Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

A DFT Study on Lignin Dissolution in Imidazolium-based Ionic Liquids

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GG (Fig. S1) model compound is consisting of two G units connected by β-O-4 linkages and it also represents the building blocks of natural lignin. In addition, dimers are rarely chosen as subject to study the interaction between lignin and ILs, thus GG was studied in this work to reveal the dissolution mechanism at molecular level.

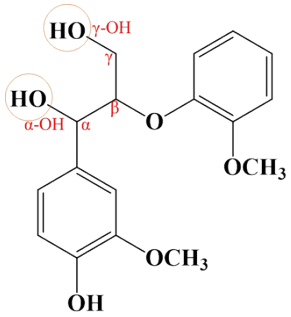


Fig. S1 Structure of guaiacyl glycerol-β-guaiacyl ether.

Since the cations and anions are the basic components of the ionic liquids, to study on the structures and properties of cations and anions are of great importance. The stable geometries of four anions and four imidazolium-based cations were optimized at B3LYP/6-31++G(d,p) level. The electrostatic potential of all the cations, anions and GG are calculated at the same level in Fig. S2. Anions have the negative ESP and cations have positive ESP and it is more concentrated on the imidazolium rings. GG is a neutral compound that negative ESP is located around oxygen atoms and positive ESP is on hydrogen atoms. These regions show the possible sites to form hydrogen bonds with cations and anions.

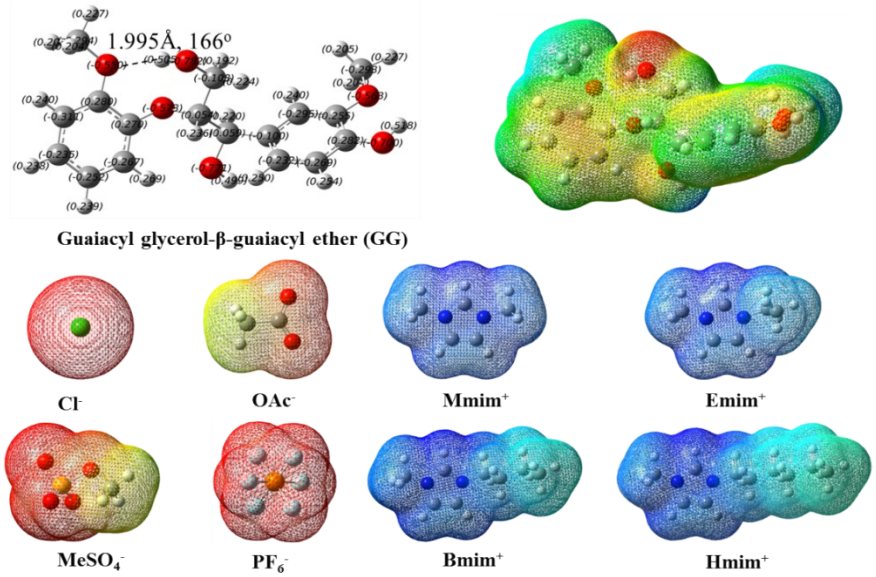


Fig. S2 Electrostatic potential surface of optimized cations, anions, and GG model compound.

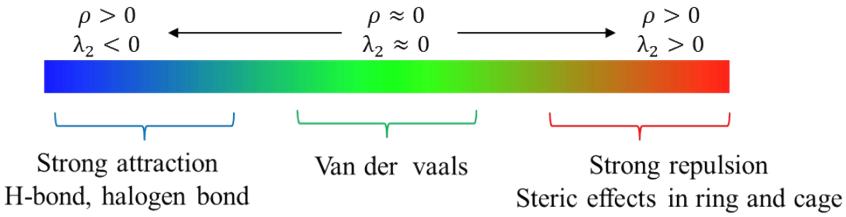


Fig. S3 Clarification of non-bonding interaction.

The GG dimer is a complexed flexible structure compared to the previous work. Resulted from the direction difference of methoxy group on the β-carbon of guaiacylglycerol-β-guaiacyl ether (GG), the six isomers of GG were calculated in Fig. S4 and their single point energies were compared. GG-1 had the lowest energy and it was set to zero, and then other structures had high energies than GG-1 which were labeled in parentheses. According to Boltzmann distribution, the conformers with the lowest energy would bear the most proportion of distribution. Therefore, GG-1 is the most stable structure extensively present in the natural structure of lignin polymers. It is analyzed that the hydroxyl group on the γ-carbon of GG-1 is very close to the methoxy group on benzene ring, thus the oxygen atom would attract the hydrogen atoms to form hydrogen bonds and the isomer is stabilized at the lower energy. In this work, GG-1 is chosen as the subject to study how ionic liquids interact with lignin model compound.

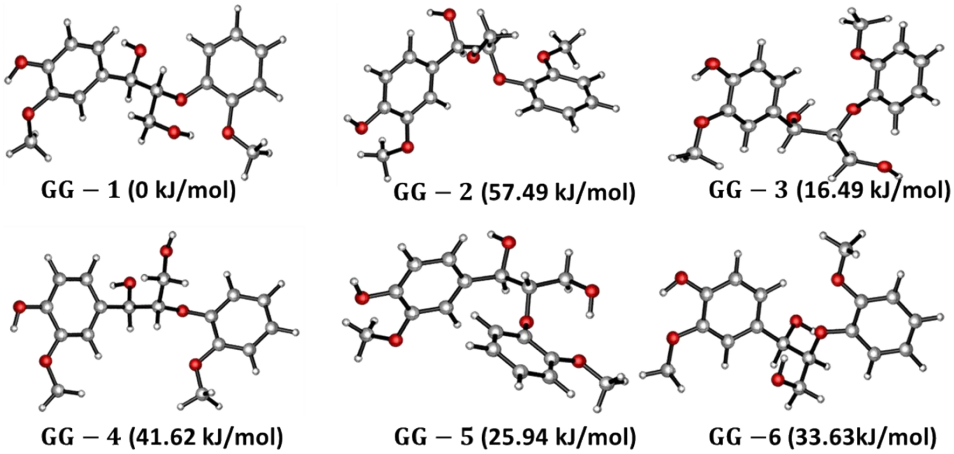


Fig. S4 Conformational isomers of GG model compound, and the relative energies to GG-1 are labeled in parentheses.

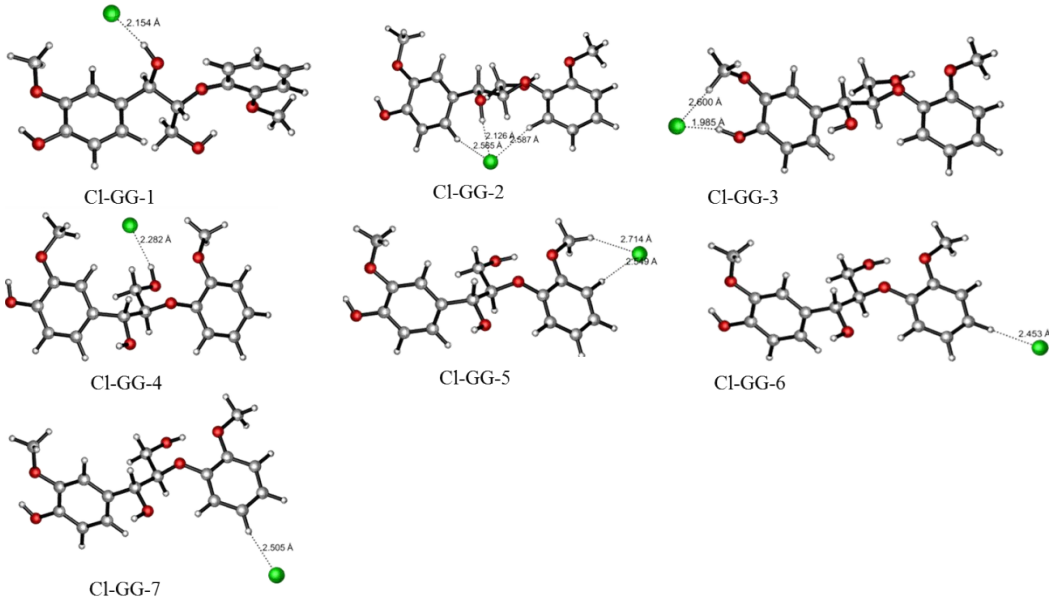


Fig. S5 The optimized configurations of Cl-GG-n (n=1-7) at B3LYP/6-31++g(d,p) level. The hydrogen bonds are indicated by dashed lines and bond distances are given in Å.

Table S1 Hydrogen bonds and interaction energy between model compound and Cl.

Structures	H bonding	Length[Å]	Angle [°]	ΔE (kJ/mol)	ΔΔE (kJ/mol)
Cl-GG-1	Cl···H43-O42	2.154	166.92	-95.21	0.00
Cl-GG-2	Cl···H43-O42	2.126	174.06	-85.12	10.08
	Cl···H7-C2	2.565	156.94		
	Cl···H27-C24	2.587	159.35		
Cl-GG-3	Cl···H11-O10	1.985	164.56	-75.68	19.52
	Cl···H15-C13	2.600	136.66		
Cl-GG-4	Cl···H36-O35	2.282	154.01	-59.07	36.13
Cl-GG-5	Cl···H29-C25	2.549	170.19	-49.85	45.36
	Cl···H41-C38	2.714	132.50		
Cl-GG-6	Cl···H31-C28	2.453	179.98	-28.72	66.48
Cl-GG-7	Cl···H30-C26	2.505	164.27	-22.54	72.67

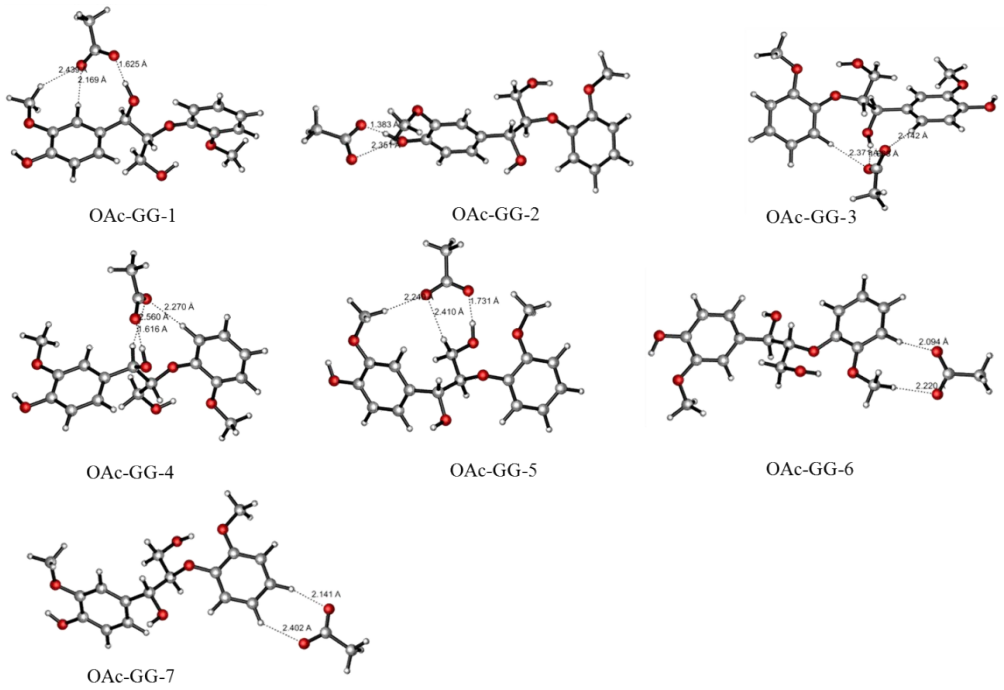


Fig. S6 Optimized configurations of OAc-GG-n (n=1-7) at B3LYP/6-31++g(d,p) level. The hydrogen bonds are indicated by dashed lines and bond distances are given in Å.

Table S2 Hydrogen bonds and interaction energy between model compound and OAc.

Structures	H bonding	Length[Å]	Angle [°]	ΔE (kJ/mol)	ΔΔE (kJ/mol)
OAc-GG-1	O50…H43-O42	1.625	175.97	-121.46	0.00
	O49…H9-C6	2.169	153.97		
	O49…H15-C13	2.439	141.06		
OAc-GG-2	O50…H11-O10	1.383	165.25	-104.96	16.50
	O49…H15-C13	2.351	148.28		
OAc-GG-3	O49…H43-O42	1.663	167.43	-104.66	16.80
	O49…H27-C24	2.371	156.45		
	O50…H7-C2	2.142	170.71		
OAc-GG-4	O50…H43-O42	1.616	177.57	-101.87	19.59
	O49…H18-C17	2.560	136.07		
	O49…H27-C24	2.270	174.92		
OAc-GG -5	O50…H36-O35	1.731	172.58	-88.36	33.10
	O49…H16-C13	2.240	153.13		
	O50…H33-C32	2.410	142.93		
OAc-GG -6	O50…H29-C25	2.094	168.74	-62.42	59.04
	O49…H41-C38	2.220	151.26		
OAc-GG -7	O49…H31-C28	2.141	164.37	-37.67	83.79
	O50…H30-C26	2.402	137.08		

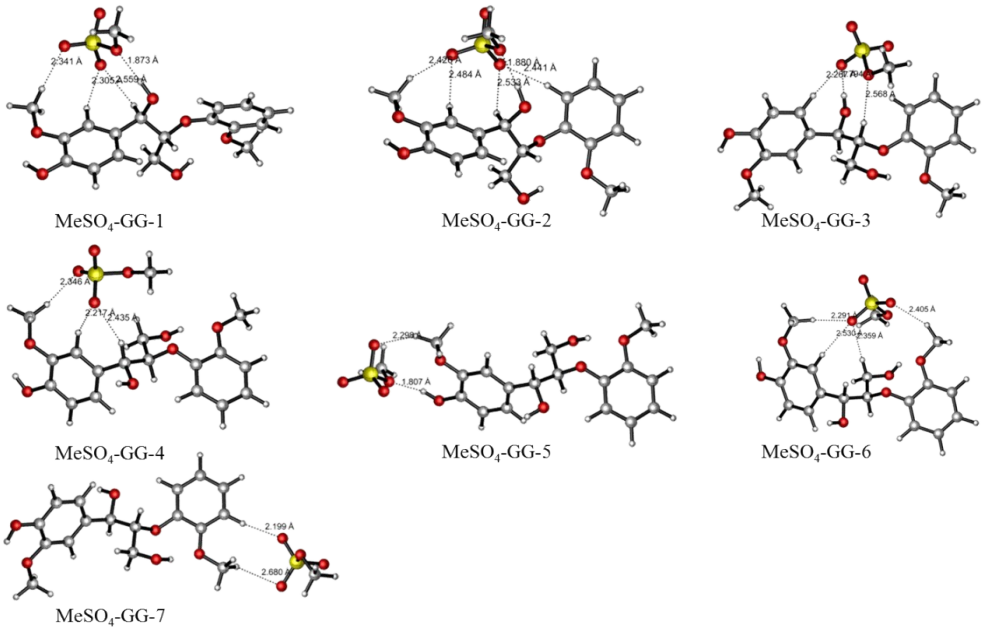


Fig. S7 Optimized configurations of $MeSO_4$-GG-n (n=1-7) at B3LYP/6-31++g(d,p) level. The hydrogen bonds are indicated by dashed lines and bond distances are given in Å.

Table S3 Hydrogen bonds and interaction energy between model compound and $MeSO_4$.

Structures	H bonding	Length[Å]	Angle [°]	ΔE (kJ/mol)	ΔΔE (kJ/mol)
$MeSO_4$-GG-1	O48···H43-O42	1.873	178.40	-84.89	0.00
	O46···H9-C6	2.305	148.41		
	O46···H18-C17	2.560	135.33		
	O45···H15-C13	2.341	168.64		
$MeSO_4$-GG-2	O48···H43-O42	1.880	173.45	-74.17	10.72
	O46···H27-C24	2.441	168.92		
	O46···H18-C17	2.533	140.08		
	O45···H15-C13	2.426	148.06		
	O45···H9-C6	2.484	141.68		
$MeSO_4$-GG-3	O46···H43-O42	1.794	178.44	-66.52	18.37
	O46···H7-C2	2.267	145.25		
	O48···H20-C19	2.568	167.90		
$MeSO_4$-GG-4	O46···H16-C13	2.346	143.17	-65.09	19.80
	O45···H9-C6	2.217	155.94		
	O45···H18-C17	2.435	155.69		
$MeSO_4$-GG-5	O48···H11-O10	1.807	154.98	-62.21	22.68
	O45···H14-C13	2.298	146.18		
$MeSO_4$-GG-6	O46···H40-C38	2.405	152.13	-51.01	33.88
	O47···H16-C13	2.291	149.68		
	O47···H33-C32	2.359	174.34		
	O47···H9-C6	2.530	144.21		
$MeSO_4$-GG-7	O46···H29-C25	2.199	170.04	-43.75	41.14

	O47⋯H41-C38	2.680	105.14

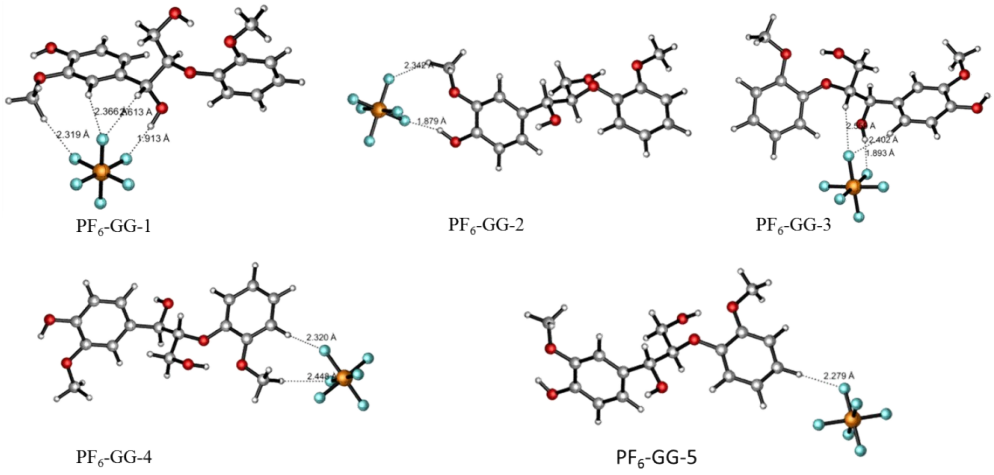


Fig. S8 Optimized configurations of PF6-GG-n (n=1-7) at B3LYP/6-31++g(d,p) level. The hydrogen bonds are indicated by dashed lines and bond distances are given in Å.

Table S4 Hydrogen bonds and interaction energy between model compound and PF_6.

Structures	H bonding	Length[Å]	Angle [°]	ΔE (kJ/mol)	ΔΔE (kJ/mol)
PF_6-GG-1	F50⋯H43-O42	1.913	172.13	-61.69	0.00
	F49⋯H15-C13	2.319	169.75		
	F48⋯H9-C6	2.366	144.49		
	F48⋯H18-C17	2.613	135.13		
PF_6-GG-2	F50⋯H14-C13	2.342	144.33	-45.01	16.68
	F49⋯H11-O10	1.879	155.81		
PF_6-GG-3	F50⋯H43-O42	1.893	165.66	-41.70	19.99
	F48⋯H7-C2	2.402	122.20		
	F48⋯H20-C19	2.559	150.09		
PF_6-GG-4	F45⋯H29-C25	2.320	171.71	-34.06	27.63
	F46⋯H47-C38	2.448	147.21		
PF_6-GG-5	F46⋯H31-C28	2.279	179.25	-16.21	45.48

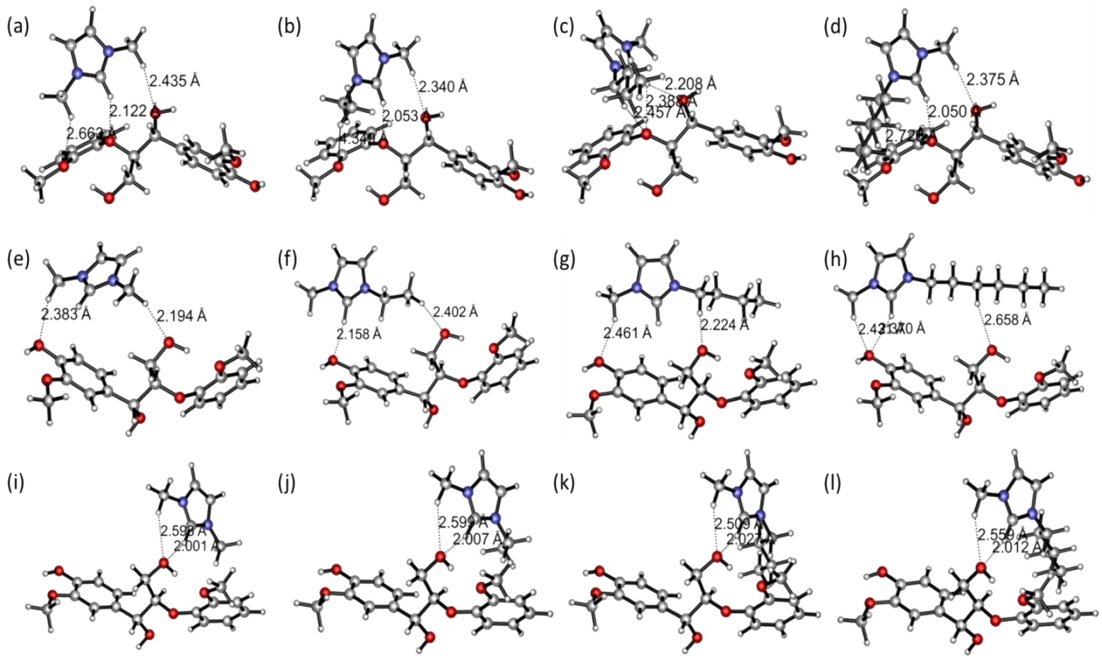


Fig. S9 The most stable structures of cation-GG model compound. (a)-(d) indicate the interaction of four cations with hydroxyl group at the α-C position of GG; (e)-(h) means the interaction with –OH at the benzene ring; (i)-(l) means the interaction with –OH at the γ-C position of GG. All structures were optimized at the b3lyp/6-31++g(d,p) level.

Table S5 hydrogen bonds in different cation-GG structures. The symbols of structures are marked as the above Fig. S9.

Structure	H-bond	Length (Å)	Angle (°)	ΔE (kJ/mol)	Structure	H-bond	Length (Å)	Angle (°)	ΔE (kJ/mol)
a	O21···H50-C46	2.122	149.75	-68.44	b	O56···H11-C9	2.612	159.23	-65.55
	O42···H59-C56	2.435	157.77			O40···H7-C3	2.053	158.24	
	O37···H53-C52	2.663	143.14			O61···H18-C16	2.340	166.40	
e	O10···H59-C56	2.383	163.94	-55.60	f	O29···H7-C3	2.158	169.15	-53.06
	O35···H54-C52	2.194	155.47			O54···H14-C12	2.402	162.24	
i	O35···H50-C46	2.001	155.75	-72.93	j	O54···H7-C3	2.007	155.72	-70.76
	O35···H53-C52	2.593	144.70			O54···H18-C16	2.599	144.86	
c	O46···H7-C3	2.388	131.03	-63.51	d	O73···H17-C15	2.375	164.58	-63.47
	O67···H7-C3	2.208	155.30			O52···H7-C3	2.050	158.06	
	O46···H11-C9	2.457	150.67			O68···H11-C9	2.720	158.64	
g	O35···H17-C15	2.461	153.19	-54.29	h	O41···H17-C15	2.431	154.09	-47.74
	O60···H11-C9	2.224	171.10			O66···H21-C19	2.658	161.52	
k	O60···H7-C3	2.027	152.66	-68.46	l	O66···H7-C3	2.013	154.36	-67.94
	O60···H17-C15	2.509	146.41			O66···H17-C15	2.559	145.43	

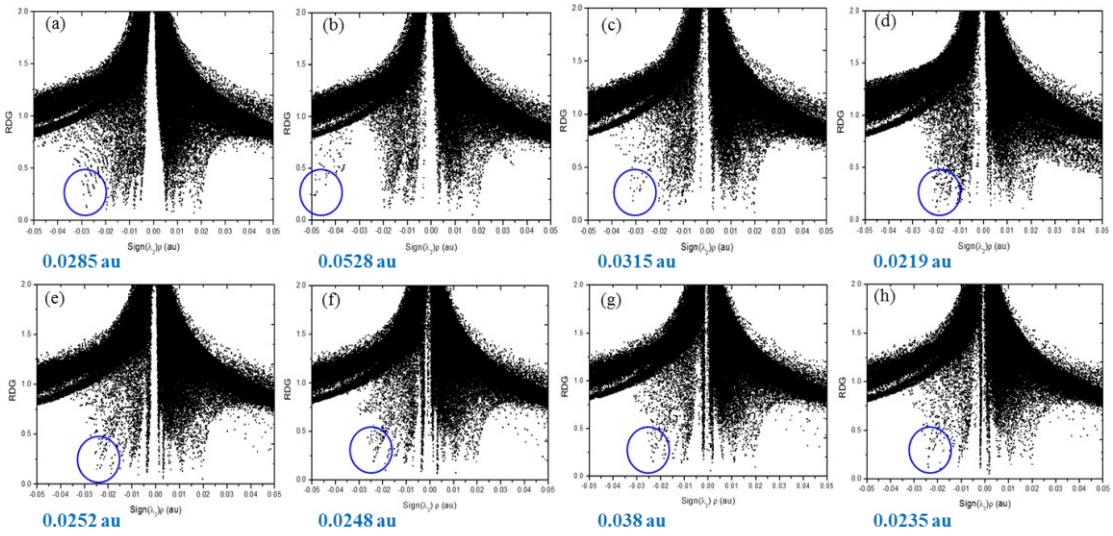


Fig. S10 Scatter plots of the strongest anion-GG and cation-GG interactions. (a) Cl-GG, (b) OAc-GG, (c) MeSO4-GG, (d) PF6-GG; (e) Mmim-GG, (f) Emim-GG, (g) Bmim-GG, (h) Hmim-GG.

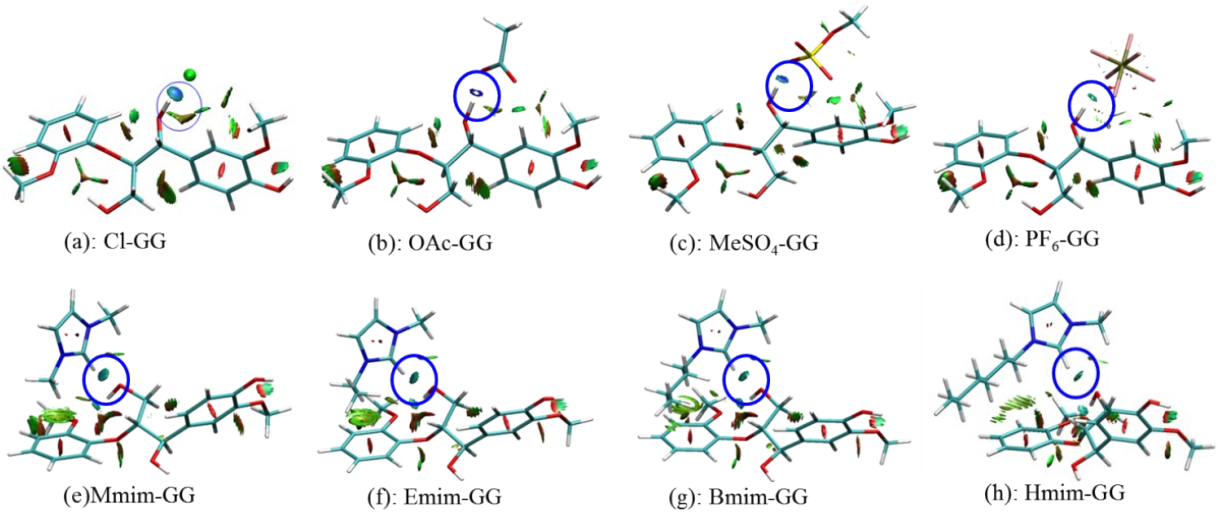
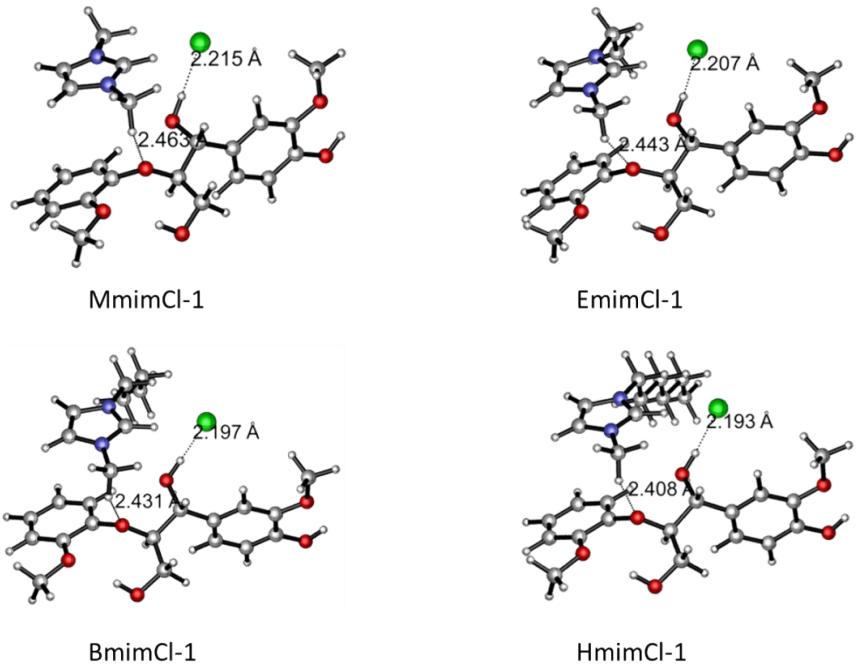
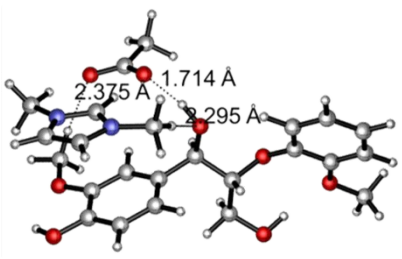


Fig. S11 Isosurfaces plots of the strongest anion-GG and cation-GG interaction. (a) Cl-GG, (b) OAc-GG, (c) MeSO4-GG, (d) PF6-GG; (e) Mmim-GG, (f) Emim-GG, (g) Bmim-GG, (h) Hmim-GG.

(1) Results of interaction energy calculation for the 16 kinds of ionic liquids with GG model compound at α-carbon position:





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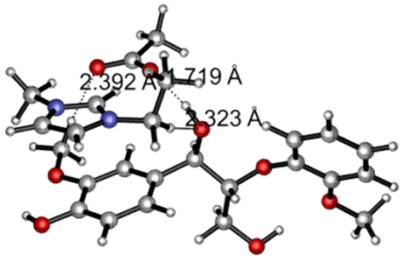

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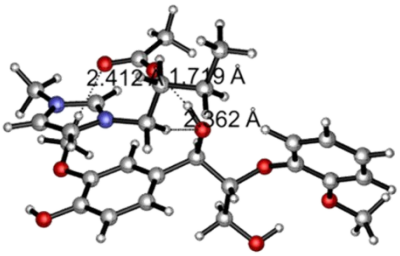
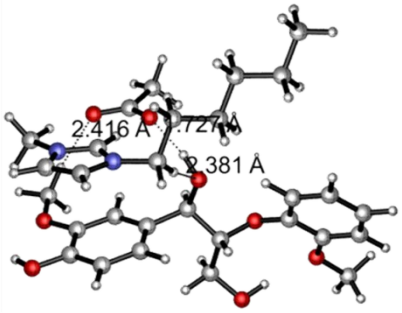
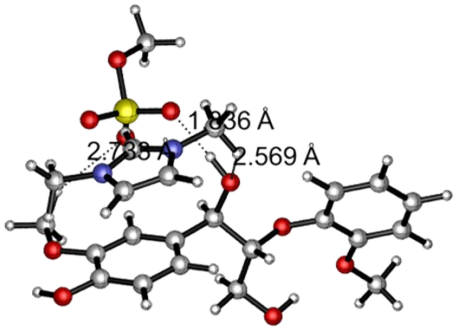


BmimOAc-1



HmimOAc-1



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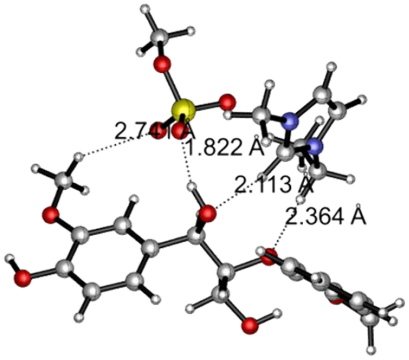

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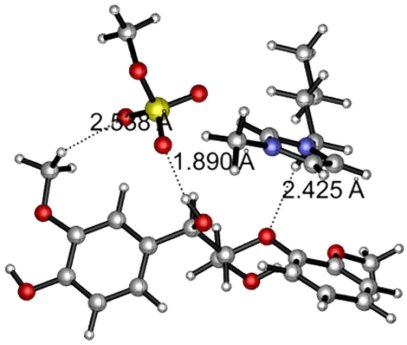

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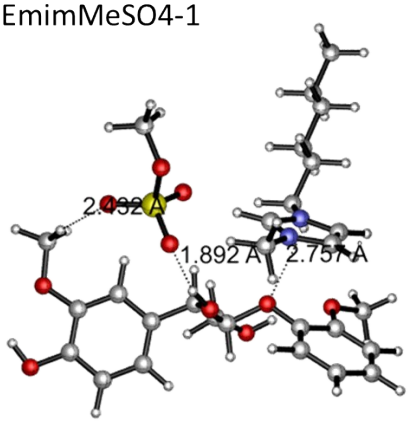

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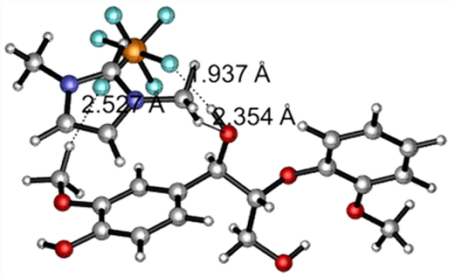

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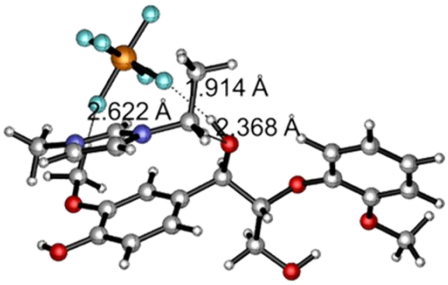

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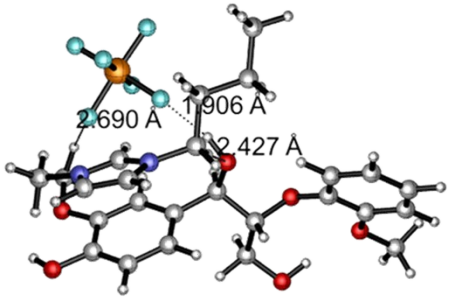

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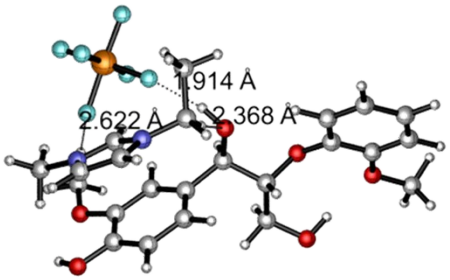

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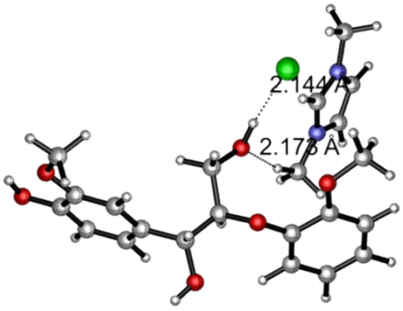
(2) Results of interaction energy calculation for the 16 kinds of ionic liquids with GG model compound at γ-carbon position:



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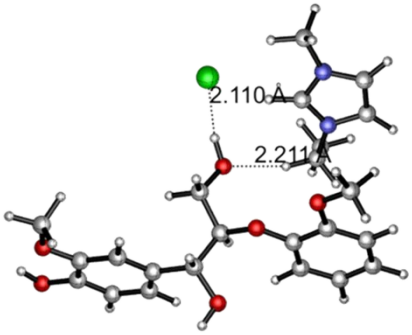

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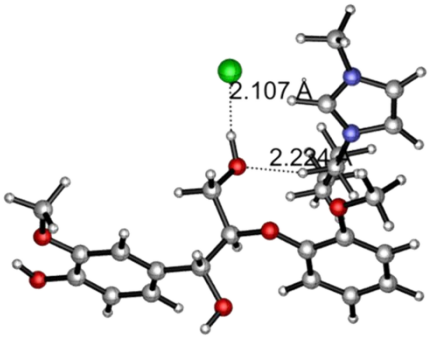

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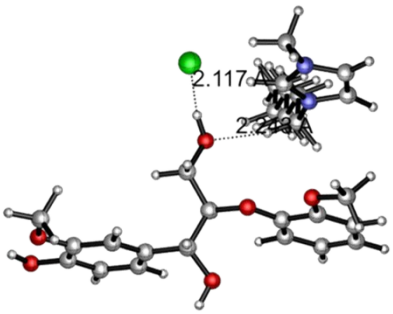

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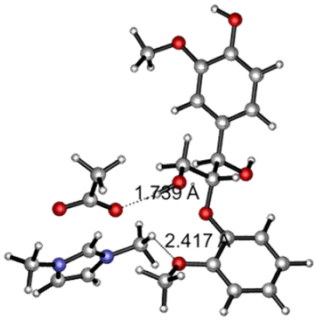

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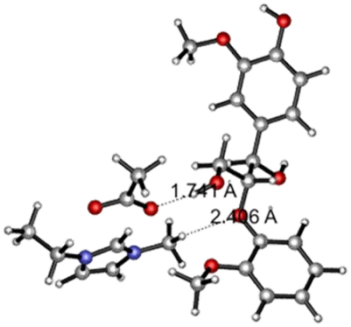

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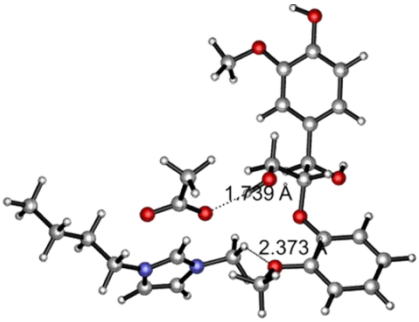
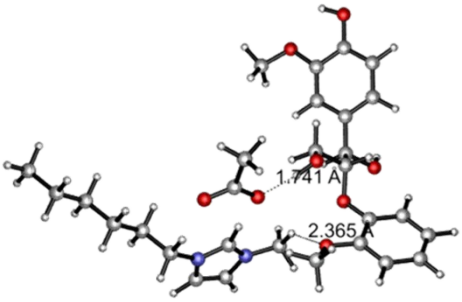


BmimOAc-2



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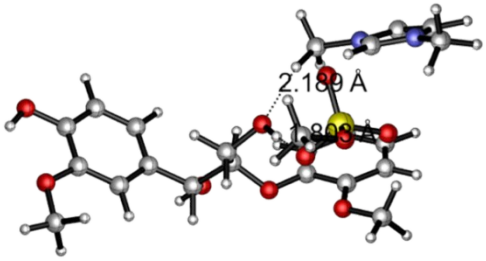

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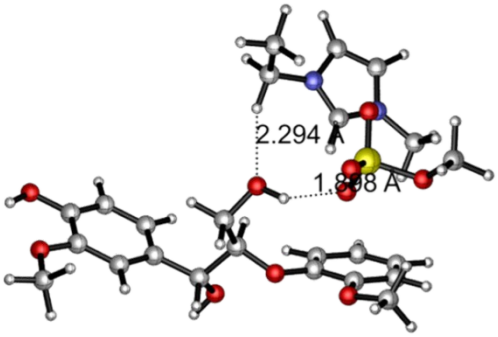

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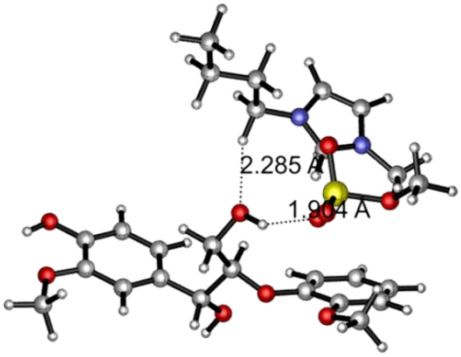

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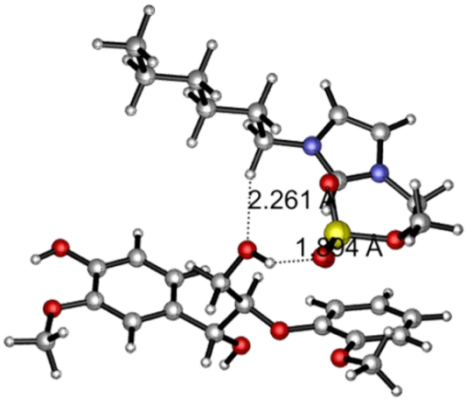

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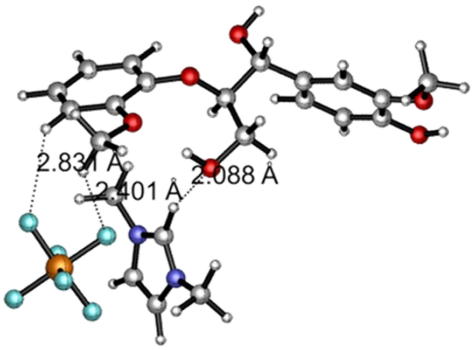

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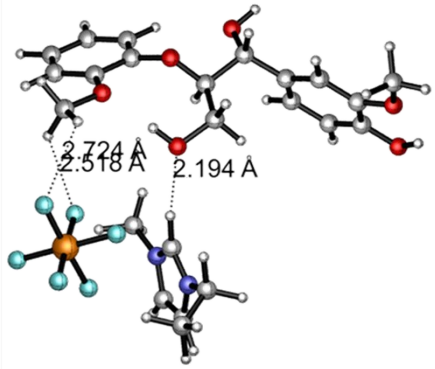

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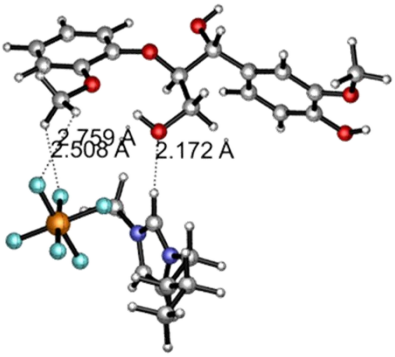

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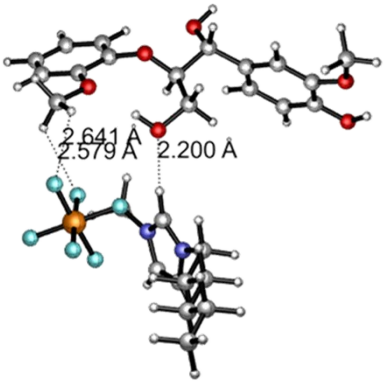
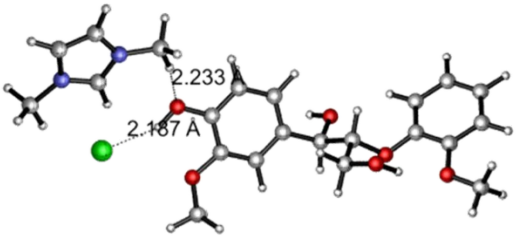


HmimPF6-2

(3) Results of interaction energy calculation for the 16 kinds of ionic liquids with GG model compound at phenolic position:



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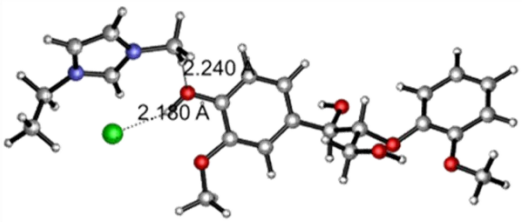

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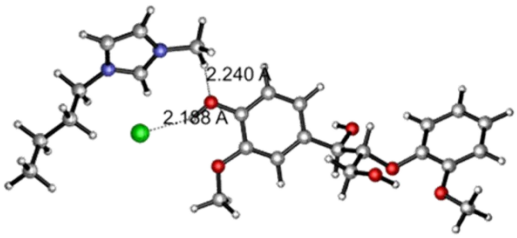

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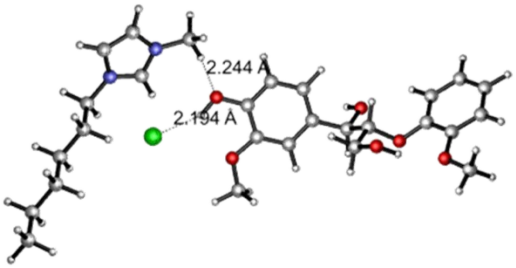

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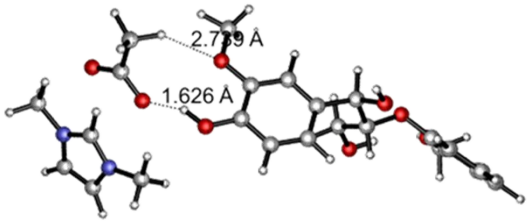

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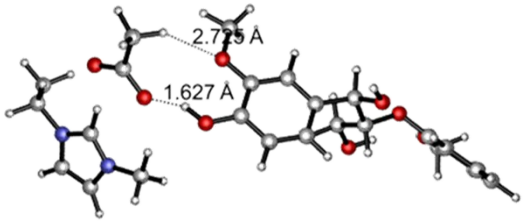

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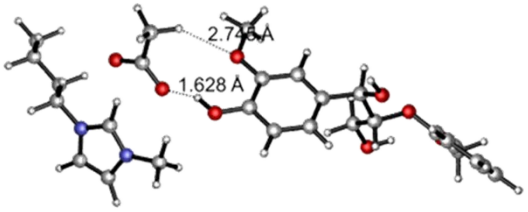

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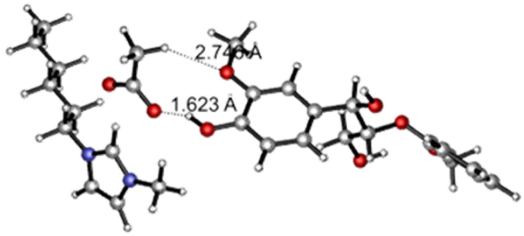

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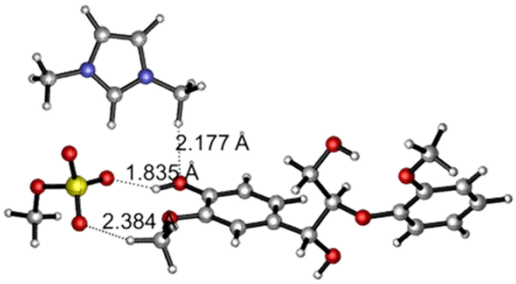
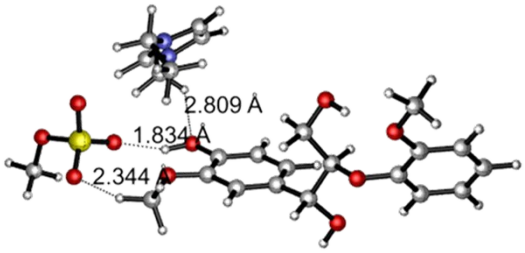


MmimMeSO4-3



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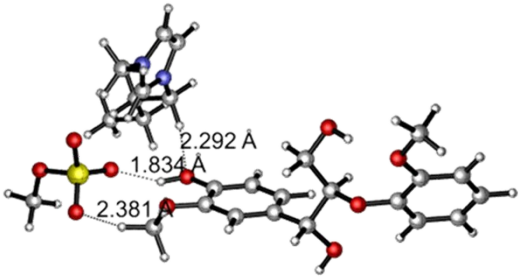

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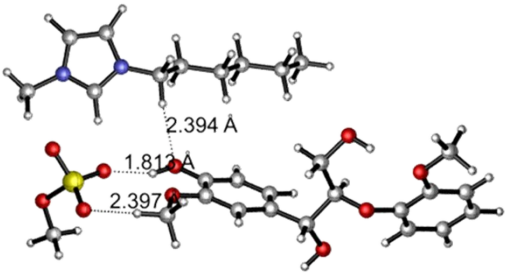

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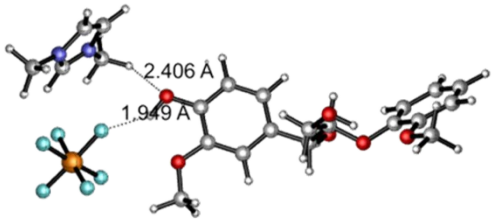
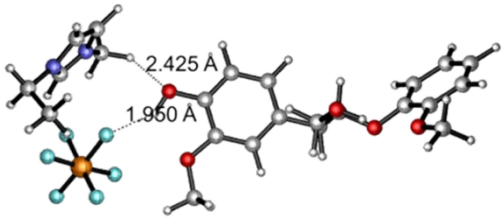


MmimPF6-3



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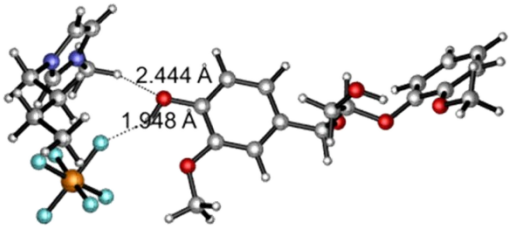

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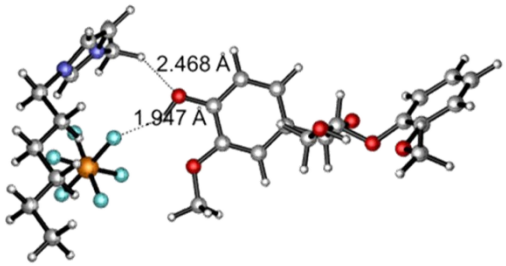


HmimPF6-3

All the 48 complexes are the most stable structures of the interaction between ion pairs and GG model compound, and the interaction energies are summarized in Table S6.

Table S6 The interaction energies of the 48 IL-GG complexes computed at the level of B3LYP/6-31++g(d,p) using the DFT theory.

Entry	**Structure**	ΔE_1**(kJ/mol)**	ΔE_2**(kJ/mol)**	ΔE_3**(kJ/mol)**
1	MmimCl-1	-444.49	-427.74	-423.43
2	EmimCl-1	-440.20	-423.55	-420.46
3	BmimCl-1	-437.35	-420.47	-417.19
4	HmimCl-1	-436.41	-419.08	-415.70
5	MmimOAc-1	-481.99	-463.72	-459.60
6	EmimOAc-1	-478.30	-458.99	-454.20
7	BmimOAc-1	-474.53	-455.36	-450.71
8	HmimOAc-1	-473.13	-454.03	-449.22
9	MmimMeSO4-1	-428.06	-409.62	-398.36
10	EmimMeSO4-1	-423.21	-408.11	-390.21
11	BmimMeSO4-1	-417.87	-403.76	-387.77
12	HmimMeSO4-1	-415.47	-397.89	-386.56
13	MmimPF6-1	-369.82	-360.78	-356.96
14	EmimPF6-1	-368.24	-358.67	-353.73
15	BmimPF6-1	-365.09	-356.44	-347.81
16	HmimPF6-1	-364.22	-354.96	-346.38

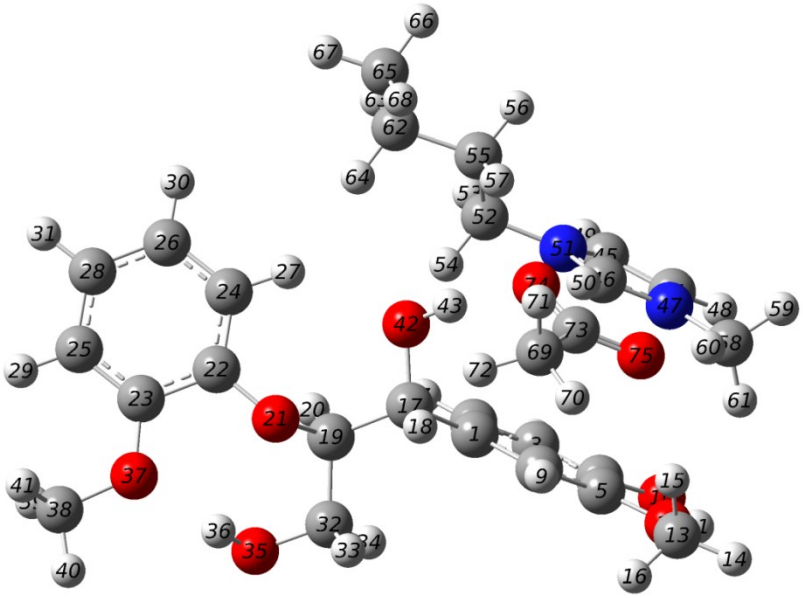
Table S7 Second-Order Perturbation Stabilization Energy E(2) (kJ/mol) for ion pairs-GG.

	π stacking, kJ/mol			**H-bond, kJ/mol**		
	Donor	**Acceptor**	**E(2)**	**Donor**	**Acceptor**	***E(2)***
BmimCl-GG	π (C1-C2)	π* (C46-N47)	3.77	LP (Cl69)	σ* (O42-H43)	71.57
	π (C44-C45)	π* (C3-C4)	0.81	LP (Cl69)	σ* (C13-H15)	5.42
	σ (C62-H64)	π* (C22-C24)	0.60	LP (O42)	σ* (C52-H54)	2.86
	π (C1-C2)	σ* (C52-H54)	0.56	LP (O12)	σ* (C58-H61)	1.81
	σ (C58-H61)	π* (C5-C6)	0.47	LP (O42)	σ* (C52-H53)	1.05
	π (C22-C24)	π* (C62-N64)	0.39	LP (O10)	σ* (C58-H61)	0.92
	π (C5-C6)	σ* (C58-H59)	0.30	LP (O42)	σ* (C46-H50)	0.92
	σ (C62-H64)	π* (C26-C28)	0.30	LP (O42)	σ* (C55-H57)	0.42
	π (C5-C6)	π* (C46-N47)	0.21			
BmimOAc-GG	π (C1-C2)	π (C46-N47)	2.77	LP (O74)	σ* (O42-H43)	94.08
	π (C1-C2)	σ* (C52-H54)	0.84	LP (O75)	σ* (C13-H15)	7.27
	π (C44-C45)	π* (C3-C4)	0.63	LP (O42)	σ* (C52-H54)	6.59
	σ (C52-H54)	π* (C1-C2)	0.42	LP (O12)	σ* (C58-H61)	1.55
	σ (C58-H61)	π* (C5-C6)	0.38	LP (O10)	σ* (C58-H61)	0.88
	π (C5-C6)	π* C46-N47)	0.25	LP (O42)	σ* (C62-H64)	0.71
	π (C5-C6)	σ* (C58-H59)	0.21	LP (O42)	σ* (C52-H53)	0.55
BmimMeSO$_4$-GG	π (C1-C2)	π* (C46-N47)	1.47	LP (O62)	σ* (O42-H43)	69.97
	π (C44-C45)	π* (C3-C4)	0.92	LP (O61)	σ* (C13-H15)	9.70
	π (C1-C2)	σ* (C52-H54)	0.67	LP (O60)	σ* (C6-H9)	7.52
	π (C5-C6)	π* (C46-N47)	0.50	LP (O60)	σ* (C17-H18)	3.28
	π (C3-C4)	π* (C46-N47)	0.38			
	π (C46-N47)	π* (C1-C2)	0.34			
	σ (C55-H56)	π* (C5-C6)	0.34			
	σ (C52-H54)	π* (C1-C2)	0.25			
	σ (C55-H56)	π* (C3-C4)	0.25			
BmimPF$_6$-GG	σ (C1-C2)	π* (C46-N47)	3.36	LP (F69)	σ* (O42-H43)	26.25
	π (C1-C2)	σ* (C52-H54)	0.67	LP (O42)	σ* (C52-H54)	14.66
	π (C44-C45)	π* (C3-C4)	0.67	LP (F73)	σ* (C13-H15)	4.28
	π (C5-C6)	π* (C46-N47)	0.42	LP (F74)	σ* (C6-H9)	3.70
	π (C5-C6)	σ* (C46-H50)	0.25	LP (O10)	σ* (C58-H61)	2.98
	σ (C58-H61)	π* (C3-C4)	0.25	LP (F74)	σ* (O42-H43)	1.22
				LP (F74)	σ* (C17-H18)	0.92
				LP (O42)	σ* (C62-H64)	0.67
				LP (F74)	σ* (C17-C19)	0.46
				LP (O42)	σ* (C52-H53)	0.42
				LP (F72)	σ* (C13-H15)	0.25

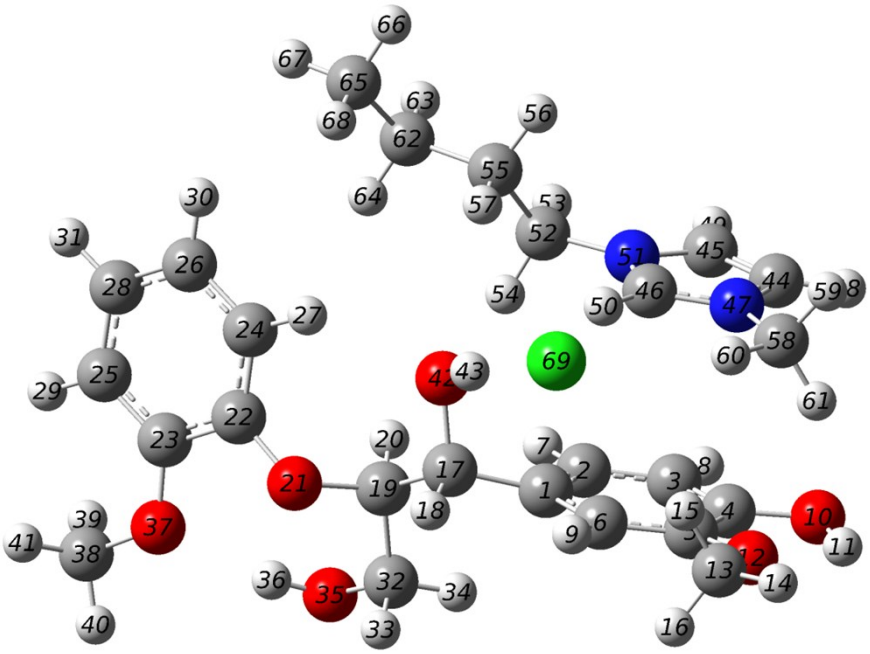
Table S8 Comparison of interaction energies at the B3LYP/6-31++g** and B3LYP-D3/6-311+g** , and M06-2X/6-311+g** levels of theory.

	B3LYP/6-31++g**, kJ/mol			B3LYP-D3/6-311+g**, kJ/mol			M06-2X/6-311+g**, kJ/mol		
Structures	$\Delta E_{1,CA}$	$\Delta E_{1,CA\text{-}GG}$	$\Delta E_{1,C\text{-}A\text{-}GG}$	$\Delta E_{2,CA}$	$\Delta E_{2,CA\text{-}GG}$	$\Delta E_{2,C\text{-}A\text{-}GG}$	$\Delta E_{3,CA}$	$\Delta E_{3,CA\text{-}GG}$	$\Delta E_{3,C\text{-}A\text{-}GG}$
MmimCl-GG	-382.12	-62.37	-444.49	-391.21	-116.72	-507.92	-393.50	-129.13	-522.63
EmimCl-GG	-378.22	-61.98	-440.20	-389.77	-117.87	-507.64	-394.83	-130.56	-525.39
BmimCl-GG	-374.99	-62.36	-437.35	-386.98	-121.53	-508.51	-391.86	-133.85	-525.71
HmimCl-GG	-373.85	-62.56	-436.41	-385.79	-124.13	-509.92	-390.77	-141.26	-532.03
MmimOAc-GG	-421.44	-60.55	-481.99	-434.10	-121.75	-555.85	-439.62	-129.22	-568.84
EmimOAc-GG	-416.53	-61.77	-478.30	-429.77	-127.03	-556.79	-435.15	-131.27	-566.42
BmimOAc-GG	-412.81	-61.72	-474.53	-428.94	-129.28	-558.22	-434.01	-137.97	-571.98
HmimOAc-GG	-411.52	-61.61	-473.13	-427.60	-132.34	-559.93	-437.14	-136.90	-574.04
$MmimMeSO_4$-GG	-363.00	-65.06	-428.06	-392.37	-123.91	-516.28	-402.31	-123.74	-526.05
$EmimMeSO_4$-GG	-356.81	-66.40	-423.21	-386.54	-131.81	-518.35	-397.66	-130.50	-528.16
$BmimMeSO_4$-GG	-353.72	-64.15	-417.87	-384.77	-135.21	-519.98	-390.58	-139.56	-530.14
$HmimMeSO_4$-GG	-352.53	-62.94	-415.47	-383.58	-138.85	-522.43	-401.03	-131.85	-532.88
$MmimPF_6$-GG	-324.77	-45.05	-369.82	-354.59	-100.18	-454.77	-365.25	-94.45	-459.70
$EmimPF_6$-GG	-323.32	-44.92	-368.24	-356.29	-97.85	-454.14	-368.21	-96.42	-464.63
$BmimPF_6$-GG	-321.08	-44.01	-365.09	-357.15	-99.44	-456.59	-368.47	-95.33	-463.81
$HmimPF_6$-GG	-319.98	-44.24	-364.22	-356.61	-102.33	-458.94	-367.94	-98.25	-466.19

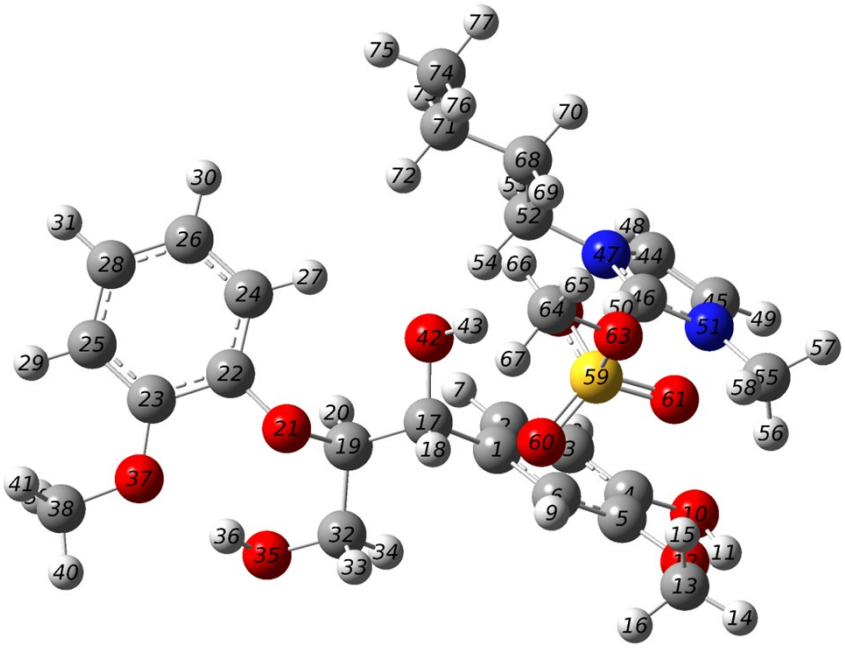
C-cation, A-anion, CA-ion pairs, $\Delta E_{CA\text{-}GG}$ and $\Delta E_{C\text{-}A\text{-}GG}$ are the two body and three body interaction energies.



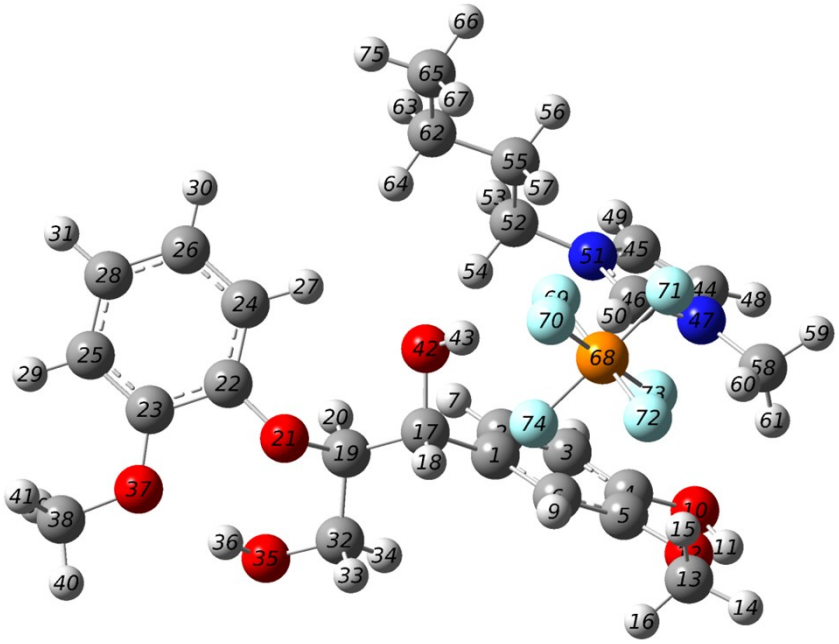
(a) BmimOAc-GG



(b) BmimCl-GG

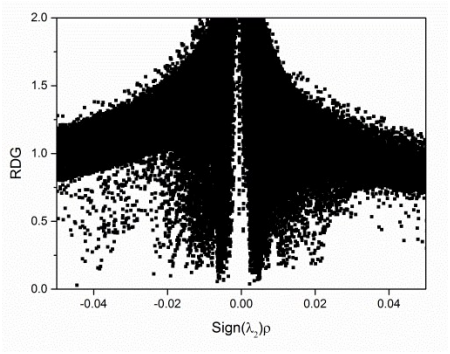


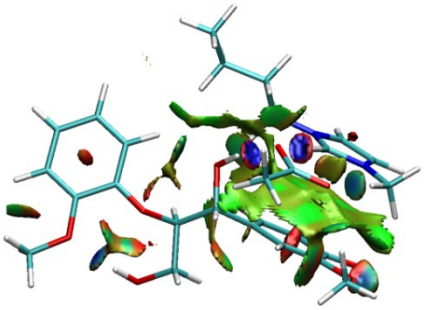
(c) $BmimMeSO_4$-GG



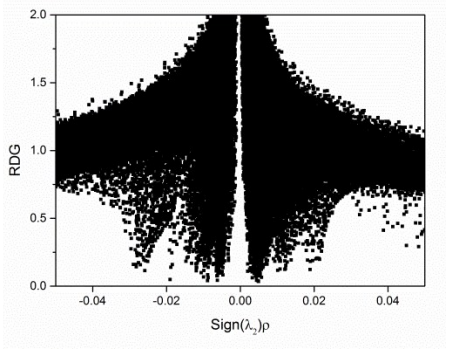
(d) $BmimPF_6$-GG

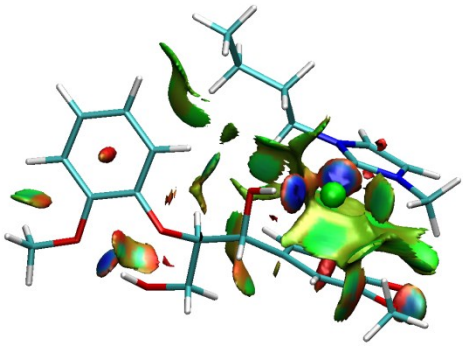
Fig. S12 Atom labels of the conformers: BmimOAc-GG, BmimCl-GG and $BmimPF_6$-GG. The geometries are optimized at B3LYP-D3/6-311+g** level.



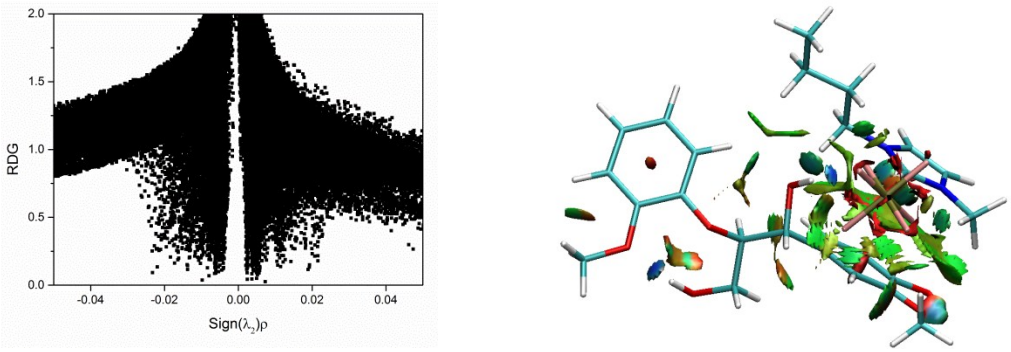


BmimOAc-GG: (a) RDG scatter plot (isovalue=0.5), (b) RDG isosurfaces (s=0.7)





BmimCl-GG: (c) RDG scatter plot (isovalue=0.5), (d) RDG isosurfaces (s=0.7)



BmimPF$_6$-GG: (e) RDG scatter plot (isovalue=0.5), (f) RDG isosurfaces (s=0.7)

Fig. S13 RDG scatter plot (isovalue =0.5) and isosurfaces (s=0.7) plots of the conformers: BmimOAc-GG, BmimCl-GG and BmimPF$_6$-GG. The isosurfaces are colored on a blue-green-red scale according to values of sign(λ_2)ρ, ranging from -0.05 to 0.05 a.u.. Blue indicates strong attractive interactions and green indicates the π-stacking interaction.

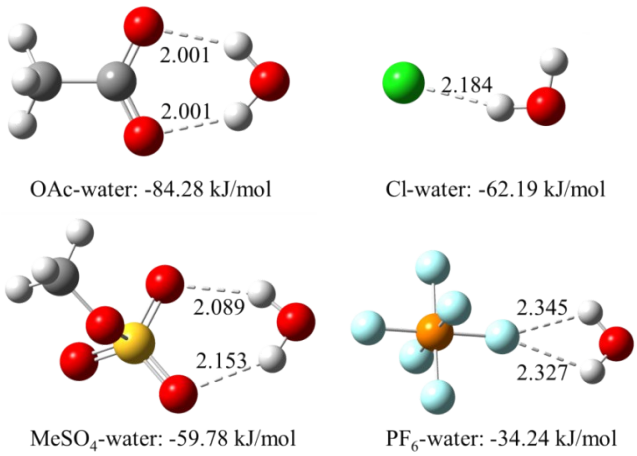


Fig. S14 the conformers of the interaction between four kinds of anions and water calculated at the B3LYP/6-31++g** level.

Table S9 Comparison ofsecond order pueterbation energies of anions-GG and anions-water interaction by NBO at the B3LYP/6-31++g** level.

Structure	**Donor (i)**	**Acceptor(j)**	***E(2)*, kJ/mol**	**total *E(2)***	**ΔE, kJ/mol**
OAc-GG	Lp O 49	σ* C6-H9	29.97	283.51	-121.46
	Lp O 49	σ* C13-H15	8.62		
	Lp O 50	σ* O42-H43	244.92		
Cl-GG	Lp Cl 44	σ* C6-H9	20.43	112.1	-95.21
	Lp Cl 44	σ* O42-H43	91.67		
MeSO$_4$-GG	Lp O 45	σ* C13-H15	6.82	96.32	-81.98
	Lp O 46	σ* C6-H9	16.62		
	Lp O 46	σ* O42-H43	72.88		
PF$_6$-GG	Lp F 48	σ* C6-H9	8.92	64.97	-61.69

	Lp F 48	σ* C17-H18	3.14		
	Lp F 49	σ* C13-H15	11.64		
	Lp F 50	σ* O42-H43	41.27		
OAc-water	Lp O9	σ* O1-H2	38.72	77.53	-84.28
	Lp O10	σ* O1-H3	38.81		
Cl-water	Lp Cl	σ* O1-H3	74.89	74.89	-62.19
$MeSO_4$-water	Lp O6	σ* O1-H2	19.40	44.90	-59.78
	Lp O7	σ* O1-H3	25.49		
PF_6-water	Lp O5	σ* O1-H2	1.97	4.12	-34.24
	Lp O5	σ* O1-H3	2.14		

Table S10 viscosity of ionic liquids from Bioresource Technol, 2015, 178, 2-18.

Ionic liquids	**Temp. (°C)**	**η (mPa s)**
EmimCl	80	65
BmimCl	80	142
EmimOAc	80	17
BmimOAc	80	26

Table S11 viscosity of ionic liquids from AIChE J, 2012, 58, 2885-2899.

Ionic liquids	**Temp. (°C)**	**Pres.**	**η (mPa s)**
BmimOAc	0	0.1	139.7
$BmimPF_6$	0	0.1	265
$BmimMeSO_4$	0	0.1	188
$EmimPF_6$	55	0.1	15
$BmimPF_6$	55	0.1	25.77
$HmimPF_6$	55	0.1	34.7

Table S12 H-bonds, lengths and angles of ion pairs-GG conformers at the level of B3LYP/6-31++g** and B3LYP-D3/6-311+g**.

Structure	**B3LYP/6-31++g****			**B3LYP-D3/6-311+g****		
	H-bonds	**Length(Å)**	**Angle(°)**	**H-bonds**	**Length(Å)**	**Angle(°)**
Ion pairs-GG interaction:						
BmimCl-GG	Cl69⋯O42-H43	2.197	161.59	Cl69⋯O42-H43	2.150	166.86
	O21⋯C58-H59	2.431	138.58	O12⋯C58-H61	2.578	124.05
BmimOAc-GG	O74⋯O42-H43	1.719	168.21	O74⋯O42-H43	1.694	167.38
	O75⋯C13-H15	2.412	166.41	O75⋯C13-H15	2.401	158.57
$BmimMeSO_4$-GG	O71⋯O42-H43	1.890	165.18	O62⋯O42-H43	1.780	168.04
	O70⋯C13-H15	2.538	144.92	O61⋯C13-H15	2.358	156.58
$BmimPF_6$-GG	F73⋯O42-H43	1.906	159.03	F69⋯O42-H43	1.922	156.62
	F71⋯C13-H15	2.690	136.34	F73⋯C13-H15	2.356	143.38

Anions-GG interaction:						
Cl-GG	Cl⋯H43-O42	2.154	166.92	Cl⋯H43-O42	2.157	165.74
	Cl⋯H9-C6	2.604	139.29	Cl⋯H9-C6	2.567	136.67
OAc-GG	O50⋯H43-O42	1.625	175.97	O50⋯H43-O42	1.644	176.68
	O49⋯H9-C6	2.169	153.97	O49⋯H9-C6	2.115	150.93
	O49⋯H15-C13	2.439	141.06	O49⋯H15-C13	2.433	140.23
$MeSO_4$-GG	O48⋯H43-O42	1.873	172.46	O48⋯H43-O42	1.802	166.79
	O45⋯H15-C13	2.341	139.02	O45⋯H15-C13	2.194	175.07
	O46⋯H9-C6	2.305	149.38	O46⋯H9-C6	2.360	136.41
PF_6-GG	F50⋯H43-O42	1.913	172.13	F50⋯H43-O42	1.883	165.94
	F49⋯H15-C13	2.319	169.75	F49⋯H15-C13	2.297	154.28
	F48⋯H9-C6	2.366	144.49	F48⋯H9-C6	2.251	141.43
	F48⋯H18-C17	2.613	135.13	F48⋯H18-C17	2.435	137.84
Cations-GG interaction:						
Mmim-GG	O35⋯H50-C46	2.001	155.75	O35⋯H50-C46	1.987	150.78
	O35⋯H53-C52	2.593	144.70	O35⋯H53-C52	3.215	123.06
Emim-GG	O54⋯H7-C3	2.007	155.72	O54⋯H7-C3	1.992	153.77
	O54⋯H18-C16	2.560	144.86	O54⋯H18-C16	2.893	132.04
Bmim-GG	O60⋯H7-C3	2.027	152.66	O60⋯H7-C3	1.934	160.21
	O60⋯H17-C15	2.509	146.41	O60⋯H17-C15	2.685	142.24
Hmim-GG	O66⋯H7-C3	2.013	154.36	O66⋯H7-C3	2.038	149.31
	O66⋯H17-C15	2.559	145.43	O66⋯H17-C15	2.398	147.68