Electronic Supporting Information for

"Controlling the outcome of S_N2 reactions in ionic liquids: From rational data set design to predictive linear regression models"

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Correlation of reaction outcome to Kamlet-Taft parameters using multivariate regression analysis

Correlating reaction outcome with Kamlet–Taft solvent parameters has been used previously to identify how the solvent properties influence the rate constant for the process.[1-5] Kamlet–Taft parameters consist of α, which is the hydrogen bond donating ability of the solvent[6] and associated with the cation of the ionic liquid; β, which is the hydrogen bond accepting ability of the solvent[7] and associated with the anion of the ionic liquid; and π^*, which is the polarizability of the solvent[8] and associated with both components of the ionic liquid. Multivariate regression analysis allows for determination of any relationship between the reaction outcome, in this case k_2, and a combination of parameters as shown in equation S1[9]:

$$\ln(k_2) = \text{intercept} + a\alpha + b\beta + c\pi^* \qquad \text{(S1)}$$

where a, b, and c are coefficients that indicate the relative contribution of each parameter to the fit. In order for a relationship to be significant, the p-value for each coefficient must be less than 0.05.

Due to the nature of measuring Kamlet–Taft parameters, which can involve different dyes and conditions, only parameters that have been determined from one source have been used for this analysis.[10] This limits the analysis to contain only 11 ionic liquids from this study, specifically [bmim][$N(SO_2CF_3)_2$], [bm_2im][$N(SO_2CF_3)_2$], [bm_4im][$N(SO_2CF_3)_2$], [bpy][$N(SO_2CF_3)_2$], [$h_x$py][$N(SO_2CF_3)_2$], [bmpyr][$N(SO_2CF_3)_2$], [bmpi][$N(SO_2CF_3)_2$], [$h_x$mim][$N(SO_2CF_3)_2$], [omim][$N(SO_2CF_3)_2$], [dmim][$N(SO_2CF_3)_2$], and [mTOA][$N(SO_2CF_3)_2$].

Initially, only the first seven ionic liquids listed (those that had available rate constant date for the reaction investigated at the inception of the project) were considered. A significant correlation was found between the rate constant for the process and a combination of α and π^* parameters:

$$\ln(k_2) = 4.66\alpha - 10.35\pi^*$$

with p-values of 0.046 and 0.00013 respectively. This correlation can be represented graphically in Figure S1. Other combinations were also analysed; these are shown below with the respective p-values in italics and parentheses.

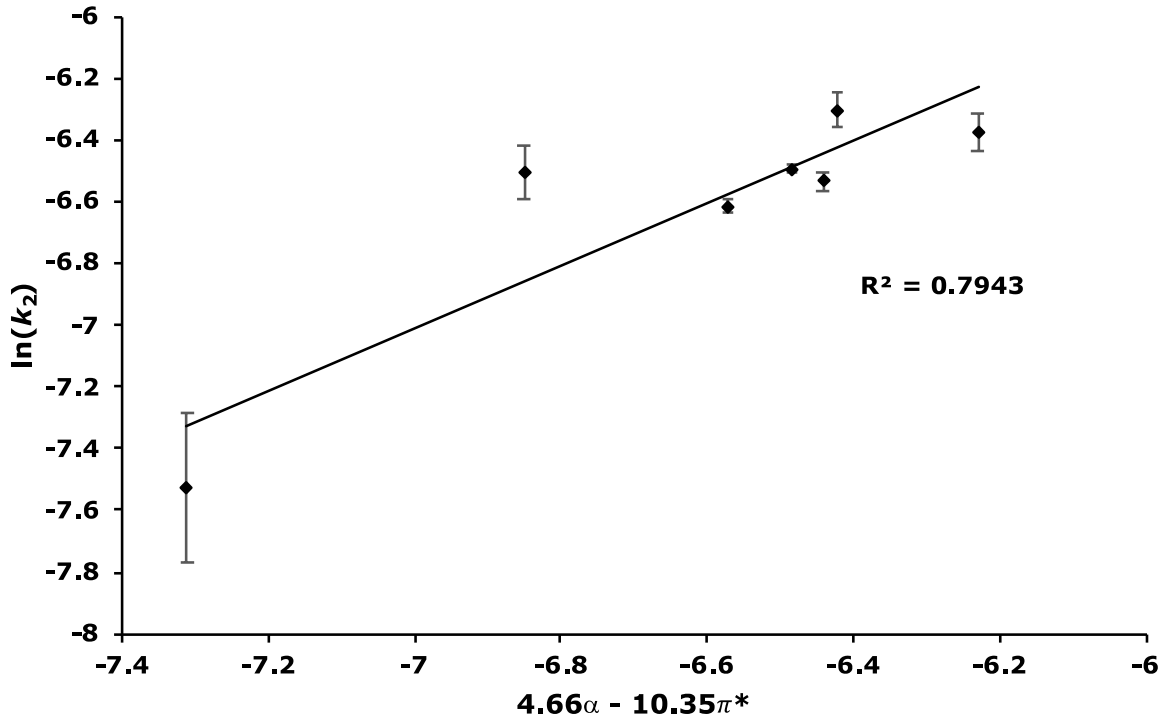


Figure S1. The relationship between the natural logarithm of k_2 and a combination of the α and π^* parameters for the reaction between benzyl bromide **1** and pyridine **2** in mixtures of one of seven ionic liquids. Uncertainties reported by transforming reported errors on calculating the natural logarithm.

The analysis was then extended to all eleven ionic liquids and found a similar significant correlation:

$$\ln(k_2) = 6.20\alpha - 11.33\pi^*$$

with p-values of 0.0026 and 2.51 x 10^{-7} respectively. This correlation can be represented graphically in Figure S2. Significant correlations were also found between ln(k_2) and the β parameter (including the intercept), as well as with β and π^* (correlations listed below). In both cases, the coefficients in front of these parameters were negative, indicating that high β and π^* values disfavour this reaction and would result in a low k_2 value. Once again, other combinations were also analysed; these are shown below with the respective p-values in italics and parentheses.

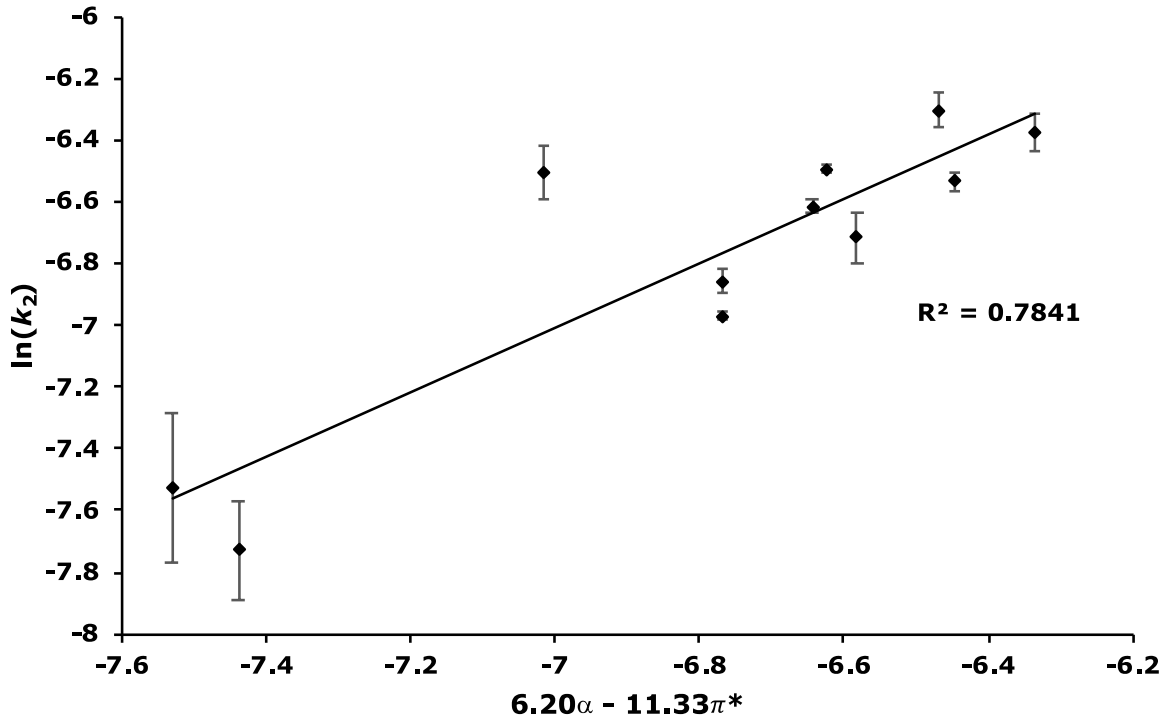


Figure S2. The relationship between the natural logarithm of k_2 and a combination of the α and π^* parameters for the reaction between benzyl bromide **1** and pyridine **2** in mixtures of one of eleven ionic liquids. Uncertainties reported by transforming reported errors on calculating the natural logarithm.

Analyses for seven ionic liquids

Combination of α, β, and π^* with intercept

$\ln(k_2) = -4.03(0.39) - 0.81(0.87)\alpha - 15.96(0.29)\beta + 5.51(0.70)\pi^*$

Combination of α and β with intercept

$\ln(k_2) = -2.45(0.16) + 1.01(0.58)\alpha - 10.74(0.010)\beta$

Combination of α and π^* with intercept

$\ln(k_2) = 0.22(0.93) + 4.63(0.081)\alpha - 10.61(0.022)\pi^*$

Combination of β and π^* with intercept

$\ln(k_2) = -3.51(0.22) - 13.96(0.033)\beta + 3.44(0.49)\pi^*$

Combination of α and intercept

$\ln(k_2) = -7.99(0.0054) + 2.89(0.46)\alpha$

Combination of β and intercept

$\ln(k_2) = -1.82(0.11) - 11.09(0.0034)\beta$

Combination π^* and intercept

$\ln(k_2) = 1.02(0.78) - 8.97(0.069)\pi^*$

Combination of α, β, and π^*

$\ln(k_2) = 2.58(0.46)\alpha - 5.59(0.47)\beta - 6.37(0.28)\pi^*$

Combination of α and β

$\ln(k_2) = -1.05(0.47)\alpha - 14.15(0.00021)\beta$

Combination of α and π^*

$\ln(k_1) = 4.66(0.046)\alpha - 10.36(0.00013)\pi^*$

Combination of β and π^*

$\ln(k_2) = -10.25(0.047)\beta - 2.57(0.25)\pi^*$

Analyses for eleven ionic liquids

Combination of α, β, and π^* with intercept

$\ln(k_2) = -1.66(0.40) + 2.12(0.23)\alpha - 7.23(0.012)\beta - 3.32(0.35)\pi^*$

Combination of α and β with intercept

$\ln(k_2) = -3.22(0.011) + 1.09(0.40)\alpha - 9.00(8.85 \times 10^{-5})\beta$

Combination of α and π^* with intercept

$\ln(k_2) = 1.02(0.70) + 6.08(0.005)\alpha - 12.45(0.0026)\pi^*$

Combination of β and π^* with intercept

$\ln(k_2) = -2.17(0.28) - 9.37(0.00027)\beta - 0.44(0.87)\pi^*$

Combination of α and intercept

$\ln(k_2) = -9.28(5.35 \times 10^{-5}) + 5.31(0.086)\alpha$

Combination of β and intercept

$\ln(k_2) = -2.47(0.000070) - 9.53(9.75 \times 10^{-6})\beta$

Combination π^* and intercept

$\ln(k_2) = 2.85(0.48) - 11.26(0.034)\pi^*$

Combination of α, β, and π^*

$\ln(k_2) = 2.42(0.16)\alpha - 6.39(0.011)\beta - 5.88(0.0097)\pi^*$

Combination of α and β

$\ln(k_2) = -2.36(0.027)\alpha - 12.52(2.75 \times 10^{-7})\beta$

Combination of α and π^*

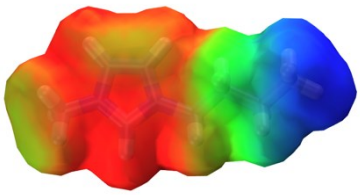
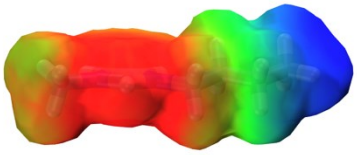
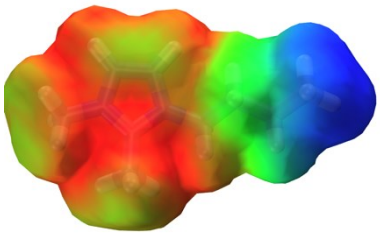
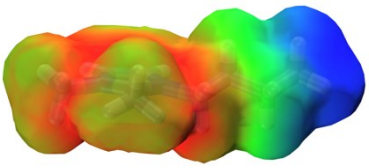
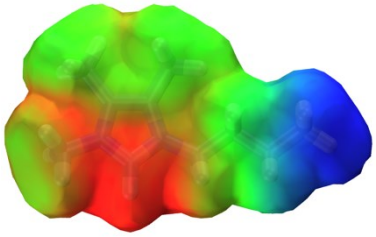
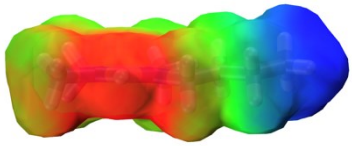
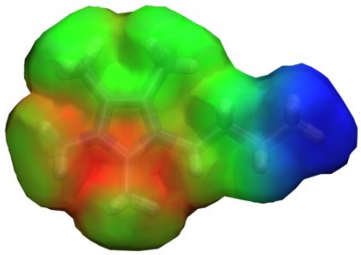
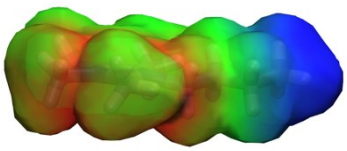
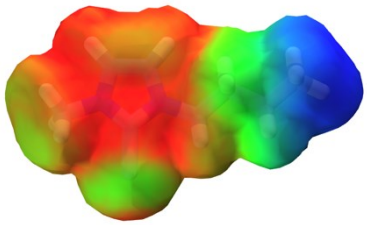
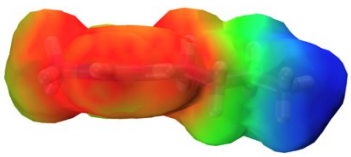
$\ln(k_2) = 6.20(0.0026)\alpha - 11.33(2.52 \times 10^{-7})\pi^*$

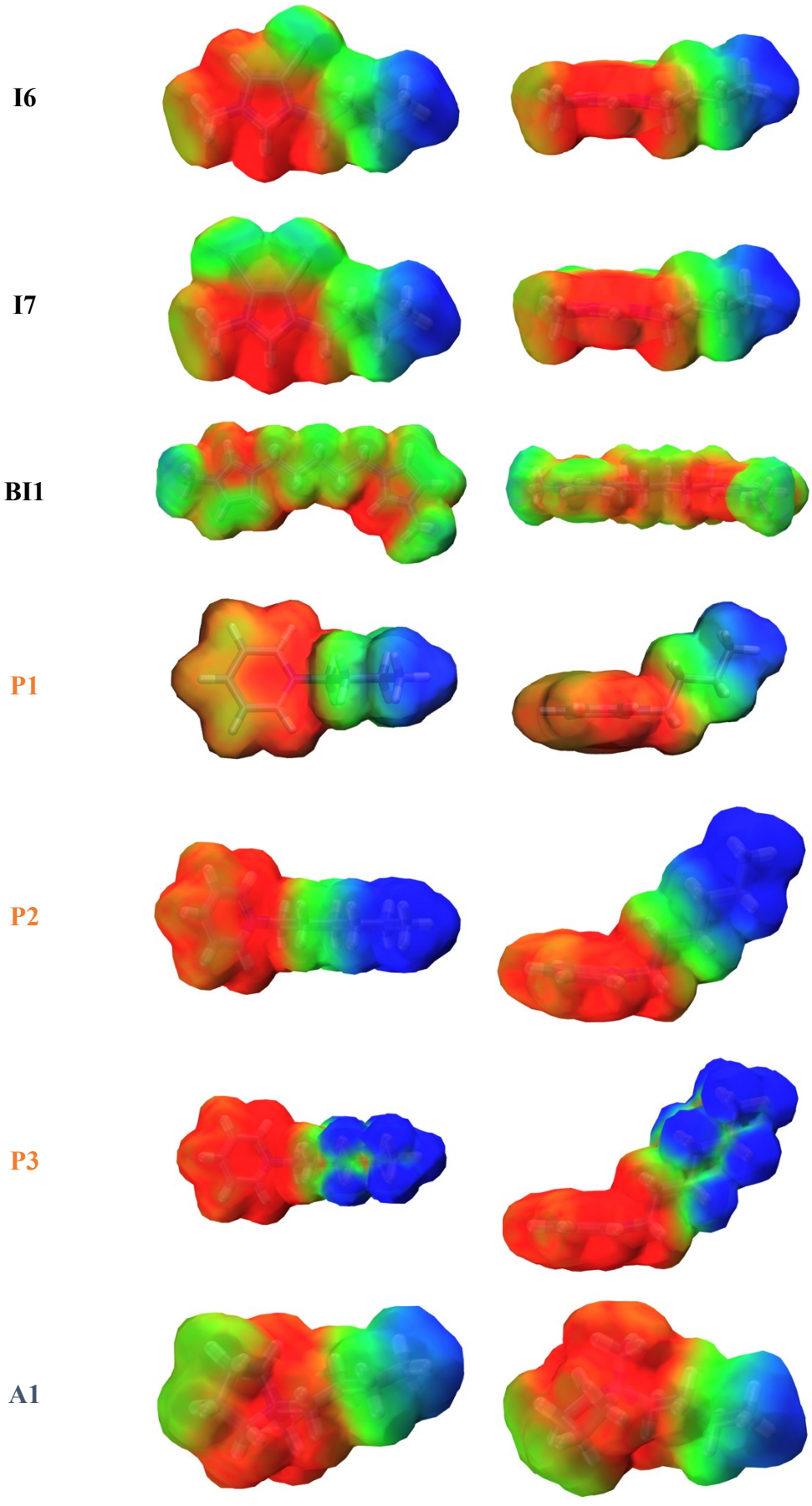
Combination of β and π^*

$\ln(k_2) = -8.62(0.00016)\beta - 3.37(0.0014)\pi^*$

Molecular electrostatic potentials for the cations considered

Table S1. The molecular electrostatic potential (MEP) for each of the cations of the ionic liquids considered in the original analysis. MEP colour range is represented on a blue-green-red colour scale ranging from 50 to 100 kcal mol^{-1} (100 to 150 for compound **BI1**) mapped onto the molecular electronic isodensity surface (isovalue 0.02 *e* $Å^{-3}$).

Ionic liquid cation	Molecular electrostatic potential of cation	
	Top view	Side view
I1		
I2		
I3		
I4		
I5		


I6
I7
BI1
P1
P2
P3
A1

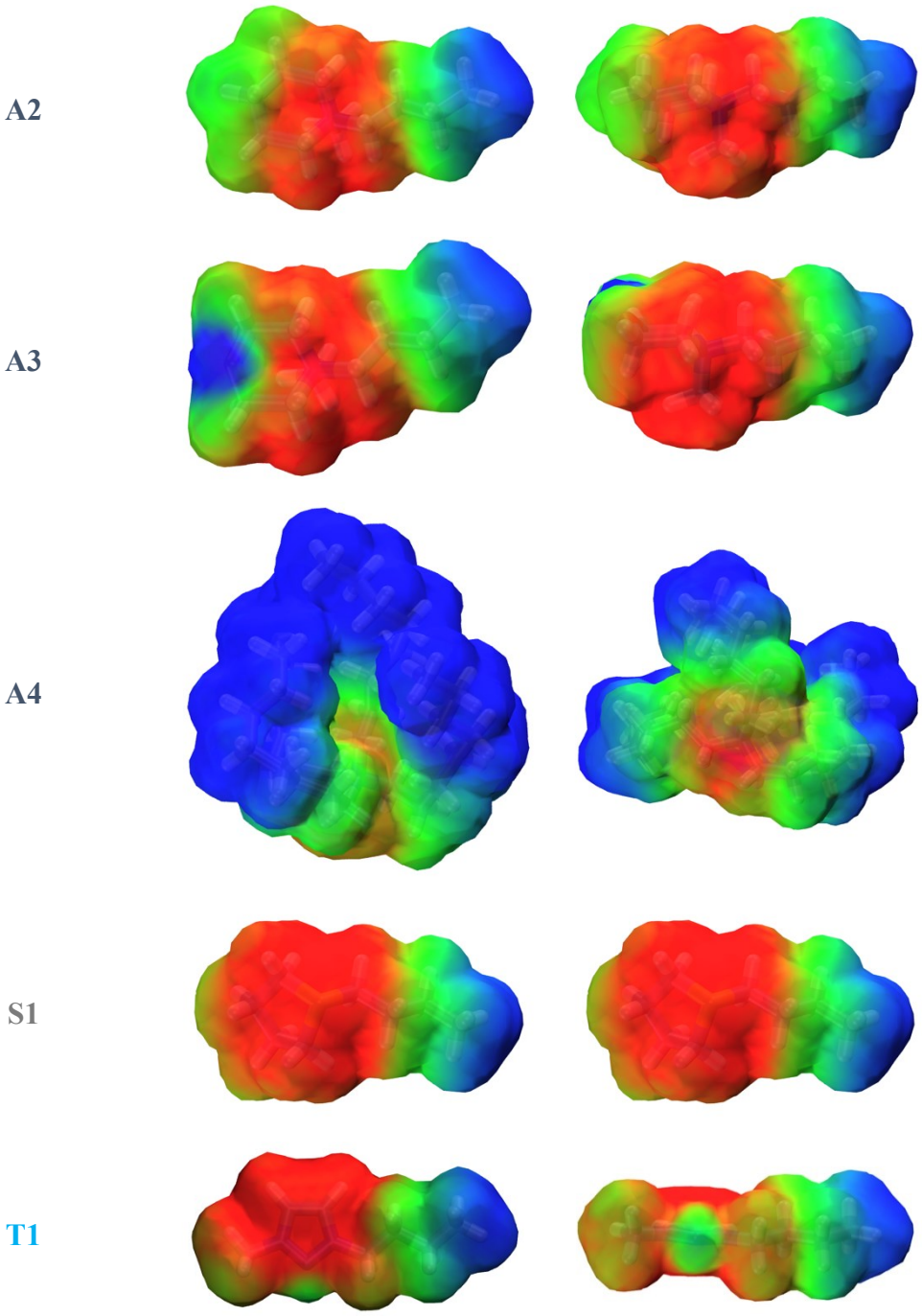
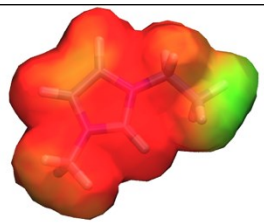
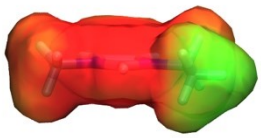
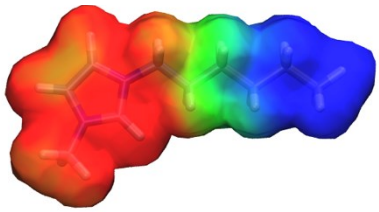
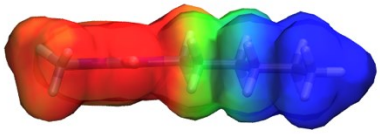
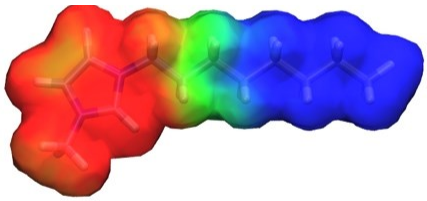
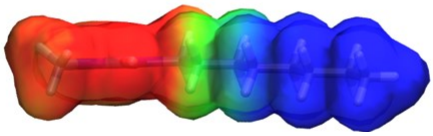
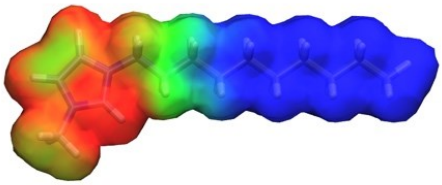
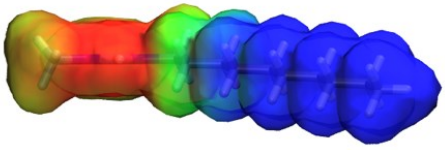
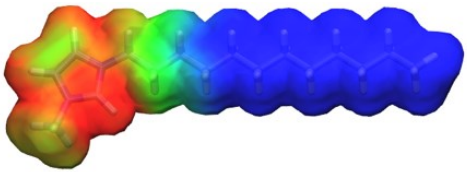
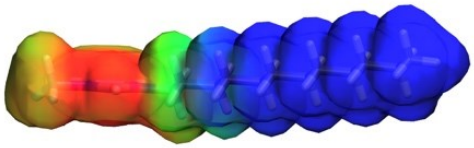
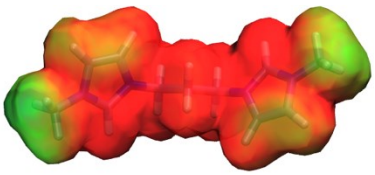
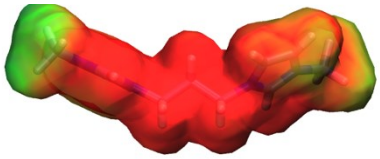
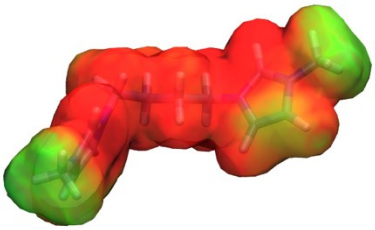
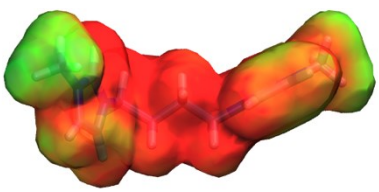
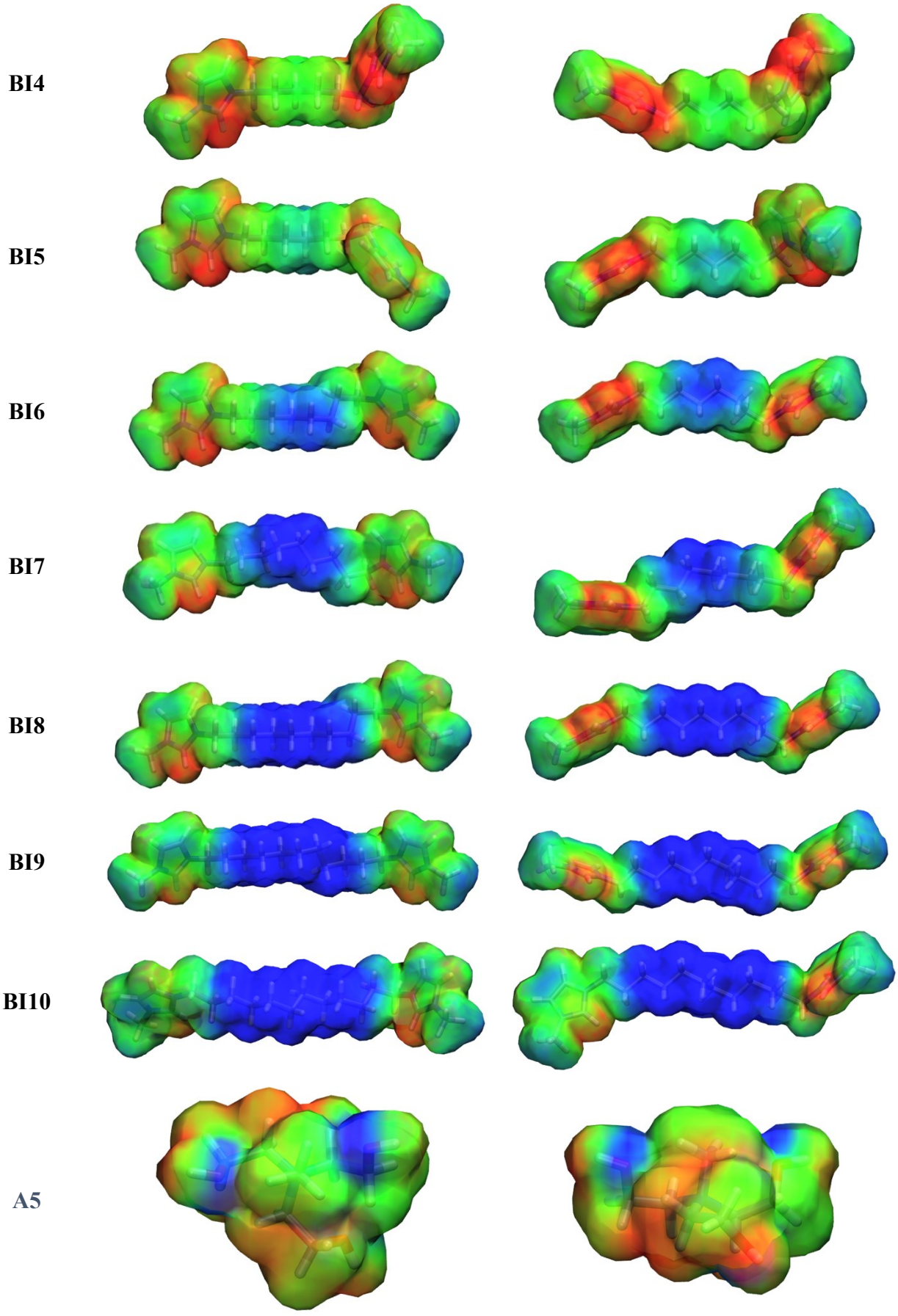
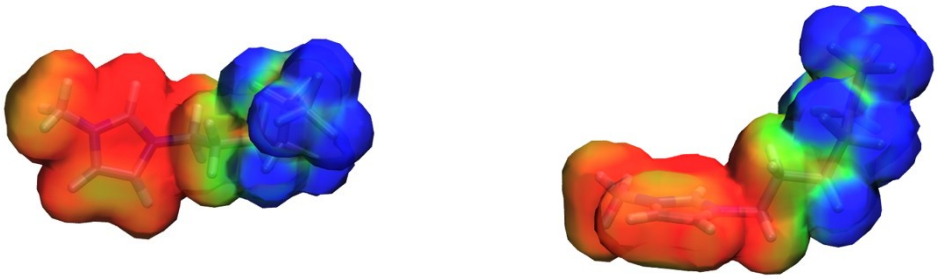

A2
A3
A4
S1
T1

Table S2. The molecular electrostatic potential (MEP) for each of the cations of the ionic liquids considered of the second data set. MEP colour range is represented on a blue-green-red colour scale ranging from 50 to 100 kcal mol^{-1} (100 to 150 for compounds **BI2-BI0**) mapped onto the molecular electronic isodensity surface (isovalue 0.02 *e* $Å^{-3}$).

Ionic liquid cation	Molecular electrostatic potential of cation	
	Top view	Side view
I8		
I9		
I10		
I11		
I12		
BI2		
BI3		


BI4
BI5
BI6
BI7
BI8
BI9
BI10
A5

I13



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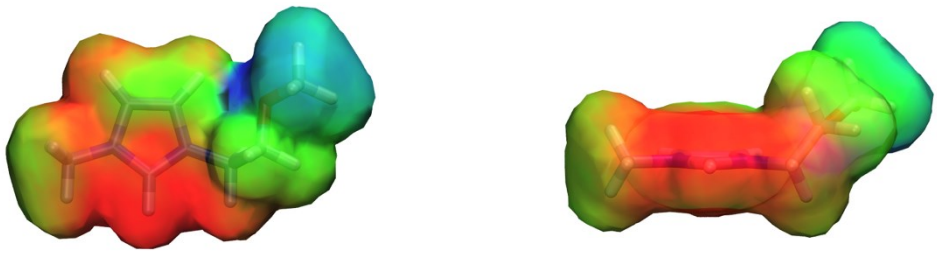

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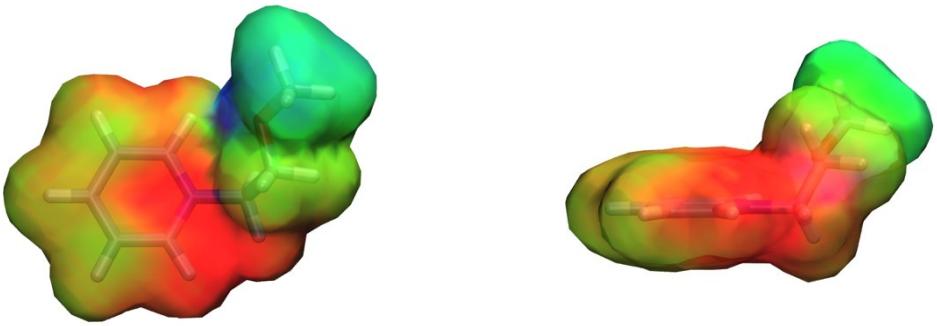

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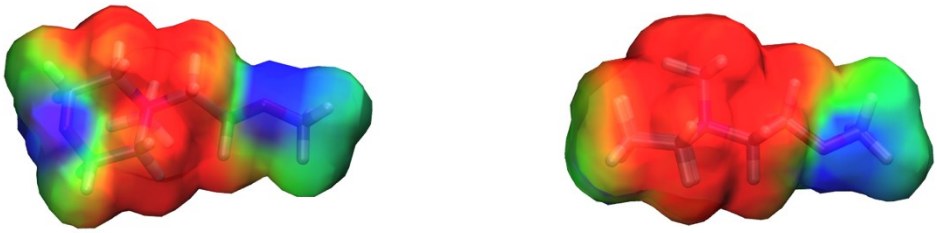

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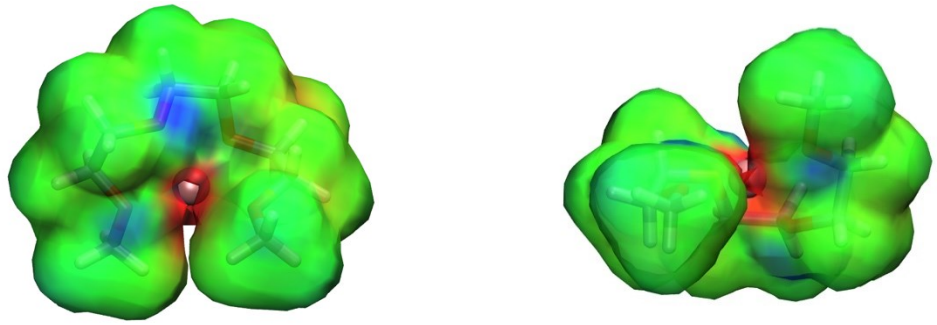

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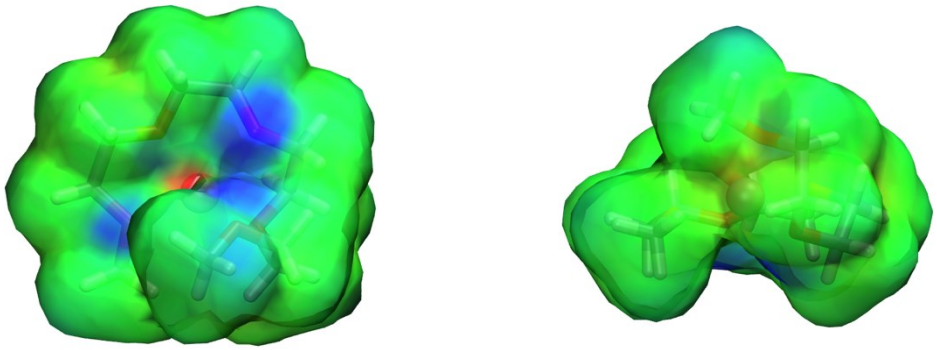


The full set of calculated descriptors used for each cation

The description of local properties and all calculated descriptors can be found at the following Figshare repository:

The repository contains:

- Full list of descriptors (.xlsx file)
- Linear regression and ANN model and cross-correlation results (xlsx files)
- QM (EMPIRE) input, output, wave function files; structure files (xyz input, dat output)
- Parasurf input and output files
- Gaussian cube files of electron density, Electrostatic Potential, ionisation energy, electron affinity, electronegativity, and molecular hardness

Figshare repository DOI: 10.6084/m9.figshare.1274963

Linear correlation and dependency analysis of molecular descriptors

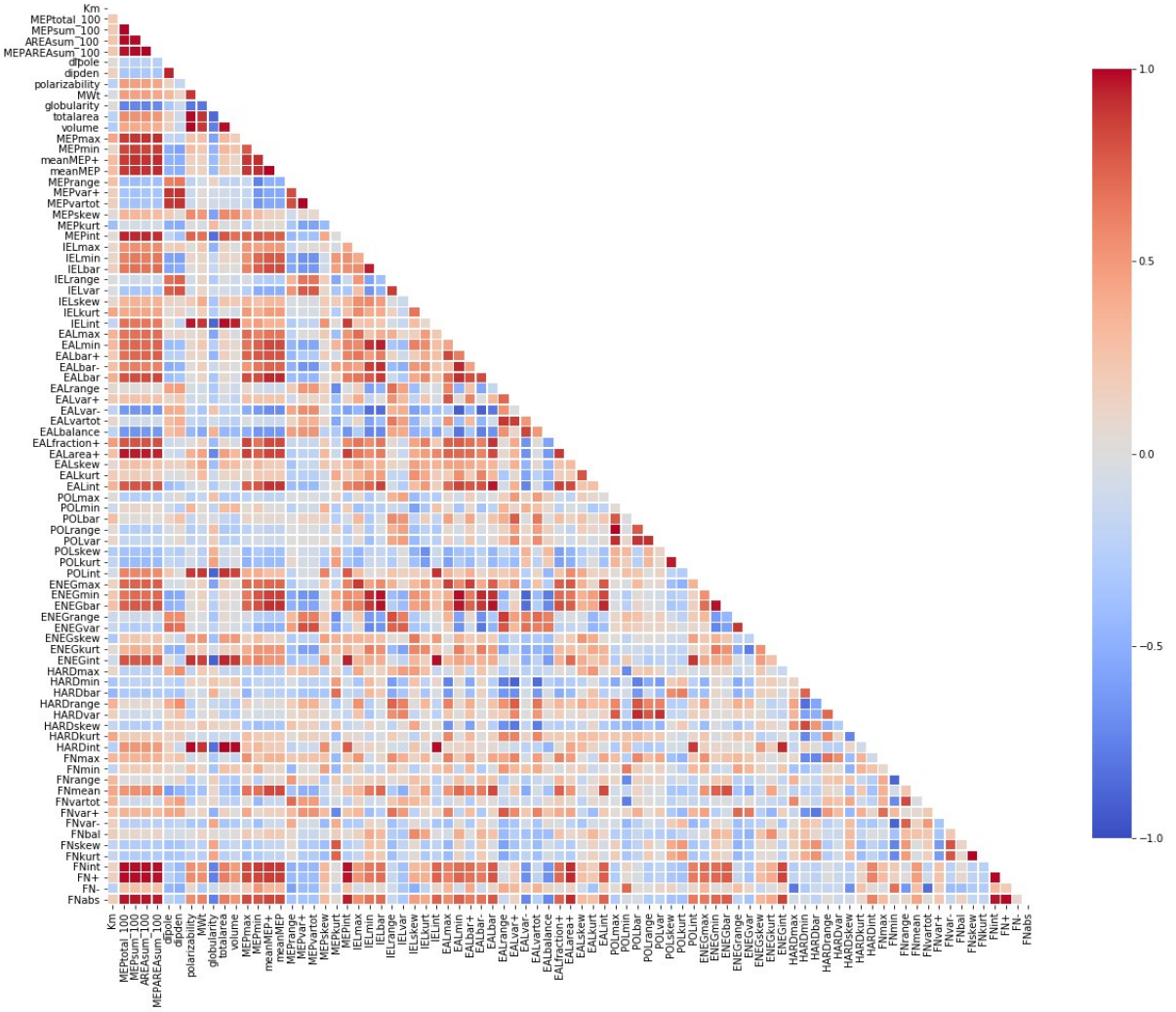


Figure S3. Correlation matrix heat map of the local molecular property descriptors analysed in this work.

Table S3. Selected results for F-Tests and Mutual Information (MI) Tests.

Parameter	F-test	MI-Test
MEPmax	1.00	0.00
meanMEP	0.46	0.20
MEPrange	0.72	0.36
EALbar-	0.70	0.05
EALbar	0.75	0.28
EALfraction	0.91	0.86
EALarea	0.57	0.28
EALint	0.81	0.33
POLkur	0.67	0.40
ENEGmin	0.45	0.50
ENEGbar	0.70	0.32
ENEGskew	0.87	0.96
HARDkurt	0.84	0.00
HARDint	0.56	0.43
FNmin	0.51	0.59
FNmean	0.94	0.39

Summary of regression models in this study

Table S4. R^2 correlation analysis for linear regression models using different combinations of three molecular descriptors using (a) data set 1 without **BI1**, (b) data set 1 without **BI1** and **S1**, and (c) data set 1 without **BI1**, **S1** and **A3**.

(a)

Parameter	MEPareasum	MEPtotal
	0.50	0.52
dipden	0.62	0.63
ENEGmin	0.53	0.53
dipole	0.59	0.59
EALfraction+	0.57	0.56
dipden and ENEGmin	0.69	0.69

(b)

Parameter	MEPareasum	MEPtotal
	0.61	
dipden	0.68	0.71
ENEGmin	0.68	0.70
dipole	0.66	
EALfraction+	0.61	
dipden and ENEGmin	0.78	0.81

(c)

Parameter	MEPareasum	MEPtotal
	0.72	
dipden	0.72	
ENEGmin	0.83	0.84
dipole	0.72	
EALfraction+	0.77	0.78
dipden and ENEGmin	0.85	0.86

Table S5. R^2 correlation analysis for newly defined MEP based descriptors with measured reaction constant for (a) data set 1 and (b) data set 1 without **BI1**.

(a)

Parameter	Cutoff MEP 80	Cutoff MEP 90	Cutoff MEP 100
MEPtotal	0.09	0.14	0.12
MEPsum	0.15	0.10	0.09
MEParea	0.09	0.14	0.12
MEPareasum	0.08	0..11	0.10

(b)

Parameter	Cutoff MEP 80	Cutoff MEP 90	Cutoff MEP 100	Cutoff MEP 100
MEPtotal	0.23	0.30	0.51	0.35
MEPsum	0.15	0.34	0.50	0.35
MEParea	0.21	0.29	0.51	0.34
MEPareasum	0.32	0.33	0.50	0.34

Table S6. R^2 correlation analysis for linear regression models using different combinations of three molecular descriptors (including one newly defined descriptor) using (a) data set 1 without **BI1**, (b) data set 1 without **BI1** and **S1**, and (c) data set 1 without **BI1**, **S1** and **A3**.

(a)

Parameter	ENEGmin	ENEGmax	ENEGrange	dipden	
EALfraction+	0.625	0.635	0.689	0.653	
EALmin	0.557	0.647	0.689	0.733	
EALbar-	0.610	0.712	0.710	0.758	**MEPtotal**
EALbar	0.565	0.749	0.746	0.637	
dipden	0.696	0.693	0.745	0.634	
EALfraction+	0.545	0.628	0.699	0.517	
EALmin	0.539	0.627	0.654	0.673	
EALbar-	0.584	0.678	0.684	0.651	**MEPtop25**
EALbar	0.550	0.751	0.753	0.530	
dipden	0.613	0.546	0.627	0.488	

(b)

Parameter	ENEGmin	ENEGmax	ENEGrange	dipden	
EALfraction+	0.725	0.688	0.746	0.714	
EALmin	0.722	0.711	0.739	0.837	
EALbar-	0.713	0.765	0.771	0.840	**MEPtotal**
EALbar	0.732	0.752	0.782	0.720	
dipden	0.811	0.731	0.777	0.714	
EALfraction+	0.579	0.607	0.691	0.513	
EALmin	0.530	0.519	0.540	0.596	
EALbar-	0.545	0.533	0.550	0.517	**MEPtop25**
EALbar	0.530	0.658	0.683	0.430	
dipden	0.555	0.345	0.443	0.322	

(c)

Parameter	ENEGmin	ENEGmax	ENEGrange	dipden	
EALfraction+	0.861	0.810	0.859	0.787	
EALmin	0.848	0.8267	0.828	0.866	
EALbar-	0.850	0.832	0.836	0.848	**MEPtotal**
EALbar	0.848	0.861	0.883	0.792	
dipden	0.856	0.744	0.767	0.744	
EALfraction+	0.841	0.802	0.855	0.774	
EALmin	0.728	0.724	0.724	0.726	
EALbar-	0.744	0.640	0.643	0.653	**MEPtop25**
EALbar	0.741	0.809	0.825	0.707	
dipden	0.719	0.562	0.578	0.560	

Table S7. Descriptors used, correlation and statistics for best scoring regression models trained in this study. Data in brackets represents statistics for 6-fold random cross-validation. Models *D*', *E*', and *F*' represent forward propagation artificial neural networks (ANNs). MAE: Mean absolute error; MSE: Mean standard error; RC: Rank correlation.

Model	Training data set	Descriptors	R^2	MAE / 10^{-4} L mol^{-1} s^{-1}	MSE / 10^{-4} L mol^{-1} s^{-1}	RC / %	Figure
A	16 ions w.o. **S1**	MEPmax, MEPmean, MEPrange	0.87	2.19	6.76	79.4	3
B	16 ions w.o. **BI1**	MEPtotal100, dipden, EALbar-	0.64	4.33	29.57	82.1	S4
C	15 ions w.o. **S1**, **BI1**	MEPtotal100, dipden, EALbar-	0.74	3.49	19.45	78.2	S5
D	14 ions w.o. **S1**, **BI1, A3**	MEPtotal100, EALbar, ENEGrange	0.88	1.45	4.11	85.9	4
A	37 ions w.o. **S1**	MEPmax, MEPmean, MEPrange	0.49	4.65	37.31	65.5	S6
B	28 ions w.o. **BI1-9**	MEPtotal100, dipden, EALbar-	0.74	3.85	23.97	90.1	S7
C	27 ions w.o. **S1, BI1-9**	MEPtotal100, dipden, EALbar-	0.81	3.30	13.97	90.2	S8
D	26 ions w.o. **S1, A3, BI1-9**	MEPtotal100, EALbar, ENEGrange	0.82 (0.69, 85%)	3.01 (3.58)	12.30	88.2	6a
D'	26 ions w.o. **S1**, **A3**, **BI1-9**	MEPtotal100, EALbar, ENEGrange	0.89 (0.72, 81%)	1.78 (3.02)		95.8	6b

D'	All 38 ions	MEPtotal100, EALbar, ENEGrange	0.81 (0.53, 65%)	2.88 (4.24)		87.7	6c
E	26 ions w.o. **S1**, **A3**, **BI1-9**	EALfraction+, POLskew, HARDmax	0.82 (0.75, 91%)	2.66 (2.96)	12.24	89.9	S9
E'	26 ions w.o. **S1**, **A3**, **BI1-9**	EALfraction+, POLskew, HARDmax	0.91 (0.68, 75%)	2.01 (3.61)		92.3	S10
E'	All 38 ions	EALfraction+, POLskew, HARDmax	0.82 (0.32, 39%)	2.56 (5.67)		84.6	S11
F	26 ions w.o. **S1**, **A3**, **BI1-9**	MEPtotal100, EALarea+, ENEGrange	0.80	3.03	13.20	86.7	S12
F'	26 ions w.o. **S1**, **A3**, **BI1-9**	MEPtotal100, EALarea+, ENEGrange	0.91 (0.67, 0.74%)	1.85 (3.88)		95.0	S13
F'	All 38 ions	MEPtotal100, EALarea+, ENEGrange	0.80 (0.51, 63%)	2.87 (4.30)		85.5	S14

The optimization of the ANNs included cross-validations optimization by altering the number of nodes, layers, and optimization cycles for the ANNs; The details of those can be found online on the Figshare repository (DOI: 10.6084/m9.figshare.1274963).

Table S8. Parameters for linear regression models corresponding to linear regression equations of the form $a\times A + b\times B + c\times C + d$, where A, B, C denote the molecular descriptors of the corresponding models in order as listed in Table S7 above. Coefficients are rounded to 3 significant figures.

Model	Data set	*a*	*b*	*c*	*d*
A	1	0.479	0.835	0.611	-41.5
A	2	-0.263	0.548	0.418	-31.4
B	1	9.98×10^{-3}	-264	0.338	17.8
B	2	10.1×10^{-3}	-87.5	0.132	5.15
C	1	8.48×10^{-3}	-184	0.273	15.0
C	2	7.97×10^{-3}	-9.28	0.146	5.61
D	1	3.24×10^{-3}	0.232	-0.113	28.8
D	2	3.24×10^{-3}	0.232	0.113	28.8
E	2	23.9	-5.47	29.4×10^{-3}	2.84
F	2	7.18×10^{-3}	30.9×10^{-3}	-72.2×10^{-3}	10.3

Evaluation of efficacy of final models not included in main text

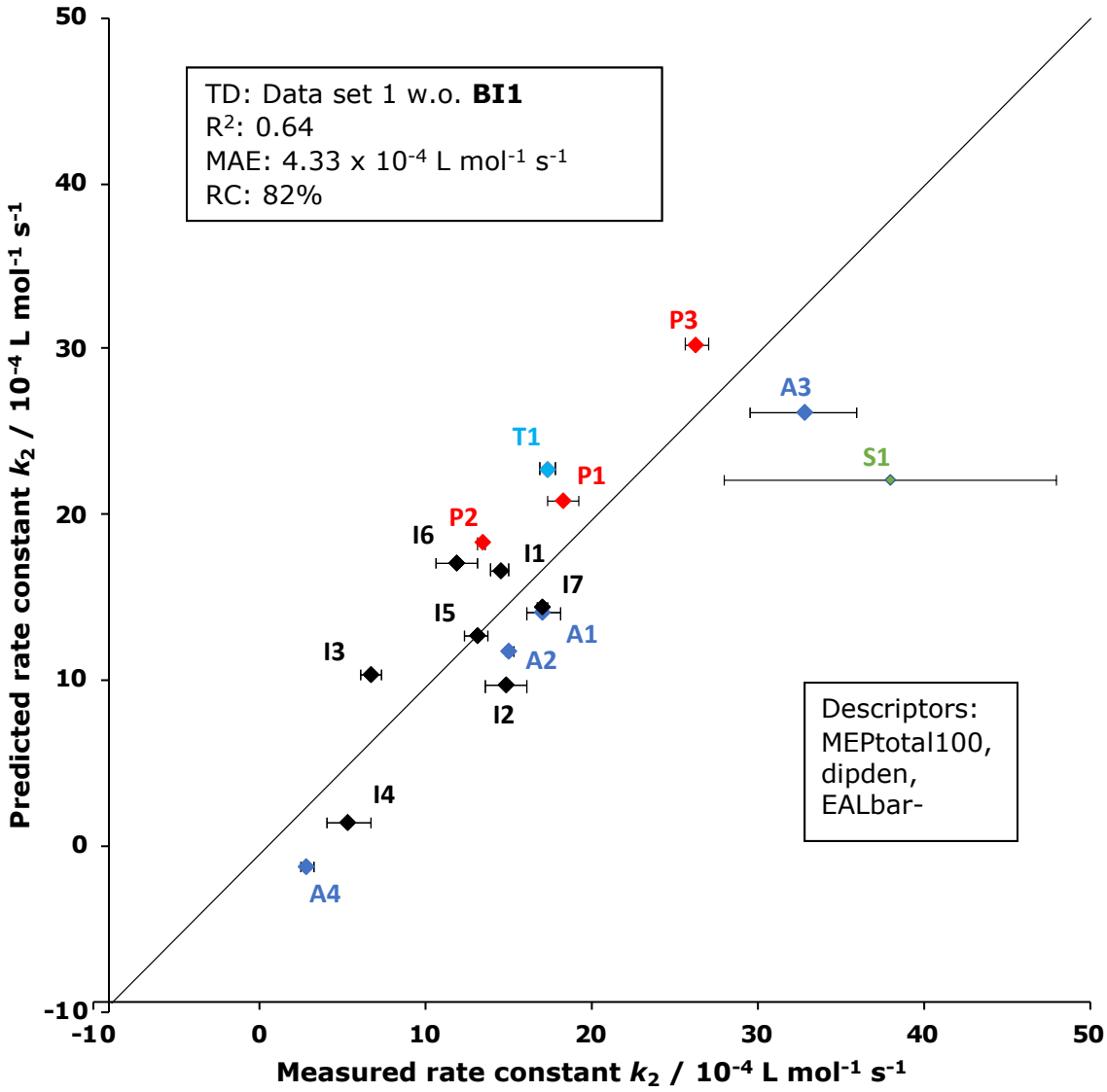


Figure S4. Correlation of linear regression model *B* with experimentally observed kinetic data, using the descriptors MEPtotal100, dipden, EALbar-. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

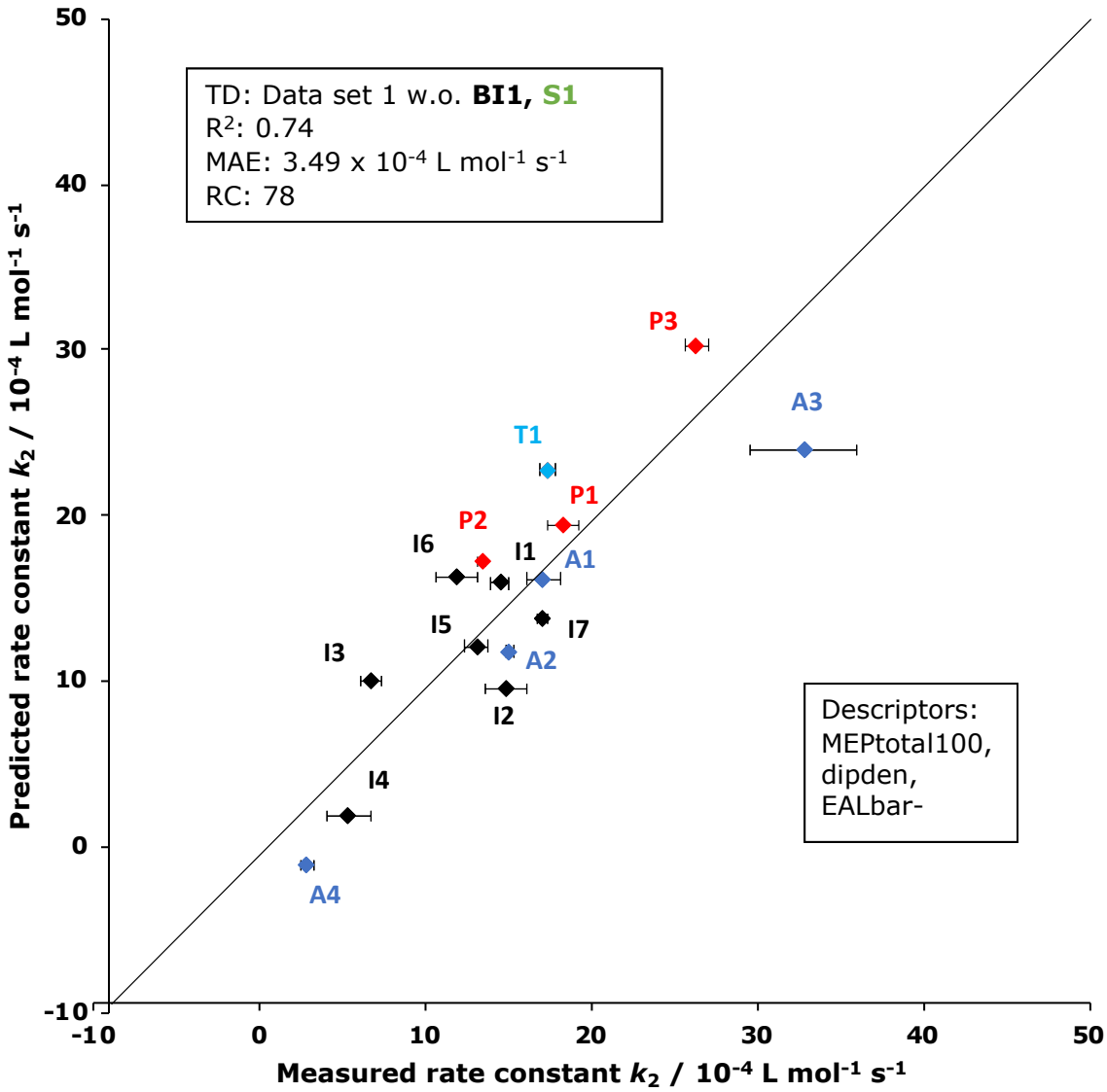


Figure S5. Correlation of linear regression model *C* with experimentally observed kinetic data, using the descriptors MEPtotal100, dipden, EALbar-. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

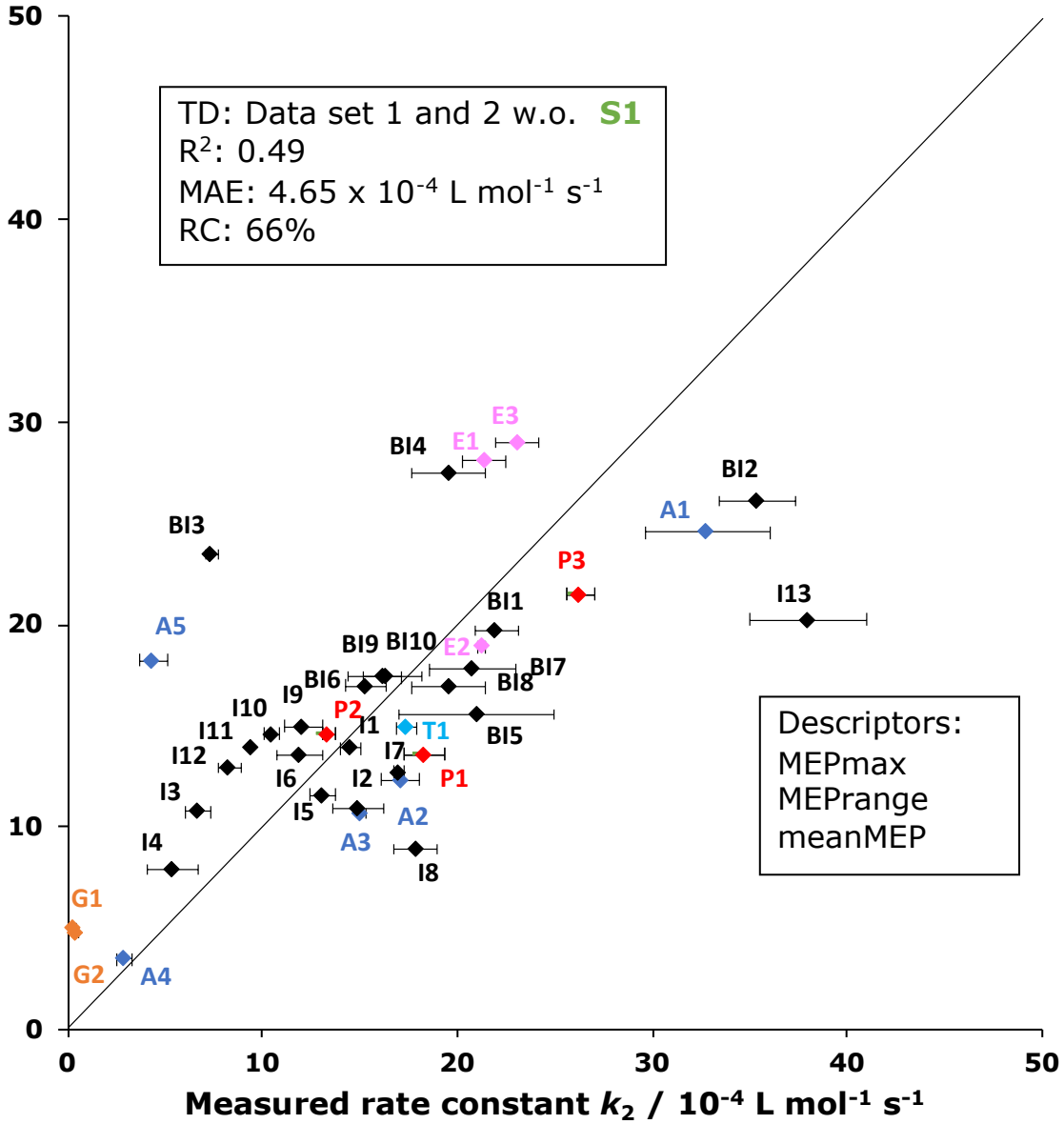


Figure S6. Correlation of linear regression model *A* with experimentally observed kinetic data, using the descriptors MEPmax, MEPmean, MEPrange. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

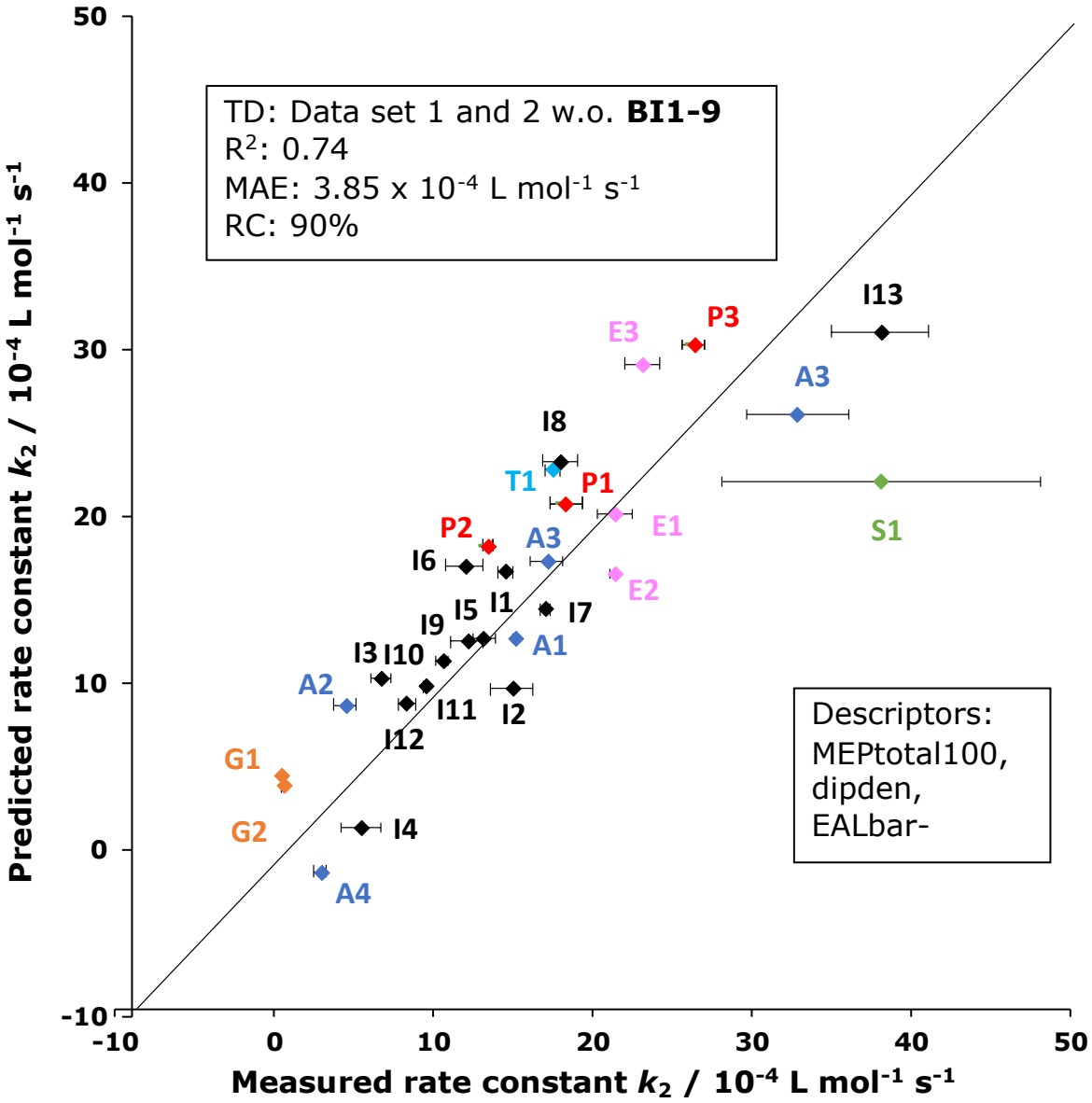


Figure S7. Correlation of linear regression model *B* with experimentally observed kinetic data, using the descriptors MEPtotal100, dipden, EALbar-. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

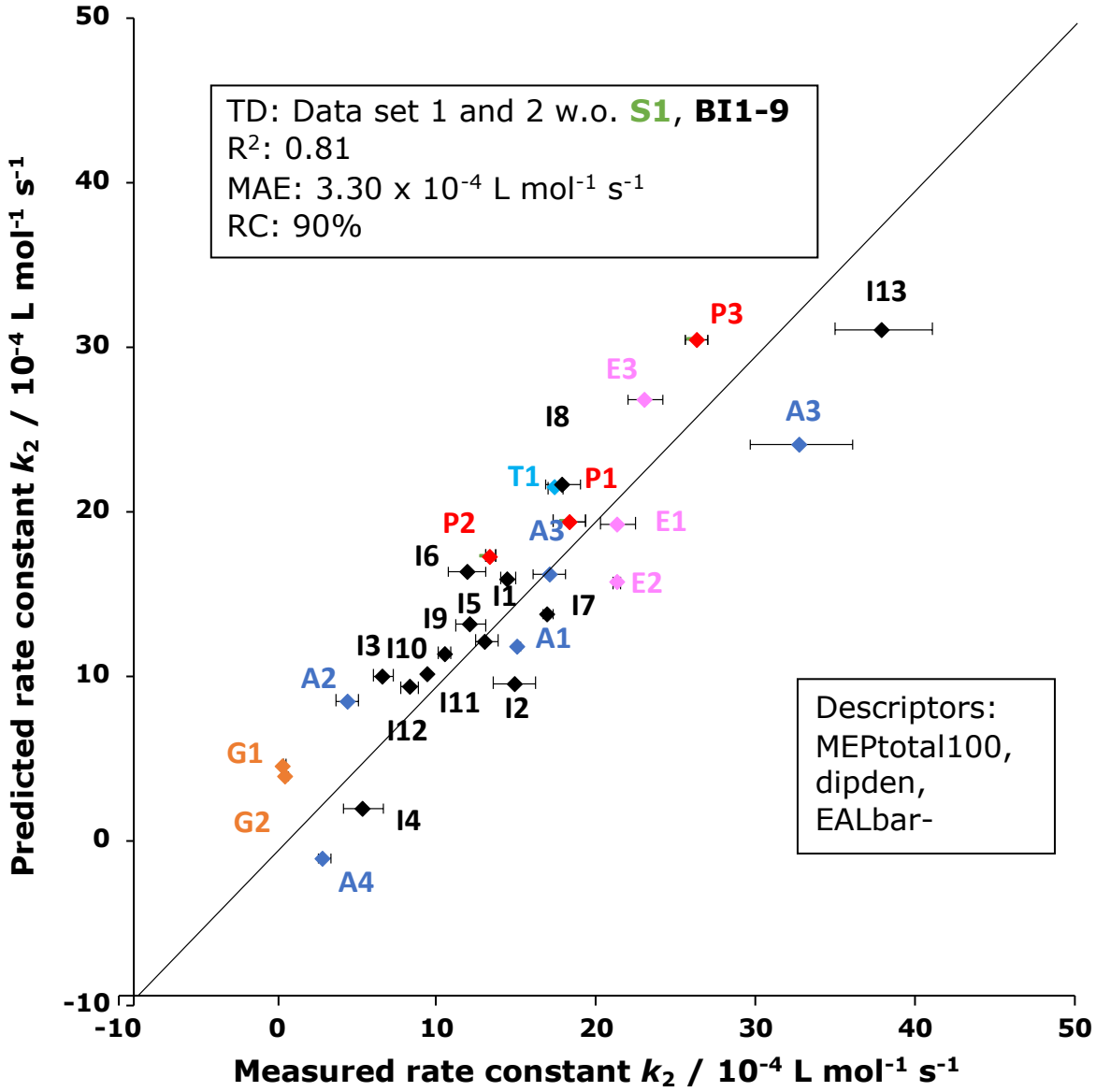


Figure S8. Correlation of linear regression model *C* with experimentally observed kinetic data, using the descriptors MEPtotal100, dipden, EALbar-. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

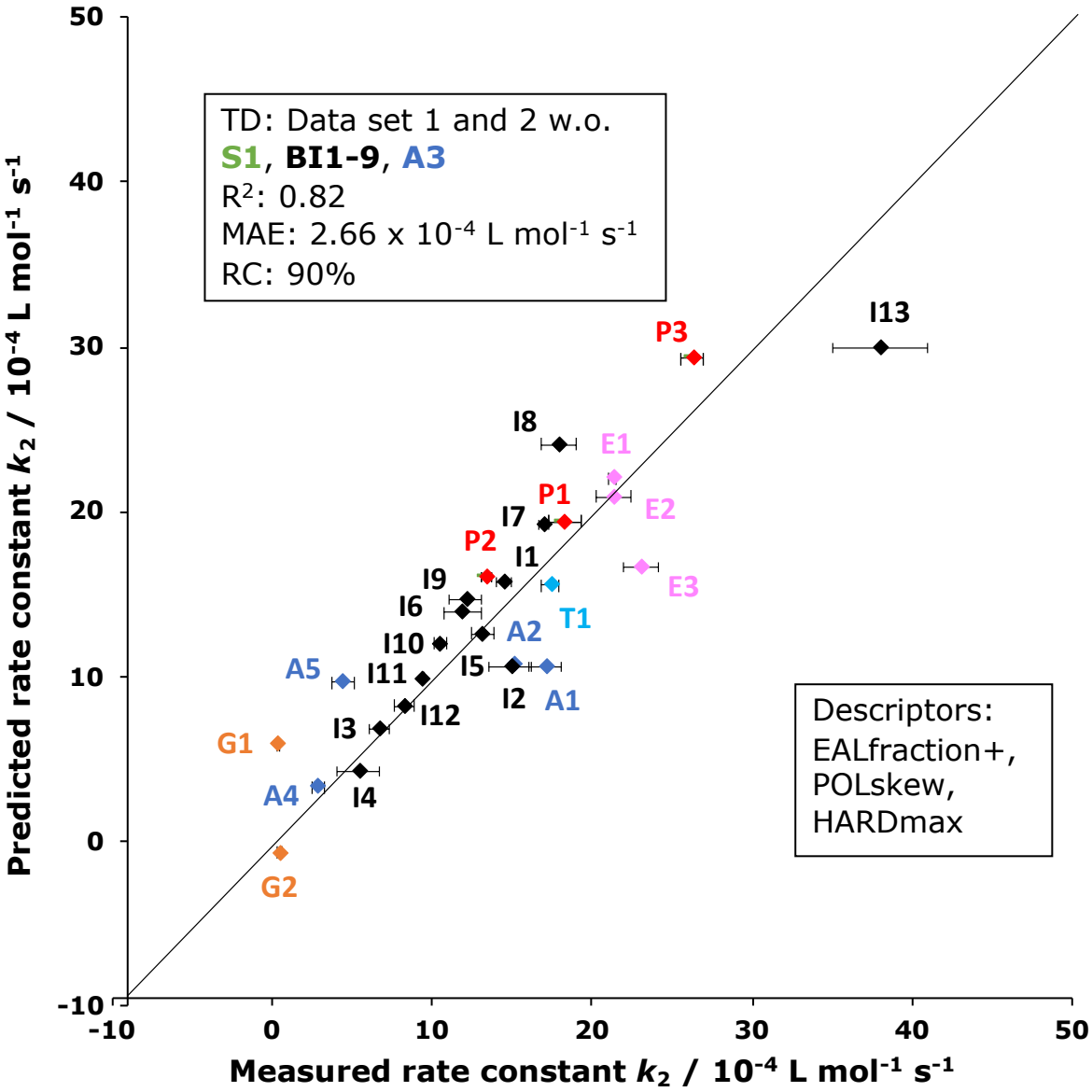


Figure S9. Correlation of linear regression model *E* with experimentally observed kinetic data, using the descriptors EALfraction+, POLskew, HARDmax. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

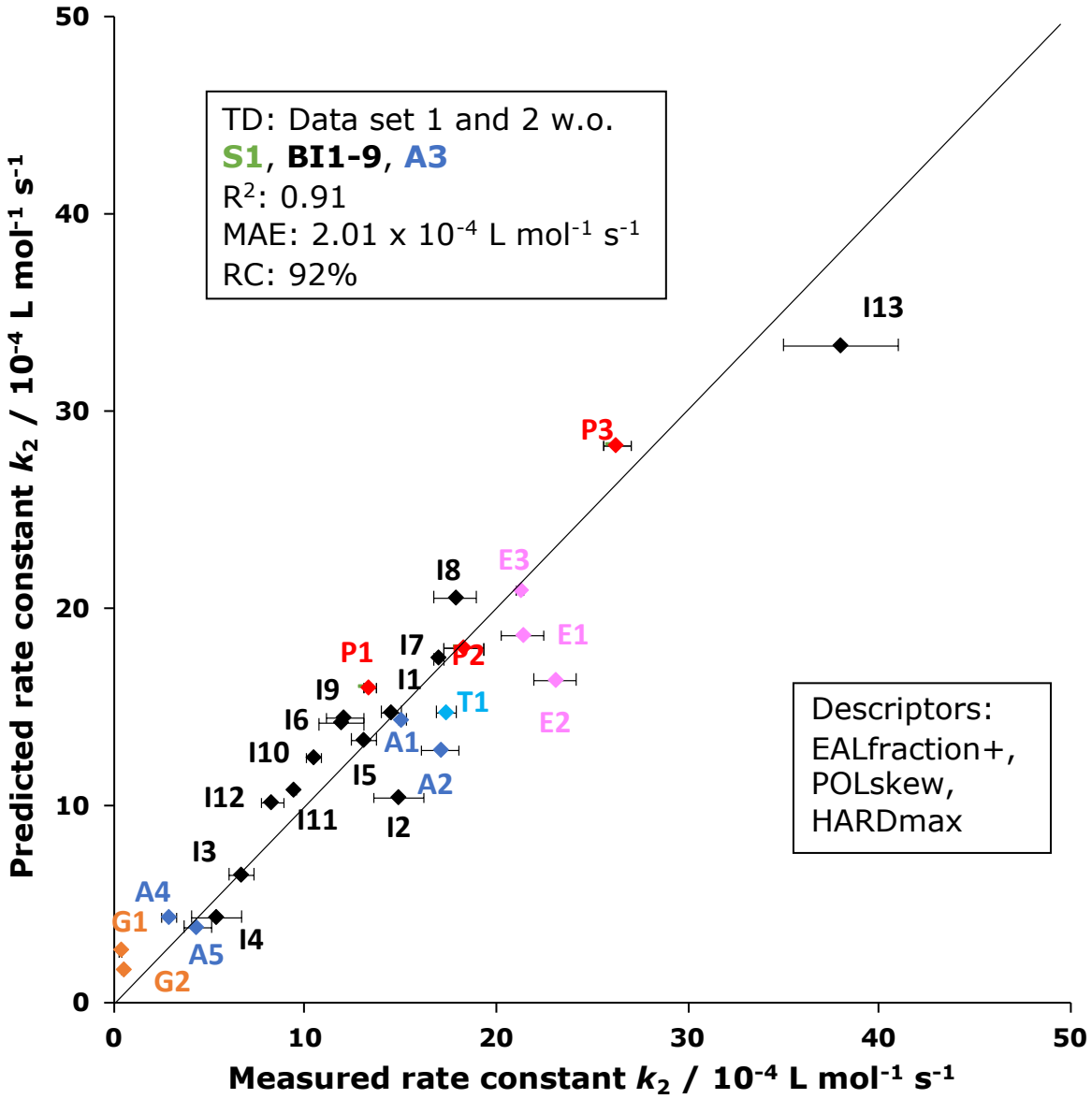


Figure S10. Correlation of the artificial neural network model *E*' with experimentally observed kinetic data, using the descriptors EALfraction+, POLskew, HARDmax. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

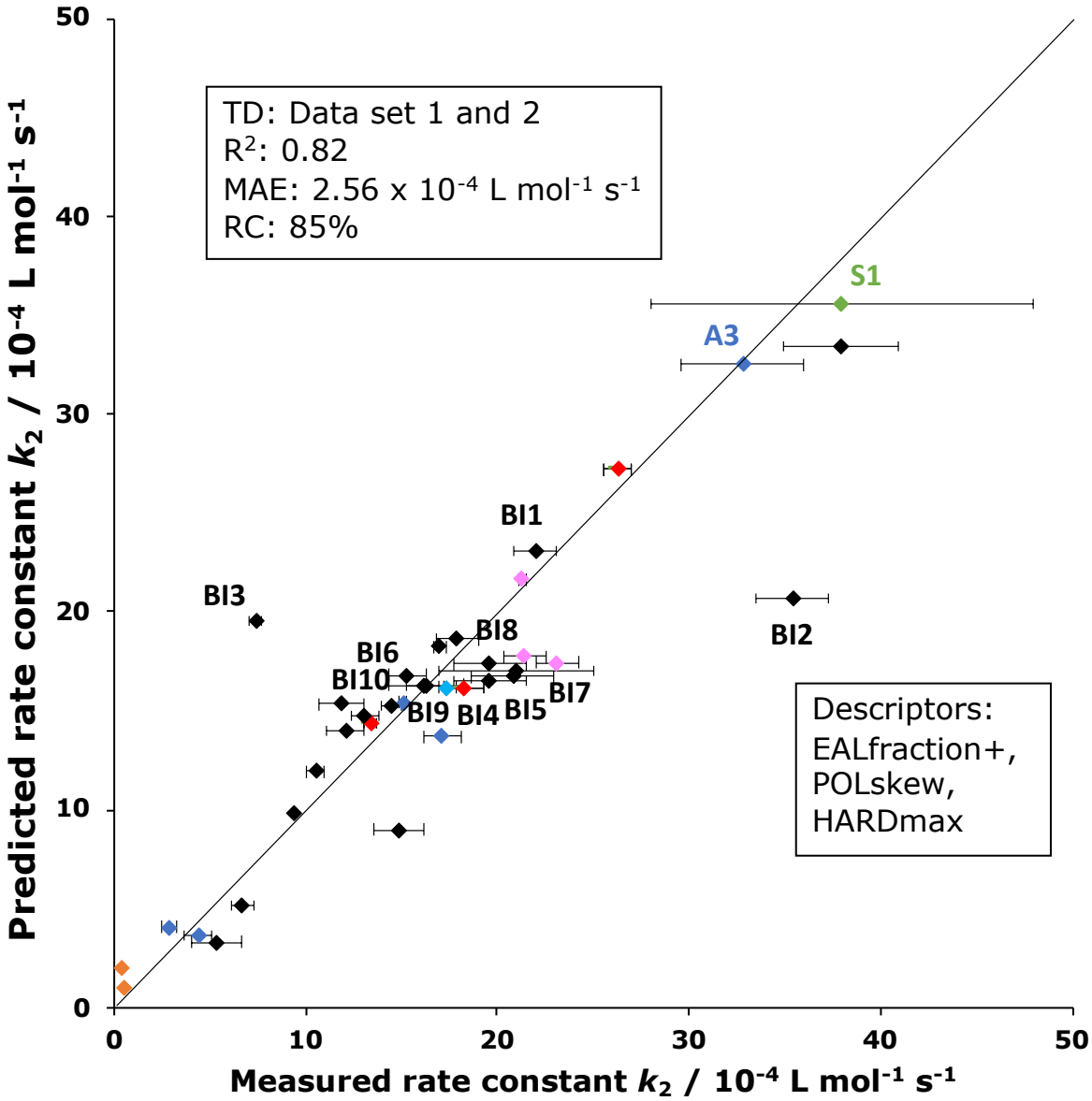


Figure S11. Correlation of the artificial neural network model *E*' with experimentally observed kinetic data, using the descriptors EALfraction+, POLskew, HARDmax. TD: Training data; MAE: Mean absolute error; RC: Rank correlation. As per the main text, for clarity, only ions not present in Figure S9 are listed here.

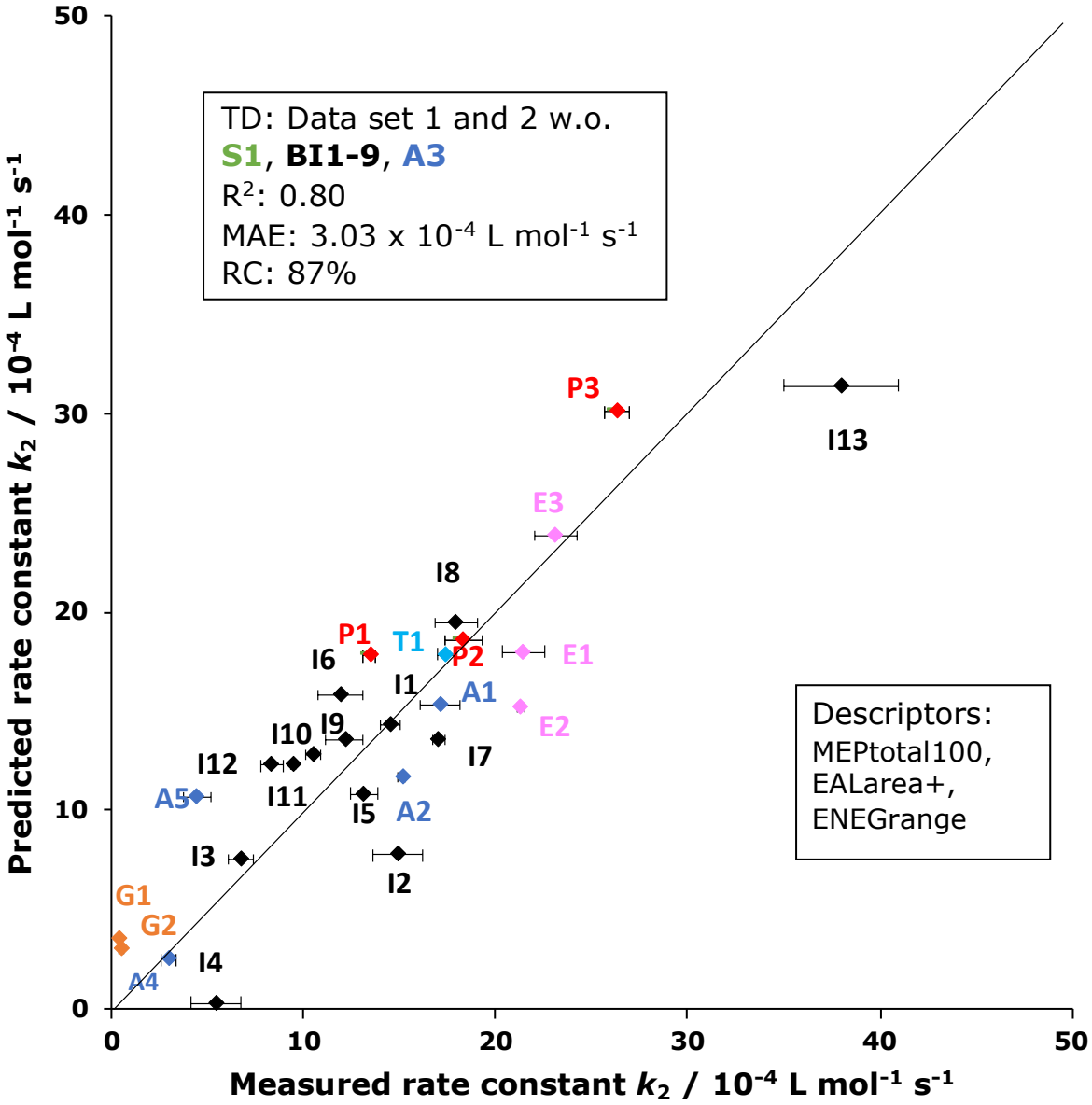


Figure S12. Correlation of linear regression model *F* with experimentally observed kinetic data, using the descriptors MEPtotal100, EALarea+, ENEGrange. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

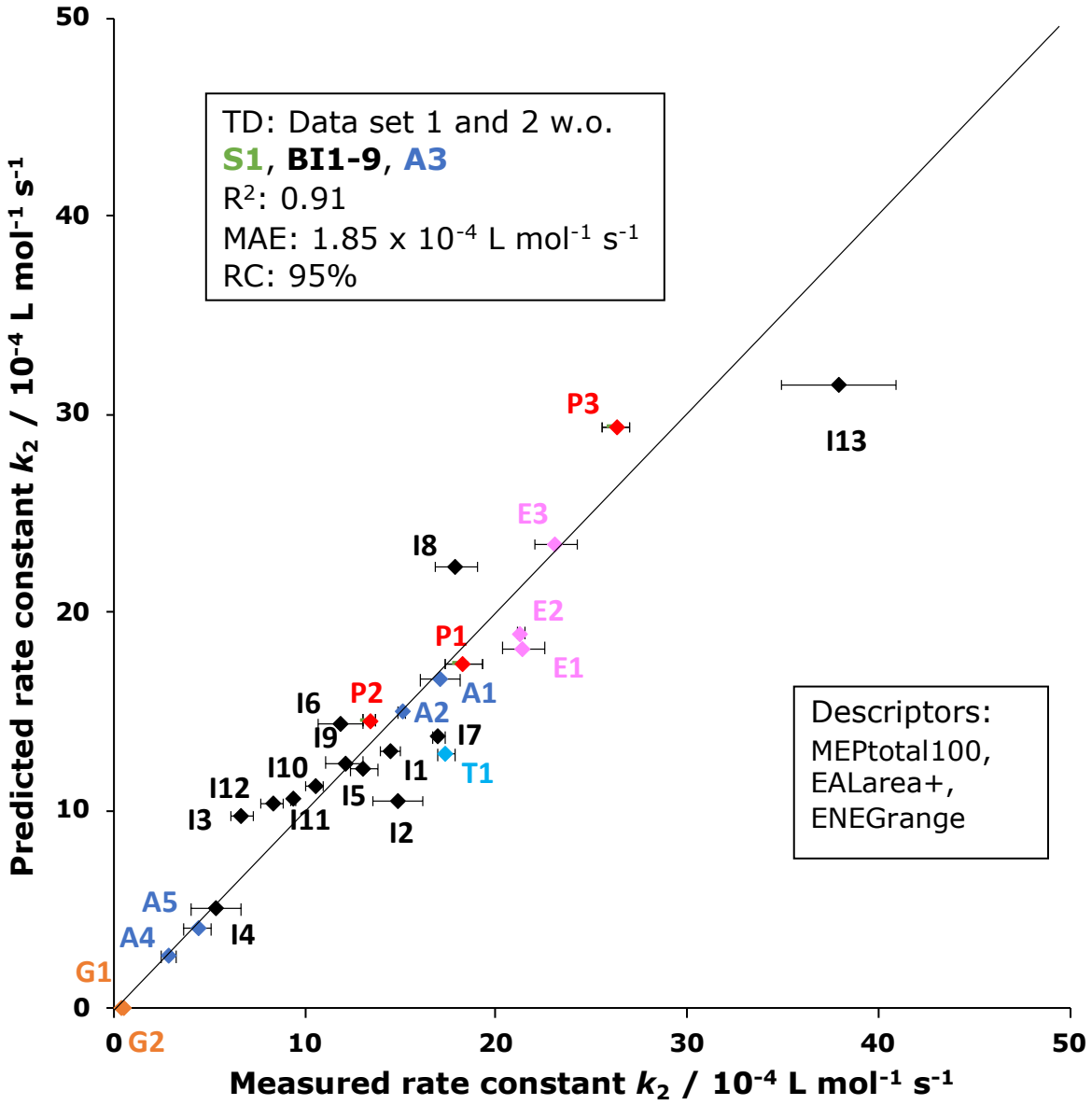


Figure S13. Correlation of the artificial neural network model *F*' with experimentally observed kinetic data, using the descriptors MEPtotal100, EALarea+, ENEGrange. TD: Training data; MAE: Mean absolute error; RC: Rank correlation.

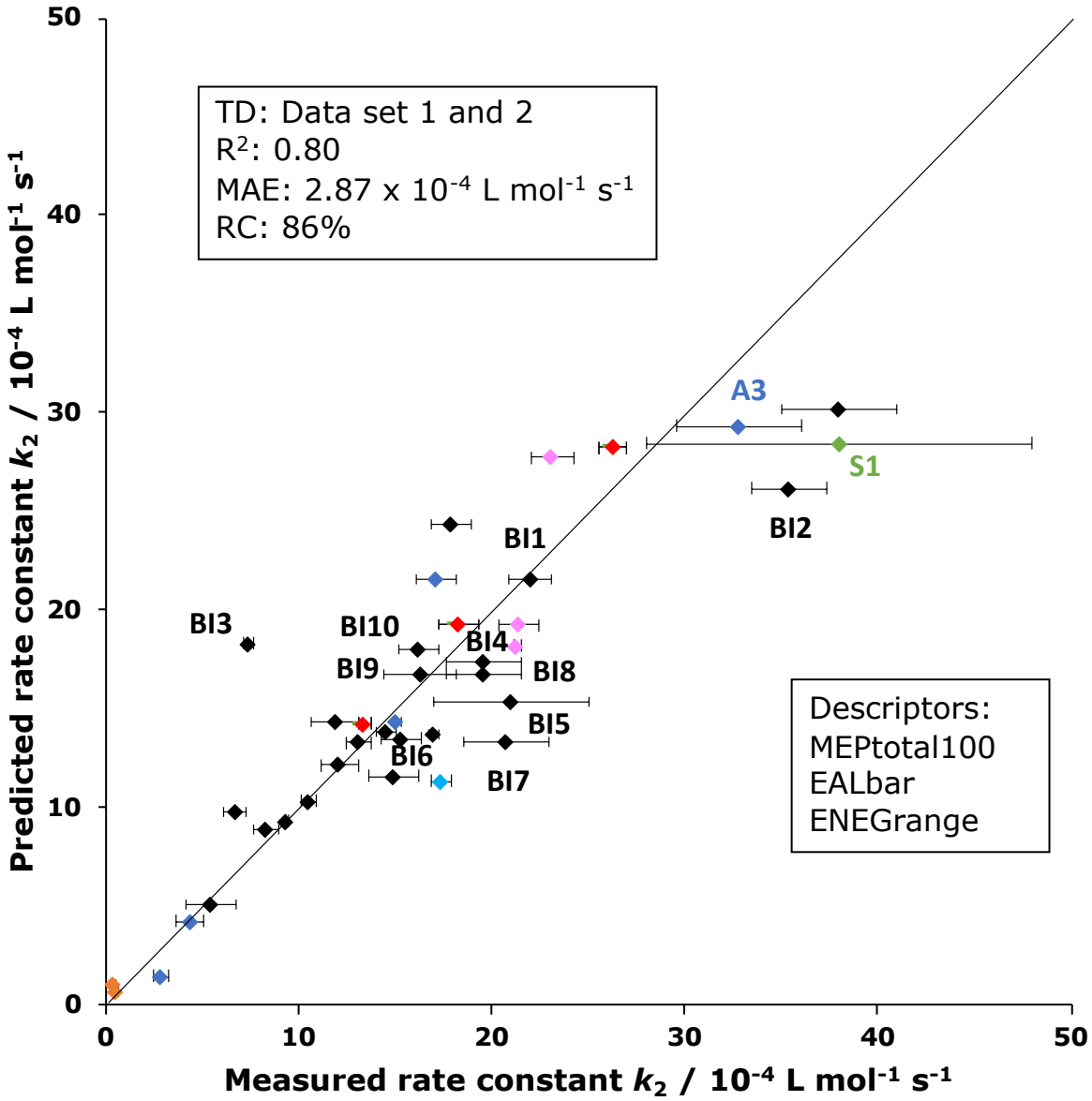


Figure S14. Correlation of the artificial neural network model *F*' with experimentally observed kinetic data, using the descriptors MEPtotal100, EALarea+, ENEGrange. TD: Training data; MAE: Mean absolute error; RC: Rank correlation. As per the main text, for clarity, only ions not present in Figure S12 are listed here.

General experimental

Unless otherwise stated all chemicals were purified prior to use as according to standard protocols.[11] Samples of [emim][$N(SO_2CF_3)_2$] were obtained from IoLiTec and used without further purification. Where water is mentioned Milli-Q™ water was used unless otherwise stated. The terms 'under reduced pressure' and '*in vacuo*' refer to the use of a rotary evaporator fitted with a variable pressure pump and a Schlenk line apparatus, respectively. Before use in the kinetic studies, all ionic liquids were dried *in vacuo* (< 1 mbar) at room temperature until a constant, sustained pressure was obtained unless otherwise stated. Under these conditions the water content of all the ionic liquids considered was < 200 ppm as measured by Karl-Fischer titrimetry. Ion chromatography showed that all the ionic liquids contained < 1% bromide content.

NMR spectra for the characterisation of the synthesised ionic liquids and their precursor bromides was conducted on either a Bruker Avance III 300 (300 MHz, ^{1}H), a Bruker Avance III 400 (400 MHz, ^{1}H), a Bruker Avance III 500 (500 MHz, ^{1}H) or a Bruker Avance III 600 (600 MHz, ^{1}H) spectrometer. Multiplicities are reported as singlet (s), doublet (d), triplet (t) quartet (q), pentet (p), and multiplet (m). ^{1}H NMR spectra used in the kinetic studies were conducted on either a Bruker Avance III 400 (400 MHz, ^{1}H), a Bruker Avance III 500 (500 MHz, ^{1}H) or a Bruker Avance III 600 (600 MHz, ^{1}H) spectrometer. The results were shown to be reproducible regardless of the NMR spectrometer used.

The reaction mixtures for the kinetic studies were prepared under pseudo first order conditions such that they contained at least a 10-fold excess of pyridine relative to benzyl bromide. Reaction progress was monitored using ^{1}H NMR spectroscopy following depletion of the signal corresponding benzylic protons of benzyl bromide at approximately 4.0 ppm. The reactions were monitored until > 95% completion. The pseudo first order rate constants were obtained using Equation S2 and the software MestReNova and the second order rate constant was determined using Equation S3 in the LINEST function in Microsoft Excel. The exception was the kinetic data determined with the ionic liquid [Fhmim][$N(SO_2CF_3)_2$] where reaction progress was monitored using ^{1}H NMR spectroscopy following formation of the signal corresponding to the benzylic protons of the product at approximately 5.6 ppm. In this instance Equation S4 and the three-parameter linear regression fit in MestReNova were used to determine the pseudo-first order rate constant and the second order rate constant was determined in the same manner as for the other ionic liquids using Equation S3.

$$\ln [A] = -k_{obs}t$$

Equation S2: Logarithmic form of the integrated first order rate equation; [A] = integral of benzyl bromide, k_{obs} = the pseudo first order rate constant and t = time.

$$k_{obs} = k_2[B]$$

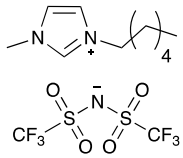
Equation S3: Relationship used to convert pseudo first order rate constants into the corresponding bimolecular rate constants; k_2 = the bimolecular rate constant, k_{obs} = the pseudo first order rate constant and [B] = the concentration of pyridine.

$$[C] = 1 - e^{-k_{obs}t}$$

Equation S4: Exponential function used to determine the observed pseudo first order rate constant through monitoring product formation; [C] = the integral of the product, k_{obs} = the pseudo first order rate constant and t = time.

Synthesis of ionic liquids

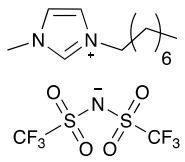
1-Hexyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([$h_x$mim][$N(SO_2CF_3)_2$])



A mixture of *n*-hexyl bromide (19.9 g, 120 mmol) and *N*-methylimidazole (12.2 g, 149 mmol) was stirred at 45 °C for 2 days. Additional *n*-hexyl bromide (3.62 g, 21.9 mmol) was added to the solution and the reaction was stirred for a further 4 days. A clear viscous liquid resulted, which was then mixed thoroughly with ethyl acetate (20 mL) and the mixture was stored -19 °C overnight. Two separate liquid layers formed with no crystallisation. The ethyl acetate was removed under reduced pressure and a mixture of acetonitrile (20 mL) and ethyl acetate (20 mL) was added to the residue and the biphasic system mixed thoroughly. The mixture was stored at -19 °C overnight but again no crystallisation occurred. The acetonitrile-ethyl acetate mix was removed under reduced pressure. Acetonitrile (30 mL) was added to the residue and the resulting system was mixed before addition of ethyl acetate (10 mL). The solution was cooled using liquid nitrogen, but no crystallisation occurred. The organic solvent was decanted, diethyl ether (25 mL) was added and the resulting system was mixed thoroughly. The mixture was allowed to settle before cooling with liquid nitrogen. A viscous, opaque, white lower layer separated from the ether. The ether was decanted and the process was repeated twice more. The residue was then heated to 90 °C *in vacuo* for 6 hours to yield 1-hexyl-3-methylimidazolium bromide as a clear viscous liquid (34.4 g, 139 mmol, 98%) that was used without any further purification. ^{1}H NMR (500 MHz, $CDCl_3$-*d*) δ 10.48 (s, 1H, NC<u>H</u>N), 7.52 (m, 1H, NCHC<u>H</u>N), 7.39 (m, 1H, NC<u>H</u>CHN), 4.33 (t, J = 7.5 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 4.14 (s, 3H, NC<u>H</u>$_3$), 1.92 (m, 2H, NCH$_2$C<u>H</u>$_2$), 1.33 (m, 6H, CH$_2$(C<u>H</u>$_2$)$_3$CH$_3$), 0.88 (t, J = 7.0 Hz, 3H, CH$_2$C<u>H</u>$_3$).

1-Hexyl-3-methylimidazolium bromide (34.4 g, 13.9 mmol) was dissolved in water (20 mL) and combined with lithium *bis*(trifluoromethanesulfonyl)imide (41.1 g, 14.3 mmol) dissolved in water (25 mL). The resulting solution was stirred for three days at room temperature, during which time two immiscible layers formed. The organic layer was extracted using dichloromethane (3 x 30 mL), and subsequently washed with water (3 x 30 mL). The organic layer was concentrated under reduced pressure and the resulting liquid was stirred under reduced pressure for 5 hours, to give 1-hexyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide as a viscous, pale yellow liquid (56.5 g, 0.126 mol, 91%) that was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.10 (s, 1H, NC<u>H</u>N), 7.77 (m, 1H, NCHC<u>H</u>N), 7.70 (s, 1H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 3.85 (s, 3H, NC<u>H</u>$_3$), 1.78 (m, 2H, NCH$_2$C<u>H</u>$_2$), 1.27 (m, 6H, CH$_2$(C<u>H</u>$_2$)$_3$CH$_3$), 0.87 (t, J = 6.9 Hz, 3H, CH$_2$C<u>H</u>$_3$).

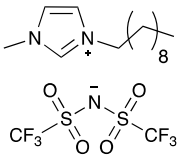
1-Octyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([omim][$N(SO_2CF_3)_2$])



N-Methylimidazole (8.94 g, 109 mmol) was combined with *n*-octyl bromide (20.5 g, 106 mmol). The resultant mixture was seen to separate into two immiscible layers. To this mixture, diethyl ether (5 mL) and acetonitrile (5 mL) were added; after this addition a single layer formed. The solution was stirred under a nitrogen atmosphere at reflux for eight days. During this time, a clear, viscous liquid formed, which was combined with ethyl acetate (40 mL) and mixed thoroughly before being allowed to settle; the result was two phases, the lower being white and opaque. The upper layer was decanted off before repeating this procedure twice more. Solvent was removed from the cloudy layer under reduced pressure before drying *in vacuo*, to yield a clear, viscous liquid. ^{1}H NMR analysis of the residue showed residual *N*-methylimidazole (*ca.* 1.7%) as indicated by the singlet at δ 7.5. The above process was repeated three times with ether (30 mL each time). Again, the mixture was concentrated under reduced pressure and subsequently dried *in vacuo* to give a clear, viscous liquid. NMR analysis of this liquid again showed residual *N*-methylimidazole (*ca.* 1%, analysed as above). The residue was dissolved in a minimum amount of acetonitrile (*ca.* 15 mL) before addition of ethyl acetate (5 mL). The mixture was stirred vigorously, during which time hexane (40 mL) was added slowly; two phases formed. The upper layer was decanted from the mixture before the bottom layer was washed with hexane (2 x 40 mL). The resulting solution was concentrated under reduced pressure before drying at *ca*. 50 °C *in vacuo* for 5 hours to yield 1-octyl-3-methylimidazolium bromide (26.9 g, 97.7 mmol, 92%) as a clear, viscous liquid, which was used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.14 (s, 1H, NC<u>H</u>N), 7.78 (m, 1H, NCHC<u>H</u>N), 7.71 (m, 1H, NC<u>H</u>CHN), 4.16 (t, J = 7.2 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 3.85 (s, 3H, NC<u>H</u>$_3$), 1.78 (m, 2H, NCH$_2$C<u>H</u>$_2$, 1.26 (m, 10H, CH$_2$(C<u>H</u>$_2$)$_5$CH$_3$), 0.87 (t, J = 6.9 Hz, 3H, CH$_2$C<u>H</u>$_3$).

1-Octyl-3-methylimidazolium bromide (26.9 g, 97.7 mmol) was dissolved in water (50 ml) and subsequently combined with lithium *bis*(trifluoromethanesulfonyl)imide (29.8 g, 10.4 mmol) and the mixture was stirred vigorously for 12 hours. During this time, two cloudy, immiscible layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with dichloromethane (3 x 30 mL). The organic solution was then washed with water (3 x 40 mL). The organic layer was retained and concentrated under reduced pressure before being dried *in vacuo* at 60 °C to yield 1-octyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (44.6 g, 93.9 mmol, 96%), as a viscous, clear liquid which was used without any further purification. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.10 (s, 1H, NC<u>H</u>N), 7.77 (m, 1H, NCHC<u>H</u>N), 7.70 (s, 1H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 3.85 (s, 3H, NC<u>H</u>$_3$), 1.77 (m, 2H, CH$_2$C<u>H</u>$_2$(CH$_2$)$_7$),1.26 (m, 10H, CH$_2$(C<u>H</u>$_2$)$_7$CH$_3$), 0.86 (t, J = 6.9 Hz, 3H, CH$_2$C<u>H</u>$_3$).

1-Decyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide [dmim][N(SO_2CF_3)$_2$]

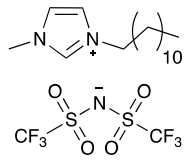


N-Methylimidazole (7.59 g, 92.4 mmol) was combined with *n*-decyl bromide (20.3 g, 91.7 mmol). The resultant mixture was seen to separate into two immiscible layers. To this mixture, diethyl ether (5 mL) and acetonitrile (5 mL) were added, after this addition a single layer formed. The solution was stirred under a nitrogen atmosphere at reflux for eight days. Addition of diethyl ether (40 mL), resulted in a cloudy white solution which was stirred vigorously. The mixture was allowed to settle, the top layer was decanted off, and this process was repeated twice more. The residue was concentrated under reduced pressure to give a viscous clear liquid, and subsequently dried *in vacuo* to give a clear liquid of higher viscosity. ^{1}H NMR analysis of the residue found *N*-methylimidazole as an impurity (*ca.* 1%) by the singlet at δ7.5. Toluene (5 mL) and cyclohexane (25 mL) were added and the resulting system was mixed thoroughly, before the upper layer was decanted off. The residue was again washed with ether (40 mL), which was decanted off, before drying *in vacuo*. ^{1}H NMR analysis of the residue found no change in the proportion of *N*-methylimidazole, using the same analysis method as above. The crude product was dissolved in a minimum amount of acetonitrile (*ca.* 30 mL), before addition of ethyl acetate (10 mL). The mixture was stirred vigorously, during which ether (40 mL) was added slowly; two layers formed. The upper layer was decanted off, the bottom layer was then washed with hexane (3 x 40 mL). Hexane (30 mL) was added to the mixture, before allowing it to settle overnight at -19 °C. A white solid precipitated, and excess solvent was decanted. Upon equilibrating to room temperature, the solid melted. Excess hexane was decanted from the mixture and the residue was dried *in vacuo* at *ca*. 50 °C for 5 hours to yield 1-decyl-3-methylimidazolium bromide as a highly viscous, clear liquid (27.1 g, 89.3 mmol, 97 %), which was used without any further purification. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.14 (s, 1H, NC<u>H</u>N), 7.78 (m, 1H, NCHC<u>H</u>N), 7.71 (m, 1H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 3.85 (s, 3H, NC<u>H</u>$_3$), 1.78 (m, 2H, NCH$_2$C<u>H</u>$_2$), 1.26 (m, 14H, CH$_2$(C<u>H</u>$_2$)$_7$CH$_3$), 0.86 (t, J = 6.9 Hz, 3H, CH$_2$C<u>H</u>$_3$).

1-Decyl-3-methylimidazolium bromide (22.7 g, 74.7 mmol) was dissolved in acetonitrile (30 mL) and water (40 mL). To this solution, lithium *bis*(trifluoromethanesulfonyl)imide was added (22.7 g, 79.0 mmol) and the mixture was stirred vigorously at room temperature for 12 hours. During this time, two clear immiscible layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with dichloromethane (3 x 30 mL). The organic solution was then washed with water (3 x 40 mL). The organic layer was retained and concentrated under reduced pressure before being dried *in vacuo* at 60 °C to yield 1-decyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (36.8 g, 73.1 mmol, 98%), as a viscous, clear liquid which was used without any further purification. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.10 (s, 1H, NC<u>H</u>N), 7.77

(m, 1H, NCHC<u>H</u>N), 7.70 (s, 1H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 3.85 (s, 3H, NC<u>H</u>$_3$), 1.77 (m, 2H, NCH$_2$C<u>H</u>$_2$), 1.26 (m, 14H, CH$_2$(C<u>H</u>$_2$)$_7$CH$_3$), 0.86 (t, *J* = 6.9 Hz, 3H, CH$_2$C<u>H</u>$_3$).

1-Dodecyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide [ddmim][N(SO$_2$CF$_3$)$_2$]

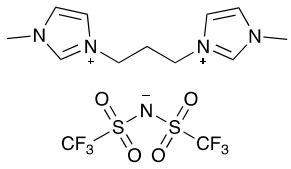


N-Methylimidazole (7.51 g, 91.5 mmol) was combined with *n*-dodecyl bromide (18.9 g, 75.8 mmol). The resultant mixture was seen to separate into two immiscible layers. To this mixture, diethyl ether (5 mL) and acetonitrile (5 mL) were added, after which phase separation was still observed. Further diethyl ether (5 mL) and acetonitrile (5 mL) was added, resulting in a single phase. The solution was stirred under a nitrogen atmosphere at reflux for eight days. Diethyl ether (40 mL) was added and the mixture was shaken, resulting in precipitation. Excess solvent was decanted off, before the residue was dried *in vacuo* for 1 hour. This process was repeated twice more. The residue was found to contain *N*-methylimidazole through NMR analysis (*ca.* 14%, as indicated by the singlet at δ7.5). Acetonitrile (20 mL) was used to dissolve the residue before addition of ether (60 mL), which resulted in precipitation of a white powder. The solvent was decanted off before the residue was dried *in vacuo*. The resulting pale, yellow amorphous substance was washed with ether (2 x 40 mL), before being dried under *in vacuo* for 5 hours. During this time, an off-white solid formed, which was triturated with toluene (10 mL) and cyclohexane (40 mL). This process was repeated once more. To the white solid, a minimum amount of acetonitrile was added (*ca*. 25 ml), resulting in two distinct, clear phases, the top presumed to be residual cyclohexane and toluene. The bottom layer was retained and combined with ether (50 ml) resulting in a white precipitate forming. Excess solvent was decanted off and the residue was dried *in vacuo* to give a white solid. ^{1}H NMR analysis of the solid showed remaining *N*-methylimidazole (*ca.* 2%, as indicated by the singlet at δ7.5). The white solid was crushed and combined with a mixture of ethyl acetate (5 mL) and hexane (25 mL), which was then stirred vigorously. The solvent was decanted off and the residue was washed with hexane (3 x 20 mL) to give a white solid. This solid was *in vacuo* for 5 hours, to give 1-dodecyl-3-methylimidazolium bromide as a bright, white, crystalline solid (22.9 g, 69.0 mmol, 91%) which was used without further purification. m.p. 44–46 °C (lit.[12] 43-46 °C) ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.10 (s, 1H, NC<u>H</u>N), 7.77 (m, 1H, NCHC<u>H</u>N), 7.70 (m, 1H, NC<u>H</u>CHN), 4.15 (t, *J* = 7.2 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 3.85 (s, 3H, NC<u>H</u>$_3$), 1.77 (m, 2H, NCH$_2$C<u>H</u>$_2$), 1.26 (m, 18H, CH$_2$(C<u>H</u>$_2$)$_9$CH$_3$), 0.86 (t, *J* = 6.9 Hz, 3H, CH$_2$C<u>H</u>$_3$).

1-Dodecyl-3-methylimidazolium bromide (22.8 g, 68.7 mmol) was dissolved in acetonitrile (30 mL) and water (40 mL). To this solution, lithium *bis*(trifluoromethanesulfonyl)imide was added (20.7 g, 72.0 mmol) and stirred vigorously at room temperature for 12 hours. During this time, two pale yellow, immiscible layers formed. The bottom layer was retained, and the top, aqueous layer,

was extracted with dichloromethane (3 x 30 mL). The organic solution was then washed with water (3 x 40 mL). The organic layer was retained and concentrated under reduced pressure before being dried *in vacuo* at 60 °C to yield 1-dodecyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (35.4 g, 66.6 mmol, 97%), as a viscous, pale yellow liquid which was used without any further purification. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.10 (s, 1H, NC<u>H</u>N), 7.77 (m, 1H, NCHC<u>H</u>N), 7.70 (s, 1H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 3.85 (s, 3H, NC<u>H</u>$_3$), 1.77 (m, 2H, NCH$_2$C<u>H</u>$_2$), 1.26 (m, 18H, CH$_2$(C<u>H</u>$_2$)$_9$CH$_3$), 0.86 (t, J = 6.9 Hz, 3H, CH$_2$C<u>H</u>$_3$).

1,3-*bis*(3-Methylimidazolium-1-yl)propane *bis*(trifluoromethanesulfonyl)imide [(mim)$_2$p$_r$][N(SO$_2$CF$_3$)$_2$]

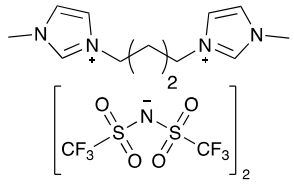


A solution of *N*-methylimidazole (8.65 g, 105 mmol) in acetonitrile (10 mL) was added to a solution of 1,3-dibromopropane (10.0 g, 49.5 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to give the precursor 1,3-*bis*(3-methylimidazolium-1-yl)propane bromide as a white solid (17.6 g, 48.1 mmol, 97%), m.p. 167-169 °C (lit.[13] 172.8 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 2H, NC<u>H</u>N), 7.81 (m, 2H, NCHC<u>H</u>N), 7.75 (m, 2H, NC<u>H</u>CHN), 4.25 (t, J = 7.0 Hz, 4H, NC<u>H</u>$_2$CH$_2$C<u>H</u>$_2$N), 3.88 (s, 6H, NC<u>H</u>$_3$), 2.40 (p, J = 7.0 Hz, 2H, NCH$_2$C<u>H</u>$_2$CH$_2$N).

1,3-*bis*(3-Methylimidazolium-1-yl)propane bromide (17.6 g, 48.1 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (29.0 g, 101 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, a white powder formed. Dichloromethane (50 mL) was added, and three colourless, immiscible layers formed. The bottom two layers were retained, and the top, aqueous layer, was extracted with dichloromethane (3 x 20 mL). The combined organic phases were then washed with water (10 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,3-*bis*(3-methylimidazolium-1-yl)propane *bis*(trifluoromethanesulfonyl)imide (36.3 g, 47.3 mmol, 98%) as a white, crystalline solid, which was used without any further purification. m.p. 47-48 °C (lit.[14] 49-50 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.73 (m, 4H, (NC<u>H</u>C<u>H</u>N), 4.20 (t, J = 7.0 Hz, 4H, NC<u>H</u>$_2$CH$_2$C<u>H</u>$_2$N), 3.85 (s, 6H, NC<u>H</u>$_3$), 2.37 (p, J = 7.0 Hz, 2H, NCH$_2$C<u>H</u>$_2$CH$_2$N).

1,4-*bis*(3-Methylimidazolium-1-yl)butane *bis*(trifluoromethanesulfonyl)imide

$[(mim)_2b][N(SO_2CF_3)_2]$

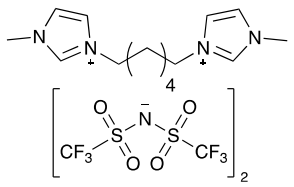


A solution of *N*-methylimidazole (23.1 g, 281 mmol) in acetonitrile (10 mL) was added to a solution of 1,4-dibromobutane (30.3 g, 140 mmol) in acetonitrile (15 mL). The reaction mixture was stirred for 3 days at room temperature, wherein a light beige powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to give the precursor 1,4-*bis*(3-methylimidazolium-1-yl)butane bromide as a light beige solid (52.1 g, 136 mmol 97%). m.p. 150-151 °C (lit.[13] 158.3 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.16 (s, 2H, NC<u>H</u>N), 7.77 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.21 (m, 4H, (NC<u>H</u>$_2$CH$_2$)$_2$), 3.85 (s, 6H, NC<u>H</u>$_3$), 1.78 (m, 4H, (NCH$_2$C<u>H</u>$_2$)$_2$).

1,4-*bis*(3-Methylimidazolium-1-yl)butane bromide (25.8 g, 66.2 mmol) was dissolved in water (50 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (38.9 g, 135 mmol) in water (50 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, a white powder formed. Ethyl acetate (50 mL) was added, and two immiscible layers formed, the bottom of which was a beige colour. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 50 mL). The combined organic phases were then washed with water (10 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,3-*bis*(3-methylimidazolium-1-yl)butane *bis*(trifluoromethanesulfonyl)imide (52.6 g, 67.4 mmol, 99%) as a white, crystalline solid, which was used without any further purification. m.p. 54-55 °C (lit.[15] 54-56 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 2H, NC<u>H</u>N), 7.74 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.30-4.10 (m, 4H, NC<u>H</u>$_2$(CH$_2$)$_2$C<u>H</u>$_2$N), 3.85 (s, 6H, NC<u>H</u>$_3$), 1.76 (m, 4H, NCH$_2$(C<u>H</u>$_2$)$_2$CH$_2$N).

1,6-*bis*(3-Methylimidazolium-1-yl)hexane *bis*(trifluoromethanesulfonyl)imide

$[(mim)_2h_x][N(SO_2CF_3)_2]$



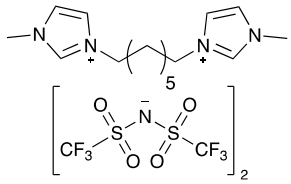
A solution of *N*-methylimidazole (20.1 g, 244 mmol) in acetonitrile (25 mL) was added to a solution of 1,6-dibromohexane (28.2 g, 115 mmol) in acetonitrile (25 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 50 mL), and the residue was dried *in vacuo* to give the precursor 1,6-*bis*(3-methylimidazolium-1-yl)hexane bromide as a white solid (44.0 g, 108 mmol, 94%). m.p.

146-148 °C (lit.[16] 150-151 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (s, 2H, NC<u>H</u>N), 7.76 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.86 (s, 6H, NC<u>H</u>$_3$), 1.84-1.72 (m, 4H, (NCH$_2$C<u>H</u>$_2$CH$_2$)$_2$), 1.39-1.13 (m, 4H, (N(CH$_2$)$_2$C<u>H</u>$_2$)$_2$).

1,6-*bis*(3-Methylimidazolium-1-yl)hexane bromide (24.7 g, 60.5 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (36.0 g, 125 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, a white powder formed. The bottom later was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (10 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,6-*bis*(3-methylimidazolium-1-yl)hexane *bis*(trifluoromethanesulfonyl)imide (44.6 g, 55.2 mmol, 91%) as a beige liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.14 (t, J = 7.2 Hz, 4H, (NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.84-1.70 (m, 4H, (NCH$_2$C<u>H</u>$_2$CH$_2$)$_2$), 1.33-1.21 (m, 4H, (N(CH$_2$)$_2$C<u>H</u>$_2$)$_2$).

1,7-*bis*(3-Methylimidazolium-1-yl)heptane *bis*(trifluoromethanesulfonyl)imide

[(mim)$_2$h$_p$][N(SO$_2$CF$_3$)$_2$]

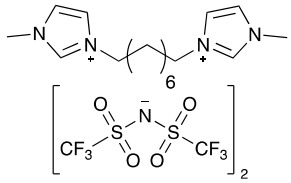


A solution of *N*-methylimidazole (4.89 g, 59.6 mmol) in acetonitrile (10 mL) was added to a solution of 1,7-dibromoheptane (7.03 g, 27.3 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 4 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to give the precursor 1,7-*bis*(3-methylimidazolium-1-yl)heptane as a white solid (11.2 g, 26.5 mmol, 97%). m.p. 132-134 °C (lit.[17] reported as a liquid). ^{1}H NMR (300 MHz, CD$_3$CN-d_3) δ 9.26 (s, 2H, NC<u>H</u>N), 7.51 (m, 2H, NCHC<u>H</u>N), 7.40 (m, 2H, NC<u>H</u>CHN), 4.23 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.90 (s, 6H, NC<u>H</u>$_3$), 1.88 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$CH$_2$)$_2$CH$_2$), 1.56-1.23 (m, 6H, (NCH$_2$CH$_2$C<u>H</u>$_2$)$_2$C<u>H</u>$_2$).

1,7-*bis*(3-Methylimidazolium-1-yl)heptane bromide (8.97 g, 21.2 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (12.86 g, 101.16 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,7-*bis*(3-methylimidazolium-1-yl)heptane

bis(trifluoromethanesulfonyl)imide (16.2 g, 19.6 mmol, 92%) as a white powder, which was used without any further purification. m.p. 59-61 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, (NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$CH$_2$)$_2$CH$_2$), 1.43-1.11 (m, 6H, (NCH$_2$CH$_2$C<u>H</u>$_2$)$_2$C<u>H</u>$_2$).

1,8-*bis*(3-Methylimidazolium-1-yl)octane *bis*(trifluoromethanesulfonyl)imide [(mim)$_2$o][N(SO$_2$CF$_3$)$_2$]

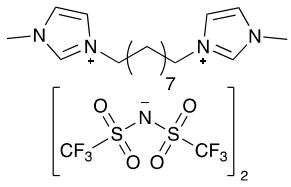


A solution of *N*-methylimidazole (3.03 g, 36.9 mmol) in acetonitrile (10 mL) was added to a solution of 1,8-dibromooctane (4.55 g, 16.7 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and was dried *in vacuo* to give the precursor 1,8-*bis*(3-methylimidazolium-1-yl)octane bromide as a white solid (7.05 g, 16.2 mmol, 97%). m.p. 124-125 °C (lit. [18] 127 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 2H, NCHN), 7.81 (m, 2H, NCHC<u>H</u>N), 7.73 (m, 2H, NC<u>H</u>CHN), 4.17 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.86 (s, 6H, NC<u>H</u>$_3$), 1.77 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_2$)$_2$), 1.38-1.13 (m, 8H, (N(CH$_2$)$_2$(C<u>H</u>$_2$)$_2$)$_2$).

1,8-*bis*(3-Methylimidazolium-1-yl)octane bromide (7.05 g, 16.2 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (12.0 g, 41.9 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,8-*bis*(3-methylimidazolium-1-yl)octane *bis*(trifluoromethanesulfonyl)imide (13.1 g, 15.7 mmol, 97%) as a colourless liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NCHN), 7.75 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, (NC<u>H</u>$_2$(CH$_2$)$_3$)$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_2$)$_2$), 1.25 (m, 8H, (N(CH$_2$)$_2$(C<u>H</u>$_2$)$_2$)$_2$).

1,9-*bis*(3-Methylimidazolium-1-yl)nonane *bis*(trifluoromethanesulfonyl)imide

$[(mim)_2n][N(SO_2CF_3)_2]$

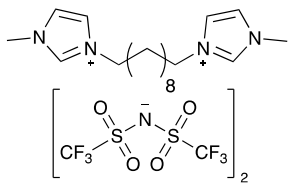


A solution of *N*-methylimidazole (3.62 g, 59.7 mmol) in acetonitrile (10 mL) was added to a solution of 1,9-dibromononane (4.90 g, 12.7 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 7 days at room temperature, wherein the mixture turned light beige. The volatile components of the mixture were removed under reduced pressure, the residue was triturated with ethyl acetate (5 x 30 mL), and the resulting powder was dried *in vacuo* to give the precursor 1,9-*bis*(3-methylimidazolium-1-yl)nonane bromide as a colourless, viscous liquid (7.53 g, 16.7 mmol, 98%). (lit.[13] reported as liquid). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.17 (s, 2H, NC<u>H</u>N), 7.78 (m, 2H, NCHC<u>H</u>N), 7.72 (m, 2H, NC<u>H</u>CHN), 4.16 (t, J = 7.3 Hz, 4H, NC<u>H</u>$_2$), 3.86 (s, 6H, NC<u>H</u>$_3$), 1.78 (p, J = 7.3 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_2$)$_2$CH$_2$), 1.33-1.18 (m, 10H, (N(C<u>H</u>$_2$)$_2$C<u>H</u>$_2$)$_2$C<u>H</u>$_2$).

1,9-*bis*(3-Methylimidazolium-1-yl)nonane bromide (6.99 g, 15.5 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (10.1 g, 35.3 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phases were removed *in vacuo* to yield 1,9-*bis*(3-methylimidazolium-1-yl)nonane *bis*(trifluoromethanesulfonyl)imide (12.8 g, 15.1 mmol, 97%) as a light beige liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.69 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.75 (p, J = 7.2 Hz, 4H, (NCH$_2$C<u>H</u>$_2$(CH$_2$)$_2$)$_2$CH$_2$), 1.29-1.17 (m, 10H, (N(C<u>H</u>$_2$)$_2$C<u>H</u>$_2$)$_2$C<u>H</u>$_2$).

1,10-*bis*(3-Methylimidazolium-1-yl)decane *bis*(trifluoromethanesulfonyl)imide

$[(mim)_2d][N(SO_2CF_3)_2]$

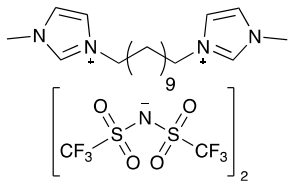


A solution of *N*-methylimidazole (15.1 g, 184 mmol) in acetonitrile (10 mL) was added to a solution of 1,10-dibromodecane (27.4 g, 91.0 mmol) in acetonitrile (30 mL). The reaction mixture was stirred for 7 days at room temperature, wherein the viscosity of the mixture was observed to increase. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to isolate the precursor 1,10-*bis*(3-methylimidazolium-1-yl)decane bromide as a white solid (41.0 g, 88.3 mmol, 97%). m.p. 145-146 °C (lit.[18] 145 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.11 (s, 2H, NC<u>H</u>N), 7.77

(m, 2H, NCHCHN), 7.71 (m, 2H, NCHCHN), 4.15 (t, J = 7.2 Hz, 4H, NCH_2), 3.85 (s, 6H, NCH_3), 1.78 (q, J = 7.2 Hz, 4H, $(NCH_2CH_2(CH_2)_3)_2$), 1.39-1.09 (m, 12H, $(N(CH_2)_2(CH_2)_3)_2$).

1,10-*bis*(3-Methylimidazolium-1-yl)decane bromide (29.2 g, 62.9 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (43.4 g, 151 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,10-*bis*(3-methylimidazolium-1-yl)decane *bis*(trifluoromethanesulfonyl)imide (51.4 g, 59.4 mmol, 95%) as a light beige liquid, which was used without any further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NCHN), 7.75 (m, 2H, NCHCHN), 7.69 (m, 2H, NCHCHN), 4.13 (t, J = 7.2 Hz, 4H, NCH_2), 3.84 (s, 6H, NCH_3), 1.76 (p, J = 7.2 Hz, 4H, $(NCH_2CH_2(CH_2)_3)_2$), 1.33-1.18 (m, 12H, $(N(CH_2)_2(CH_2)_3)_2$).

1,11-*bis*(3-Methylimidazolium-1-yl)undecane *bis*(trifluoromethanesulfonyl)imide $[(mim)_2u][N(SO_2CF_3)_2]$

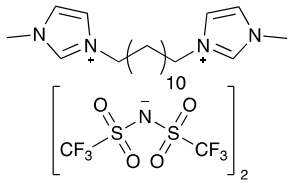


A solution of *N*-methylimidazole (3.69 g, 44.9 mmol) in acetonitrile (5 mL) was added to a solution of 1,11-dibromoundecane (4.76 g, 15.1 mmol) in acetonitrile (5 mL). The reaction mixture was stirred for 3 days at room temperature, wherein the mixture turned a beige colour. The volatile components of the mixture were removed under reduced pressure, and the resulting viscous beige liquid was triturated with ethyl acetate (10 x 20 mL), and the residue was dried *in vacuo* to isolate the precursor 1,11-*bis*(3-methylimidazolium-1-yl)undecane bromide as a colourless, viscous liquid (7.23 g, 15.1 mmol, quant.). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.14 (s, 2H, NCHN), 7.78 (m, 2H, NCHCHN), 7.72 (m, 2H, NCHCHN), 4.15 (t, J = 7.2 Hz, 4H, NCH_2), 3.86 (s, 6H, NCH_3), 1.77 (p, J = 7.2 Hz, 4H, $(NCH_2CH_2(CH_2)_3)_2CH_2$), 1.37-1.10 (m, 14H, $(N(CH_2CH_2(CH_2)_3)_2CH_2$).

1,11-*bis*(3-Methylimidazolium-1-yl)undecane bromide (7.23 g, 15.1 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (9.37 g, 32.6 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,11-*bis*(3-methylimidazolium-1-yl)undecane *bis*(trifluoromethanesulfonyl)imide (12.2 g, 13.9 mmol, 92%) as a colourless liquid, which was used

without any further purification.[1]H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.75 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (N(CH_2C<u>H</u>$_2$(CH_2)$_3$)$_2CH_2$), 1.32-1.18 (m, 14H, (N(CH_2CH_2(C<u>H</u>$_2$)$_3$)$_2C$<u>H</u>$_2$).

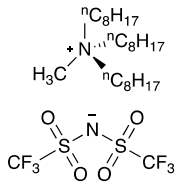
1,12-*bis*(3-Methylimidazolium-1-yl)dodecane *bis*(trifluoromethanesulfonyl)imide [(mim)$_2$dd][N(SO_2CF_3)$_2$]



A solution of *N*-methylimidazole (11.6 g, 141 mmol) in acetonitrile (10 mL) was added to a solution of 1,12-dibromododecane (21.7 g, 66.1 mmol) in acetonitrile (30 mL). The reaction mixture was stirred for 7 days at room temperature, wherein a white powder precipitated from solution. The volatile components of the mixture were removed under reduced pressure, the resulting white solid was triturated with ethyl acetate (5 x 30 mL), and the residue was dried *in vacuo* to isolate the precursor 1,12-*bis*(3-methylimidazolium-1-yl)decane bromide as a white solid (31.6 g, 64.1 mmol, 97%). m.p. 153-154 °C (lit.[13] reported as liquid). [1]H NMR (400 MHz, DMSO-d_6) δ 9.13 (d, J = 1.8 Hz, 2H, NC<u>H</u>N), 7.78 (m, 2H, NCHC<u>H</u>N), 7.71 (m, 2H, NC<u>H</u>CHN), 4.15 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.85 (s, 6H, NC<u>H</u>$_3$), 1.77 (m, 4H, (NCH_2C<u>H</u>$_2$(CH_2)$_4$)$_2$), 1.34-1.15 (m, 16H, (NCH_2CH_2(C<u>H</u>$_2$)$_4$)$_2$).

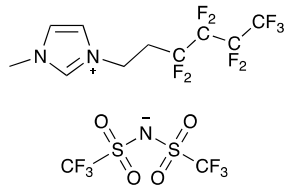
1,12-*bis*(3-Methylimidazolium-1-yl)decane bromide (24.7 g, 50.2 mmol) was dissolved in water (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (33.6 g, 117 mmol) in water (25 mL) was added and the resulting mixture was stirred vigorously at room temperature for 24 hours. During this time, two immiscible, colourless layers formed. The bottom layer was retained, and the top, aqueous layer, was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were then washed with water (20 x 50 mL). The volatile components of the organic phase were removed *in vacuo* to yield 1,12-*bis*(3-methylimidazolium-1-yl)decane *bis*(trifluoromethanesulfonyl)imide (39.3 g, 44.0 mmol, 88%) as a light beige liquid, which was used without any further purification. [1]H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H, NC<u>H</u>N), 7.76 (m, 2H, NCHC<u>H</u>N), 7.70 (m, 2H, NC<u>H</u>CHN), 4.13 (t, J = 7.2 Hz, 4H, NC<u>H</u>$_2$), 3.84 (s, 6H, NC<u>H</u>$_3$), 1.76 (p, J = 7.2 Hz, 4H, (NCH_2C<u>H</u>$_2$(CH_2)$_4$)$_2$), 1.30-1.17 (m, 16H, (NCH_2CH_2(C<u>H</u>$_2$)$_4$)$_2$).

Methyltrioctylammonium *bis*(trifluoromethanesulfonyl)imide [mTOA][N(SO_2CF_3)$_2$]



A solution of lithium *bis*(trifluoromethansulfonyl)imide (5.56 g, 19.4 mmol) in water (50 mL) was added to a solution of methyltrioctylammonium bromide (6.94 g, 15.5 mmol) in acetone (50 mL). This reaction mixture was stirred at room temperature for 48 hours. The acetone was removed under reduced pressure with two layers forming after its removal. The reaction mixture was then extracted with dichloromethane (3 x 50 mL), the organic extracts combined and extracted with water (8 x 50 mL) until a negative silver nitrate test was achieved. The excess organic solvent was removed *in vacuo* to give methyltrioctylammonium *bis*(trifluoromethanesulfonyl)imide as a pale yellow, viscous liquid (8.69 g, 13.3 mmol, 87%). ^{1}H NMR (300 MHz, CD_2Cl_2-d_2) δ 3.14-3.23 (m, 6H, NC<u>H</u>$_2$(CH$_2$)$_6$CH$_3$), 3.00 (s, 3H, NC<u>H</u>$_3$), 1.63-1.75 (m, 6H, NCH$_2$C<u>H</u>$_2$(CH$_2$)$_5$CH$_3$), 1.26-1.46 (m, 30H, N(CH$_2$)$_2$(C<u>H</u>$_2$)$_5$CH$_3$), 0.93 (t, 9H, J = 6.8 Hz, N(CH$_2$)$_7$CH$_3$).

1-(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide [Fbmim][N(SO_2CF_3)$_2$]

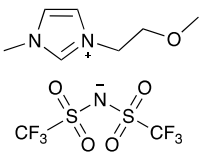


N-Methylimidazole (1.97 g, 24.0 mmol) was added to 3,3,4,4,5,5,6,6,6-nonafluorohexyl iodide (11.2 g, 30.0 mmol) and the reaction mixture was stirred under a nitrogen atmosphere at 40 °C for 7 days. After this time the reaction had proceeded to *ca.* 60% (as evidenced through analysis of the ^{1}H NMR signals for the *N*-methylimidazole singlet at δ 7.5 and the corresponding imidazolium singlet at δ 8.0). The temperature was increased to 50 °C and acetonitrile (5 mL) was added to the reaction mixture which was then stirred for a further 15 days. Intermittent ^{1}H NMR analysis over these 15 days showed that the reaction had stagnated at *ca.* 75%. The reaction mixture was then titrated with diethyl ether (10 x 20 mL) and the excess solvent and reagents were removed *in vacuo* to yield 1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-3-methylimidazolium iodide as a viscous, dark brown liquid (7.43 g, 16.3 mmol, 68%) which was used without further purification. ^{1}H NMR (400 MHz, acetone-d_6) δ 9.74 (s, 1H, NC<u>H</u>N), 8.07 (m, 1H, NC<u>H</u>CHN), 7.86 (m, 1H, NCHC<u>H</u>N), 4.88 (t, J = 7.1 Hz, 2H, NC<u>H</u>$_2$CH$_2$(CF$_2$)$_3$CF$_3$), 4.10 (s, 3H, NC<u>H</u>$_3$), 3.11-3.25 (m, 2H, NCH$_2$C<u>H</u>$_2$).

1-(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)-3-methylimidazolium iodide (7.43 g, 16.3 mmol) was dissolved in water (50 mL) and acetone (25 mL). To this solution, a solution of lithium *bis*(trifluoromethanesulfonyl)imide (5.51 g, 19.2 mmol) in water (25 mL) was added and the resulting mixture wasstirred vigorously at room temperature for 24 hours, during which time two immiscible layers formed. The mixture was extracted with dichloromethane (3 x 10 mL) and the combined organic layers were washed with a sodium iodide and water mixture (4 x 20 mL), a sodium bisulfite

and water mixture (2 x 50 mL) and water (3 x 20 mL). The solvent was removed from the organic phase under reduced pressure and the residue was dried *in vacuo* to give 1-(1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide as a brown liquid (6.57 g, 10.8 mmol, 66%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H, NC<u>H</u>N), 7.71-7.89 (m, 2H, NC<u>H</u>C<u>H</u>N), 4.57 (t, J = 4.6 Hz, 2H, NC<u>H</u>$_2$CH$_2$), 3.87 (s, 3H, NC<u>H</u>$_3$), 3.01 (m, 2H, NCH$_2$C<u>H</u>$_2$).

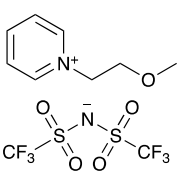
1-(2-Methoxyethyl)-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide [(eOm)mim][N(SO$_2$CF$_3$)$_2$]



N-Methylimidazole (1.92 g, 23.4 mmol) and 1-bromoethane methyl ether (4.84 g, 34.8 mmol) were combined and stirred at room temperature under nitrogen for 5 days. The mixture was then titrated with ethyl acetate (5 x 20 mL) and the residue was dried *in vacuo* to yield the precursor 1-(2-methoxyethyl)-3-methylimidazolium bromide as a colourless liquid. (4.31 g, 19.4 mmol, 83%). ^{1}H NMR (400 MHz, CD$_3$CN-d_3) δ 8.66 (s, 1H, NC<u>H</u>N), 7.43 (m, 1H, NC<u>H</u>CHN), 7.37 (m, 1H, NCHC<u>H</u>N), 4.32 (t, J = 4.8 Hz, 2H, NCH$_2$C<u>H</u>$_2$O), 3.87 (s, 3H, NC<u>H</u>$_3$), 3.71 (t, J = 4.8 Hz, 2H, NC<u>H</u>$_2$CH$_2$O), 3.52 (s, 3H, OC<u>H</u>$_3$).

Lithium *bis*(trifluoromethane)sulfonylimide (6.72 g, 23.4 mmol) was rinsed into a solution of the bromide precursor (4.31 g, 19.4 mmol) with water (45 mL) and the resultant mixture was stirred at room temperature overnight. The aqueous reaction mixture was extracted with dichloromethane (3 x 50 mL) with the organic extracts being collected and combined. The organic extracts were then washed with water (8 x 100 mL) until a negative silver nitrate test was achieved. Excess organic solvent was then removed *in vacuo* resulting in an off-white, viscous liquid (8.23 g, 16.8 mmol, 86%). ^{1}H NMR (400 MHz, CD$_3$CN-d_3) δ 8.48 (s, 1H, NC<u>H</u>N), 7.40 (m, 1H, NC<u>H</u>CHN), 7.35 (m, 1H, NC<u>H</u>CHN), 4.30 (t, J = 4.8 Hz, 2H, NCH$_2$C<u>H</u>$_2$O), 3.86 (s, 3H, NCH$_3$), 3.70 (t, J = 4.8 Hz, 2H, NC<u>H</u>$_2$CH$_2$O), 3.34 (s, 3H, OC<u>H</u>$_3$).

1-(2-Methoxyethyl)pyridinium *bis*(trifluoromethanesulfonyl)imide [(eOm)py][N(SO$_2$CF$_3$)$_2$]

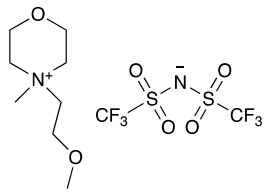


2-Bromoethyl methyl ether (5.86 g, 42.2 mmol) was added to a solution of pyridine (3.31 g, 41.8 mmol) in acetone (15 mL). This mixture was stirred at room temperature for four days. During this time, white powder was observed in the solution. The mixture was then stirred at reflux for a further two days, during which time the solvent evaporated. The residue was triturated with diethyl ether (50 mL), ethyl acetate (4 x

50 mL), and hexane (50 mL) and any remaining solvent removed *in vacuo* to yield 1-(2-methoxyethyl)pyridinium bromide as an off-white solid (8.84 g, 40.5 mmol, 96%). m.p. 125-128 °C (lit.[19] 128-130 °C). ^{1}H NMR (400 MHz, CD_3CN-d_3) δ 8.82-8.88 (m, 2H, ArH2/6), 8.52-8.59 (m, 1H, ArH4), 8.07 (t, J = 6.9 Hz, 2H, ArH3/5), 4.76-4.81 (m, 2H, $NCH_2CH_2OCH_3$), 3.85 (t, J = 5.0 Hz, 2H, $NCH_2CH_2OCH_3$), 3.31 (s, 3H, OCH_3).

1-(2-Methoxyethyl)pyridinium bromide (8.75 g, 40.1 mmol) and lithium *bis*(trifluoromethanesulfonyl)imide (11.6 g, 40.5 mmol) were dissolved in water (50 mL) and the resulting mixture was stirred at room temperature for a day, during which time two immiscible layers formed. The mixture was extracted with dichloromethane (3 x 20 mL) and the combined organic layers were washed with water (5 x 20 mL). The solvent was removed from the organic phase under reduced pressure and the residue was dried *in vacuo* to give 1-(2-methoxyethyl)pyridinium *bis*(trifluoromethanesulfonyl)imide as a pale blue liquid (13.7 g, 32.8 mmol, 81%). ^{1}H NMR (400 MHz, CD_3CN-d_3) δ 8.67-8.72 (m, 2H, ArH2/6), 8.55 (m, 1H, ArH4), 8.05 (t, J = 6.8 Hz, 2H, ArH3/5), 4.69 (t, J = 4.7 Hz, 2H, $NCH_2CH_2OCH_3$), 3.83 (*t*, J = 4.7 Hz, 2H, $NCH_2CH_2OCH_3$), 3.32 (s, 3H, OCH_3).

4-(2-Methoxyethyl)-4-methylmorpholinium *bis*(trifluoromethanesulfonyl)imide [(eOm)mmo][N(SO$_2$CF$_3$)$_2$]



2-Bromoethyl methyl ether (5.92 g, 42.6 mmol) was added to a solution of 4-methylmorpholine (3.75 g, 37.1 mmol). This mixture was stirred at room temperature for four days. During this time, white powder was observed in the solution. The mixture was then stirred at reflux for a further two days, during which time the mixture became a brown solid. The residue was triturated with diethyl ether (4 x 50 mL) and the solvent removed under reduced pressure to yield 4-(2-methoxyethyl)-4-methylmorpholinium bromide (8.30 g, 34.6 mmol, 93%) as a light brown solid. m.p. 118-120 °C (lit.[20] 121 °C). ^{1}H NMR (400 MHz, CD_3CN-d_3) δ 3.92-3.98 (m, 4H, $N(CH_2CH_2)_2O$), 3.79-3.84 (m, 2H, $NCH_2CH_2OCH_3$), 3.68 (t, J = 4.5 Hz, 2H, $NCH_2CH_2OCH_3$), 3.39-3.57 (m, 4H, $N(CH_2CH_2)_2O$), 3.36 (s, 3H, NCH_3), 3.22 (s, 3H, OCH_3).

4-(2-Methoxyethyl)-4-methylmorpholinium bromide (8.18 g, 34.1 mmol) and lithium *bis*(trifluoromethanesulfonyl)imide (10.1 g, 35.2 mmol) were dissolved in water (50 mL) and the resulting mixture stirred at room temperature for a day, during which time two immiscible layers formed. The mixture was extracted with dichloromethane (3 x 20 mL) and the combined organic layers were washed with water (5 x 20 mL). The solvent was removed from the organic phase *in vacuo* and the residue was dried under reduced pressure to give

4-(2-methoxyethyl)-4-methylmorpholinium *bis*(trifluoromethanesulfonyl)imide salt as an orange liquid (11.0 g, 25.0 mmol, 73%). ^{1}H NMR (400 MHz, CD_3CN-d_3) δ 3.92-3.97 (m, 4H, $N(CH_2C\underline{H}_2)_2O$), 3.78-3.84 (m, 2H, $NC\underline{H}_2CH_2OCH_3$), 3.59 (t, J = 4.7 Hz, 2H, $NCH_2C\underline{H}_2OCH_3$), 3.34-3.52 (m, 7H, $N(C\underline{H}_2CH_2)_2O$ and $NC\underline{H}_3$), 3.17 (s, 3H, $OC\underline{H}_3$).

Stock solution compositions and rate constants

Table S9. Composition of stock solutions by mass, including resultant mole fraction, and concentration of pyridine, used for the kinetic studies of the reaction between pyridine **2** and benzyl bromide **1** in an ionic liquid; the stock solutions are made up to 2 ml with acetonitrile.

Ionic liquid	Mass IL / g	Mass Pyridine / g	[Pyridine] / mol L^{-1}	χ_{IL}
[emim][$N(SO_2CF_3)_2$]	2.830	0.080	0.51	0.81
[$h_x$mim][$N(SO_2CF_3)_2$]	2.561	0.082	0.52	0.79
[omim][$N(SO_2CF_3)_2$]	2.513	0.079	0.50	0.80
[dmim][$N(SO_2CF_3)_2$]	2.425	0.081	0.51	0.80
[ddmim][$N(SO_2CF_3)_2$]	2.375	0.080	0.50	0.80
[$(mim)_2p_r$][$N(SO_2CF_3)_2]_2$	2.905	0.080	0.51	0.43[a]
[$(mim)_2$b][$N(SO_2CF_3)_2]_2$	2.677	0.083	0.52	0.35[a]
[$(mim)_2h_x$][$N(SO_2CF_3)_2]_2$	2.934	0.084	0.53	0.76
[$(mim)_2h_p$][$N(SO_2CF_3)_2]_2$	2.321	0.081	0.51	0.22[a]
[$(mim)_2$o][$N(SO_2CF_3)_2]_2$	2.850	0.086	0.54	0.74
[$(mim)_2$n][$N(SO_2CF_3)_2]_2$	2.822	0.083	0.53	0.75
[$(mim)_2$d][$N(SO_2CF_3)_2]_2$	2.780	0.081	0.51	0.74
[$(mim)_2$u][$N(SO_2CF_3)_2]_2$	2.752	0.083	0.52	0.74
[$(mim)_2$dd][$N(SO_2CF_3)_2]_2$	2.703	0.086	0.54	0.72
[mTOA][$N(SO_2CF_3)_2]_2$	2.128	0.084	0.53	0.76
[Fbmim][$N(SO_2CF_3)_2]_2$	3.100	0.081	0.51	0.80
[(eOm)mim][$N(SO_2CF_3)_2]_2$	2.812	0.082	0.52	0.81
[(eOm)py][$N(SO_2CF_3)_2]_2$	2.862	0.080	0.50	0.82
[(eOm)mmo][$N(SO_2CF_3)_2]_2$	2.832	0.082	0.52	0.82

[a]Solubility issues in the co-solvent acetonitrile and the reagents prevented achievement of a higher mole fraction of ionic liquid in the reaction mixture.

Table S10. Rate constants determined in the kinetic studies of the reaction between pyridine **2** and benzyl bromide **1** in an ionic liquid at 22.2 ºC. Also included are the corresponding mole fractions and concentrations of pyridine used. Uncertainties are reported as the standard deviation of triplicate results.

Ionic liquid	χ_{IL}	[Pyridine] / mol L^{-1}	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}
[emim][$N(SO_2CF_3)_2$]	0.81	0.51	8.95	17.7
			8.60	17.0
			8.98	17.7
			9.87	19.5
[$h_x$mim][$N(SO_2CF_3)_2$]	0.79	0.52	6.45	12.5
			5.67	10.9
			6.68	12.9
[omim][$N(SO_2CF_3)_2$]	0.80	0.50	5.46	10.9
			5.11	10.2
			5.16	10.3
[dmim][$N(SO_2CF_3)_2$]	0.80	0.51	4.77	9.36
			4.85	9.52
			4.75	9.32
[ddmim][$N(SO_2CF_3)_2$]	0.80	0.50	3.88	7.70
			4.37	8.68
			3.98	7.91
			4.48	8.90
[$(mim)_2p_r$][$N(SO_2CF_3)_2]_2$	0.43	0.51	19.1	37.5
			17.8	35.0
			17.2	33.8
[$(mim)_2$b][$N(SO_2CF_3)_2]_2$[a]	0.35	0.52	3.72	7.11
			4.04	7.73
[$(mim)_2h_x$][$N(SO_2CF_3)_2]_2$	0.76	0.53	8.96	17.4
			10.7	20.9
			10.4	20.5
[$(mim)_2h_p$][$N(SO_2CF_3)_2]_2$	0.22	0.51	12.6	24.5
			11.6	22.6
			8.48	16.5
[$(mim)_2$o][$N(SO_2CF_3)_2]_2$	0.74	0.54	8.36	15.4
			8.84	16.3
			7.73	14.2
[$(mim)_2$n][$N(SO_2CF_3)_2]_2$	0.75	0.53	11.8	23.0
			10.7	20.9
			9.53	18.6
[$(mim)_2$d][$N(SO_2CF_3)_2]_2$	0.74	0.51	8.96	17.4
			10.7	20.9
			10.4	20.5

$[(mim)_2u][N(SO_2CF_3)_2]_2$	0.74	0.52	9.39	18.3
			8.22	16.0
			7.44	14.5
$[(mim)_2dd][N(SO_2CF_3)_2]_2$	0.72	0.54	8.39	15.5
			9.35	17.2
		0.51	8.18	15.8
$[mTOA][N(SO_2CF_3)_2]_2$	0.76	0.53	2.02	3.80
			2.74	5.16
			2.25	4.26
$[Fbmim][N(SO_2CF_3)_2]_2$	0.80	0.51	20.0	39.4
			20.0	39.5
			17.2	33.8
$[(eOm)mim][N(SO_2CF_3)_2]_2$	0.81	0.52	11.7	22.6
			10.8	21.0
			10.5	20.4
$[(eOm)py][N(SO_2CF_3)_2]_2$	0.82	0.50	11.1	21.1
			11.3	21.5
			10.9	21.1
$[(eOm)mmo][N(SO_2CF_3)_2]_2$	0.82	0.52	10.3	23.1
			12.8	24.2
			11.4	22.1

[a]Only two data sets are represented here as solidification of the sample *in situ* prevented collection of a triplicate data point despite multiple attempts.

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