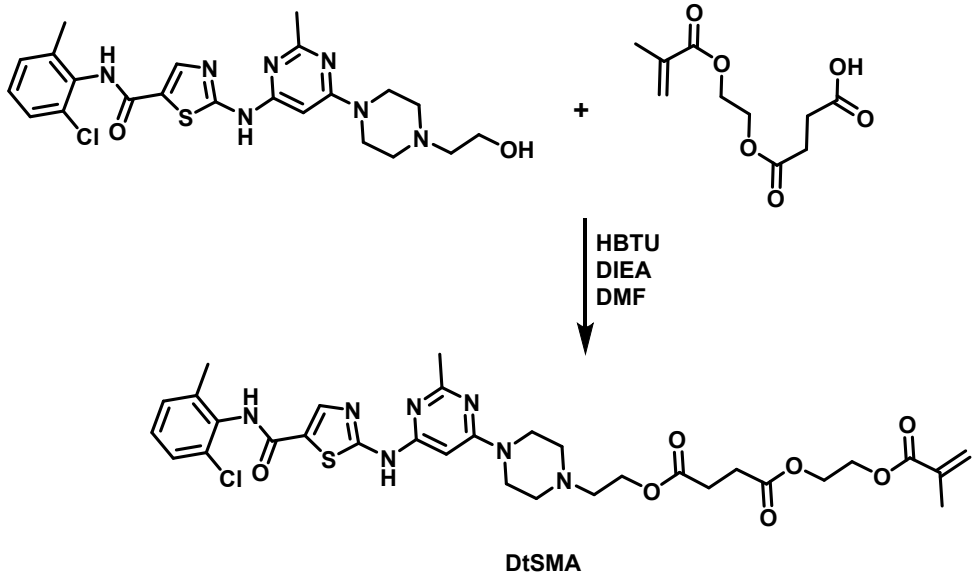
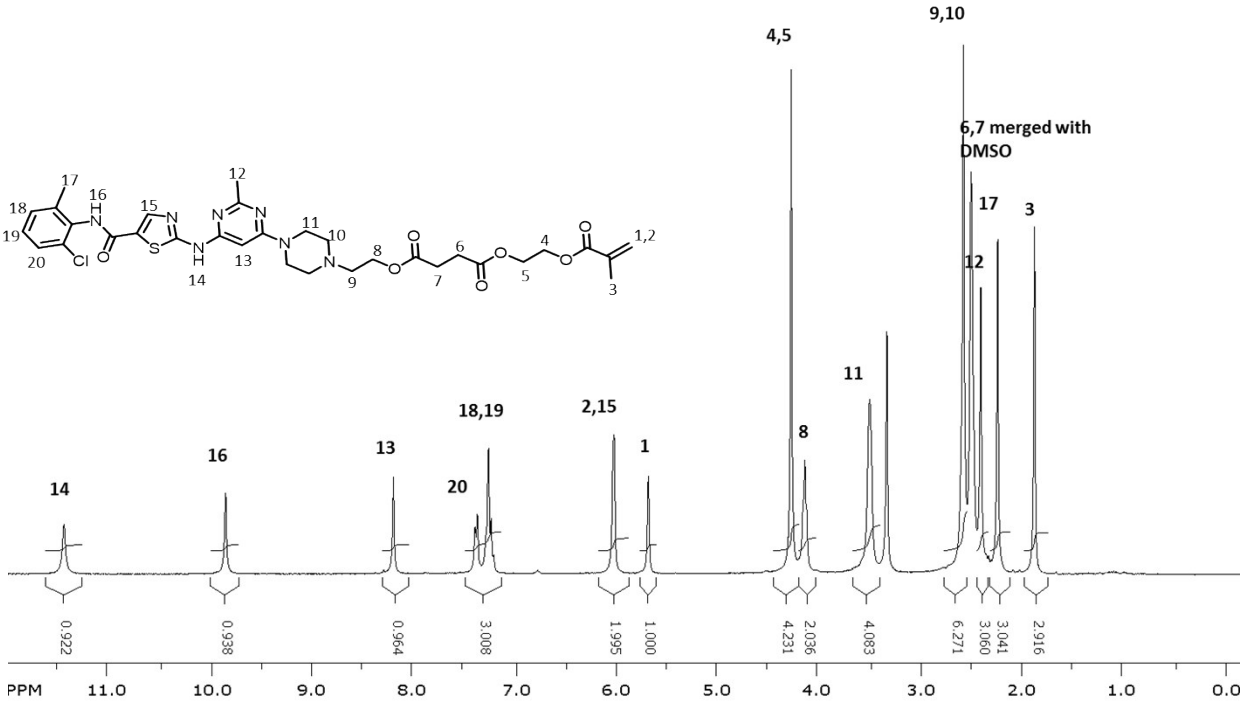
Supplementary Information



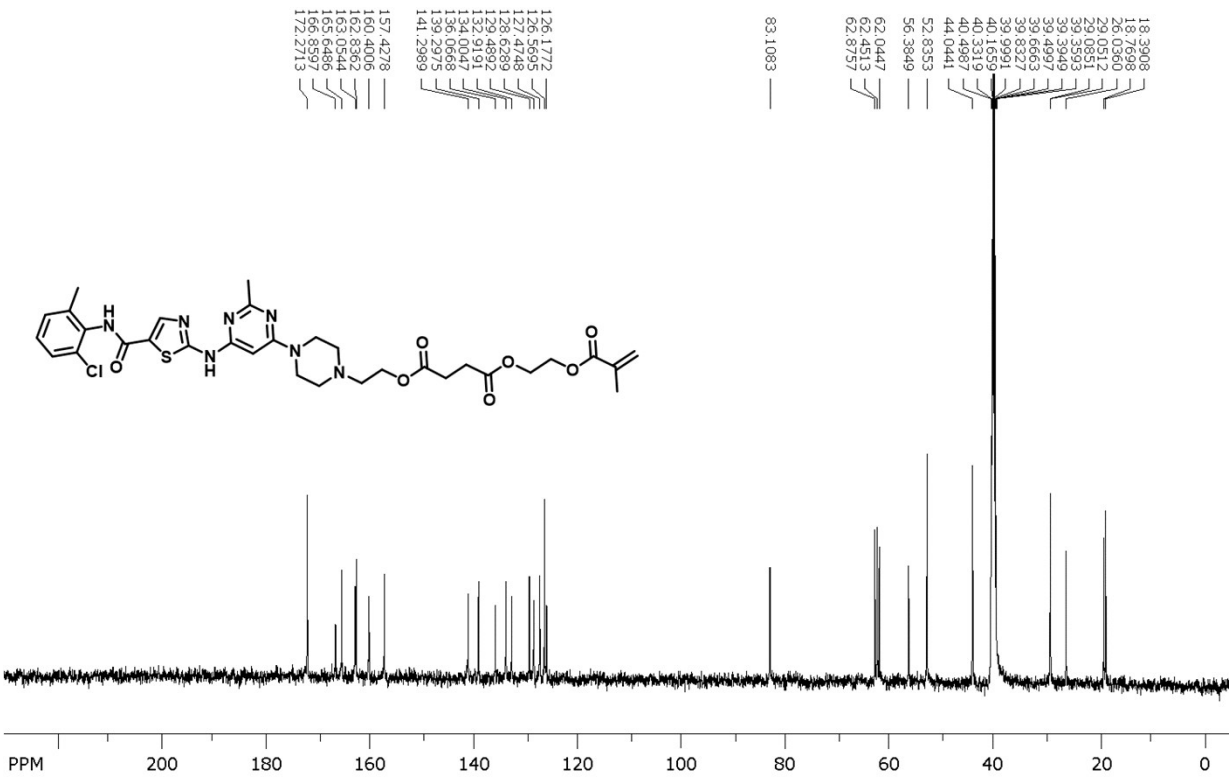
DtSMA

Synthesis of *N*-(2-Chloro-6-methylphenyl)-2-[[6-[4-(2-methacryloxyethylsuccinylethyl)-1-piperazinyl)]-2-methyl-4-pyrimidinyl]amino)]-1,3-thiazole-5-carboxamide (**Dt-SMA**). To a mixture of 2-(methacryloyloxyethyl) monosuccinate (SMA) 920 mg (4 mmol) and N,N,N',N'-tetramethyl-O-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU) 1.9 g (5 mmol) in 25 mL anhydrous DMF was added N,N-diisopropylethylamine 1.4 mL (8 mmol) at 0 ^{0}C. After 10 min. at 0 ^{0}C, the solution was stirred at room temperature for 20 min. *N*-(2-Chloro-6-methylphenyl)-2-[[6-[4-(2-hydroxyethyl)-1-piperazinyl)]-2-methyl-4-pyrimidinyl]amino)]-1,3-thiazole-5-carboxamide 976 mg (2 mmol) was then introduced as solid, and stirring was continued at room temperature for 6 h. The reaction mixture was poured into ice cold water and stirred for 20 min. The off-white solid obtained was filtered, washed with water and dried under high vacuum. The crude ester was dissolved in 15 mL of 15 % methanol in chloroform and purified by column chromatography using 10 % methanol in chloroform containing 0.3 % NH_4OH. Yield = 990 mg (70.7 %). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ 11.46 (s, 1H, **H14**), 9.87 (s, 1H, **H16**), 8.20 (s, 1H, **H13**), 7.38 (d, *J* = 6.2 Hz,1H, **H20**), 7.31-7.18 (m, 2H, **H18 & H19**), 6.08-5.97 (m, 2H, **H2 & H15**), 5.58 (s, 1H, **H1**), 4.27 (s, 4H, **H4 & H5**), 4.13 (t, *J* = 5.7 Hz, 2H, **H8**), 3.49 (s, 4H, **H11**), 2.63-2.52 (m, 6H, **H9 & H10**), 2.48 (m, 4H, **H6 & H7** merged with DMSO peak), 2.39 (s, 3H, **H12**), 2.22 (s, 3H, **H17**), 1.85 (s, 3H, **H3**); ^{13}C NMR (125 MHz,

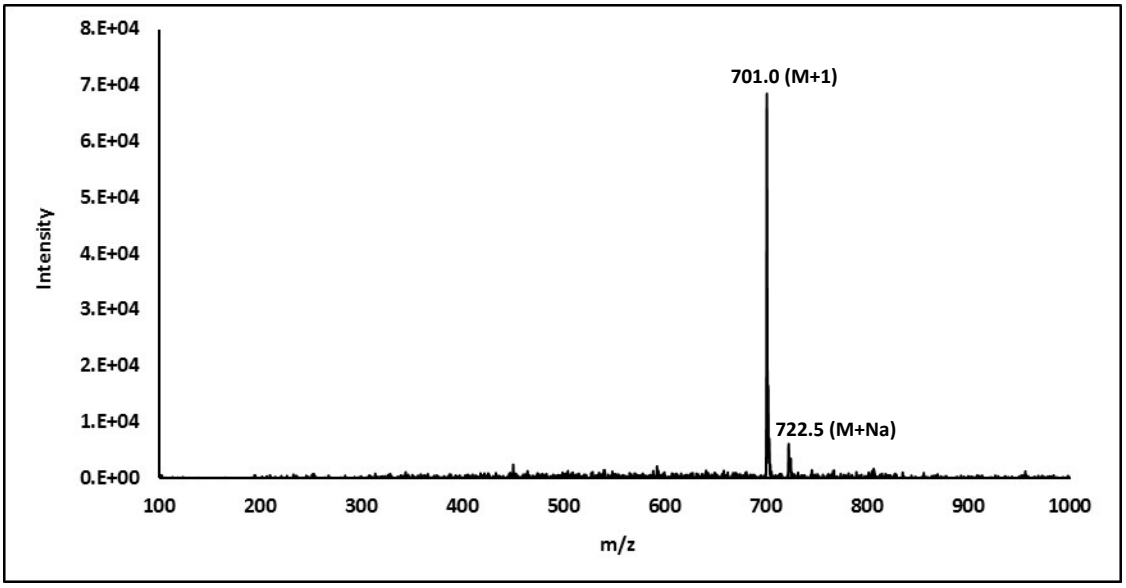
DMSO-d_6, ppm) δ 172.3, 166.9, 165.6, 163.1, 162.8, 160.4, 157.4, 141.3, 139.3, 136.1, 134.0, 132.9, 129.5, 128.6, 127.5, 126.6, 126.2, 83.1, 62.9, 62.5, 62.0, 56.4, 52.8, 44.0, 29.08, 29.05, 26.0, 18.8, 18.4; ESI-MS ($C_{32}H_{38}ClN_7O_7S$): *m/z* = 701.0 $[M+1]^+$ and 722.5 $[M+Na]^+$.



Supporting Information Fig 1. 1H NMR of Dt-SMA with peek assignments in D6 DMSO

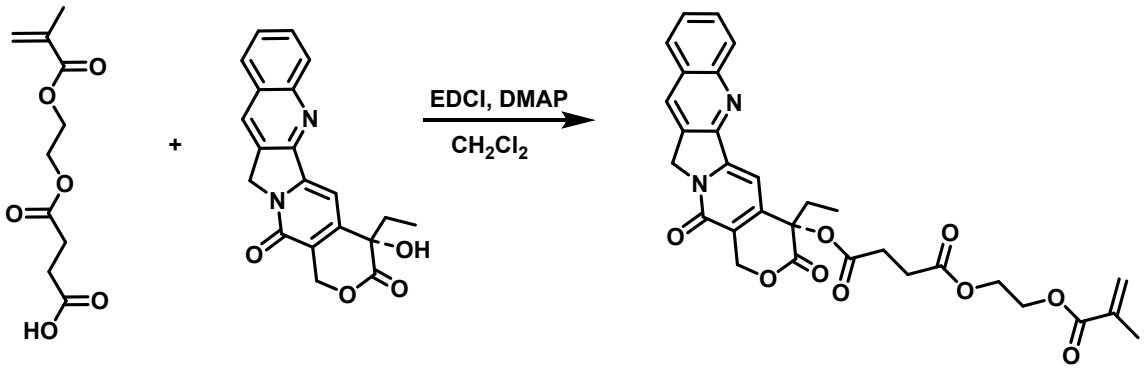


Supporting Information Fig 2. ^{13}C-NMR spectrum of Dt-SMA in DMSO-d_6

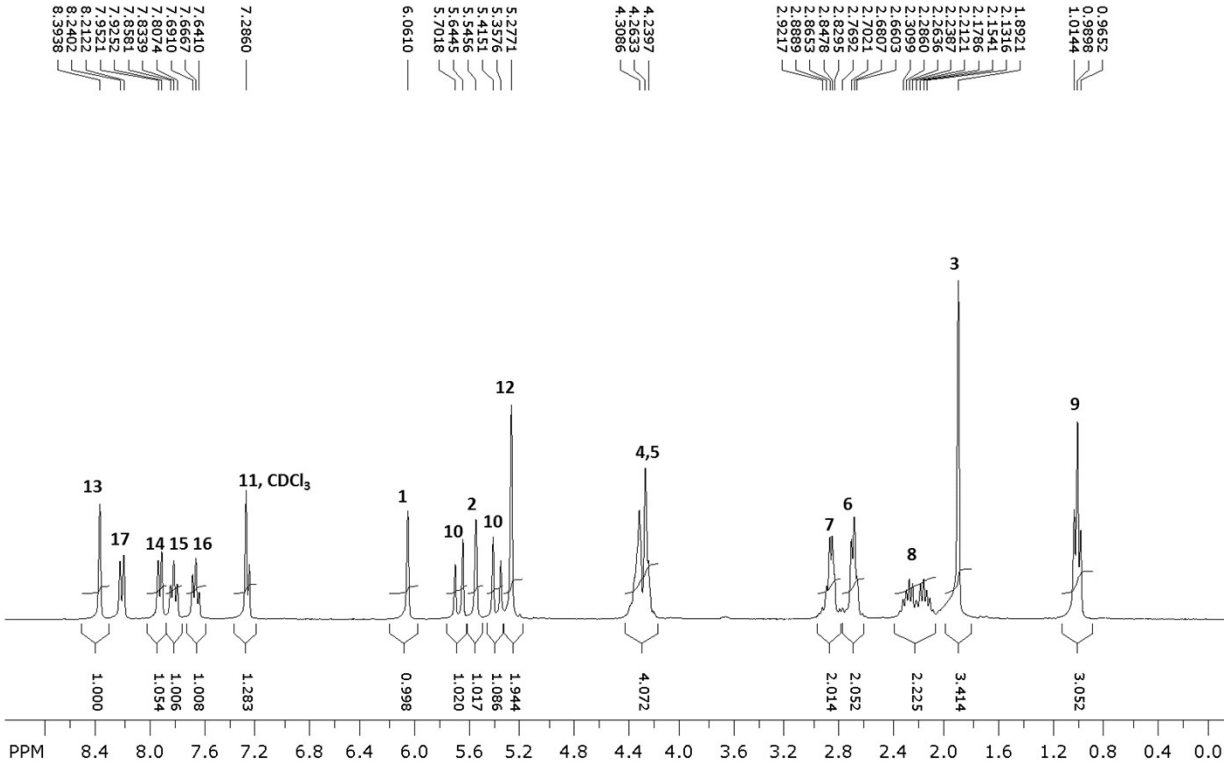


Supporting Information Fig 3. Electrospray ionization mass spectrum of Dt-SMA

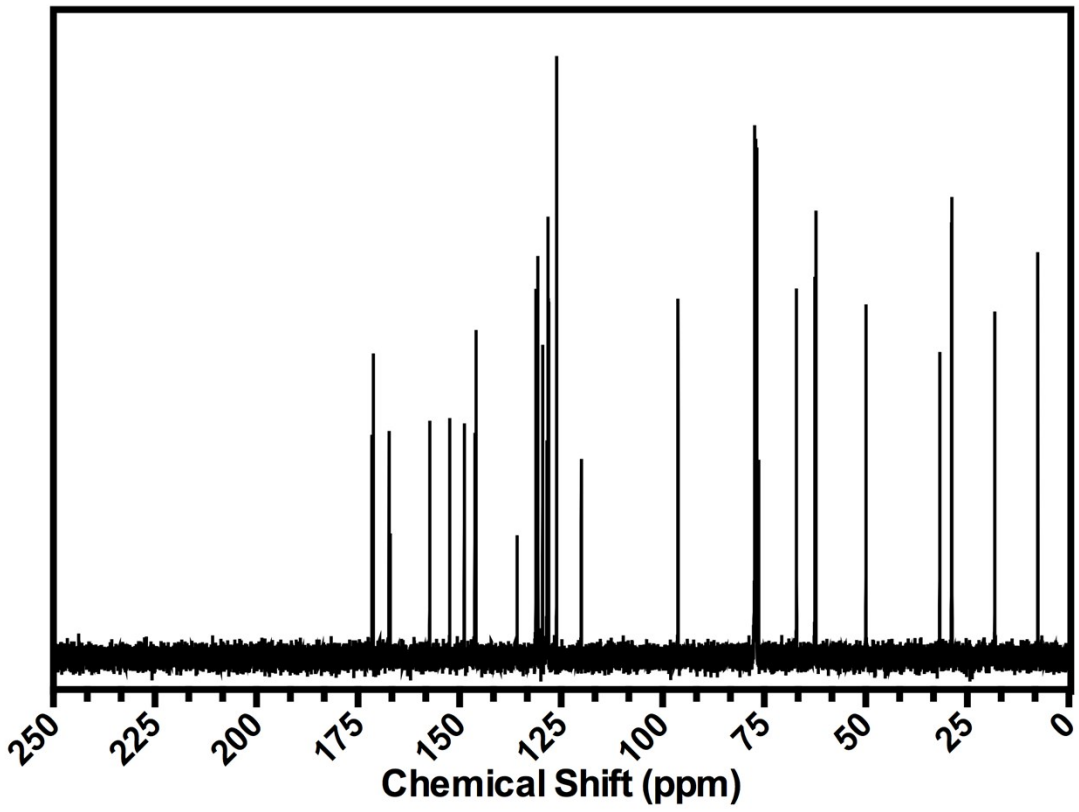
Synthetic procedure: Cam-SMA



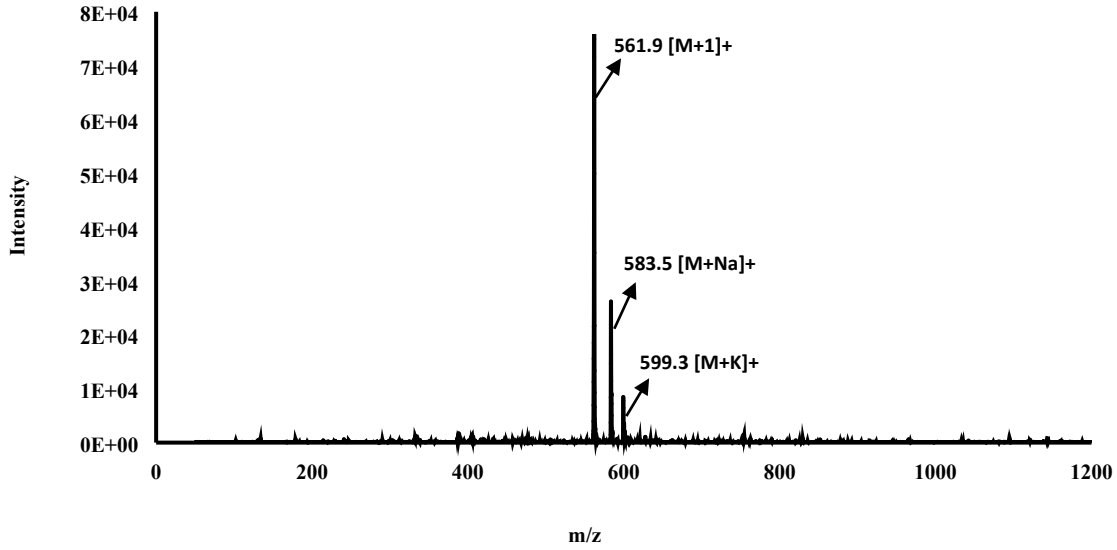
To a solution of mono-2-(methacryloyloxy)ethyl succinate (SMA) 460 mg (2 mmol), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodimide hydrochloride (EDCI.HCl) 767 mg (4 mmol) and N,N-dimethylpyridin-4-amine (DMAP) 122 mg (1 mmol) in 60 mL CH_2Cl_2 was added camptothecin 348 mg (1 mmol) as solid. After stirring at RT for 6 h, the reaction mixture was washed with water (2 X 30mL) and the organic phase was dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the resulting crude product was purified by silica gel column chromatography using 7 % methanol in chloroform. Yield = 544 mg (97.0 %). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.39 (s, 1H, **H13**), 8.23 (d, *J* = 8.4 Hz, 1H, **H17**), 7.94 (d, *J* = 8.1 Hz, 1H, **H14**), 7.83 (t, *J* = 7.6 Hz, 1H, **H15**), 7.67 (t, *J* = 7.5 Hz, 1H, **H16**), 7.29 (s, 1H, **H11**), 6.06 (s, 1H, **H1**), 5.67 (d, *J* = 17.2 Hz,1H, **H10**), 5.55 (s, 1H, **H2**), 5.39 (d, *J* = 17.2 Hz,1H, **H10**), 5.28 (s, 1H, **H12**), 4.20 – 4.40 (m, 4H, **H4 & H5**), 2.85 (m, 2H, **H7**), 2.70 (m, 2H, **H6**), 2.06-2.39 (m, 2H, **H8**), 1.89 (s, 3H, **H3**), 0.99 (t, *J* = 7.4 Hz, 3H, **H9**); ^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 171.5, 171.2, 167.3, 167.0, 157.3, 152.3, 148.8, 146.2, 145.9, 135.8, 131.2, 130.7, 129.5, 128.5, 128.2, 128.1, 128.0, 126.0, 120, 96.2, 76.3, 67.0, 62.5, 62.2, 49.9, 31.8, 28.9, 28.7, 18.2, 7.60. ESI-MS ($C_{30}H_{28}N_2O_9$): *m/z* = 561.9 $[M+1]^+$, 583.5 $[M+Na]^+$ and 599.3 $[M+K]^+$.



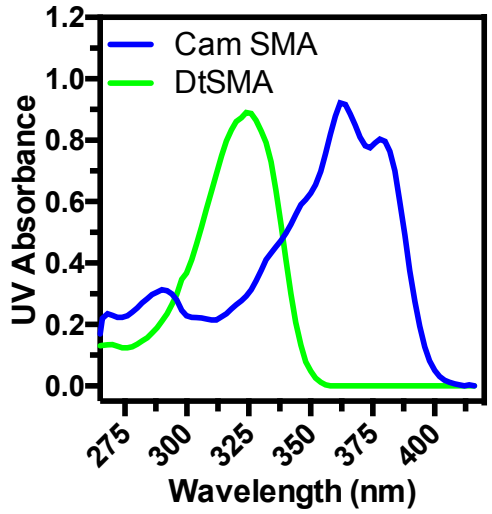
Supporting Information Fig 4. 1H-NMR spectrum of Cam-SMA in $CDCl_3$



Supporting Information Fig 5. ^{13}C NMR spectrum of Cam-SMA in $CDCl_3$



Supporting Information Fig 6. Electrospray ionization mass spectrum of Cam-SMA



Supporting Information Fig 7. UV-VS absorbance spectrums for Cam-SMA and Dt-SMA in DMF

Table 1. Molecular weight, composition, and molar mass dispersity (Đ) values for the RAFT copolymerization of DMAEMA and tBMA and subsequent block copolymerization of Dasa SMA.

Mn Block 1[a] (MAA/DMAEMA)	Đ[a] Block 1	% MAA[b] Block 1 (MA/DMAEMA)	% DMAEMA[b] Block 1 (MA/DMAEMA)	DP block 1[a,b] (MA/DMAEMA)	M_n[b] Block 2 (DASA SMA)	Đ[a] Block 2 (DASA SMA)	DP[b] Block 2 (DASA SMA)
5100	1.06	51	49	40	13800	1.19	12

a As determined by a combination size exclusion chromatography (Tosoh SEC TSK-GEL α-3000 and α-4000 columns Tosoh Bioscience, Montgomeryville, PA) connected in series to an Agilent 1200 Series Liquid Chromatography System (Santa Clara, CA) and Wyatt Technology miniDAWN TREOS, 3 angle MALS light scattering instrument and Optilab TrEX, refractive index detector (Santa Barbara, CA) and ^{1}H NMR. HPLC-grade DMF containing 0.1 wt.% LiBr at 60 ^{o}C was used as the mobile phase at a flow rate of 1 mL/min.

b As determined by ^{1}H NMR in DMSO D_6 by comparison of the $N(CH_3)_2$ resonances at 2.85 ppm to the Dasa SMA aromatic resonance at 8.25 ppm.