Supporting information

Gold Nanorods coated with a Thermo-responsive Poly(ethylene glycol)-*b*poly(*N*-vinylcaprolactam) Corona as Drug Delivery System for Remotely Near Infrared-Triggered Release

Ji Liu,^{*a,c*} Christophe Detrembleur,*^{*a*} Marie-Claire De Pauw-Gillet,^{*b*} Stéphane Mornet,^{*c*} Etienne Duguet*^{*c*} and Christine Jérôme*^{*a*}

^a Center for Education and Research on Macromolecules (CERM), Department of Chemistry, University of Liege, Sart Tilman B6A, B-4000 Liège, Belgium

christophe.detrembleur@ulg.ac.be, c.jerome@ulg.ac.be

Fax: (32)4-36663497, Tel: (32)4-3663565

^b Laboratory of Mammalian Cell Culture (GIGA-R), University of Liege, B6 Sart Tilman, B-4000 Liège, Belgium ^c CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France,

<u>duguet@icmcb.u-bordeaux1.fr</u>

Fax: +33 540 002 761, Tel: +33 540 002 651



Figure S1. NMR spectra (a) and SEC traces (b) of the mPEG₁₁₄-Br and mPEG₁₁₄-X CTA; and molecular weight M_n is obtained from SEC analysis in THF with polystyrene as the calibration standard.



Figure S2. Gold nanorods systhesized from the seed-mediated grwoth strategy



Figure S3. Schematic illustration of the home-designed apparatus to follow the NIR-induced heating profiles of the GNR@PCL-b-PEG aqueous suspension

Figure S4. Representative UV/*vis* spectra (a), size distribution diagrams from DLS analysis of the resultant $GNR@PEG_{114}$ -*b*-PNVCL₂₃₇ (b), and the corresponding correlograms for the DLS analysis (c).

Figure S5. Representative XRD (a), XPS (b) and FTIR spectra (c) of the resultant $GNR@PEG_{114}-b-PNVCL_{237}$, and pictures of the $GNR@PEG_{114}-b-PNVCL_{237}$ dispersion in different solvents, (d-1): de-ionized water, (d-2): THF, (d-3): CH₂Cl₂, and

(d-4) DMSO. XPS spectrum shows the signals originating from gold at 86.6 (Au 4f7), 333.1 eV (Au 4d5) and 353.4 eV (Au 4d3), moreover, presence of the intrinsic peak of silver at 372.3 eV (Ag 3d) could be explained by the feeding of AgNO₃ as catalyst during the preparation of GNRs. The XPS spectrum also shows peaks of C 1s (284.8 eV: C-H bond and 292.1 eV: C-C bond), O 1s (531.1 eV: C=O or C-O bonds) and N 1s (398.7 eV: N-C bond), that might arising from the PEG₁₁₄-*b*-PNVCL₂₃₇ polymer corona.

Figure S6. TGA traces of the GNR@PEG-*b*-PNVCL before and after five cycles of heating/cooling treatment, a slight difference in the polymer fraction of *ca*. 0.85 *wt*.% was detected, which might probably evidence slight detachment of the polymers during the heating/cooling treatment.

Figure S7. Evolution of temperature of GNR@PEG-b-PNVCL aqueous solution with

different concentrations upon the NIR radiation (100 mW, 802 nm) within 10 min (a), and evolution of temperature of PBS buffer solution (pH 7.4, 10 mM) upon the NIR radiation (802 nm) with different power within 10 min (b). Aside by the blank of PBS buffer solution in (a), another blank of gold nanosphere aqueous suspension (GNP, *ca*. 30 nm in diameter, 100 mg/L) was also taken to evidence dependence of heating capacity on the structure of the gold nanoparticles