Electronic Supplementary Material (ESI) for RSC Advances

PEGylated Gold Nanoparticles: Polymer Quantification as a Function of PEG lengths and Nanoparticle Dimensions

Kamil Rahme,* [a,b,c], Richard G. Hobbs, [a,b] Lan Chen [a,b,d], Michael A. Morris [a,b], Caitriona O'Driscoll[e] and Justin D. Holmes [a,b]

[a]*Materials Chemistry and Analysis Group, Department of Chemistry and the Tyndall National Institute, University College Cork, Cork, Ireland.*

[b]*Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland.*

[c]*Department of Sciences, Faculty of Natural and Applied Science, Notre Dame University (Louaize), Zouk Mosbeh, Lebanon*

[d]*Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street Cambridge, CB2 3RA, UK.*

[e]*Pharmocodelivery group, School of Pharmacie, University College Cork, Cork, Ireland.*

*To whom correspondence should be addressed: Fax:+961 9 225164; Tel:+961 9 218950

E-mail: kamil.rahme@ndu.edu.lb

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

SUPPORTING INFORMATION.

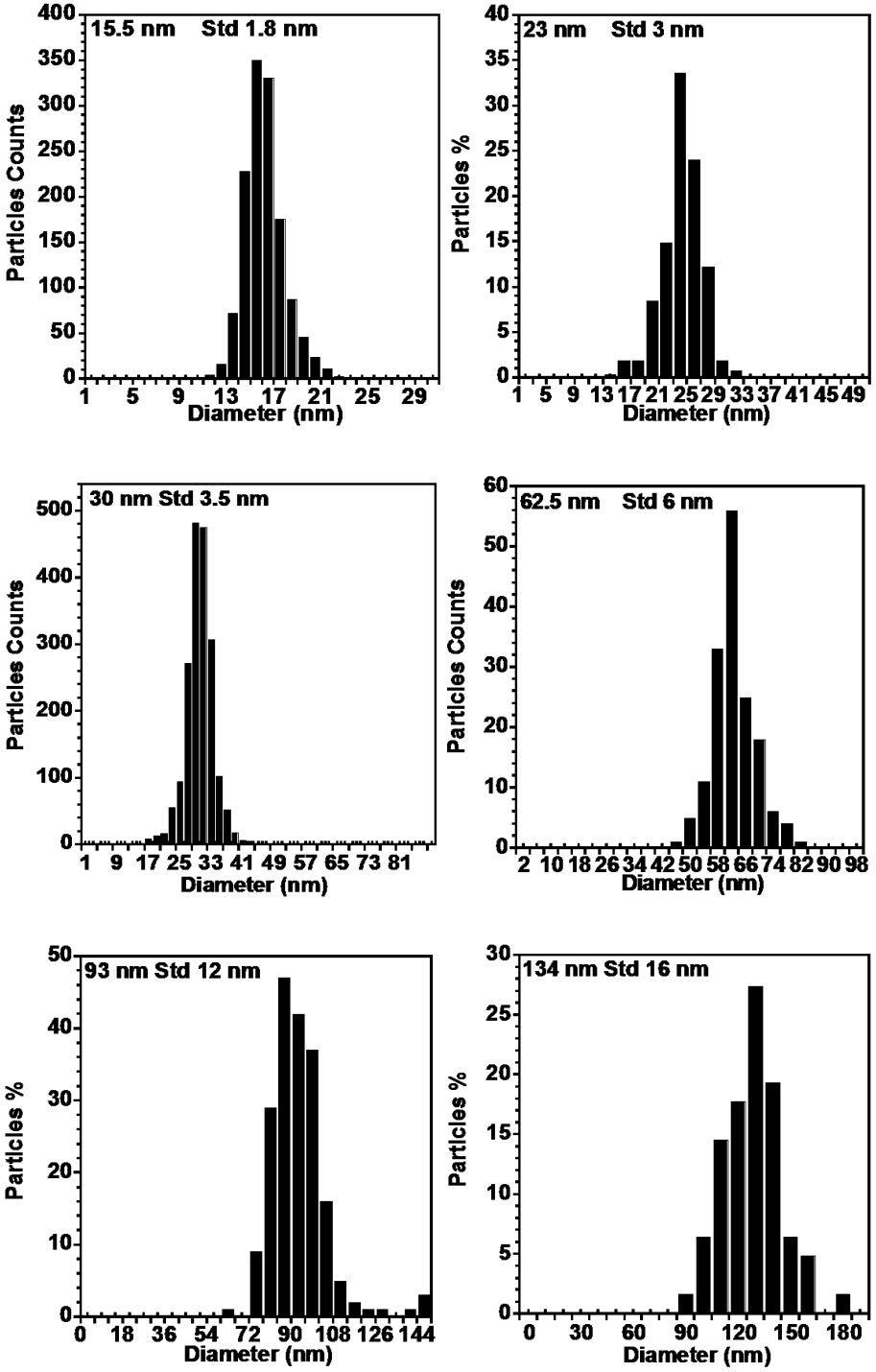


Figure S1. Statistical histograms from TEM images of different AuNPs sizes synthesized in this work analysed using Image J software.

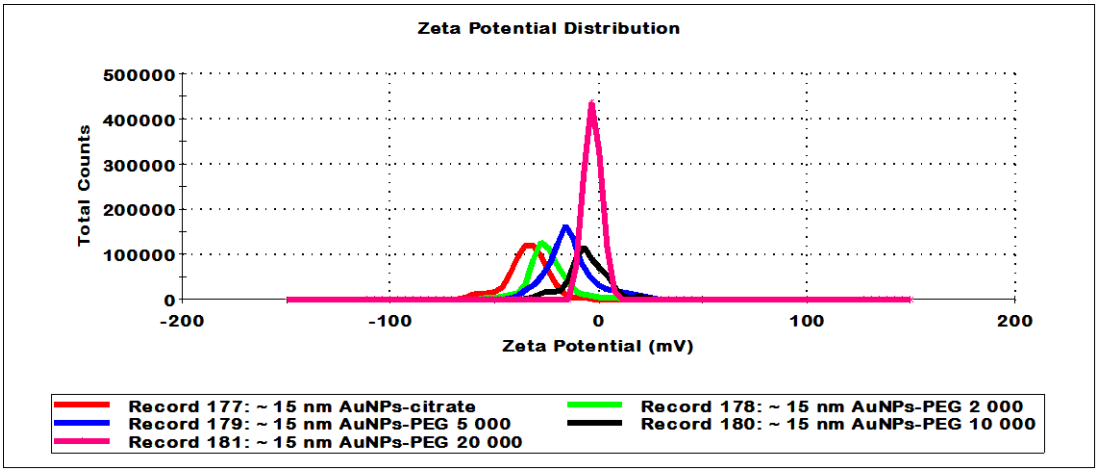


Figure S2. Zeta Potential of approximately 15 nm AuNPs coated with mPEG-SH of different molecular weight.

Example for the estimation of the numbers of PEG/AuNPs

The volume of a gold atom is

$$V_{Au} = \frac{M_{Au}}{d.N_A} = 1.7.10^{-29}\ m^3$$

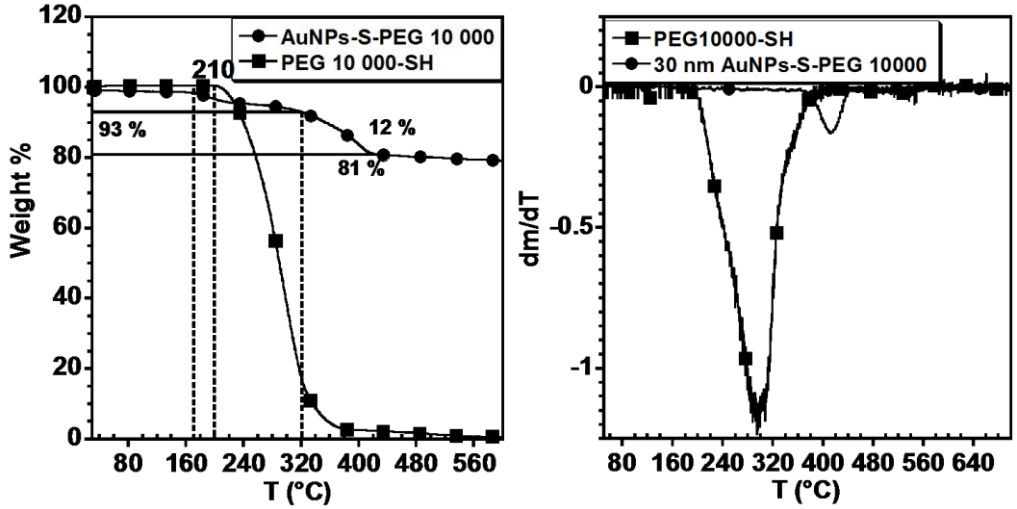
Were d is the density of gold (19.3 x 10^3 Kg/m^3), M_{Au} ~197 g/mol and N_A the Avogadro number. The number of gold atom per particle is considered to

$$N_{Au/Np} = \frac{V_{Np}}{V_{Au}}$$

For 15 nm spherical nanoparticle the volume is; V_{Np} ~ 1.767 x 10^{-24} m^3; so the number of gold atom per particle $N_{Au/Np}$ ~ 1.03 x10^5 atomes/particle. So the estimated molecular weight of 15 nm AuNPs is M_{AuNp} = 2.03 x 10^7 g/mol. For example from figure S1 (a) 12 % of weight are considered to correspond to PEG attached to AuNPs and 81 % correspond to pure gold while the weight loss below 300 °C correspond to water (<100 °C) the left citrate and free PEG. So this correspond in 1 mg to N_{AuNPs} = 2.403 x 10^{13} and N PEG $_{10000}$-SH = 6.692 x 10^{15} so from this experiment we estimate that 15 nm AuNPs contain 278 PEG $_{10\ 000}$-SH. The grafting density correspond to 278/176.71 ~ 1.573 PEG 10 000/nm^2 and finally the foot print of the PEG 10 000 correspond to 1/1.573 ~ 0.635 nm^2.

Thermogravimetric analysis measurements:

(a) (b)



(c)

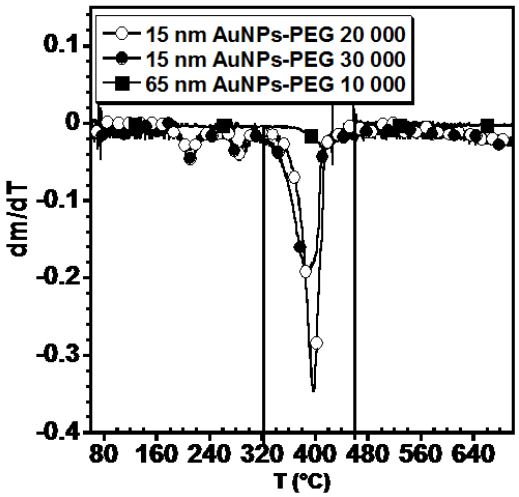


Figure S3. (a) Weight loss in function of the temperature for the mPEG$_{10\ 000}$-SH and AuNPs-S-PEG$_{10\ 000}$.(b) first derivative of the weight loss, shows clearly that PEG degrade at ~300°C while PEG grafted to AuNPs degrade at higher temperature. (c) first derivative of the weight loss for some samples used in this study.

Polymer conformation:

The Flory radius for the different PEG used in this study is calculated using the formula ($F=\alpha n^{3/5}$), these values were compared to the value of the effective distance between 2 polymer graft points D

For PEG 2 000 the value of F is $0.35 \times 45.45^{0.6} = 3.46$

For PEG 5 000 the value of F is $0.35 \times 122.73^{0.6} = 6.27$

For PEG 10 000 the value of F is $0.35 \times 245.45^{0.6} = 9.50$

For PEG 20 000 the value of F is $0.35 \times 443^{0.6} = 13.5$

For PEG 30 000 the value of F is $0.35 \times 670^{0.6} = 17.3$

For PEG 48 000 the value of F is $0.35 \times 1168.18^{0.6} = 24.24$

In order to estimate the value of D (effective distance between two grafting point), we simply estimate the surface area of empty space on the AuNPs between two grafted site and conclude the distance D. Since the PEG-SH is attached to the AuNPs through tiol-gold linkage, D can be simply obtained by calculating the square root of the NP surface area divided by the number of PEG ligands (D= √ NP surface area/number of polymer).

***ie.* for 15 nm AuNPs-PEG$_{2\ 000}$**

The distance D between the 2 PEG chain is D = √707/695 = 1.00 < F = 3.46 'brush' conformation.

For AuNPs –PEG$_{48\ 000}$

The distance D between the 2 PEG chain is D = √707/50 = 3.76 < F = 24.24 so 'brush' conformation

For 60 nm AuNPs-PEG$_{10\ 000}$

The distance D between the 2 PEG chain is D = √11304/2572 = 2.1 < F = 9.50 'brush' conformation.