Unveiling Noncovalent Interactions in Imidazolium, Pyrrolidinium or Quaternary Ammonium Cation and Acetate Anion Based Protic Ionic Liquids: Structure and Spectral Characteristics

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Supporting Information

Figure S1 MESP isosurfaces (isovalue= 0.002 au) in the dication and acetate anion.

Figure S2 Optimized $[C4qm](OAc)_2$ conformers shown as C1-C6. The relative stabilization energies (in kJ mol^{-1}) are shown in parentheses.

Figure S3 Optimized $[C4im](OAc)_2$ conformers shown as C1-C5. The relative stabilization energies (in kJ mol^{-1}) are shown in parentheses.

Figure S4 Optimized $[C1pyr](OAc)_2$ conformers shown as C1-C5. The relative stabilization energies (in kJ mol^{-1}) are shown in parentheses.

Figure S5 Optimized $[C4pyr](OAc)_2$ conformers shown as C1-C6. The relative stabilization energies (in kJ mol^{-1}) are shown in parentheses.

Table S1 Selected Structural Parameters in Isolated Cations $[C4qm]^{2+}$, $[C1pyr]^{2+}$, $[C4pyr]^{2+}$ and $[C4im]^{2+}$ and Their Complexes.

Table S2 Selected Structural Parameters in the Isolated $[OAc]^-$ anion and Dication-(OAc) Complexes.

Table S3 ZPE Corrected Binding energies (ΔE) and Free Energy Change (ΔG) or Enthalpy Change (ΔH), in kcal mol^{-1}, Accompanying the Dication-$(OAc)_2$ Complexes.

Table S4 Occupancies of Antibonding, σ*(N-H) or σ*(N-C) Natural Orbitals in the Dication-anion Complexes.

Table S5 NBO Charges (in au) in Isolated OAc^- Anion and their Dication-$(OAc)_2$ Complexes.

Figure S6 G(r), V(r), and E_{HB} parameters as a function of electron density in (a) $[C1pyr](OAc)_2$, (b)$[C1pyr](OAc)_2$, (c)$[C1pyr](OAc)_2$ and (d) $[C1pyr](OAc)_2$ complexes. See the text for details.

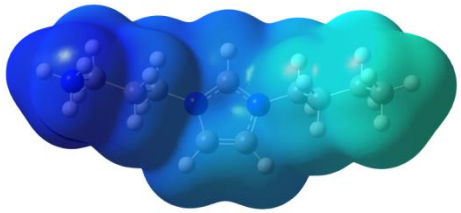
Figure S7 NCI isosurfaces for (a) $[C1pyr](OAc)_2$, (b)$[C1pyr](OAc)_2$, (c)$[C1pyr](OAc)_2$ and (d) $[C1pyr](OAc)_2$. The surfaces are displayed on a blue–green–red scale with respect to the values of $\sin(\lambda_2)\rho$, ranging from −0.05 to 0.05 au. The strongest attractions related to hydrogen bonds are displayed in blue, weak interactions such as van der Waals forces are displayed in light green, and steric repulsions are shown in red. The gradient isosurfaces with s = 0.5 au carbon atoms are displayed in light blue, nitrogen atoms are in dark blue, oxygen atoms are in red, fluor atoms are in pink, hydrogen atoms are in white, and the boron atom is in gray.

Figure S8 NCI-RDG scattered plots for a) $[C1pyr](OAc)_2$, (b)$[C1pyr](OAc)_2$, (c)$[C1pyr](OAc)_2$ and (d) $[C1pyr](OAc)_2$ ion pair complexes in the range −0.05 to 0.05 au.

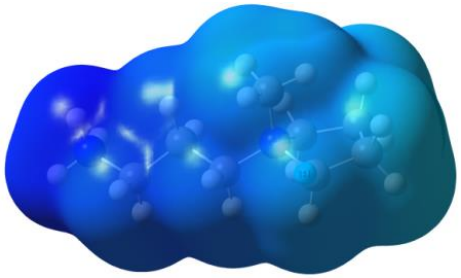
Figure S9 Calculated IR frequencies for the dication, $[C1pyr]^{2+}$, anion $[OAc]^{-}$ and $[C1pyr](OAc)_2$ complex in the ranges of (a) 3400–3000 cm^{-1}, and (b) 1600–800 cm^{-1}.

Figure S10 Calculated IR frequencies for dication, $[C4im]^{2+}$, anion $[OAc]^{-}$ and $[C4im](OAc)_2$ complex in the ranges of (a) 3800–3000 cm^{-1}, and (b) 1800–400 cm^{-1}.

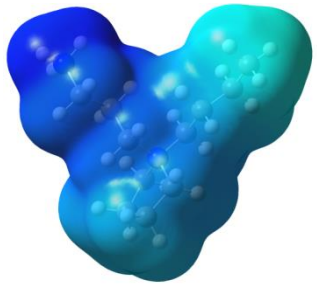
Figure S11 Calculated IR frequencies for dication, $[C4pyr]^{2+}$, anion $[OAc]^{-}$ and $[C4pyr](OAc)_2$ complex in the ranges of (a) 3800–3000 cm^{-1}, and (b) 1800–400 cm^{-1}.



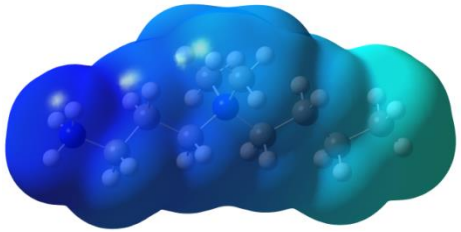
$[C4im]^{2+}$ ($V_{s,max}$ = 217)



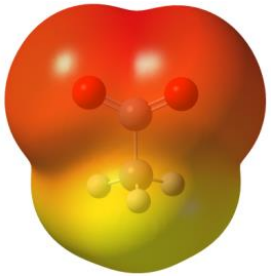
$[C1pyr]^{2+}$ ($V_{s,max}$ = 223)



$[C4pyr]^{2+}$ ($V_{s,max}$ = 221)

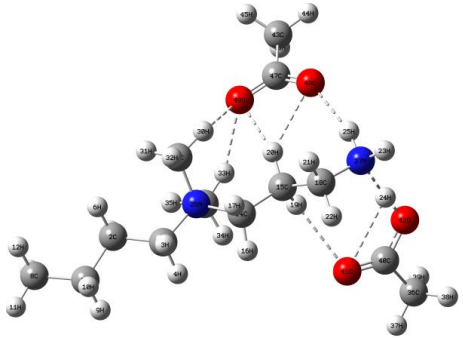


$[C4qm]^{2+}$($V_{s,max}$ = 222)



$[Ac^{-}]$ ($V_{s,min}$ = -157)

Figure S1



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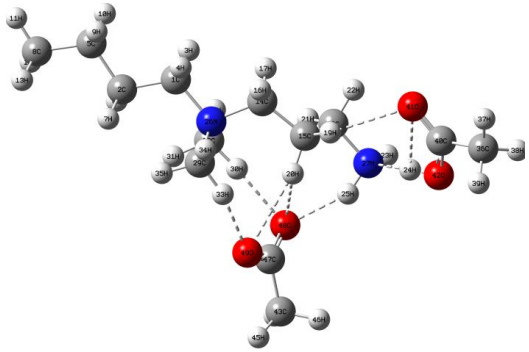

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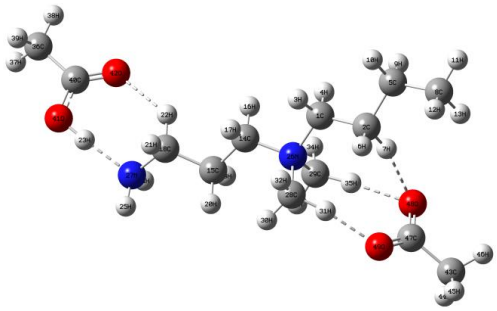

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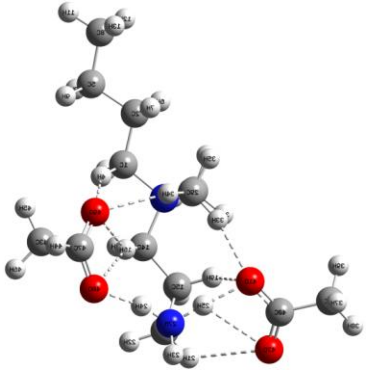

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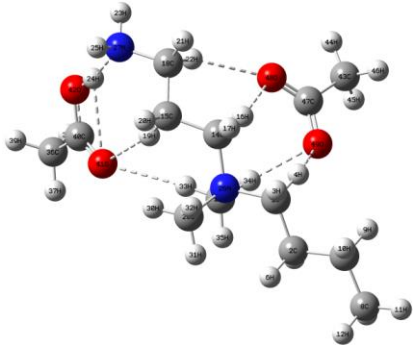

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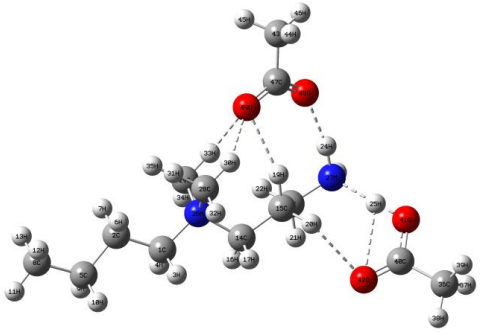
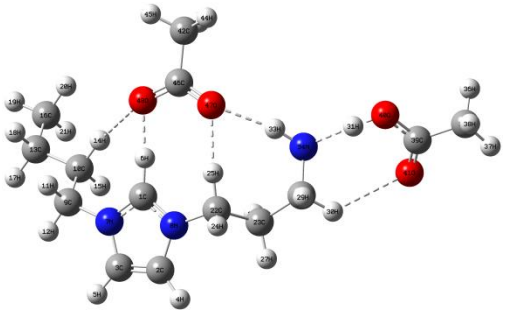


C6 (20.2)

Figure S2



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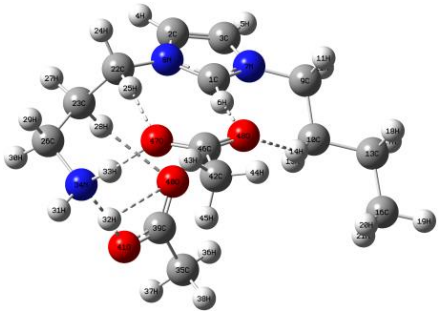

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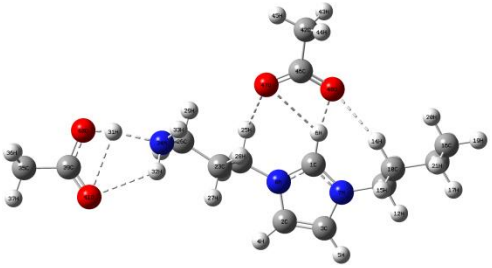

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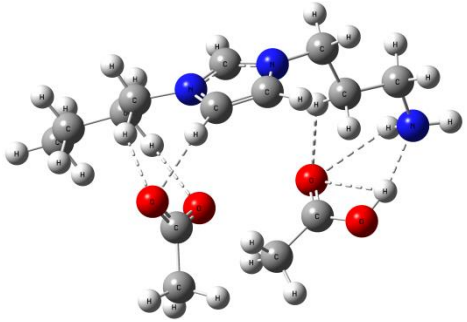

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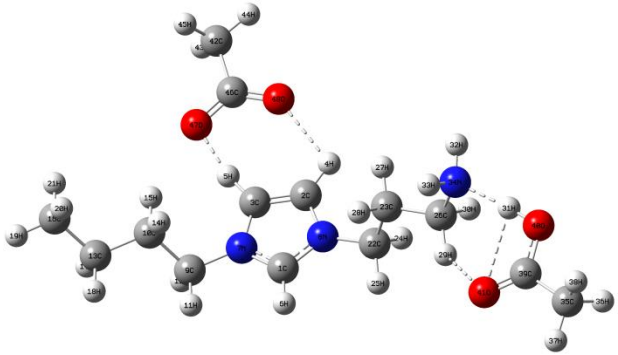
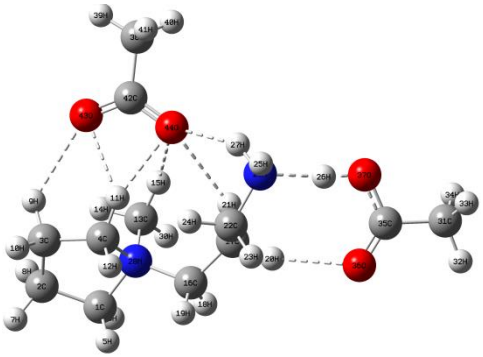


C5 (76.4)

Figure S3



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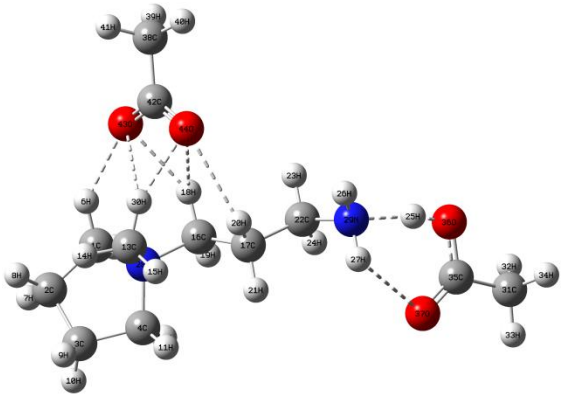

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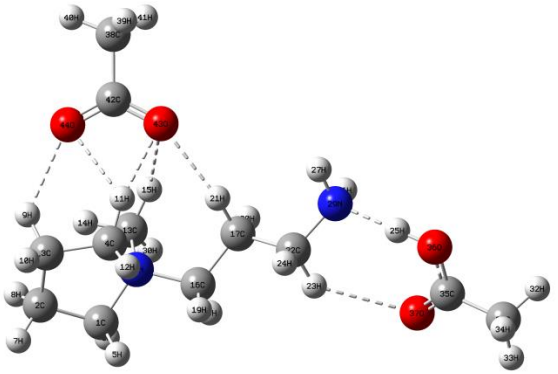

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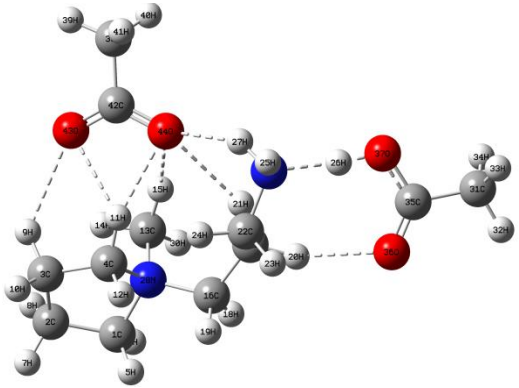

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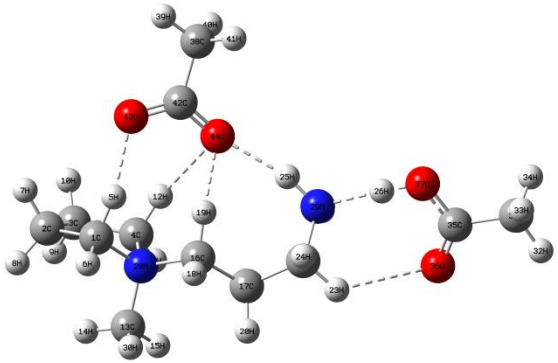

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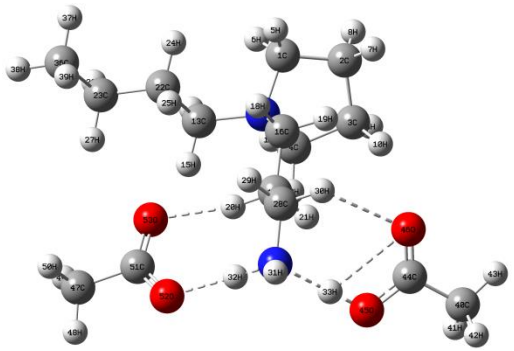
Figure S4



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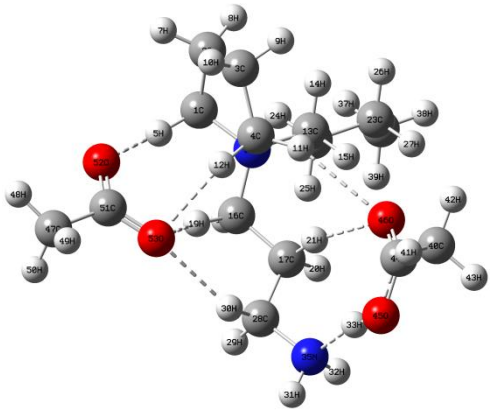

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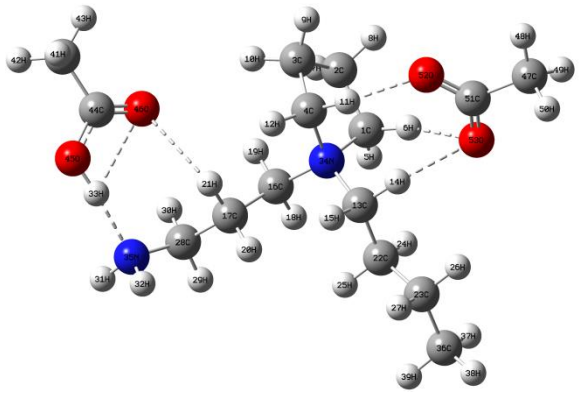

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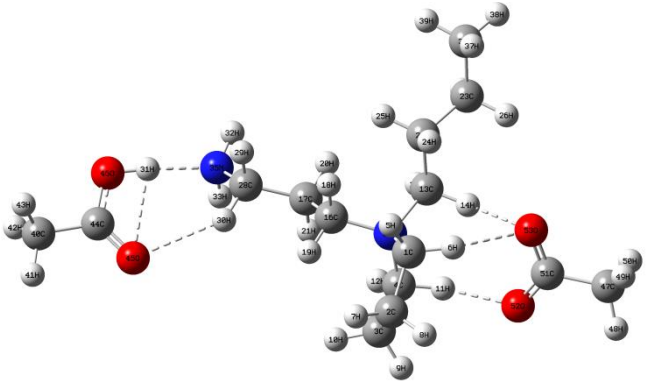

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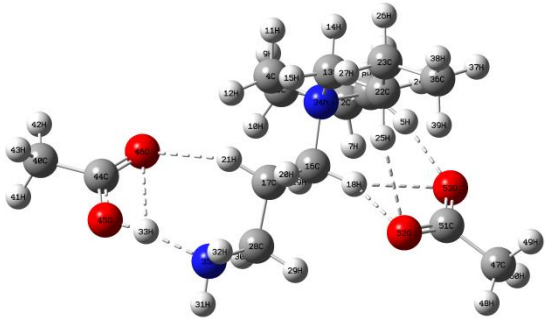

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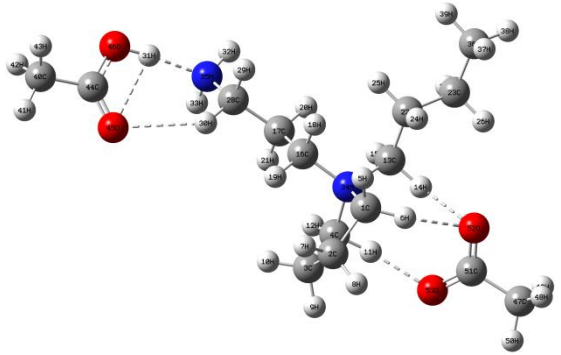


C6 (128.8)

Figure S5

Table S1. Selected Structural Parameters in Isolated Cations $[C4qm]^{2+}$, $[C1pyr]^{2+}$, $[C4pyr]^{2+}$ and $[C4im]^{2+}$ and Their Complexes.

	$[C4qm]^{2+}$	$[C4qm][OAc]_2$	$[C1pyr]^{2+}$	$[C1pyr][OAc]_2$	$[C4py]^{2+}$	$[C4pyr][OAc]_2$	$[C4im]^{2+}$	$[C4im][OAc]_2$
N1-H1	1.027	1.066	1.027	1.025	1.027	1.015	1.026	1.035
N1-H2	1.027	1.017	1.027	1.018	1.026	1.016	1.027	1.016
N1-H3	1.027	1.111	1.028	1.642	1.026	1.742	1.026	1.617
C3-H4	1.093	1.093	1.092	1.093	1.092	1.089	1.091	1.092
C3-H5	1.093	1.093	1.093	1.094	1.091	1.092	1.092	1.092
C2-H6	1.094	1.091	1.095	1.094	1.094	1.093	1.094	1.092
C2-H7	1.094	1.092	1.094	1.094	1.094	1.094	1.095	1.093
C3-H8	1.091	1.093	1.091	1.094	1.091	1.092	1.091	1.099
C3-H9	1.091	1.088	1.091	1.092	1.091	1.097	1.091	1.093
C4-H10	1.090	1.091	1.089	1.089	1.086	1.090	1.079	1.084
C4-H11	1.088	1.091	1.092	1.091	1.091	1.090	-	-
C5-H12	-	-	1.089	1.088	1.090	1.089	-	-
C6-H14	1.093	1.091	1.089	1.088	1.090	1.090	-	-
C7-H16/C7-H11	-	-	1.091	1.090	1.088	1.091	1.091	1.090
C8-H12	-	-	-	-	-	-	1.095	1.092
a(N2-C3-C2)	116.0	115.1	114.7	114.7	115.1	111.6	111.8	111.9
a(N2-C4-H11)	109.5	109.6	106.3	105.4	115.1	107.1	125.7	126.1
a(C2-C1-N1)	111.2	109.3	111.2	114.5	111.1	108.1	111.1	110.5
a(C1-N1-H1)	112.0	110.3	111.1	113.6	111.2	110.5	111.8	112.5
a(C1-N1-H2)	111.0	109.7	111.9	109.1	111.9	113.7	111.2	110.0
a(C1-N1-H3)	112.0	109.0	111.9	105.2	111.9	110.2	111.8	118.2
a(N1-C1-H6)	106.2	107.9	106.2	107.6	109.6	109.6	106.2	112.1
d(C3-C2-C1-N1)	-178.4	69.7	177.8	-71.3	178.4	173.6	179.4	-74.7
d(C2-C1-N1-H1)	-60.7	-80.9	179.6	63.4	-179.9	160.2	59.9	61.0
d(C2-C1-N1-H2)	179.7	161.0	59.9	-56.7	-60.2	-82.2	179.7	179.3
d(C2-C1-N1-H3)	60.1	44.2	-60.9	-158.3	60.4	34.0	-60.5	-53.8
d(C4-C5-C6-C7)	-	-	-2.28	1.60	0.914	28.4	-	-

Table S2: Selected structural parameters in the isolated $[OAc]^-$ anion and dication-$(OAc)_2$ complexes.

	$[OAc]^-$	$[C4qm][OAc]_2$	$[C1pyr][OAc]_2$	$[C4im][OAc]_2$	$[C4pyr][OAc]_2$
C-O1	1.249	1.284 (1.265)	1.321 (1.267)	1.317 (1.266)	1.321(1.256)
C-O2	1.249	1.235 (1.249)	1.213 (1.248)	1.215 (1.248)	1.213 (1.259)
C-CH_3	1.558	1.519 (1.521)	1.506 (1.524)	1.506 (1.527)	1.506 (1.528)
a(O1CO2)	129.0	123.9 (125.0)	123.7 (124.7)	123.8 (125.0)	124.3 (125.0)

Note: Geometrical parameters of second OAc-anion (atoms shown with prime notation in Figure 3) are given in parenthesis.

Table S3. ZPE Corrected Binding energies (ΔE) and Free Energy Change (ΔG) or Enthalpy Change (ΔH), in kcal mol^{-1}, Accompanying the Dication-$(OAc)_2$ Complexes.

	$[C4qm](OAc)_2$	$[C1pyr](OAc)_2$	$[C4im](OAc)_2$	$[C4pyr](OAc)_2$
ΔE	317 (40)	316 (38)	316 (41)	310 (36)
ΔG	–294	–293	–288	–286
ΔH	–317	–316	–316	–310

Note: A value in parenthesis represents binding energies of solvent (DMSO) optimized structure of dication-anion complexes.

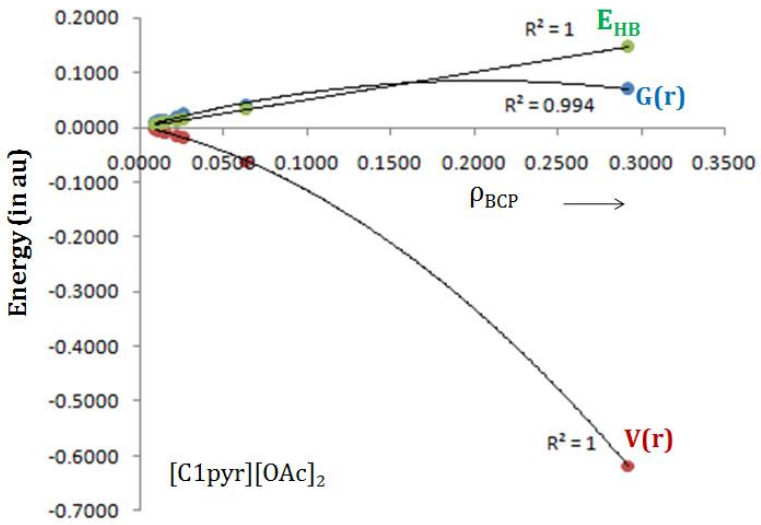
Table S4. Occupancies of antibonding,σ*(N-H) or σ*(N-C) natural orbitals in ion pair complexes.

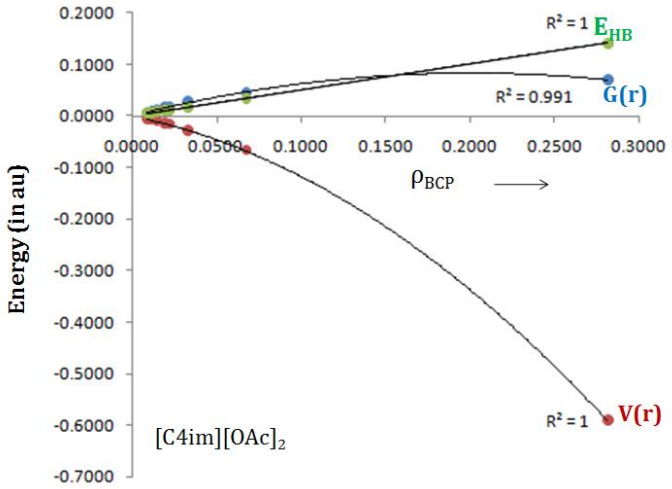
	$[C1pyr]^{2+}$	$[C1pyr][OAc]_2$	$[C4qm]^{2+}$	$[C4qm][OAc]_2$	$[C4pyr]^{2+}$	$[C4pyr][OAc]_2$	$[C4im]^{2+}$	$[C4im][OAc]_2$
σ*(N-H1)	0.0079	-	0.0079	0.1361	0.0079	-	0.0080	-
σ*(N-H2)	0.0052	0.0212	0.0079	0.0868	0.0052	0.0056	0.0080	0.0393
σ*(N-H3)	0.0079	0.0094	0.0052	0.0066	0.0079	0.0074	0.0054	0.0061
σ*(N-C3)	0.0139	0.0102	0.0138	0.0136	0.0140	0.0083	0.0141	0.0116

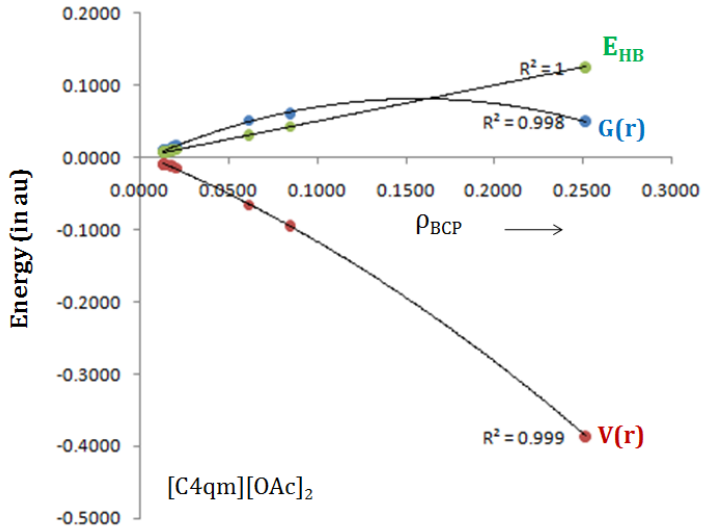
Table S5. Selected charges (in au) driven from the NBO analysis for isolated dication and their dication-$(OAc)_2$ complexes.

Atom	$[C1pyr]^{2+}$	$[C1pyr][OAc]_2$	Atom	$[C4qm]^{2+}$	$[C4qm][OAc]_2$
N1	-0.689	-0.897	N1	-0.689	-0.809
H1	0.450	0.515	H1	0.450	0.467
H2	0.451	0.434	H2	0.450	0.470
H3	0.463	0.376	H3	0.462	0.403
H4	0.239	0.228	H4	0.237	0.233
H5	0.239	0.228	H5	0.238	0.237
H6	0.232	0.246	H6	0.229	0.225
H7	0.231	0.238	H7	0.232	0.226
H8	0.232	0.229	H8	O.236	0.209
H9	0.236	0.251	H9	0.239	0.278
H10	0.229	0.260	H10	0.217	0.261
H11	0.222	0.234	H11	0.221	0.223
O1	-0.812	-0.670 (-0.807)	O1	-0.812	-0.844 (-0.837)
O2	-0.812	-0.748 (-0.879)	O2	-0.812	-0.753 (-0.815)
Atom	$[C4pyr]^{2+}$	$[C4pyr][OAc]_2$	Atom	$[C4im]^{2+}$	$[C4im][OAc]_2$
N1	-0.689	-0.728	N1	-0.689	-0.743
H1	0.450	0.461	H1	0.449	0.458
H2	0.450	0.485	H2	0.449	0.474
H3	0.462	0.432	H3	0.461	0.438
H4	0.237	0.253	H4	0.237	0.239
H5	0.238	0.227	H5	0.238	0.226
H6	0.229	0.239	H6	0.231	0.216
H7	0.232	0.238	H7	0.228	0.249
H8	O.236	0.247	H8	0.233	0.232
H9	0.239	0.220	H9	0.237	0.247
H10	0.221	0.256	H1’	0.249	0.263
H11	0.235	0.220	H2’	0.252	0.280
-	-	-	H3’	0.266	0.238
O1	-0.812	-0.743 (-0.845)	O1	-0.812	-0.690 (-0.797)
O2	-0.812	-0.672 (-0.826)	O2	-0.812	-0.752 (-0.857)

Note: NBO charges of the second OAc-anion (atoms shown with prime notation in Figure 3) are given in parenthesis.


Energy (in au)
ρBCP
EHB
G(r)
V(r)
R² = 1
R² = 0.994
R² = 1
[C1pyr][OAc]2


Energy (in au)
ρBCP
EHB
G(r)
V(r)
R² = 1
R² = 0.991
R² = 1
[C4im][OAc]2


Energy (in au)
ρBCP
EHB
G(r)
V(r)
R² = 1
R² = 0.998
R² = 0.999
[C4qm][OAc]2

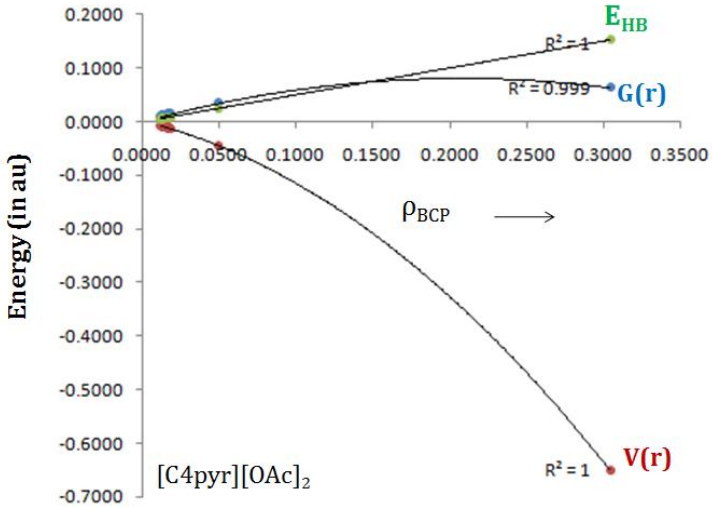
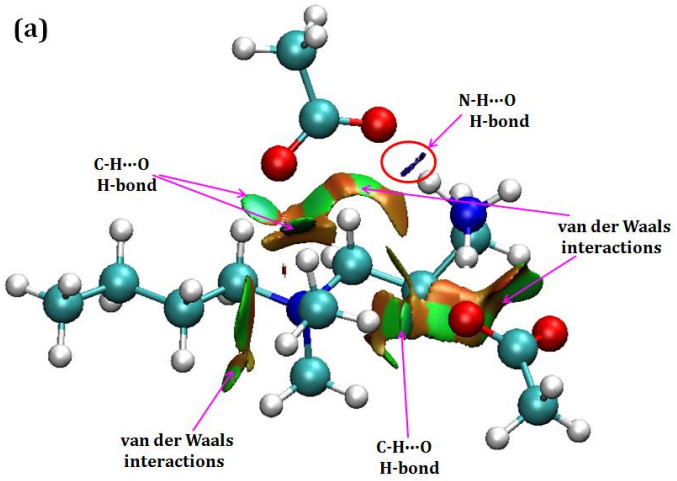
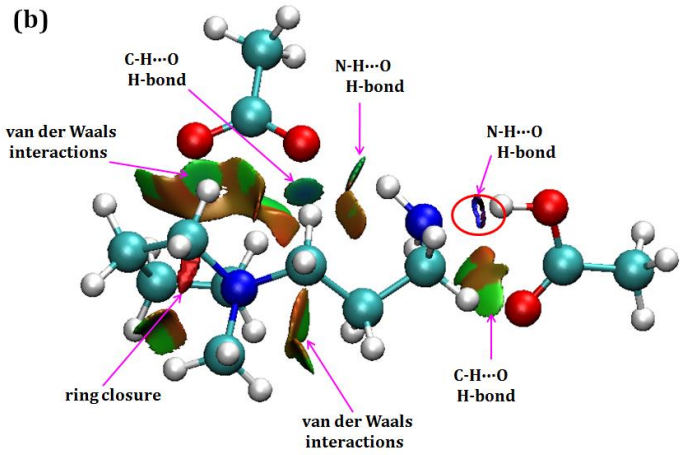

Energy (in au)
ρBCP
EHB
G(r)
V(r)
R² = 1
R² = 0.999
R² = 1
[C4pyr][OAc]2

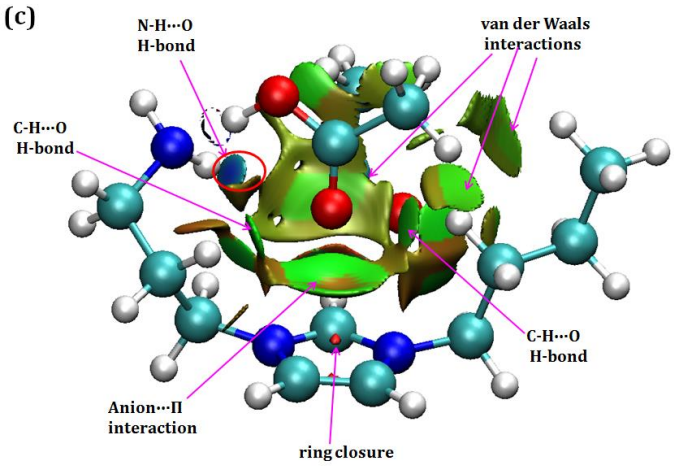
Figure S6



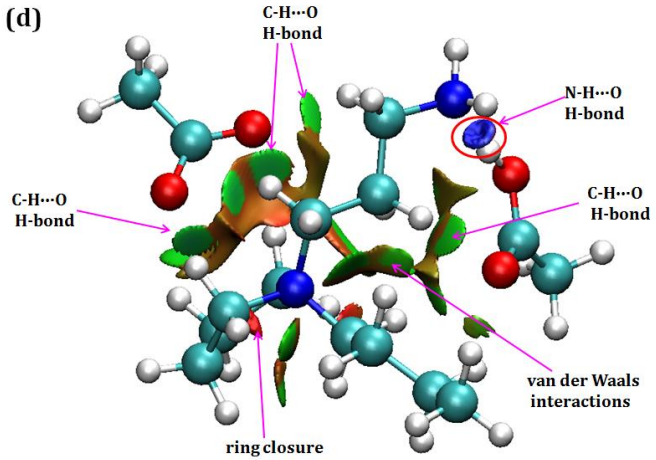
[C4qm][OAc]$_2$



[C1pyr][OAc]$_2$



[C4im][OAc]$_2$



[C4pyr][OAc]$_2$

Figure S7

Discussion on NCI: As is evident from Figure S7, the [C1qm][OAc]$_2$ ion pair complex reveal hydrogen-bonding and nonbonding interactions near the overlapping density regions with the acetate anion rendering strong N-H···O interactions with ammonium protons which emerge with dark blue colored disc-shaped blocks. The light green isosurface imply attractive interactions arising from the C-H···O as well as the van der Waals interactions between anionic oxygens and protons from either quaternary ammonium or those from the alkyl linkage. Furthermore a 'cyan' isosurface dispersed between the cation and acetate anion suggests the coexistence of weak hydrogen bonding and steric interactions. Alternatively the RDG-NCI scattered plots of [C1qm][OAc]$_2$ ion-pair complexes (*cf.* Figure S8(a)) reveal spikes in low density and low gradient regions with their depth being proportional to the strength of interactions. The spike at -0.020 corresponds to strong N-H···O interactions while existence of spike around -0.010 to −0.015 au imply the presence of C-H···O and the van der Waals interactions. Similar inferences are drawn for rest of the dication-(OAc)$_2$ complexes displayed in Figures. S7 and Figure S8.

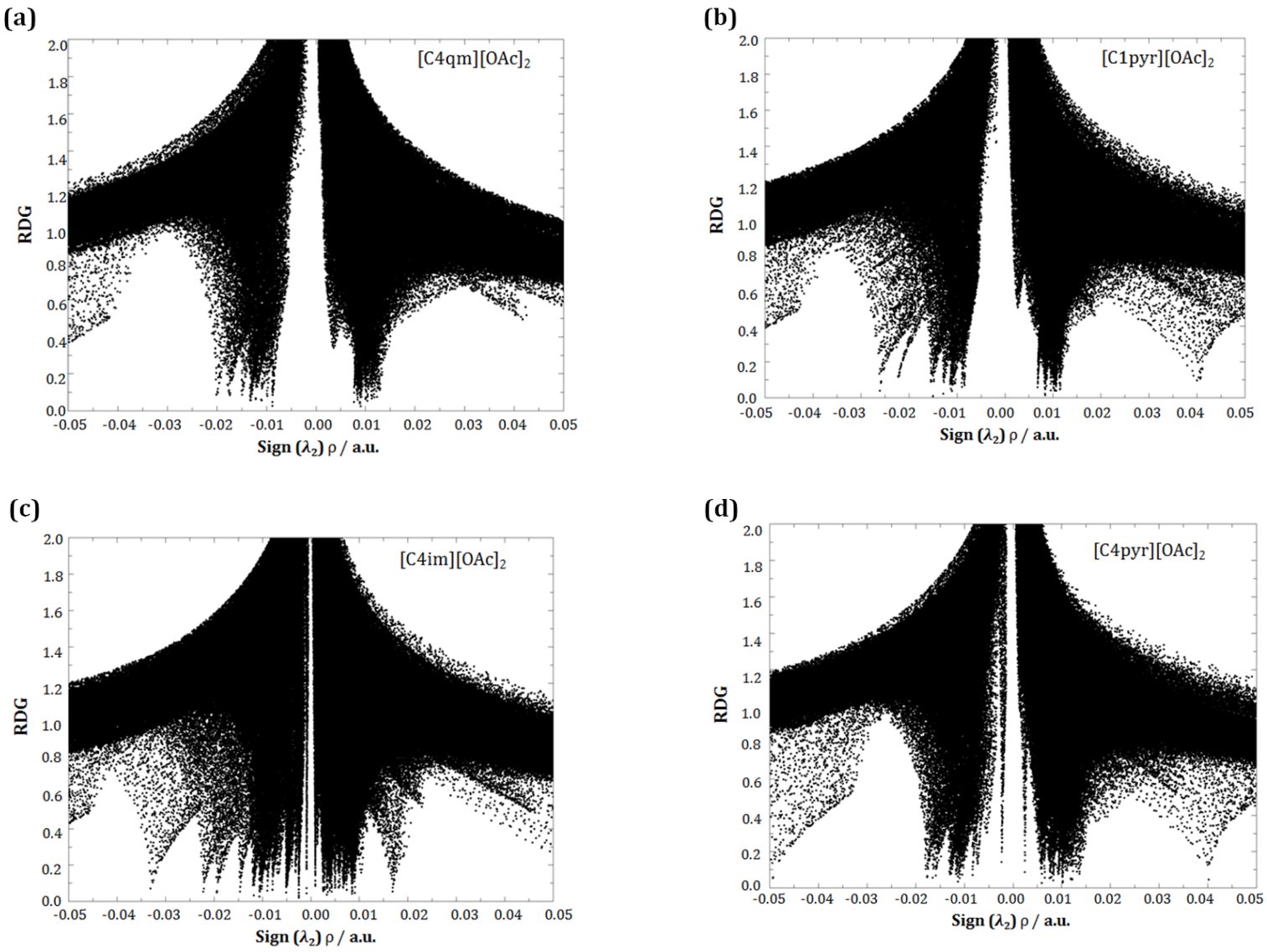

(a)
[C4qm][OAc]2
RDG
Sign (λ2) ρ / a.u.
(b)
[C1pyr][OAc]2
RDG
Sign (λ2) ρ / a.u.
(c)
[C4im][OAc]2
RDG
Sign (λ2) ρ / a.u.
(d)
[C4pyr][OAc]2
RDG
Sign (λ2) ρ / a.u.

Figure S8

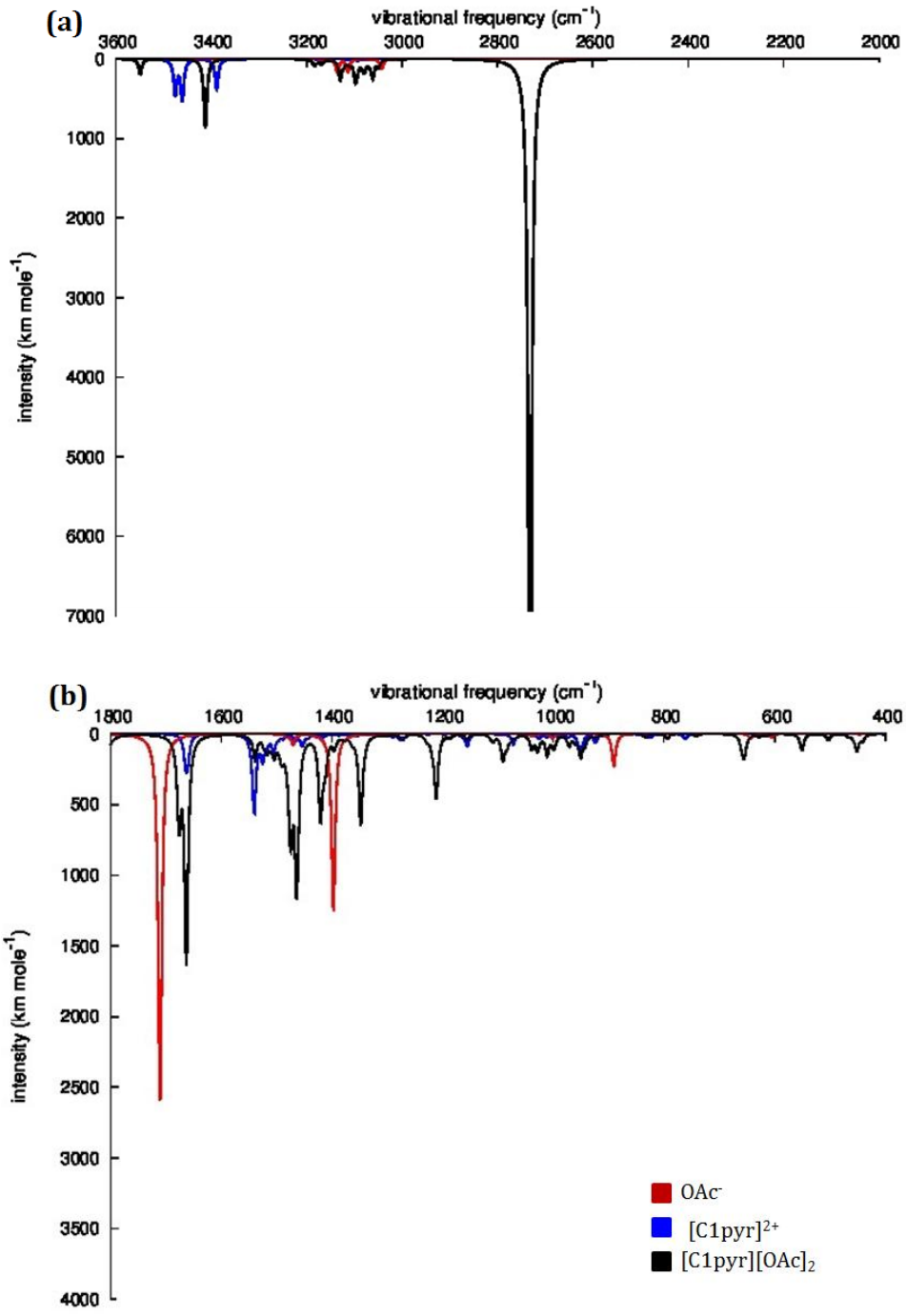

(a)
vibrational frequency (cm^{-1})
3600
3400
3200
3000
2800
2600
2400
2200
2000
0
1000
2000
3000
4000
5000
6000
7000
intensity (km mole^{-1})
(b)
vibrational frequency (cm^{-1})
1800
1600
1400
1200
1000
800
600
400
0
500
1000
1500
2000
2500
3000
3500
4000
intensity (km mole^{-1})
OAc$^-$
[C1pyr]$^{2+}$
[C1pyr][OAc]$_2$

Figure S9

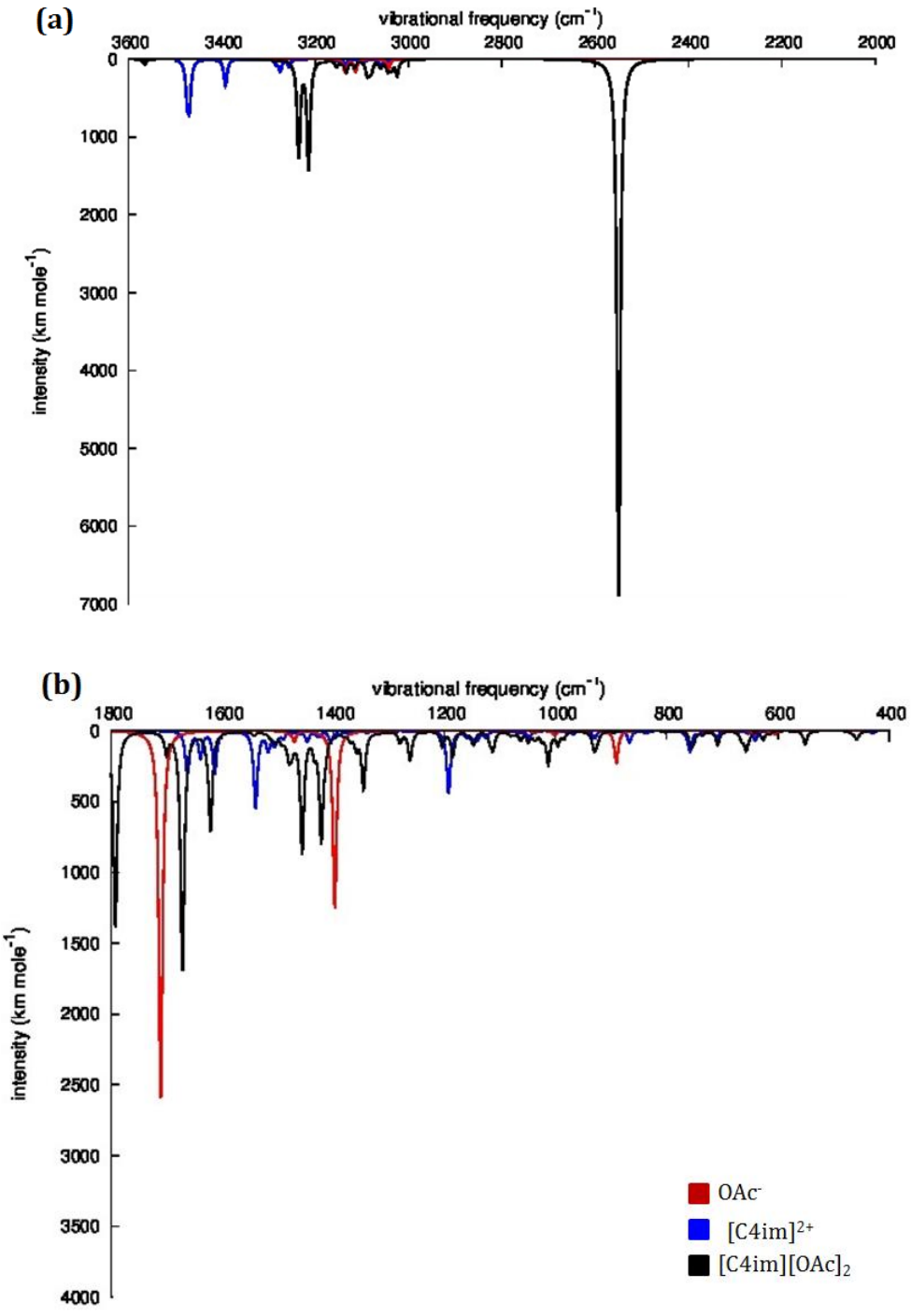

(a)
vibrational frequency (cm^{-1})
3600
3400
3200
3000
2800
2600
2400
2200
2000
0
1000
2000
3000
4000
5000
6000
7000
intensity (km mole^{-1})
(b)
vibrational frequency (cm^{-1})
1800
1600
1400
1200
1000
800
600
400
0
500
1000
1500
2000
2500
3000
3500
4000
intensity (km mole^{-1})
OAc$^-$
[C4im]$^{2+}$
[C4im][OAc]$_2$

Figure S10

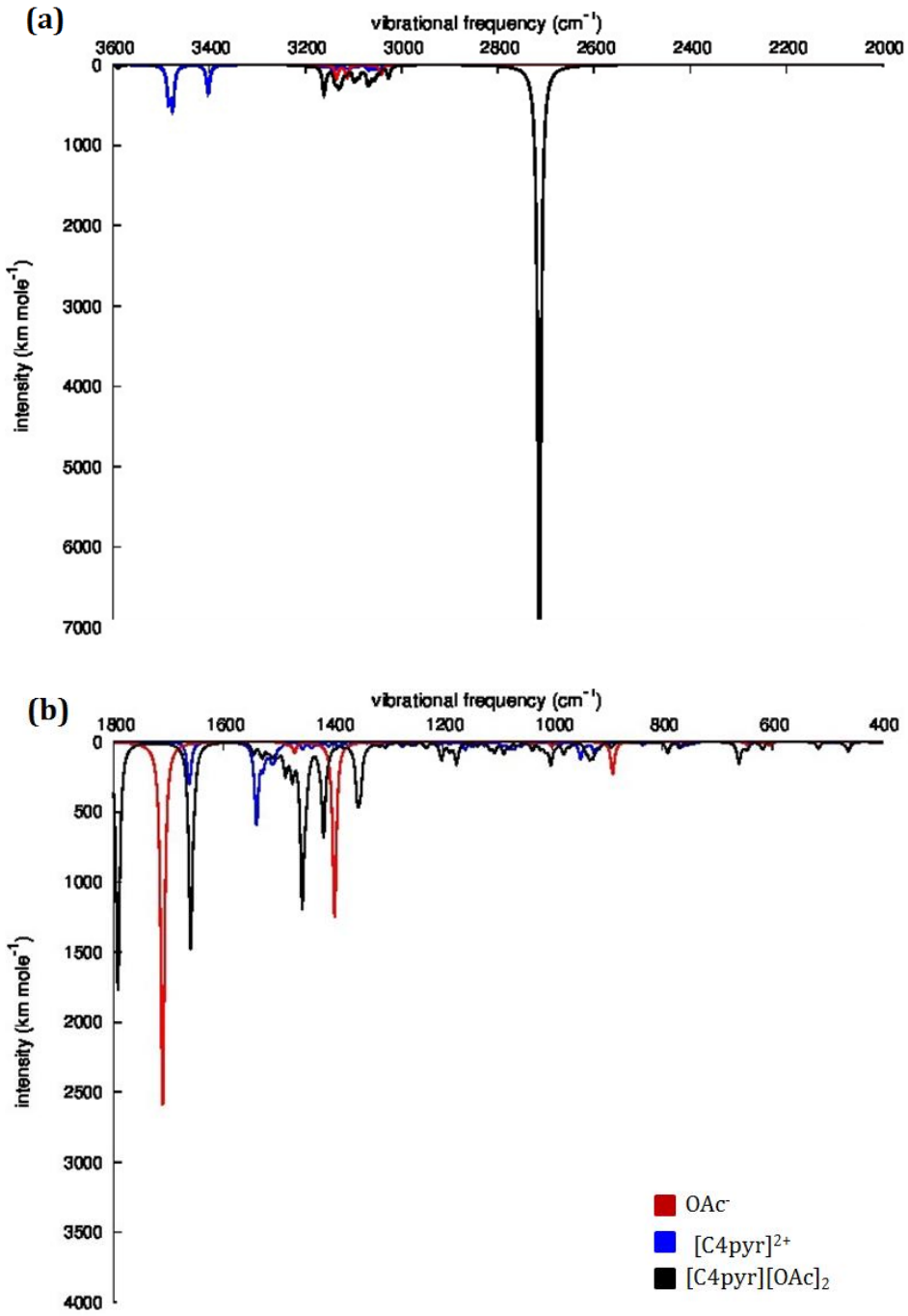

(a)
vibrational frequency (cm^{-1})
3600
3400
3200
3000
2800
2600
2400
2200
2000
0
1000
2000
3000
4000
5000
6000
7000
intensity (km mole^{-1})
(b)
vibrational frequency (cm^{-1})
1800
1600
1400
1200
1000
800
600
400
0
500
1000
1500
2000
2500
3000
3500
4000
intensity (km mole^{-1})
OAc$^-$
[C4pyr]$^{2+}$
[C4pyr][OAc]$_2$

Figure S11