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Supplementary information for

Amphiphilic polymers based on Polyoxazoline as relevant nanovectors for Photodynamic Therapy



Figure S1. Synthetic routes for CmPMMA and CmPOX.



Figure S2. ¹H NMR spectra of CmOTs and CmPOX in CDCl₃.



Figure S3. SEC trace of CmPOX in DMF (RI detection).



Figure S4. Experimental set-up for the irradiation of self-assembly solutions



Figure S5. Zoom of ¹H NMR spectra (300 MHz; $CDCl_3$) of CmMMA, CmPOX and CmPOX/CmMMA showing the evolution of coumarin protons upon irradiation



Figure S6. TEM images of CmPOX/CmMMA before and after irradiation/crosslinking



Figure S7. ¹**H NMR CmPOX/CmMMA after irradiation and polymerization**. The water was removed by freeze-drying and the polymer redispersed in deuterated chloroform for characterization. Signals at 5.54 and 6.02 ppm are signs of residual monomer.



Figure S8. ¹H NMR spectrum of CmPMMA



Figure S9. SEC traces of CmMMA (black line) and CmPMMA (brown line) in THF (dotted lines MALS detection, full lines RI detection)



Figure S10. Cryo-TEM images of CmPOX micelles (A), uncrosslinked CmPOX/CmPMMA micelles (B), and crosslinked CmPOX/CmPMMA micelles loaded in Pheo (C).



Pheo in water

100nm

Figure S11. Typical image of Pheophorbide a nano-objects formed by dispersion of Pheo in water following the same process than for the nanovectors.



Figure S12. DLS analysis (intensity average, number average, and correlogramms) of CmPOX/CmPMMA micelles, uncrosslinked, crosslinked and loaded with Pheo



CmPox/CmMMA irrad.



CmPox/CmVIVA irrad. Polym.



Crosslinked CmPOX/CmPMMA selfassemblies

Figure S13. Examples of large nano-objects observed by TEM.



Figure S14. CmPOX/CmPMMA cross-linked micelles (sample 10 times diluted with respect to the sample analyzed at 173°): **a)** Correlation curve at 150° and relative weight average distribution function ; **b)** plot of $\overline{\Gamma}$ versus Dq^2 .



Figure S15. Plots of $\overline{\Gamma}$ versus Dq^2 of CmPOX/CmPMMA cross-linked micelles after 200µm filtration (sample 10 times diluted with respect to the sample analyzed at 173°).



Figure S16. Efficacy of Pheo-loaded (0.1μ M or 0.5μ M) nanovectors on cell viability after photodynamic therapy protocol assessed with the metabolic test PrestoBlue 24h after treatment. X: crosslinked nanovector; Pheo: pheophorbide Experiments were led two times independently, with 6 biological replicates at each experiment. Statistical analysis was led by one-way ANOVA followed by a Dunnett's multiple comparisons test comparing each condition with the control one. Statistical significance was compared between pheo-loaded crosslinked and non-crosslinked nanovector using t-test. Statistical difference p value <0.05 = *; p<0.0001 = ****; ns = non-significant.