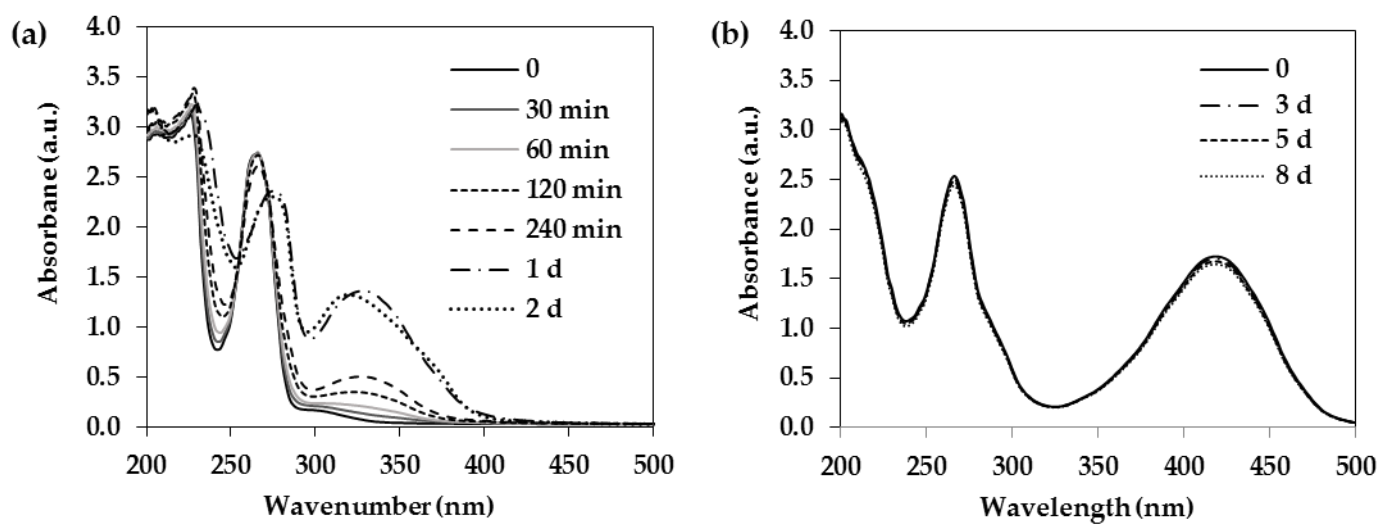
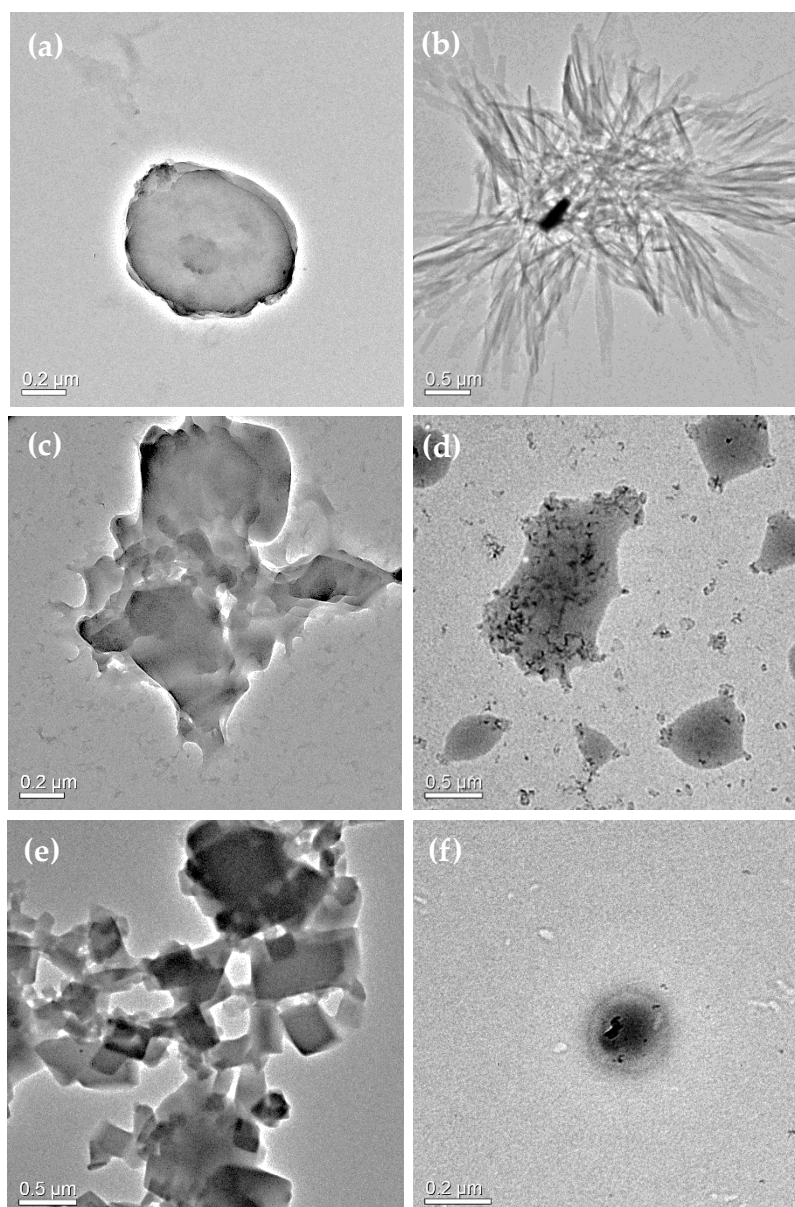


## Supplementary material



**Figure S1.** UV-Vis spectra of (a) pristine BH4 and (b) pristine SP solutions in water (1% w/v) at different times.



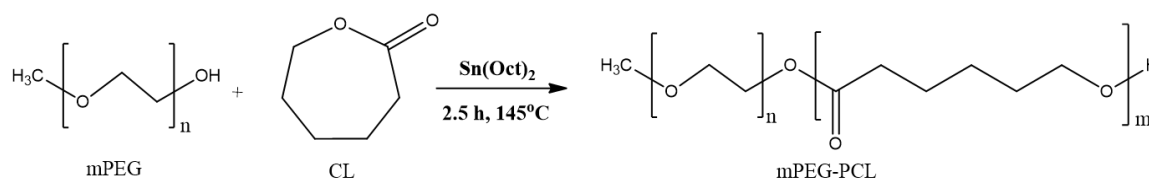
**Figure S2.** TEM micrographs of (a) processed TA $\beta$ CD, (b) processed SP, (c) SP1/TA $\beta$ CD1 PM, (d) spray-dried SP1/TA $\beta$ CD1 complex, (e) SP1/TA $\beta$ CD2 PM and (f) spray-dried SP1//TA $\beta$ CD2 complex.

**Table S1.** The number average molecular weight ( $M_n$ ), the weight average molecular weight ( $M_w$ ) and the dispersity ( $\mathcal{D}$ ,  $M_w/M_n$ ), as determined by  $^1\text{H-NMR}$  and GPC.

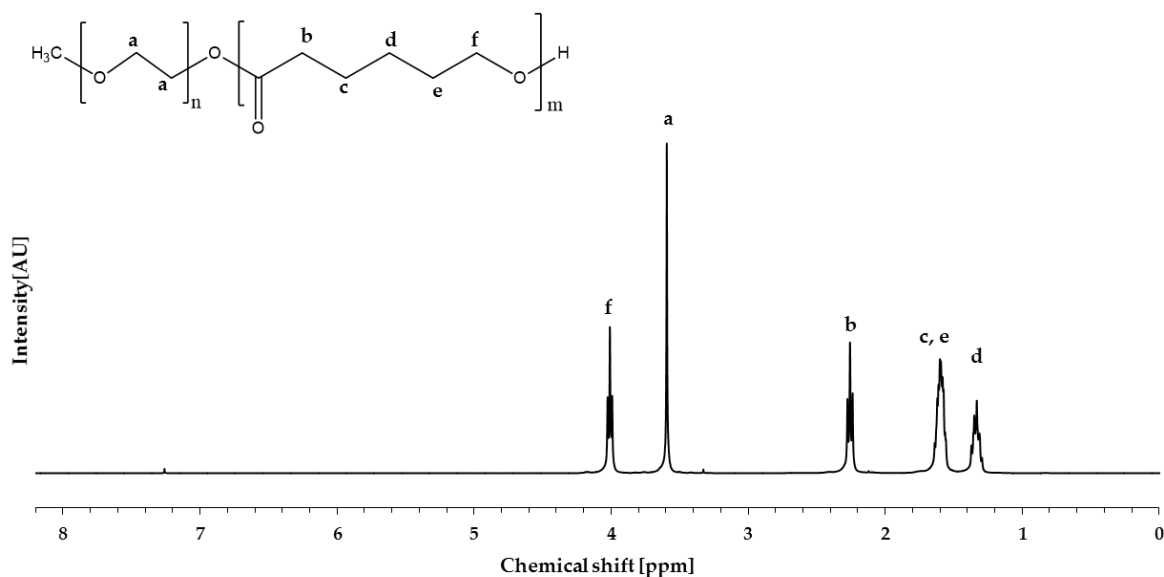
| Copolymer | $M_n$<br>(theoretical)<br>[g mol $^{-1}$ ] | $M_n$<br>( $^1\text{H-NMR}$ )<br>[g mol $^{-1}$ ] | $M_n$<br>(GPC)<br>[g mol $^{-1}$ ] | $M_w$<br>(GPC)<br>[g mol $^{-1}$ ] | $\mathcal{D}$ <sup>13</sup><br>( $M_w/M_n$ )<br>GPC <sup>14</sup> |
|-----------|--|---|------------------------------------|------------------------------------|---|
| mPEG-PCL  | 24,000                                     | 25,000  | 19,000                             | 32,600                             | 1.71 <sup>15</sup>  |

**Table S2.** Equivalent amounts of the different components used for the encapsulation of SP within mPEG-PCL NPs.

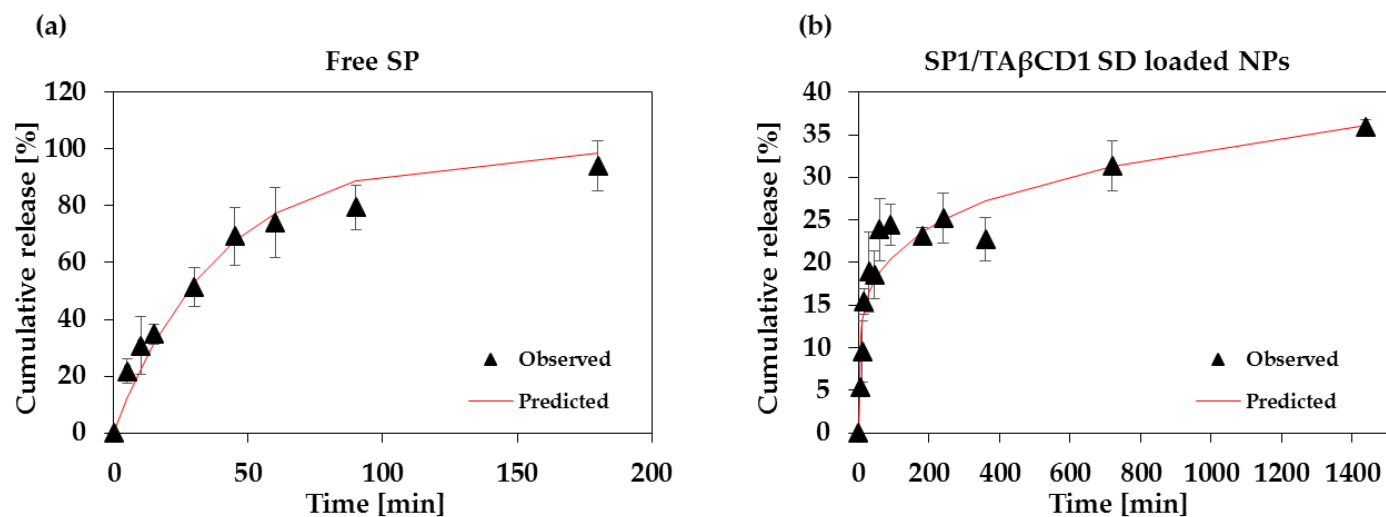
| Formulation | Equivalent amount used for encapsulation |         |                    |
|-------------|--|---------|--------------------|
|             | mPEG-PCL [mg]                            | SP [mg] | TA $\beta$ CD [mg] |
| Pristine SP | 50                                       | 1       | -                  |
|             |  | 2       | -                  |
| 1           |  | 8.5     |                    |
| 2           |  | 17      |                    |
| 1           |  | 17      |                    |
| 2           |  | 34      |                    |
| 1           |  | 8.5     |                    |
| 2           |  | 17      |                    |
| 1           |  | 17      |                    |
| 2           |  | 34      |                    |



**Figure S3.** Ring opening polymerization reaction of CL initiated by the terminal hydroxyl group of mPEG with a molecular weight of  $4000 \text{ g mol}^{-1}$ .



**Figure S4.**  $^1\text{H-NMR}$  spectrum of the mPEG-PCL copolymer in  $\text{CDCl}_3$ .



**Figure S5.** Fitting of average release data of (a) free SP to a first-order kinetics and (b) SP from SP1/TA $\beta$ CD1 encapsulated PEG-PCL NPs to the Korsmeyer-Peppas model, as determined with DDSolver Software 1.0 [41].