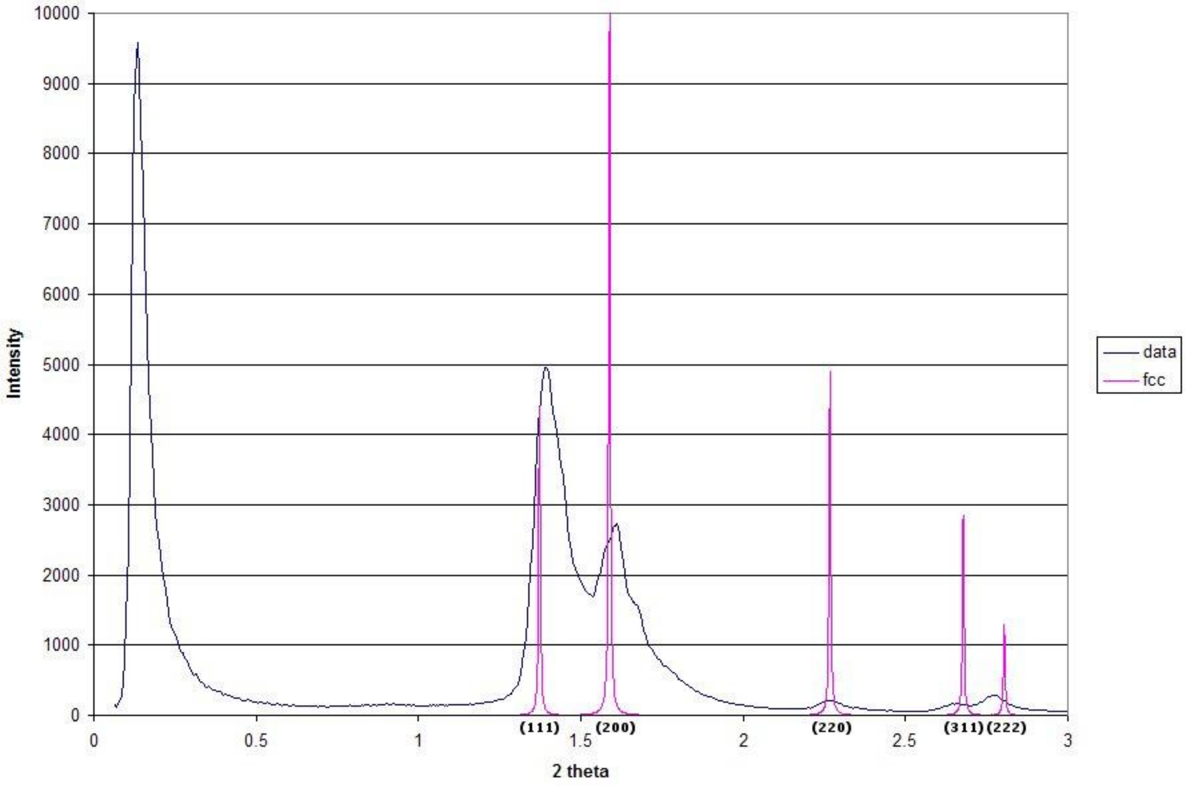
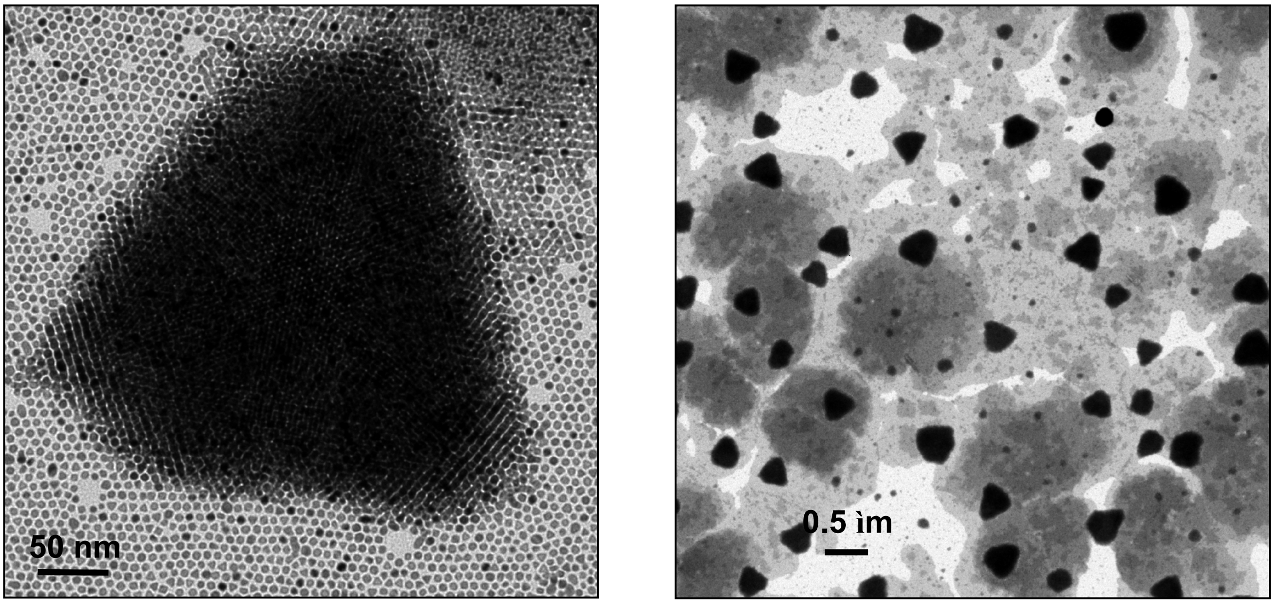


Figure S13. Low magnification TEM images of AuNP(C)



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(b) A. Courty, A. Mermet, P. A. Albouy, E. Duval and M. P. Pileni, *Nat. Mater.,* 2005, **4**, 395.

(c) S. H. Wang, S. Sato and K. Kimura, *Chem. Mater.,* 2003, **15**, 2445;

(d) A. L. Rogach, D. V. Talapin, E. V. Shevchenko, A. Kornowski, M. Haase and H. Weller, *Adv. Funct. Mater.,* 2002, **12**, 653;

(e) C. B. Murray, C. R. Kagan and M. G. Bawendi, *Annu. Rev. Mater. Sci.,* 2000, **30**, 545.

(f) R. L. Whetten, M. N. Shafigullin, J. T. Khoury, T. G. Schaaff, I. Vezmar, M. M. Alvarez and A. Wilkinson, *Acc. Chem. Res.,* 1999, **32**, 397.

(g) C. P. Collier, T. Vossmeyer and J. R. Heath, *Annu. Rev. Phys. Chem.,* 1998, **49**, 371.

(h) R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney and R. G. Osifchin, *Science,* 1996, **273**, 1690.