

Supporting Information

Evaluation of Cation-Anion Interaction Strength in Ionic Liquids

Ana M. Fernandes^{§*}, Marisa A. A. Rocha[†], Mara G. Freire[‡], Isabel M. Marrucho[‡], João A. P. Coutinho[‡], Luis M. N. B. F. Santos[†]

[‡]CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

[§]QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

[†] CIQ, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, 4169-007

Porto, Portugal

*Corresponding author

Tel: +351-234-370200; Fax: +351-234-370084;

E-mail address: afernandes@ua.pt

Computational Details

Table S1. Electronic energies (E_{ele}) and BSSE corrected electronic energies (E_{ele} ($BSSE$)), for each specie, calculated at the B3LYP/6-31+G(d) level of theory.

Species	E_{ele}	E_{ele} ($BSSE$)
	Hartree	
$[\text{C}_4\text{mim}]^+$	-423.18615	---
$[\text{C}_4\text{C}_1\text{mim}]^+$	-462.51281	---
Cl^-	-460.27473	---
BF_4^-	-424.56698	---
PF_6^-	-940.71596	---
TfO^-	-961.55341	---
Tf_2N^-	-1827.28343	---
$[\text{C}_4\text{mim}][\text{Cl}]$	-883.60256	-883.60225
$[\text{C}_4\text{mim}][\text{BF}_4]$	-847.88392	-847.88296
$[\text{C}_4\text{mim}][\text{PF}_6]$	-1364.02383	-1364.02256
$[\text{C}_4\text{mim}][\text{TfO}]$	-1384.86667	-1384.86511
$[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$	-2250.58868	-2250.58589
$[\text{C}_4\text{C}_1\text{mim}][\text{Tf}_2\text{N}]$	-2289.90797	-2289.90493
$[\text{C}_4\text{mim}][\text{Cl}_2]^-$	-1343.92565	-1343.92504
$[\text{C}_4\text{mim}][(\text{BF}_4)_2]^-$	-1272.49333	-1272.49199
$[\text{C}_4\text{mim}][(\text{PF}_6)_2]^-$	-2304.77942	-2304.77762
$[\text{C}_4\text{mim}][(\text{TfO})_2]^-$	-2346.46143	-2346.45950
$[\text{C}_4\text{mim}][(\text{Tf}_2\text{N})_2]^-$	-4077.91100	-4077.90701
$[\text{C}_4\text{C}_1\text{mim}][(\text{Tf}_2\text{N})_2]^-$	-4117.22608	-4117.22028
$[(\text{C}_4\text{mim})_2]^+[\text{Cl}]$	-1306.84121	-1306.84069
$[(\text{C}_4\text{mim})_2]^+[\text{BF}_4]$	-1271.11698	-1271.11576
$[(\text{C}_4\text{mim})_2]^+[\text{PF}_6]$	-1787.25355	-1787.25145
$[(\text{C}_4\text{mim})_2]^+[\text{TfO}]$	-1808.09766	-1808.09548
$[(\text{C}_4\text{mim})_2]^+[\text{Tf}_2\text{N}]$	-2673.81984	-2673.81557
$[(\text{C}_4\text{C}_1\text{mim})_2]^+[\text{Tf}_2\text{N}]$	-2752.45995	-2752.45450

Table S2. BSSE uncorrected and corrected dissociation energies for the ionic liquid pairs ([cation][anion]), [(cation)₂anion]⁺ and [(anion)₂cation]⁻ aggregates, calculated at the B3LYP/6-31+G(d) level of theory.

Reaction Scheme	$E_{Diss} / \text{kJ}\cdot\text{mol}^{-1}$			$E_{Diss}(BSSE) / \text{kJ}\cdot\text{mol}^{-1}$		
	(1)	(2)	(3)	(1)	(2)	(3)
	[cation][anion]	[cation(anion) ₂] ⁻	[(cation) ₂ anion] ⁺	[cation][anion]	[cation(anion) ₂] ⁻	[(cation) ₂ anion] ⁺
[C ₄ mim][Cl]	372	127	138	371	126	137
[C ₄ mim][BF ₄]	343	111	123	341	110	122
[C ₄ mim][PF ₆]	320	104	114	316	103	112
[C ₄ mim][TfO]	334	109	118	330	108	116
[C ₄ mim][Tf ₂ N]	313	102	118	305	99	114
[C ₄ C ₁ mim][Tf ₂ N]	293	91	103	285	84	97

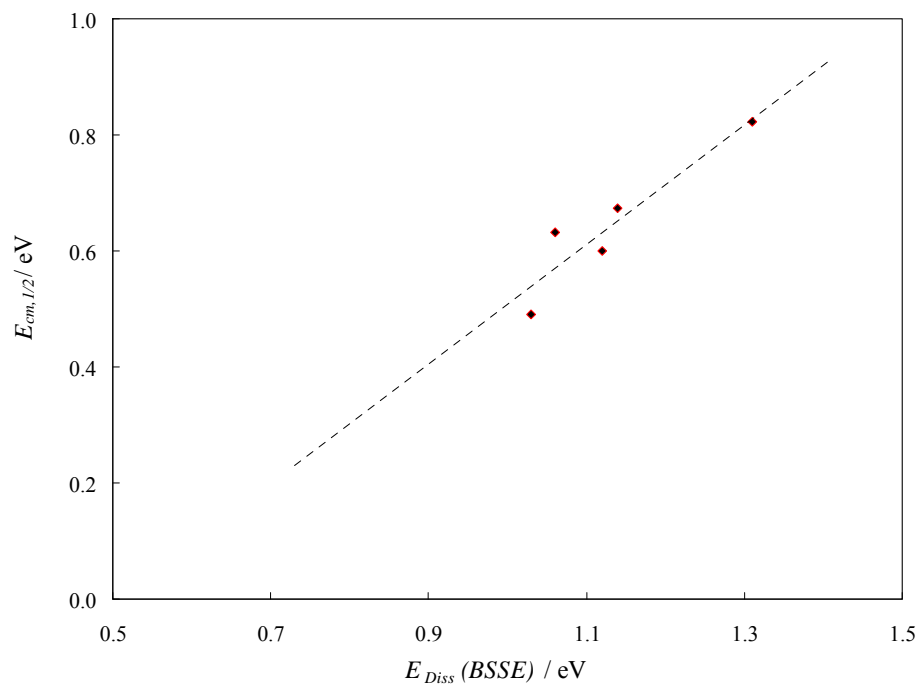


Figure S2. Plot of the calculated dissociation energies ($E_{Diss}(BSSE)$) versus the relative interaction energies ($E_{cm,1/2}$), $E_{cm,1/2} = 1.0 \times E_{Diss}(BSSE) - 0.52$.