Supplementary Materials

Synthesis and characterization of ionic graft copolymers: introduction and *in-vitro* release of antibacterial drug by anion exchange

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Content:

S1. Synthesis of multifunctional macroinitiators P(MMA-*co*-BIEM) (example for Ia)

Comonomers HEMA (1.40 mL, 11.50 mmol) and MMA (3.70 mL, 34.50 mmol), anisole (0.50 mL), dNbpy (62.66 mg, 15.30 × 10^{-2} mmol) and CuBr (10.99 mg, 7.67 × 10^{-2} mmol) were placed into a Schlenk flask and degassed by two freeze–pump–thaw cycles. The initial sample was taken and EBiB initiator (113.77 μL, 7.67 × 10^{-2} mmol) was introduced to the mixture. Next, the reaction flask was immersed in an oil bath at 70°C. The reaction was stopped by exposing to air. The reaction mixture diluted in THF was passed through a neutral alumina column to remove copper catalyst, then the polymer was precipitated in diethyl ether and vacuum dried. ^{1}H NMR of P(MMA-*co*-HEMA) (Figure S1a) (DMSO-d_6, δ, ppm): 5.01–4.72 (1H, –CH_2–O**H**), 3.90–3.82 (2H, –C**H**$_2$–OH), 4.17–4.05 (2H, –COO–C**H**$_2$–), 3.56–3.48 3H, –O–C**H**$_3$), 1.94–1.57 (2H, –C**H**$_2$– backbone), 1.4–0.51 (3H, –C**H**$_3$ backbone). FT-IR (Figure S2a) (cm^{-1}): 3600–3100 ν(O–H), 3000–2800 ν(C–H), 1750 ν(C=O), 1150 ν(C–O).

The obtained hydroxyl-functionalized polymer **I** (0.70 g, including 0.90 mmol of HEMA units) was dissolved in pyridine (6 mL). Next, the mixture was placed in an ice bath to cool it down to 0 °C. After cooling α-bromoisobutyrate bromide (BIBB) (166.21 μL, 1.34 mmol) was added dropwise. The mixture was stirred overnight. Next, the bromoester-functionalized polymer **Ia** was precipitated in cooled water and vacuum dried. ^{1}H NMR of P(MMA-*co*-BIEM) (Figure S1b) (DMSO-d_6, δ, ppm): 4.47–4.28 (2H, –C**H**$_2$–OOC–C–(CH_3)$_2$Br), 4.28–4.08 (2H, –COO–C**H**$_2$), 3.74–3.44 (3H, –O–C**H**$_3$), 2.02–1.91 (6H, –(C**H**$_3$)$_2$Br initiating moiety), 1.94–1.57 (2H, –C**H**$_2$– backbone), 1.4–0.51 (3H, –C**H**$_3$ backbone). FT-IR (Figure S2b) (cm^{-1}): 3000-2800 ν(C–H), 1750 ν(C=O), 1150 ν(C–O).

Table S1. Conversion values in synthesis of macroinitiator precursors determined by ^{1}H NMR.

	HEMA conversion	**MMA conversion**	**total conversion**
I	32	31	31
II	44	53	49

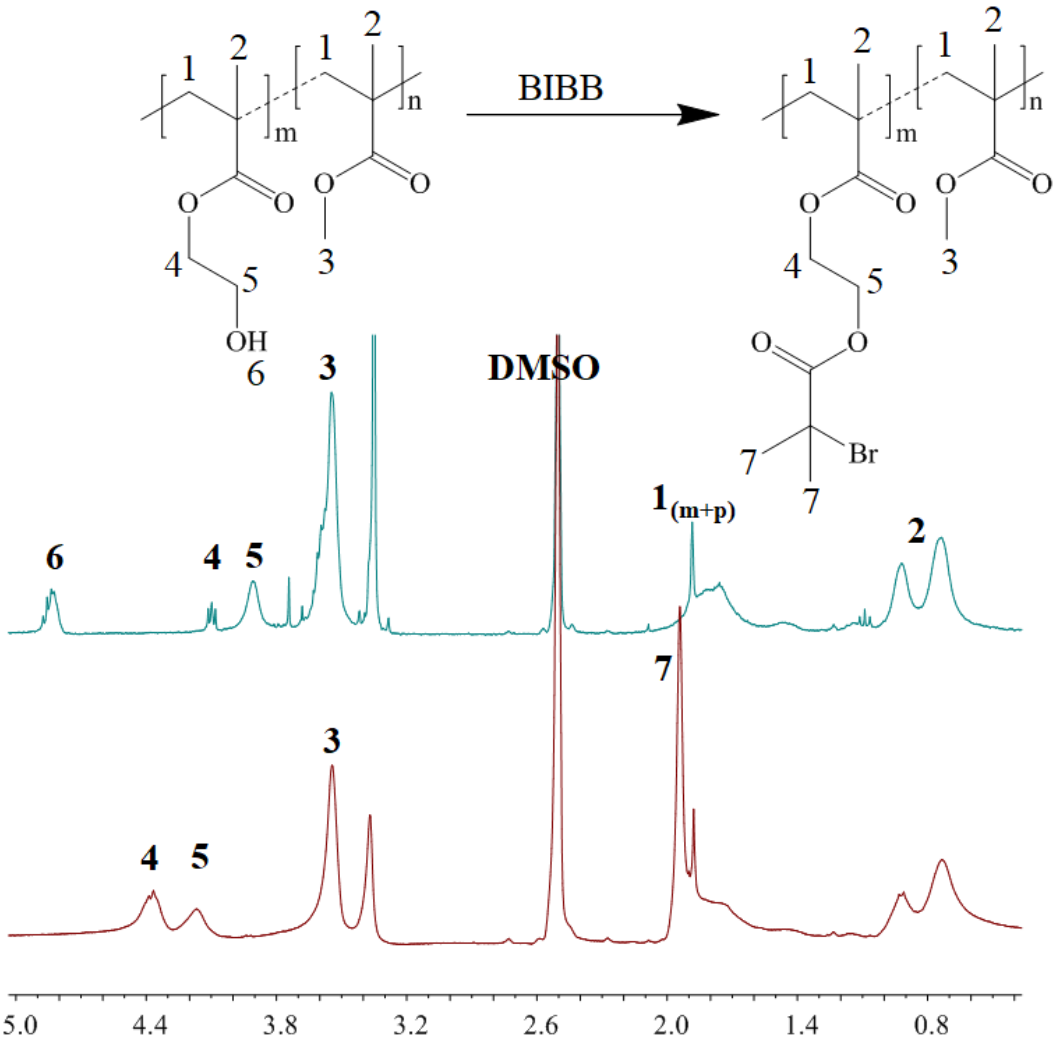

Figure S1. ^{1}H NMR spectra of a) precursor I, and b) multifunctional macroinitiator Ia**.**

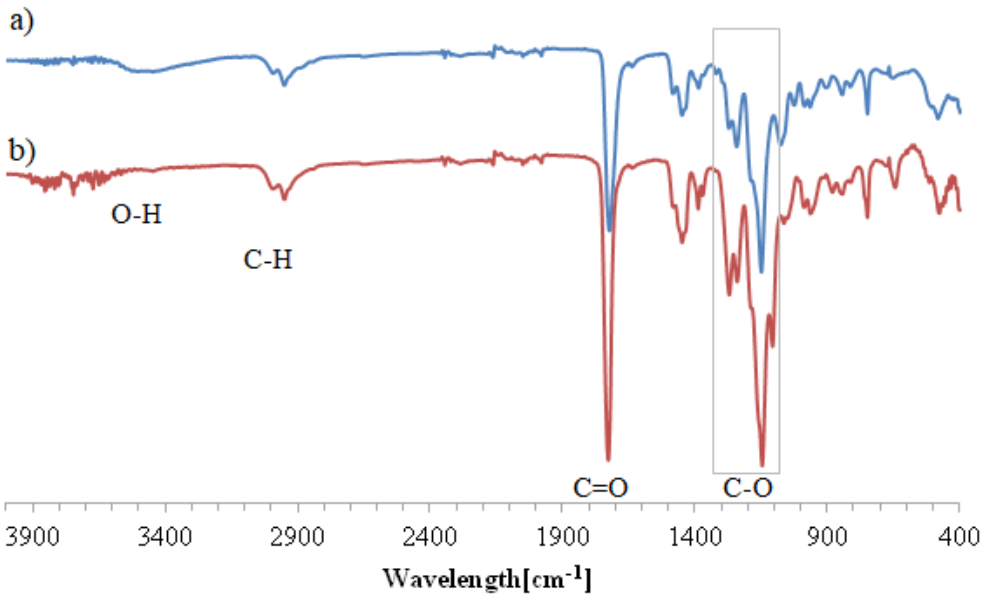

Figure S2. FT-IR spectra for (a) precursor **I**, and (b) multifunctional macroinitiator **Ia**.

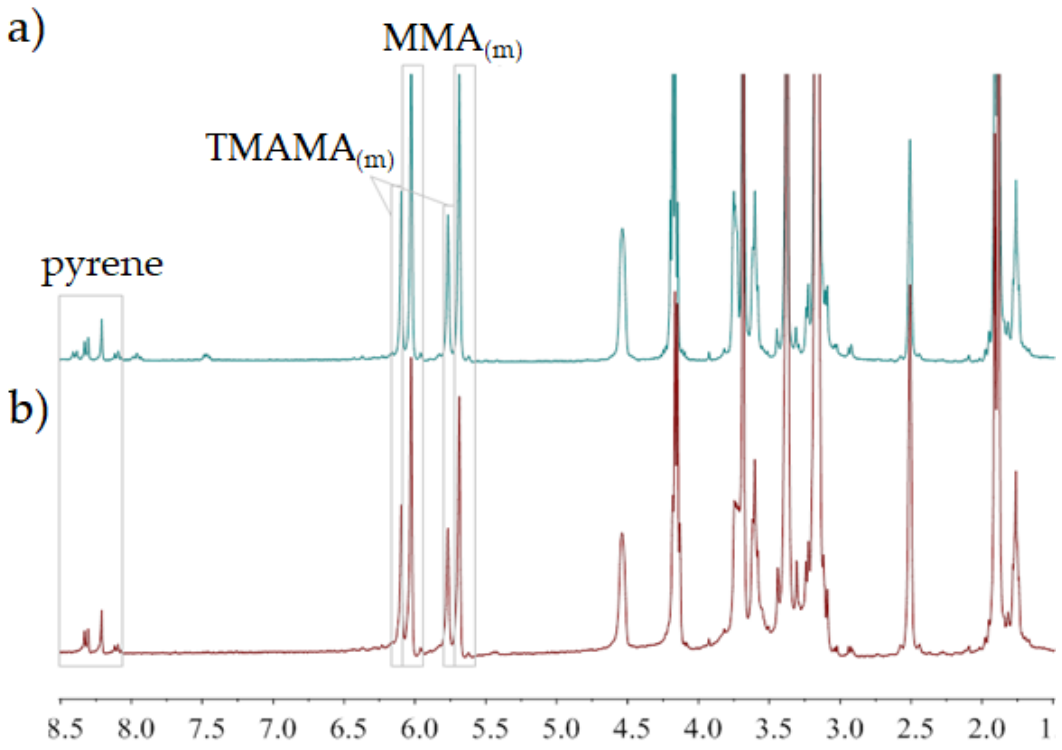

Figure S3. ^{1}H NMR spectra of a mixture a) before starting of reaction, and b) at the end of copolymerization resulting in grafted copolymer G2**.**

^{1}H NMR (DMSO-d$_6$, δ, ppm): 4.63-4.43 (2H, -C**H$_2$**-O-), 4.47-4.28 (2H, -C**H$_2$**-OOC-C-(CH$_3$)$_2$Br), 4.28-4.08 (2H, -COO-C**H$_2$**), 3.86-3.65 (2H, -C**H$_2$**-N$^+$), 3.65-3.47 (3H, -O-C**H$_3$**), 3.42-3.01 (9H, -N$^+$-(C**H$_3$**)$_3$, 1.98-1.82 (6H, -(C**H$_3$**)$_2$Br initiating moiety), 1.4-0.51 (3H, -C**H$_3$** backbone).

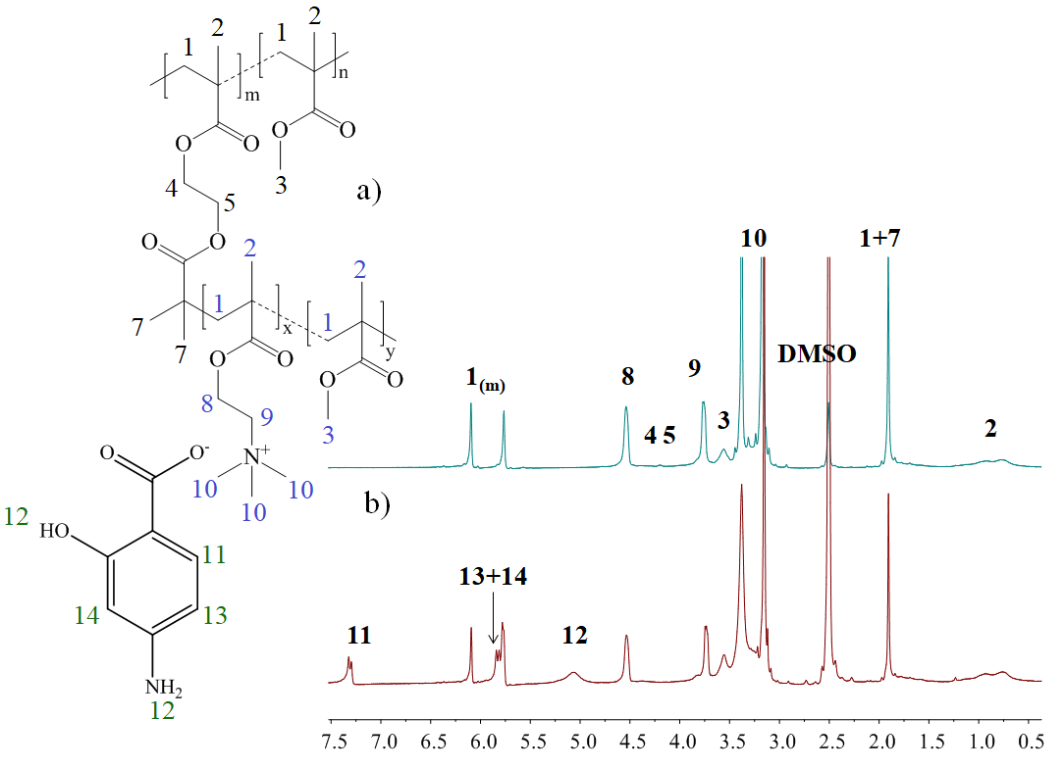

Figure S4. [1]H NMR spectra of grafted copolymers a) G2, and b) G2_PAS, where * **1**$_{(m)}$ is related to monomer residue.

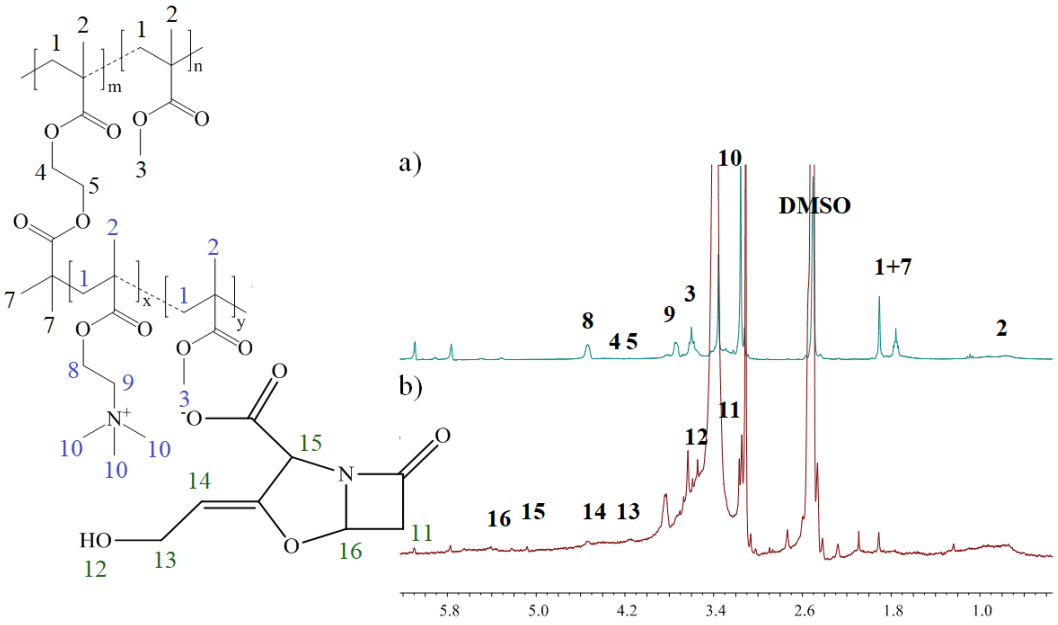

Figure S5. . [1]H NMR spectra of grafted copolymers a) G5, and b) G5_CLV, where * **1**$_{(m)}$ is related to monomer residue.

Table S2. Hydrodynamic diameters of nanoparticles determined with DLS[a].

	Cl$^-$			**PAS$^-$**			**CLV$^-$**		
	PDI	Size [nm]	Intensity [%]	PDI	Size [nm]	Intensity	PDI	Size [nm]	Intensity
G1	0.361	88 368 21	56 25 17	0.503	145 23	59 40	0.601	148 18	75 25
G2	0.427	124 21	60 40	0.114	261	100	0.365	21 357	80 20
G3	0.295	203	98	0.775	354	100	0.442	26 250	69 31
G4	0.454	18 125	64 32	0.264	24	89	0.397	25 240	83 11
G5	0.444	114	94	0.265	75	100	0.268	91	100
G6	0.293	105	99	0.291	127	100	0.253	86	100
G7	0.241	72	100	0.443	194 37	82 18	0.316	75	98
G8	0.349	95	98	0.459	206 40	54 46	0.163	48	98

[a]concentration of copolymer in water: 1mg/mL.

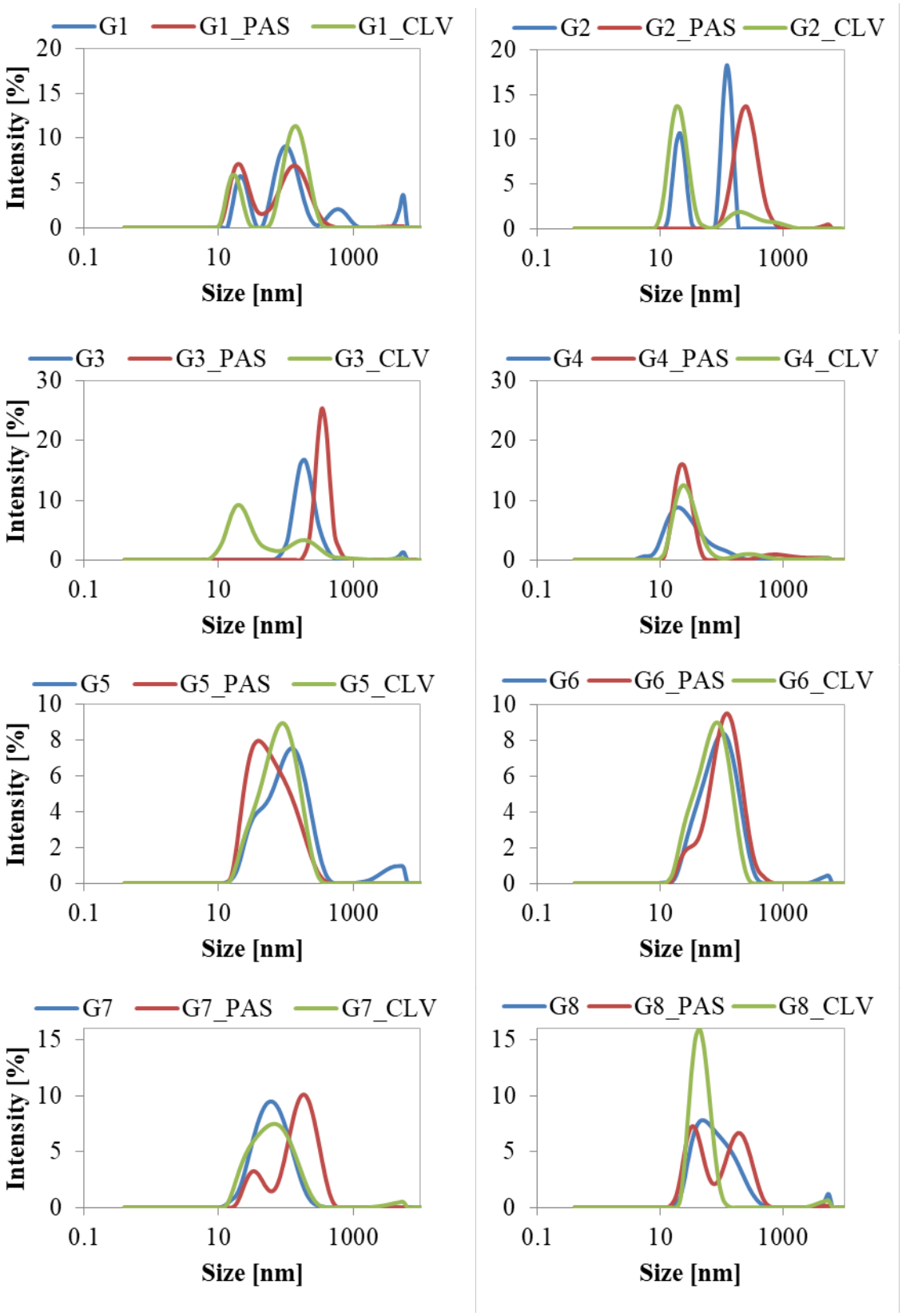

Figure S6. DLS histograms of particles formed by graft copolymers (1 mg/mL aq. solution).

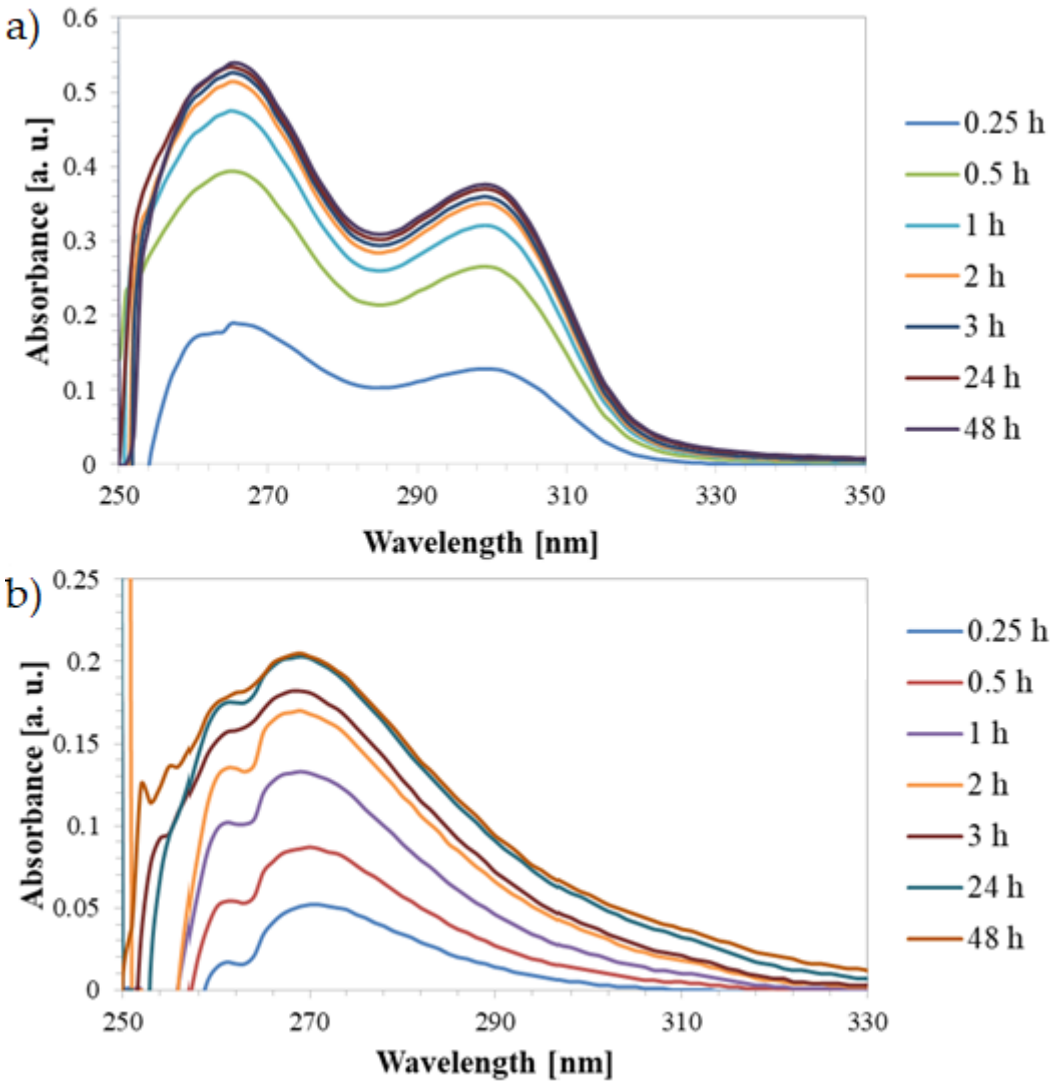

Figure S7. UV-Vis spectra of released drug for a) G2_PAS, and b) G2_CLV systems.