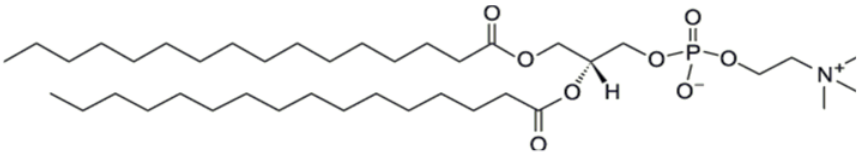
Electronic Supplementary Information

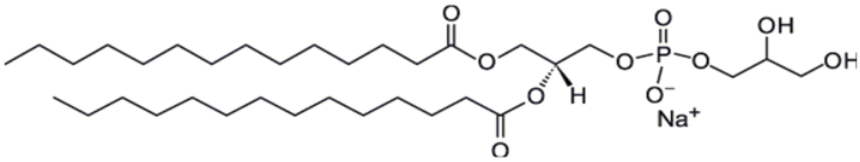
Shape directed biomineralization of gold nanoparticles using self-assembled lipid structures

Rukan Genc,[1*] Gael Clergeaud[2], Mayreli Ortiz[2], Ciara O'Sullivan[2,3] *

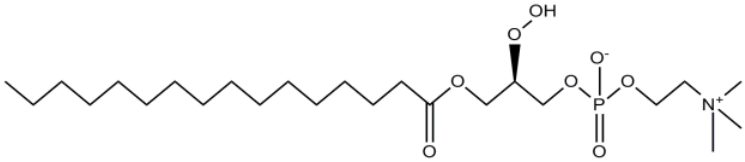
FIGURES and SCHEMES



1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC)



1,2-dimyristoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (DMPG)



1-palmitoyl-2-hydroxy-sn-glycero-3-phosphocholine (lyso-PPC)

Scheme ESI1: Chemical structures of the phospholipids used in the work.

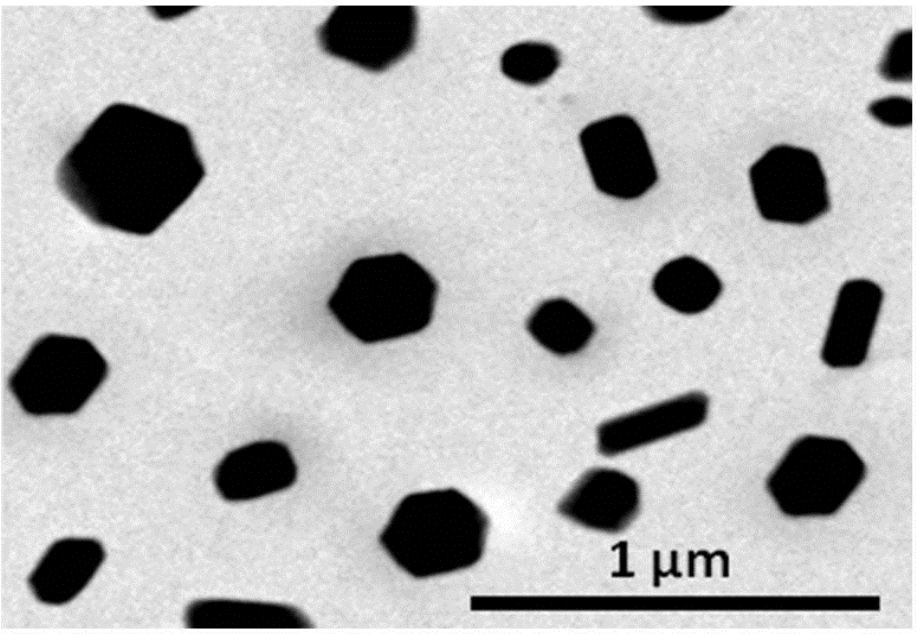


Figure ESI 1. TEM images representing the hexagonal shaped gold nanostructures formed from DPPC: lyso PPC lipids as template.

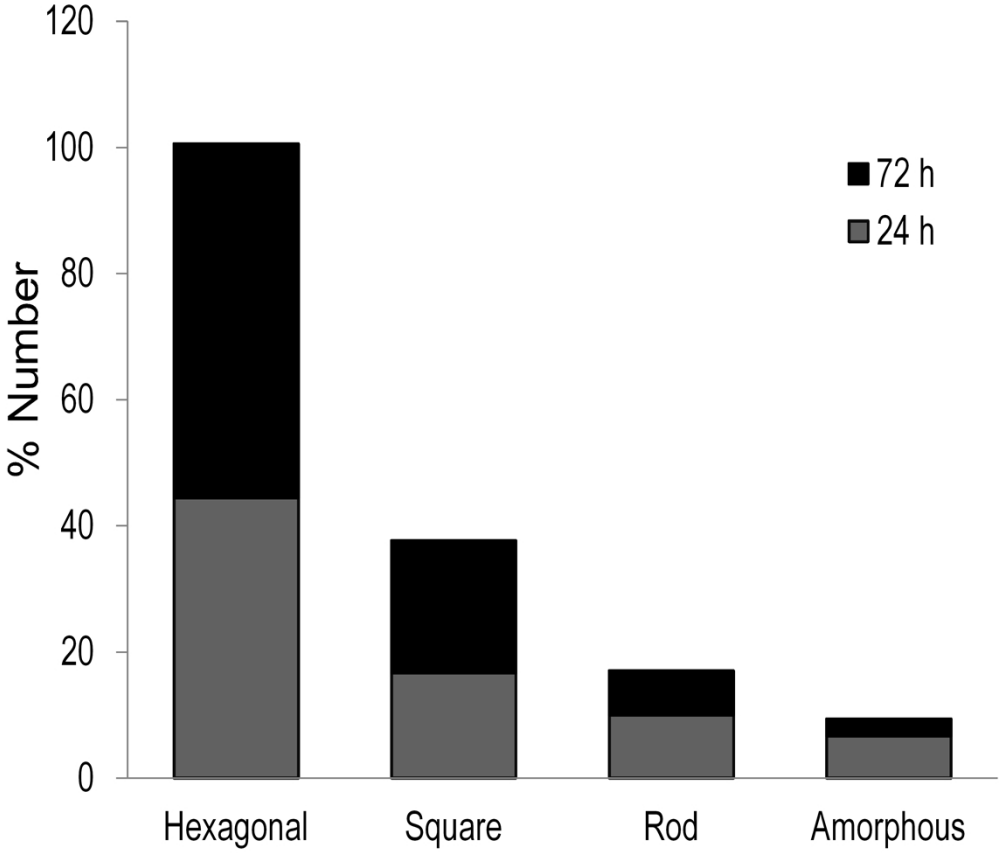


Figure ESI 2. Particle distribution by means of the shape after 24 hours and 72 hours of reaction time. Increased number of hexagonal shaped gold nanostructures were formed after 72 hours in compared to 24 hours.

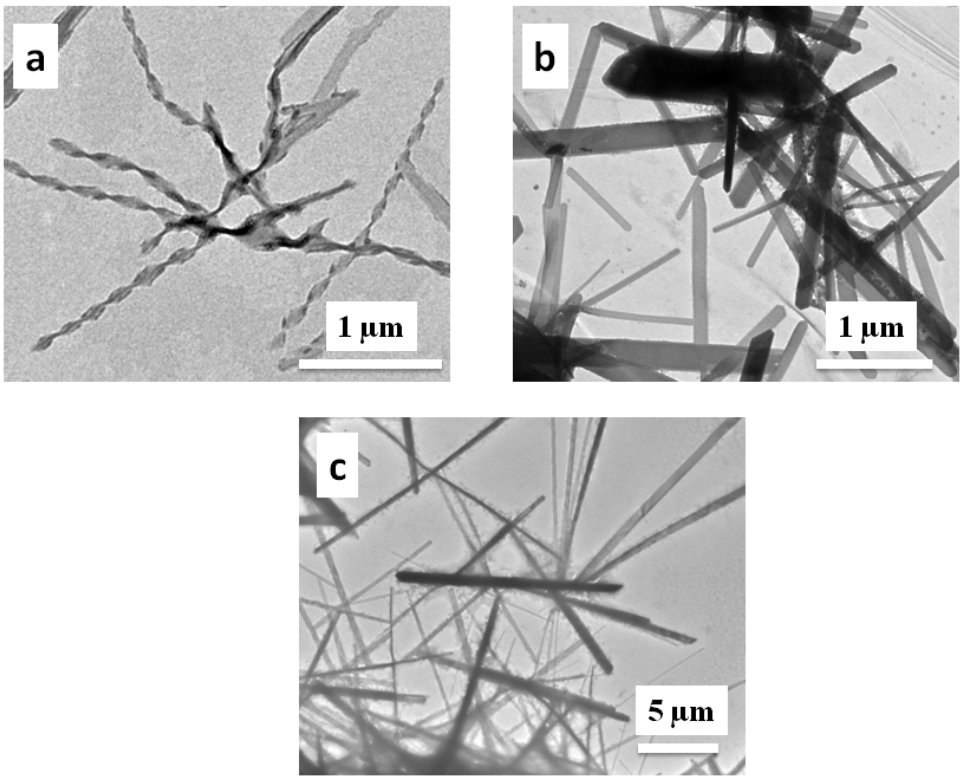


Figure ESI3: TEM images of twisted ribbons prepared at 25 ^{o}C, nanostrips at 45 ^{o}C and nanotubes prepared at 65 ^{o}C from negatively charged short tail phospholipid, DMPG.

Formation of lipid nanostructures

There are several structural factors that determine the final structure of lipid self-assembly. The packing factor, P, is fundamental in determining the effective shape of the lipid molecule and their organization which is directly proportional to the effective volume occupied by a single lipid molecule (*V*) and inversely proportional to the length of the lipid tail (*l*) and head group size (*a*). [1,2]Another important lipid property is the critical melting temperature (T_M), which is the temperature at which lipids change phase

from gel to liquid crystalline. The T_M is indicative of the thermal behavior of the lipids as well as their physical characteristics, such as lipid tail length, head group size and the effective volume occupied by a single lipid, under changing thermal conditions.[1]

In our previous study, Curvature tuned preparation liposome method was developed and conducted to several phospholipid types to evaluate the effect of head group size (***a)*** on the lipid phase behavior and organization at different temperatures.[2] Formation of spherical lipid nanovesicles from long tailed charged lipids (DPPG, DOPG, DOTAP) in all the conditions studied and temperature dependence of the other nanostructures obtained from the zwitterionic lipids (DOPC and DPPC) were discussed. Hexagonal and rectangular lipid nanodisks used in the presented report as templates were of the zwitterionic DPPC (T_M = 41 ^oC) with lyso-PPC (88:12 mol/mol). At 25 ^oC, sub-micron sized hexagonal disks and rectangular shaped lipid structures were obtained (Figure 2a), whilst at 45 ^oC nano-sized lipidic rectangles were observed (Figure 1a).

In a further study on the effect of lipid tail length (***l***), and thus of the lipid packing factor, on aggregate shape and the lipid superstructure, was also evaluated. As reported previously, negatively charged –long tail lipids (18C-16C) were resulted on nanosized liposomes regardless of the temperature changes. On the other hand, interesting superstructures were obtained with the lipid formulation of the short tailed, negatively charged DMPG (14C, T_M = 23 ºC):lyso-PPC (88:12 mol/mol), which formed twisted ribbons of ~100-150 nm width, ~200 nm pitch and several microns in length, at T_0=25 ºC . When the T_0 was increased to 45 ºC, nano-sized planar strips of 200 nm in width and of several microns in length were observed, and at 65 ºC, tubes with a width of approximately 1 µm were obtained (Figure ESI3.). Oda et al. also reported that short tailed amphiphiles have a higher tendency to form twisted ribbons than longer tailed

ones.[3] In a more recent study of Spector et al., they reported that the formation of these kinds of lipid assemblies is related to the molecular packing of the two lipids and their chirality, which force the lipid molecules to pack into membranes tilted at a small angle where planar bilayers form twisted ribbons and helices, which close into tubes.[3,4] Although, nanotubes and nanostrips have high potential as template, this study focused only on ribbon shaped nanostructure, since, there were plenty of other studies on the potential use of softmatter nanotubes.

(1) Mouritsen, P. O. G. *Life — As a Matter of Fat*; Springer-Verlag: Berlin/Heidelberg, 2005.

(2) Genç, R.; Ortiz, M.; O'Sullivan, C. K. *Langmuir* **2009**, *25*, 12604–12613.

(3) Oda, R.; Huc, I.; Schmutz, M.; Candau, S. J.; MacKintosh, F. C. *Nature* **1999**, *399*, 566–9.

(4) Inagaki, M.; Shibakami, M.; Regen, S. L. *Journal of the American Chemical Society* **1997**, *119*, 7161–7162.