Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Importance of dispersion forces for prediction of thermodynamic and transport properties of routinely used ionic liquids

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SUPPLEMENTARY INFORMATION

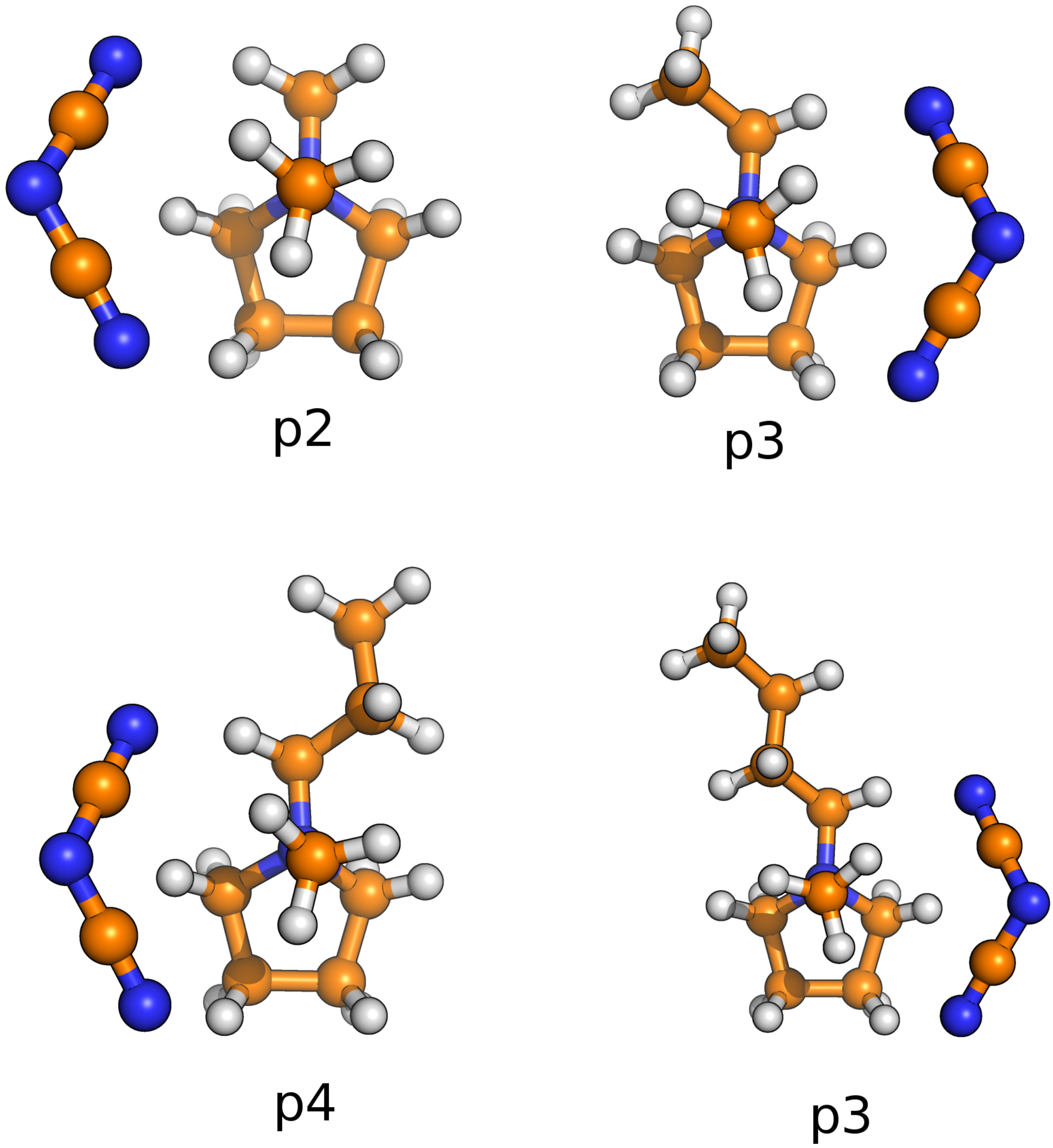

Figure S1. Lowest energy conformations of pyrrolidinium-based ion pairs coupled with the $N(CN)_2$ anion.

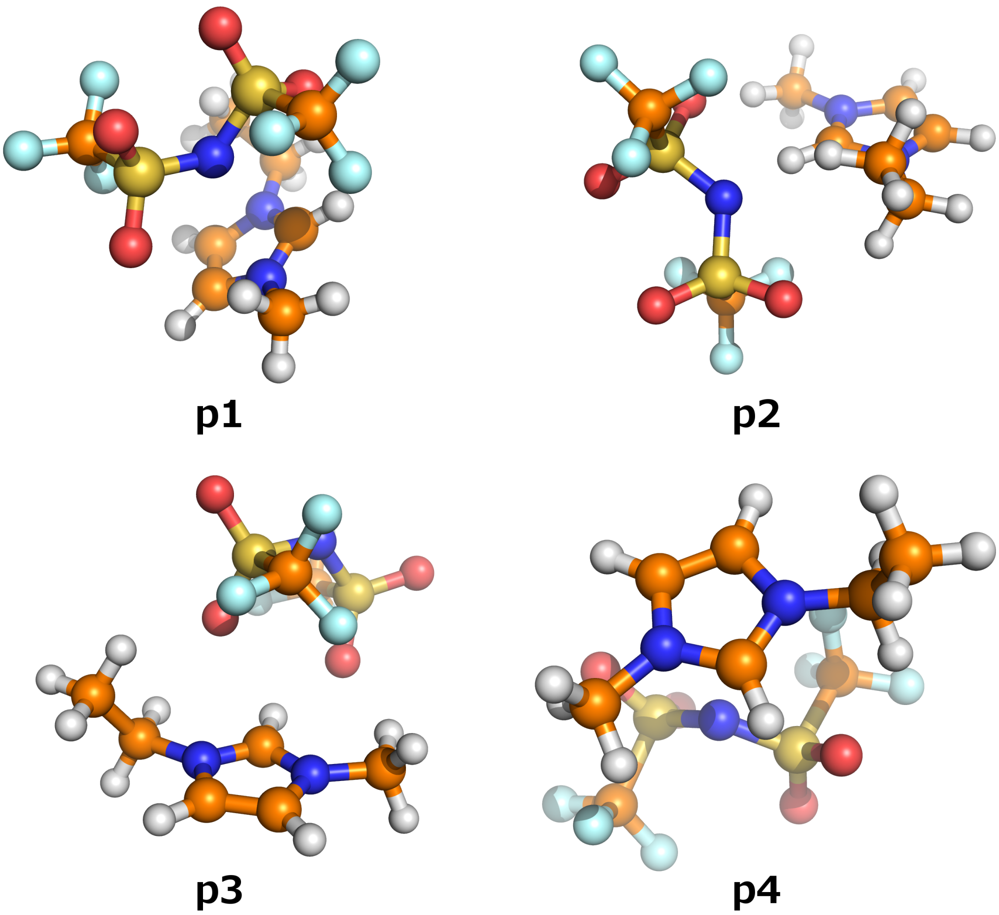

Figure S2. Imidazolium-based ion pair conformations coupled with the NTf_2 anion.

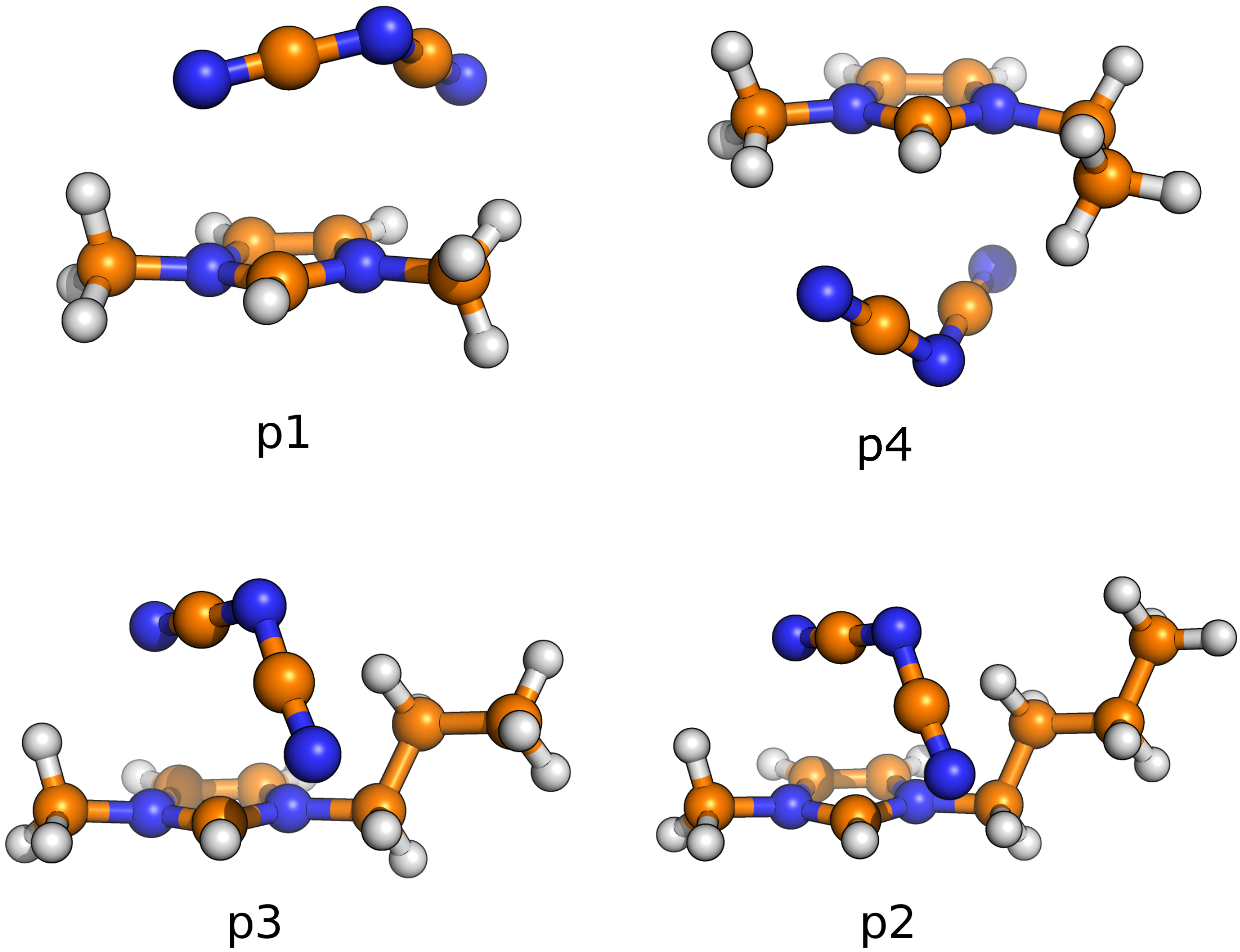

Figure S3. Lowest energy conformations of imidazolium-based ion pairs coupled with the $N(CN)_2$ anion.

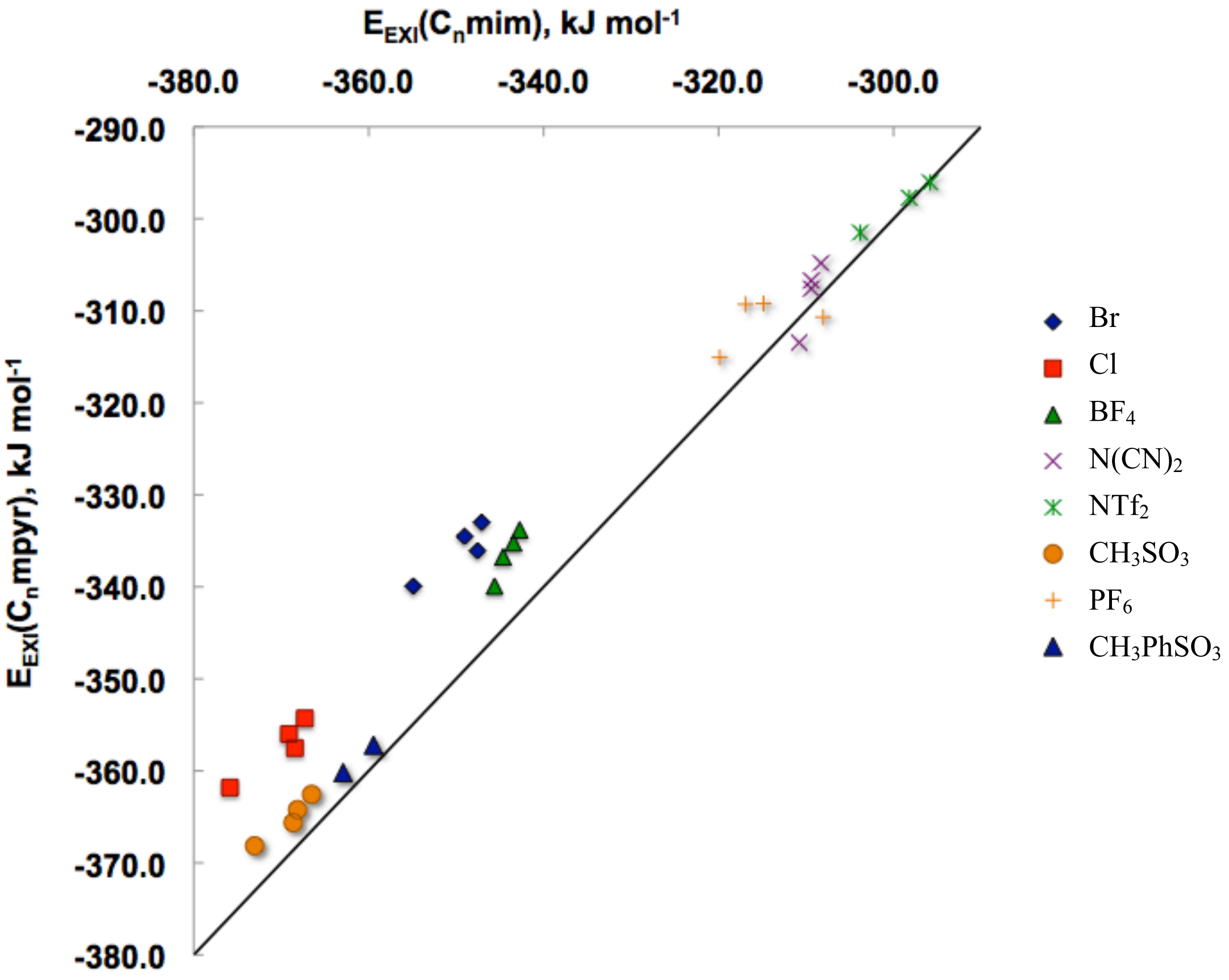

Figure S4. Comparison of the E_{EXI} contribution for imidazolium and pyrrolidinium ion pairs.

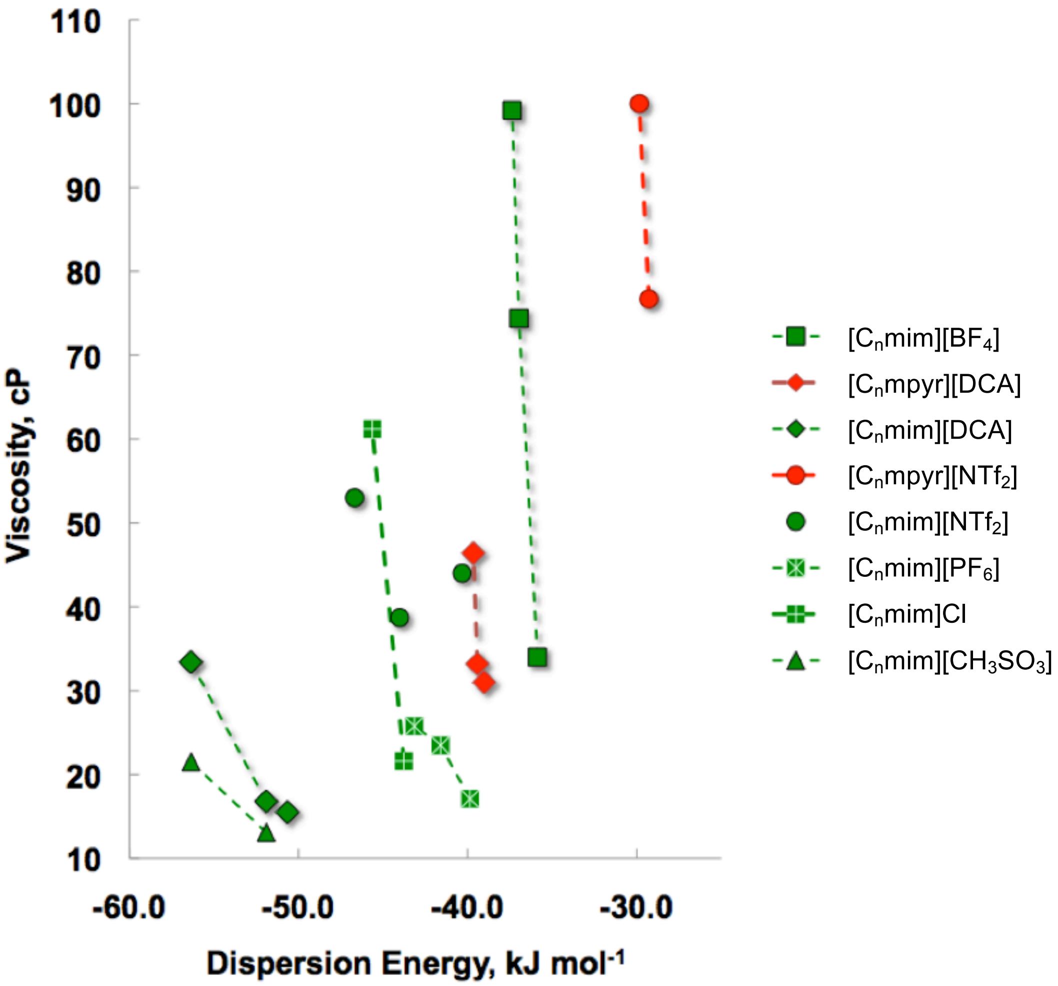

Figure S5. Correlation between conductivity (in cP) and dispersion component of interaction energy in kJ mol^{-1}. Viscosity data are taken at 293/295 K with the exception of [$C_n$mim][PF_6] taken at 353 K and [$C_n$mim]Cl and [$C_n$mim][Mesylate] taken at 363 K.

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Table S1. SAPT interaction energy, E_{Int}(SAPT) in kJ mol^{-1}, and its components (in kJ mol^{-1}) of ion pairs and corresponding conformations. The lowest energy conformation for each ion pair is given in bold.

Cation	**Anion**	**Conformation**	E_{Elst}	$E^{(10)}_{Exch}$	$E^{(20)}_{Ind,resp}$	$E^{(20)}_{Exch-Ind,resp}$	$E^{(20)}_{Disp}$	$E^{(20)}_{Exch-Disp}$	$\delta HF_{int,resp}$	$E_{tot}(SAPT)$
C_1mim	**BF_4**	**p1**	**-383.3**	**73.7**	**-50.5**	**23.2**	**-42.2**	**7.1**	**-8.0**	**-380.1**
C_2mim	**BF_4**	**p1**	**-382.1**	**78.0**	**-54.1**	**24.0**	**-45.6**	**7.6**	**-8.8**	**-380.9**
C_2mim	BF_4	p4	-375.8	73.8	-51.6	22.9	-42.1	7.1	-8.5	-374.2
C_3mim	**BF_4**	**p1**	**-380.1**	**79.0**	**-56.0**	**24.3**	**-47.0**	**7.8**	**-9.0**	**-381.1**
C_3mim	BF_4	p4	-377.3	75.9	-54.0	23.1	-45.0	7.4	-8.7	-378.6
C_4mim	**BF_4**	**p1**	**-378.5**	**79.3**	**-57.1**	**24.3**	**-47.7**	**7.9**	**-9.0**	**-380.8**
C_4mim	BF_4	p4	-375.2	75.9	-54.7	23.1	-45.3	7.5	-8.7	-377.5
C_1mpyr	**BF_4**	**p1**	**-367.6**	**70.3**	**-46.7**	**15.3**	**-37.5**	**6.0**	**-10.8**	**-371.0**
C_1mpyr	BF_4	p2	-362.3	70.0	-45.6	15.1	-34.1	5.7	-11.4	-362.5
C_2mpyr	**BF_4**	**p1**	**-362.4**	**69.6**	**-47.6**	**15.3**	**-38.5**	**6.2**	**-10.8**	**-368.3**
C_2mpyr	BF_4	p2	-351.0	69.9	-45.9	14.8	-35.6	5.7	-11.0	-353.0
C_2mpyr	BF_4	p3	-358.2	71.8	-47.4	15.7	-35.5	5.9	-11.8	-359.5
C_3mpyr	**BF_4**	**p1**	**-358.9**	**68.3**	**-48.2**	**15.0**	**-39.0**	**6.2**	**-10.6**	**-367.3**
C_3mpyr	BF_4	p2	-346.3	68.4	-46.4	14.3	-35.9	5.8	-10.9	-351.1
C_3mpyr	BF_4	p3	-355.0	71.2	-48.2	15.6	-36.0	6.0	-11.8	-358.1
C_4mpyr	**BF_4**	**p1**	**-356.8**	**68.3**	**-49.0**	**15.0**	**-39.3**	**6.2**	**-10.6**	**-366.1**
C_4mpyr	BF_4	p2	-343.8	67.9	-47.0	14.3	-36.2	5.7	-10.8	-349.9
C_4mpyr	BF_4	p3	-353.4	71.9	-49.1	15.8	-36.4	6.0	-11.9	-357.1
C_1mim	**Br**	**p1**	**-462.6**	**178.6**	**-244.8**	**193.7**	**-65.7**	**20.3**	**-19.8**	**-400.3**
C_1mim	Br	p2	-411.3	141.9	-133.0	84.5	-41.8	10.5	-34.7	-383.9
C_2mim	Br	p1	-449.6	175.6	-227.8	177.1	-67.4	20.4	-18.9	-390.7
C_2mim	Br	p2	-411.8	147.0	-138.1	86.3	-46.6	11.5	-36.1	-387.8

C_2mim	Br	p3	-412.0	144.8	-139.9	91.0	-47.3	12.1	-32.4	-383.5
C_2mim	**Br**	**p4**	**-455.0**	**177.1**	**-241.9**	**190.3**	**-66.9**	**20.6**	**-19.3**	**-395.2**
C_3mim	Br	p1	-447.7	177.0	-231.1	179.0	-68.9	20.7	-19.4	-390.5
C_3mim	Br	p2	-408.7	147.1	-138.8	86.1	-47.5	11.7	-36.3	-386.3
C_3mim	Br	p3	-413.3	148.8	-146.1	95.5	-52.8	13.6	-30.8	-385.1
C_3mim	**Br**	**p4**	**-457.7**	**183.2**	**-252.8**	**198.5**	**-70.7**	**21.6**	**-20.1**	**-398.1**
C_4mim	Br	p1	-446.6	177.6	-231.5	178.4	-70.2	21.0	-19.4	-390.6
C_4mim	Br	p2	-407.1	147.7	-139.9	85.9	-48.9	11.9	-36.4	-386.9
C_4mim	Br	p3	-412.4	150.3	-148.9	97.0	-55.2	14.3	-30.5	-385.4
C_4mim	**Br**	**p4**	**-455.2**	**182.7**	**-252.2**	**197.2**	**-71.3**	**21.7**	**-19.9**	**-397.0**
C_1mpyr	**Br**	**p1**	**-410.5**	**136.1**	**-136.1**	**91.2**	**-52.2**	**13.6**	**-20.4**	**-378.3**
C_1mpyr	Br	p2	-403.9	132.9	-128.4	84.4	-48.8	12.7	-20.9	-372.1
C_2mpyr	**Br**	**p1**	**-405.5**	**135.7**	**-137.8**	**92.4**	**-54.0**	**14.1**	**-20.2**	**-375.4**
C_2mpyr	Br	p2	-388.8	132.7	-123.1	79.1	-50.8	12.9	-22.1	-360.2
C_2mpyr	Br	p3	-398.8	133.4	-130.5	85.8	-50.6	13.2	-20.8	-368.2
C_3mpyr	**Br**	**p1**	**-403.2**	**136.1**	**-139.1**	**92.5**	**-55.3**	**14.4**	**-20.2**	**-374.7**
C_3mpyr	Br	p2	-383.6	129.9	-123.6	79.7	-51.1	13.1	-21.6	-357.1
C_3mpyr	Br	p3	-396.4	133.7	-131.8	86.3	-51.8	13.5	-20.8	-367.3
C_4mpyr	**Br**	**p1**	**-401.2**	**136.5**	**-140.0**	**92.7**	**-55.8**	**14.5**	**-20.3**	**-373.5**
C_4mpyr	Br	p2	-380.9	129.3	-124.0	79.4	-51.6	13.1	-21.5	-356.1
C_4mpyr	Br	p3	-394.8	134.5	-133.0	86.8	-52.3	13.6	-20.9	-366.0
C_1mim	**Cl**	**p1**	**-473.5**	**173.7**	**-216.1**	**161.8**	**-61.6**	**19.0**	**-21.7**	**-418.5**
C_1mim	Cl	p2	-439.0	158.1	-132.9	76.6	-43.3	11.0	-39.1	-408.6
C_2mim	Cl	p1	-460.6	170.3	-200.0	145.0	-63.6	19.1	-20.4	-410.1
C_2mim	Cl	p2	-437.1	160.2	-136.3	76.4	-46.9	11.6	-40.3	-412.5
C_2mim	Cl	p3	-436.9	157.4	-137.7	81.2	-47.7	12.3	-36.0	-407.5

C_2mim	**Cl**	**p4**	**-464.8**	**171.1**	**-213.4**	**158.4**	**-62.5**	**19.1**	**-21.0**	**-413.1**
C_3mim	Cl	p1	-456.9	170.5	-201.0	144.5	-64.6	19.4	-20.6	-408.7
C_3mim	Cl	p2	-433.4	159.9	-136.9	75.9	-47.4	11.7	-40.6	-410.7
C_3mim	Cl	p3	-435.8	157.7	-141.6	83.6	-51.9	13.4	-33.8	-408.3
C_3mim	**Cl**	**p4**	**-466.0**	**175.8**	**-220.9**	**163.2**	**-65.6**	**20.0**	**-21.8**	**-415.4**
C_4mim	Cl	p1	-454.8	170.2	-200.4	143.0	-65.4	19.5	-20.5	-408.5
C_4mim	Cl	p2	-431.2	159.8	-137.6	75.4	-48.4	11.8	-40.6	-410.9
C_4mim	Cl	p3	-434.0	158.0	-143.7	84.3	-53.7	13.9	-33.2	-408.4
C_4mim	**Cl**	**p4**	**-463.4**	**175.3**	**-220.9**	**162.3**	**-66.1**	**20.1**	**-21.6**	**-414.3**
C_1mpyr	**Cl**	**p1**	**-419.4**	**124.9**	**-117.6**	**69.8**	**-48.0**	**12.5**	**-19.4**	**-397.3**
C_1mpyr	Cl	p2	-415.4	124.5	-113.7	66.4	-45.8	11.9	-19.9	-392.0
C_2mpyr	**Cl**	**p1**	**-413.2**	**123.9**	**-118.5**	**70.0**	**-49.3**	**12.8**	**-19.3**	**-393.6**
C_2mpyr	Cl	p2	-397.3	121.9	-108.0	60.7	-46.6	11.9	-20.9	-378.3
C_2mpyr	Cl	p3	-408.3	123.4	-114.0	65.9	-46.8	12.2	-19.9	-387.5
C_3mpyr	**Cl**	**p1**	**-409.9**	**123.3**	**-119.1**	**69.5**	**-50.2**	**13.0**	**-19.2**	**-392.6**
C_3mpyr	Cl	p2	-393.0	121.3	-109.0	60.8	-47.3	12.1	-20.9	-376.1
C_3mpyr	Cl	p3	-404.9	122.7	-114.5	65.7	-47.5	12.3	-19.8	-386.0
C_4mpyr	**Cl**	**p1**	**-407.3**	**122.9**	**-119.6**	**69.3**	**-50.3**	**13.0**	**-19.2**	**-391.2**
C_4mpyr	Cl	p2	-390.9	121.5	-109.8	60.3	-48.2	12.2	-20.9	-375.8
C_4mpyr	Cl	p3	-402.3	122.2	-114.8	65.3	-47.6	12.4	-19.8	-384.5
C_1mim	**$N(CN)_2$**	**p1**	**-382.8**	**106.7**	**-74.5**	**50.3**	**-62.5**	**11.7**	**-10.5**	**-361.6**
C_1mim	$N(CN)_2$	p2	-362.4	102.4	-58.7	26.6	-47.6	8.1	-19.2	-350.7
C_2mim	**$N(CN)_2$**	**p1**	**-381.2**	**110.2**	**-77.8**	**51.1**	**-64.9**	**12.2**	**-11.6**	**-362.1**
C_2mim	$N(CN)_2$	p2	-377.8	107.8	-76.3	51.2	-63.4	12.0	-10.7	-357.2
C_2mim	$N(CN)_2$	p3	-373.1	103.6	-73.8	49.9	-62.5	11.8	-9.7	-353.8
C_3mim	$N(CN)_2$	p1	-369.3	103.1	-71.4	45.0	-64.4	11.5	-11.8	-357.3

C_3mim	$N(CN)_2$	p2	-359.3	102.1	-61.2	29.1	-57.1	9.5	-16.7	-353.6
C_3mim	**$N(CN)_2$**	**p3**	**-381.5**	**111.3**	**-78.1**	**50.6**	**-68.7**	**12.7**	**-11.2**	**-364.9**
C_4mim	$N(CN)_2$	p1	-368.1	103.6	-72.0	45.0	-65.3	11.7	-11.8	-356.9
C_4mim	**$N(CN)_2$**	**p2**	**-379.9**	**111.7**	**-78.6**	**50.3**	**-70.4**	**12.9**	**-11.1**	**-365.1**
C_4mim	$N(CN)_2$	p3	-369.3	102.3	-69.1	45.0	-64.1	11.8	-10.4	-353.8
C_1mpyr	$N(CN)_2$	p1	-348.2	79.2	-51.0	21.7	-44.8	7.5	-11.9	-347.6
C_1mpyr	**$N(CN)_2$**	**p2**	**-350.6**	**75.1**	**-48.9**	**22.3**	**-46.5**	**7.5**	**-10.9**	**-352.1**
C_1mpyr	$N(CN)_2$	p3	-328.5	73.0	-48.5	20.0	-43.2	7.1	-11.7	-331.8
C_1mpyr	$N(CN)_2$	p4	-354.1	77.0	-49.1	23.5	-45.5	7.6	-10.9	-351.5
C_2mpyr	$N(CN)_2$	p1	-341.8	78.1	-50.8	21.2	-45.3	7.6	-12.0	-343.1
C_2mpyr	$N(CN)_2$	p2	-342.7	74.6	-47.8	21.5	-46.8	7.6	-11.3	-344.9
C_2mpyr	**$N(CN)_2$**	**p3**	**-345.1**	**74.9**	**-49.1**	**22.0**	**-47.3**	**7.7**	**-11.0**	**-348.0**
C_3mpyr	$N(CN)_2$	p1	-338.6	74.6	-50.7	21.2	-46.3	7.6	-11.8	-344.0
C_3mpyr	$N(CN)_2$	p2	-339.1	74.1	-48.2	21.2	-47.1	7.6	-11.3	-342.7
C_3mpyr	$N(CN)_2$	p3	-311.6	65.1	-42.0	15.3	-41.9	6.5	-10.4	-319.0
C_3mpyr	**$N(CN)_2$**	**p4**	**-342.5**	**74.0**	**-49.4**	**21.6**	**-47.6**	**7.7**	**-11.0**	**-347.1**
C_4mpyr	$N(CN)_2$	p1	-336.8	73.7	-48.4	21.0	-47.2	7.6	-11.3	-341.4
C_4mpyr	$N(CN)_2$	p2	-336.2	72.3	-50.8	21.2	-46.9	7.6	-11.2	-344.1
C_4mpyr	**$N(CN)_2$**	**p3**	**-340.1**	**73.7**	**-49.6**	**21.6**	**-47.7**	**7.7**	**-11.0**	**-345.3**
C_1mim	**CH_3SO_3**	**p1**	**-431.9**	**106.0**	**-84.2**	**47.4**	**-59.9**	**11.4**	**-10.4**	**-421.5**
C_2mim	**CH_3SO_3**	**p1**	**-427.0**	**111.8**	**-89.9**	**49.0**	**-64.9**	**12.3**	**-12.4**	**-421.1**
C_2mim	CH_3SO_3	p4	-423.5	106.2	-85.5	47.3	-61.0	11.7	-10.7	-415.6
C_3mim	**CH_3SO_3**	**p1**	**-427.0**	**116.6**	**-93.9**	**50.0**	**-68.4**	**12.9**	**-13.4**	**-423.3**
C_3mim	CH_3SO_3	p4	-419.7	106.4	-86.5	47.4	-61.7	11.8	-10.8	-413.0
C_4mim	**CH_3SO_3**	**p1**	**-424.9**	**117.5**	**-95.4**	**50.1**	**-69.9**	**13.1**	**-13.6**	**-423.0**
C_4mim	CH_3SO_3	p4	-417.4	106.4	-87.1	47.4	-61.8	11.9	-10.8	-411.4

C_1mpyr	**CH_3SO_3**	**p1**	**-406.8**	**97.8**	**-69.0**	**27.0**	**-51.3**	**9.1**	**-16.7**	**-409.8**
C_1mpyr	CH_3SO_3	p2	-403.2	107.5	-69.3	27.1	-46.5	8.8	-20.4	-396.1
C_2mpyr	**CH_3SO_3**	**p1**	**-401.0**	**95.5**	**-69.5**	**26.8**	**-52.9**	**9.3**	**-16.4**	**-408.2**
C_2mpyr	CH_3SO_3	p2	-385.5	89.9	-64.1	24.1	-48.4	8.4	-15.7	-391.2
C_2mpyr	CH_3SO_3	p3	-396.7	102.5	-68.9	26.6	-48.0	8.9	-19.5	-395.1
C_3mpyr	**CH_3SO_3**	**p1**	**-396.1**	**92.2**	**-69.6**	**26.3**	**-53.6**	**9.3**	**-15.9**	**-407.5**
C_3mpyr	CH_3SO_3	p2	-381.1	89.3	-64.9	23.9	-48.8	8.4	-15.8	-388.9
C_3mpyr	CH_3SO_3	p3	-393.4	102.0	-70.0	26.5	-49.1	9.0	-19.3	-394.4
C_4mpyr	**CH_3SO_3**	**p1**	**-393.3**	**91.8**	**-70.1**	**26.1**	**-53.7**	**9.3**	**-16.0**	**-406.0**
C_4mpyr	CH_3SO_3	p2	-378.3	88.7	-65.5	23.7	-49.4	8.5	-15.7	-387.9
C_4mpyr	CH_3SO_3	p3	-391.1	102.0	-70.7	26.5	-49.4	9.0	-19.4	-393.1
C_1mim	NTf_2	p1	-366.1	101.6	-64.8	41.3	-49.2	8.6	-7.1	-335.7
C_1mim	**NTf_2**	**p2**	**-363.8**	**107.7**	**-62.0**	**24.2**	**-35.3**	**5.7**	**-21.4**	**-344.9**
C_1mim	NTf_2	p3	-357.3	90.4	-54.2	22.9	-37.5	5.7	-12.1	-342.0
C_2mim	NTf_2	p1	-365.0	107.3	-66.7	42.1	-54.0	9.1	-8.1	-335.4
C_2mim	**NTf_2**	**p2**	**-358.4**	**105.1**	**-60.3**	**24.4**	**-40.6**	**6.1**	**-18.9**	**-342.5**
C_2mim	NTf_2	p3	-357.2	96.0	-56.9	23.6	-40.6	6.2	-13.5	-342.4
C_2mim	NTf_2	p4	-358.1	99.4	-59.1	34.8	-48.5	8.1	-7.6	-331.1
C_3mim	NTf_2	p1	-364.8	110.9	-68.5	42.9	-56.9	9.6	-8.6	-335.4
C_3mim	NTf_2	p2	-358.0	108.1	-61.8	25.0	-43.8	6.6	-18.7	-342.6
C_3mim	**NTf_2**	**p3**	**-356.5**	**97.9**	**-58.3**	**23.9**	**-42.2**	**6.4**	**-14.0**	**-342.8**
C_3mim	NTf_2	p4	-348.2	96.1	-57.2	33.7	-48.3	8.0	-6.9	-322.9
C_1mpyr	**NTf_2**	**p1**	**-326.1**	**60.6**	**-40.2**	**13.8**	**-32.7**	**4.4**	**-9.3**	**-329.4**
C_1mpyr	NTf_2	p2	-322.7	59.3	-40.5	11.5	-29.1	4.0	-10.1	-327.7
C_1mpyr	NTf_2	p3	-331.1	68.9	-42.9	15.0	-32.6	4.7	-11.0	-329.0
C_1mpyr	NTf_2	p5	-324.9	60.8	-41.1	11.6	-29.7	4.0	-9.9	-329.1

C_2mpyr	**NTf_2**	**p1**	**-319.4**	**55.6**	**-38.7**	**12.8**	**-33.4**	**4.3**	**-8.6**	**-327.5**
C_2mpyr	NTf_2	p2	-317.8	60.4	-40.9	11.6	-30.9	4.1	-10.7	-324.4
C_2mpyr	NTf_2	p3	-316.8	58.8	-38.4	12.8	-33.0	4.4	-8.5	-320.7
C_2mpyr	NTf_2	p4	-322.9	65.2	-41.7	14.2	-32.7	4.6	-10.8	-323.9
C_2mpyr	NTf_2	p5	-313.2	58.6	-38.6	10.8	-30.9	4.0	-9.0	-318.3
C_2mpyr	NTf_2	p6	-315.8	58.4	-40.0	11.0	-29.8	4.0	-9.9	-322.1
C_3mpyr	**NTf_2**	**p1**	**-317.7**	**57.6**	**-40.0**	**12.8**	**-35.3**	**4.6**	**-8.7**	**-326.8**
C_3mpyr	NTf_2	p2	-314.2	61.4	-41.3	11.7	-31.0	4.1	-10.6	-319.8
C_3mpyr	NTf_2	p3	-314.7	60.5	-39.3	13.0	-33.5	4.5	-8.9	-318.4
C_3mpyr	NTf_2	p4	-321.2	66.2	-42.6	14.2	-34.3	4.7	-10.9	-323.9
C_3mpyr	NTf_2	p5	-309.8	57.3	-38.7	10.6	-31.0	4.0	-9.0	-316.7
C_3mpyr	NTf_2	p6	-312.3	58.0	-40.2	11.0	-30.8	4.0	-10.0	-320.4
C_4mpyr	NTf_2	p1	-315.8	58.0	-40.7	13.0	-35.6	4.7	-9.0	-325.5
C_4mpyr	**NTf_2**	**p2**	**-315.6**	**58.5**	**-41.7**	**11.3**	**-33.5**	**4.3**	**-9.8**	**-326.5**
C_4mpyr	NTf_2	p3	-314.5	63.4	-41.0	13.4	-34.8	4.7	-9.5	-318.3
C_4mpyr	NTf_2	p4	-319.2	66.0	-43.1	14.2	-35.0	4.8	-10.9	-323.1
C_4mpyr	NTf_2	p5	-308.2	56.9	-38.8	10.5	-31.5	4.0	-9.0	-316.0
C_4mpyr	NTf_2	p6	-311.3	58.3	-40.7	11.1	-31.7	4.1	-10.0	-320.2
C_1mim	**PF_6**	**p1**	**-358.5**	**71.3**	**-46.2**	**21.7**	**-43.0**	**6.6**	**-8.1**	**-356.3**
C_2mim	**PF_6**	**p1**	**-358.3**	**77.2**	**-50.4**	**23.7**	**-47.8**	**7.3**	**-8.9**	**-357.2**
C_2mim	PF_6	p4	-350.7	70.4	-46.6	21.5	-43.3	6.6	-8.1	-350.2
C_3mim	PF_6	p1	-342.2	73.4	-46.5	20.2	-46.9	7.1	-7.4	-342.2
C_3mim	**PF_6**	**p4**	**-347.4**	**70.4**	**-47.0**	**21.5**	**-43.5**	**6.7**	**-8.2**	**-347.6**
C_4mim	**PF_6**	**p1**	**-356.2**	**80.0**	**-53.7**	**24.7**	**-51.3**	**7.8**	**-9.3**	**-358.1**
C_4mim	PF_6	p4	-345.5	70.2	-47.4	21.4	-43.6	6.7	-8.2	-346.3
C_1mpyr	**PF_6**	**p1**	**-339.0**	**61.2**	**-40.5**	**13.2**	**-36.1**	**5.2**	**-9.8**	**-345.6**

C_1mpyr	PF_6	p2	-334.8	61.1	-39.9	13.3	-33.1	4.9	-10.1	-338.5
C_2mpyr	**PF_6**	**p1**	**-333.8**	**62.7**	**-41.6**	**13.7**	**-36.8**	**5.3**	**-10.1**	**-340.4**
C_2mpyr	PF_6	p2	-322.8	59.6	-39.1	12.4	-34.3	4.9	-9.7	-328.9
C_2mpyr	PF_6	p3	-330.1	61.4	-40.7	13.5	-34.1	5.1	-10.3	-335.2
C_3mpyr	**PF_6**	**p1**	**-331.8**	**60.1**	**-41.7**	**13.2**	**-38.0**	**5.3**	**-9.7**	**-342.5**
C_3mpyr	PF_6	p2	-319.0	58.7	-39.4	12.2	-34.4	4.9	-9.6	-326.7
C_3mpyr	PF_6	p3	-327.3	60.9	-41.3	13.4	-34.7	5.1	-10.3	-334.2
C_4mpyr	**PF_6**	**p1**	**-329.9**	**60.3**	**-42.4**	**13.3**	**-38.2**	**5.4**	**-9.7**	**-341.3**
C_4mpyr	PF_6	p2	-317.0	58.4	-40.0	12.2	-34.9	4.9	-9.6	-325.9
C_4mpyr	PF_6	p3	-325.5	60.6	-41.7	13.4	-35.0	5.1	-10.2	-333.4
C_1mim	**CH_3PhSO_3**	**p1**	**-415.6**	**104.2**	**-81.6**	**42.5**	**-60.0**	**11.2**	**-12.5**	**-411.7**
C_2mim	**CH_3PhSO_3**	**p1**	**-414.1**	**109.6**	**-91.0**	**48.7**	**-66.2**	**12.1**	**-12.4**	**-413.3**
C_2mim	CH_3PhSO_3	p4	-409.5	104.1	-85.1	45.0	-61.2	11.3	-11.5	-407.0
C_3mim	**CH_3PhSO_3**	**p1**	**-413.5**	**112.9**	**-94.1**	**49.5**	**-69.9**	**12.7**	**-13.0**	**-415.2**
C_3mim	CH_3PhSO_3	p4	-410.0	109.4	-86.8	43.7	-67.1	12.3	-12.3	-410.8
C_4mim	**CH_3PhSO_3**	**p1**	**-412.3**	**115.1**	**-95.9**	**50.0**	**-72.3**	**13.1**	**-13.3**	**-415.6**
C_4mim	CH_3PhSO_3	p4	-408.0	109.7	-92.3	47.3	-66.9	12.1	-13.4	-411.5
C_1mpyr	**CH_3PhSO_3**	**p1**	**-394.4**	**95.5**	**-69.4**	**25.8**	**-51.5**	**8.8**	**-17.2**	**-402.4**
C_1mpyr	CH_3PhSO_3	p2	-384.0	90.3	-64.8	23.7	-45.4	7.9	-17.2	-389.5
C_2mpyr	**CH_3PhSO_3**	**p1**	**-388.9**	**93.6**	**-69.7**	**25.7**	**-53.2**	**9.0**	**-17.1**	**-400.7**
C_2mpyr	CH_3PhSO_3	p2	-373.5	87.4	-63.9	23.0	-48.6	8.1	-16.1	-383.7

Table S2. Average interaction, E_{Int}(ave), and dispersion, E_{Disp+X}(ave), energies in kJ mol^{-1} and the proposed ratio (as defined in equation 4) for imidazolium- and pyrrolidinium-based ionic liquids.

Ionic Liquid		E_{Int}(ave)	E_{Disp+X}(ave)	$Ratio = \frac{E_{Int}(\text{ave})}{E_{Disp+X}(\text{ave})}$
Cation	Anion			
C_1mim	Cl	-418.4	-42.5	9.8389
C_2mim		-412.2	-43.8	9.4170
C_3mim		-414.3	-45.2	9.1742
C_4mim		-412.9	-45.6	9.0478
C_1mpyr		-396.8	-35.0	11.3432
C_2mpyr		-393.1	-35.6	11.0406
C_3mpyr		-392.2	-36.2	10.8231
C_4mpyr		-390.7	-36.5	10.7185
C_1mim	Br	-400.3	-45.4	8.8248
C_2mim		-394.2	-46.7	8.4497
C_3mim		-397.6	-48.6	8.1842
C_4mim		-396.3	-49.2	8.0508
C_1mpyr		-377.9	-38.0	9.9534
C_2mpyr		-375.0	-38.9	9.6429
C_3mpyr		-374.4	-39.9	9.3939
C_4mpyr		-373.2	-40.2	9.2824
C_1mim	BF_4	-380.1	-34.5	11.0136
C_2mim		-380.5	-35.9	10.6078
C_3mim		-380.4	-37.0	10.2926
C_4mim		-380.1	-37.4	10.1712
C_1mpyr		-370.7	-30.8	12.0317

C_2mpyr		-368.0	-31.3	11.7599
C_3mpyr		-367.0	-31.8	11.5411
C_4mpyr		-365.9	-32.0	11.4230
C_1mim	PF_6	-356.3	-36.4	9.7804
C_2mim		-356.8	-39.9	8.9514
C_3mim		-347.1	-39.1	8.8852
C_4mim		-358.0	-43.2	8.2969
C_1mpyr		-345.3	-30.2	11.4307
C_2mpyr		-339.8	-30.5	11.1523
C_3mpyr		-342.2	-31.5	10.8539
C_4mpyr		-341.0	-31.7	10.7404
C_1mim	CH_3SO_3	-421.5	-48.5	8.6933
C_2mim		-420.5	-51.9	8.1018
C_3mim		-423.1	-55.0	7.6920
C_4mim		-422.9	-56.4	7.5042
C_1mpyr		-409.7	-41.6	9.8490
C_2mpyr		-408.1	-42.5	9.6036
C_3mpyr		-407.5	-43.2	9.4228
C_4mpyr		-405.9	-43.3	9.3688
C_1mim	CH_3PhSO_3	-411.7	-48.8	8.4347
C_2mim		-412.9	-53.4	7.7311
C_3mim		-414.6	-56.5	7.3352
C_4mim		-414.9	-58.6	7.0861
C_1mpyr		-402.3	-42.1	9.5493
C_2mpyr		-400.7	-43.5	9.2166
C_3mpyr				

C_4mpyr				
C_1mim	$N(CN)_2$	-361.4	-50.7	7.1350
C_2mim		-361.3	-51.9	6.9595
C_3mim		-364.5	-55.1	6.6148
C_4mim		-364.7	-56.4	6.4687
C_1mpyr		-351.5	-38.0	9.2434
C_2mpyr		-346.6	-39.0	8.8830
C_3mpyr		-346.1	-39.4	8.7796
C_4mpyr		-344.5	-39.7	8.6856
C_1mim	NTf_2	-344.1	-40.3	8.5335
C_2mim		-342.2	-44.0	7.7747
C_3mim		-342.5	-46.7	7.3366
C_4mim		-329.0	-27.5	11.9800
C_1mpyr		-325.8	-28.1	11.6114
C_2mpyr		-325.3	-29.3	11.1124
C_3mpyr		-325.4	-29.8	10.9025
C_4mpyr		-329.0	-27.5	11.9800

Table S3. Melting point (T_m in K), density (ρ in g cm^{-3}), conductivity (σ in mScm^{-1}) and viscosity (η in cP).

Ionic Liquid	T_m	Ref.	ρ g cm^{-3}	Ref.	σ mScm^{-1}	Ref.	η cP	Ref.
[C_1mpyr]Cl	533	1						
[C_2mpyr]Cl								
[C_3mpyr]Cl	495	2						
[C_4mpyr]Cl	468	2						
[C_1mim]Cl	398	3						
[C_2mim]Cl	362	This work	1.221 (363K)	This work	10.37 (363 K)	This work	21.6 (363 K)	This work
[C_3mim]Cl	333	4						
[C_4mim]Cl*	341	This work	1.207 (363K)	This work	3.30 (363 K)	This work	61.2 (363 K)	This work
[C_1mpyr]Br	608	5						
[C_2mpyr]Br	533	2						
[C_3mpyr]Br	482	2						
[C_4mpyr]Br*	489	2						
[C_1mim]Br	382.65	6						
[C_2mim]Br	344	7			16.49 (363 K)	This work		
[C_3mim]Br	301	2			0.3 (298 K)	8		
[C_4mim]Br*	347.45	9						
[C_1mpyr][BF_4]	613	10			1.3×10^{-8}(297K)	11		
[C_2mpyr][BF_4]	567	12			7.3×10^{-8} (297K)	11		
[C_3mpyr][BF_4]	337	10			8.8×10^{-7} (325K)	11		
[C_4mpyr][BF_4]	411	10			4.2×10^{-11} (300K)	11		
[C_1mim][BF_4]	376.55	13						
[C_2mim][BF_4]	288	2	1.240 (293 K)	2	12 (293K)	2	34 (293K)	2
[C_3mim][BF_4]	256	14	1.239 (298 K)	2	5.9 (298K)	14	74.4 (298K)	2
[C_4mim][BF_4]	202	21	1.203 (298 K)	2	3.145 (293K)	2	99.2 (298K)	15

[C_1mpyr][PF_6]	663	16						
[C_2mpyr][PF_6]	479	This work						
[C_3mpyr][PF_6]	386	16						
[C_4mpyr][PF_6]	343	16			0.17 (363 K)	This work		
[C_1mim][PF_6]	362	17						
[C_2mim][PF_6]	336	This work	1.422 (353 K)	18	18.01 (353K)	This work	17.1 (353 K)	19
[C_3mim][PF_6]	314	This work	1.368 (353 K)	20	10.24 (353 K)	This work	23.47 (353K)	20
[C_4mim][PF_6]	285	21	1.368 (295 K)	22	1.373 (293 K)	2	25.77 (353 K)	23
[C_1mpyr][CH_3SO_3]	473	24						
[C_2mpyr][CH_3SO_3]	313	24						
[C_3mpyr][CH_3SO_3]*	353	24						
[C_4mpyr][CH_3SO_3]*	336	24						
[C_1mim][CH_3SO_3]	364.15	25						
[C_2mim][CH_3SO_3]	303.75	25	1.199 (363 K)	This work	15.88 (363 K)	This work	13.1 (363K)	This work
[C_3mim][CH_3SO_3]*	312.95	25						
[C_4mim][CH_3SO_3]*	346.85	25	1.130 (363 K)	This work	7.30 (363 K)	This work	21.5 (363K)	This work
[C_1mpyr][CH_3PhSO_3]	440	24						
[C_2mpyr][CH_3PhSO_3]	393	24						
[C_3mpyr][CH_3PhSO_3]	353	24						
[C_4mpyr][CH_3PhSO_3]	388	24						
[C_1mim][CH_3PhSO_3]	372.6	26						
[C_2mim][CH_3PhSO_3]	322.9	27						
[C_4mim][CH_3PhSO_3]*	340	28						
[C_1mpyr][$N(CN)_2$]	388	29			57.67 (393 K)	This work		
[C_2mpyr][$N(CN)_2$]	263.15	30	1.047 (293 K)	This work	15.3 (293 K)	This work	31.0 (293 K)	This work
[C_3mpyr][$N(CN)_2$]	262.85	30	1.038 (293 K)	30	15.7 (293 K)	30	33.2 (293K)	30
[C_4mpyr][$N(CN)_2$]	218	29	1.023 (293 K)	2	9.83 (293 K)	2	46.4 (293 K)	2
[C_1mim][$N(CN)_2$]	307	31	1.14 (293 K)	31	36 (298 K)	31	15.5 (298 K)	31

$[C_2mim][N(CN)_2]$	252	2	1.101 (293 K)	2	25.3 (293K)	2	16.8 (294K)	2
$[C_4mim][N(CN)_2]^*$	263	31	1.0621 (293 K)	32	9.53 (293K)	2	33.4 (293K)	2
$[C_1mpyr][NTf_2]$	410	This work						
$[C_2mpyr][NTf_2]$	359	33			25.02 (393 K)	This work		
$[C_3mpyr][NTf_2]$	285	33	1.432 (293 K)	30	3.2 (293K)	30	76.7 (293K)	30
$[C_4mpyr][NTf_2]$	267	21	1.400 (293 K)	30	2.2 (293K)	30	100 (293K)	30
$[C_1mim][NTf_2]$	299	34	1.559 (295 K)	35	8.4 (293K)	35	44 (293K)	35
$[C_2mim][NTf_2]$	258	21	1.524 (293 K)	30	7.5 (293K)	30	38.7 (293K)	30
$[C_3mim][NTf_2]$	-	-	1.454 (295 K)	22	4.22 (295K)	22	53(294 K)	22
$[C_4mim][NTf_2]^*$	275	21	1.425 (295 K)	22	3.23 (295K)	22	54 (294K)	22

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