Mutual Solubility of Water and Structural/Positional Isomers of *N*-Alkylpyridinium-based Ionic Liquids

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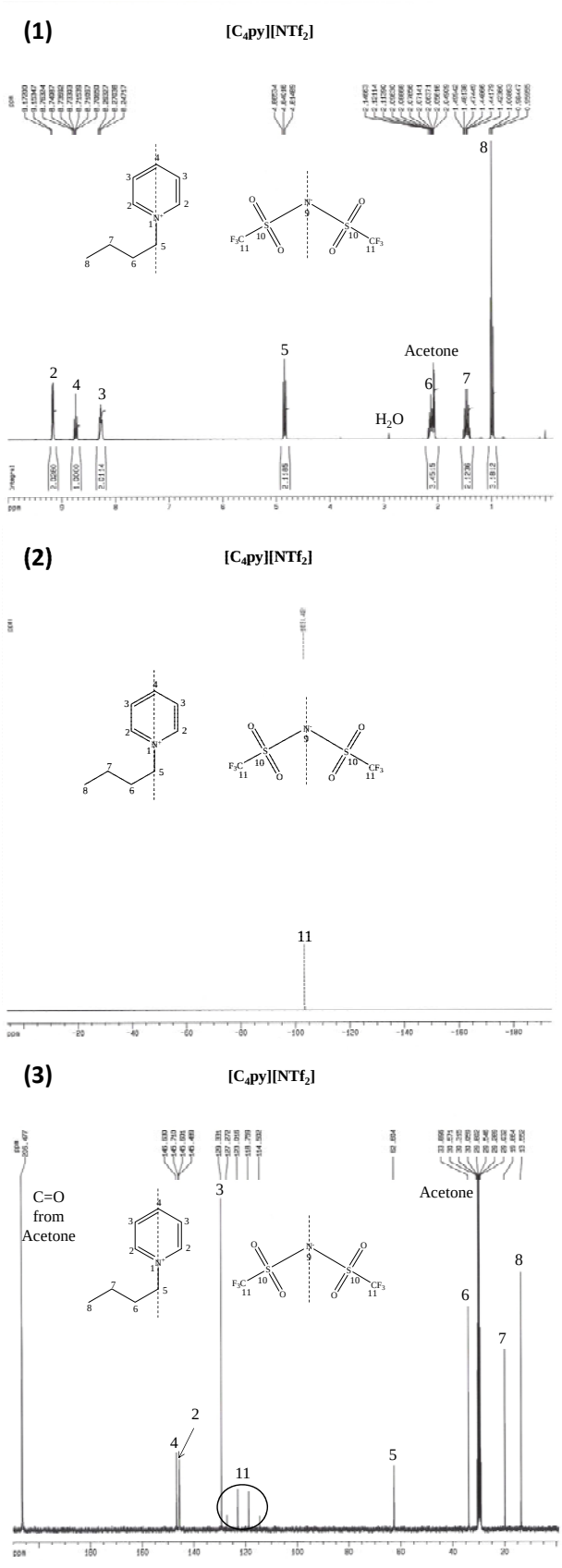

Figure S1. ^{1}H (1), ^{19}F (2), ^{13}C (3) NMR spectra of $[C_4py][NTf_2]$ in CD_3COCD_3.

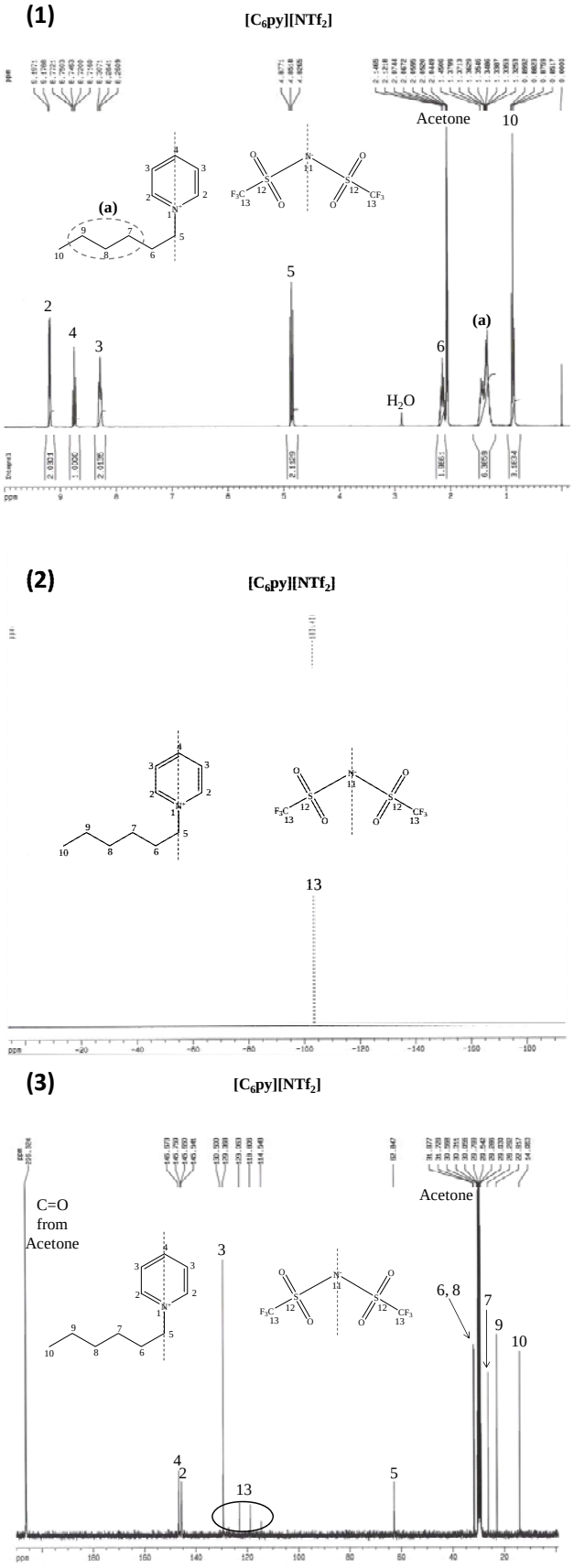

Figure S2. ^{1}H (1), ^{19}F (2), ^{13}C (3) NMR spectra of $[C_6py][NTf_2]$ in CD_3COCD_3.

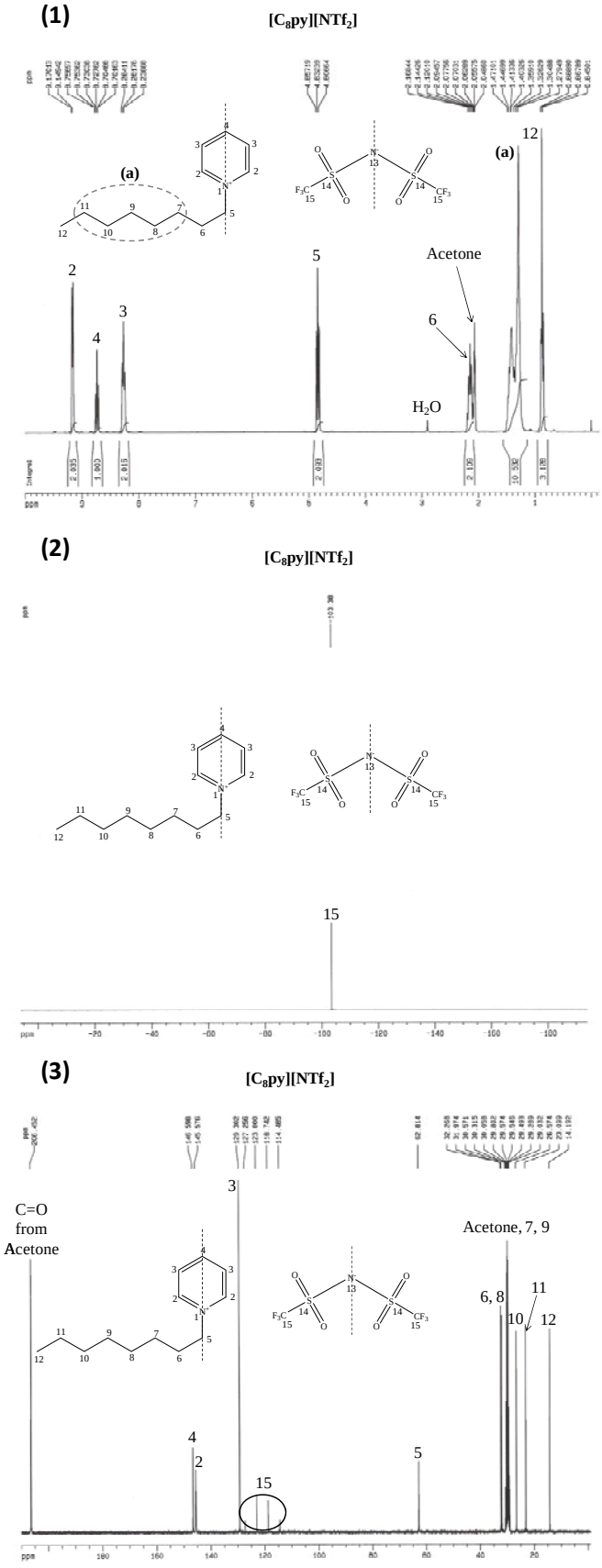

Figure S3. ^{1}H (1), ^{19}F (2), ^{13}C (3) NMR spectra of $[C_8py][NTf_2]$ in CD_3COCD_3.

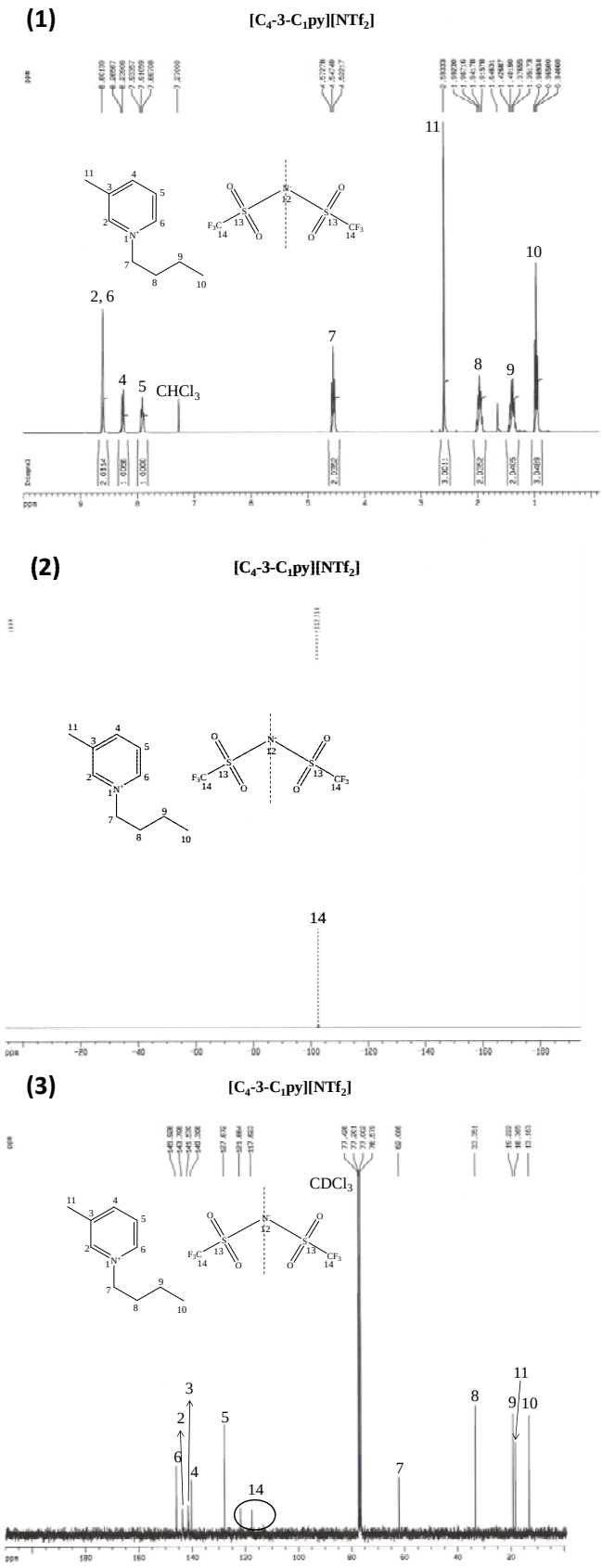

Figure S4. ^{1}H (1), ^{19}F (2), ^{13}C (3) NMR spectra of $[C_4\text{-}3\text{-}C_1py][NTf_2]$ in CD_3COCD_3.

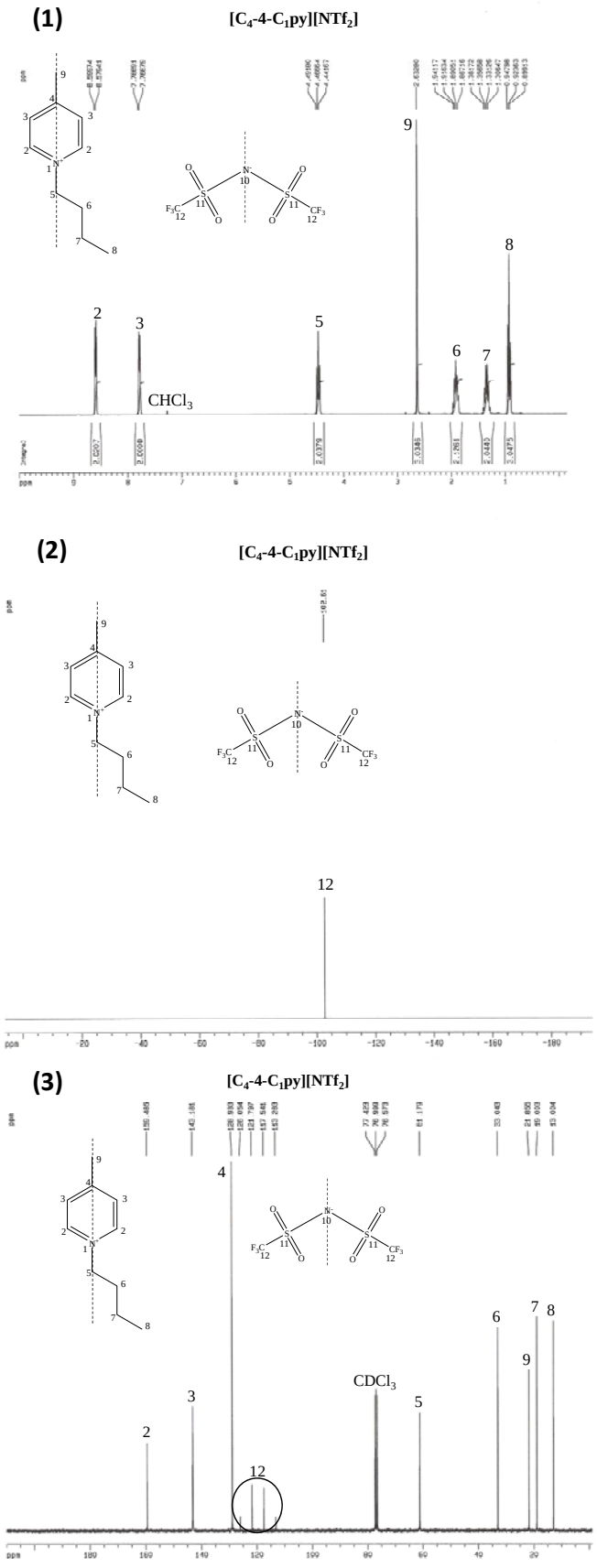

Figure S5. ^{1}H (1), ^{19}F (2), ^{13}C (3) NMR spectra of $[C_4\text{-}4\text{-}C_1py][NTf_2]$ in CD_3COCD_3.

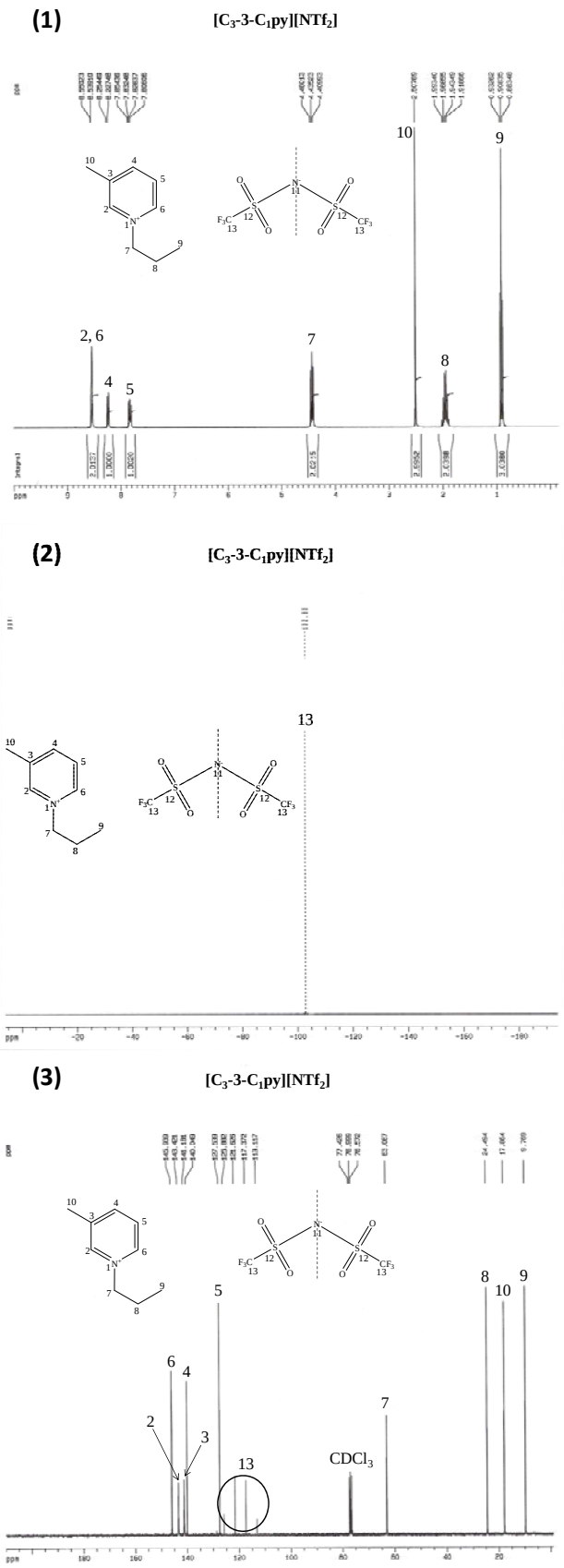

Figure S6. ^{1}H (1), ^{19}F (2), ^{13}C (3) NMR spectra of $[C_3\text{-}3\text{-}C_1py][NTf_2]$ in CD_3COCD_3.

TABLE S1: Weight Fraction Solubility of Water in the IL-rich Phase (w_w) and Weigth Fraction Solubility of IL in the Water-rich Phase (w_{IL}) at Different Temperatures

	$[C_4py][NTf_2]$	$[C_6py][NTf_2]$	$[C_8py][NTf_2]$	$[C_4\text{-}3\text{-}C_1py][NTf_2]$	$[C_4\text{-}4\text{-}C_1py][NTf_2]$
T / K			$100(w_w \pm \sigma^a)$		
288.15	1.212 ± 0.014	1.029 ± 0.007	0.804 ± 0.012	0.970 ± 0.009	1.159 ± 0.004
293.15	1.334 ± 0.004	1.107 ± 0.004	0.873 ± 0.005	1.049 ± 0.004	1.262 ± 0.013
298.15	1.435 ± 0.005	1.165 ± 0.007	0.927 ± 0.003	1.119 ± 0.006	1.353 ± 0.014
303.15	1.571 ± 0.015	1.307 ± 0.011	1.037 ± 0.022	1.248 ± 0.009	1.479 ± 0.010
308.15	1.741 ± 0.005	1.408 ± 0.003	1.153 ± 0.010	1.362 ± 0.005	1.643 ± 0.011
313.15	1.896 ± 0.011	1.528 ± 0.020	1.252 ± 0.003	1.460 ± 0.014	1.776 ± 0.010
318.15	2.056 ± 0.011	1.659 ± 0.004	1.369 ± 0.008	1.579 ± 0.001	1.919 ± 0.005
T / K			$100(w_{IL} \pm \sigma^a)$		
288.15	0.760 ± 0.004	0.454 ± 0.001	0.0810 ± 0.0026	0.473 ± 0.002	0.490 ± 0.006
293.15	0.778 ± 0.006	0.481 ± 0.005	0.0883 ± 0.0007	0.489 ± 0.003	0.505 ± 0.008
298.15	0.815 ± 0.011	0.491 ± 0.001	0.0917 ± 0.0008	0.500 ± 0.010	0.526 ± 0.015
303.15	0.855 ± 0.004	0.508 ± 0.012	0.1018 ± 0.0010	0.518 ± 0.009	0.565 ± 0.008
308.15	0.911 ± 0.004	0.554 ± 0.019	0.1102 ± 0.0005	0.546 ± 0.012	0.598 ± 0.016
313.15	0.942 ± 0.002	0.596 ± 0.022	0.1168 ± 0.0019	0.579 ± 0.004	0.623 ± 0.018
318.15	1.036 ± 0.006	0.628 ± 0.015	0.1328 ± 0.0046	0.604 ± 0.006	0.670 ± 0.018

[a]Standard Deviation

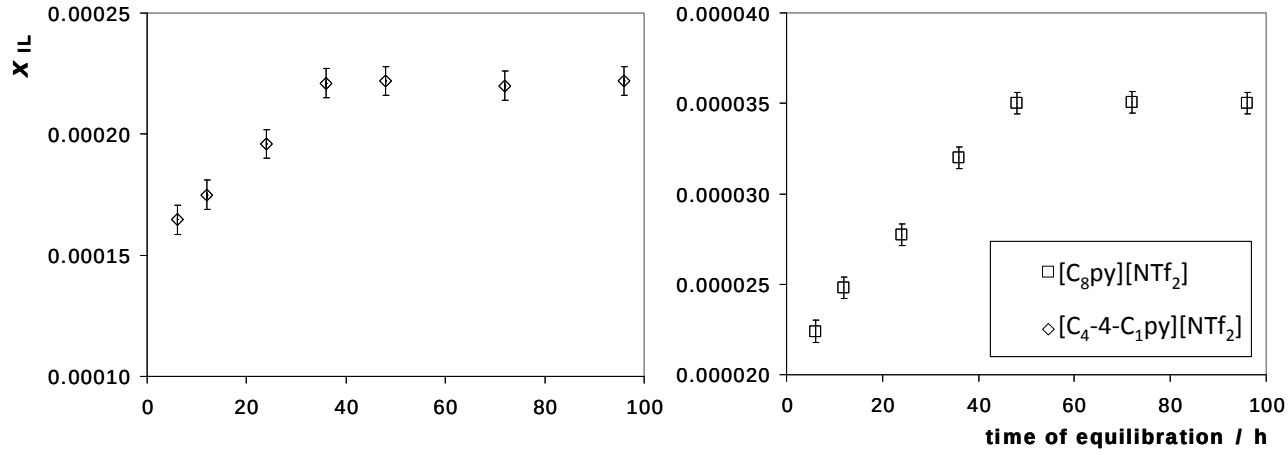

Figure S7. Solubility of $[C_4\text{-}4\text{-}C_1py][NTf_2]$ and $[C_8py][NTf_2]$ *versus* time of equilibration at 298.15 K.

Supplementary Information 2

MD Force Field Parameterization

Mutual Solubility of Water and Structural/Positional Isomers of *N*-Alkylpyridinium-based Ionic Liquids

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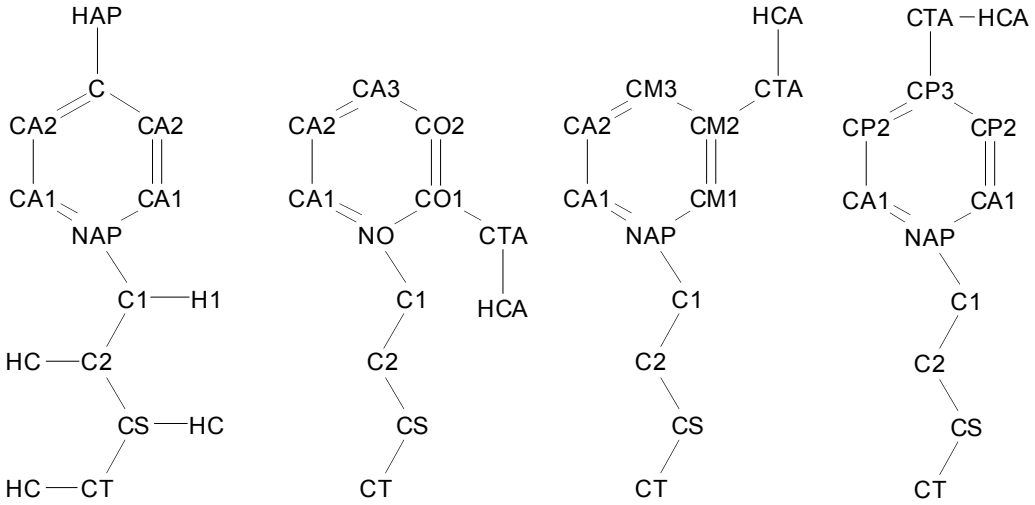
parameters (kJ/mol, A, deg)
Molecular force field for ionic liquids
DL_POLY format except dihedral functions that may have 4 cosine terms.



ATOMS

# i	m/amu	q/e	field	sig	eps	
# dialkylimidazolium JPCB108:2038(2004)						
C1	12.011	-0.17	lj	3.50	0.27614	0.0
C2	12.011	0.01	lj	3.50	0.27614	0.0
CE	12.011	-0.05	lj	3.50	0.27614	0.0
CS	12.011	-0.12	lj	3.50	0.27614	0.0
CT	12.011	-0.18	lj	3.50	0.27614	0.0
CR	12.011	-0.11	lj	3.55	0.29288	0.0
CW	12.011	-0.13	lj	3.55	0.29288	0.0
HA	1.008	0.21	lj	2.42	0.12552	0.0
HCR	1.008	0.21	lj	2.42	0.12552	0.0
HCW	1.008	0.21	lj	2.42	0.12552	0.0
HC	1.008	0.06	lj	2.50	0.12552	0.0
H1	1.008	0.13	lj	2.50	0.12552	0.0
NA	14.007	0.15	lj	3.25	0.71128	0.0
# pyridinium JCSPerkin2:2365(1999)						
NAP	14.007	0.15	lj	3.25	0.71128	0.0
NO	14.007	0.06	lj	3.25	0.71128	0.0
CA1	12.011	0.00	lj	3.55	0.29288	0.0
CA2	12.011	-0.07	lj	3.55	0.29288	0.0
CA3	12.011	0.02	lj	3.55	0.29288	0.0
CO1	12.011	0.26	lj	3.55	0.29288	0.0
CO2	12.011	-0.16	lj	3.55	0.29288	0.0
CM1	12.011	-0.09	lj	3.55	0.29288	0.0
CM2	12.011	0.19	lj	3.55	0.29288	0.0
CM3	12.011	-0.07	lj	3.55	0.29288	0.0
CP2	12.011	-0.16	lj	3.55	0.29288	0.0
CP3	12.011	0.28	lj	3.55	0.29288	0.0
HAP	1.008	0.15	lj	2.42	0.12552	0.0
CTA	12.011	-0.11	lj	3.50	0.27614	0.0
HCA	1.008	0.06	lj	2.50	0.12552	0.0
# bistriflylamide JPCB108:16893(2004)						
FBT	18.998	-0.16	lj	2.95	0.22175	0.0
CBT	12.011	0.35	lj	3.50	0.27614	0.0
SBT	32.066	1.02	lj	3.55	1.04600	0.0
OBT	15.999	-0.53	lj	2.96	0.87864	0.0
NBT	14.000	-0.66	lj	3.25	0.71128	0.0

```
TRANSLATION
# equivalence between atoms and labels in bonds, angles and dihedrals
# this is because atoms that have the same role in bonds, angles and
# dihedrals have many times different electrostatic charges and therefore
# differrent labels for the purpose of nonbonded interactions
HA HCW
HA HCR
HA HAP
HC H1
HC HCA
CT C1
CT C2
CT CE
CT CS
CT CTA
CA CA1
CA CA2
CA CA3
CA CO1
CA CO2
CA CM1
CA CM2
CA CM3
CA CP2
CA CP3
NA NAP
NA NO

BONDS
# i  j    type    re/A    ka/kJmol-1 (negative means a rigid constraint)
# alkanes OPLS-AA JACS118:11225(1996); JPC100:18010(1996)
CT   CT   harm    1.529   2242
# dialkylimidazolium JPCB108:2038(2004)
CR   HA   harm    1.080  -2845
CW   HA   harm    1.080  -2845
CR   NA   harm    1.315   3992
CW   NA   harm    1.378   3574
CW   CW   harm    1.341   4352
NA   CT   harm    1.466   2820
# pyridinium OPLS-AA Theochem424:145(1998)
CA   HA   harm    1.080  -3071
CA   CA   harm    1.380   3925
CA   NA   harm    1.340   4042
CA   CT   harm    1.510   2654
NA   CT   harm    1.480   2820
# bistriflylamide JPCB108:16893(2004)
CBT  FBT  harm    1.323   3698
CBT  SBT  harm    1.818   1950
SBT  OBT  harm    1.437   5331
NBT  SBT  harm    1.570   3137

ANGLES
# i  j    k     type      th/deg   ka/kjmol-1
# alkanes OPLS-AA JACS118:11225(1996); JPC100:18010(1996)
CT   CT   CT    harm      112.7    488.3
CT   CT   HC    harm      110.7    313.8
HC   CT   HC    harm      107.8    276.1
# dialkylimidazolium JPCB108:2038(2004)
```

```
CW   NA   CR    harm      108.0    585.8
CW   NA   CT    harm      125.6    585.8
CR   NA   CT    harm      126.4    585.8
NA   CR   HA    harm      125.1    292.9
NA   CR   NA    harm      109.8    585.8
NA   CW   CW    harm      107.1    585.8
NA   CW   HA    harm      122.0    292.9
CW   CW   HA    harm      130.9    292.9
NA   CT   HC    harm      110.7    313.8
NA   CT   CT    harm      112.7    488.3
# pyridinium OPLS-AA Theochem424:145(1998), JCSPerkin2:2365(1999)
CA   CA   CA    harm      120.0    527.2
CA   CA   HA    harm      120.0    292.9
CA   CA   NA    harm      120.0    585.8
CA   NA   CA    harm      120.4    585.8
CA   NA   CT    harm      119.8    585.8
NA   CA   HA    harm      120.0    292.9
NA   CT   HC    harm      109.5    292.9
CA   CT   HC    harm      109.5    293.1
NA   CA   CT    harm      120.0    586.2
CA   CA   CT    harm      120.0    586.2
# bistriflylamide JPCB108:16893(2004)
FBT  CBT  FBT   harm      107.1    781
FBT  CBT  SBT   harm      111.7    694
OBT  SBT  OBT   harm      118.5    969
CBT  SBT  OBT   harm      102.6    870
NBT  SBT  OBT   harm      113.6    789
NBT  SBT  CBT   harm      103.5    764
SBT  NBT  SBT   harm      125.6    671

DIHEDRALS
# i  j    k    l    type     v1         v2          v3          v4
# alkanes OPLS-AA JACS118:11225(1996); JPC100:18010(1996)
HC   CT   CT   HC   cos3     0.0000     0.0000      1.3305      0.0000
CT   CT   CT   HC   cos3     0.0000     0.0000      1.5313      0.0000
CT   CT   CT   CT   cos3     7.2800    -0.6569      1.1673      0.0000
# dialkylimidazolium JPCB108:2038(2004)
CW   NA   CR   NA   cos3     0.0000    19.4600      0.0000      0.0000
CW   NA   CR   HA   cos3     0.0000    19.4600      0.0000      0.0000
CT   NA   CR   NA   cos3     0.0000    19.4600      0.0000      0.0000
CT   NA   CR   HA   cos3     0.0000    19.4600      0.0000      0.0000
CR   NA   CW   CW   cos3     0.0000    12.5500      0.0000      0.0000
CR   NA   CW   HA   cos3     0.0000    12.5500      0.0000      0.0000
CT   NA   CW   CW   cos3     0.0000    12.5500      0.0000      0.0000
CT   NA   CW   HA   cos3     0.0000    12.5500      0.0000      0.0000
NA   CW   CW   NA   cos3     0.0000    44.9800      0.0000      0.0000
NA   CW   CW   HA   cos3     0.0000    44.9800      0.0000      0.0000
HA   CW   CW   HA   cos3     0.0000    44.9800      0.0000      0.0000
CW   NA   CT   HC   cos3     0.0000     0.0000      0.5190      0.0000
CR   NA   CT   HC   cos3     0.0000     0.0000      0.0000      0.0000
CW   NA   CT   CT   cos3    -7.1535     6.1064      0.7939      0.0000
CR   NA   CT   CT   cos3    -5.2691     0.0000      0.0000      0.0000
NA   CT   CT   CT   cos3    -7.4797     3.1642     -1.2026      0.0000
NA   CT   CT   HC   cos3     0.0000     0.0000      0.3670      0.0000
# improper dialkylimidazolium ring AMBER
CR   CW   NA   C1   cos3     0.0000     8.3700      0.0000      0.0000
NA   NA   CR   HA   cos3     0.0000     9.2000      0.0000      0.0000
NA   CW   CW   HA   cos3     0.0000     9.2000      0.0000      0.0000
# pyridinium AMBER (cycle) JPCB110:19586(2006)
```

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CA   CA   CA   CA   cos3     0.0000    30.3340      0.0000      0.0000
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HA   CA   CA   CA   cos3     0.0000    30.3340      0.0000      0.0000
HA   CA   CA   NA   cos3     0.0000    30.3340      0.0000      0.0000
HA   CA   CA   HA   cos3     0.0000    30.3340      0.0000      0.0000
CA   NA   CA   HA   cos3     0.0000    12.5520      0.0000      0.0000
CT   NA   CA   HA   cos3     0.0000    12.5520      0.0000      0.0000
CA   NA   CA   CA   cos3     0.0000    12.5520      0.0000      0.0000
CT   NA   CA   CA   cos3     0.0000    12.5520      0.0000      0.0000
HC   CT   NA   CA   cos3     0.0000     0.0000      0.0000      0.0000
CT   CT   NA   CA   cos4     0.0000     1.1120      0.0000      0.6900
CA   CA   CA   CT   cos3     0.0000    30.3340      0.0000      0.0000
HA   CA   CA   CT   cos3     0.0000    30.3340      0.0000      0.0000
CA   NA   CA   CT   cos3     0.0000    12.5520      0.0000      0.0000
CT   NA   CA   CT   cos3     0.0000    12.5520      0.0000      0.0000
NA   CA   CT   HC   cos3     0.0000     0.0000      0.0000      0.0000
CA   CA   CT   HC   cos3     0.0000     0.0000      0.0000      0.0000
NA   CA   CA   CT   cos3     0.0000    30.3340      0.0000      0.0000
# improper pyridinium ring AMBER
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CA   CA   NA   HA   cos3     0.0000     9.2000      0.0000      0.0000
CA   CA   NA   CT   cos3     0.0000     8.3700      0.0000      0.0000
# bistriflylamide JPCB108:16893(2004)
OBT  SBT  CBT  FBT  cos3     0.0000     0.0000      1.4510      0.0000
NBT  SBT  CBT  FBT  cos3     0.0000     0.0000      1.3220      0.0000
OBT  SBT  NBT  SBT  cos3     0.0000     0.0000     -0.0150      0.0000
SBT  NBT  SBT  CBT  cos3    32.7730   -10.4200     -3.1950      0.0000
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