

Supporting information  
for  
Unravelling the interactions of magnetic  
ionic liquids by energy decomposition  
schemes: Towards a transferable  
polarisable force field

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**Table S1.** Contributions to the interaction energy (kcal mol<sup>-1</sup>) using SAPT0. Dist is the distance of the minimum interaction energy between the CM, E<sub>Elec</sub> is the electrostatic contribution, E<sub>Exch</sub> is the exchange contribution, E<sub>Ind</sub> is the induction contribution, E<sub>Disp</sub> is the dispersion contribution, E<sub>Tot</sub> is the total interaction energy in SAPT0 and E<sub>CCSD(T)</sub> is the interaction energy with DLPNO-CCSD(T)

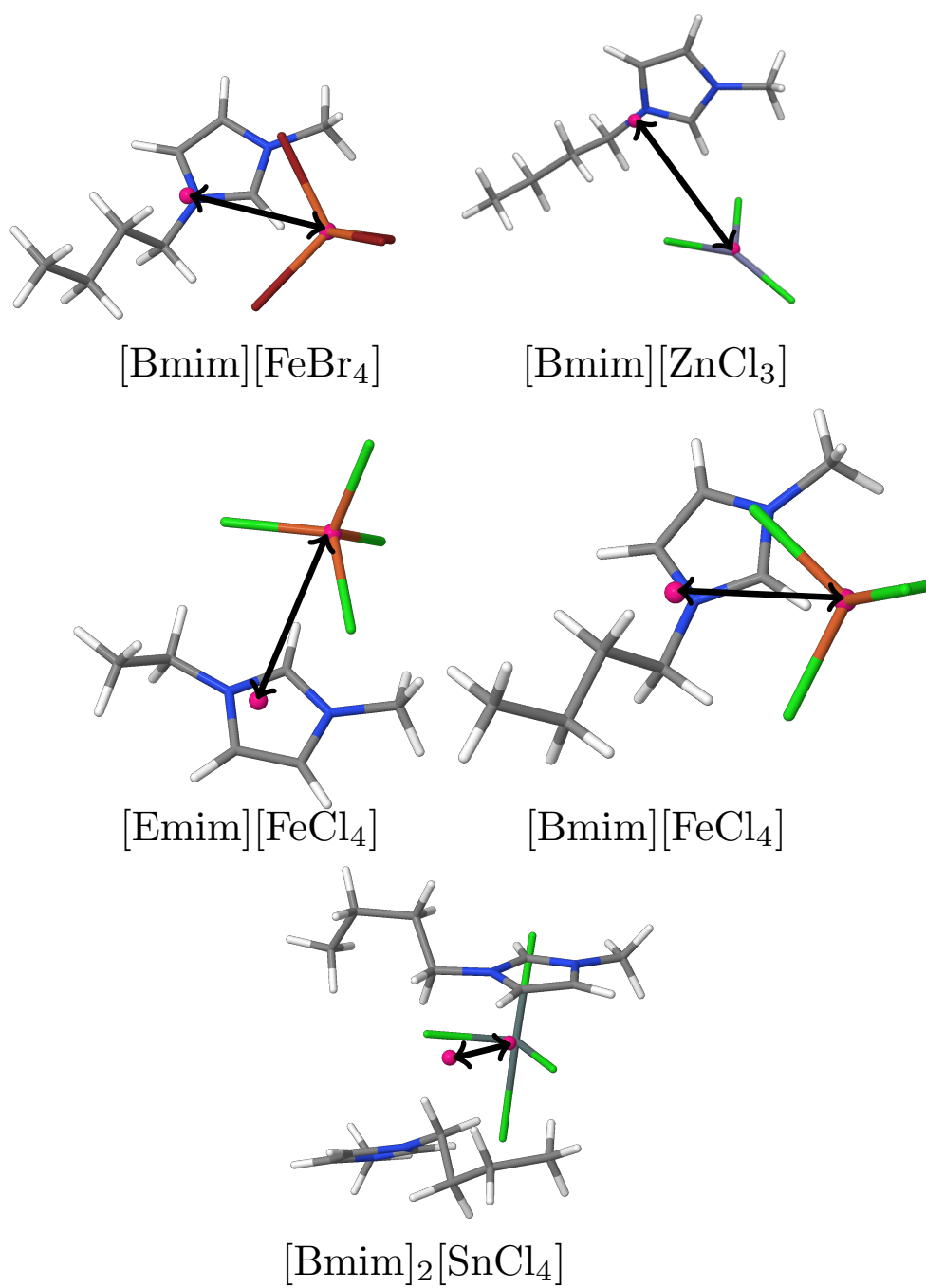
Molecule	Dist(Å)	E <sub>Elec</sub>	E <sub>Exch</sub>	E <sub>Ind</sub>	E <sub>Disp</sub>	E <sub>Tot</sub>	E <sub>CCSD(T)</sub>
[Bmim][FeCl <sub>4</sub> ](C <sub>4</sub> -C <sub>5</sub> )	5.341	-65.19	17.89	-5.50	-7.91	-60.71	-58.82
[Bmim][FeCl <sub>4</sub> ](Chain)	9.599	-35.11	5.63	-2.44	-2.40	-34.32	-33.79

**Table S2.** Charge of the MIL anion according to Mulliken and Natural Population Analysis (NPA) at the minimum geometry.

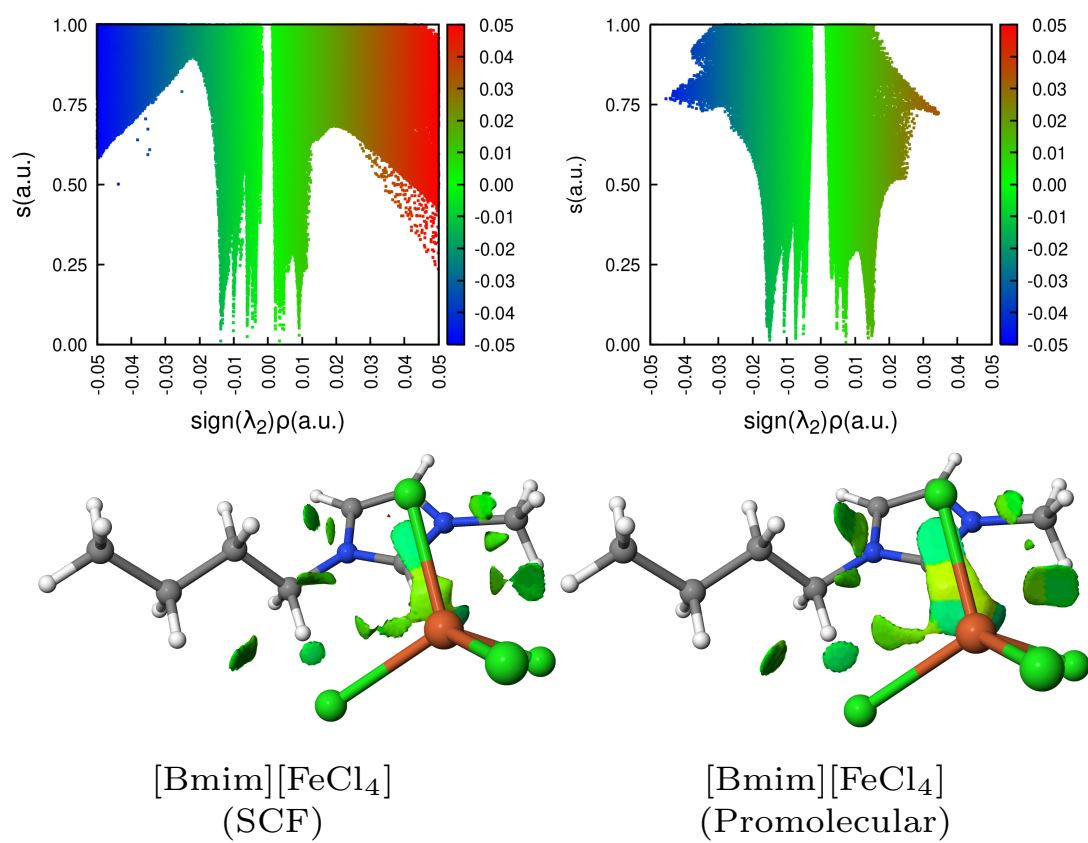
MIL	Q <sub>Mull</sub>	Q <sub>NPA</sub>
[Emim][FeCl <sub>4</sub> ]	-1.0620	-0.95775
[Bmim][FeCl <sub>4</sub> ]	-1.1317	-0.94044
[Bmim][FeBr <sub>4</sub> ]	-1.1196	-0.93520
[Bmim][ZnCl <sub>3</sub> ]	-1.0517	-0.93843
[Bmim] <sub>2</sub> [SnCl <sub>4</sub> ]	-2.1194	-1.79151

**Table S3.** Comparison between minimum distance and energies between SAPT0 and LED-DLPNO-CCSD(T).

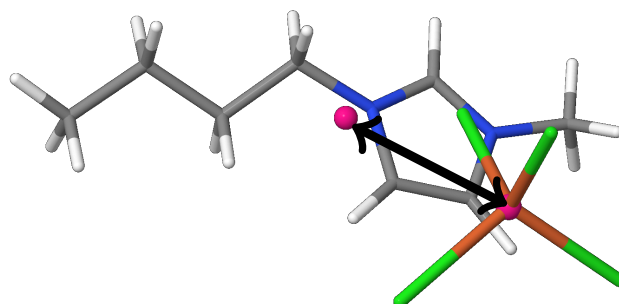
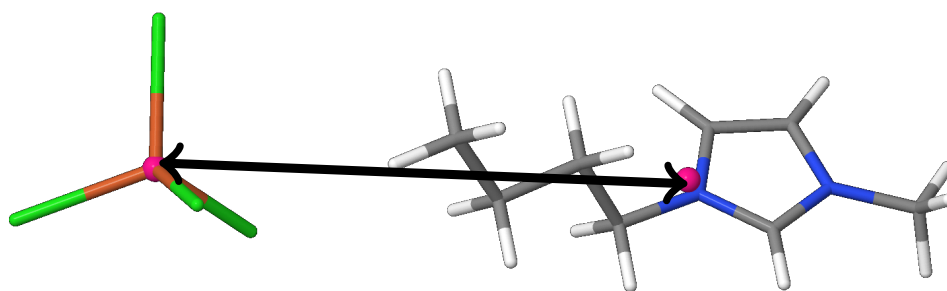
MIL	Method	Dist (Å)	E (kcal mol <sup>-1</sup> )
[Emim][FeCl <sub>4</sub> ]	LED	4.108	-73.441
	SAPT	4.017	-76.282
[Bmim][FeCl <sub>4</sub> ]	LED	4.341	-71.634
	SAPT	4.273	-73.955
[Bmim][FeBr <sub>4</sub> ]	LED	4.426	-71.343
	SAPT	4.342	-74.596
[Bmim][ZnCl <sub>3</sub> ]	LED	4.640	-70.364
	SAPT	4.574	-72.251
[Bmim] <sub>2</sub> [SnCl <sub>4</sub> ]	LED	3.680	-260.076
	SAPT	3.513	-270.503



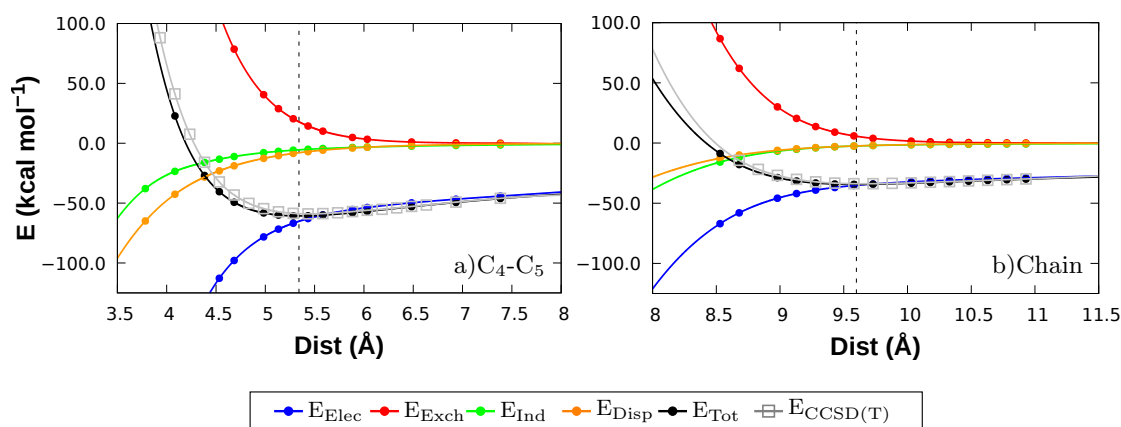
**Figure S1.** Distance between the centre of mass of the different monomers.



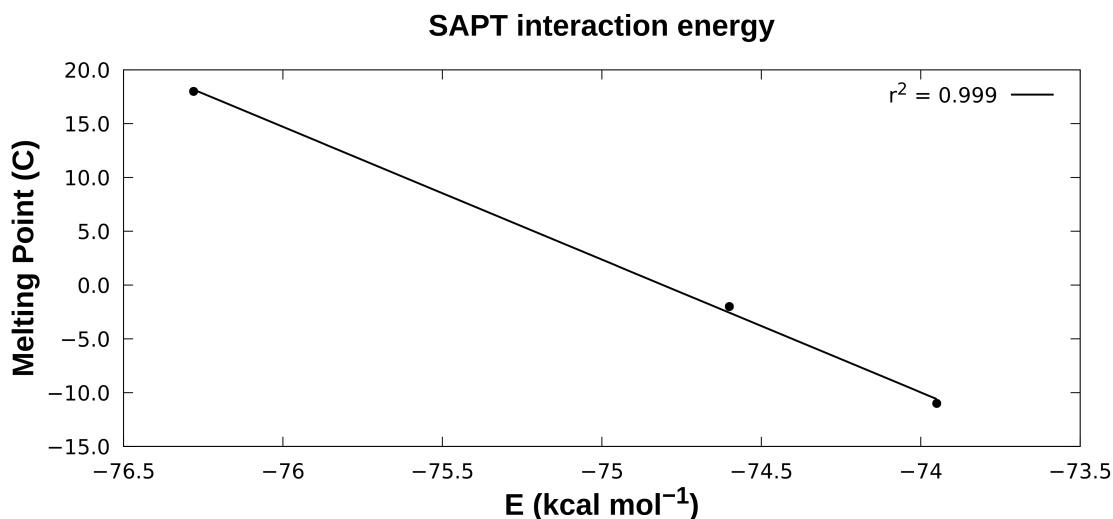
**Figure S2.** Comparison between SCF calculation and promolecular calculation in NCIPlot.



**Figure S3.** Distance between the centre of mass of the different additional configurations of [Bmim][FeCl<sub>4</sub>]



**Figure S4.** SAPT decomposition for an increase distance between the monomers in [Bmim][FeCl<sub>4</sub>] with different dispositions.



**Figure S5.** Relationship between SAPT energy and the experimental melting points for different MILs. Relationship between SAPT energy and the experimental melting points for different MILs.

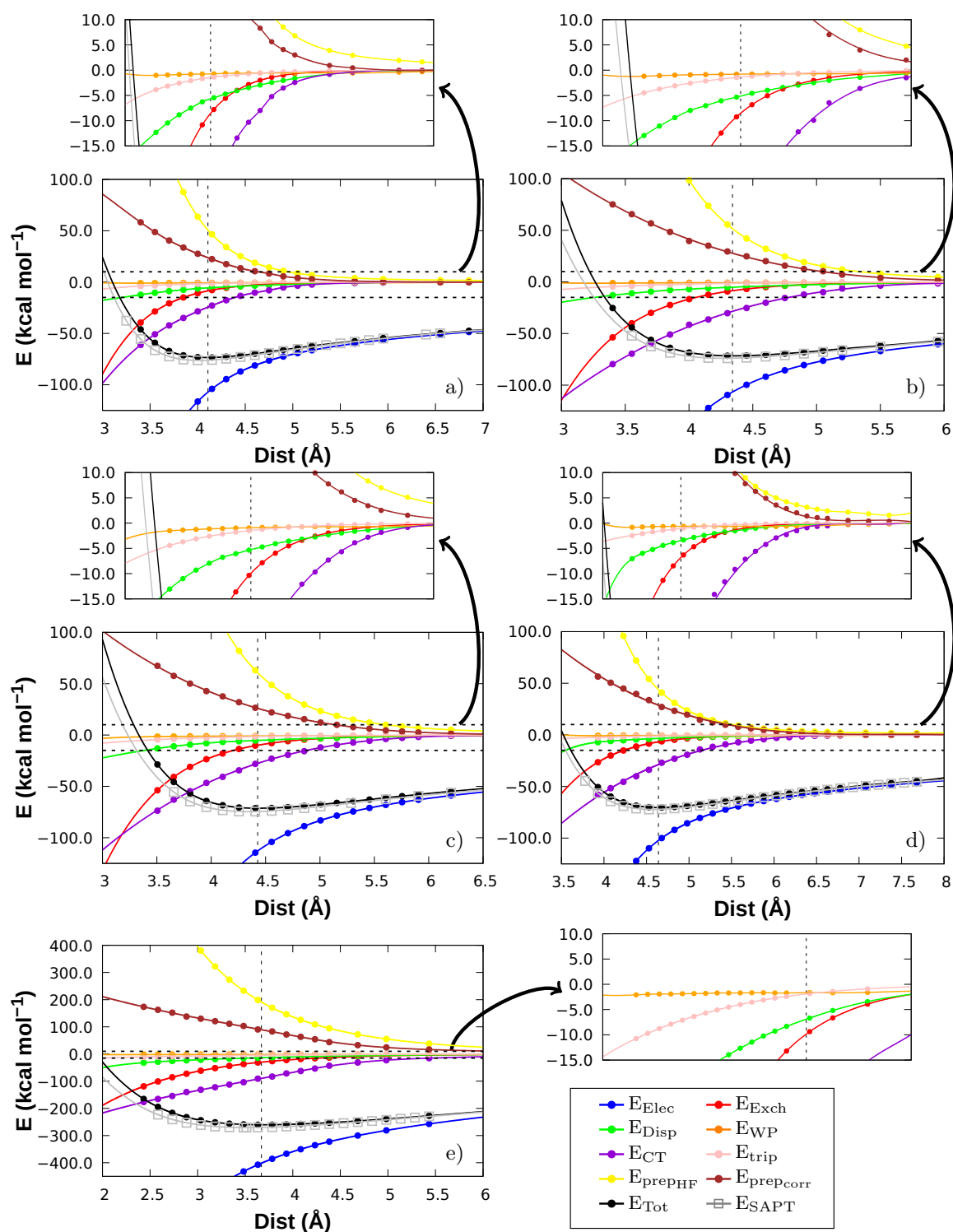
Experimental data taken from Refs. [1,2,3].

<sup>1</sup>Yoshida, Y.; Otsuka, A.; Saito, G.; Natsume, S.; Nishibori, E.; Takata, M.; Sakata, M.; Takahashi, M.; Yoko, T. Conducting and Magnetic Properties of 1-Ethyl-3-Methylimidazolium (EMI) Salts Containing Paramagnetic Irons: Liquids [EMI][M<sup>III</sup>Cl<sub>4</sub>] (M = Fe and Fe<sub>0.5</sub>Ga<sub>0.5</sub>) and Solid [EMI]<sub>2</sub>[Fe<sup>II</sup>Cl<sub>4</sub>]. Bull. Chem. Soc. Jpn. 2005, 78, 1921–1928, doi:10.1246/bcsj.78.1921.

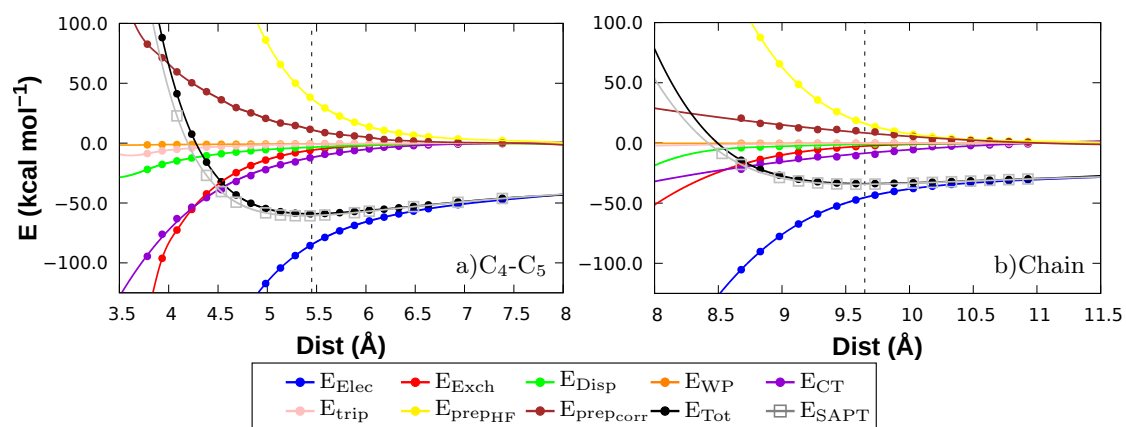
<sup>2</sup>Krieger, B.M.; Lee, H.Y.; Emge, T.J.; Wishart, J.F.; Edward W. Castner, J. Ionic Liquids and Solids with Paramagnetic Anions. Phys. Chem. Chem. Phys. 2010, 12, 8919–8925, doi:10.1039/B920652N.

<sup>3</sup>Yoshida, Y.; Saito, G. Influence of Structural Variations in 1-Alkyl-3-Methylimidazolium Cation and Tetrahalogenoferrate(III) Anion on the Physical Properties of the Paramagnetic Ionic Liquids. J. Mater. Chem. 2006, 16, 1254–1262, doi:10.1039/b515391c.

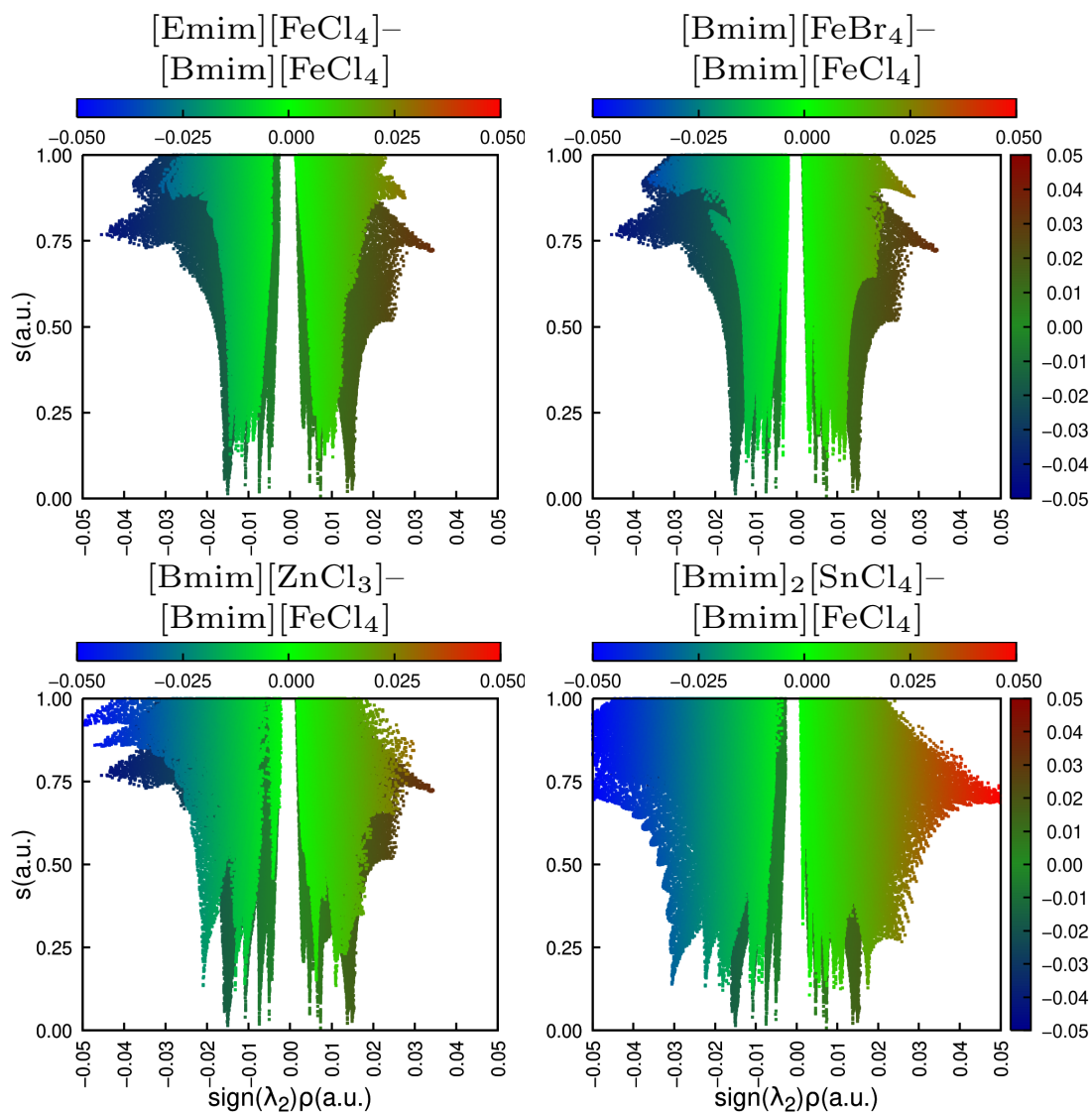




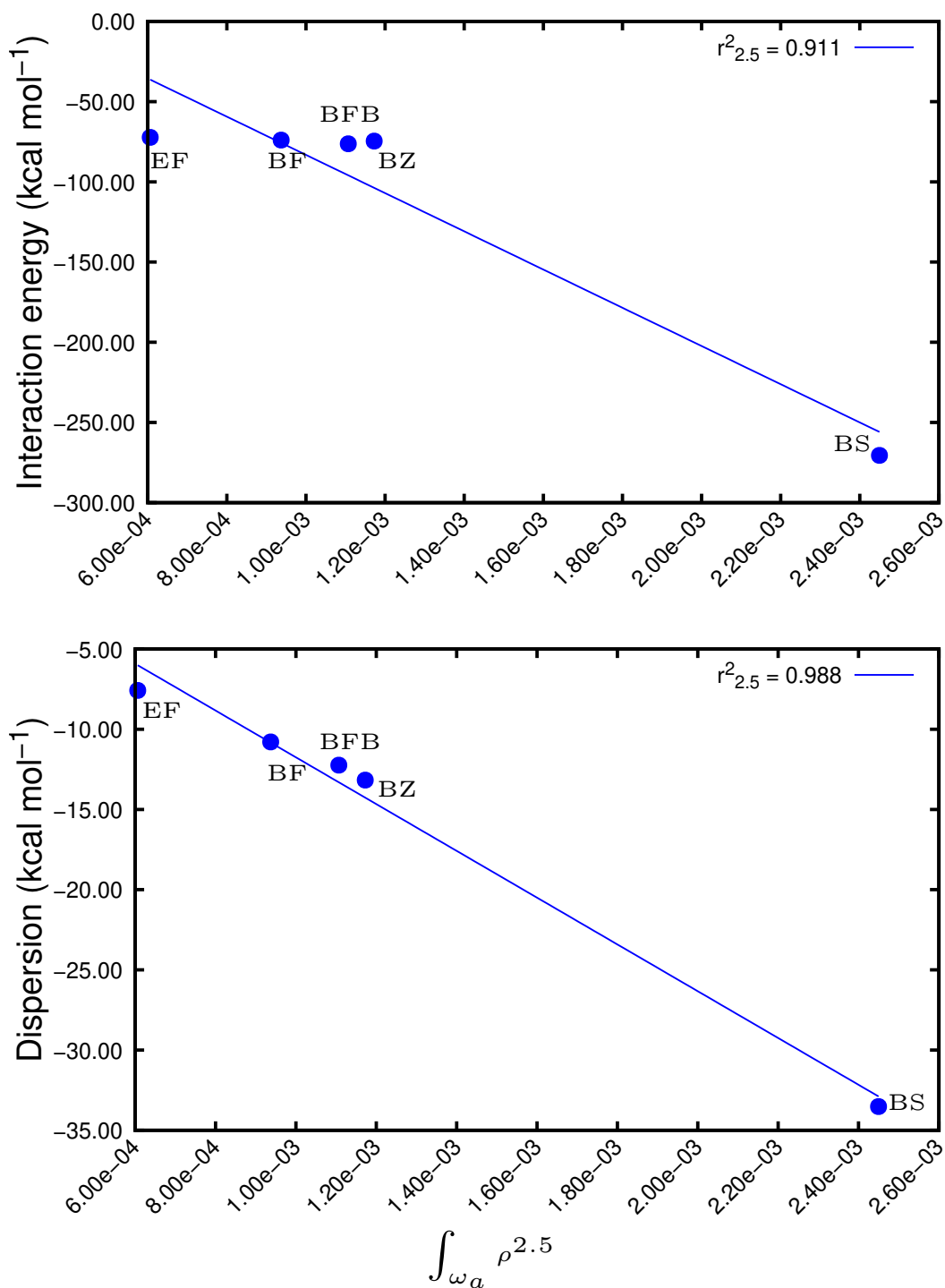
**Figure S6.** The LED-DLPNO-CCSD(T) decomposition for an increase distance between the monomers. The SAPT0 energy is included with the purpose to compare the results. a) [Emim][FeCl<sub>4</sub>], b) [Bmim][FeCl<sub>4</sub>], c) [Bmim][FeBr<sub>4</sub>], d) [Bmim][ZnCl<sub>3</sub>], e) [Bmim]<sub>2</sub>[SnCl<sub>4</sub>]



**Figure S7.** The LED-DLPNO-CCSD(T) decomposition for an increase distance between the monomers in [Bmim][FeCl<sub>4</sub>] with different dispositions.



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