## Supplementary Materials: Biodegradable Polyphosphazene Based Peptide-Polymer Hybrids

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**Figure S1.** GPC chromatographs of polymer **1–5**. All polymers elute at similar retention volumes indicating similar molecular weights.



**Figure S2.** (**A**) <sup>31</sup>P NMR spectrum of polymer **1–5**. A broad peak at about 0 ppm indicates complete substitution of the chlorine atoms at polyphosphazene backbone and the absence of degradation products. (**B**) <sup>31</sup>P NMR spectrum of the monomer (*N*-(trimethylsilyl)-trichlorophosphoranimine), the precursor polymer (poly(dichlorophosphazene) and polymer 2 to show complete monomer conversion and macromolecular substitution of the chlorine atoms at the polyphosphazene backbone.



**Figure S3.** UV–Vis spectra in acetonitrile of polymer **5** loaded with 2.4 wt % imiquimod (black), of imiquimod (red) and of Gly-Phe-Leu-Gly-imiquimod (blue).



**Figure S4.** Normalized FFF analysis illustrating the degradation of polymer **2** at 37 °C in an aqueous solution at pH 2. Broadening and decrease in intensity and a shift to earlier retention time of the polymer peak are observed.



**Figure S5.** Hydrolytic and enzymatic release of imiquimod from polymer **5** during 3.5 days shown in two different studies to confirm reproducibility.



Figure S6. ATR-FTIR spectra of polymer 1–5.



**Figure S7.** Enzymatic degradation of polymer 2 followed by <sup>31</sup>P NMR spectroscopy after 14 days in citrate buffer (pH 6) containing L-cysteine and papain (black), hydrolytic degradation of polymer **2** in the same buffer system without papain (red), with papain and cystamine as inhibitor (blue). All samples were stored at 37 °C.



**Figure S8.** Enzymatic degradation of polymer **2** followed by <sup>31</sup>P NMR spectroscopy of two different samples a-1 and a-2) under the same conditions (28 days in citrate buffer (pH 6) containing L-cysteine and papain). All samples were stored at 37 °C.



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