Electronic Supplementary Information for

One-pot Synthesis of sub-3 nm gold nanoparticle networks connected by thio-based multidentate fullerene adducts

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Experimental Details

Synthesis of the fullerene hexaadduct

General. Reagents were purchased as reagent grade and used without further purification. Absolute THF was purchased from Sigma Aldrich and used without further purification. Compound **1** has been prepared according to a literature procedure.[1] All reactions were performed in standard glassware under an inert argon atmosphere. Evaporation and concentration were done using a Vacuubrand Vacuum Pumping Unit PC 101 NT and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (70-230 mesh, 0.063-0.200 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization by UV light. IR spectra (cm^{-1}) were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on Bruker Avance 300 apparatus with solvent peaks as reference. Mass measurements were carried out on an UltraflexTM matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany) equipped with SCOUT^{TM} High Resolution Optics, an X-Y multi-sample probe and a gridless reflector. This instrument was used at a maximum accelerating potential of 25 kV in positive mode and was operated in mode reflector at 26 kV and a matrix suppression deflection (cut off) set to 500 m/z. A saturated solution of 1,8-dihydroxy-9,10-dihydroanthracen-9-one (dithranol, ALDRICH) in CH_2Cl_2 was used as matrix.

Compound 2. A solution of **1** (1.50 g, 4.33 mmol) and KSCN (1.53 g, 15.70 mmol) in EtOH (10 mL) / H_2O (2 mL) was refluxed for 1h. Water was added and the aqueous phase extracted three times with Et_2O. The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and evaporated. Column chromatography (SiO_2, EtOAc / toluene 1:1) yielded malonate **2** (1.12 g, 84%) as a colorless oil. IR: 1729 cm^{-1} (C=O), 2154 cm^{-1} (SCN); ^1H NMR ($CDCl_3$, 300MHz): $\delta = 4.28$ (t, 4H, $J = 6$Hz, CH_2O), 3.39 (s, 2H, $COCH_2CO$), 3.02 (t, 4H, $J = 7$Hz, CH_2SCN), 2.17 (m, 4H, $CH_2C\underline{H_2}CH_2$) ppm; ^{13}C NMR ($CDCl_3$, 75MHz): $\delta = 166.2$ (CO), 111.8 (SCN), 62.6 (CH_2O), 41.2 ($COCH_2CO$), 30.5 (CH_2SCN), 28.9 ($CH_2\underline{C}H_2CH_2$) ppm.

Compound 3. DBU (0.83 mL, 5.55 mmol) was added to a solution of C_{60} (200 mg, 0.28 mmol), **2** (840 mg, 2.8 mmol) and CBr_4 (9.19 g, 27.7 mmol) in *o*-DCB (50 mL) under argon atmosphere. The resulting mixture was stirred at room temperature for 3d. Cyclohexane was added and the precipitate filtered off using a plug of silica gel followed by a mixture of CH_2Cl_2 and cyclohexane (1:1) to eliminate *o*-DCB. Then CH_2Cl_2 was used to elute the crude product. Column chromatography (SiO_2, EtOAc / toluene 3:2) yielded **3** (412 mg, 29%) as an orange-red solid. IR: 1743 cm^{-1} (C=O), 2156 cm^{-1} (SCN); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 245 (65500), 281 (52400), 315 (33300), 340 (23700), 380 (4900 mol^{-1} dm^3 cm^{-1}) nm; ^{1}H NMR ($CDCl_3$, 300MHz): δ = 4.44 (t, 24H, J = 6Hz, $C\underline{H}_2O$), 3.01 (t, 24H, J = 7Hz, $C\underline{H}_2SCN$) 2.23 (m, 24H, $CH_2C\underline{H}_2CH_2$) ppm; ^{13}C NMR ($CDCl_3$, 75MHz): δ = 163.1 (CO), 145.5 (C_{60}-sp^2), 140.9 (C_{60}-sp^2), 111.4 (SCN), 68.8 (C_{60}-sp^3), 64.1 (CH_2O), 45.0 ($\underline{C}(COOR)_2$), 30.2 (CH_2SCN), 28.7 ($CH_2\underline{C}H_2CH_2$) ppm; MALDI-TOF-MS (matrix): m/z (%) calcd. for $C_{126}H_{72}N_{12}O_{24}S_{12}$: 2522.2 [M]$^+$, found: 2522.0.

Characterization data

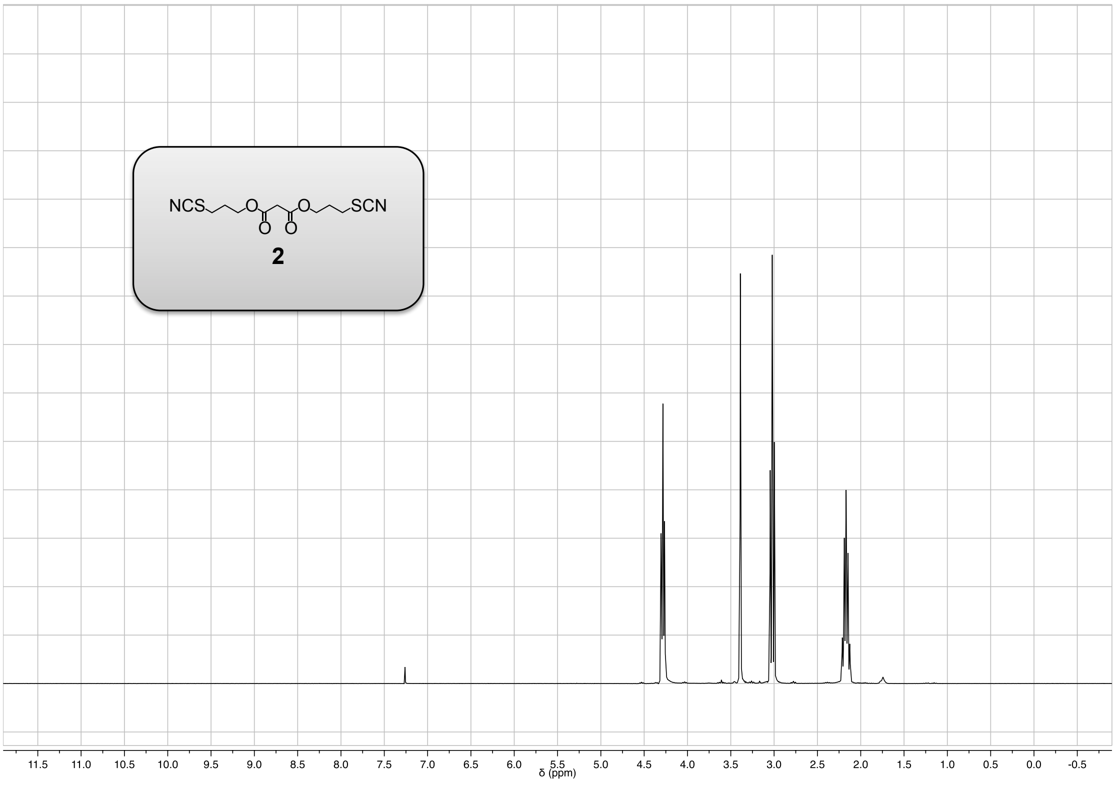

Fig. S1. ^{1}H NMR spectrum of malonate **2** ($CDCl_3$, 300 MHz).

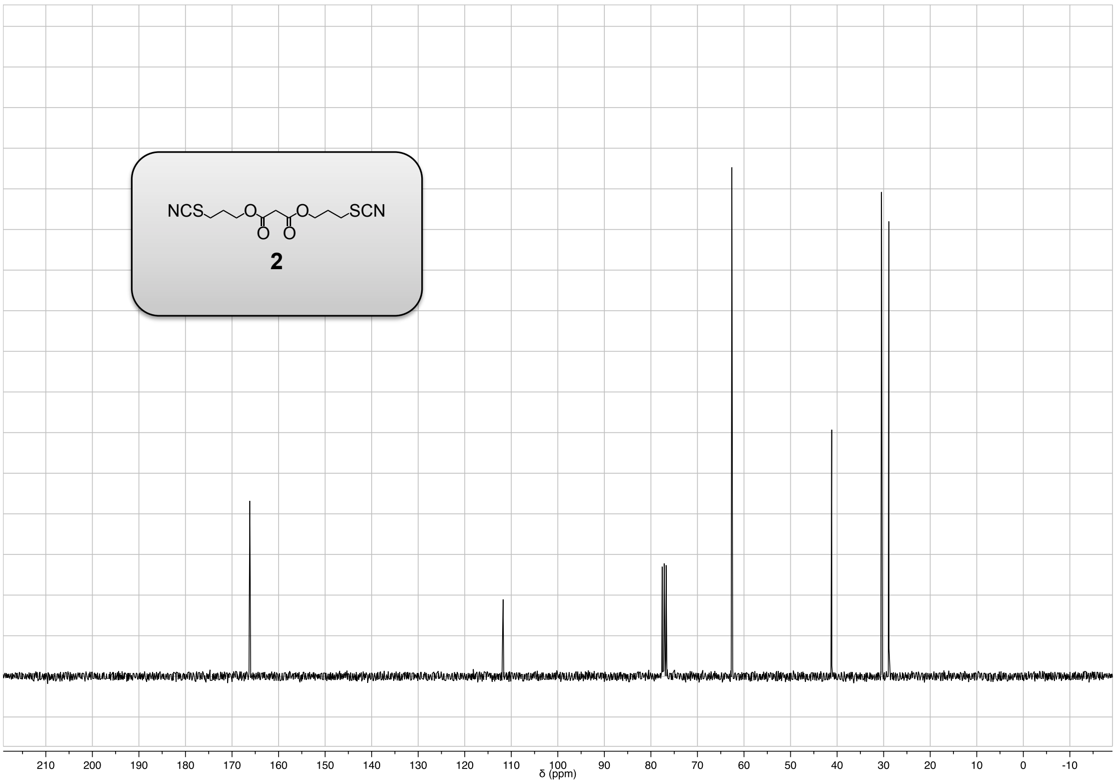

Fig. S2. ^{13}C NMR spectrum of malonate **2** ($CDCl_3$, 75 MHz).

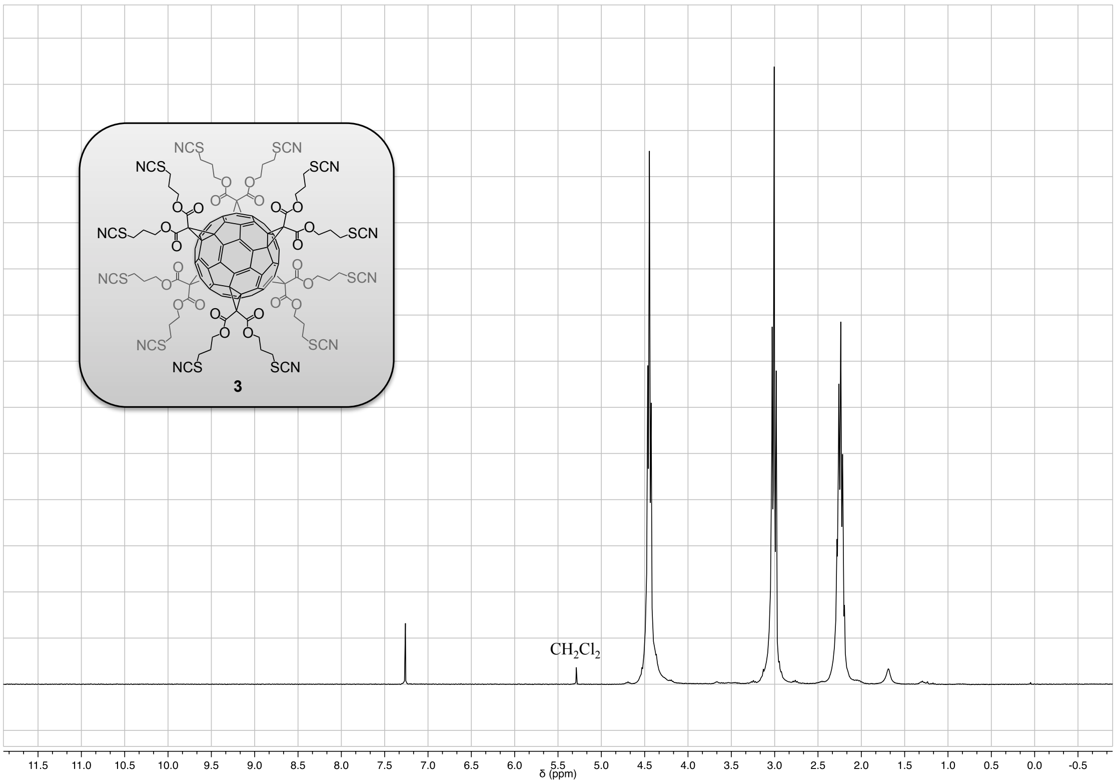

Fig. S3. ^{1}H NMR spectrum of hexaadduct **3** ($CDCl_3$, 300 MHz).

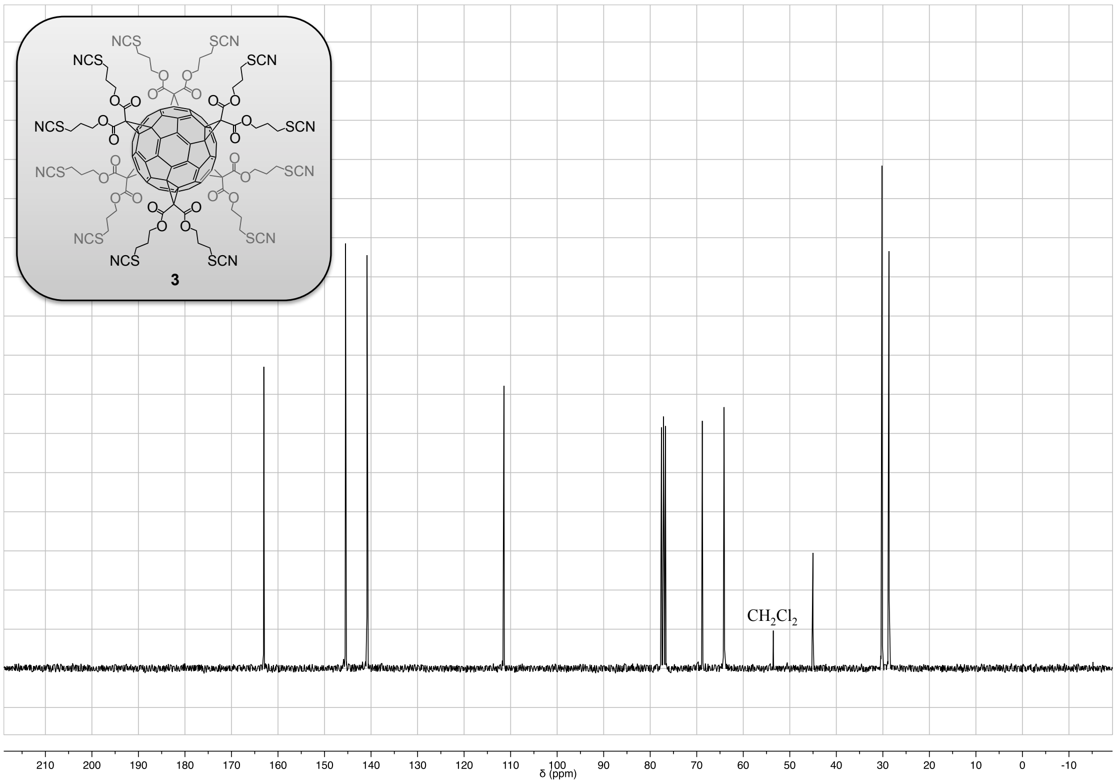

Fig. S4. ^{13}C NMR spectrum of hexaadduct **3** (CDCl$_3$, 75 MHz).

Preparation of AuNPs.

General. 4-Aminothiophenol was purchased from TCI. Tetrachloroauric acid trihydrate $HAuCl_4.3H_2O$, lithium borohydride $LiBH_4$ solution (2 M in THF) and THF (Chromasolv®) were purchased from Aldrich Chemical Company, Inc. All reagents and solvents were of commercial quality and used without further purification. The glassware used in the synthesis were cleaned with aqua regia (aqua regia is a very corrosive product and should be handled with extreme care) and then rinsed with copious amount of distilled water, then dried overnight prior to use. All reactions were carried out in atmospheric conditions.

General procedure for the preparation of AuNPs. The experimental procedure is common for every sample, the difference between the four experiments is only the amount of starting ligands, HATP and/or **3**, used during the synthesis (see table 1). Typically, tetrachloroauric acid trihydrate (45.7 mg, 1 eq, 116 µmol) was dissolved in 10 mL of tetrahydrofuran. This mixture and a lithium borohydride solution (0.46 mmol; 4 eq, 0.23 mL of a 2M commercial solution, in 10 mL THF) were added dropwise and simultaneously with two distinct syringe pumps (addition speed fixed at 1 mL.min^{-1}), to a 100 mL trineck round-bottom flask, equipped with an ice bath, containing a stirred solution of ligand(s) (in 10 mL THF) over a 15 minutes period. After the end of the addition of $LiBH_4$ and $HAuCl_4$, the mixture was left under stirring (300 rpm) for five hours (from 0°C to RT). The mixture turned quickly from orange to a brown and afterwards to a black solution plus the formation of a black precipitate, which indicates the aggregation of the prepared functionalized gold particles. Tetrahydrofuran is removed by rotary evaporation and ethanol is added. The black precipitate is collected by centrifugation (15 minutes, 11000 rpm). The product is then washed with ethanol three times and dichloromethane three times to completely remove the HATP and **3** excess and salts. The washed black precipitate is dried at air under atmospheric conditions and stored under these conditions. Compounds incorporating ATP have also been washed three times with dimethylformamide to remove possible $Au_{25}(ATP)_{17}$ traces that may be present in the crude product.[2] The so-obtained products are insoluble in all solvents.

Table 1. Amount of ligands introduced in the reaction medium for each experiment. Equivalents are given compared to $HAuCl_4.3H_2O$ (1 eq). *Yields are given compared to Au and have been calculated by considering the remaining mass of sample at the end of TGA (900°C) as bulk gold.

		AuNP@ [(3)$_{1/11}$(ATP)$_{1.5}$]	**AuNP@ [(3)$_{1/5}$(ATP)$_{1.5}$]**	**AuNP@ [(3)$_{1/11}$]**	**AuNP@ [(3)$_{1/5}$]**
3	(mg)	26.6	58.5	26.6	58.5
	(µmol)	10.5	23.2	10.5	23.2
	(eq.)	1/11	1/5	1/11	1/5
HATP	(mg)	21.9	21.9	-	-
	(µmol)	175	175	-	-
	(eq.)	1.5	1.5	-	-
Mass obtained	(mg)	23.5	28.5	22.0	26.1
Yield (/ Au)*	(%)	54.8	33.2	57.0	51.7

Characterization of AuNPs

Powder X-ray diffraction (PXRD) is carried out on a Bruker D8 Advance A25 diffractometer using Cu Kα radiation equipped with a 1-dimensional position-sensitive detector (Bruker LynxEye). At high angles, between 4° and 80° (2θ), X-Ray scattering was recorded with 0.02° steps and 0.5 s per step. Divergence slit was fixed to 0.2° and the detector aperture to 191 channels (2.9°). At small angles, between 0.45° and 7° (2θ), X-Ray scattering was recorded with 0.01° steps and 2 s per step. Divergence slit was variable and programed at 20 mm and the detector aperture to 59 channels (0.9°).

Transmission electron microscopy (TEM) was carried out on a JEOL 2010 LaB_6 microscope operating at 200 kV. Samples were dispersed in EtOH with an ultrasonic bath and then a drop was deposited on a copper grid and let to dry under ambient conditions of atmosphere and temperature. Despite our efforts, it has not been possible to observe clearly fullerene units owing to the relative low stability of this kind of organic moiety under the electron beam, even by decreasing the tension from 200 to 80 kV.

Thermogravimetric analysis (TGA) was performed with a TGA/DSC 1 STARe System from Mettler Toledo. Around 2 mg of sample was heated at a rate of 10 °C min^{-1} from 25 to 900 °C, in a 70 μL alumina crucible, under air atmosphere (20 mL min^{-1}). Shining droplets were observed at the end of experiment, which corresponds to bulk gold.

The infrared spectra were obtained on a Bruker Vector 22 FT-IR spectrometer with KBr pellets at room temperature and registered from 4000 to 400 cm^{-1}.

microRaman spectra were performed, on the solids dehydrated in air at 673 K, using a LabRam HR (Jobin Yvon-Horiba) spectrometer equipped interference and edge filters and CCD detector. The exciting line of a diode laser at 785 nm was focused on the samples with a power of 100 μW using a long working objective (magnification 50×). Such low laser power was chosen to avoid thermal degradation of the samples.

X-ray photoelectron spectroscopy (XPS) measurement was carried out using monochromatized Al Kα source in a commercial instrument (AXIS Ultra DLD KRATOS) All spectra reported here were acquired with the sample held at room temperature in UHV. XPS revealed well-resolved peaks corresponding to C 1s, Au 4f, S 2p and N 1s. Each high-resolution spectrum was decomposed into a combination of Voigt functions.

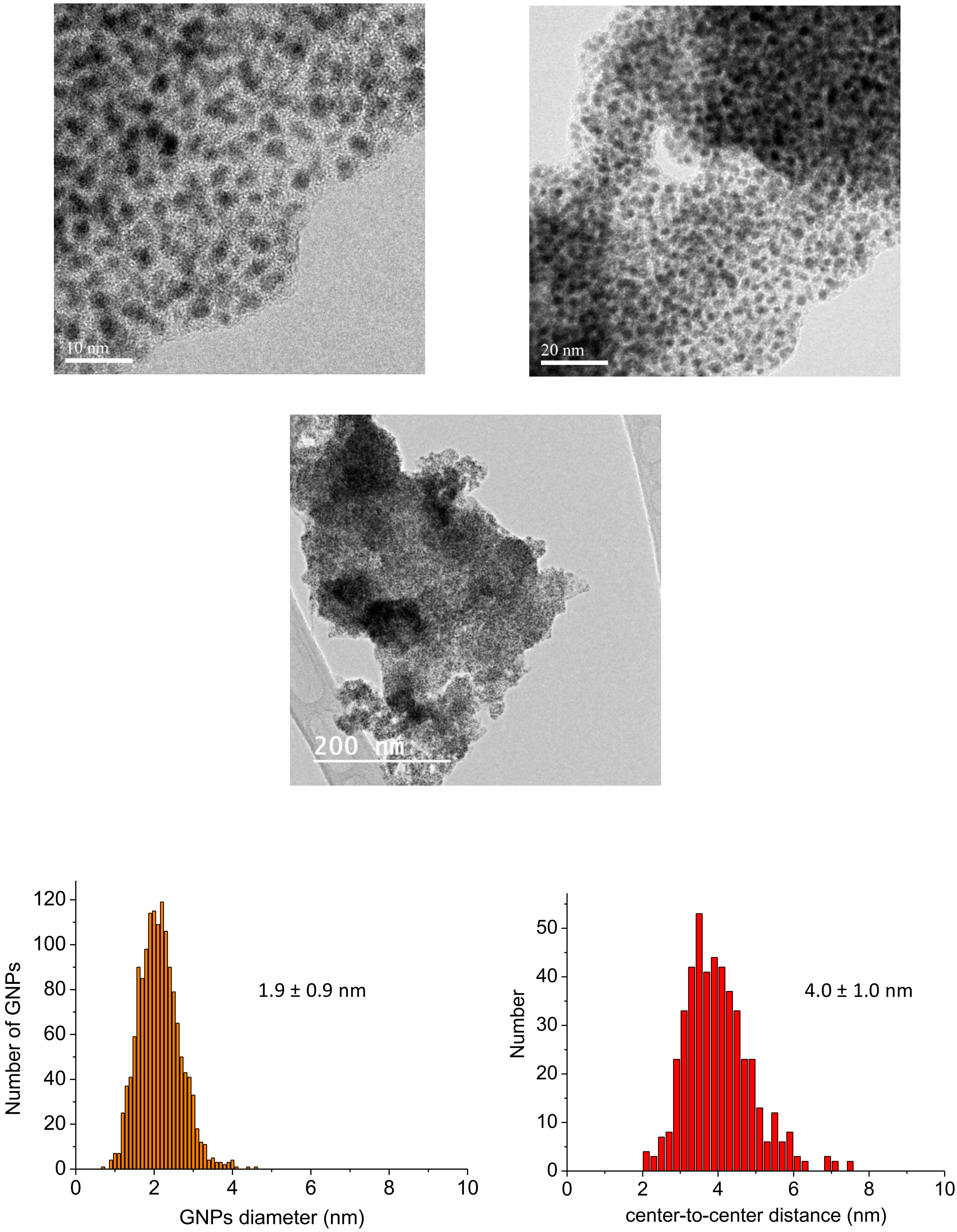

Fig. S5. TEM images, diameter of GNPs and center-to-center distance histograms of AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$].

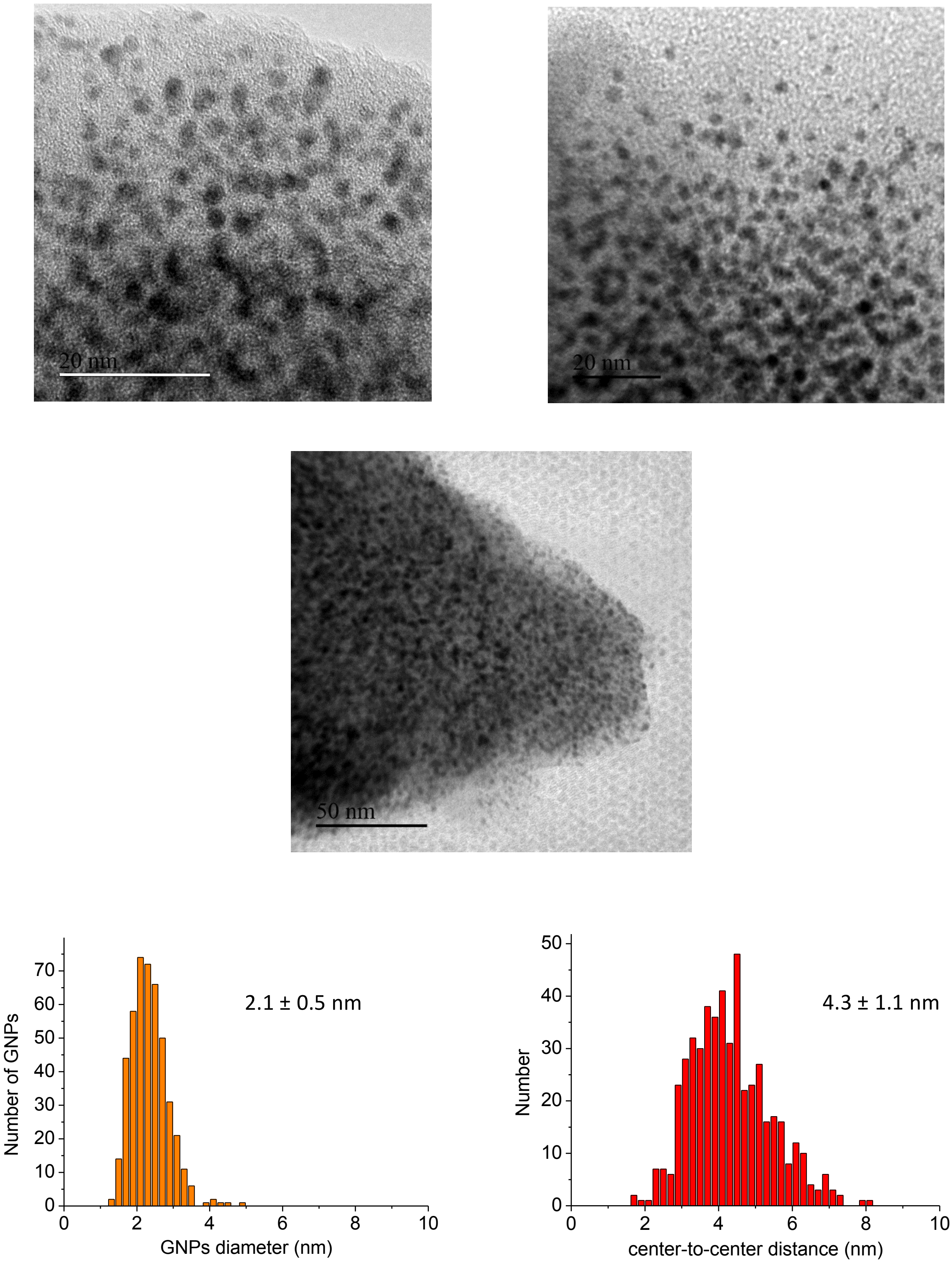

Fig. S6. TEM images, diameter of GNPs and center-to-center distance histograms of AuNP@[($\mathbf{3}$)$_{1/5}$(ATP)$_{1.5}$].

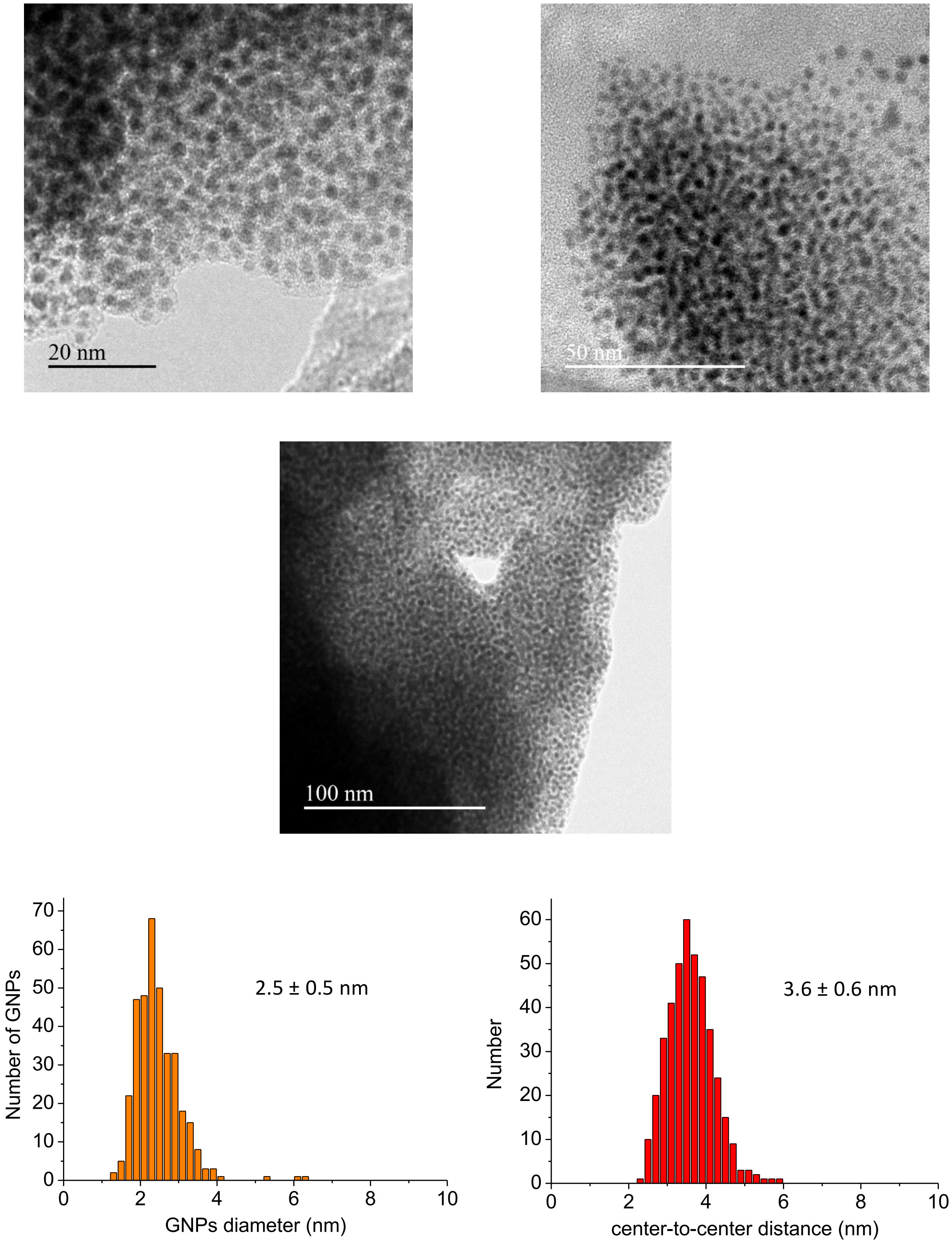

Fig. S7. TEM images, diameter of AuNPs and center-to-center distance histograms of AuNP@[(**3**)$_{1/11}$].

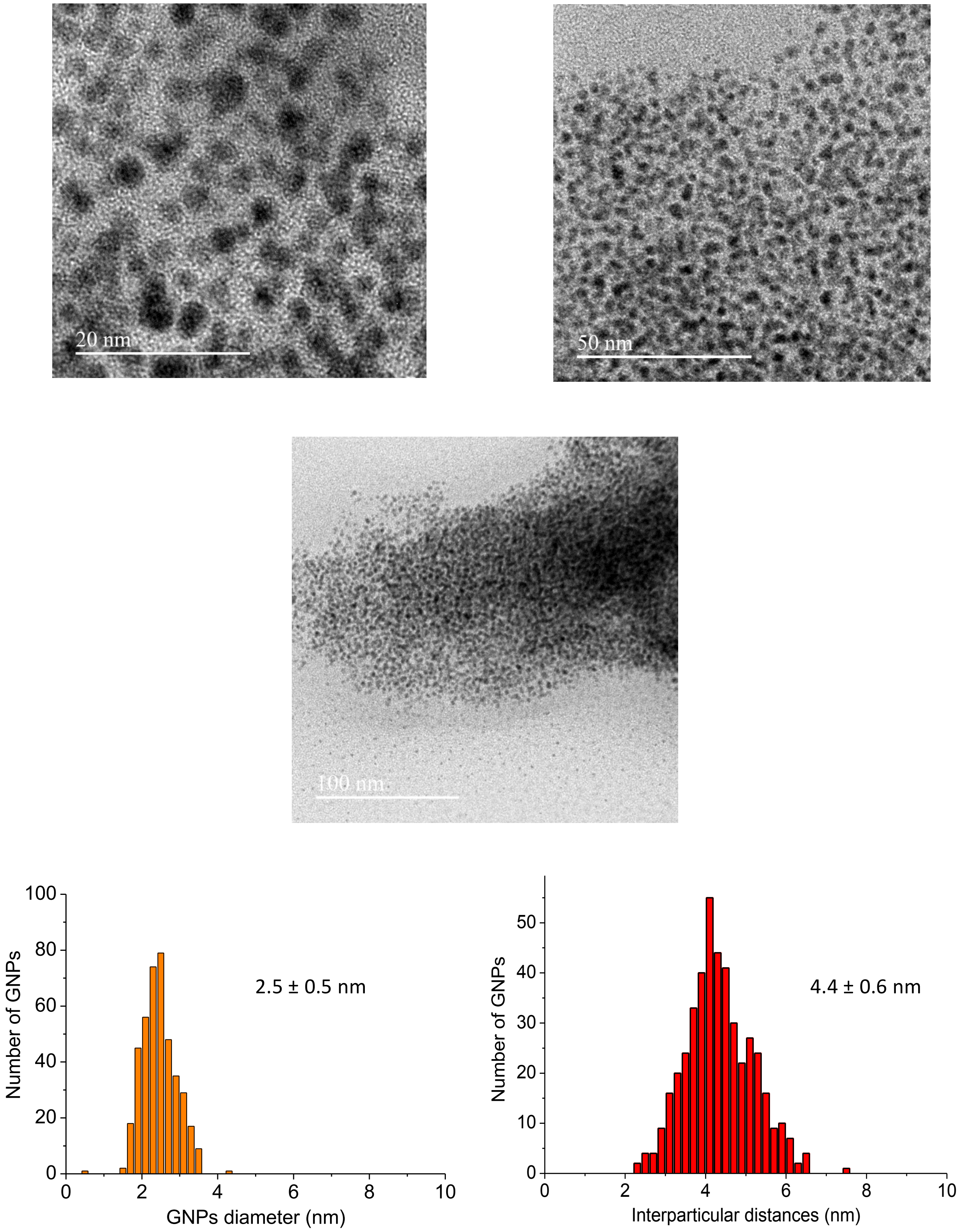

Fig. S8. TEM images, diameter of AuNPs and center-to-center distance histograms of AuNP@[(**3**)$_{1/5}$].

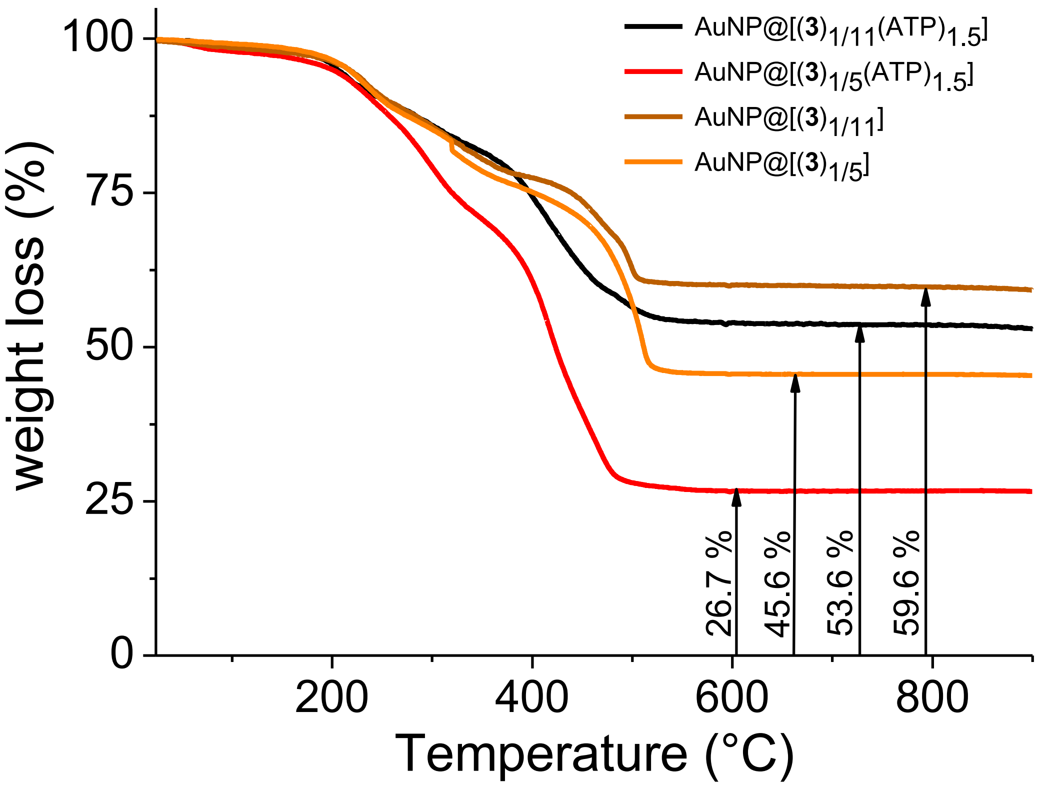

Fig. S9. Thermogravimetric analysis (TGA) of materials carried out under air at 10°C/min. Shinning droplets of bulk gold have been observed for each sample at the end of the experiment.

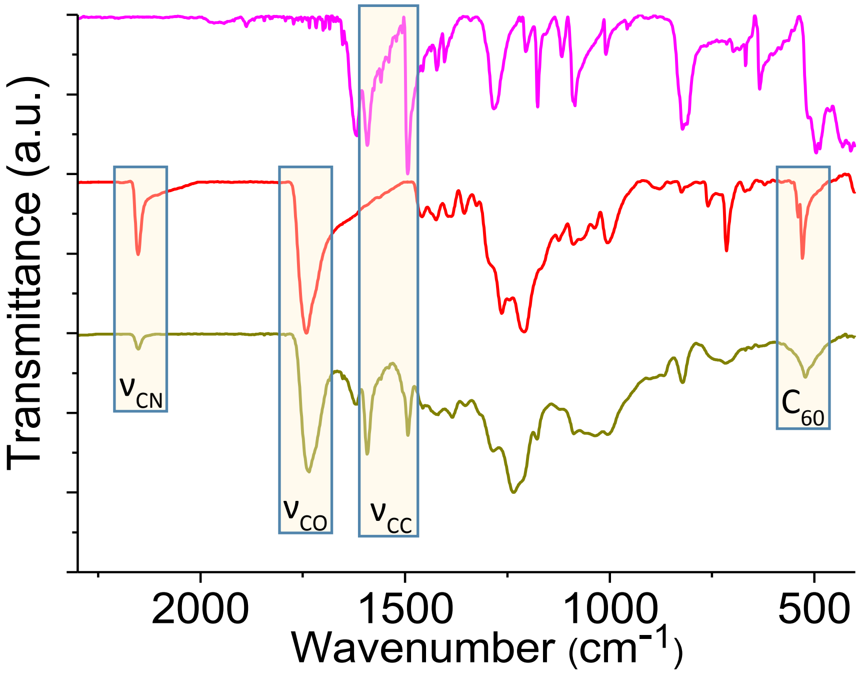

Fig. S10. FTIR spectra of AuNP@[(**3**)$_{1/5}$(ATP)$_{1.5}$] (dark yellow), **3** (red) and 4-ATP (pink).

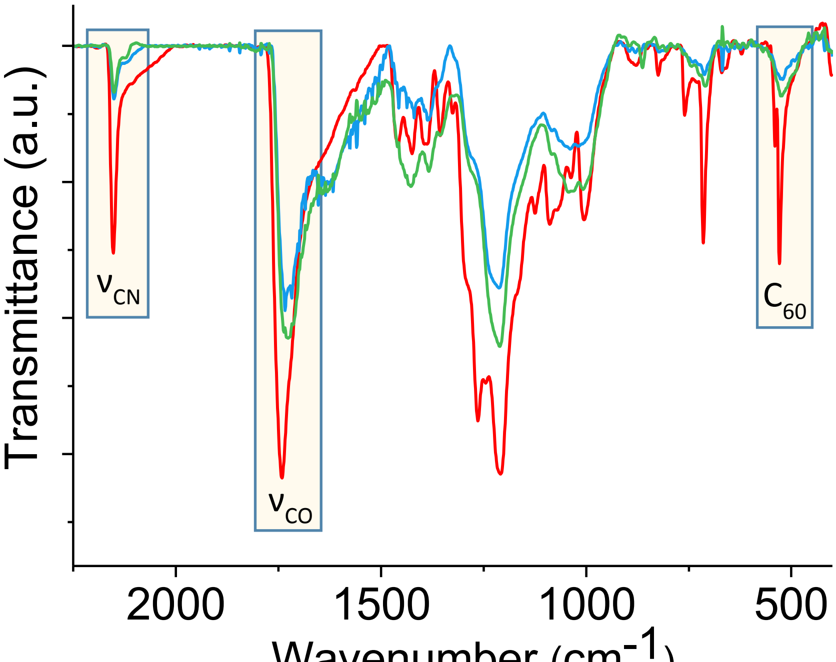

Fig. S11. FTIR spectra of AuNP@[(**3**)$_{1/11}$] (green), AuNP@[(**3**)$_{1/5}$] (blue) and **3** (red).

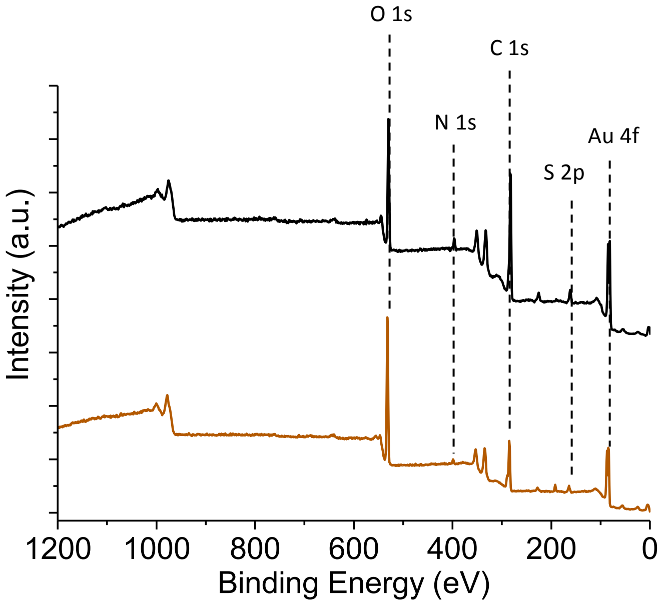

Fig. S12. Survey scan of XPS analysis of compound AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$] (black) and compound AuNP@[(**3**)$_{1/11}$] (brownish).

Table 2. Atomic percentage of elements present at the surface of compounds AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$] and AuNP@[(**3**)$_{1/11}$]. *Bore contamination from LiBH$_4$.

	Au	S	N	O	C	B*
AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$]	2.2	4.8	2.6	30.6	48.8	11.0
AuNP@[(**3**)$_{1/11}$]	3.8	4.0	1.6	33.9	47.1	9.6

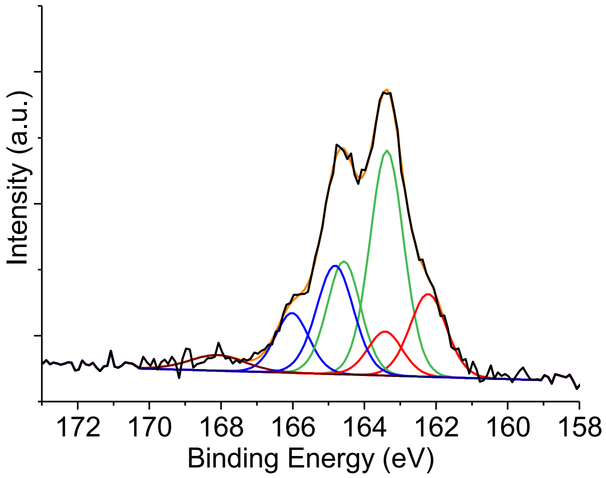

Fig. S13. XPS S 2p of compound AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$]: S-Au (red), S-H (green), S-CN (blue) and SOx (brownish).

References

1 J. Iehl, R. Pereira de Freitas, B. Delavaux-Nicot and J.-F. Nierengarten, *Chem. Commun.*, 2008, 2450.

2 C. Lavenn, F. Albrieux, G. Bergeret, R. Chiriac, P. Delichere, A. Tuel and A. Demessence, *Nanoscale*, 2012, **4**, 7334.