Osmotic pressure-dependent release profiles of payloads from nanocontainers by co-encapsulation of simple salts

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Table S1 Composition of the dispersed phase for the dispersion of nanocapsules used in the experiments. NP means nanocapsules and D is added for samples containing 2-nitrophenol sodium salt (dye). X refers to the addition of diethylentriamine (crosslinker) and $[Salt]_c$ indicates that the concentration of encapsulated salt in aqueous dispersed phase is equal to "c".

Entry	1,4-diaminobutane [mg]	diethylentriamine [mg]	KCl [mol.L ⁻¹]	CaCl ₂ [mol.L ⁻¹]	2-nitrophenol sodium salt [mg]
NPD	88	-	-	-	23
NPD[KCI] _{0.1}	88	-	0.1	-	23
NPD[KCl] _{0.25}	88	-	0.25	-	23
NPD[KCl] _{0.5}	88	-	0.5	-	23
NPD[KCl] ₁	88	-	1	-	23
NPD[KCl] ₂	88	-	2	-	23
NPD[KCl] ₃	88	-	3	-	23
NPD[KCl] ₄	88	-	4	-	23
NPD[CaCl ₂] _{0.067}	88	-	-	0.067	23
NPD[CaCl ₂] _{0.167}	88	-	-	0.167	23
NPD[CaCl ₂] _{0.33}	88	-	-	0.33	23
NPD[CaCl ₂] _{0.67}	88	-	-	0.67	23
NPD[CaCl ₂] _{1.3}	88	-	-	1.3	23
$NPD[CaCl_2]_2$	88	-	-	2	23
NPD[CaCl ₂] _{2.67}	88	-	-	2.67	23
NP	88	-	-	-	-
NPX	76	14		-	-
NPDX[KCI] ₁	76	14	1	-	23
NP[KCI] ₁	88	-	1	-	-
NPX[KCI] ₁	76	14	1	-	-

Table S2 Osmotic pressure inside the NCs containing KCl with initial concentration in dispersed phase between 0.1and 4 M.

	KCI [mol.L ⁻¹]	Osmotic Coefficient	The sumplies of issue (i)	Osmotic pressure (π)
Entry		(φ)	The number of lons (I)	[MPa]
NPD[KCI] _{0.1}	0.1	0.927	2	0.46
NPD[KCI] _{0.25}	0.25	0.913	2	1.15
NPD[KCI] _{0.5}	0.5	0.900	2	2.23
NPD[KCl]1	1	0.898	2	4.45
NPD[KCI]2	2	0.912	2	9.04
NPD[KCI] ₃	3	0.950	2	14.2
NPD[KCI]4	4	0.990	2	19.7

Table S3 Composition of the dispersed phase for the dispersion of nanocapsules used in the experiments. NP means nanocapsules and X refers to the addition of diethylentriamine (crosslinker) and $[Salt]_c$ indicates that the concentration of encapsulated salt in aqueous dispersed phase is equal to "*c*".

Entry	1,4-diaminobutane [mg]	diethylentriamine [mg]	KSCN [mol.L ⁻¹]	Foscarnet [mol.L ⁻¹]
NP[KSCN] _{0.1}	88	-	0.1	-
NP[KSCN] ₁	88	-	1	-
NPX[KSCN]1	76	14	1	-
NP[Foscarnet] _{0.1}	88	-	-	0.1
NPX[Foscarnet] _{0.1}	76	14	-	0.1

Characterization methods

The morphology of the NCs was examined with a transmission electron microscope (TEM) (Jeol 1400) operating at an accelerating voltage of 120 kV and a Gemini 1530 (Carl Zeiss AG, Oberkochem, Germany) scanning electron microscope (SEM) operating at 0.35 kV. Droplets of 10 µL of the diluted dispersions were placed on small silica platelets for scanning electron microscopy and on copper grids for TEM measurements. The UV-Vis absorption spectra were recorded with a Perkin Elmer Lambda 25 UV/VIS spectrometer. All dynamic light scattering (DLS) measurements were carried out at 22 °C on a commercially available instrument from ALV GmbH (Langen, Germany) consisting of a goniometer and an ALV-5000 multiple tau full-digital correlators with 320 channels. A helium-neon laser from JDS Uniphase (Milpitas, USA) with an operating intensity of 25 mW and a laser wavelength of λ = 632.8 nm was used as a light source. All solutions for the light scattering experiments were prepared in dustfree quartz cuvettes from Hellma (Müllheim, Germany) with an inner diameter of 18 mm, which were cleaned before with distilled acetone. For the measurements of NCs size, their dispersion was diluted against an aqueous SDS solution (X=40, the same dilution condition with the release experiment). The amount of dispersed phase percentage in the NCs dispersion was ~ 0.05wt% after dilution. Samples were very slightly hazy after dilution. Samples were then withdrawn at two certain times, at t = 0 min and t = 240 min. Dust was removed from the withdraw samples via filtration using 5 micrometer filter LS (PTFE) (Merck Millipore, Germany) before measurements. The Stokes-Einstein equation was applied to calculate diffusion coefficient while viscosity value was set for water at 22 °C. The values of hydrodynamic average diameters of the samples were calculated by independent extrapolation for q = 0 (zero angle). An Activa M spectrometer (Horiba Jobin Yvon, Bernsheim, Germany) equipped with a Meinhardt-type nebulizer and a cyclone chamber was used for ICP-OES measurements. The device was controlled by an ACTIVAnalyst 5.4 software. For the measurement the following conditions were chosen: 1250 W forward plasma power, 12 L·min-1 Ar flow, and 15 rpm pump flow. The Ar emission at 404.442 nm was employed as a reference line t. The emission lines chosen for calibration and guantification of potassium were 766.490 nm and 769.896 nm with a 5 s integration time. For calibration and quantification of calcium, the emission lines 373.690 and 422.673 with a 5 s integration time were chosen. The emission lines 213.618 and 253.560 were selected for calibration and quantification of phosphorus with a 5 s integration time. For the calibration 5 different standard concentrations were used, baseline correction, and a dynamic underground correction were provided by the software. Each measurement was an average of three repetitions and repeated two times.



Fig. S1 UV-Vis spectra of 2-nitrophenol sodium salt dissolved in water with different concentration (a). Calibration curve of 2-nitrophenol sodium salt in water for UV-Vis spectroscopy (b).



Fig. S2 Calibration curves for potassium (a), calcium (b), and phosphorus (c) for ICP-OES.



Fig. S3 Temporal release profiles of the dye for NPD, NPD[KCl]_{0.1}, NPD[KCl]₁, NPD[CaCl₂]_{0.067}, NPD[CaCl₂]_{0.67}, and NPD[CaCl₂]_{2.67}.



Fig. S4 Release profiles of the dye and KCl versus time for sample NPD[KCl]_{0.1} where the dye and KCl were encapsulated at concentration 0.1 M in the dispersed aqueous phase.



Fig. S5 TEM micrograph of sample NP[KCl]₁ (Table S1). The average shell thickness for these NCs was calculated to be 36 ± 13 nm.



Fig. S6 DLS results of sample NP (a and b), NP[KCl]₁ (c and d), NPX (e and f), and NPX[KCl]₁ (g and h) after dilution at time t = 0 and t = 240 min. The values of the hydrodynamic avarage radii were calculated by independent extrapolation of for q = 0 (zero angle). The polydispersity index (PDI) was mesured at an angle of 90°.



Fig. S7. Photograph of the dispersion of nanocontainers with encapsulated KSCN before (a) and after (b) addition of a solution of ferric ions.

References

[1] W. J. Hamer, Y. C. Wu, J. Phys. Chem. Ref. Data 1972, 1, 1047-1100.