Electronic Supplementary Material (ESI) for Polymer Chemistry.


## Supplementary Information

# Fluorescent gold nanoparticles with chain-end grafted RAFT copolymers: Influence of the polymer molecular weight and of the chromophore

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**Synthesis of the polymer-chromophore conjugates.**

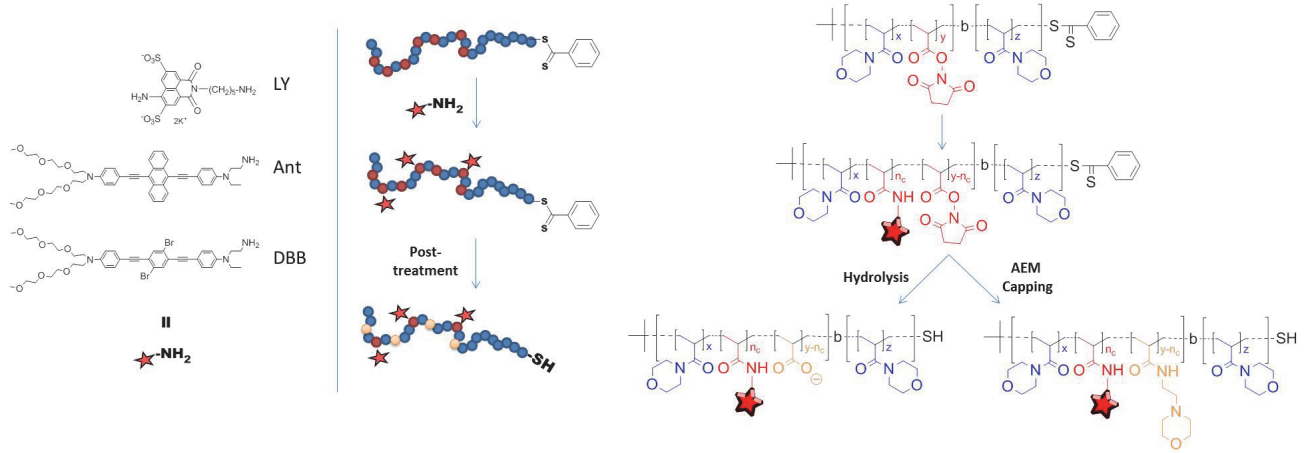


**Fig. S1.** Amino-functionalized chromophores used for this study and schematic representation of the synthesis of the various polymer-chromophore conjugates (for the P(NAM-*stat*-NAS) backbones, z = 0).

## TEM images.

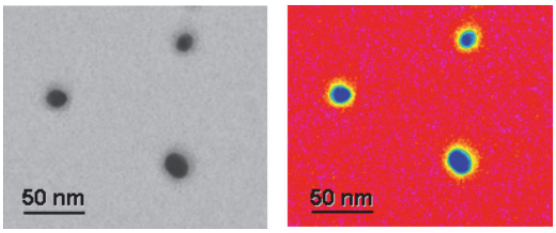


**Fig. S2.** Grey- (left) and multicolor-scale (right) TEM image of a PNAM@GNP sample prepared by the two-step ligand exchange approach and stained with $RuO_4$

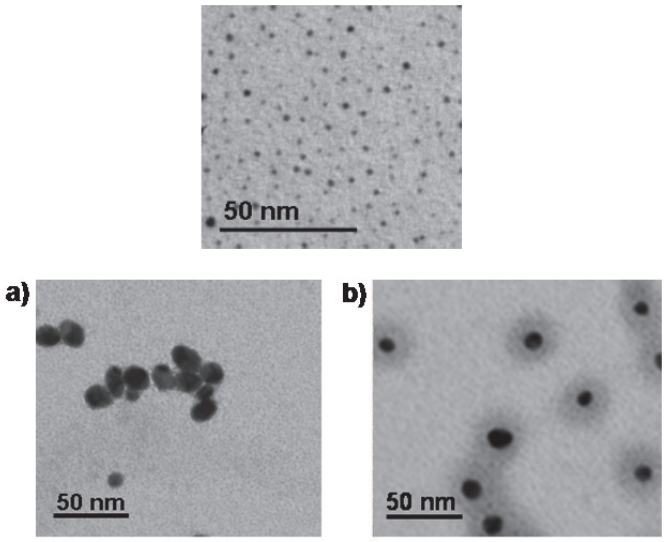


**Fig. S3.** Typical TEM images of a PNAM@GNP sample obtained by the one-step approach (top) and GNPs obtained by the two-step approach (bottom): (a) citrate-stabilized ones and (b) the corresponding PNAM@GNP.

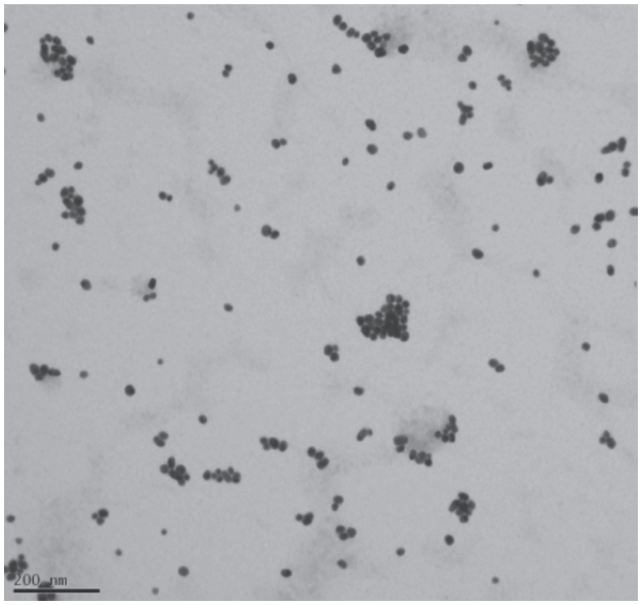

**Fig. S4.** TEM images of citrate-stabilized GNPs prepared using the Turkevitch method. Without polymer stabilization, they tend to aggregate on the TEM grid upon drying

## Thermogravimetric analyses (TGA).

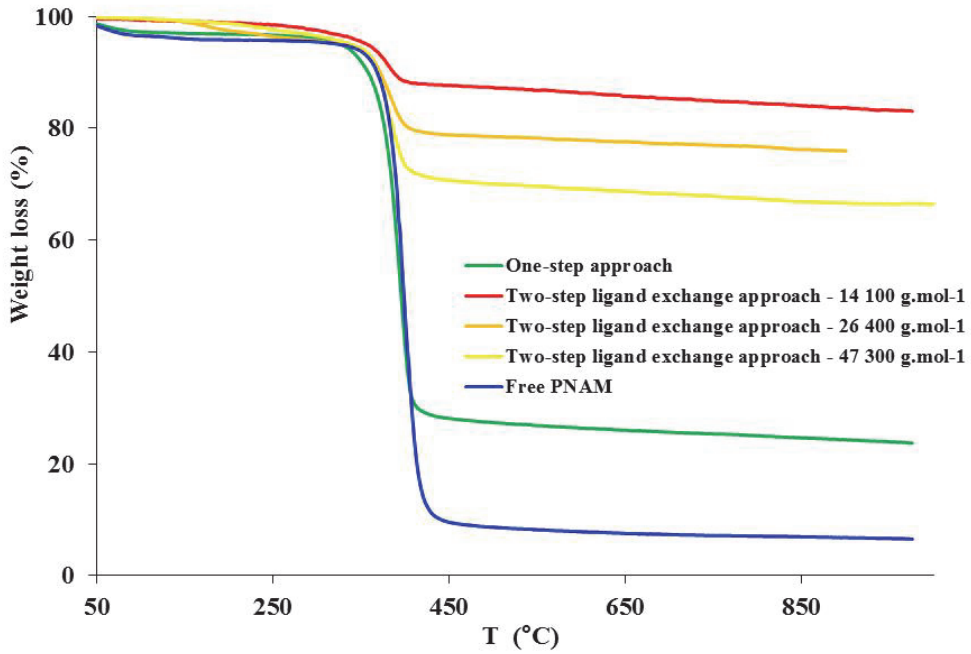


**Fig. S5.** Comparative TGA thermograms of the free PNAM homopolymer and the corresponding PNAM@GNP samples obtained through the one- and two-step grafting approaches (10°C/min, $N_2$ atmosphere).

Except a first small weight loss around 100°C corresponding to the evaporation of some water, the thermogram obtained for the PNAM sample exhibited one significant weight loss between 400 and 500°C corresponding to the decomposition of PNAM. This weight loss represented 92 % of the initial sample weight, the remaining being non-volatile organic residues.
The thermograms obtained for the purified PNAM@GNP samples prepared either by the one-step or the two-step approaches were qualitatively similar with a weight loss between 400 and 500°C corresponding to the decomposition of PNAM that was more or less important depending on the PNAM/Au ratio. It is noteworthy that no weight loss due to the eventual presence of citrate ligands was observed for the sample prepared by the two-step approach, confirming their complete elimination after the grafting and purification processes.
No decomposition of gold was observed in these conditions. As a result, the Au/polymer weight ratio was calculated from Equation 1.

$$m_{Au}/m_{PNAM} = \frac{m_{residues} - (0.08*0.92)\times(m_{sample} - m_{water})}{m_{sample} - m_{residues} - m_{water}} \quad (1)$$

$m_{Au}$, $m_{PNAM}$, $m_{sample}$, $m_{residues}$ and $m_{water}$ are respectively the mass of the gold, the PNAM, the sample and of the residues and water determined from the thermograms.

**Grafting density.** From the TEM and the TGA results, the number of polymer chains per GNP can be calculated from Equation 2:

$$Polymer\ chains/GNP = \frac{N_a \times \rho_{Au} \times V_{GNP}}{Mn_{PNAM} \times (m_{Au}/m_{PNAM})} \quad (2)$$

Where $N_a$ is the Avogadro constant, $\rho_{Au}$ is the density of gold (19.82 g.cm$^{-3}$), $V_{GNP}$ the volume of the gold core calculated from the diameter determined by TEM, $M_{n\ PNAM}$ the number-average molecular weight of the PNAM chains and $m_{Au}/m_{PNAM}$ the weight ratio determined from **Equation 1**.
The grafting density expressed in number of chains per nm² is obtained by dividing this number of polymer chains per GNP by the surface area of the gold core (calculated from the diameter determined by TEM).

## Purification of the grafted gold nanoparticles.

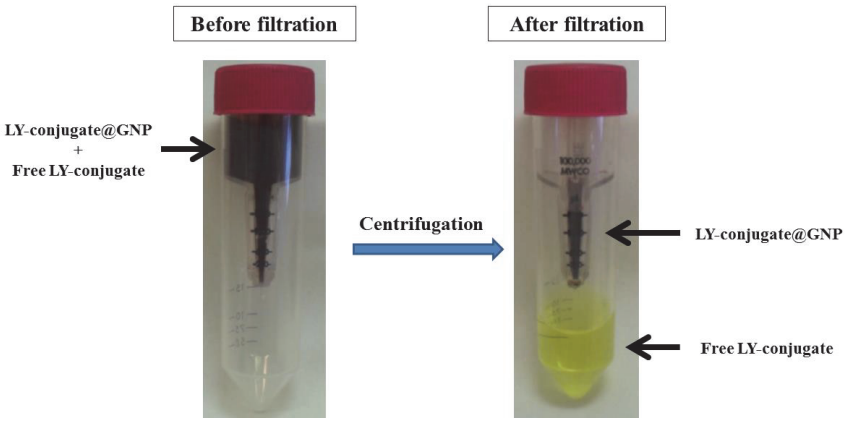


**Fig. S6.** Purification of the LY-conjugate@GNP samples by ultrafiltration

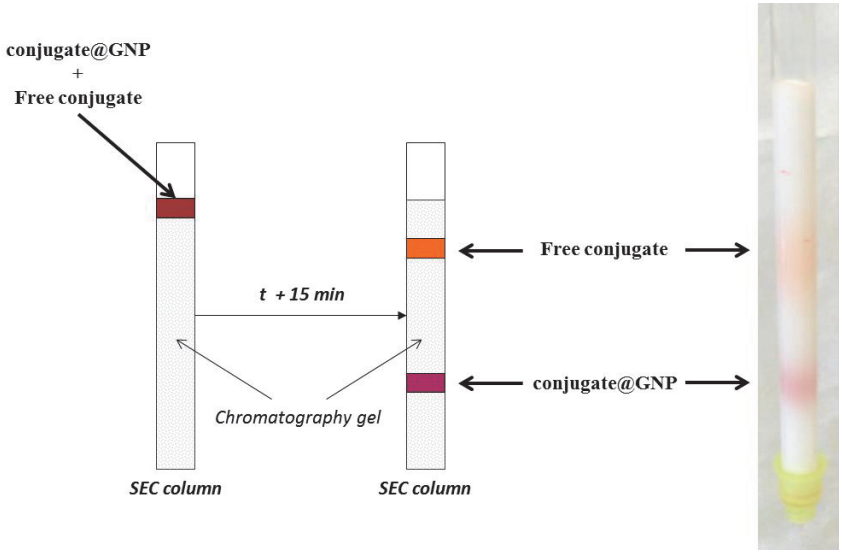


**Fig. S7.** Purification of the conjugate@GNP samples by size exclusion chromatography

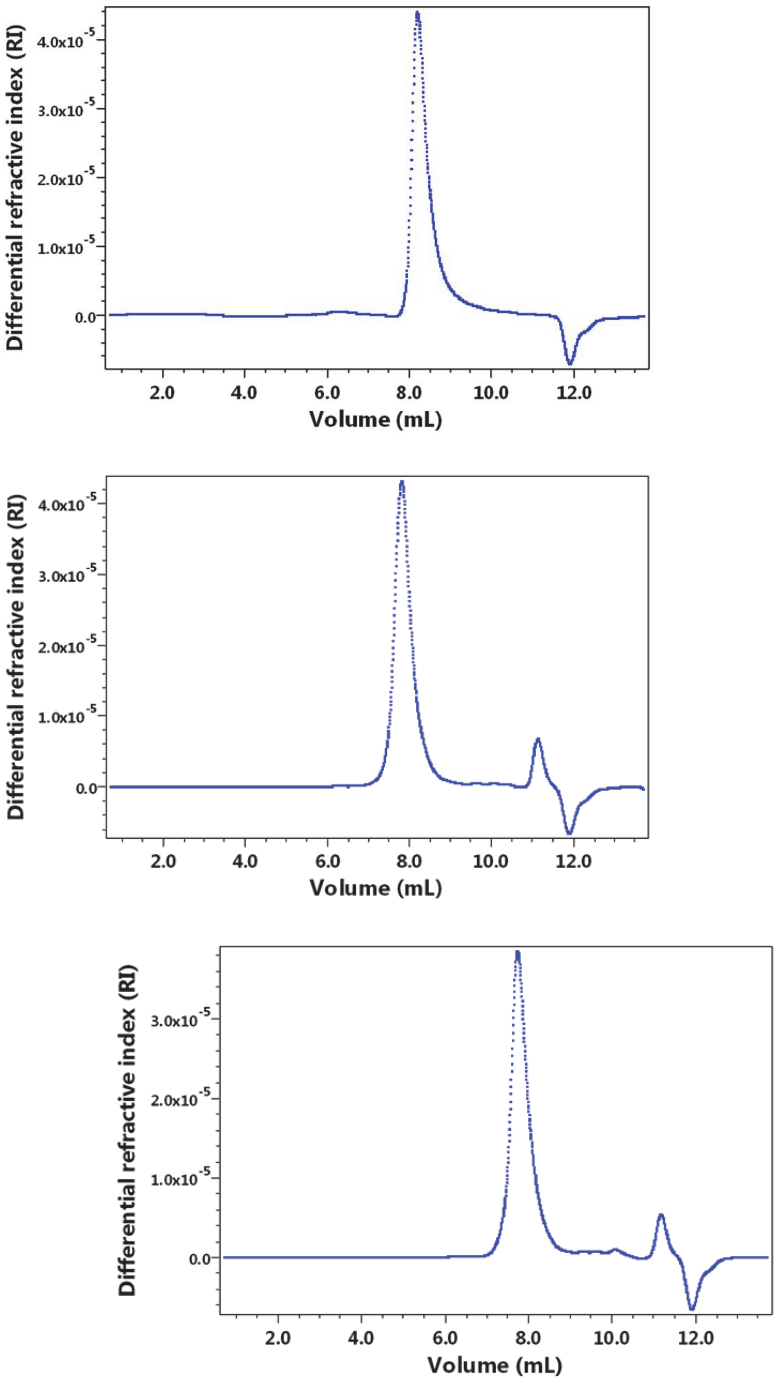


**Fig. S8.** Typical SEC chromatograms of the homo- (top, **P2**) and co-polymers (middle, **C4**; bottom **B2**) used for this study