Electronic Supporting Information

Pre- and post-functionalization of thermoresponsive cationic microgels with ionic liquid moieties carrying different counterions

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Content

Table S1 $VIM^+C_nH_{2n+1}[X]^-$ comonomer synthesis feed amounts and yields.

$VIM^+C_nH_{2n+1}[X]^-$ comonomer	***V*(*N*-vinylimidazole) [mL]**	***n*(VIM) [mmol]**	***V*($C_nH_{2n+1}X$) [mL]**	***n*($C_nH_{2n+1}X$) [mmol]**	**yield [%]**
$VIM^+C_1H_3[I]^-$	1.5	16.6	3.1	49.8	92
$VIM^+C_{12}H_{25}[Br]^-$	3.00	33.2	7.94	33.2	93
$VIM^+C_{16}H_{33}[Br]^-$			10.15		76

1-vinyl-3-methylimidazolium iodide

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.43 (s, 1H), 8.18 (s, 1H), 7.85 (s, 1H), 7.32 (dd, J = 15.6, 8.7 Hz, 1H), 5.95 (dd, J = 15.6, 2.4 Hz, 1H), 5.43 (dd, J = 8.7, 2.3 Hz, 1H), 3.90 (s, 3H) ppm.
^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ = 135.8, 128.8, 124.4, 118.9, 108.5, 39.5, 36.1 ppm.

1-vinyl-3-dodecanylimidazolium bromide

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.70 (s, 1H), 8.27 (t, J = 1.7 Hz, 1H), 7.99 (t, J = 1.5 Hz, 1H), 7.34 (dd, J = 15.7, 8.8 Hz, 1H), 6.00 (dd, J = 15.6, 2.3 Hz, 1H), 5.41 (dd, J = 8.7, 2.3 Hz, 1H), 4.21 (t, J = 7.3 Hz, 2H), 1.91 – 1.73 (m, 2H), 1.24 (s, 18H), 0.83 (t, 3H) ppm.
^{13}C {^{1}H} NMR (101 MHz, D_2O) δ = 128.18, 123.03, 119.67, 109.56, 49.94, 31.90, 29.88, 29.82, 29.78, 29.77, 29.60, 29.42, 29.16, 26.14, 22.56, 13.79 ppm.

1-vinyl-3-hexadecanylimidazolium bromide

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.66 (s, 1H), 8.26 (t, J = 1.7 Hz, 1H), 7.98 (t, J = 1.6 Hz, 1H), 7.33 (dd, J = 15.7, 8.8 Hz, 1H), 5.99 (dd, J = 15.6, 2.3 Hz, 1H), 5.41 (dd, J = 8.7, 2.3 Hz, 1H), 4.21 (t, J = 7.3 Hz, 2H), 1.90 – 1.71 (m, 2H), 1.22 (s, 26H), 0.83 (t, 3H) ppm.

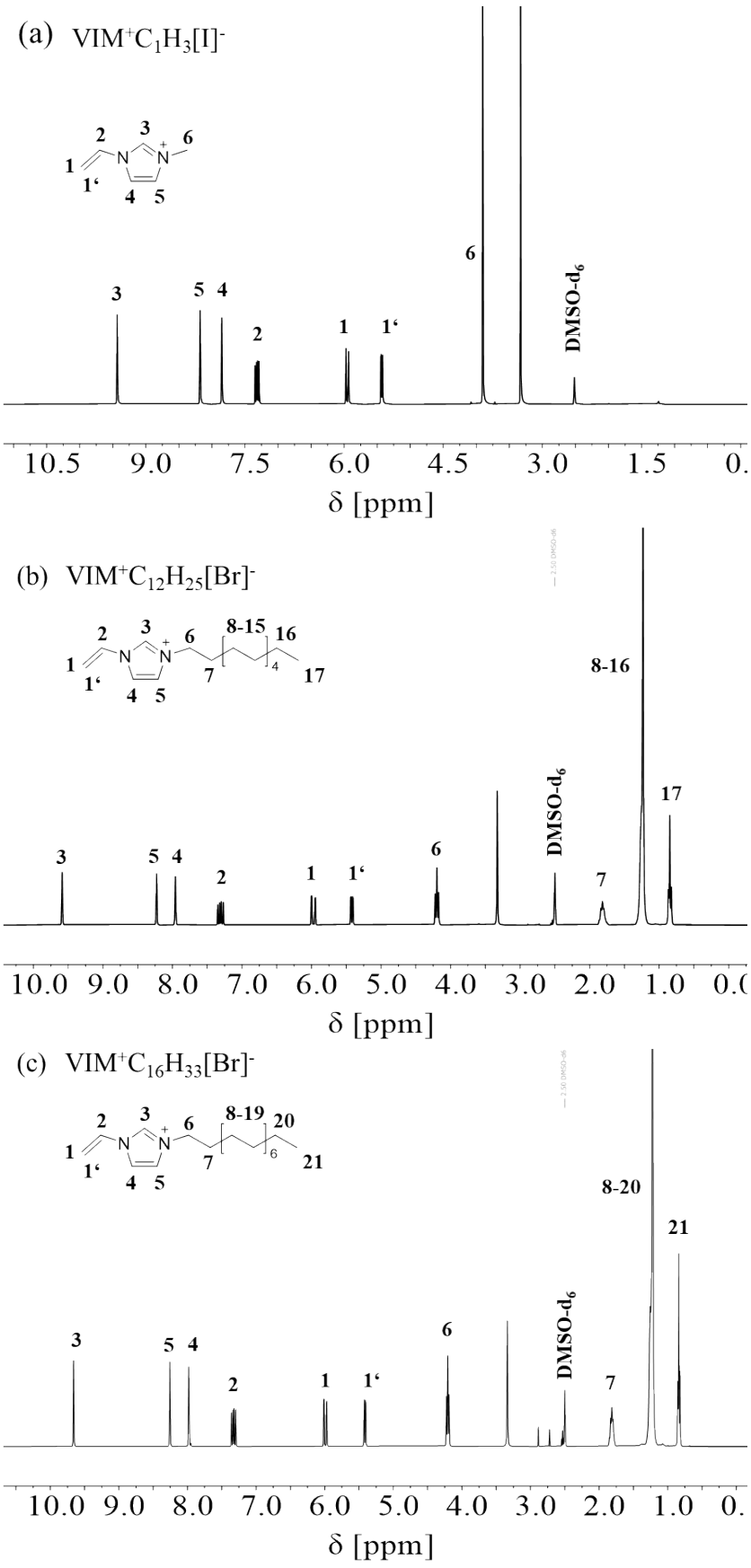

Fig. S1 ^{1}H NMR spectra of alkylated vinylimidazolium comonomers with halides as counterions ($VIM^{+}C_nH_{2n+1}[X]^{-}$) measured in DMSO-$d_6$. (a) n =1, (b) n = 12, and (c) n = 16.

Table S2 Comonomer and salt amounts for the pre-functionalization of $VIM^+C_nH_{2n+1}$ (n = 1, 12, 16) monomers via anion exchange.

$VIM^+C_nH_{2n+1}[A]^-$ comonomer	***m*($VIM^+C_nH_{2n+1}[X]^-$) [mg]**	***m*(NaMeS) [mg]**	***m*($NaBF_4$) [mg]**	***m*($LiNTf_2$) [mg]**	**yield [%]**
$VIM^+C_1H_3[MeS]^-$	590.1	442.8	-	-	86
$VIM^+C_1H_3[BF_4]^-$	590.1	-	411.7	-	82
$VIM^+C_1H_3[NTf_2]^-$	590.1	-	-	1077	61
$VIM^+C_{12}H_{25}[MeS]^-$	171.7	88.6	-	-	83
$VIM^+C_{12}H_{25}[BF_4]^-$	343.4	-	164.6	-	81
$VIM^+C_{12}H_{25}[NTf_2]^-$	171.7	-	-	215.3	70
$VIM^+C_{16}H_{33}[MeS]^-$	199.7	88.6	-	-	81
$VIM^+C_{16}H_{33}[BF_4]^-$	499.3	-	205.8	-	73
$VIM^+C_{16}H_{33}[NTf_2]^-$	199.7	-	-	215.3	75

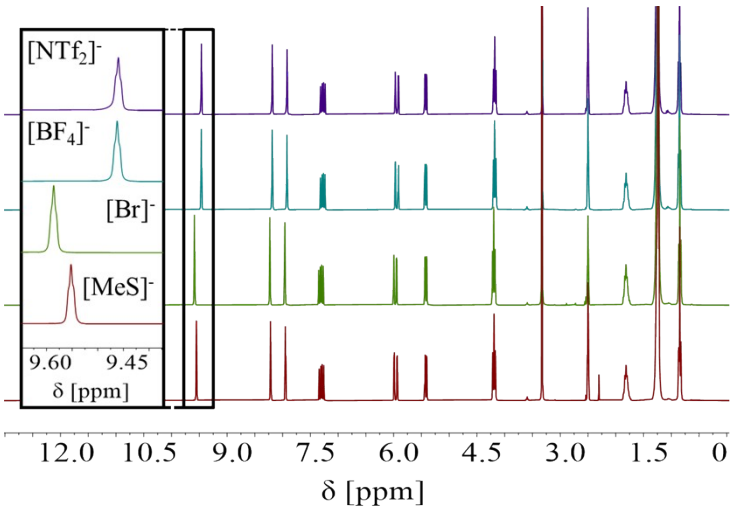

Figure S2 ^{1}H NMR spectra of the VIM^{+}C$_{12}$H$_{25}$[A]$^{-}$ monomers functionalized with different anions. Magnification shows the shift of the most acidic proton in the vinylimidazolium ring.

1-vinyl-3-methylimidazolium methanesulfonate (VIM^{+}C$_1$H$_3$[MeS]$^{-}$)
^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.40 (s, 1H), 8.17 (t, J = 1.8 Hz, 1H), 7.84 (t, J = 1.8 Hz, 1H), 7.31 (dd, J = 15.6, 8.7 Hz, 1H), 5.94 (dd, J = 15.6, 2.4 Hz, 1H), 5.42 (dd, J = 8.7, 2.4 Hz, 1H), 3.89 (s, 3H) ppm.
^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ = 128.8, 124.5, 118.7, 116.9, 108.6, 52.0, 36.1 ppm.

1-vinyl-3-methylimidazolium tetrafluoroborate (VIM^{+}C$_1$H$_3$[BF$_4$]$^{-}$)
^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.40 (s, 1H), 8.16 (t, J = 1.8 Hz, 1H), 7.83 (t, J = 1.8 Hz, 1H), 7.30 (dd, J = 15.6, 8.7 Hz, 1H), 5.94 (dd, J = 15.6, 2.4 Hz, 1H), 5.42 (dd, J = 8.7, 2.4 Hz, 1H), 3.88 (s, 3H) ppm.
^{19}F {^{1}H} NMR (376 MHz, DMSO-d_6) δ = -148.21 – -148.27 (d, 4F) ppm.

1-vinyl-3-methylimidazolium bistriflimide (VIM^{+}C$_1$H$_3$[NTf$_2$]$^{-}$)
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.39 (s, 1H), 8.15 (t, J = 1.8 Hz, 1H), 7.81 (t, J = 1.8 Hz, 1H), 7.29 (dd, J = 15.6, 8.7 Hz, 1H), 5.93 (dd, J = 15.6, 2.4 Hz, 1H), 5.41 (dd, J = 8.7, 2.4 Hz, 1H), 3.89 (s, 3H) ppm.
^{19}F {^{1}H} NMR (376 MHz, DMSO-d$_6$): δ = -78.78 (s, 6F) ppm.

1-vinyl-3-dodecanylimidazolium methanesulfonate (VIM^{+}C$_{12}$H$_{25}$[MeS]$^{-}$)
^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.55 (t, J = 1.7 Hz, 1H), 8.22 (t, J = 1.9 Hz, 1H), 7.95 (t, J = 1.9 Hz, 1H), 7.30 (dd, J = 15.7, 8.8 Hz, 1H), 5.96 (dd, J = 15.6, 2.3 Hz, 1H), 5.42 (dd, J = 8.8, 2.4 Hz, 1H), 4.19 (t, J = 7.3 Hz, 2H), 1.90 – 1.71 (m, 2H), 1.25 (s, 18H), 0.84 (t, 3H) ppm.

1-vinyl-3-dodecanylimidazolium tetrafluoroborate (VIM^{+}C$_{12}$H$_{25}$[BF$_4$]$^{-}$)
^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.46 (t, J = 1.7 Hz, 1H), 8.19 (t, J = 1.9 Hz, 1H), 7.92 (t, J = 1.9 Hz, 1H), 7.28 (dd, J = 15.7, 8.8 Hz, 1H), 5.94 (dd, J = 15.6, 2.4 Hz, 1H), 5.42 (dd, J = 8.8, 2.4 Hz, 1H), 4.18 (t, J = 7.3 Hz, 2H), 1.89 – 1.71 (m, 2H), 1.25 (s, 18H), 0.84 (t, 3H) ppm.

^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ = -150.74 – -149.79 (d, 4F) ppm.

1-vinyl-3-dodecanylimidazolium bistriflimide ($VIM^+C_{12}H_{25}[NTf_2]^-$)
^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.46 (t, J = 1.7 Hz, 1H), 8.18 (t, J = 1.9 Hz, 1H), 7.92 (t, J = 1.9 Hz, 1H), 7.28 (dd, J = 15.6, 8.7 Hz, 1H), 5.94 (dd, J = 15.6, 2.3 Hz, 1H), 5.42 (dd, J = 8.8, 2.4 Hz, 1H), 4.18 (t, J = 7.2 Hz, 2H), 1.90 – 1.72 (m, 2H), 1.25 (s, 19H), 0.86 (t, 3H) ppm.
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$): δ = -78.98 (s, 6F) ppm.

1-vinyl-3-hexadecanylimidazolium methanesulfonate ($VIM^+C_{16}H_{33}[MeS]^-$)
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.55 (t, J = 1.7 Hz, 1H), 8.22 (t, J = 2.0 Hz, 1H), 7.95 (d, J = 2.0 Hz, 1H), 7.30 (dd, J = 15.7, 8.8 Hz, 1H), 5.96 (dd, J = 15.6, 2.4 Hz, 1H), 5.42 (dd, J = 8.8, 2.3 Hz, 1H), 4.19 (t, J = 7.3 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.23 (s, 26H), 0.84 (t, 3H) ppm.

1-vinyl-3- hexadecanylimidazolium tetrafluoroborate ($VIM^+C_{16}H_{33}[BF_4]^-$)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.30 (s, 1H), 7.68 (s, 1H), 7.43 (s, 1H), 7.18 (dd, J = 15.6, 8.7 Hz, 1H), 5.83 (dd, J = 15.6, 3.0 Hz, 1H), 5.37 (dd, J = 8.7, 3.0 Hz, 1H), 4.25 (t, J = 7.5 Hz, 2H), 1.98 – 1.83 (m, 2H), 1.49 – 1.18 (m, 26H), 0.87 (t, J = 6.8 Hz, 3H) ppm.
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ = -150.80 – -150.86 (d, 4F) ppm.

1-vinyl-3- hexadecanylimidazolium bistriflimide ($VIM^+C_{16}H_{33}[NTf_2]^-$)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.07 (s, 1H), 7.62 (s, 1H), 7.41 (s, 1H), 7.15 (dd, J = 15.6, 8.7 Hz, 1H), 5.78 (dd, J = 15.6, 3.1 Hz, 1H), 5.44 (dd, J = 8.6, 3.1 Hz, 1H), 4.23 (t, J = 7.5 Hz, 2H), 1.96 – 1.82 (m, 2H), 1.24 (s, 26H), 0.87 (t, J = 6.8 Hz, 3H) ppm.
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$): δ = -78.96 (s, 6F) ppm.

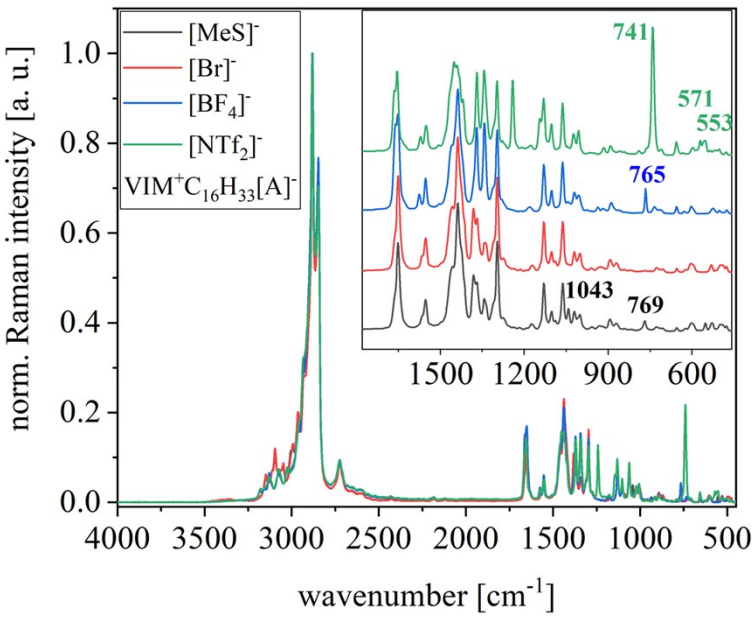

Fig. S3 Raman spectra overlay of $VIM^+C_{16}H_{33}[A]^-$ monomers functionalized with different anions. Insight shows characteristic signals of the applied anions. $[MeS]^-$ ion shows signals at

symmetric stretching at $\nu_s = 1043$ (S=O), $\nu = 772$ cm^{-1}, and $\delta_s = 553$ cm^{-1} (SO_2). Tetrafluoroborate shows FBF symmetric stretching at $\nu_s = 765$ cm^{-1}, and bending at $\delta_s = 522$ cm^{-1}.[1] The bistriflimide anion is present by CF_3 symmetric stretching at $\nu_s = 1243$ cm^{-1}, and $\nu_s = 741$ cm^{-1} (SNS), as well as asymmetric deformation of CF_3 at $\delta_{as} = 571$ cm^{-1}, and symmetric deformation $\delta_s = 553$ cm^{-1} (SO_2).[2]

Table S3 Synthesis feed amounts for poly(VCL-*co*-$VIM^+C_nH_{2n+1}[A]^-$) microgel synthesis (n = 1, 12, 16; x = 10 mol%) via pre-functionalization.

microgel sample	*m*(VCL) [mg]	*m*($VIM^+C_nH_{2n+1}[A]^-$) [mg]	*m*(BIS) [mg]	*m*(AMPA) [mg]	yield [%]
$VIM^+C_1H_3[I]^-$*	660.1	124.5	16.2	8.4	80
$VIM^+C_{12}H_{25}[Br]^-$*	660.2	180.9	16.2	8.6	89
$VIM^+C_{16}H_{33}[Br]^-$*	660.2	210.5	16.	8.6	87
$VIM^+C_1H_3[MeS]^-$*	660.2	107.6	16.3	8.6	73
$VIM^+C_{12}H_{25}[MeS]^-$ **	330.1	94.5	8.1	4.3	83
$VIM^+C_{16}H_{33}[MeS]^-$ **	330.7	109.5	8.1	4.3	74
$VIM^+C_1H_3[BF_4]^-$*	660.2	103.3	16.3	8.6	42
$VIM^+C_{12}H_{25}[BF_4]^-$ **	330.7	92.5	8.1	4.3	53
$VIM^+C_{16}H_{33}[BF_4]^-$ **	330.1	107.1	8.1	4.3	72
$VIM^+C_1H_3[NTf_2]^-$*	660.2	205.2	16.5	8.6	n.d.
$VIM^+C_{12}H_{25}[NTf_2]^-$ **	329.9	143.1	8.1	4.3	n.d.
$VIM^+C_{16}H_{33}[NTf_2]^-$	330.1	158.3	8.1	4.3	n.d.

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* Synthesis in V = 50 mL (100 mol% monomer ≡ 5.27 mmol)
**Synthesis in V = 25 mL (100 mol% monomer ≡ 2.64 mmol)

Table S4 Salt $M^+[A]^-$ amounts for post-modification of poly(VCL-*co*-$VIM^+C_nH_{2n+1}[I]^-$) microgels (n = 1, 12, 16) via anion exchange.

microgel sample	*m*(microgel) [mg]	*n*($M^+[A]^-$) [mmol]	*m*(NaMeS) [mg]	*m*($NaBF_4$) [mg]	*m*($LiNTf_2$) [mg]
VIM^+C_1-10 $[A]^-$	73	0.074	8.7	8.1	21.3
VIM^+C_{12}-10 $[A]^-$	100	0.06	7.3	6.7	17.7
VIM^+C_{16}-10 $[A]^-$			7.0	6.5	16.9

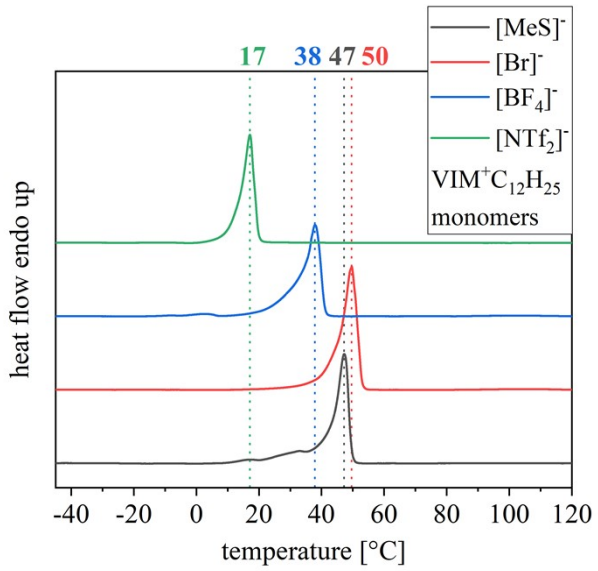

Figure S4 Stacked DSC thermogram of VIM+C12H25[A]- before (Br-) and after anion exchange with bistriflimide (NTf2-), tetrafluoroborate (BF4-), and methanesulfonate (MeS-). Change in melting temperature is visible by the reported endothermic peaks.

Table S5 Melting temperatures T_m and corresponding onsets determined by DSC of functional $VIM^+C_nH_{2n+1}[A]^-$ ionic liquid monomers.

counterion	$VIM^+C_1H_3[A]^-$		$VIM^+C_{12}H_{25}[A]^-$		$VIM^+C_{16}H_{33}[A]^-$	
	T_m [°C]	Onset [°C]	T_m [°C]	Onset [°C]	T_m [°C]	Onset [°C]

$[X]^-$	69.9	67.6	49.62	44.71	69.78	66.32
$[MeS]^-$	60.6	45.9	47.18	42.75	64.81	58.26
$[BF_4]^-$	56.8	46.7	37.89	33.22	60.54	57.36
$[NTf_2]^-$	32.8	30.2	17.06[§]	12.55	44.04	41.90

[§] In line with the T_m reported for the non-polymerizable analogue.[3]

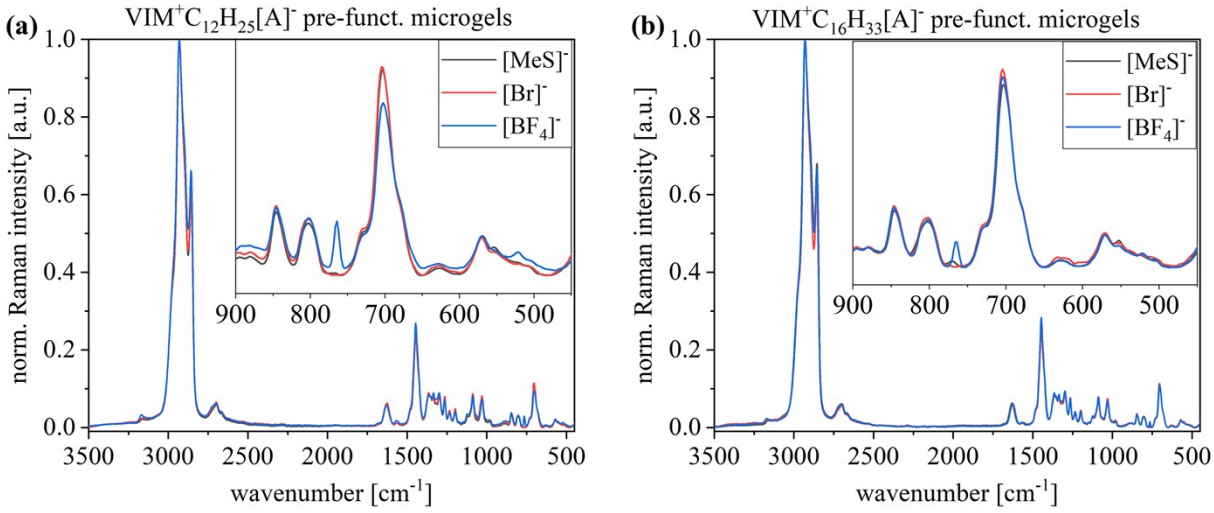

Fig. S5 Raman spectra of poly(VCL-*co*-VIM$^+$C$_n$H$_{2n+1}$[A]$^-$) microgels from pre-functionalization with bromide, methanesulfonate, and tetrafluoroborate. Insight shows characteristic signals of the anions for (a) n = 12, and (b) n = 16.

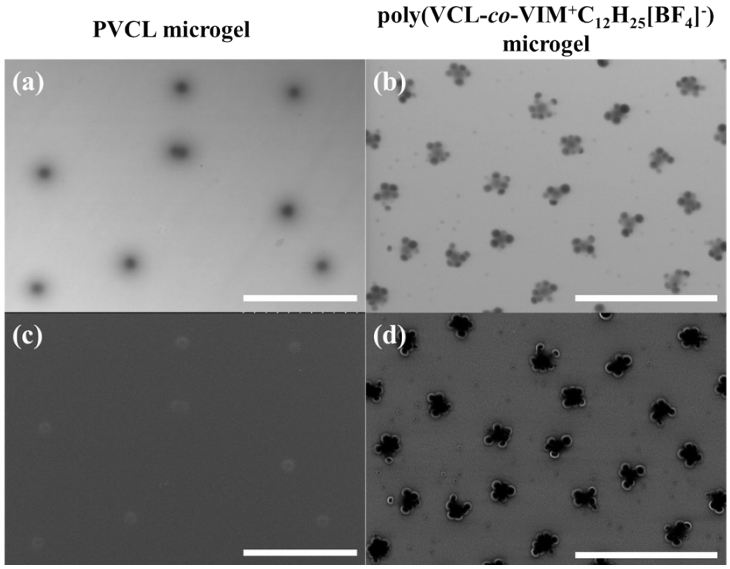

Fig. S6 Electron microscopy images of reference PVCL microgel and poly(VCL-*co*-VIM$^+$C$_{12}$H$_{25}$[BF$_4$]$^-$) microgels from pre-functionalization approach recorded in STEM mode (a+b), and SEM mode (c+d). Scale bar is set to 2 µm and accelerating voltage is 30.0 kV.

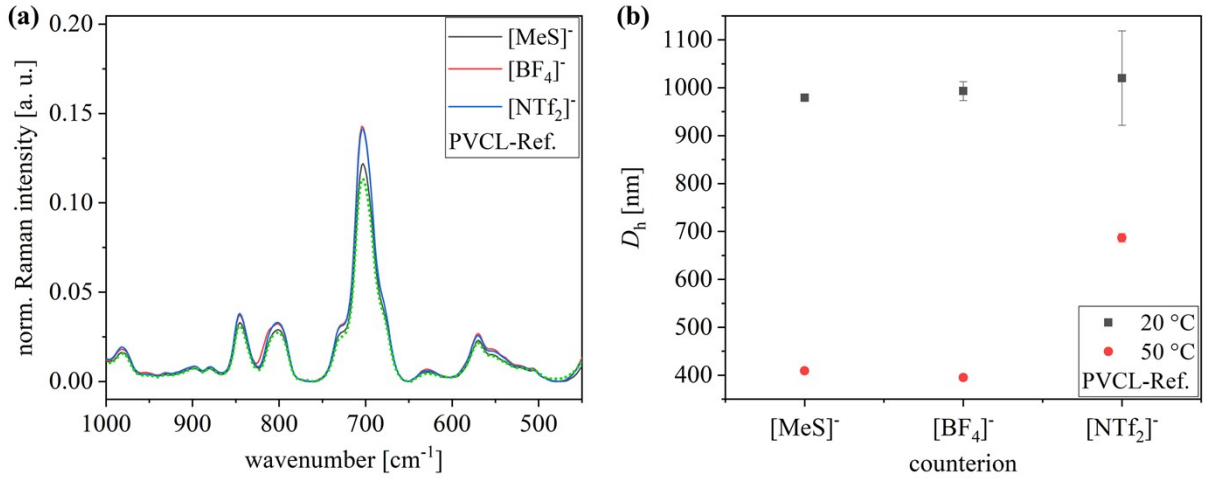

Fig. S7 (a) Raman spectra insight, and (b) hydrodynamic diameter at $T = 20$ °C and 50 °C in H_2O of PVCL microgels after treatment with anion salt. Dotted green line depicts PVCL microgel spectra before salt treatment.

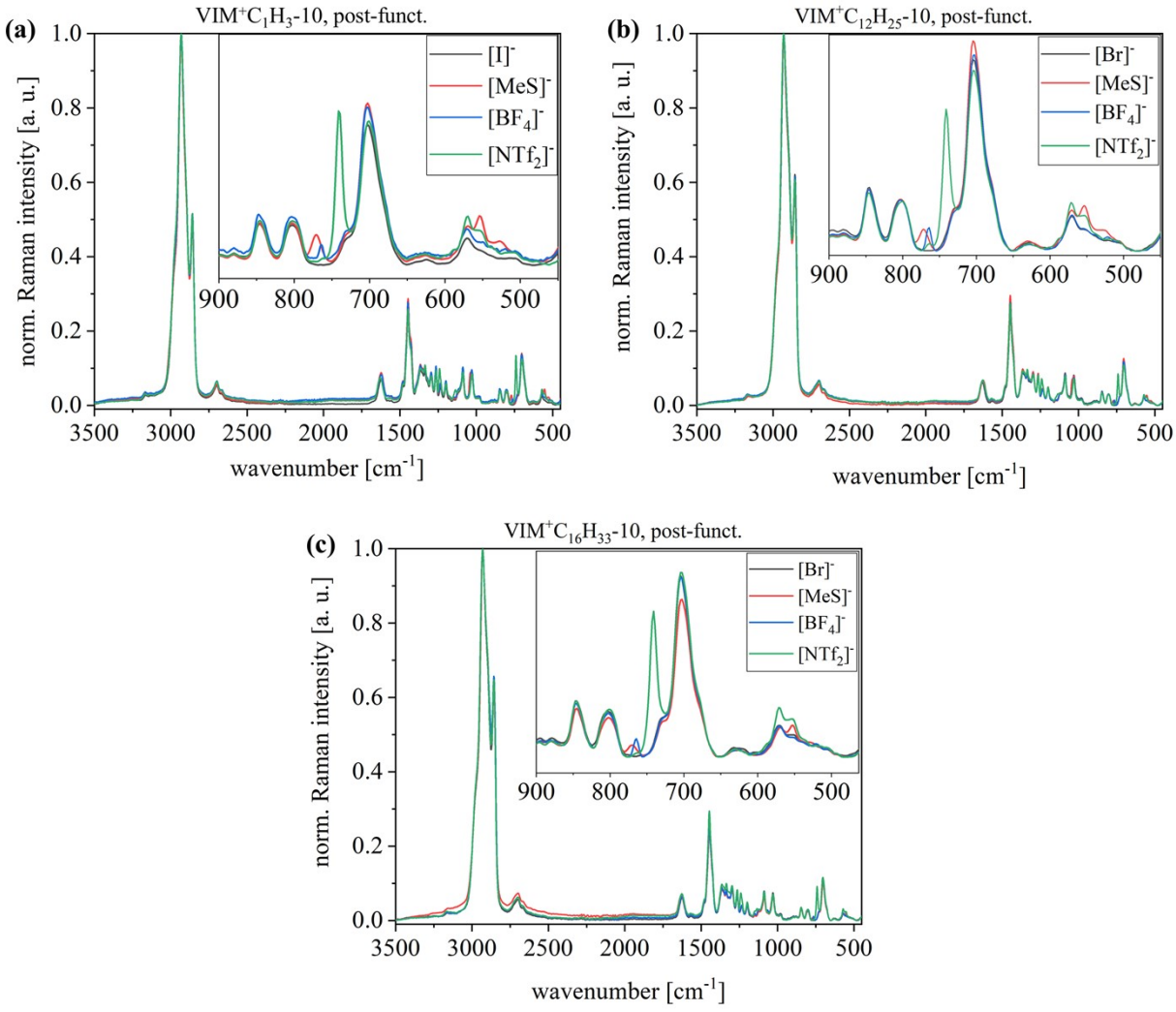

Fig. S8 Raman spectra of poly(VCL-*co*-VIM$^+$C$_n$H$_{2n+1}$[A]$^-$) microgels from post-functionalization with methanesulfonate, tetrafluoroborate, and bistriflimide. Insight shows characteristic signals of the anions for (a) n = 1, (b) n = 12, and (c) n = 16.

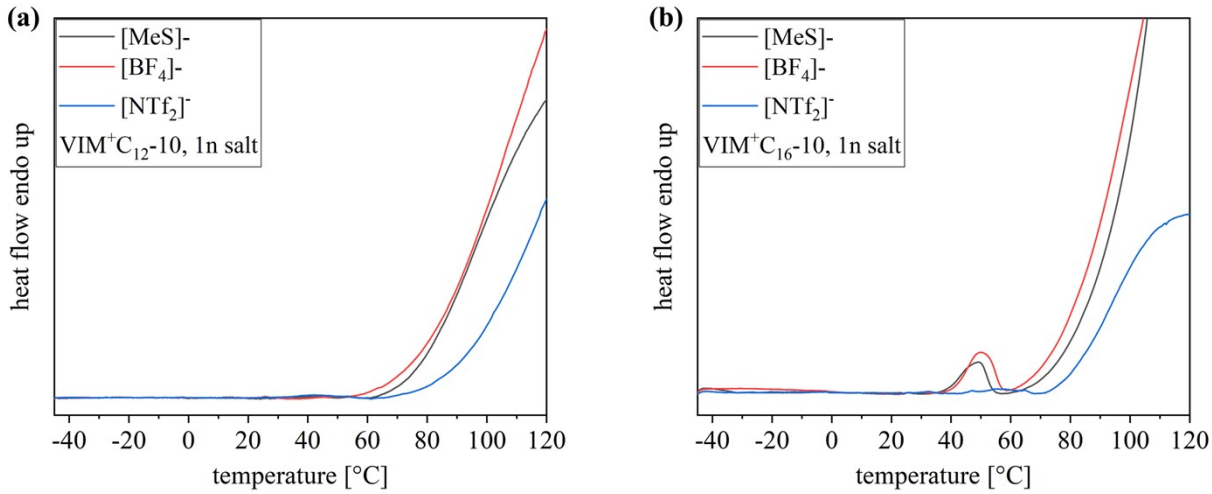

Fig. S9 DSC thermograms of poly(VCL-*co*-VIM$^+$C$_n$H$_{2n+1}$[A]$^-$) microgels from post-functionalization with methanesulfonate, tetrafluoroborate, and bistriflimide for (a) n = 12, and (b) n = 16.

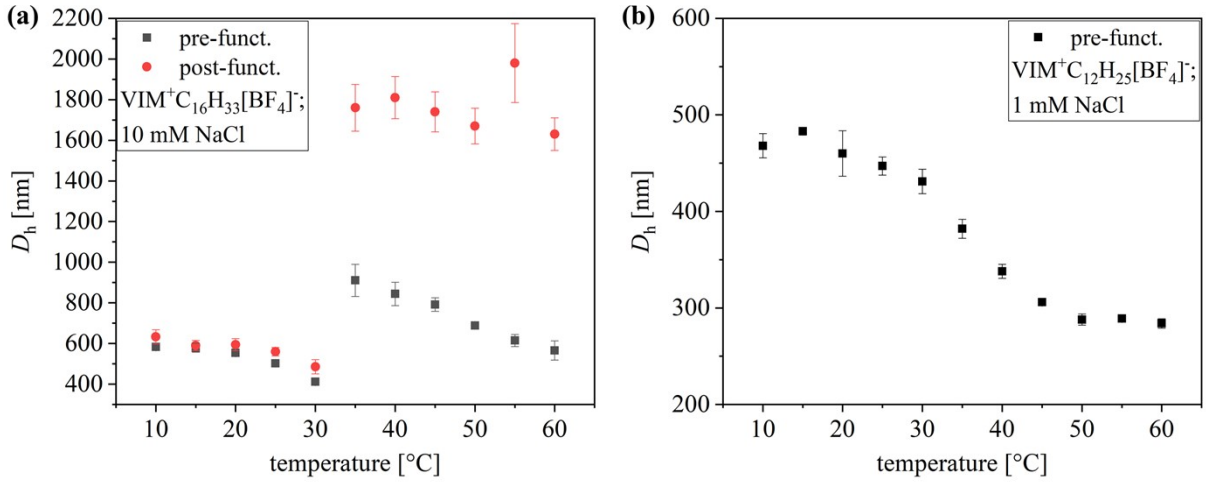

Fig. S10 Hydrodynamic diameter as a function of temperature. (a) Comparison of poly(VCL-*co*-VIM$^+$C$_{16}$H$_{33}$[BF$_4$]$^-$) microgels from pre- and post-functionalization measured in 10 mM NaCl. (b) Poly(VCL-*co*-VIM$^+$C$_{12}$H$_{25}$[BF$_4$]$^-$) microgels from pre-functionalization measured in 1 mM NaCl.

References

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2. Y. F. Hu, Z. C. Liu, C. M. Xu and X. M. Zhang, *Chem Soc Rev*, 2011, **40**, 3802-3823.
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