Supplementary Information (SI) for Polymer Chemistry.

Supplementary Material

for

Temperature-Triggered Self-Separating Swelling Poly(Ionic Liquid)s as Efficient Catalysts for CO_2 Cycloaddition Reactions

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Text 1：Preparation of Ionic Liquid Monomer VC_mIm

The synthesis of five ionic liquid monomers VC_mIm with different alkyl chain lengths on the imidazole ring (m represents the number of carbon atoms in the imidazole side chain, 3, 6, 12, 14, 18) follows the nucleophilic substitution mechanism. Taking the synthesis of 1-vinyl-3-dodecylimidazolium bromide ($VC_{12}Im$) as an example, the detailed experimental steps are as follows: in a 50 mL three-neck flask, a mixture of 1-Vinylimidazole (20 mmol, 1.88 g) and CH_2Cl_2 (10 mL) was prepared under a N_2 atmosphere.Then, a solution of 1-Bromododecane (20 mmol, 4.98 g) in CH_2Cl_2 (10 mL) was added dropwise. Subsequently, the mixture was heated in an oil bath preheated to 75°C and reacted for 10 hours. After the reaction, the solvent was removed using a rotary evaporator, and the unreacted substances were washed with ethyl acetate to obtain a white solid. The target product $VC_{12}Im$ was obtained in 94.6% yield. Similarly, 1-vinyl-3-propylimidazolium bromide (VC_3Im), 1-vinyl-3-hexylimidazolium bromide (VC_6Im), 1-vinyl-3-tetradecylimidazolium bromide ($VC_{14}Im$), 1-vinyl-3-octadecylimidazolium bromide ($VC_{18}Im$) were prepared. The structure was confirmed by ^1H NMR and ^{13}C NMR spectroscopy (see Figures S2-S11).

Text 2：Preparation of Crosslinker VIm-C_n-VIm

Four crosslinkers VIm-C_n-VIm with different chain lengths (n represents the number of carbon atoms in the central alkyl chain, 3, 6, 12, 14) were synthesized following the route shown in Figure 1(b). Taking the synthesis of 3,3'-(dodecane-1,12-diyl)bis(1-vinyl-3-imidazolium) dibromide (VIM-C_{12}-VIM) as an example, the specific synthesis steps are as follows: 1-vinylimidazole (25.0 mmol, 4.10 g), 1,12-Dibromododecane (12.5 mmol, 2.52 g), and CH_2Cl_2 (30 mL) were simultaneously added to a 100 mL round-bottom flask and mixed uniformly. Then, the mixture was heated at 60°C for the reaction. After the reaction, the mixture was allowed to settle and separate into layers. The lower yellow oily layer was the product layer. The upper turbid liquid was discarded, and the yellow oily crude product was washed with dichloromethane to remove unreacted starting materials. The product was dried at 75°C to obtain a white solid VIM-C_{12}-VIM. The yield of VIm-C_{12}-VIm reached 97.2%. Similarly, 3,3'-(propane-1,3-diyl)bis(1-vinyl-3-imidazolium) dibromide (VIM-C_3-VIM), 3,3'-(hexane-1,6-diyl)bis(1-vinyl-3-imidazolium) dibromide (VIM-C_6-VIM), and 3,3'-(tetradecane-1,14-diyl)bis(1-vinyl-3-imidazolium) dibromide (VIM-C_{14}-VIM) were prepared. The structures were confirmed by ^1H NMR and ^{13}C NMR spectroscopy (see Figures S12-S21).

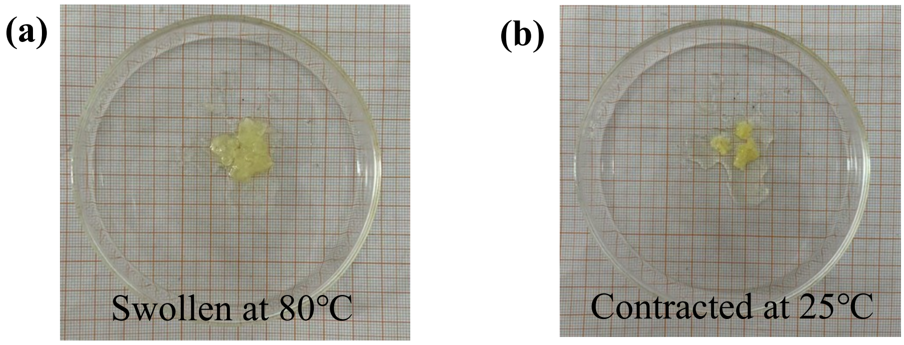


Figure S1 (a)-(b) Images of P-[$VC_{12}Im$]-C_{12}-Br in reaction medium under different tempreture

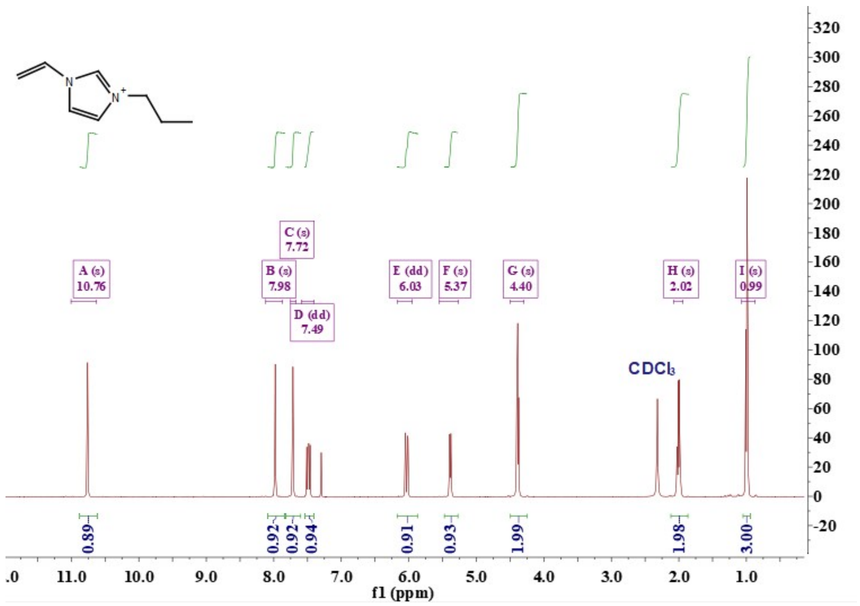


Figure S2 ^{1}H NMR spectra of the ionic liquid monomer VC_3Im

VC_3Im: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.98 (s, 1H), 7.72 (s, 1H), 7.49 (dd, J = 15.7, 8.7 Hz, 1H), 6.03 (dd, J = 15.7, 2.8 Hz, 1H), 5.37 (s, 1H), 4.40 (s, 2H), 2.02 (s, 2H), 0.99 (s, 3H).

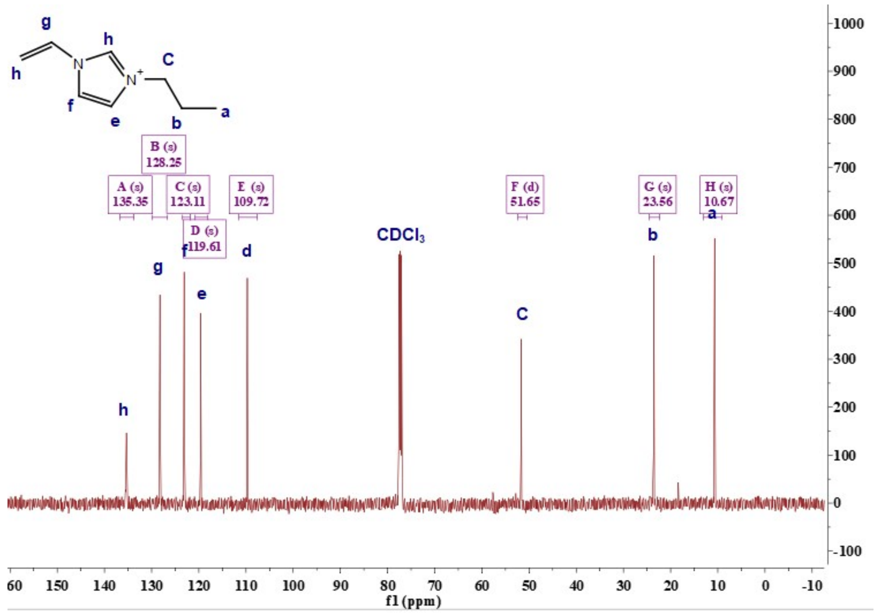


Figure S3 ^{13}C NMR spectra of the ionic liquid monomer VC$_3$Im

VC$_3$Im: ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.35 (s), 128.25 (s), 123.11 (s), 119.61 (s), 109.72 (s), 51.65 (d, J = 4.9 Hz), 23.56 (s), 10.67 (s).

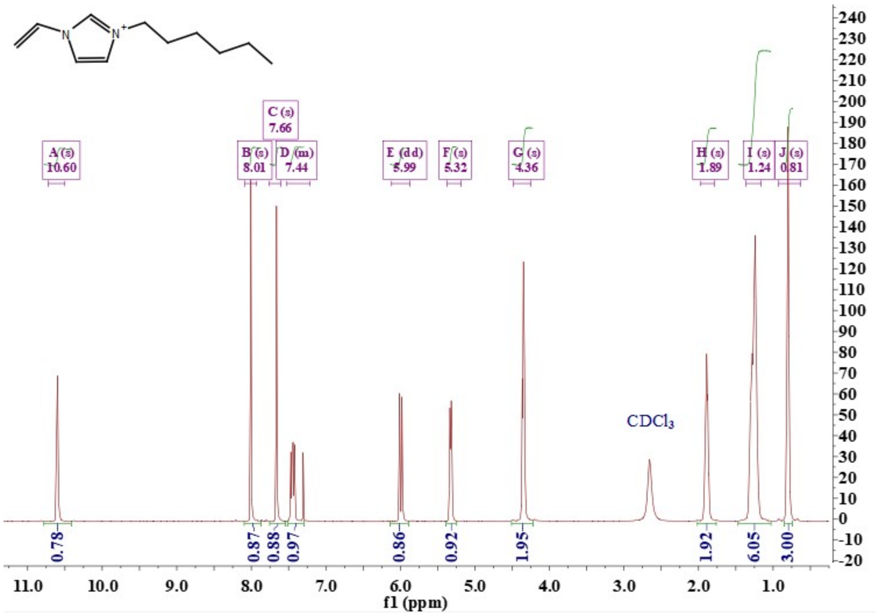


Figure S4 ^{1}H NMR spectra of the ionic liquid monomer VC$_6$Im.

VC$_6$Im: ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.60 (s, 1H), 8.01 (s, 1H), 7.66 (s, 1H), 7.52 – 7.21 (m, 1H), 5.99 (dd, J = 15.7, 2.5 Hz, 1H), 5.32 (s, 1H), 4.36 (s, 2H), 1.89 (s, 2H), 1.24 (s, 7H), 0.81 (s, 3H).

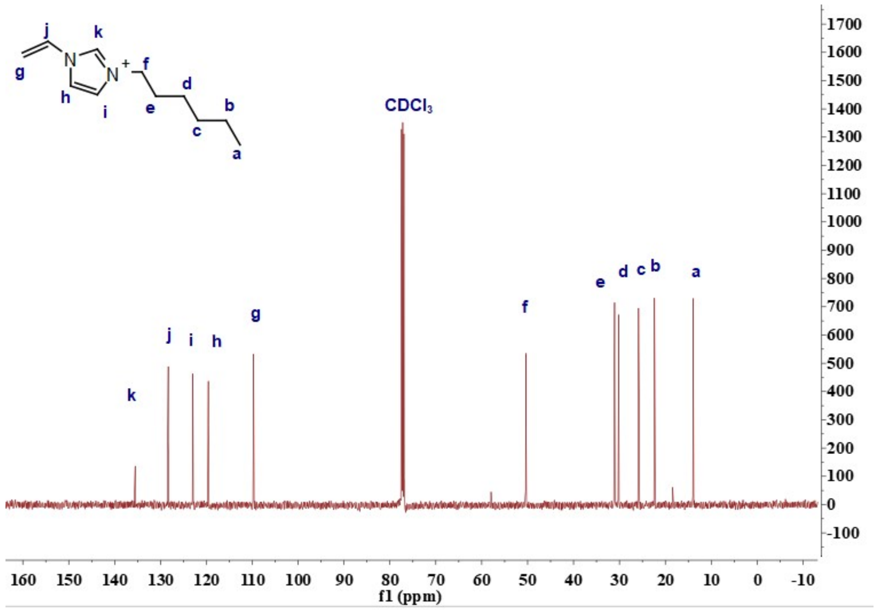


Figure S5 ^{13}C NMR NMR spectra of the ionic liquid monomer VC$_6$Im

VC$_6$Im: ^{13}C NMR (126 MHz, CDCl$_3$) δ 154.39 (s), 76.89 (s), 67.02 (s), 43.88 (s).

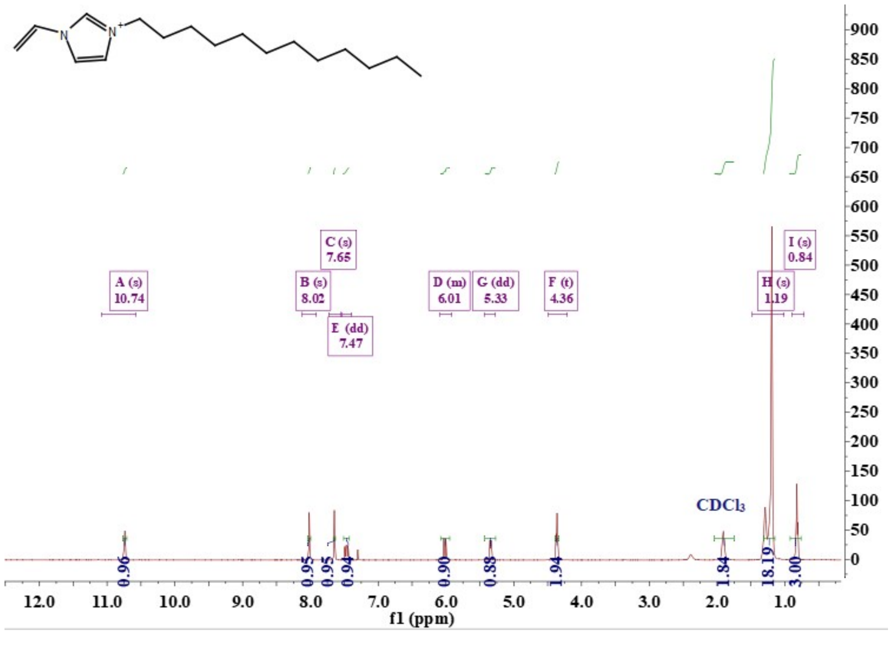


Figure S6 ^{1}H NMR spectra of the ionic liquid monomer VC$_{12}$Im

VC$_{12}$Im: ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.74 (s, 1H), 8.02 (s, 1H), 7.65 (s, 2H), 7.47 (dd, *J* = 15.6, 8.7 Hz, 2H), 6.09 – 5.92 (m, 1H), 5.33 (dd, *J* = 23.1, 16.2 Hz, 2H), 4.36 (t, *J* = 7.3 Hz, 3H), 1.19 (s, 33H), 0.84 (s, 5H).

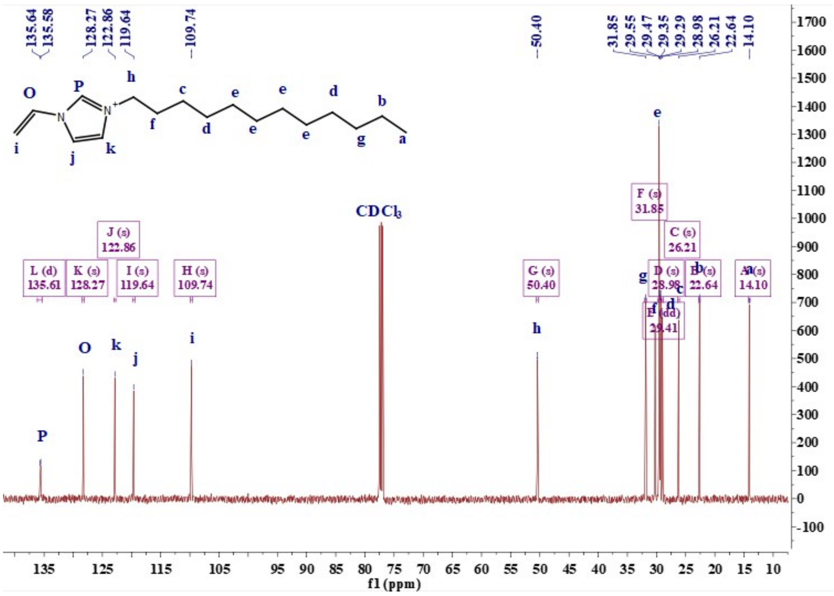


Figure S7 ^{13}C NMR NMR spectra of the ionic liquid monomer $VC_{12}Im$

$VC_{12}Im$: ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.61 (d, *J* = 8.6 Hz), 128.27 (s), 122.86 (s), 119.64 (s), 109.74 (s), 50.40 (s), 31.85 (s), 29.41 (dd, *J* = 24.3, 9.1 Hz), 28.98 (s), 26.21 (s), 22.64 (s), 14.10 (s).

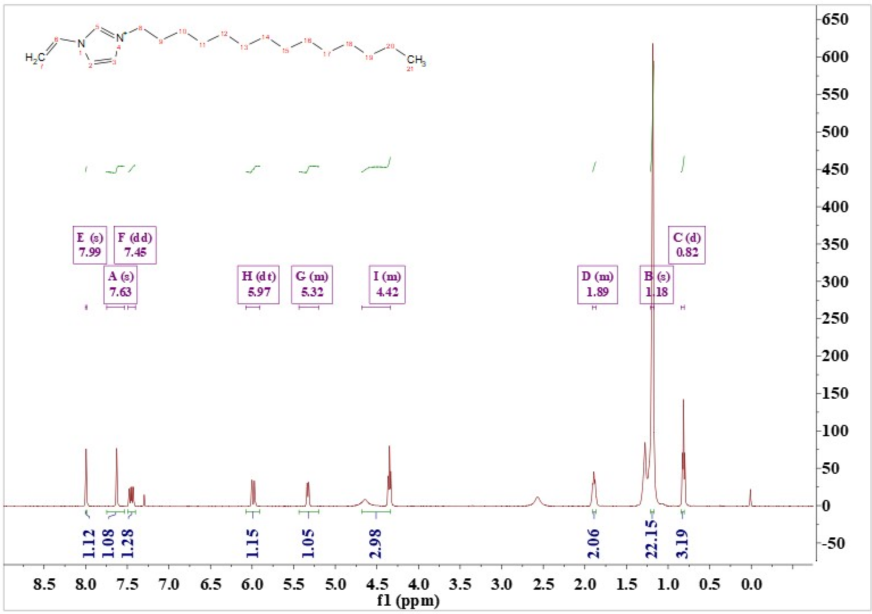


Figure S8 ^{1}H NMR spectra of the ionic liquid monomer $VC_{14}Im$

$VC_{14}Im$: ^{1}H NMR (500 MHz, CDCl3) δ7.99 (s, 1H), 7.63 (s, 1H), 7.45 (dd, J = 15.6, 8.7 Hz, 1H), 5.97 (dt, J = 31.4, 15.7 Hz, 1H), 5.44-5.20 (m, 1H), 4.68-4.34 (m, 3H), 1.91-1.87 (m, 2H), 1.18 (s, 22H), 0.82 (d, J = 6.6 Hz, 3H).

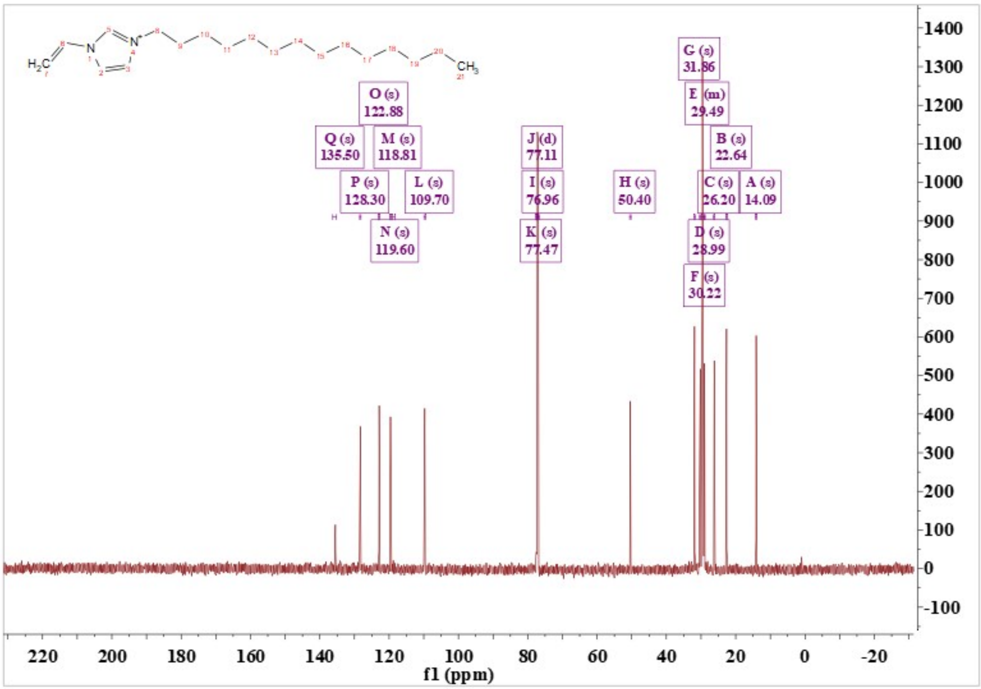


Figure S9 ^{13}C NMR spectra of the ionic liquid monomer $VC_{14}Im$

$VC_{14}Im$: ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.50 (s), 128.30 (s), 122.88 (s), 119.60 (s), 118.81 (s), 109.70 (s), 77.47 (s), 77.11 (d, J = 25.9 Hz), 76.96 (s), 50.40 (s), 31.86 (s), 30.22 (s), 29.84 – 29.16 (m), 28.99 (s), 26.20 (s), 22.64 (s), 14.09 (s).

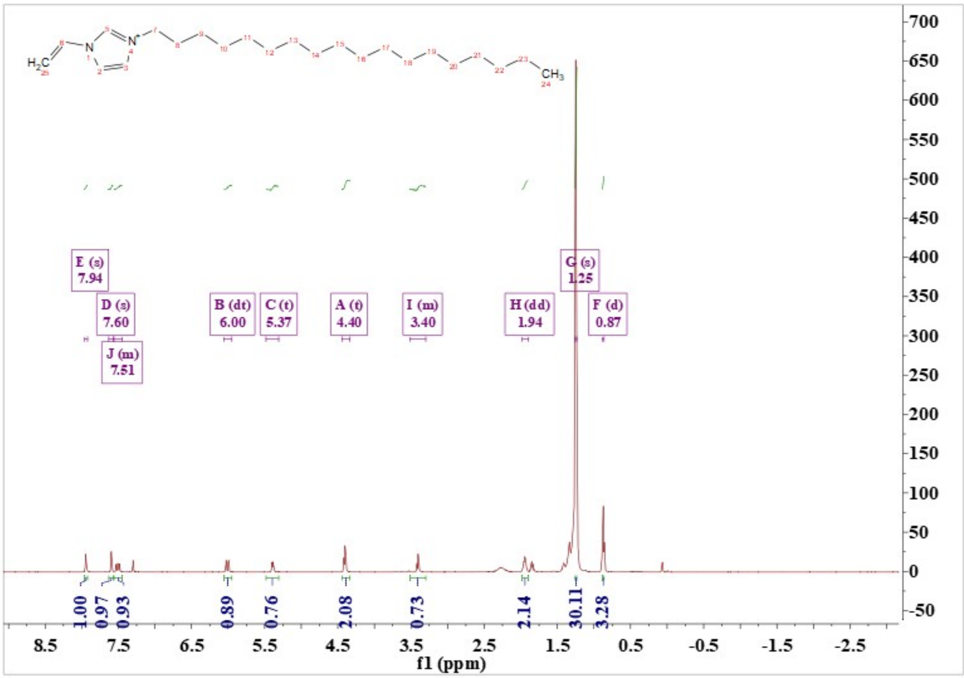


Figure S10 ^{1}H NMR spectra of the ionic liquid monomer $VC_{18}Im$

$VC_{18}Im$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.60 (s, 1H), 7.56 – 7.44 (m, 1H), 6.00 (dt, J = 23.3, 11.7 Hz, 1H), 5.37 (t, J = 22.0 Hz, 1H), 4.40 (t, J = 7.4 Hz, 2H), 3.52 – 3.30 (m, 1H), 1.94 (dd, J = 13.9, 6.9 Hz, 2H), 1.25 (s, 30H), 0.87 (d, J = 5.7 Hz, 3H).

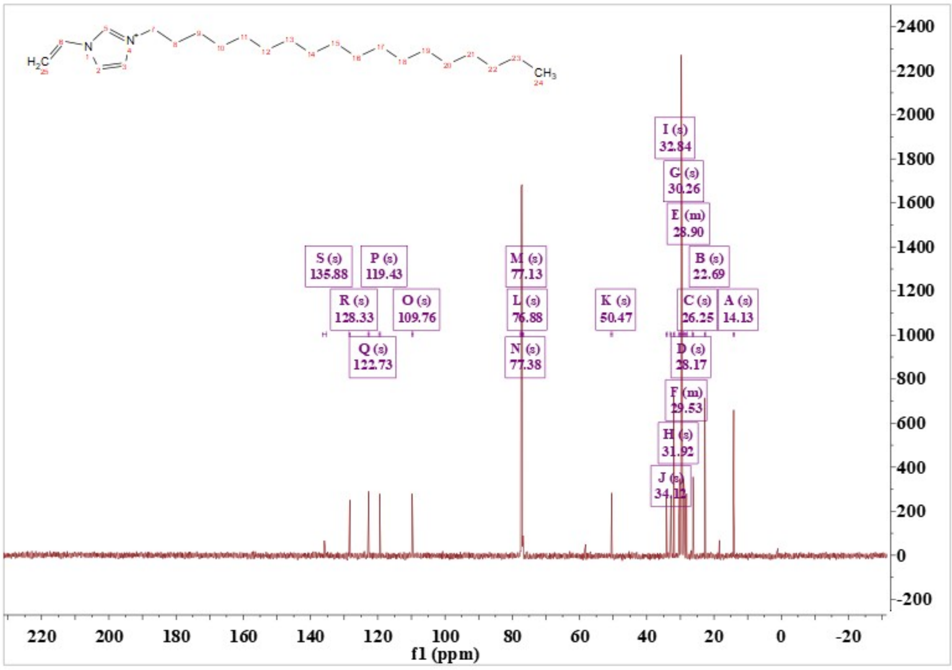


Figure S11 ^{13}C NMR spectra of the ionic liquid monomer VC$_{18}$Im

VC$_{18}$Im: ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.50 (s), 128.30 (s), 122.88 (s), 119.60 (s), 118.81 (s), 109.70 (s), 77.47 (s), 77.11 (d, *J* = 25.9 Hz), 76.96 (s), 50.40 (s), 31.86 (s), 30.22 (s), 29.84 – 29.16 (m), 28.99 (s), 26.20 (s), 22.64 (s), 14.09 (s).

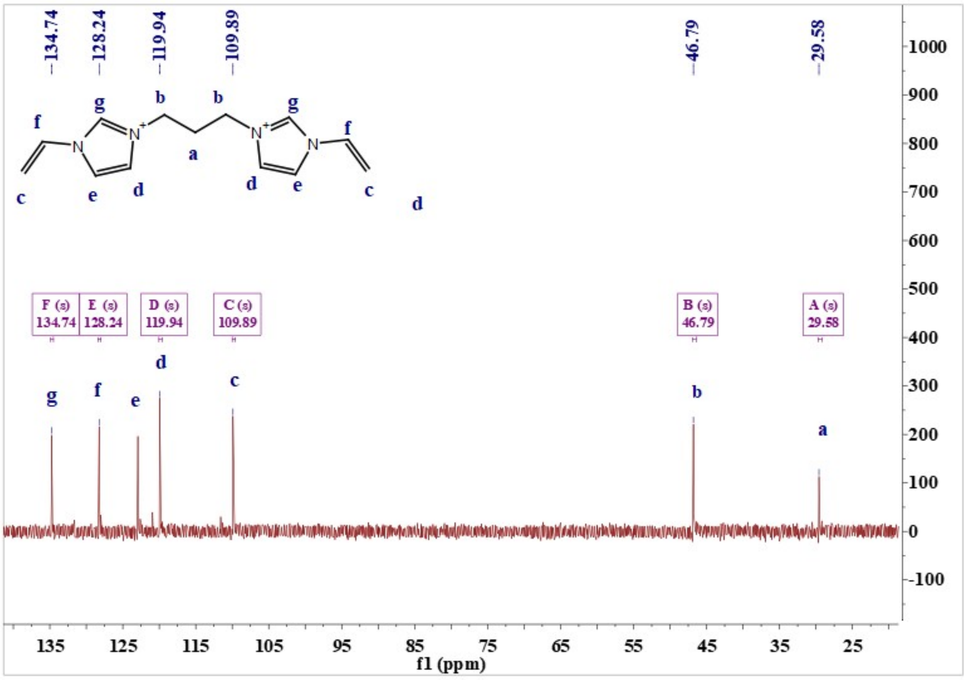


Figure S12 ^{1}H NMR spectra of the crosslinker VIm-C$_3$-VIm

VIm-C$_3$-VIm: ^{1}H NMR (500 MHz, D$_2$O) δ 9.16 (s, 1H), 7.80 (d, J = 1.8 Hz, 2H), 7.64 (d, J = 1.6 Hz, 2H), 7.14 (dt, J = 15.6, 7.8 Hz, 2H), 5.80 (dd, J = 15.6, 2.8 Hz, 2H), 5.41 (dd, J = 8.7, 2.7 Hz, 2H), 4.40 (s, 4H).

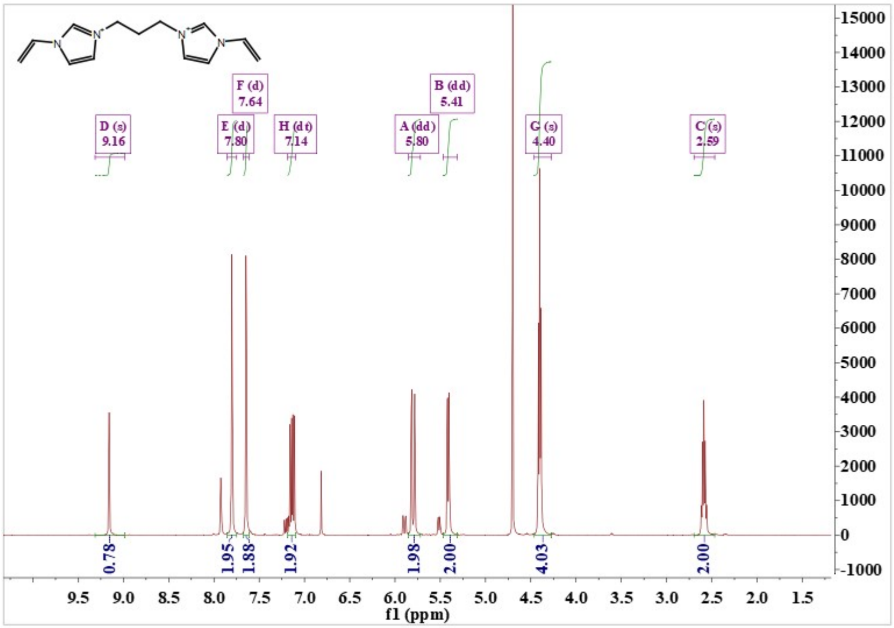


Figure S13 ^{13}C NMR spectra of the crosslinker VIm-C$_3$-VIm

VIm-C$_3$-VIm: ^{13}C NMR (126 MHz, D$_2$O) δ 134.74 (s), 128.24 (s), 119.94 (s), 109.89 (s), 46.79 (s), 29.58 (s).

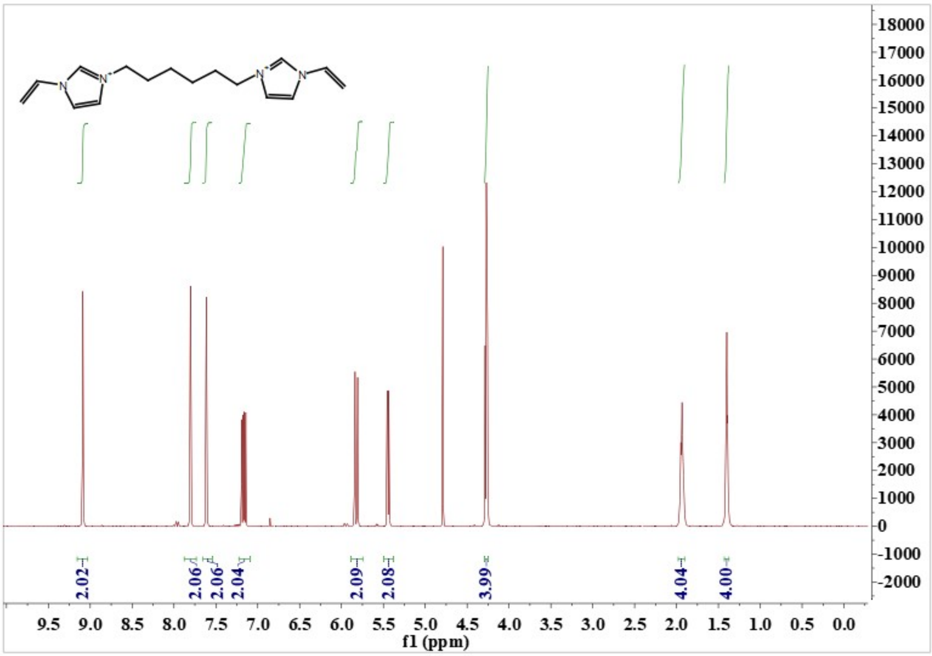


Figure S14 ^{1}H NMR spectra of crosslinker VIm-C$_6$-VIm

VIm-C$_6$-VIm: ^{1}H NMR (500 MHz, D$_2$O) δ 9.09 (s, 1H), 7.80 (t, J = 1.8 Hz, 1H), 7.61 (t, J = 1.7 Hz, 1H), 7.17 (dd, J = 15.6, 8.7 Hz, 1H), 5.82 (dd, J = 15.6, 2.8 Hz, 1H), 5.44 (dd, J = 8.7, 2.8 Hz, 1H), 4.79 (s, 1H), 4.27 (t, J = 7.2 Hz, 1H), 1.93 (s, 1H), 1.40 (s, 1H).

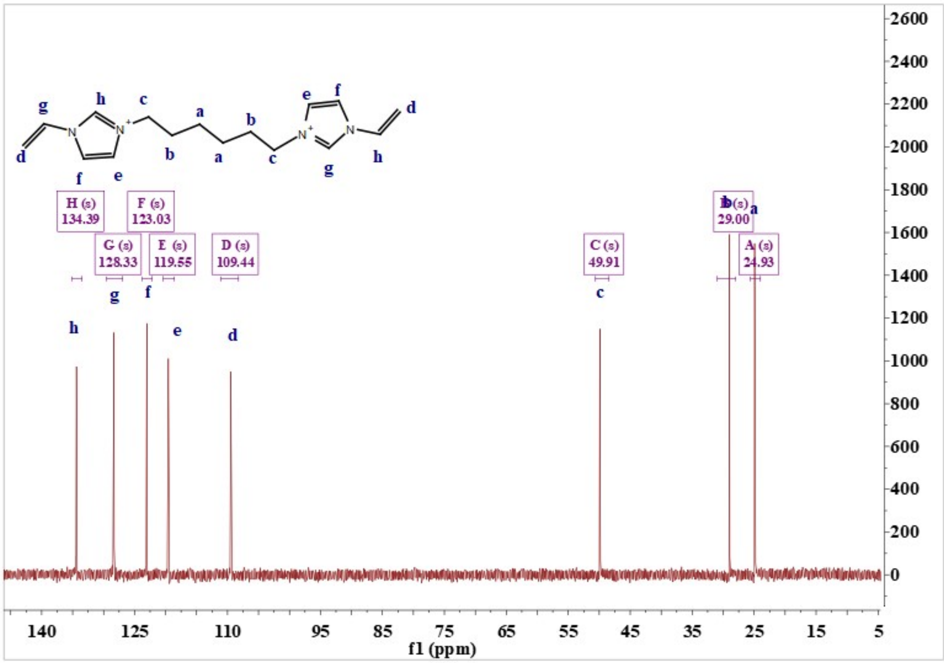


Figure S15 ^{13}C NMR spectra of the crosslinker VIm-C_6-VIm

VIm-C_6-VIm: ^{13}C NMR (126 MHz, D_2O) δ 134.39 (s), 128.33 (s), 123.03 (s), 119.55 (s), 109.44 (s), 49.91 (s), 29.00 (s), 24.93 (s).

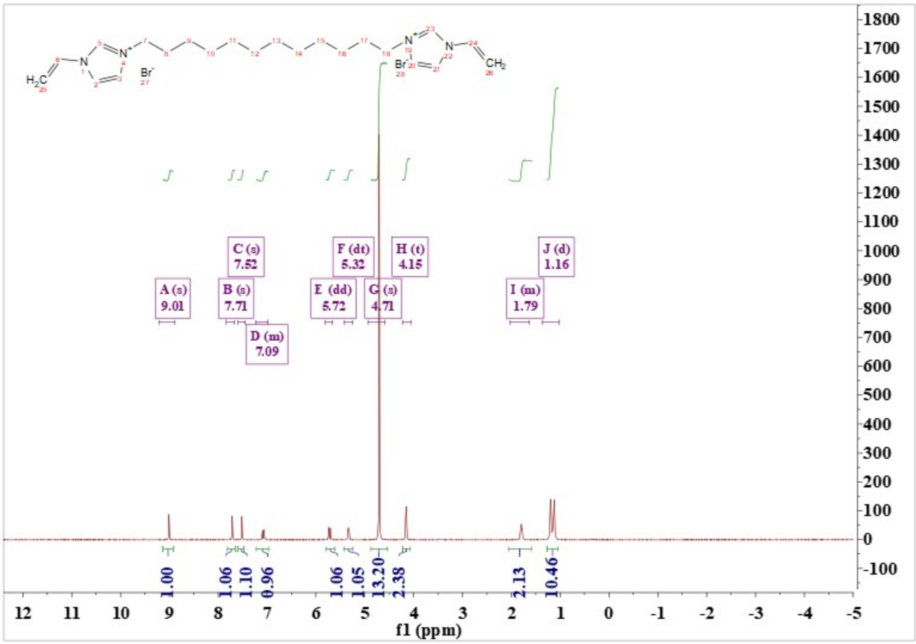


Figure S16 ^1H NMR spectra of crosslinker VIm-C_{12}-VIm

VIm-C_{12}-VIm: ^1H NMR (500 MHz, D_2O) δ 9.01 (s, 1H), 7.71 (s, 1H), 7.52 (s, 1H), 7.23 – 6.98 (m, 1H), 5.72 (dd, J = 15.6, 2.7 Hz, ^1H), 5.32 (dt, J = 40.6, 20.3 Hz, 1H), 4.71 (s, 15H), 4.15 (t, J = 7.1 Hz, 3H), 2.02 – 1.63 (m, 2H), 1.16 (d, J = 37.5 Hz, 12H).

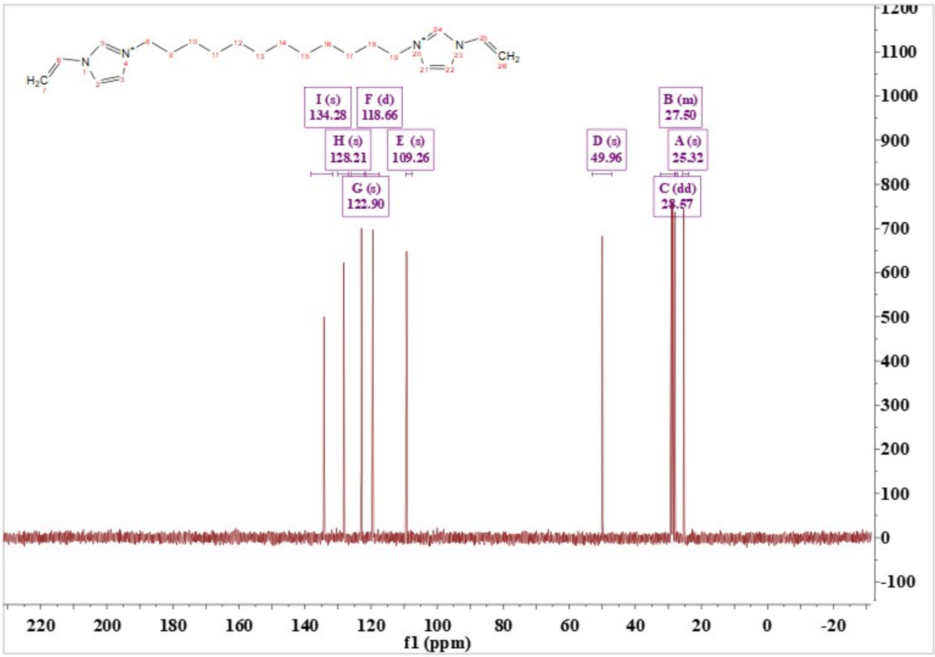


Figure S17 ^{13}C NMR spectra of crosslinker VIm-C$_{12}$-VIm

VIm-C$_{12}$-VIm: ^{13}C NMR (126 MHz, D$_2$O) δ 134.28 (s), 128.21 (s), 122.90 (s), 118.66 (d, J = 197.6 Hz), 109.26 (s), 49.96 (s), 28.57 (dd, J = 68.2, 57.8 Hz), 27.87 – 27.13 (m), 25.32 (s).

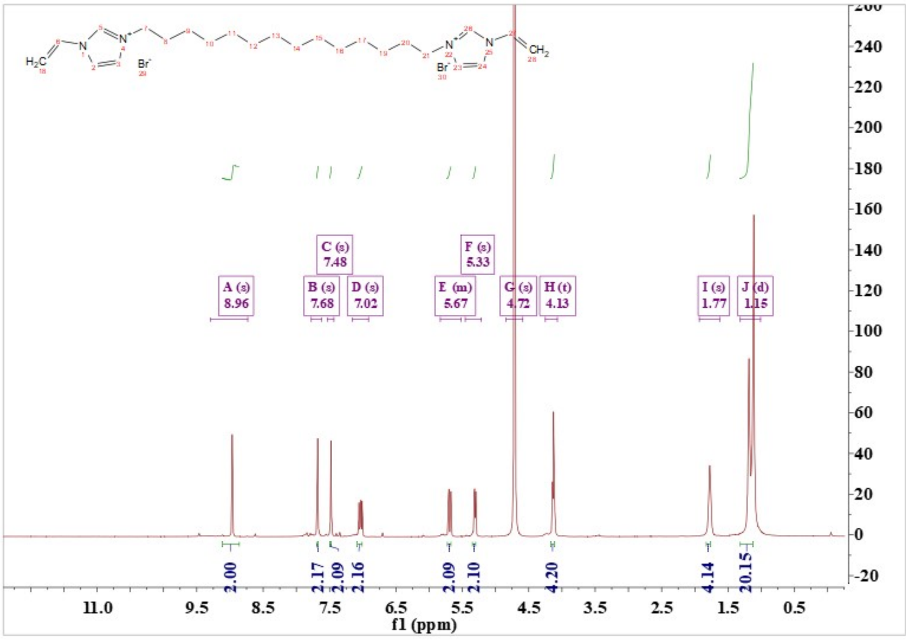


Figure S18 ^{1}H NMR spectra of crosslinker VIm-C$_{14}$-VIm

VIm-C$_{14}$-VIm: ^{1}H NMR (500 MHz, D$_2$O) δ 8.96 (s, 1H), 7.68 (s, 2H), 7.48 (s, 2H), 7.02 (s, 2H), 5.83 – 5.52 (m, 2H), 5.33 (s, 2H), 4.72 (s, 53H), 4.13 (t, J = 7.0 Hz, 5H), 1.77 (s, 6H), 1.15 (d, J = 36.0 Hz, 33H).

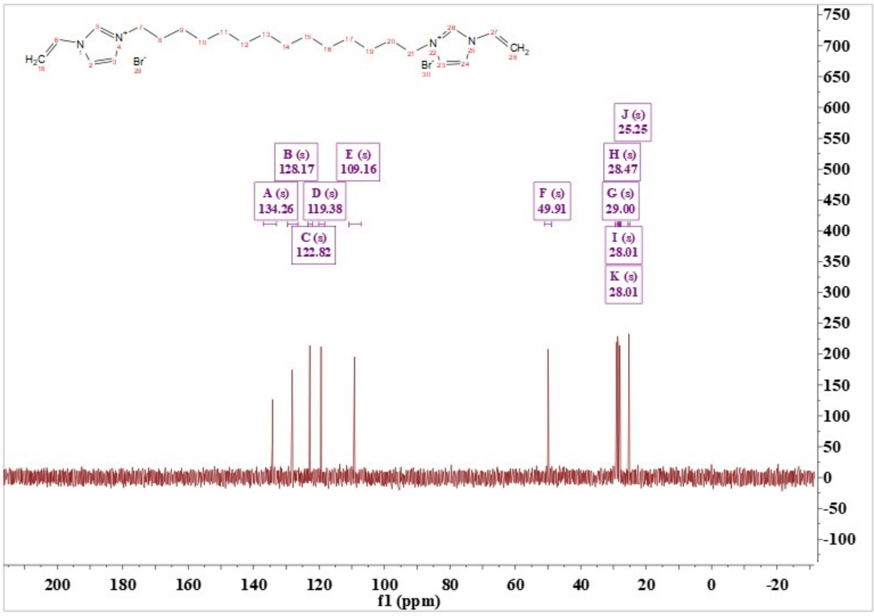


Figure S19 ^{13}C NMR spectra of crosslinker VIm-C_{14}-VIm

VIm-C_{14}-VIm: ^{13}C NMR (126 MHz, D_2O) δ 134.28 (s), 128.21 (s), 122.90 (s), 118.66 (d, J = 197.6 Hz), 109.26 (s), 49.96 (s), 28.57 (dd, J = 68.2, 57.8 Hz), 27.87 – 27.13 (m), 25.32 (s).

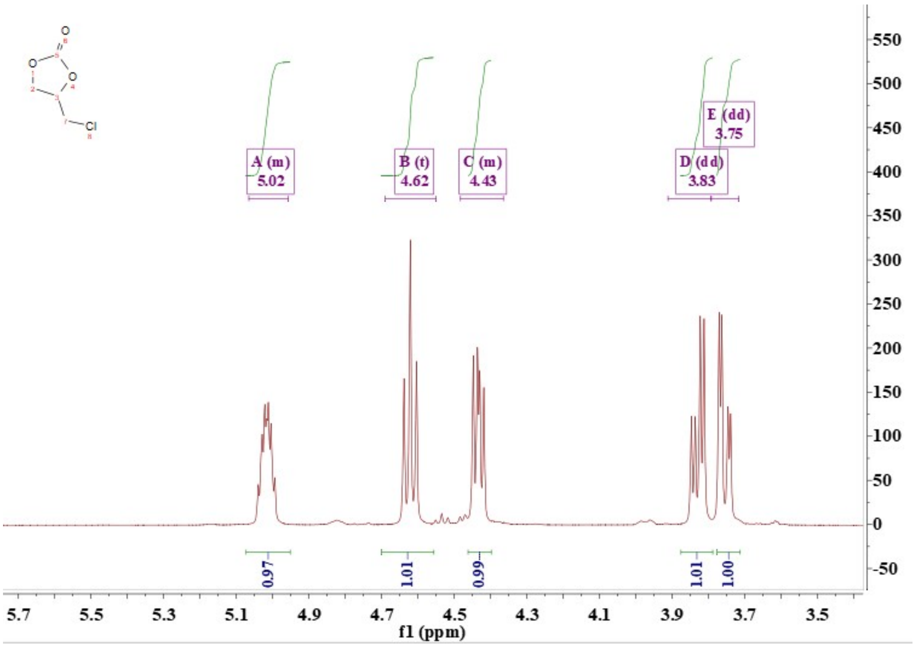


Figure S20 ^{1}H NMR spectra of chloromethyldioxane

Chloromethyldioxane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07-4.96 (m, 1H), 4.62 (t, J = 8.6 Hz, 1H), 4.48 – 4.36 (m, 1H), 3.83 (dd, J = 12.2, 5.3 Hz, 1H), 3.75 (dd, J = 12.2, 3.6 Hz, 1H).

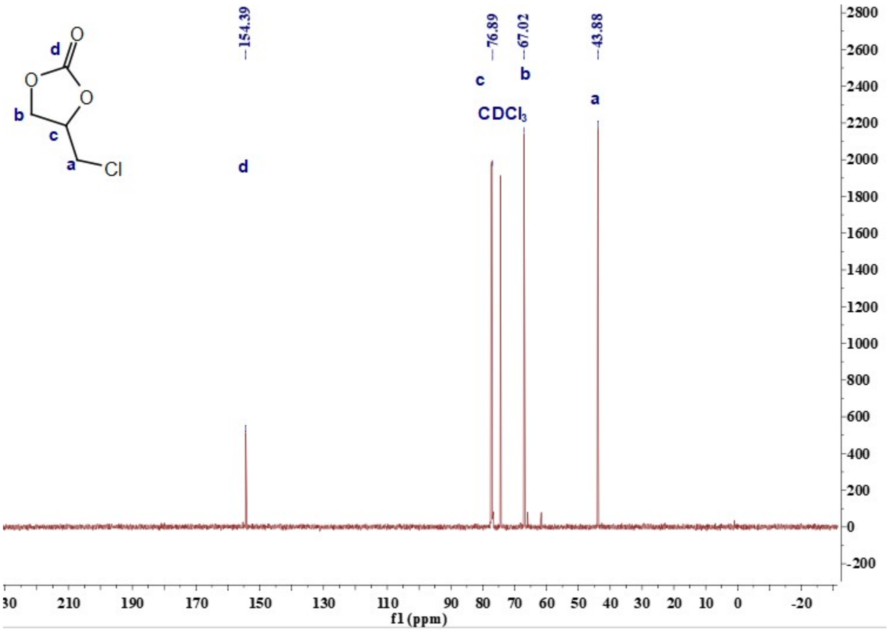


Figure S21 ^{13}C NMR spectra of chloromethyldioxane

Chloromethyldioxane: ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.39 (s), 76.89 (s), 67.02 (s), 43.88 (s).

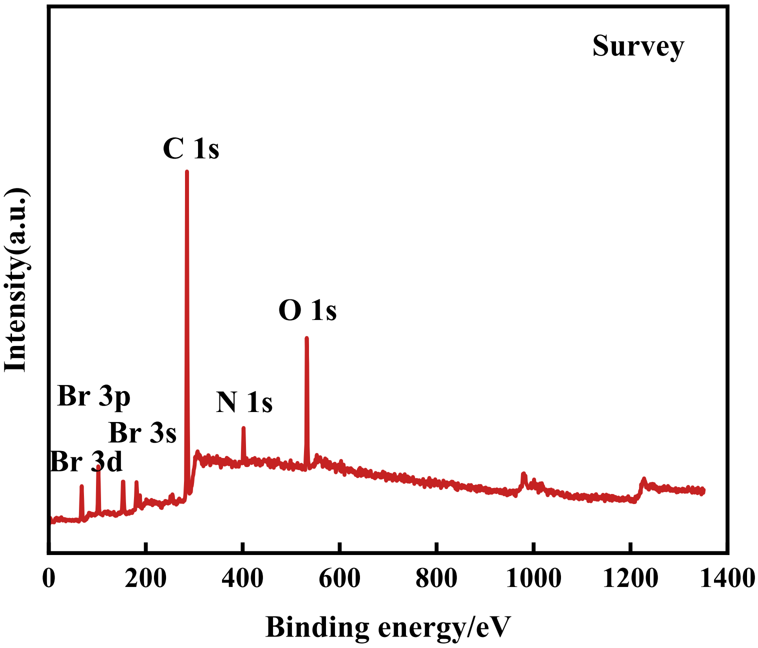


Figure S22 XPS spectra of P-[$VC_{12}Im$]-C_3-Br

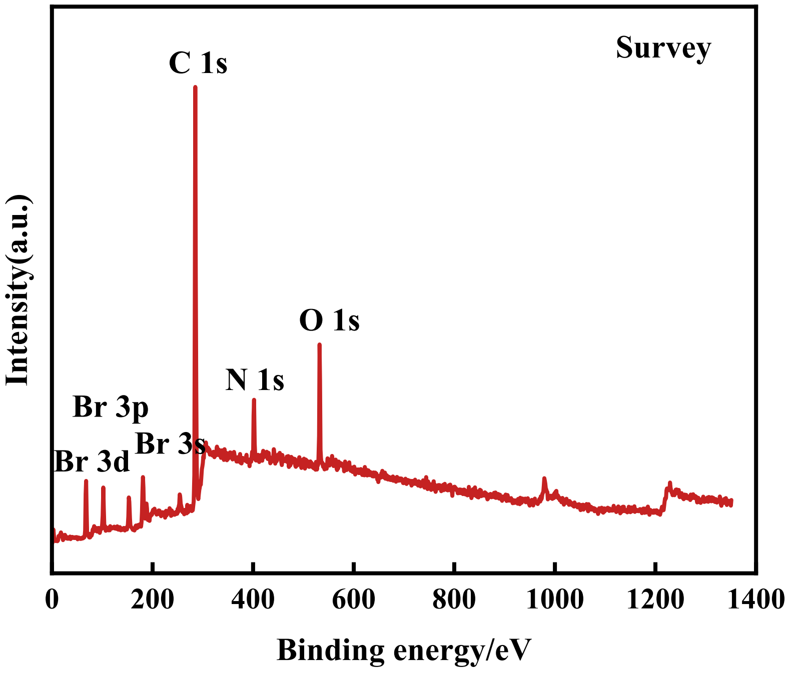


Figure S23 XPS spectra of P-[VC$_{12}$Im]-C$_6$-Br

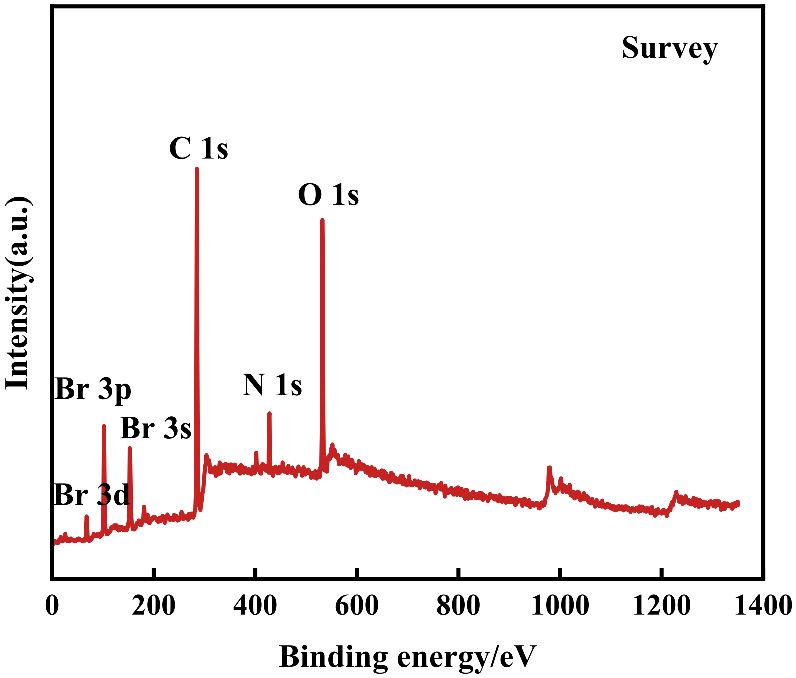


Figure S24 XPS spectra of P-[VC$_{12}$Im]-C$_{14}$-Br

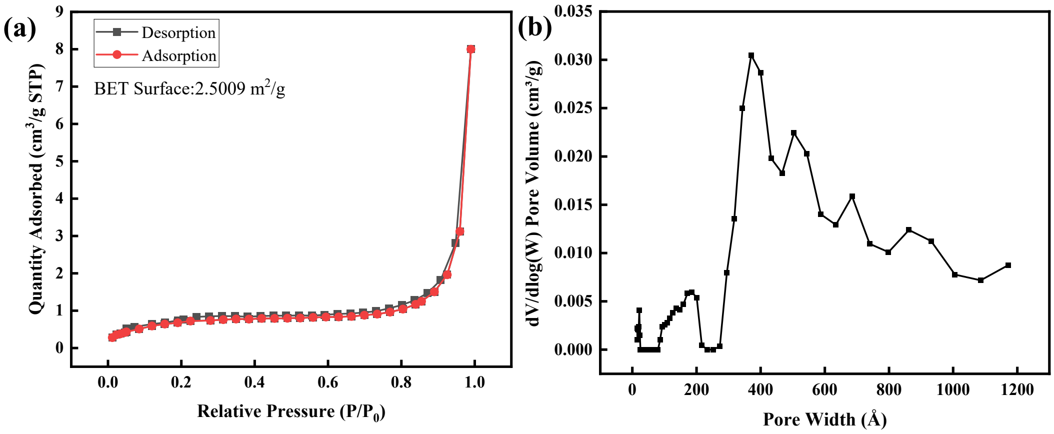


Figure S25 (a) Nitrogn adsorption-desorption isotherm and (b) pore size distribution plot of P-[VC_{12}Im]-C_{12}-Br

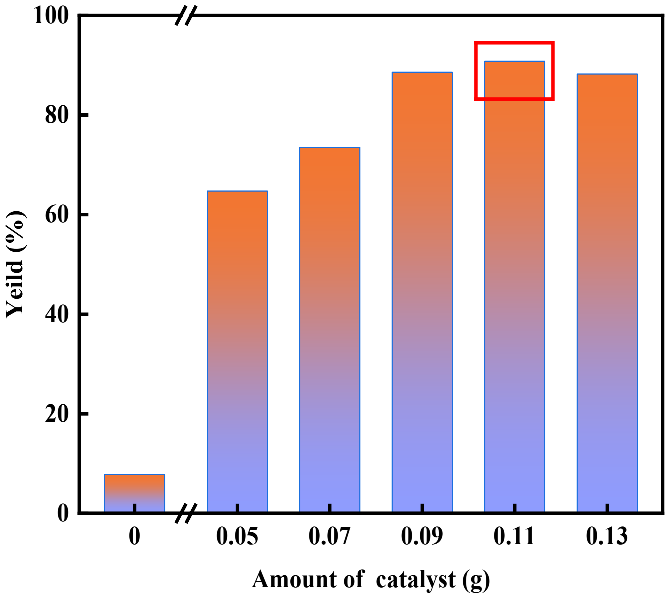


Figure S26 Effect of catalyst dosage of P-[VC_{12}Im]-C_{12}-Br on the yield of chloromethyl oxazolidinone in the CO_2 cycloaddition reaction

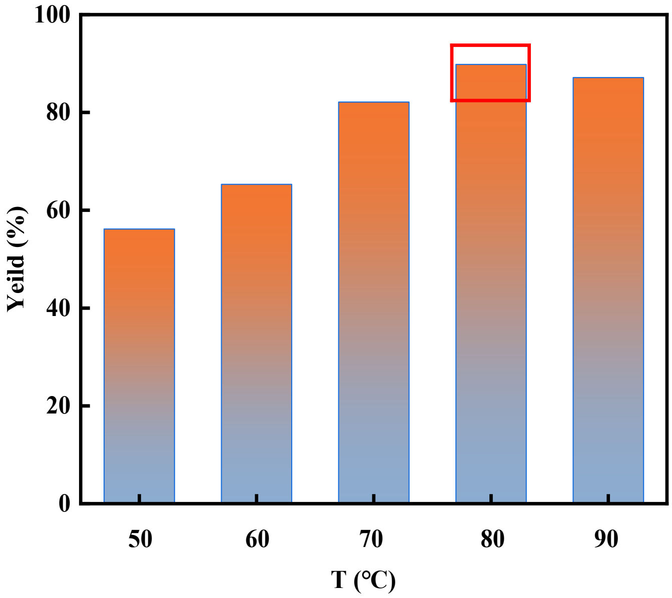


Figure S27 Effect of reaction temperature on the yield of chloromethyl oxazolidinone in the CO_2 cycloaddition reaction catalyzed by P-[$VC_{12}Im$]-C_{12}-Br

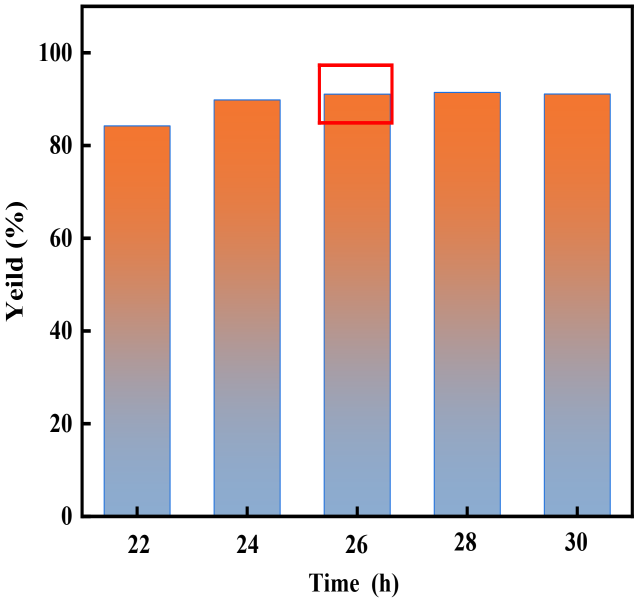


Figure S28 Effect of reaction time on the yield of chloromethyl oxazolidinone in the CO_2 cycloaddition reaction catalyzed by P-[$VC_{12}Im$]-C_{12}-Br

Table S1 Comparison of the catalytic activity for Cycloaddition of CO_2 and epichlorohydrin by the selected reported literature.

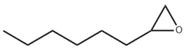
Entry	Catalyst	cocatalyst	Reaction condition	Yeild	Ref.
1	P-[$VC_{12}Im$]-C_{12}-Br	-	0.1 MPa, 80℃, 26 h	91.07%	this work
2	poly[bvbim]Cl	-	0.1MPa, 140℃, 3h	30%	1

3	POP-PBnCl-TPPMg-12	-	0.1 MPa, 30°C, 48 h	53.7%	2
4	P4FIm-7	-	0.1 Mpa, 60°C, 48 h	87.4%	3
5	PQPBrCOOH	-	0.1 Mpa, 100°C, 8 h	65.2%	4
6	P-DAEImOPy	-	0.5 MPa, 110°C, 2 h	95%	5
7	HCPs-[DmPhe]Br	-	1.3 MPa, 130°C, 8 h	97%	6
8	PVBIMCl	-	6 Mpa, 110°C, 3 h	95.8%	7
9	HPILs-Cl-2	TBAB	0.1 Mpa, 70°C, 9 h	99%	8
10	IPOP1-XL	TBAB	0.1 Mpa, 35°C, 36 h	99%	9
11	[PDVB-HAVIM-C$_{18}$]Br	-	0.1 MPa, 80°C, 16 h	96.4%	10
12	[HDBU]Br@P-DD-4/1	-	0.1 MPa, 80°C, 24 h	95%	11
13	P-[VC6Im]Br-C8-5%	-	0.1 MPa, 70°C, 24 h	93%	12

Table S2 Swelling kinetics parameters of P-[VC$_{12}$Im]-C$_n$-Br

SPILs	Parameters of exponential model			Parameters of Scott's second-order swelling kinetics model		
	n	k	R_1^2	a	b	R_2^2
P-[VC$_{12}$Im]-C$_3$-Br	0.514	0.137	0.991	0.269	3.486	0.992
P-[VC$_{12}$Im]-C$_6$-Br	0.595	0.105	0.997	0.157	3.918	0.983
P-[VC$_{12}$Im]-C$_{12}$-Br	0.828	0.049	0.991	0.087	2.905	0.992
P-[VC$_{12}$Im]-C$_{14}$-Br	0.782	0.059	0.990	0.443	2.626	0.995

Table S3 CO$_2$ cycloaddition with long-chain epoxides

Entry	Epoxides	Reaction condition	Yeild
1		0.1 Mpa, 90°C, 28 h	24.75%
2		0.1 Mpa, 90°C, 32 h	1.72%

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