Supplementary Information

The Crosslinker Matters: Vinylimidazole-based Anion Exchange Polymer for Dispersive Solid-phase Extraction of Phenolic Acids

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Optimization of the [C_6-bis-VIM] [Br] crosslinked polymer

Table S1. Extraction recoveries obtained from DSPE experiments with [C_6-bis-VIM] [Br] crosslinked polymers with different monomer to crosslinker ratios.

VIM / mmol	[C_6-bis-VIM] [Br] / mmol	Molar ratio	ER ChlorA	ER CaffA	ER DHB	ER FerA	ER CinA
5.5	4.8	1.15	92.4 ± 1.6	83.2 ± 1.1	100.5 ± 1.4	49.8 ± 0.3	29.7 ± 0.0
6.3	4.1	1.53	92.3 ± 0.6	84.6 ± 0.8	99.6 ± 0.3	54.3 ± 1.9	33.9 ± 1.6
7.2	3.1	2.30	94.4 ± 0.5	88.1 ± 1.0	100.4 ± 1.5	62.0 ± 2.8	40.6 ± 2.9
7.8	2.5	3.07	94.2 ± 1.0	89.3 ± 1.2	100.0 ± 1.1	64.2 ± 1.1	42.2 ± 1.0
8.5	1.9	4.59	93.6 ± 0.9	88.6 ± 1.1	98.4 ± 0.9	69.5 ± 1.1	49.6 ± 1.0
9.0	1.3	6.90	95.4 ± 0.0	92.6 ± 0.1	99.0 ± 0.4	79.8 ± 0.6	63.2 ± 1.0
9.3	1.0	9.20	95.4 ± 0.3	92.9 ± 0.6	99.1 ± 0.5	80.3 ± 1.3	64.1 ± 1.7
9.5	0.8	11.50	92.7 ± 0.7	91.3 ± 0.7	95.2 ± 0.4	84.8 ± 0.7	74.5 ± 0.5
9.7	0.7	13.80	91.3 ± 0.8	90.1 ± 0.8	95.5 ± 0.7	82.0 ± 1.0	70.3 ± 1.6

Extraction recovery (ER): mean ± SD /%; n = 3

Conditioning solution

Table S2. Amount of bound analyte with the poly(n-VIM/C_6-bis-VIM) polymer with a monomer to crosslinker ratio of 11.50 to 1 obtained from DSPE experiments by applying different conditioning solutions.

Conditioning solution	Bound ChlorA	Bound CaffA	Bound DHB	Bound FerA	Bound CinA
Phosphate buffer (pH 6.6)	98.7 ± 0.3	97.2 ± 0.1	99.0 ± 0.2	90.4 ± 0.1	78.2 ± 0.4

Phosphate buffer	98.7	97.6	98.9	91.9	80.9
(pH 7.0)	± 0.1	± 0.0	± 0.1	± 0.0	± 0.2
Phosphate buffer	98.4	97.7	98.6	92.7	82.2
(pH 7.7)	± 0.0	± 0.1	± 0.1	± 0.3	± 0.8
0.5 % (w/w) LiCl, 5 vol. %	98.3	94.3	99.1	85.1	71.7
MeOH in water	± 0.0	± 0.2	± 0.0	± 0.4	± 0.6
5 vol. % MeOH	98.6	94.4	99.3	85.6	73.2
in water	± 0.0	± 0.3	± 0.0	± 0.6	± 0.9

Bound analyte: mean ± SD /%; n = 3

Eluting solution

Table S3. Extraction recoveries obtained from DSPE experiments with the poly(n-VIM/C_6-bis-VIM) polymer with a monomer to crosslinker ratio of 11.50 to 1 by applying different eluting solutions.

Eluting solution	**ER ChlorA**	**ER CaffA**	**ER DHB**	**ER FerA**	**ER CinA**
1 vol. % TFA, 1.5 % (w/w) LiCl, 50 vol. % ACN in water	91.7 ± 0.6	89.8 ± 0.4	94.7 ± 0.4	81.6 ± 0.7	70.4 ± 0.9
1 vol. % TFA, 3 % (w/w) LiCl, 50 vol. % ACN in water	90.4 ± 0.7	82.2 ± 0.3	84.9 ± 0.1	72.8 ± 0.0	59.9 ± 0.0
2 vol. % TFA, 3 % (w/w) LiCl, 50 vol. % ACN in water	91.0 ± 0.9	84.6 ± 7.2	87.3 ± 9.0	76.5 ± 10.2	65.6 ± 13.7
1 vol. % TFA, 1.5 % (w/w) LiCl, 75 vol. % ACN in water	90.9 ± 1.3	87.4 ± 1.1	96.6 ± 1.3	75.6 ± 0.2	63.4 ± 0.6
1 vol. % TFA, 1.5% (w/w) LiCl, 25 vol.% ACN in water	88.8 ± 0.7	84.2 ± 0.8	92.8 ± 0.4	75.9 ± 1.0	66.2 ± 2.0
2 vol. % TFA, 1.5 % (w/w) LiCl, 50 vol. % ACN in water	92.7 ± 0.7	91.3 ± 0.7	95.2 ± 0.4	84.8 ± 0.7	74.5 ± 0.5

Extraction recovery (ER): mean ± SD /%; n = 3

Linearity of calibration

Table S4. Calibration results obtained from HPLC-UV measurements of concentrations ranging between 25 and 250 mg L^{-1}.

Analyte	**Linear**	**R^2**	**Bias (Max)**	**Bias (Min)**	**RSD (Max)**

	function		/%	/%	/%
ChlorA	y= 15.611x - 17.154	0.9997	2.5	-2.3	1.4
CaffA	y= 31.416x - 1.622	0.9997	2.1	-2.9	1.7
DHB	y= 52.314x + 14.653	0.9997	2.2	-3.5	1.4
FerA	y= 27.289x + 2.618	0.9997	2.2	-3.0	1.6
CinA	y= 39.201x + 52.516	0.9995	6.1	-5.4	2.2

Table S5. Calibration results obtained from HPLC-UV measurements of concentrations ranging between 250 and 500 mg L^{-1}.

Analyte	Linear function	R^2	Bias (Max) /%	Bias (Min) /%	RSD (Max) /%
ChlorA	y= 15.468x - 73.089	0.9985	1.5	-3.3	0.9
CaffA	y= 30.365x - 381.429	0.9983	2.0	-1.9	0.6
DHB	y= 46.088x + 1901.446	0.9959	1.7	-3.3	0.5
FerA	y= 26.552x + 296.051	0.9985	1.4	-1.9	0.6
CinA	y= 36.541x + 886.703	0.9978	1.4	-2.6	0.6

Repeatability

Table S6. Repeatability results for the HPLC-DAD method at 50 mg L^{-1}.

Value	ChlorA	CaffA	DHB	FerA	CinA
Max $RSD_{intraday}$ / %	1.02	0.95	0.83	1.00	1.01
$RSD_{interday}$ / %	1.27	1.07	1.17	1.05	0.99

Table S7. Repeatability results for the HPLC-DAD method at 500 mg L^{-1}.

Value	ChlorA	CaffA	DHB	FerA	CinA
Max $RSD_{intraday}$ / %	0.97	0.99	0.81	0.93	0.91
$RSD_{interday}$ / %	0.67	0.60	0.60	0.59	0.48

Limit of detection (LOD) and limit of quantification (LOQ)

Table S8. LOD and LOQ results for all phenolic acids.

Limit	c ChlorA	c CaffA	c DHB	c FerA	c CinA

LOD	0.04	0.02	0.02	0.03	0.02
LOQ	0.12	0.08	0.08	0.12	0.07

Analyte concentration (c) in mg L^{-1}

Adsorption time profiles

Table S9. Amount of bound analyte with the poly(n-VIM/C_6-bis-VIM) polymer with a monomer to crosslinker ratio of 11.50 to 1 obtained from DSPE experiments with different extraction times.

t /min	Bound ChlorA	Bound CaffA	Bound DHB	Bound FerA	Bound CinA
1	97.7 ± 0.3	95.9 ± 0.2	98.1 ± 0.3	87.9 ± 0.4	76.2 ± 0.6
2.5	98.2 ± 0.1	96.8 ± 0.3	98.5 ± 0.1	89.9 ± 1.0	79.0 ± 1.3
5	98.3 ± 0.1	97.1 ± 0.1	98.6 ± 0.0	90.8 ± 0.3	80.2 ± 0.4
10	98.4 ± 0.1	97.4 ± 0.1	98.6 ± 0.1	91.5 ± 0.3	80.9 ± 0.4
20	98.3 ± 0.2	97.6 ± 0.1	98.5 ± 0.2	91.7 ± 0.4	80.8 ± 0.8

Bound analyte: mean ± SD /%; n = 3

Differently crosslinked polymers

Table S10. Extraction recoveries obtained from DSPE experiments with differently crosslinked vinylimidazole-based polymers.

Crosslinker	Molar ratio	ER ChlorA	ER CaffA	ER DHB	ER FerA	ER CinA
DVB	4.6	92.9 ± 1.4	85.5 ± 1.6	95.1 ± 1.2	74.8 ± 1.3	71.9 ± 1.4
EGDMA	4.6	82.6 ± 0.6	73.2 ± 0.3	85.3 ± 0.7	61.2 ± 0.6	52.4 ± 1.1
[C_6-bis-VIM] [Br]	4.6	96.3 ± 0.8	91.1 ± 0.9	99.3 ± 0.7	71.4 ± 0.7	50.8 ± 0.7

Extraction recovery (ER): mean ± SD /%; n = 3

Sorption capacity

Table S11. Extraction recoveries obtained from DSPE experiments with the poly(n-VIM/C_6-bis-VIM) polymer with a monomer to crosslinker ratio of 11.50 to 1, by applying different loading concentrations.

c / mg L^{-1}	ChlorA	CaffA	DHB	FerA	CinA
10	89.6 ± 1.7	88.7 ± 1.7	94.4 ± 0.1	86.7 ± 0.3	76.6 ± 2.3
20	93.1 ± 0.5	92.8 ± 1.0	93.3 ± 1.3	88.6 ± 2.2	82.6 ± 2.6

50	90.7 ± 0.9	91.4 ± 1.2	92.3 ± 1.0	89.4 ± 0.8	83.3 ± 1.9
100	92.5 ± 0.7	92.0 ± 0.8	92.5 ± 0.8	90.6 ± 0.5	84.1 ± 0.2
250	92.4 ± 0.9	91.9 ± 1.0	92.9 ± 0.9	89.5 ± 0.8	82.4 ± 0.9
500	91.3 ± 0.1	89.0 ± 0.5	91.9 ± 0.6	81.6 ± 0.9	69.5 ± 1.3

Extraction recovery: mean ± SD /%; n = 3

Reusability

Table S12. Amount of bound analyte with the poly(n-VIM/C_6-bis-VIM) polymer with a monomer to crosslinker ratio of 11.50 to 1 obtained after multiple DSPE cycles.

DSPE cycle	ChlorA	CaffA	DHB	FerA	CinA
1	98.6 ± 0.1	99.3 ± 0.0	98.8 ± 0.1	97.8 ± 0.2	91.1 ± 0.8
2	93.7 ± 0.1	85.9 ± 0.2	98.2 ± 0.0	60.1 ± 0.5	41.7 ± 0.5
3	93.9 ± 0.5	87.4 ± 0.6	98.4 ± 0.0	62.3 ± 1.8	43.7 ± 1.4
4	94.1 ± 0.4	86.4 ± 0.5	98.3 ± 0.1	62.5 ± 1.0	41.6 ± 1.6
5	93.3 ± 0.2	86.3 ± 0.6	98.3 ± 0.0	60.1 ± 1.3	40.8 ± 0.6

Bound analyte: mean ± SD /%; n = 3

Polymer characterization

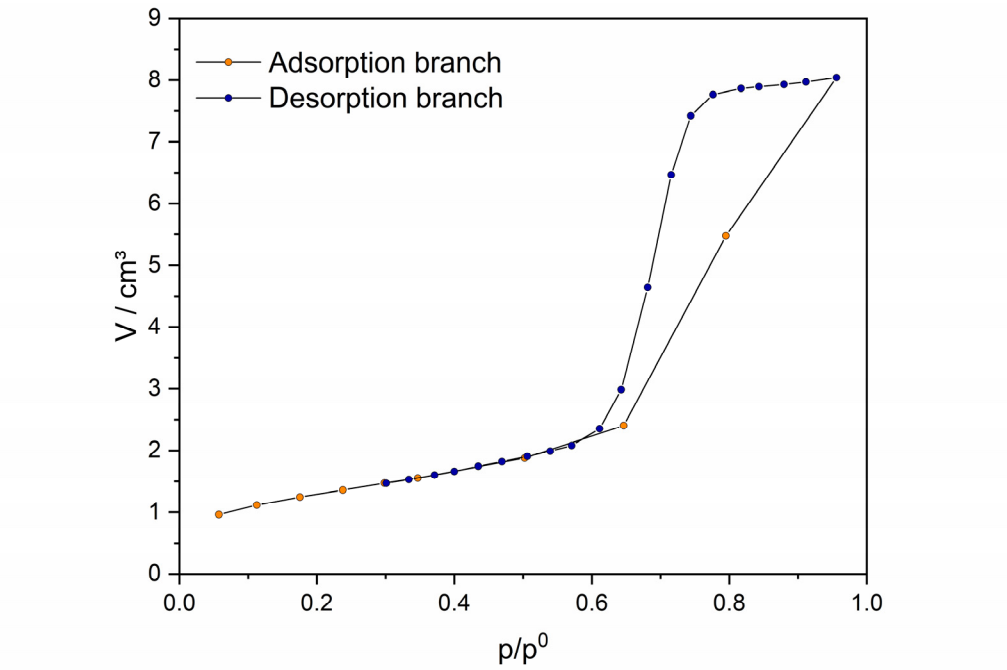

Figure S1. N_2 adsorption and desorption isotherm obtained from BET measurements with the poly(n-VIM/C_6-bis-VIM) polymer with a monomer to crosslinker ratio of 11.50 to 1.

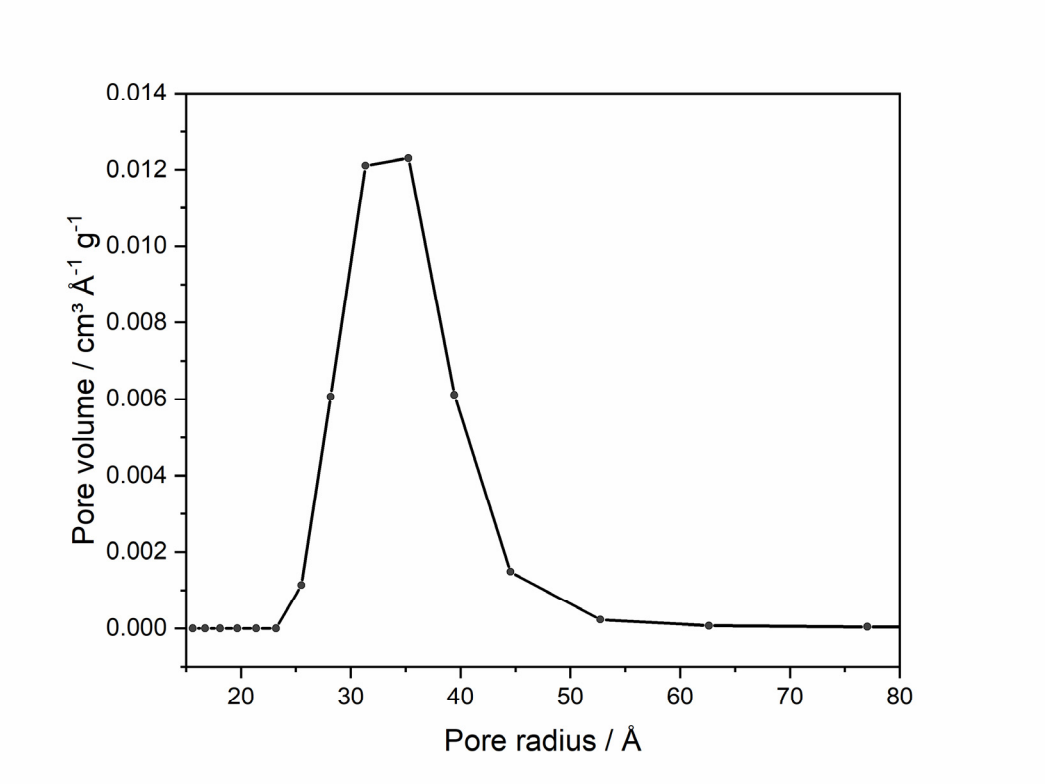

Figure S2. Calculated pore size distribution from the desorption branch of the isotherm.

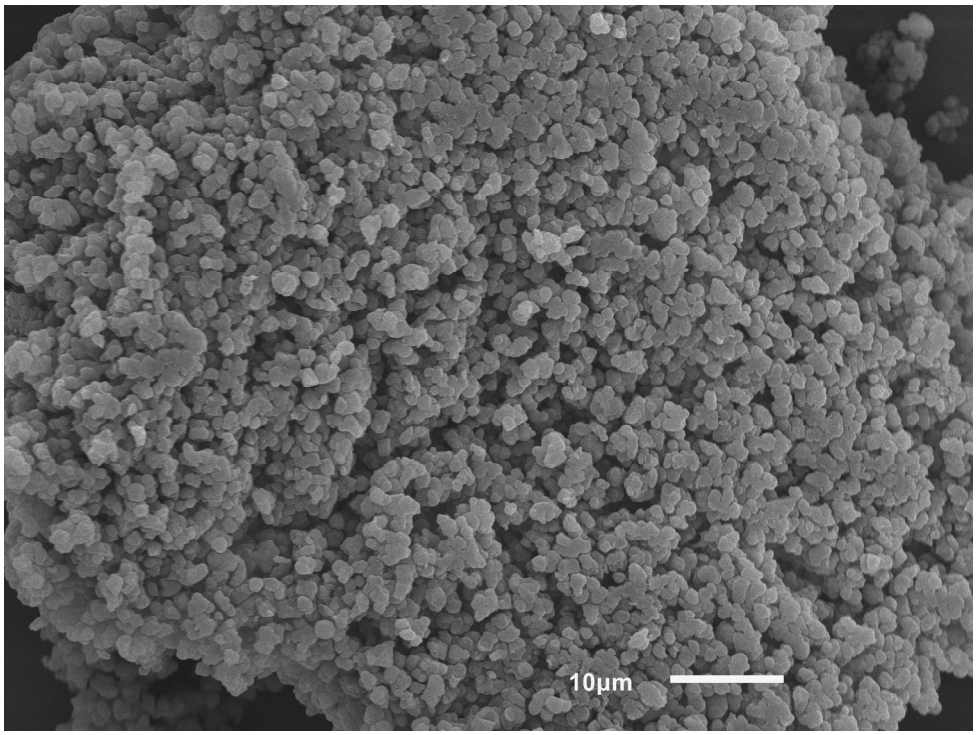

Figure S3. SEM image of the surface structure of the poly(n-VIM/C_6-bis-VIM) polymer with a monomer to crosslinker ratio of 11.50 to 1 at augmentation x1500.

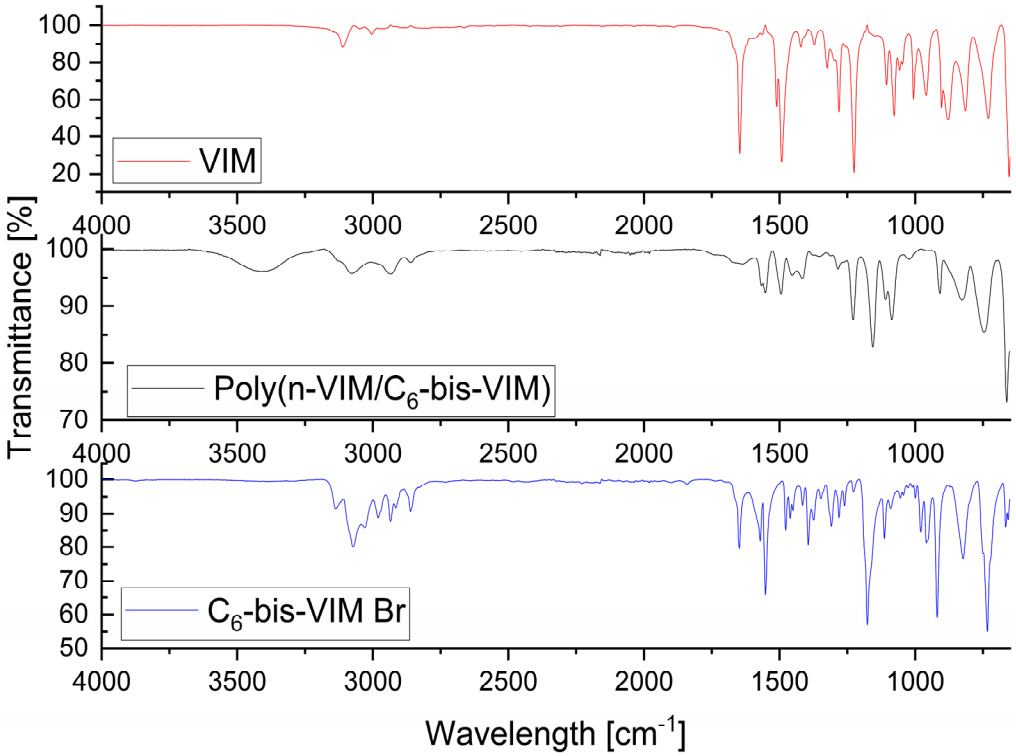

Figure S4. ATR-FTIR spectra of the monomer VIM, the poly(n-VIM/C_6-bis-VIM) polymer with a monomer to crosslinker ratio of 11.50 to 1 and the crosslinker [C_6-bis-VIM] [Br].