Supporting information for:

Chemical Encoding of an Amphiphilic Copolymer for a Dual Controlled Release from their Assemblies

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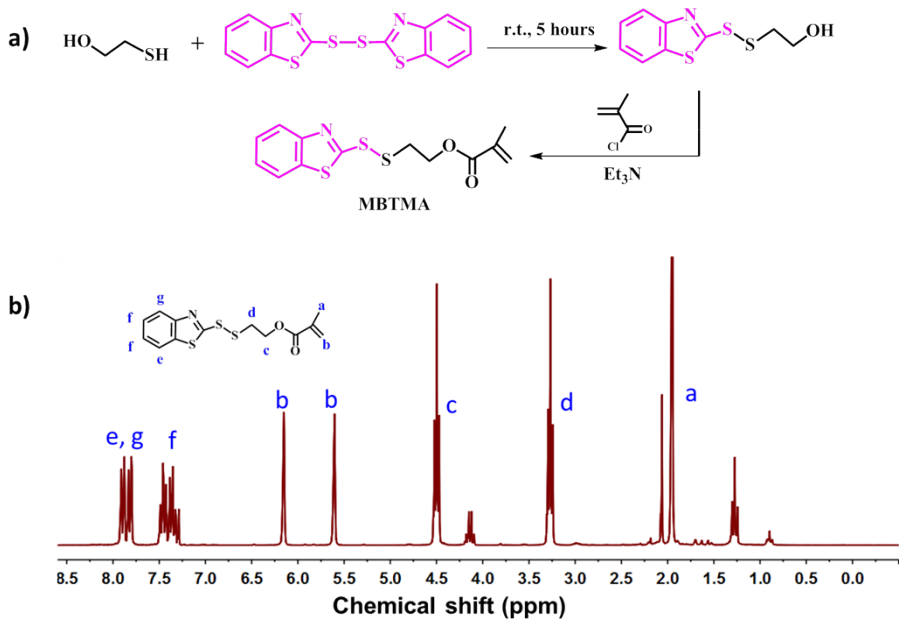

Fig. S1. a) Synthesis of polymerizable monomer MBTMA following the previously reported method [1, 2]; b) ^{1}H NMR spectrum of MBTMA in $CDCl_3$.

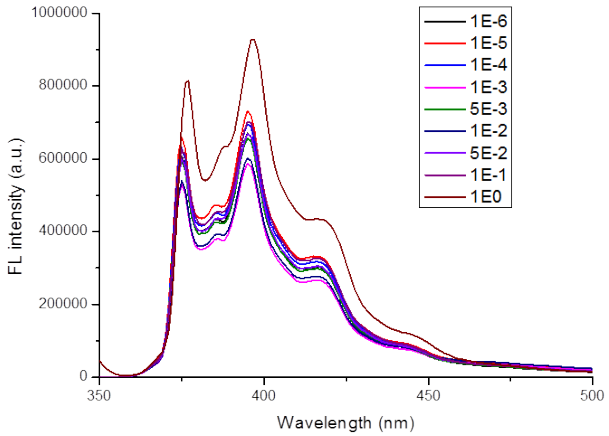

Fig. S2. Fluorescence emission spectra of pyrene in the copolymer P2 nanoparticles at the copolymer P2 at different concentrations.

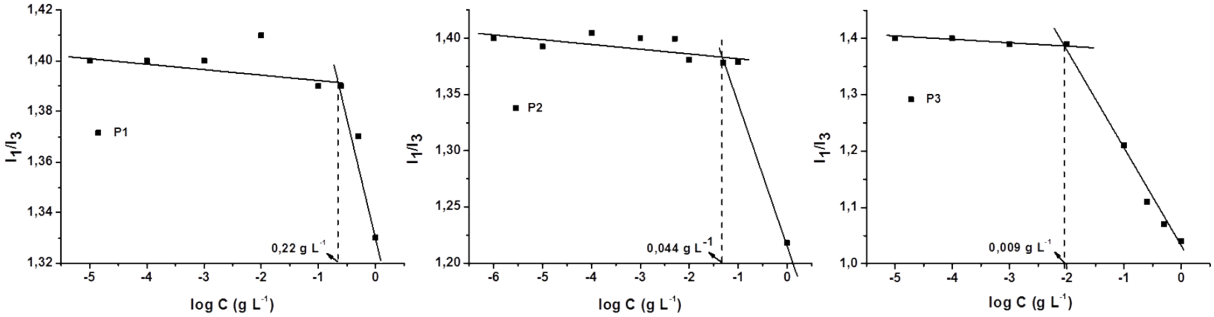

Fig. S3. Critical aggregation concentration (CAC) of polymer assemblies of the copolymers P1-P3.

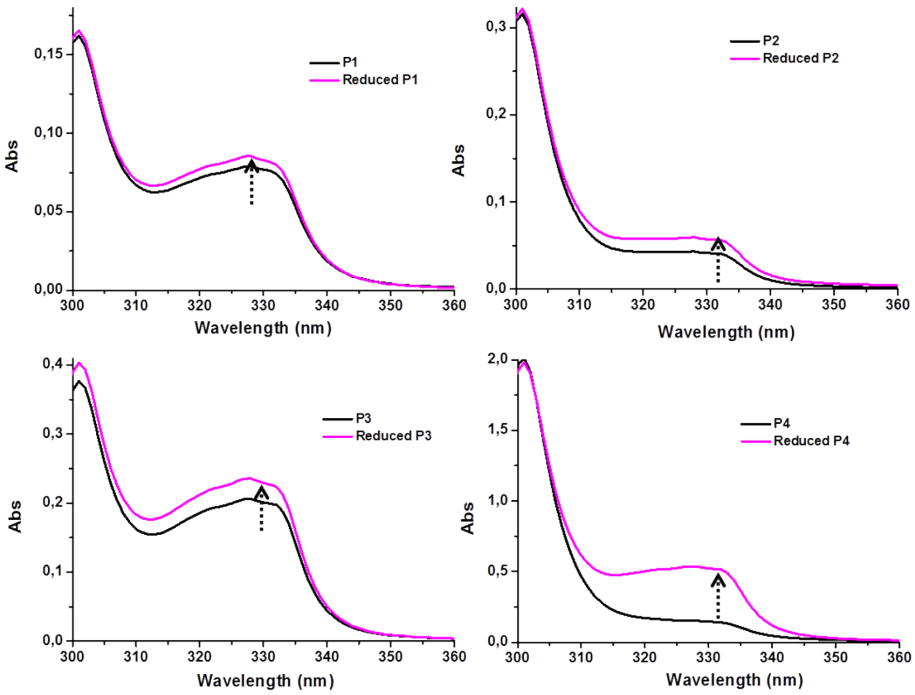

Fig. S4. UV-Vis spectra of poly(VP-*co*-MBTMA) copolymers before (black) and after (violet) reduction with DTT in THF. The molar ratio of DTT to MBTMA units in the copolymer was 50/1.

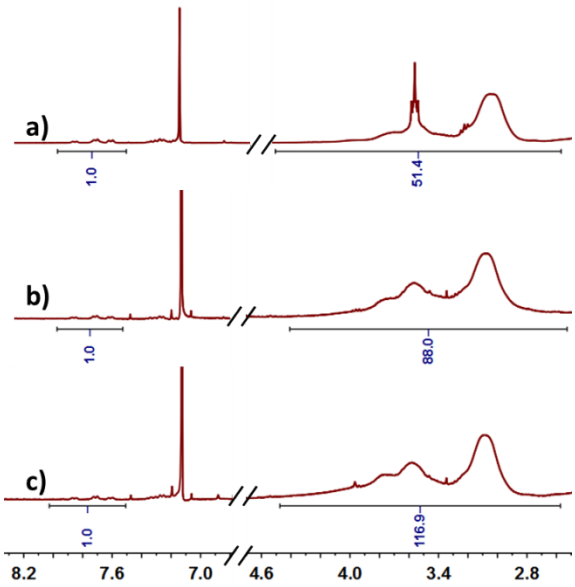

Fig. S5. ^{1}H NMR spectra of a) the copolymer P2; b) the nanoparticles of P2 after dialysis against distilled water; c) the nanoparticles of P2 after dialysis against TCEP·HCl solution. All the samples were dried and then dissolved in $CDCl_3$.

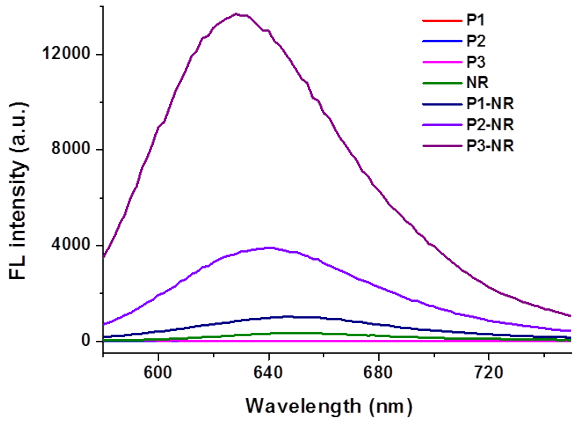

Fig. S6. Emission spectra of Nile Red in water (NR) or encapsulated in polymeric assemblies of P1 (P1-NR), P2 (P2-NR), or P3 (P3-NR).

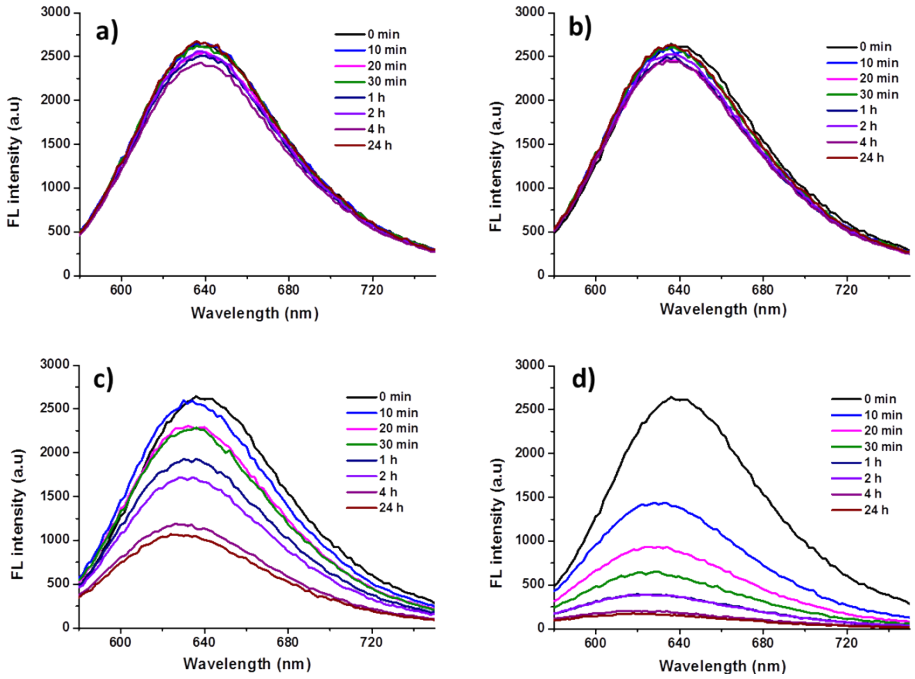

Fig. S7. Emission spectra of Nile Red in the dispersions of P2 after reduction by TCEP·HCl with different concentrations: a) 0 mM; b) 0.25 mM; c) 2.5 mM; d) 25 mM.

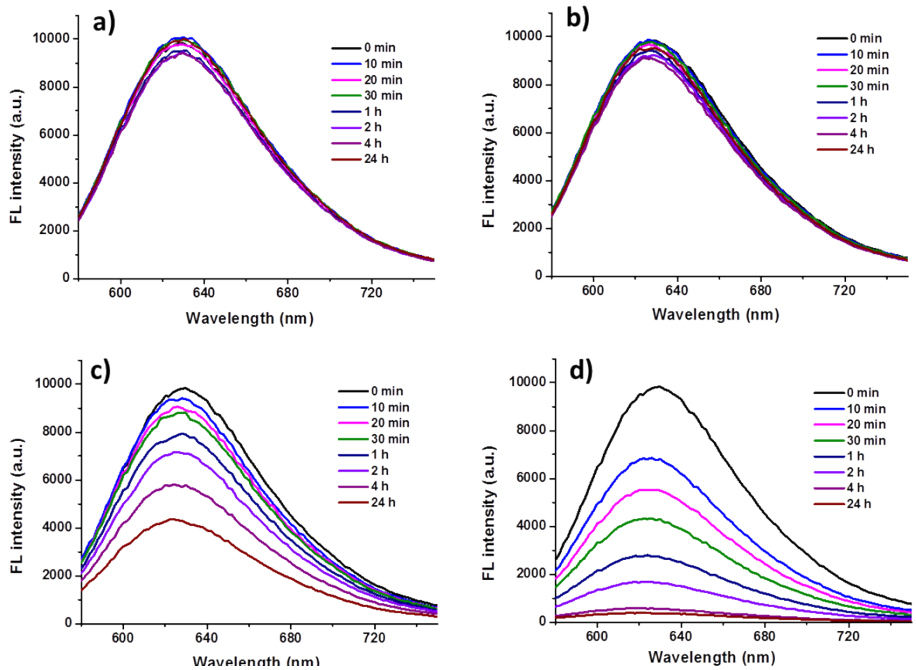

Fig. S8. Emission spectra of Nile Red in the dispersions of P3 after reduction by TCEP·HCl with different concentrations: a) 0 mM; b) 0.5 mM; c) 5 mM; d) 50 mM.

Because the hydrochloric acid coming from the TCEP·HCl could have an influence on the fluorescence behavior of Nile Red due to a possible protonation of the dye [3],

the emission spectra of the P2 nanoparticles was also examined in the presence of hydrochloric acid in a solution having the same pH value as the TCEP·HCl solution. The difference between the emission intensity of Nile Red in the dispersion of P2 treated with HCl and TCEP·HCl is displayed in Figure S9. The signal of Nile Red decreased with time after being treated with TCEP·HCl whereas it remains relatively stable in the presence of HCl. This observation indicated that the decrease of the emission intensity of Nile Red in the dispersions of P2 and P3 can be mainly attributed to the reduction of the copolymers.

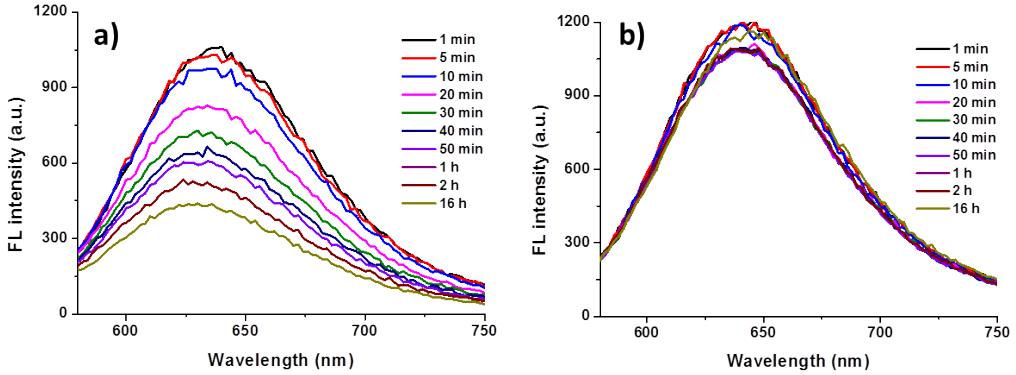

Fig. S9. Fluorescence emission spectra of Nile Red in polymer assemblies of P2 after addition of: a) TCEP·HCl with concentration of 5 mM and b) HCl aqueous solution with the same pH value to TCEP·HCl solution (pH~2.3).

References

[1] Brzezinskal, E.; Ternay Jr., A. L. *J. Org. Chem.* **1994**, *59*, 8239-8244

[2] Tsarevsky, N. V.; Huang, J.; Matyjaszewski, K. *J. Polym. Sci.: Part A: Polym. Chem.* **2009**, *47*, 6839-6851.

[3] Wagner, B. D.; Boland, P. G.; Lagona, J.; Isaacs, L. *J. Phys. Chem. B* **2005**, *109*, 7686-7691.