Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information

Theoretical Study on the Microscopic Mechanism of Lignin Solubilization in Keggin-type Polyoxometalate Ionic Liquids

Zhaoyang Ju[a,b,c], Weihua Xiao[a], Xiaoqian Yao[f], Xin Tan[f], Blake A. Simmons[c,d], Kenneth L. Sale[c,e], Ning Sun[b*]*

[a]Engineering Laboratory for AgroBiomass Recycling & Valorizing, College of Engineering, China Agricultural University, Beijing, China

[b]Advanced Biofuel Process Demonstration Unit, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

[c]Joint BioEnergy Institute, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

[d]Lawrence Berkeley National Laboratory, Berkeley, CA, USA
[e]Sandia National Laboratories, Livermore, CA, USA
[f]CAS Key Laboratory of Green Process and Engineering, Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China

Content

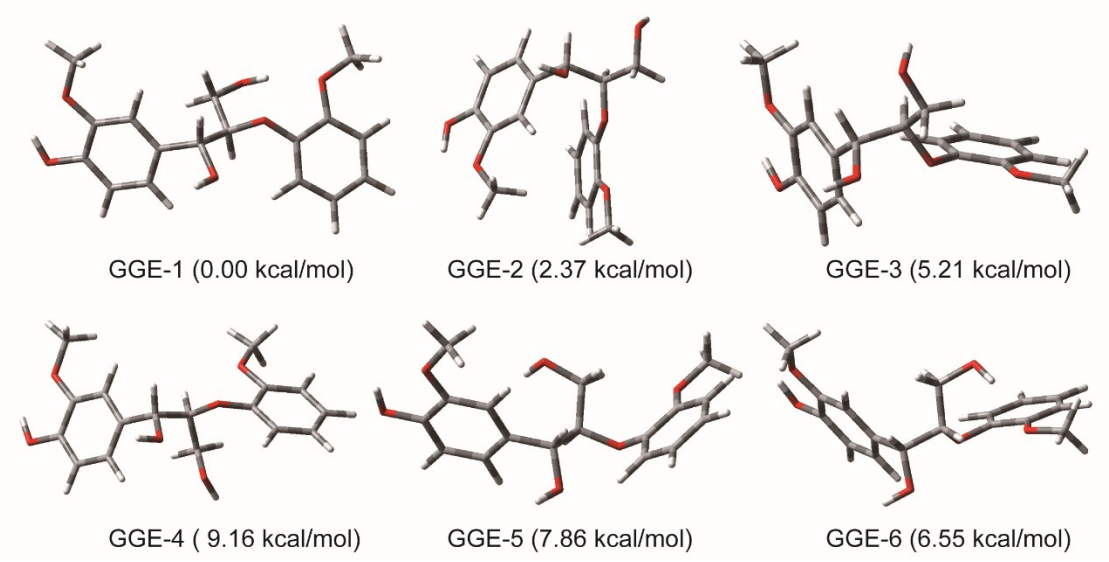

Fig. S1 Conformational isomers of GGE model compound, and the relative energies to GGE-1 are labeled in parentheses.

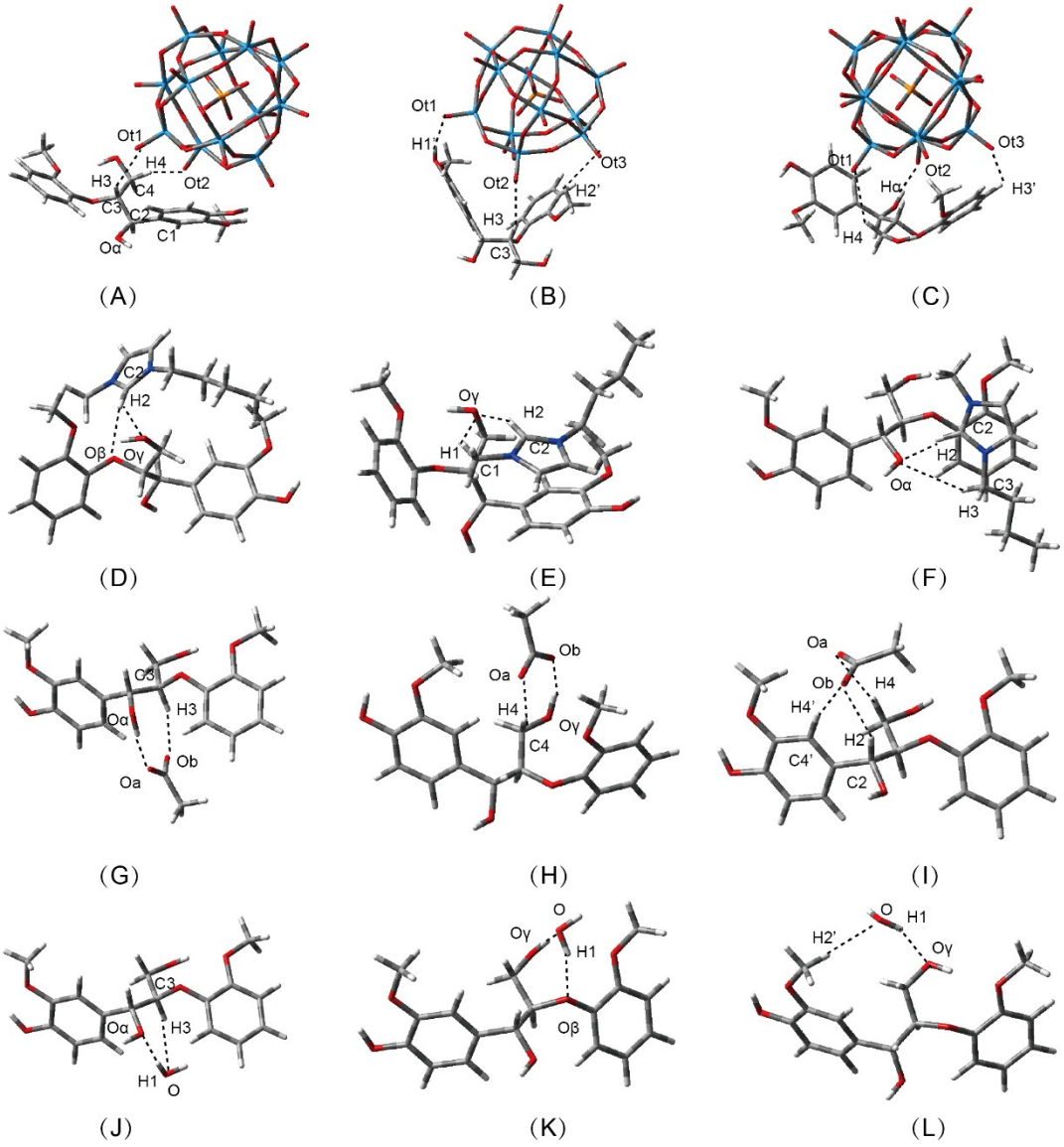

Fig. S2 Optimized geometries of GGE and isolated anion/cation: GGE-POM (A-C), GGE-C4C1Im (D-F), GGE-OAc (G-I), and GGE-H_2O (J-L).

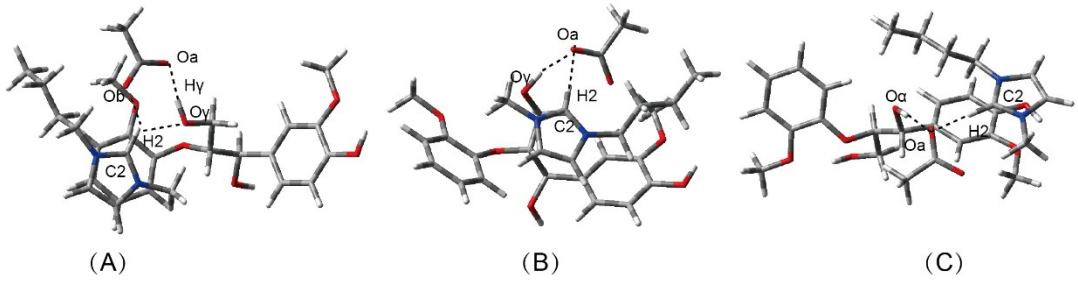

Fig. S3 Optimized the geometry of GGE-[C4C1Im][OAc].

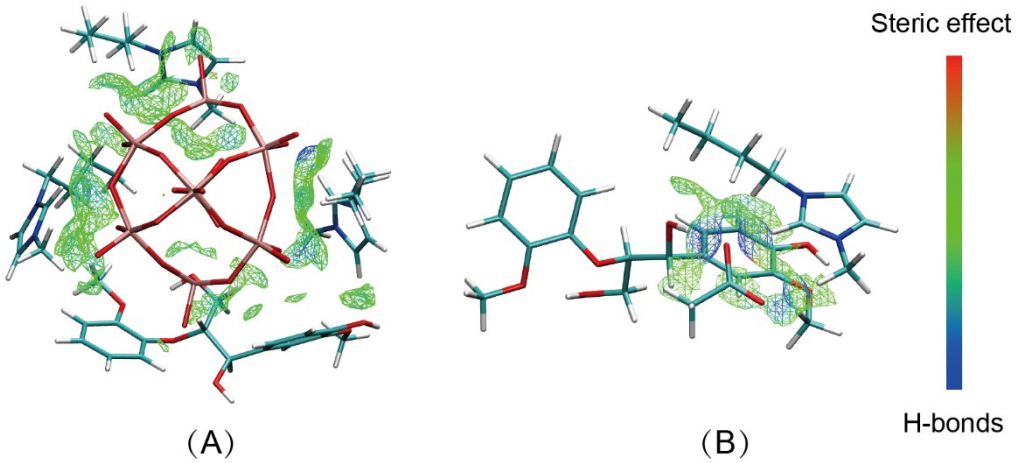

Fig. S4 Isosurfaces (isovalue = 0.5 a.u.) of (A) GGE-$[C4C1Im]_3[PW_{12}O_{40}]$ and (B) GGE-[C4C1Im][OAc]. Blue indicates strong attractive interaction like H-bonds, green indicates the π-π interaction and red indicates steric hindrance.

Table S1 The selected bond distance (Å) of the isolated $[PW_{12}O_{40}]^{3-}$ anion

bond	DFT	expt[a]
P-O_a	1.55	1.53
W-O_d	1.71	1.70
W-O_{b1}	1.93	1.91
W-O_{b2}	1.92	1.91
W-O_a	2.46	2.44

[a]Reference 40

Table S2 The corresponding H-Bonds lengths (in angstroms), bond angles (in degrees) and interaction energies (in kcal/mol) of $[C4C1Im]^+$ $[PW_{12}O_{40}]^{3-}$ structures.

Entry	**H-bonds**	**Length**	**Angle**	**ΔE_1[a]**	**ΔE_2[a]**	**Δ BSSE[a]**	**ΔE_{2C}[a]**	**ΔE_{2CR}[a]**
(A)	C1-H1…Ot1	2.23	164.30	-167.91	-171.91	5.71	-166.20	0.00
	C2-H2…Ob1	2.04	149.43					
	C3-H3…Ot2	2.55	113.70					
(B)	C1-H1…Ot1	2.23	136.74	-157.95	-161.16	4.21	-156.95	4.21
	C2-H2…Ob1	2.74	155.60					
	C3-H3…Ot2	2.60	107.92					
(C)	C1-H1…Ot1	2.51	133.09	-162.50	-166.49	5.51	-160.98	5.21
	C2-H2…Ot2	1.99	144.81					
	C3-H3…Ot2	2.26	148.45					
(D)	C2-H2…Ot1	1.94	152.85	-156.67	-159.69	4.80	-154.89	11.31
	C3-H3…Ot1	2.45	146.82					

[a] ΔE_1, ΔE_2, Δ BSSE, ΔE_{2C} and ΔE_{2CR} represent the interaction energies using M06L/6-31g** (LANL2DZ basis sets on metal atoms), the interaction energies using M06L/def2-TZVP, the values of BSSE, the interaction energies (ΔE_2) corrected by BSSE and the relative interaction energies (ΔE_{2C}).

Table S3 Bond lengths, bond energies E_{HB}, electron densities ρ(r) and Laplacian values $\nabla^2\rho(r)$ for the H-bonds of the $[C4C1Im]^+$ $[PW_{12}O_{40}]^{3-}$ complex of the POM-ILs.

Entry	Type of H-bonds	V(r) (a.u.)	E_{HB}(kJ/mol)	ρ(r) (a.u.)	$\nabla^2\rho(r)$(a.u.)
(A)	C1-H1…Ot1	-0.011	-14.92	0.015	0.041
	C2-H2…Ob1	-0.018	-23.03	0.023	0.066
	C3-H3…Ot2	-0.006	-8.27	0.009	0.034
(B)	C1-H1…Ot1	-0.012	-15.30	0.016	0.051
	C2-H2…Ob1	-0.011	-14.81	0.016	0.052
	C3-H3…Ot2	-0.006	-8.12	0.009	0.036
(C)	C1-H1…Ot1	-0.006	-7.71	0.009	0.031
	C2-H2…Ot2	-0.020	-26.48	0.026	0.080
	C3-H3…Ot2	-0.011	-14.87	0.015	0.048
(D)	C2-H2…Ot1	-0.022	-29.05	0.028	0.086
	C3-H3…Ot1	-0.007	-9.43	0.010	0.035

Table S4 The corresponding H-Bonds lengths (in angstroms), bond angles (in degrees) and interaction energies (in kcal/mol) of $[C4C1Im]_3[PW_{12}O_{40}]$ ion pairs.

Entry	H-bonds	Length	Angle	ΔE_1[a]	ΔE_2[a]	Δ BSSE[a]	ΔE_{2C}[a]	ΔE_{2CR}[a]
(A)	C2-H2…Ot1	2.39	98.64	-366.23	-376.42	15.29	-361.14	3.44
	C3-H3…Ot1	2.33	160.68					
	C2'-H2'…Ob1	2.70	160.04					
	C3'-H3'…Ot1	2.33	163.33					
	C2''-H2''…Ot3	2.01	149.90					
	C3''-H3''…Ot3	2.47	143.40					
(B)	C2-H2…Ot1	1.99	157.05	-365.24	-375.81	16.09	-359.72	4.85
	C3-H3…Ot1	2.70	143.25					
	C2'-H2'…Ot2	2.55	105.09					
	C1''-H1''…Ot3	2.50	109.20					
(C)	C2-H2…Ob1	2.21	139.91	-369.9	-379.19	14.61	-364.58	0.00
	C1-H1…Ot1	2.44	158.97					
	C2-H2'…Ot2	2.60	130.15					
	C1-H1''…Ot3	2.44	160.67					

[a] ΔE_1, ΔE_2, ΔBSSE, ΔE_{2C} and ΔE_{2CR} represent the interaction energies using M06L/6-31g** (LANL2DZ basis sets on mental atoms), the interaction energies using M06L/def2-TZVP, the values of BSSE, the interaction energies (ΔE_2) corrected by BSSE and the relative interaction energies (ΔE_{2C}).

Table S5 The NPA charge (a.u.) of $[C4C1Im]_3[PW_{12}O_{40}]$ ion pairs corresponding to the geometry in Fig. 3 (B).

	C4C1Im1	**C4C1Im2**	**C4C1Im3**	**POM**			
C	-0.695	-0.696	-0.695	P	2.739	O2-9	-0.704
H	0.247	0.231	0.245	W1	1.82	O2-10	-0.702
H	0.232	0.232	0.241	W2-1	1.859	O2-11	-0.705
H	0.231	0.248	0.227	W2-2	1.859	O2-12	-0.732
C	-0.466	-0.465	-0.461	W2-3	1.817	O2-13	-0.729
H	0.247	0.244	0.23	W2-4	1.819	O2-14	-0.734
H	0.24	0.245	0.252	W3-1	1.775	O2-15	-0.713
C	-0.467	-0.468	-0.472	W3-2	1.812	O2-16	-0.703
H	0.234	0.235	0.233	W4-1	1.819	O2-17	-0.728
H	0.232	0.232	0.242	W4-2	1.819	O2-18	-0.681
C	-0.253	-0.255	-0.243	W4-3	1.813	O2-19	-0.73
H	0.262	0.274	0.254	W4-4	1.818	O2-20	-0.729
H	0.272	0.264	0.269	W5	1.793	O2-21	-0.722
N	-0.333	-0.32	-0.335	O1-1	-1.054	O2-22	-0.699
C	0.282	0.269	0.278	O1-2	-1.048	O2-23	-0.718
H	0.275	0.271	0.274	O1-3	-1.054	O2-24	-0.681
N	-0.337	-0.33	-0.333	O1-4	-1.046	O3-1	-0.473
C	-0.044	-0.043	-0.045	O2-1	-0.683	O3-2-1	-0.523
H	0.27	0.278	0.269	O2-2	-0.683	O3-2-2	-0.527
C	-0.041	-0.042	-0.038	O2-3	-0.703	O3-2-3	-0.52
H	0.27	0.275	0.269	O2-4	-0.702	O3-2-4	-0.532
C	-0.486	-0.489	-0.484	O2-5	-0.729	O3-3-1	-0.549
H	0.276	0.28	0.25	O2-6	-0.683	O3-3-2	-0.478
H	0.249	0.265	0.275	O2-7	-0.686	O3-4-1	-0.545
H	0.264	0.25	0.265	O2-8	-0.697	O3-4-2	-0.522
						O3-4-3	-0.572
						O3-4-4	-0.538
						O3-5-1	-0.518
Sum	0.961	0.985	0.967				-2.913
∆e	0.039	0.015	0.033				0.087

Table S6 The corresponding H-Bonds lengths (in angstroms), bond angles (in degrees) and interaction energies of (A-C) GGE-POM, (D-F) GGE-C4C1Im (G-I) GGE-OAc and (J-L) GGE-H_2O.

Entry	H-bonds	Length	Angle	ΔE_1[a]	ΔE_2[a]	Δ BSSE[a]	ΔE_{2C}[a]	ΔE_{2CR}[a]
(A)	C3-H3…Ot1	2.40	130.58	-15.94	-21.81	6.14	-15.68	9.78
	C4-H4…Ot2	2.60	112.31					
(B)	C1'-H1'…Ot1	1.96	155.89	-24.89	-32.97	7.52	-25.45	0.00
	C3-H3…Ot2	2.49	151.83					
	C2'-H2'…Ot3	2.64	110.12					
(C)	C4-H4…Ot1	2.95	143.49	-23.23	-30.23	6.71	-23.52	1.93
	Oα-Hα…Ot2	1.88	178.06					
	C3'-H3'…Ot3	2.53	153.22					
(D)	C2-H2…Oβ	2.35	125.05	-23.52	-19.67	1.64	-18.02	3.07
	C2-H2…Oγ	2.34	136.55					
(E)	C1-H1…Oγ	1.97	156.53	-26.12	-22.46	1.71	-20.75	0.27
	C2-H2…Oγ	3.04	134.65					
(F)	C2-H2…Oα	2.07	163.66	-26.05	-22.73	1.83	-20.90	0.00
	C3-H3…Oα	2.99	139.21					
(G)	Oα-Hα…Oa	1.68	166.07	-36.42	-31.62	1.66	-29.96	0.00
	C3-H3…Ob	2.24	158.69					
(H)	Oγ-Hγ…Ob	1.78	162.59	-32.13	-26.54	2.02	-24.53	5.43
	C4-H4…Oa	2.25	149.50					
(I)	C2-H2…Ob	2.43	150.49	-31.51	-26.46	1.82	-24.64	5.32
	C4-H4…Oa	2.35	171.16					
	C4'-H4'…Ob	2.02	161.26					
(J)	O-H1…Oα	1.99	165.67	-9.40	-7.79	1.34	-6.45	0.09
	O…H3-C3	2.56	140.49					
(K)	O-H1…Oβ	1.95	151.74	-9.60	-7.72	1.19	-6.54	0.00
	O…Hγ-Oγ	2.06	145.47					
(L)	O-H1…Oγ	2.00	154.62	-8.82	-6.63	0.87	-5.76	0.77
	O…H2'-C2'	2.70	173.67					

[a] ΔE_1, ΔE_2, Δ BSSE, ΔE_{2C} and ΔE_{2CR} represent the interaction energies using M06L/6-31g** (LANL2DZ basis sets on mental atoms), the interaction energies using M06L/def2-TZVP, the values of BSSE, the interaction energies (ΔE_2) corrected by BSSE and the relative interaction energies (ΔE_{2C}).

Table S7 Changes in bond length (in angstroms) for GGE while it interacts with POM

Type of bonds	GGE	GGE-POM1	GGE-POM2	GGE-POM-3
C1-C2	1.50842	1.50648	1.50175	1.51493
C2-Oα	1.41980	1.43615	1.43170	1.43599
C2-C3	1.52384	1.51941	1.53147	1.54276
C3-C4	1.52463	1.51689	1.52356	1.52232
C4-Oγ	1.40039	1.40430	1.40388	1.40164
C3-Oβ	1.43844	1.46091	1.45729	1.45019
Oβ-C5	1.36791	1.35463	1.37310	1.37352

Table S8 Energy decomposition of interaction energies (in kcal/mol) for GGE and POM, OAc, C4C1Im and H_2O[a].

Entry		ΔE_{els}	ΔE_{exe}	ΔE_{ind}	ΔE_{disp}	ΔE_{tot}
(A)	GGE-POM	-30.15	37.53	-11.78	-30.25	-34.65
(B)	GGE-OAc	-42.54	39.39	-25.14	-9.79	-38.08
(C)	GGE-C4C1Im	-25.46	24.11	-9.23	-15.56	-26.14
(D)	GGE-H_2O	-18.11	17.59	-4.29	-4.54	-9.35

[a] $\Delta E_{tot} = \Delta E_{els} + \Delta E_{exe} + \Delta E_{ind} + \Delta E_{disp}$

Table S9 The corresponding H-Bonds lengths (in angstroms), bond angles (in degrees) and interaction energies (in kcal/mol) of GGE-$[C4C1Im]_3[PW_{12}O_{40}]$ structures.

Entry	H-bonds	Length	Angle	ΔE_1[a]	ΔE_2[a]	Δ BSSE[a]	ΔE_{2C}[a]	ΔE_{2CR}[a]
(A)	C2-H2…Ot1	2.40	160.08	-181.90	-191.69	7.85	-183.83	0.68
	C3-H3…Ot2	2.44	162.02					
(B)	O1-H1…Ot1	3.31	100.49	-182.15	-191.21	7.32	-183.89	0.62
	C2-H2…Ot2	2.32	117.64					
(C)	O1-H1…Ot1	2.92	79.20	-183.52	-191.53	7.01	-184.51	0.00
	C2-H2…Ot2	2.78	174.77					
(D)	C2-H2…Ot1	2.46	123.62	-379.80	-393.97	6.62	-387.35	0.06
	C3-H3…Ot2	2.13	144.54					
	O1-H1…Ot3	2.75	85.71					
(E)	C3-H3…Ot1	2.78	157.11	-381.04	-396.13	8.72	-387.41	0.00
	C2-H2…Ot3	2.53	175.61					
	C4-H4…Ot2	2.42	121.18					
(F)	C3-H3…Ot2	2.52	163.38	-378.66	-393.66	6.92	-386.75	0.66
	C1-H1…Ot1	2.51	95.82					

[a] ΔE_1, ΔE_2, ΔBSSE, ΔE_{2C} and ΔE_{2CR} represent the interaction energies using M06L/6-31g** (LANL2DZ basis sets on mental atoms), the interaction energies using M06L/def2-TZVP, the values of BSSE, the interaction energies (ΔE_2) corrected by BSSE and the relative interaction energies (ΔE_{2C}).

Table S10 Changes in bond length (in angstroms) for GGE while more cations were introduced in the system corresponding to the structures of Fig. 5.

Type of bonds	GGE	A	B	C	D	E	F
C1-C2	1.50842	1.50986	1.50826	1.51874	1.51128	1.51196	1.50896
C2-Oα	1.41980	1.42137	1.41688	1.41777	1.42028	1.41667	1.41813
C2-C3	1.52384	1.53115	1.53027	1.53078	1.52446	1.52599	1.52439
C3-C4	1.52463	1.52189	1.52164	1.53528	1.52004	1.52318	1.52503
C4-Oγ	1.40039	1.39587	1.39947	1.39001	1.40042	1.39924	1.39969
C3-Oβ	1.43844	1.44887	1.43452	1.43861	1.44981	1.44067	1.43329
Oβ-C5	1.36791	1.37684	1.37278	1.37618	1.36647	1.36928	1.37323

Table S11 The corresponding H-Bonds lengths (in angstroms), bond angles (in degrees) and interaction energies (in kcal/mol) of GGE-[C4C1Im][OAc] structures.

Entry	H-bonds	Length	Angle	ΔE_1[a]	ΔE_2[a]	ΔBSSE[a]	ΔE_{2C}[a]	ΔE_{2CR}[a]
(A)	Oγ-Hγ…Oa	1.62	175.97	-132.96	-123.31	2.06	-121.25	7.44
	C2-H2…Ob	1.87	138.14					
	C2-H2…Oγ	2.46	124.46					
(B)	Oγ-Hγ…Oa	1.81	163.95	-140.90	-130.16	2.91	-127.25	1.44
	C2-H2…Oa	1.81	175.24					
(C)	Oα-Hα…Oa	1.72	167.17	-141.06	-131.17	2.48	-128.70	0.00
	C2-H2…Oa	1.73	170.26					

[a] ΔE_1, ΔE_2, ΔBSSE, ΔE_{2C} and ΔE_{2CR} represent the interaction energies using M06L/6-31g** (LANL2DZ basis sets on mental atoms), the interaction energies using M06L/def2-TZVP, the values of BSSE, the interaction energies (ΔE_2) corrected by BSSE and the relative interaction energies (ΔE_{2C}).