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## **Supplementary information**

## Stability of biodegradable microcarriers' surface: physically adsorbed *versus* chemically linked shells.

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Figure S1. <sup>1</sup>H NMR spectra in DMSO- $d_6$  of dextran, Dex-C<sub>6</sub><sup>14</sup>, Dex-C=C<sup>27</sup> and Dex-C<sub>6</sub><sup>7</sup>-C=C<sup>10</sup>



Figure S2. <sup>1</sup>H NMR spectra in D<sub>2</sub>O of dextran, Dex-N<sup>+11</sup>, Dex-N<sup>+11</sup>-C<sub>6</sub><sup>36</sup> and Dex-N<sup>+11</sup>-C $\equiv$ C<sup>24</sup>



Figure S3. <sup>1</sup>H NMR spectra in DMSO- $d_6$  of coumarin derivatives (1) and (2), Dex-C=C<sup>25</sup> and Dex-C=C<sup>25</sup>-Coumarin<sup>1.5</sup>



Figure S4. <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> of PLA derivatives (crude PLA, Tosylated PLA, then PLA-N<sub>3</sub>)



Figure S5: A) In situ interfacial CuAAC click chemistry occurring between PLA-N<sub>3</sub> and Dex-C<sub>6</sub><sup>7</sup>-C=C<sup>10</sup>. B) Schematic representation of the interface deformation during the *In situ* interfacial CuAAC.



Figure S6: <sup>1</sup>H NMR spectra (DMSO-<sub>d6</sub>) of NPs produced without (Run 5, Table 1) or with (Run 7, Table 1) *in situ* CuAAC. Spectra are given before treatments, after SDS and culture medium treatments.





Fig. S7: Left: Scanning electronic microscopy pictures of fluorescent MCS (Entries 18 and 18, Table 2). Magnification and scale bar are done on the pictures. Right: Confocal laser scanning microscopy of the same MCs, before and after the SDS treatment. A schematic representation of the observation height is drawn.