# Supporting Information

## Insight into Physico-Chemical Properties of Oxalatoborate-Based Ionic Liquids through Combined Experimental-Theoretical Characterization

Matteo Palluzzi[a], Giorgia Mannucci[a], Akiko Tsurumaki[a,b], Matteo Busato[a], Maria Assunta Navarra*[a,b], Paola D'Angelo*[a]

[a] Department of Chemistry, Sapienza University of Rome, P.le A. Moro 5, 00185, Rome, Italy.
[b] Hydro-Eco Research Center, Sapienza University of Rome, Via A. Scarpa 16, 00161 Rome, Italy.
E-mail: mariassunta.navarra@uniroma1.it
E-mail: p.dangelo@uniroma1.it

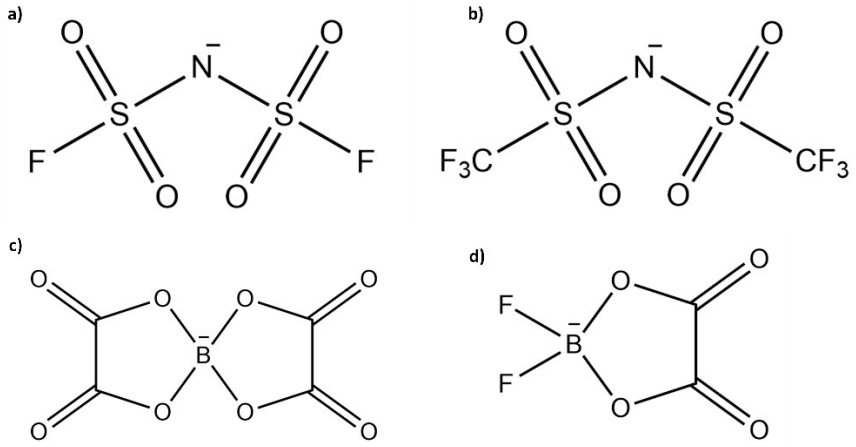



**Fig. S1** Structure of a) FSI, b) TFSI, c) BOB, d) DFOB anions.

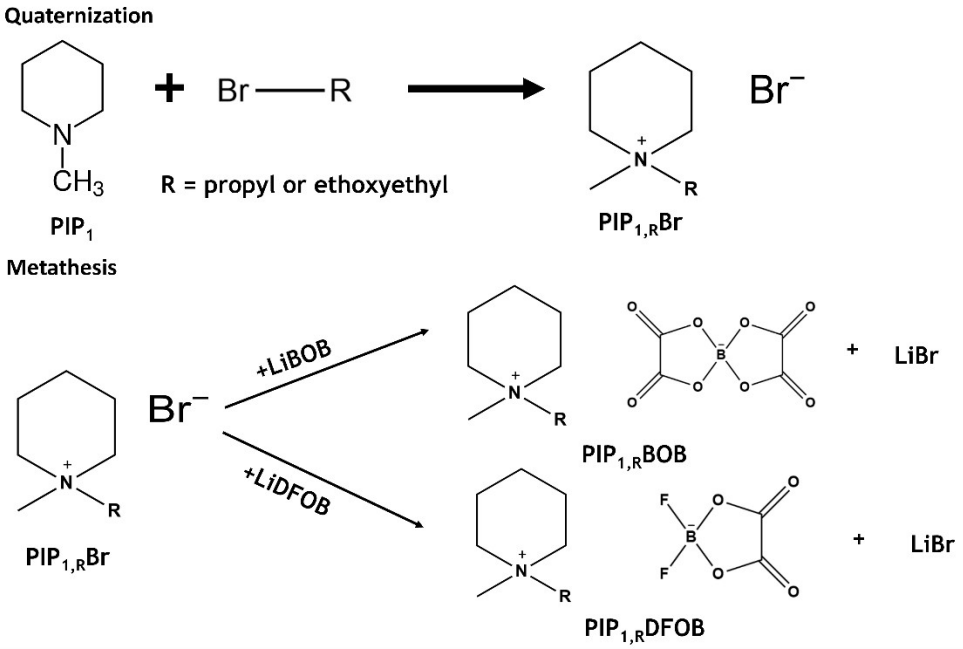



**Fig. S2** Schematic representation of the IL synthesis.

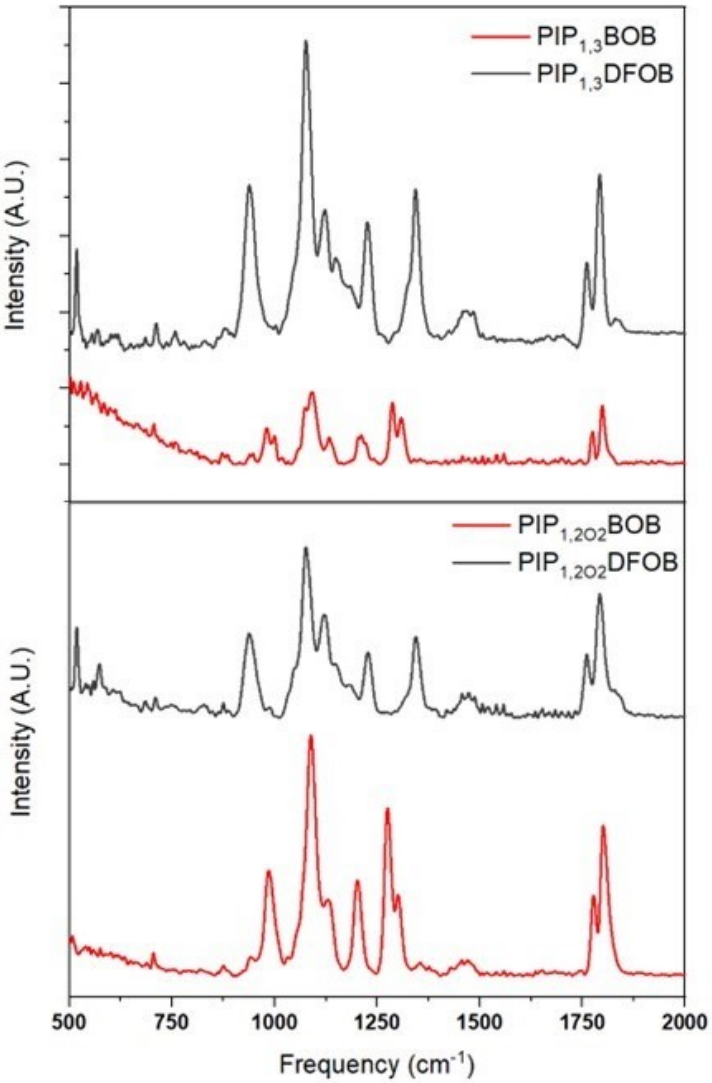



**Fig. S3** ATR-FTIR spectra of the four ILs.

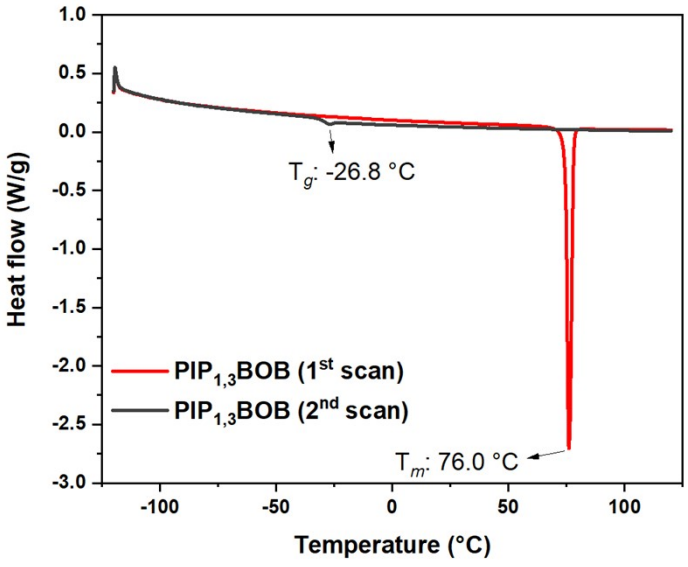



**Fig. S4** DSC curves of $PIP_{1,3}BOB$.

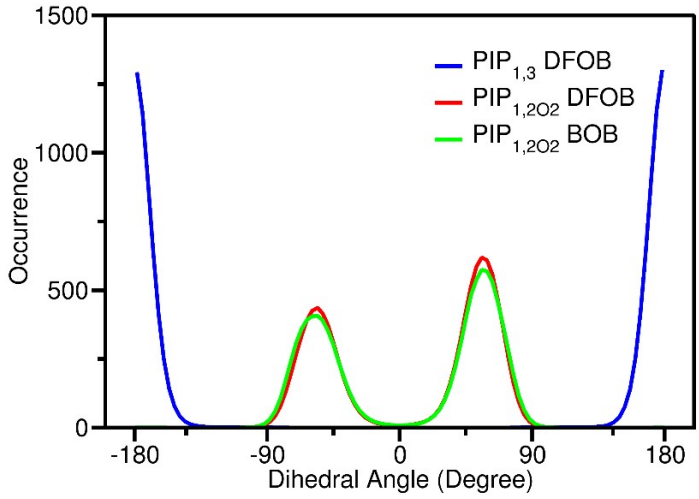



**Fig. S5** Dihedral angle distribution function of $PIP_{1,3}$ DFOB, $PIP_{1,2O2}$ DFOB, and $PIP_{1,2O2}$ BOB obtained from the MD simulations. The referred dihedral angles are the ones reported in **Fig. S6**.

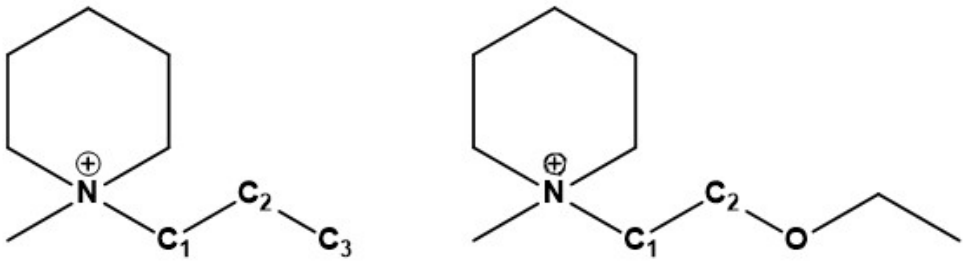



**Fig. S6** Structures of the $PIP_{1,3}$ and $PIP_{1,2O2}$ cations with highlighted the atoms forming the dihedral angles employed for the distributions shown in **Fig. S5**.

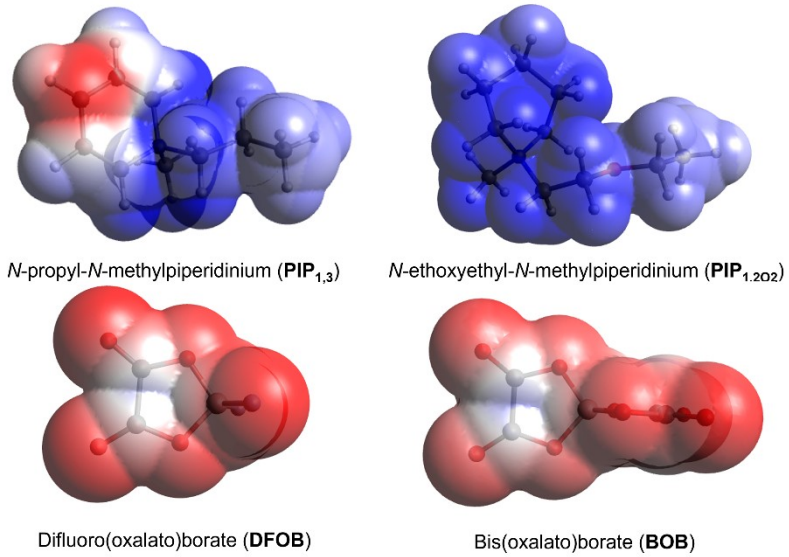



**Fig. S7** Electrostatic potential maps calculated from DFT optimizations of the isolated $PIP_{1,3}$, $PIP_{1,2O2}$, DFOB, and BOB ions at the B3LYP/def2TZVP level of theory. Color code: blue = positive, red = negative.

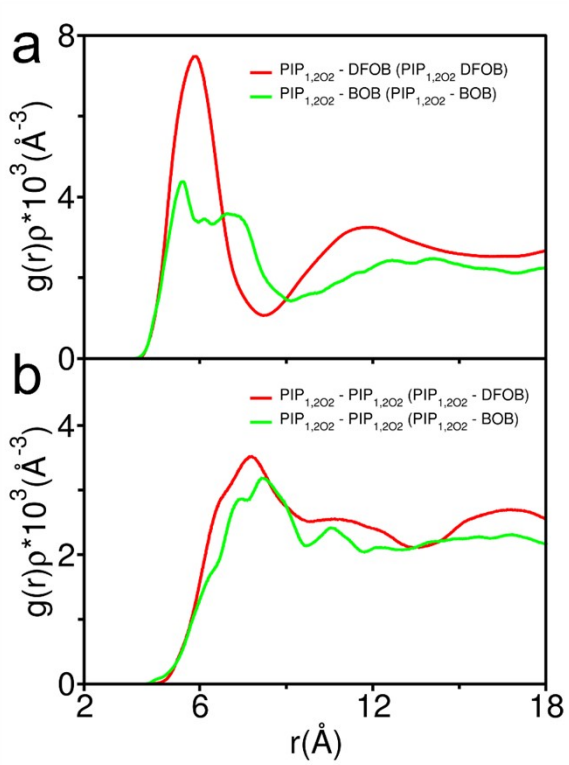



**Fig. S8** Radial distribution functions multiplied by the numerical densities of the observed species, *g(r)ρ*'s, calculated from the MD simulations for $PIP_{1,2O2}$DFOB and $PIP_{1,2O2}$BOB between a) the center of mass of $PIP_{1,2O2}$ and the center of mass of the respective anion and b) the center of mass of two cations.

**Table S1** Number of molecules, box dimensions, and densities of the MD simulated systems.

| System | $PIP_{1,3}$ | $PIP_{1,2O2}$ | DFOB | BOB | Box edge (Å) | Density (g $cm^{-3}$) |
|---|---|---|---|---|---|---|
| **$PIP_{1,3}$ DFOB** | 339 | 0 | 339 | 0 | 49.9997 | 1.2569 |
| **$PIP_{1,2O2}$ DFOB** | 0 | 306 | 306 | 0 | 49.9258 | 1.2625 |
| **$PIP_{1,2O2}$ BOB** | 0 | 270 | 0 | 279 | 50.0198 | 1.3298 |

**Table S2** Partial charges calculated using the CHELPG scheme from DFT optimizations at the B3LYP/def2TZVP level of theory for each atom of the two anions, referred to the reported structures.

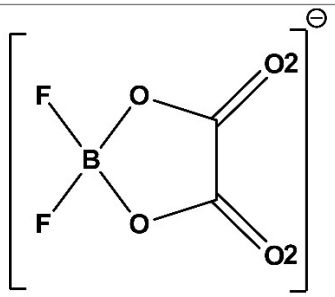
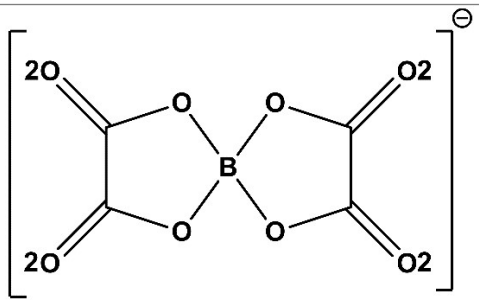
| **DFOB** | | **BOB** | |
|---|---|---|---|
|  | |  | |
| **Atom type** | **Charge** | **Atom type** | **Charge** |
| **B** | 0.943 | **B** | 0.786 |
| **F** | -0.458 | **O** | -0.498 |
| **O** | -0.524 | **C** | 0.605 |
| **C** | 0.589 | **O2** | -0.554 |
| **O2** | -0.578 | | |

**Table S3** Isovalues employed for the SDFs. The same density/maximum ratio was employed for the same observed species in different systems.

| System | Reference | Observed species | Isovalues |
|---|---|---|---|
| **$PIP_{1,3}DFOB$** | **$PIP_{1,3}$ (Figure 3a)** | DFOB C.O.M. | 8.7 |
| | | $PIP_{1,3}$ C.O.M. | 6.6 |
| | | $O_{DFOB}$ | 6.8 |
| | | $F_{DFOB}$ | 6.0 |
| **$PIP_{1,2O2}DFOB$** | **$PIP_{1,2O2}$ (Figure 3b)** | DFOB C.O.M. | 8.9 |
| | | $PIP_{1,2O2}$ C.O.M. | 4.5 |
| | | $O_{DFOB}$ | 7.7 |
| | | $F_{DFOB}$ | 6.2 |
| | **DFOB (Figure 4a)** | DFOB C.O.M. | 4.9 |
| | | $PIP_{1,2O2}$ C.O.M. | 7.0 |
| | | $O_{DFOB}$ | 4.0 |
| | | $F_{DFOB}$ | 3.6 |
| **$PIP_{1,2O2}BOB$** | **BOB (Figure 4b)** | BOB C.O.M. | 5.7 |
| | | $PIP_{1,2O2}$ C.O.M. | 6.3 |
| | | $O_{BOB}$ | 3.9 |