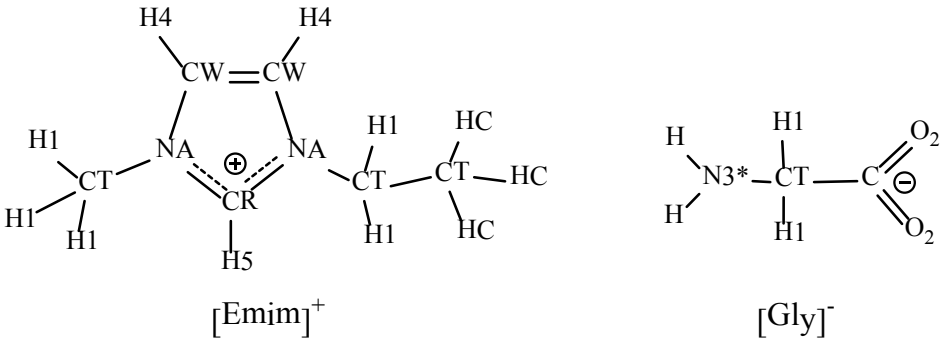


**Fig. S1** Schematic structure and atom type notations of the 1-ethyl-3-methylimidazolim cation ($[Emim]^+$) and glycine anion ($[Gly]^-$) in the AMBER force field.

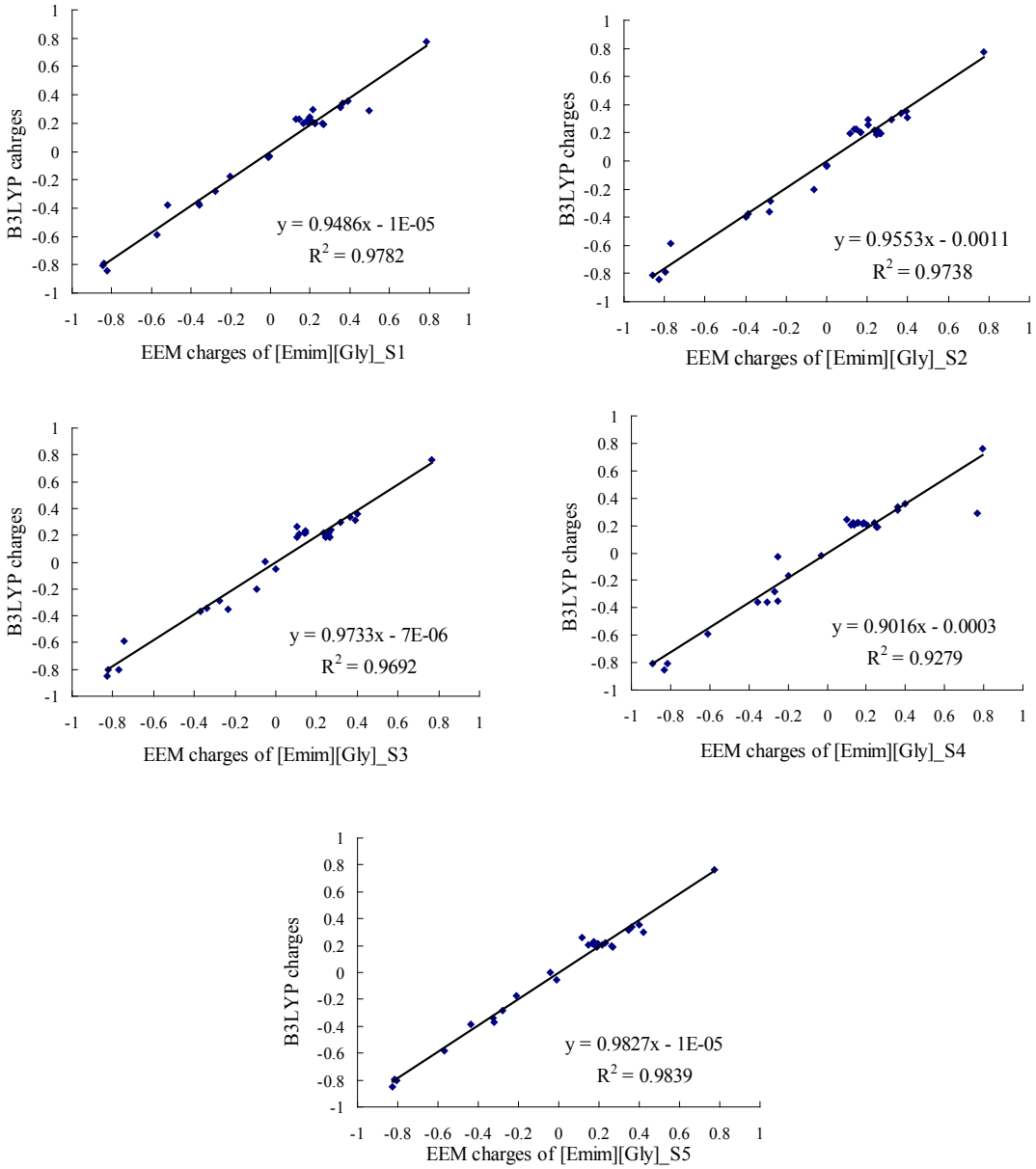


**Fig. S2** The EEM/MM charges vs the corresponding B3LYP/6-311+G(d,p) charges (*e*) of five [Emim][Gly] conformers.

**Table S1** Force field parameters for the [Emim][Gly] ILs used in this work.[a]

| | Bonds | | | | |
|---|---|---|---|---|---|
| | $K_r$ (kJ·mol $^{-1}$·Å$^{-2}$) | $r_0$ (Å) | | $K_r$ (kJ·mol $^{-1}$·Å$^{-2}$) | $r_0$ (Å) |
| CT-CT | 1297 | 1.52 | CW-CW | 1715 | 1.34 |
| CT-H1 | 1423 | 1.08 | CT-HC | 1423 | 1.09 |
| CW-H4 | 1611 | 1.07 | CT-H1 | 1359.8 | 1.0864 |
| CR-H5 | 1590 | 1.07 | CT-C | 1326.3 | 1.5499 |
| CR-NA | 1674 | 1.32 | CT-N3* | 1535.5 | 1.4608 |
| CW-NA | 1506 | 1.38 | C-O2 | 2092 | 1.2374 |
| CT-NA | 1172 | 1.47 | N3*-H | 1882.8 | 1.0036 |
| | Angles | | | | |
| | $K_\theta$ (kJ· mol$^{-1}$ ·rad$^{-2}$) | $\theta_0$(deg) | | $K_\theta$ (kJ· mol$^{-1}$ ·rad$^{-2}$) | $\theta_0$(deg) |
| CT-CT-H1 | 159 | 109.5 | H4-CW-NA | 126 | 122.1 |
| CT-CT-HC | 155 | 109.5 | H5-CR-NA | 126 | 125.7 |
| CT-CT-NA | 293 | 112.2 | CW-CW-H4 | 126 | 130.7 |
| H1-CT-H1 | 146 | 109.5 | C-CT-N3* | 376.6 | 116.5 |
| HC-CT-HC | 142 | 109.5 | C-CT-H1 | 242.7 | 108.1 |
| H1-CT-NA | 230 | 109.5 | N3*-CT-H1 | 251 | 108.8 |
| CW-NA-CT | 209 | 125.7 | H1-CT-H1 | 161.1 | 106.1 |
| CR-NA-CT | 209 | 126.3 | CT-C-O2 | 334.7 | 115.4 |
| CW-CW-NA | 502 | 107.1 | O2-C-O2 | 355.6 | 129.1 |
| CR-NA-CW | 502 | 108 | CT-N3*-H | 209.2 | 107.3 |
| NA-CR-NA | 502 | 109.9 | H-N3*-H | 209.2 | 103.4 |
| | Proper Torsion | | | | | | |
| | $K_\varphi$ (kJ mol$^{-1}$ rad$^{-2}$) | $\gamma$ (deg) | $n$ | | $K_\varphi$ (kJ mol$^{-1}$ rad$^{-2}$) | $\gamma$ (deg) | $n$ |
| NA-CR-NA-CW | 50.21 | 180 | 2 | NA-CT-CT-HC | 0.669 | 0 | 3 |
| NA-CR-NA-CT | 8.368 | 180 | 2 | H1-CT-CT-HC | 0.628 | 0 | 3 |
| H5-CR-NA-CW | 6.276 | 180 | 2 | HC-CT-CT-HC | 0.628 | 0 | 3 |
| H5-CR-NA-CT | 6.276 | 180 | 2 | H1-CT-NA-CW | 1.021 | 0 | 3 |
| CW-CW-NA-CR | 50.21 | 180 | 2 | H1-CT-NA-CR | 0.686 | 0 | 3 |
| CW-CW-NA-CT | 8.368 | 180 | 2 | CT-CT-NA-CW | -0.745 | 0 | 1 |
| H4-CW-NA-CR | 8.368 | 180 | 2 | CT-CT-NA-CR | -0.987 | 0 | 1 |
| H4-CW-NA-CT | 6.276 | 180 | 2 | N3-CT-C-O2 | 0.962 | 0 | 2 |
| NA-CW-CW-H4 | 6.276 | 180 | 2 | H1-CT-C-O2 | 0 | 0 | 2 |
| NA-CW-CW-NA | 50.21 | 180 | 2 | H1-CT-N3*-H | 0.92 | 0 | 3 |
| H4-CW-CW-H4 | 6.276 | 180 | 2 | | | | |
| | Improper Torsion | | | | | | |
| | $K_\varphi$ (kJ mol$^{-1}$ rad$^{-2}$) | $\gamma$ (deg) | $n$ | | $K_\varphi$ (kJ mol$^{-1}$ rad$^{-2}$) | $\gamma$ (deg) | $n$ |
| NA-NA-CR-H5 | 4.602 | 180 | 2 | CR-CW-NA-CT | 8.368 | 180 | 2 |
| CW-NA-CW-H4 | 4.602 | 180 | 2 | CT-O2-C-O2 | 43.93 | 180 | 2 |

[a] to be continued.

**Table S1 (continued)** Force field parameters for the [Emim][Gly] ILs used in this work.[a]

| | Van der Waals | | | | |
|---|---|---|---|---|---|
| | $\sigma_i$ (Å) | $\varepsilon_i$ (kJ/mol) | | $\sigma_i$ (Å) | $\varepsilon_i$ (kJ/mol) |
| CT | 3.3997 | 0.4577 | O2 | 2.9599 | 0.8786 |
| C | 3.3997 | 0.3598 | H | 1.0691 | 0.0657 |
| CW | 3.3997 | 0.3598 | HC | 2.6495 | 0.0657 |
| CR | 3.3997 | 0.3598 | H1 | 2.4714 | 0.0657 |
| NA | 3.2500 | 0.7113 | H4 | 2.5106 | 0.0628 |
| N3* | 3.3409 | 0.7113 | H5 | 1.782 | 0.0628 |

[a]The labels of atoms refer to those used in Fig. S1.

**Table S2** Comparison of EEM/MM and B3LYP/6-311+G(d,p) vibrational frequencies ($cm^{-1}$) for gas-phase $[Emim]^+$ and $[Gly]^-$.

| $[Emim]^+$ | | | | | | | |
|---|---|---|---|---|---|---|---|
| EEM/MM | B3LYP | EEM/MM | B3LYP | EEM/MM | B3LYP | EEM/MM | B3LYP |
| 52.2 | 46.4 | 58.3 | 70.5 | 138.6 | 135.1 | 206.6 | 208.3 |
| 245.7 | 232.8 | 295.7 | 291.9 | 370.2 | 378.1 | 453.9 | 425.3 |
| 547.7 | 591.7 | 596.3 | 632.6 | 626.6 | 660.2 | 662.1 | 698.2 |
| 717.9 | 752.9 | 818.6 | 802.5 | 885.5 | 834.0 | 896.4 | 881.0 |
| 914.1 | 962.0 | 937.8 | 1036.3 | 956.4 | 1042.8 | 982.1 | 1099.0 |
| 985.0 | 1102.3 | 1051.7 | 1124.6 | 1073.7 | 1135.8 | 1104.3 | 1149.8 |
| 1110.5 | 1175.5 | 1174.6 | 1270.3 | 1193.3 | 1311.4 | 1263.4 | 1342.8 |
| 1362.9 | 1384.9 | 1366.0 | 1411.0 | 1368.6 | 1428.0 | 1396.8 | 1437.3 |
| 1417.0 | 1461.0 | 1438.5 | 1484.1 | 1468.2 | 1491.0 | 1494.6 | 1494.3 |
| 1536.4 | 1508.9 | 1556.0 | 1510.4 | 1632.1 | 1594.4 | 1641.2 | 1603.5 |
| 2870.4 | 3046.5 | 2871.7 | 3069.4 | 2914.5 | 3079.2 | 2976.6 | 3110.2 |
| 2978.8 | 3122.3 | 2979.4 | 3134.1 | 2980.0 | 3150.0 | 2980.8 | 3165.0 |
| 3120.1 | 3273.7 | 3139.6 | 3278.0 | 3143.9 | 3291.2 | | |
| $[Gly]^-$ | | | | | | | |
| EEM/MM | B3LYP | EEM/MM | B3LYP | EEM/MM | B3LYP | EEM/MM | B3LYP |
| 40.6 | 95.7 | 295.4 | 190.0 | 332.4 | 294.8 | 464.9 | 481.3 |
| 566.6 | 573.5 | 675.2 | 672.6 | 824.8 | 854.2 | 891.7 | 935.1 |
| 1040.8 | 983.7 | 1151.3 | 1102.0 | 1207.1 | 1145.1 | 1361.4 | 1299.1 |
| 1418.2 | 1354.3 | 1494.1 | 1368.9 | 1619.9 | 1470.7 | 1678.3 | 1656.0 |
| 1752.6 | 1676.8 | 2918.8 | 2998.5 | 2977.2 | 3055.8 | 3345.8 | 3419.5 |
| 3386.8 | 3504.3 | | | | | | |