Electronic Properties of Cyano Ionic Liquids: a Valence Band Photoemission Study: Supporting Information

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DOS and PDOS of 5 pairs clusters

The electronic structure calculated for five pairs clusters of : $Im^{+}_{2,1}/SCN^{-}$, $Im^{+}_{2,1}/N(CN)_2{}^{-}$, $Im^{+}_{2,1}/C(CN)_3{}^{-}$ and $Im^{+}_{2,1}/B(CN)_4{}^{-}$ is summarized in Figure S1. Results for $Im^{+}_{2,1}/B(CN)_4{}^{-}$ are only indicated in this supporting information file as no experimental data was available for direct comparison with simulations. The total DOS (black curve) as well as the DOS projected on the cations (red curve) and anions (blue curve) are shown in the left column of Figure S1. The total DOS as well as the DOS projected on the different elements composing each ILs is shown in the right column of Figure S1. Note that the energy scale is not shifted to that of experimental results.

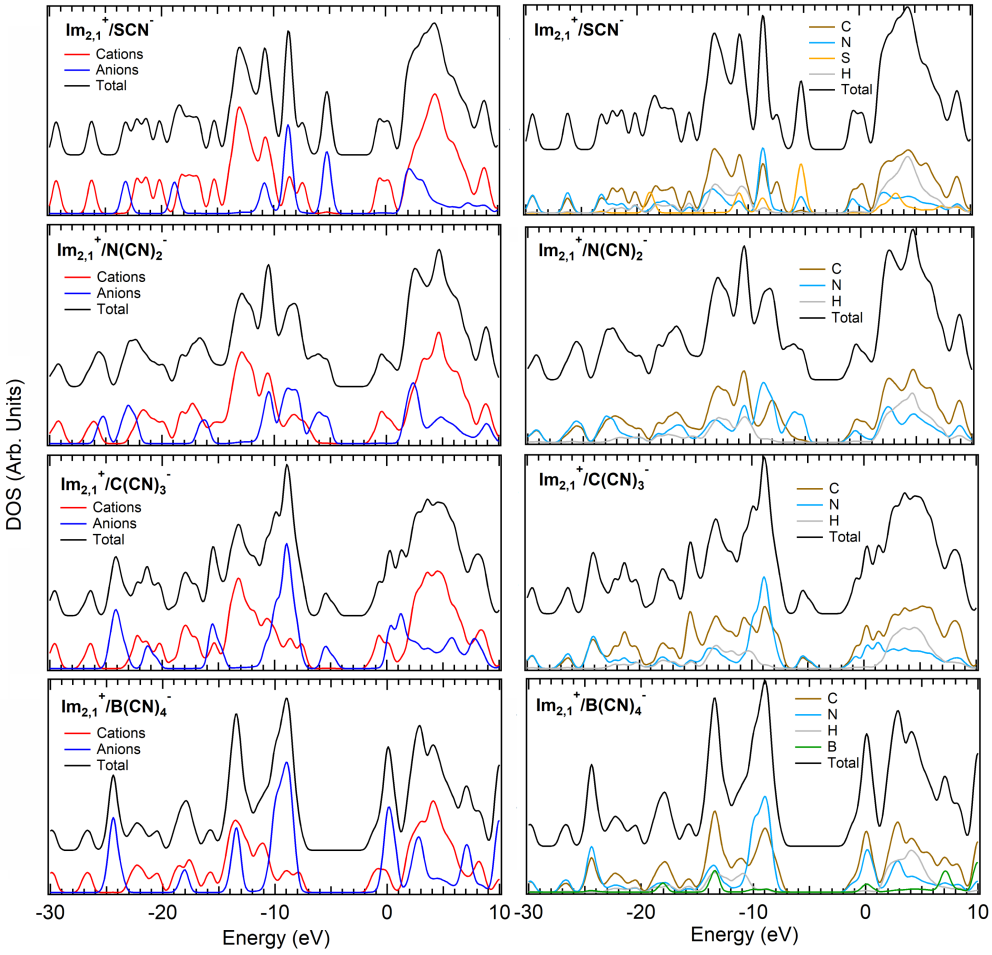

Figure S1: DOS and PDOS projected either on the cations and anions or on the different elements, calculated for five pairs clusters.

Frontier orbitals and energy gaps

The HOMO and LUMO Kohn-Sham orbitals calculated for five pairs clusters of $Im^+_{2,1}/SCN^-$, $Im^+_{2,1}/N(CN)_2{}^-$, $Im^+_{2,1}/C(CN)_3{}^-$ and $Im^+_{2,1}/B(CN)_4{}^-$ are reported in Figure S2. These orbitals can be directly compared to the simple model of Figure 8 in the main manuscript, where frontier orbitals are obtained by using isolated ions orbitals shifted by the Madelung energy.

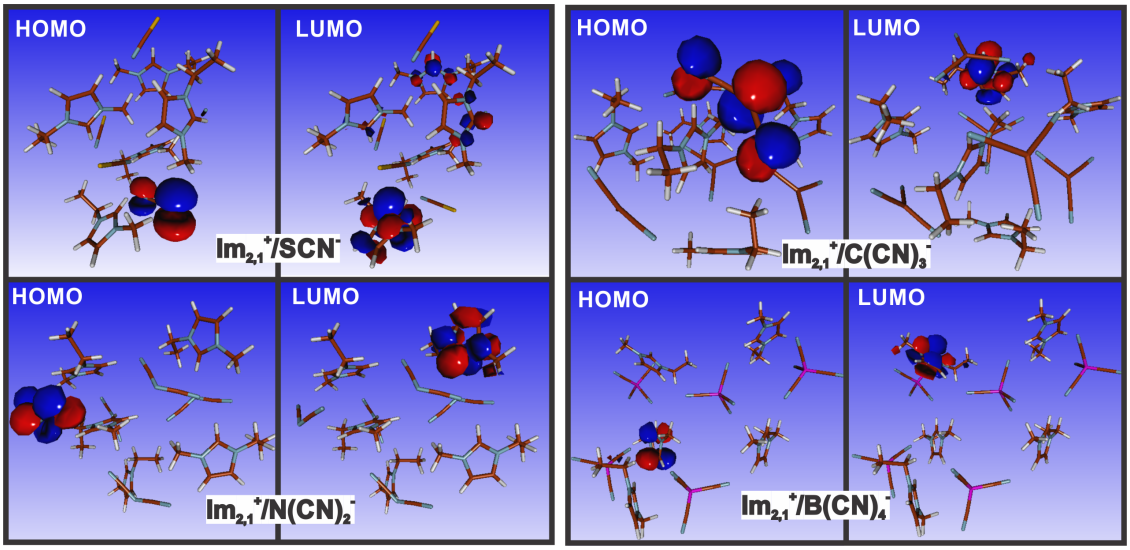

Figure S2: Frontier orbitals calculated for five pairs clusters of $Im^+_{2,1}/SCN^-$, $Im^+_{2,1}/N(CN)_2{}^-$, $Im^+_{2,1}/C(CN)_3{}^-$ and $Im^+_{2,1}/B(CN)_4{}^-$.

The HOMO-LUMO energy gap obtained using either 5 pairs cluster or shifted single ions electronic structure approaches are summarized in Table S1. For the 5 pairs clusters, the HOMO-LUMO gap is obtained from an average of the 5 HOMOs and 5 LUMOs positions. The energy gaps and trends obtained using these two methods are in good agreement.

Table S1: Comparison of the HOMO-LUMO gap obtained either from 5 pairs clusters or from orbitals of isolated ions shifted by the Madelung energy.

	5 pairs cluster	Shifted isolated ions
$Im^+_{2,1}/SCN^-$	4.52 eV	4.47 eV
$Im^+_{2,1}/N(CN)_2{}^-$	4.77 eV	4.80 eV
$Im^+_{2,1}/C(CN)_3{}^-$	4.35 eV	4.46 eV
$Im^+_{2,1}/B(CN)_4{}^-$	6.81 eV	6.69 eV