Light-Switchable Nanoparticles Based on Amphiphilic Diblock, Triblock and Heterografted Polyoxazoline

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SI I. Quantification of photo-dimerization and photo-crosslinking efficiency and reversibility for both D, H and T from absorption coumarin band according to cycloaddition and cleavage respectively monitored by UV-vis spectroscopy

Dimerization/de-dimerization rates at each times of irradiation are estimated from maximal absorbance measured for each ones. Concerning D and H, assuming that the initial absorption band corresponds to total de-dimerized form (single unimers), the maximal absorption band at t_0 ($A(t_0)$) is estimated at 100% of de-dimerization, in other terms 0% of dimerization. Other rates, where absorption band $A(t)$ going to decrease with the irradiation at 350 nm (dimerization) are deduced from these values (dimerization(t)).

Calculation of dimerization/de-dimerization rates:

$$\text{Dimerization (t)} = 100 - \frac{A(t) \times 100}{A(t0)} \ (\%) \qquad \text{(equation 1)}$$

$$\text{De-dimerization (t)} = \frac{A(t) \times 100}{A(t0)} \ (\%) \qquad \text{(equation 2)}$$

Concerning T, the initial approximation is reverse. Initial chains are already dimerized and absorption band corresponds to the minimal value of dimerization which continues to grow under irradiation at 254 nm (de-dimerization). In previous works, we estimated (by NMR and

UV-vis spectroscopy) this rate of dimerization is above 97% (3% are de-dimerized) which corresponds to the initial absorbance value (A(t0)).

Calculation of dimerization/de-dimerization rates for T:

$$\text{De-dimerization (t)} = 100 - \frac{A(t) \times 3}{A(t0)} \; (\%) = Dd(max)$$

$$\text{Dimerization (t)} = 100 - \frac{A(t) \times ddmax}{A(ddmax)} \; (\%)$$

SI II. Aging study of NP_D, NP_{Dx}, NP_H, NP_{Hx} and NP_T nanoparticles by DLS during 60 days in the dark at room temperature (20 °C), under natural light exposure at room temperature and heating at 37 °C.

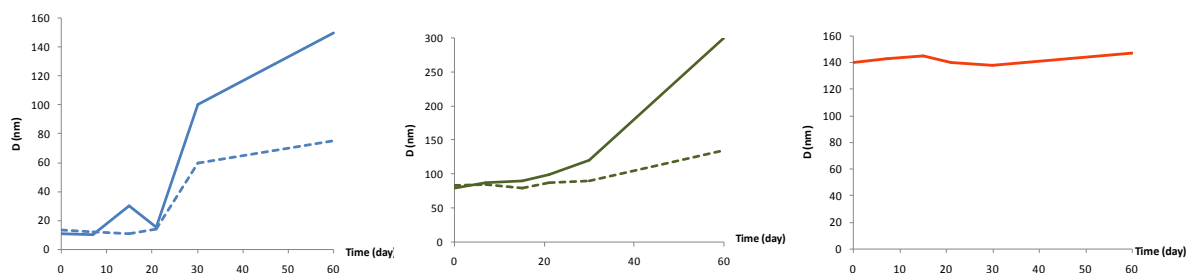Aging study monitored by DLS during 60 days

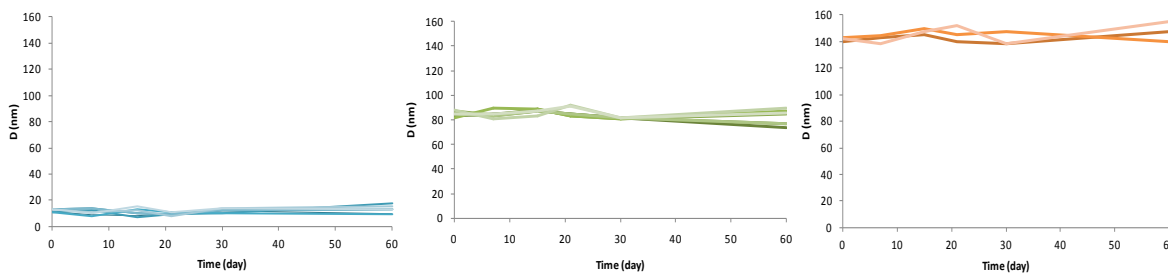**Figure SI 1.** Size distribution evolution during 60 days for D (left), H (middle) and T (right) at 60°C.

Figure SI 2. Size distribution evolution during 60 days for D (left), H (middle) and T (right) at room temperature (20 °C), under natural light exposure at room temperature and heating at 37 °C.
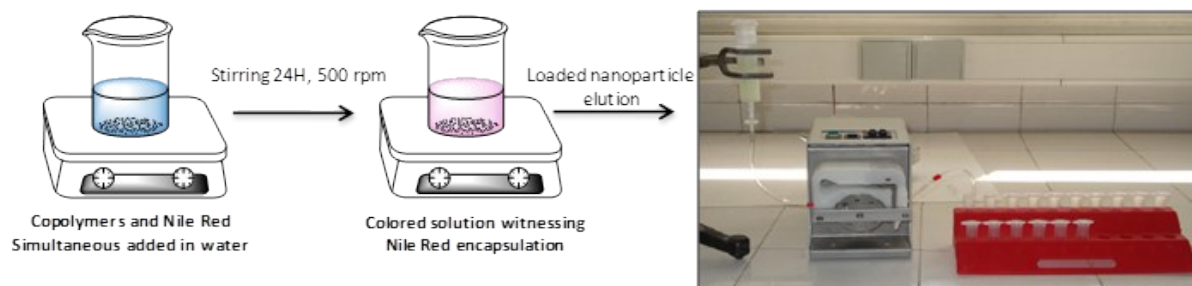
Figure SI 3. Illustration of loading processing and loaded NPs elution through a peristaltic pump.
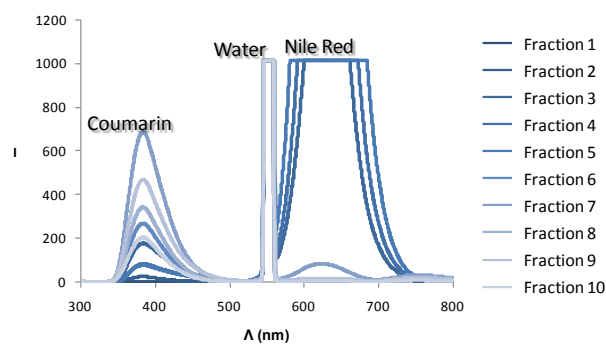

Figure SI 4. Emission spectra of eluted parts from NP$_D$ encapsulated solutions recorded from 300 to 800 nm under $\lambda_{excitation}$= 552 nm.
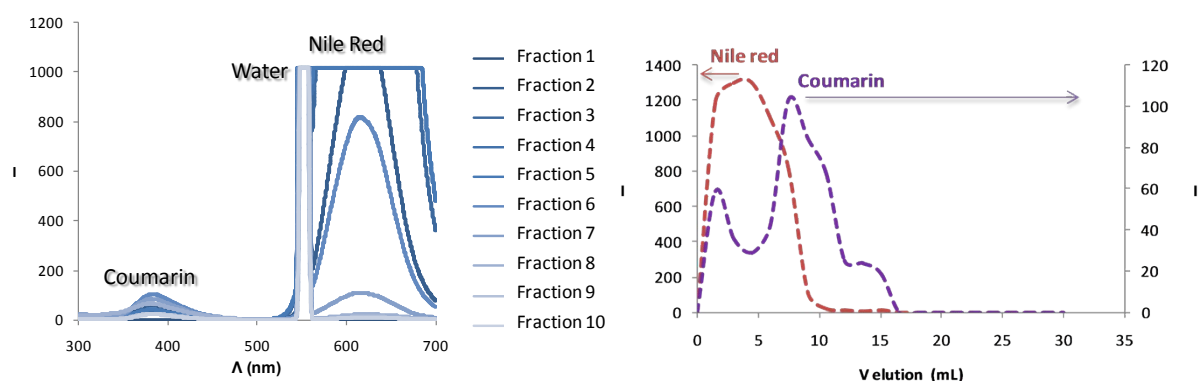

Figure SI 5. Emission spectra recorded from 300 to 700 nm under $\lambda_{excitation}$= 552 nm (left) and respective reported maxima emission intensities of Nile Red and coumarin for each eluted part from NP$_{Dx}$ encapsulated solutions.
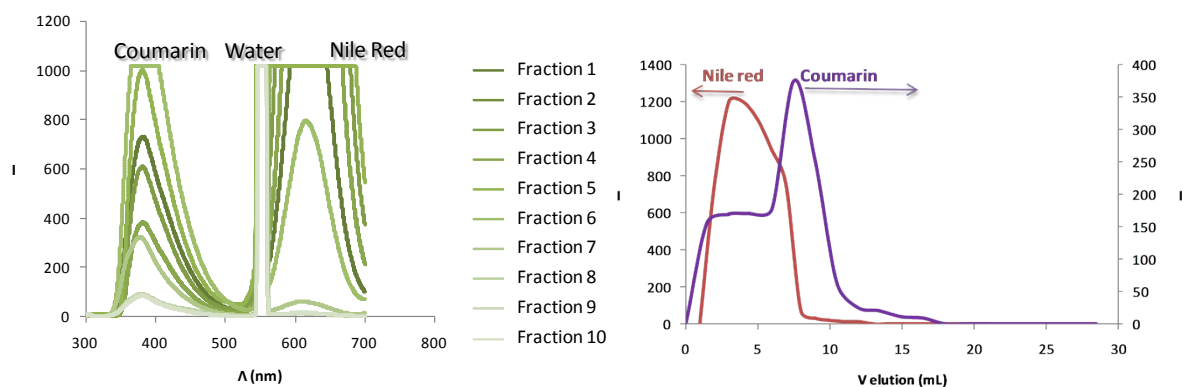
Figure SI 6. Emission spectra recorded from 300 to 700 nm under $\lambda_{excitation}$= 552 nm (left) and respective reported maxima emission intensities of Nile Red and coumarin for each eluted part from NP_H encapsulated solutions.

Figure SI 7. Emission spectra recorded from 300 to 700 nm under $\lambda_{excitation}$= 552 nm (left) and respective reported maxima emission intensities of Nile Red and coumarin for each eluted part from NP_{Hx} encapsulated solutions.
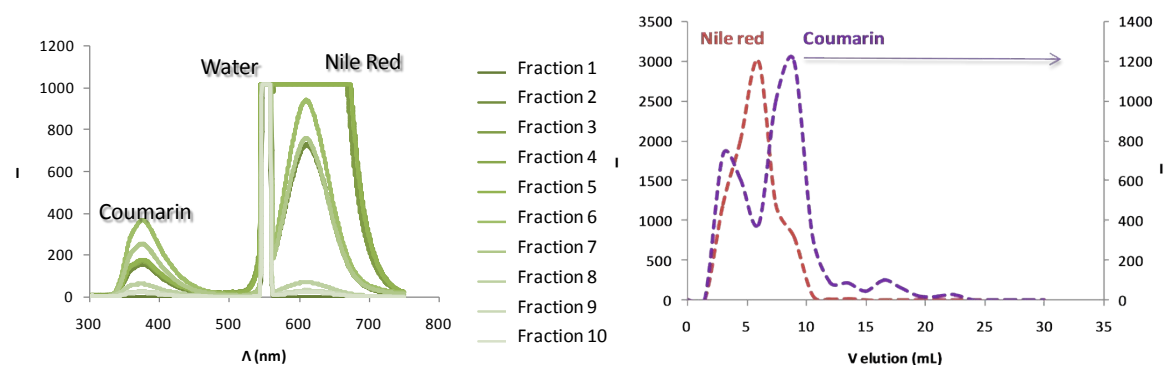

Figure SI 8. Emission spectra recorded from 300 to 700 nm under $\lambda_{excitation}$= 552 nm (left) and respective reported maxima emission intensities of Nile Red and coumarin for each eluted part from NP_T encapsulated solutions.
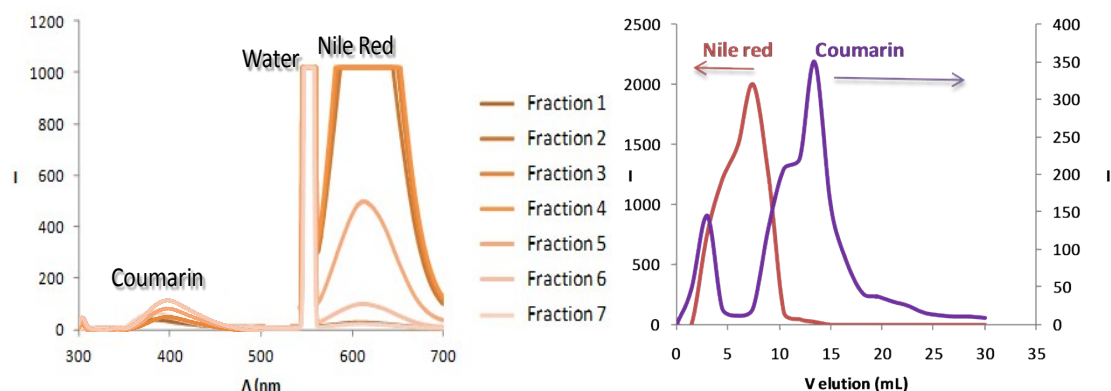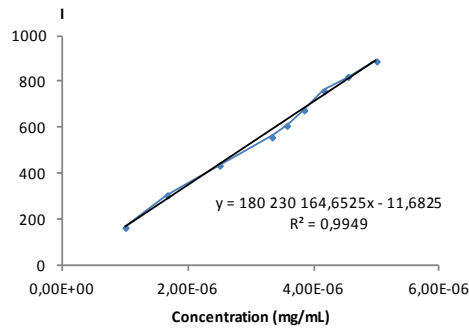
Figure SI 9. Nile Red calibration curve deduced from maxima intensities of Nile Red emission band for concentrations varying from 1.10^{-6} to 5.10^{-6} mg/mL.

Knowing initial concentration in polymer (5.10^{-5} mg/mL, Pi) and the amount of Nile Red initially introduced (5.10^{-6} mg/mL, NRi), loading efficiency (D.L.E.) and capacity (D.L.C.) are determinated for each NP solution from calibration curve to estimate the encapsulated Nile Red concentration (NRe) and then according to the following calculation:

Calculation of D.L.E. and D.L.C. rates:

$$\text{D.L.E.} = \frac{NRe}{NRi} * 100 \ (\%) \quad \text{(equation 3)} \qquad \text{D.L.C.} = \frac{\frac{NRe}{Pi} * 100}{} \ (\%) \quad \text{(equation 4)}$$