Supporting Information

Influence of ionic liquids on the electronic environment of atomically dispersed Ir on (MgO) (100)

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Experimental results of IR spectroscopy for uncoated MgO-Ir(CO)$_2$ complex

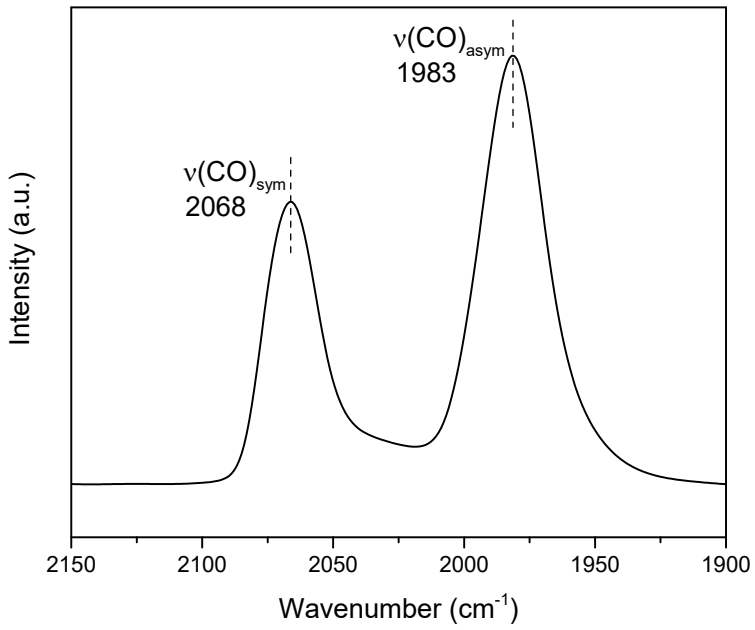
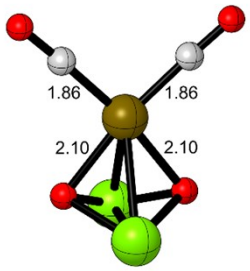
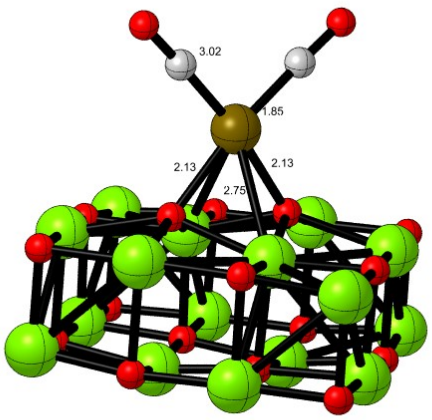


Figure S1. IR spectrum of MgO-supported Ir(CO)$_2$ catalyst in the region of 1900–2150 cm^{-1}.

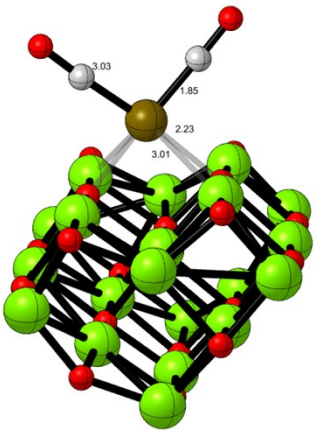
(MgO)$_n$-Ir(CO)$_2$ Complexes



1
^{2}[(MgO)$_2$Ir(0)(CO)$_2$]^0

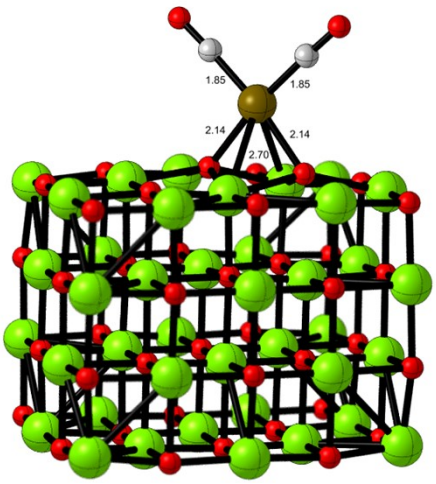


2
^{2}[(MgO)$_{16}$Ir(0)(CO)$_2$]^0 (100)



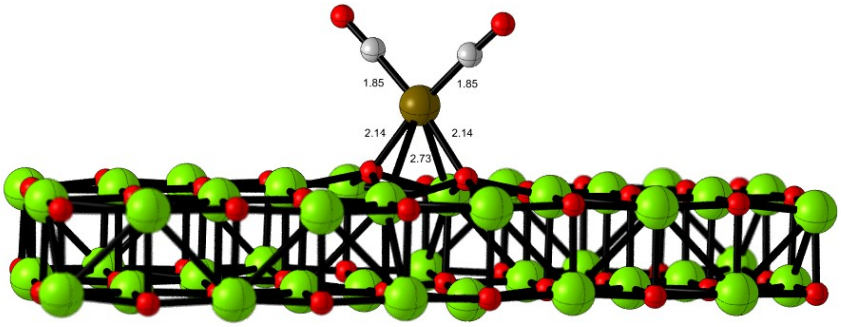
3

$^{2}[(MgO)_{20}Ir(0)(CO)_2]^{0}$ (110)



4

$^{1}[(MgO)_{40}Ir(I)(CO)_2\ ]^{+}$ (100)



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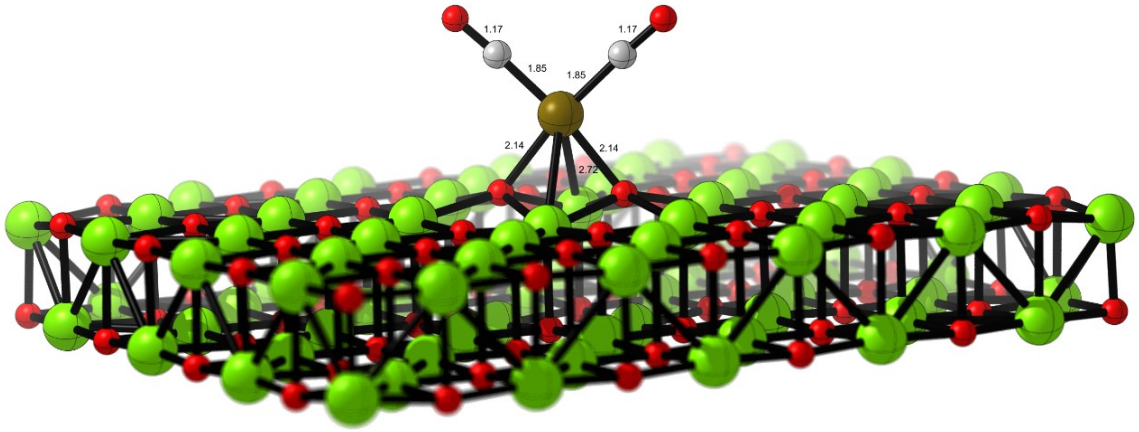
$^{1}[(MgO)_{40}Ir(I)(CO)_2\ ]^{+}$ (100)



6

$^{1}[(MgO)_{80}Ir(I)(CO)_2\ ]^{+}$ (100)

Figure S2. Optimized models for the $(MgO)_n$ supported-$Ir(CO)_2$ catalyst (bipodal) (PBE/6-31G(d,p)).

Charge Analysis for ILs

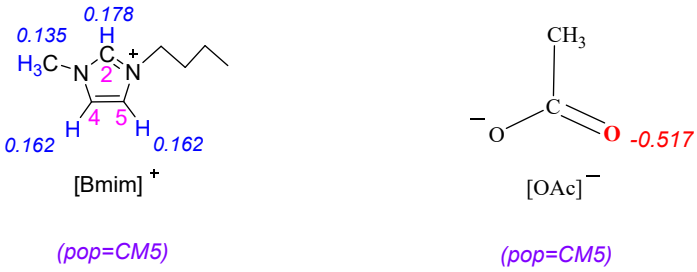


Figure S3. Charge distributions on cation and anion of IL ([**Bmim**][**OAc**]) (CM5 methods, PBE/6-31G(d,p)) (Red: negative , Blue: positive, Pink: carbon number).

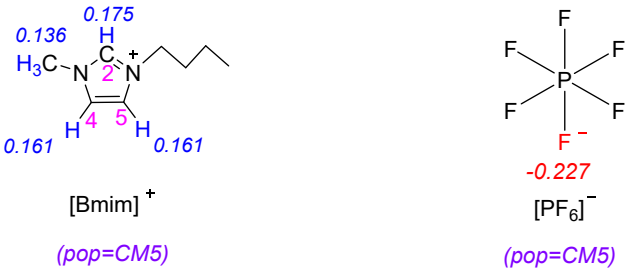


Figure S4. Charge distributions on [**Bmim**][**PF_6**] (CM5 methods, PBE/6-31G(d,p)) (Red: negative , Blue: positive).

Conformer distributions for ILs

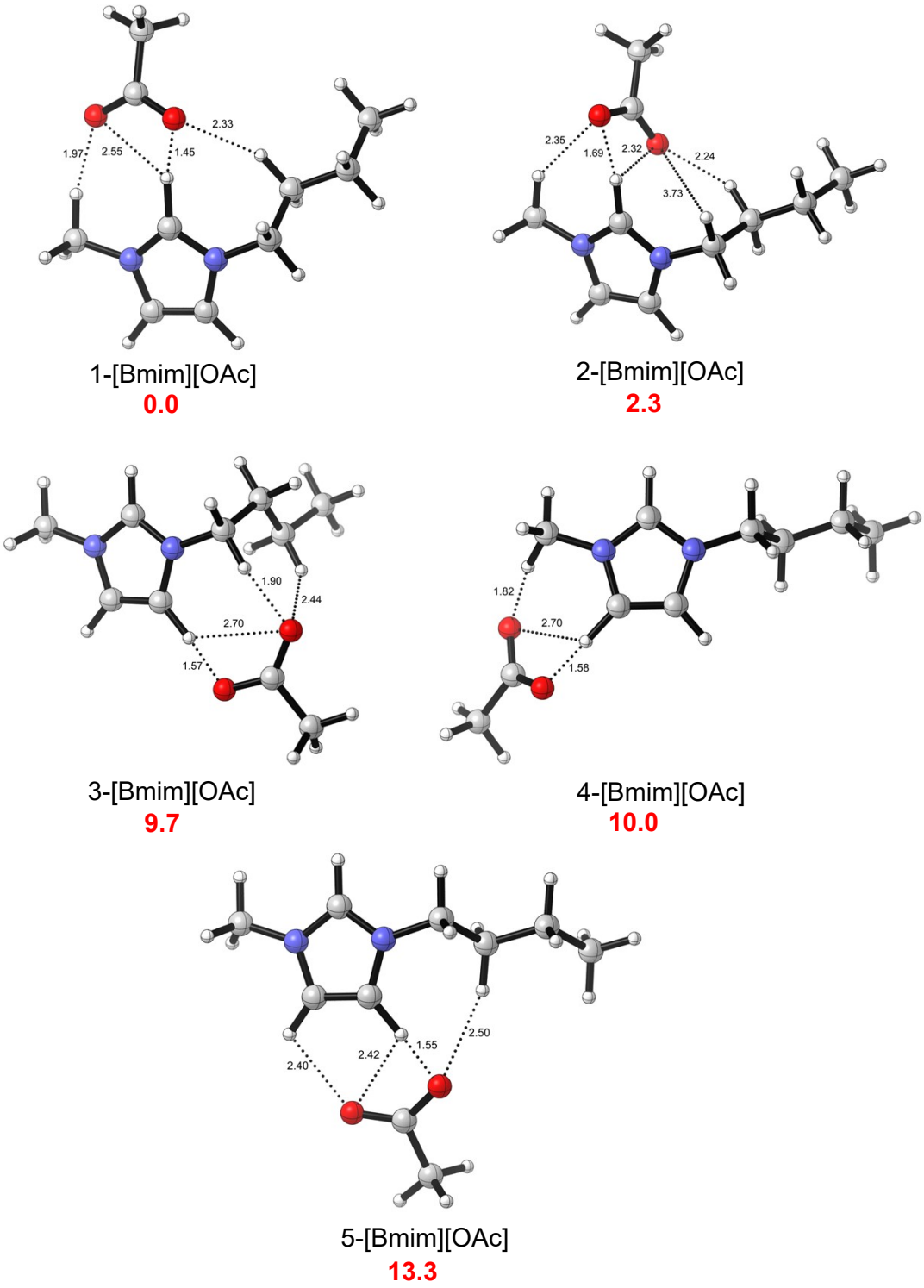
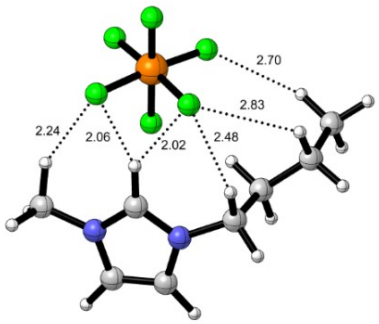
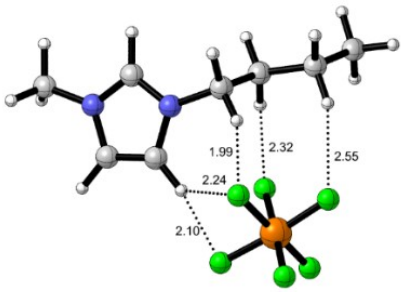


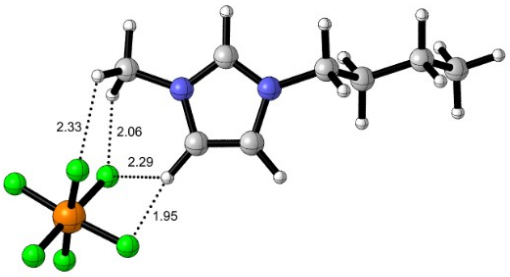
Figure S5. Conformer distributions for [Bmim][OAc] and their relative energies (**red**) shown below for each species (PBE/6-31G**, kcal.mol^{-1}).



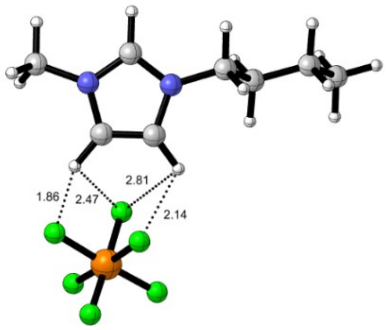
1-[Bmim][PF_6]
0.0



2-[Bmim][PF_6]
6.9



3-[Bmim][PF_6]
8.8



4-[Bmim][PF_6]
11.7

Figure S6. Conformer distributions for [Bmim][PF_6] and their relative energies (**red**) shown below for each species (PBE/6-31G**, kcal.mol^{-1}).

Experimental results of IR spectroscopy for IL coated MgO-Ir(CO)$_2$ complexes

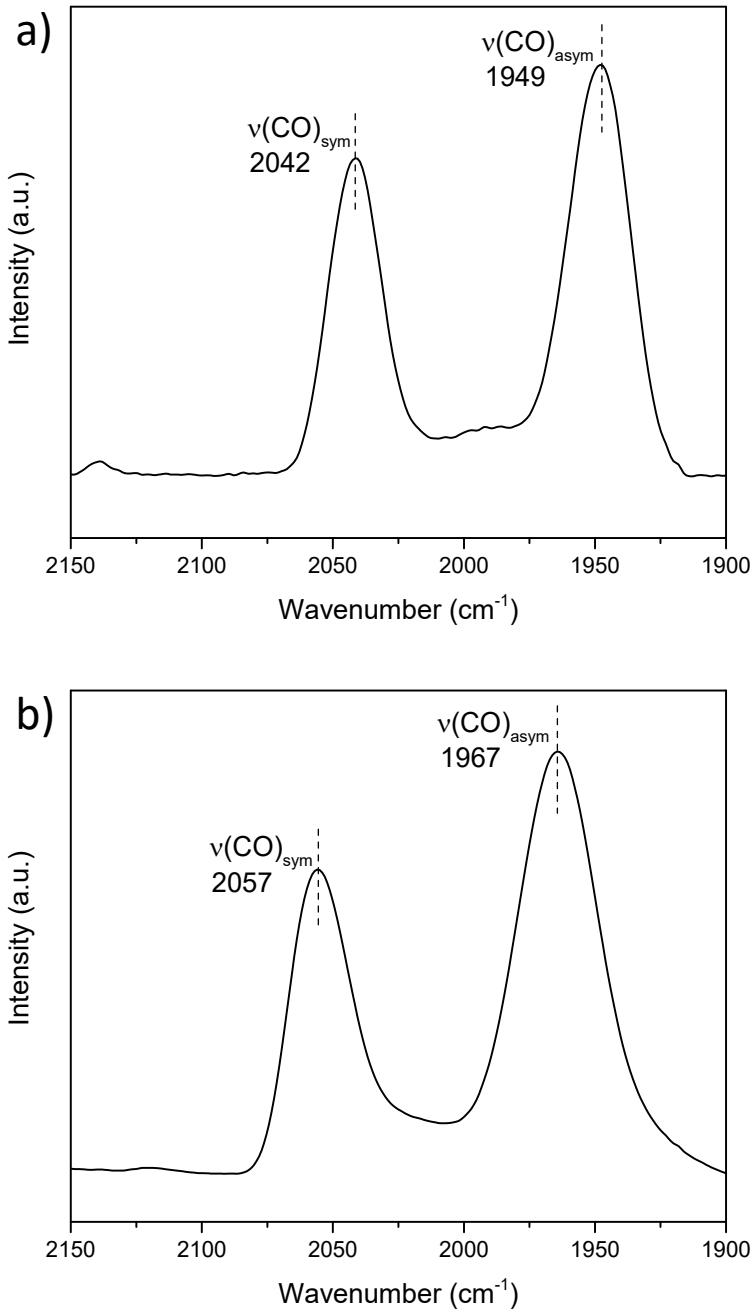


Figure S7. IR spectra of MgO-supported Ir(CO)$_2$ complexes when coated with a) [Bmim][OAc] and b) [Bmim][PF_6] in the region of 1900–2150 cm^{-1}.

Figure S8 provides the FTIR spectrum of the MgO-supported $Ir(CO)_2$ [Bmim][PF_6]-coated $Ir(CO)_2$ complex in the C–H stretching region. The region of 3100–3200 cm^{-1} presents the IR bands because of the C–H stretching vibrations of the imidazolium ring.[1] The band at 3128 cm^{-1} in Figure S8 represents the υ(C2H) of the cation of [Bmim][PF_6].[2,3]

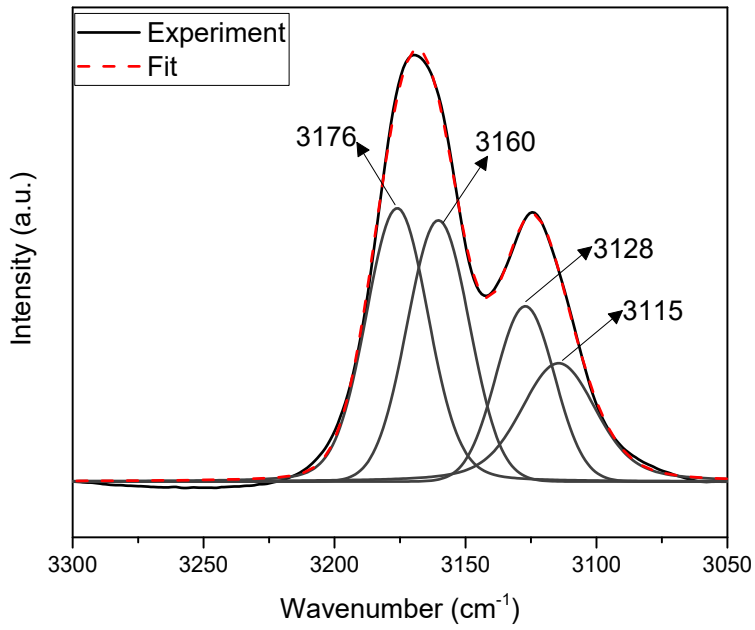
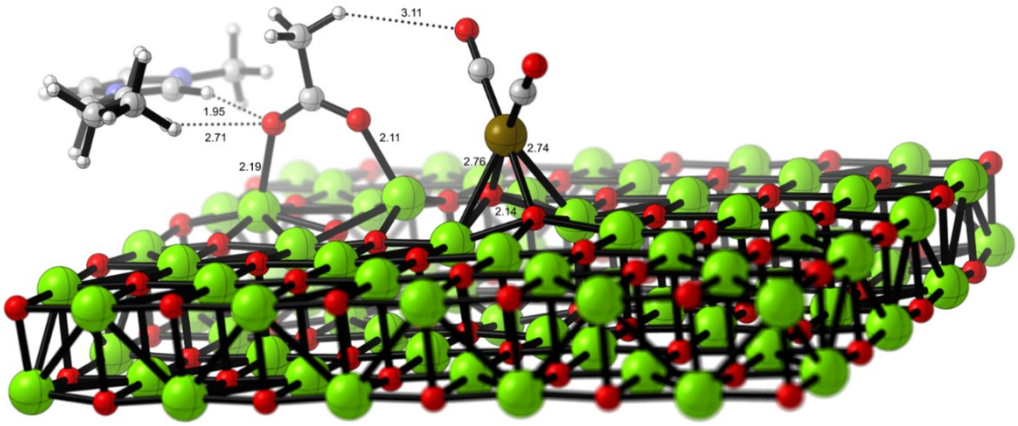
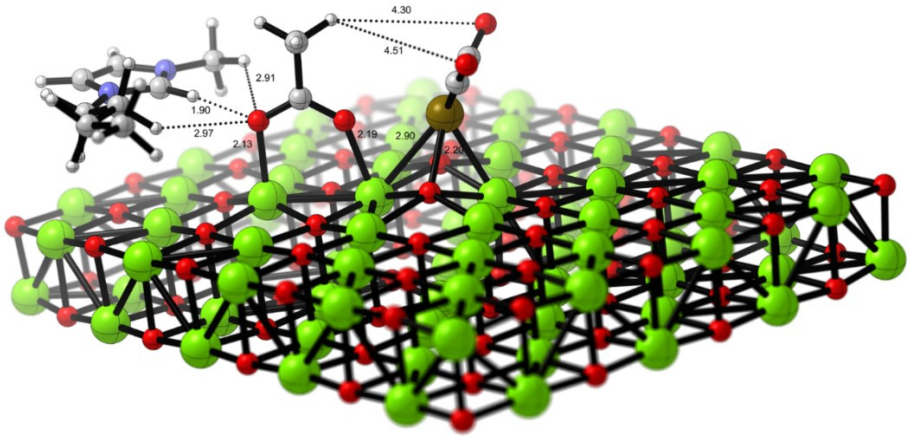


Figure S8. IR spectrum of MgO-supported $Ir(CO)_2$ complex when coated with [Bmim][PF_6] in the region of 3300–3050 cm^{-1}.

[Bmim][OAc]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^{+}$ complexes



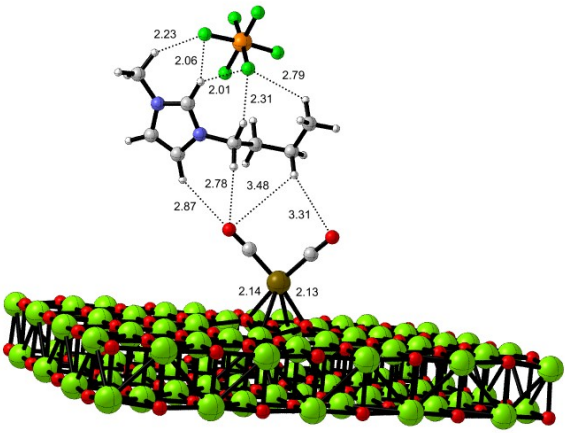
7-[Bmim][Ac]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^{+}$
0.0
(cation-anion-catalyst arrangement)
ν(CO)asym : 2008 (1980)
ν(CO)sym : 2068 (2039)
μ= 16.5



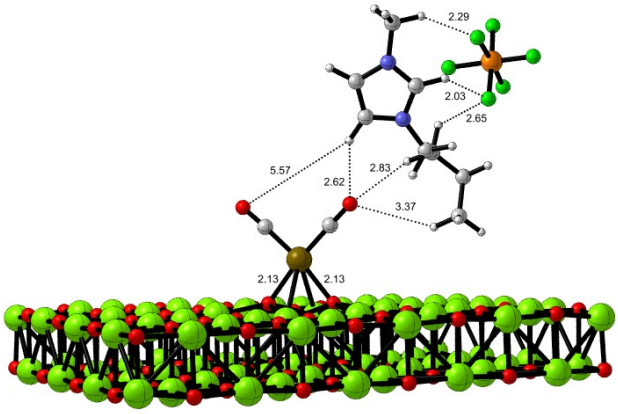
8-[Bmim][Ac]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^{+}$
6.4
(cation-anion-catalyst arrangement)
ν(CO)asym : 1993 (1965)
ν(CO)sym : 2054 (2025)
μ= 16.2

Figure S9. Structures of [Bmim][OAc] coated ^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^{+}$ catalyst (**6**) and their ν(C_xH), ν$(CO)_{asym}$/ν$(CO)_{sym}$ frequencies (**blue**), their scaled values (**black**), relative energies (**red**) and dipole moment (**green**) shown below for each species (PBE/6-31G(d,p)).

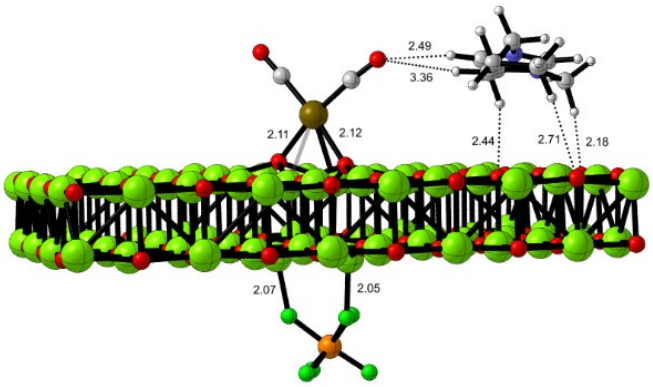
[Bmim][PF_6]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^+$ complexes



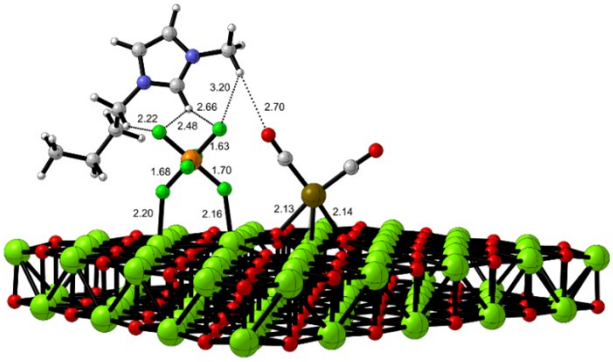
9-[Bmim][PF_6]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^+$
(anion-cation-catalyst arrangement)
$\nu(C_XH)$: 3184 (3139)
ν(CO)asym : 2001 (1973)
ν(CO)sym : 2067 (2038)
49.3
μ= 18.7



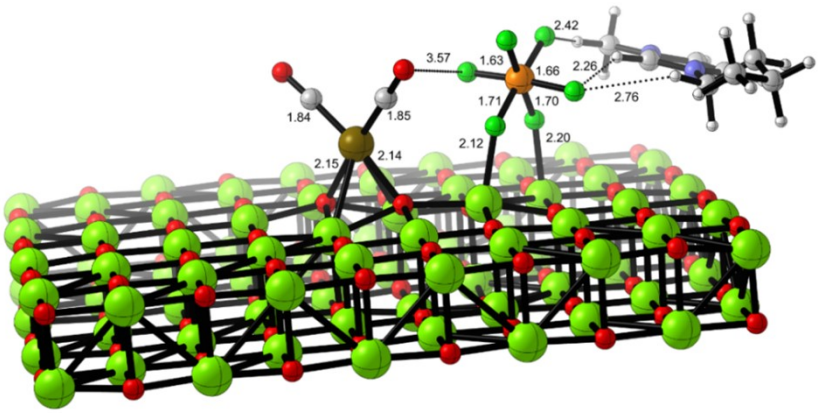
10-[Bmim][PF_6]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^+$
(anion-cation-catalyst arrangement)
$\nu(C_XH)$: 3181 (3136)
ν(CO)asym : 2001 (1973)
ν(CO)sym : 2064 (2035)
47.2
μ= 16.5



11-[Bmim][PF_6]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^+$
(cation-catalyst-anion arrangement)
$\nu(C_XH)$: 3263 (3172)
ν(CO)asym : 1973 (1945)
ν(CO)sym : 2056 (2027)
0.0
μ= 25.9



12-[Bmim][PF_6]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^+$
(cation-anion-catalyst arrangement)
$\nu(C_XH)$: 3191 (3146)
ν(CO)asym : 2001 (1973)
ν(CO)sym : 2063 (2034)
7.5
μ= 16.6



13-[Bmim][PF_6]-^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^+$
(cation-anion-catalyst arrangement)
ν(C_xH): 3209 (3164)
ν(CO)asym : 2015 (1987)
ν(CO)sym : 2077 (2048)
0.6
μ= 13.7

Figure S10. Structures of [Bmim][PF_6] coated ^{1}[$(MgO)_{80}Ir(I)(CO)_2$]$^+$ complexes (**6**) and their ν(C_xH), ν$(CO)_{asym}$/ν$(CO)_{sym}$ frequencies (**blue**), their scaled values (**black**), relative energies (**red**) and dipole moment (**green**) shown below for each species (PBE/6-31G(d,p)).

Table S1. Calculated relative Gibbs free energies (ΔG_{rel}) , dipole moments (μ), vibration frequencies (ν) and experimental band positions for the uncoated and [BMIM][PF_6] and [BMIM][OAc]coated MgO supported $Ir(CO)_2$ complexes (kcal.mol^{-1}, PBE/6-31G**, cm^{-1}).

Complexes		Calculated				*Experimental*		
	ΔG_{rel}	ν(C2H)	$\nu(CO)_{asym}$	$\nu(CO)_{sym}$	μ	*ν(C2H)*	*$\nu(CO)_{asym}$*	*$\nu(CO)_{sym}$*
6-$^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$(100)	-	-	1987	2043	-		*1983*	*2068*
7-[Bmim][OAc]-$^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$	5.1	2946	1980	2039	16.5	-	*1949*	*2042*
8-[Bmim][OAc]-$^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$	11.5	2944	1965	2025	16.2			
9-[Bmim][PF_6]-$^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$	49.3	3139	1973	2038	18.7	*3128*	*1967*	*2057*
10-[Bmim][PF_6]-$^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$	47.2	3136	1973	2035	16.5			
11-[Bmim][PF_6]-$^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$	0.0	3172	1945	2027	25.9			
12-[Bmim][PF_6]-$^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$	7.5	3146	1973	2034	16.6			
13-[Bmim][PF_6]-$^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$	0.6	3164	1987	2048	13.7			

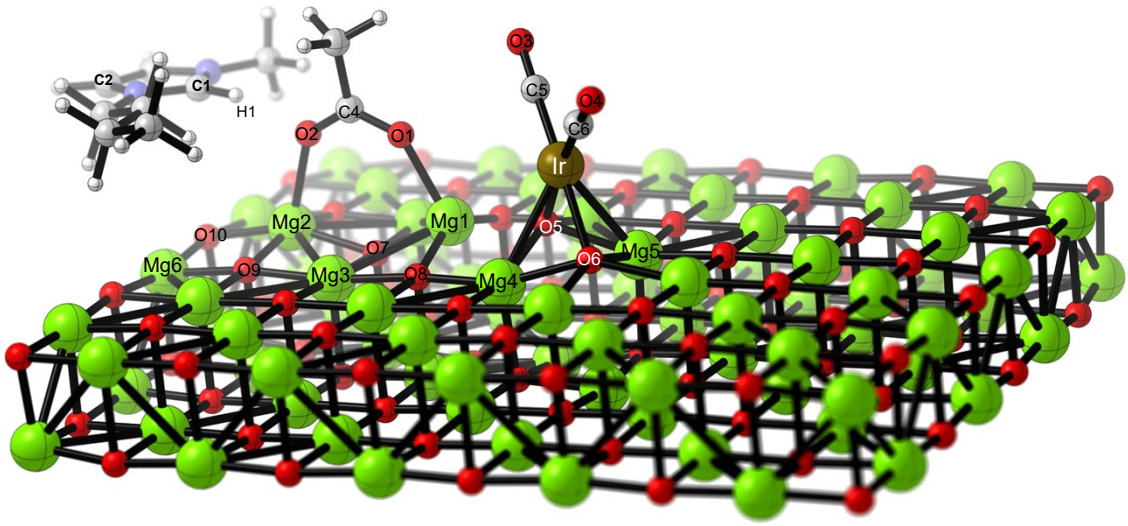


Figure S11. Optimized structure of [Bmim][Ac] coated $^{1}[(MgO)_{80}Ir(I)(CO)_2]^{+}$ (**7**) complex and its labeled atoms (PBE/6-31G**).

Table S2. Charge distributions on labeled atoms and change in their electron densities (blue: positive, red: negative) (**Figure S11**) uncoated, [Bmim][OAc] coated MgO-supported $Ir(CO)_2$ complexes and naked [Bmim][OAc] IL (PBE/6-31G**, pop=CM5).

		uncoated-complex		coated-complex	
	Atoms	Hirshfeld	CM5	Hirshfeld	CM5
	Ir	0.100	0.375	0.096	0.371
	C5	0.121	0.0819	0.125	0.0871
	O3	-0.0962	-0.143	-0.096	-0.144
	C6	0.122	0.0841	0.115	0.0762
	O4	-0.0941	-0.141	-0.103	-0.15
	O5	-0.309	-0.616	-0.308	-0.598
	Mg4	0.322	0.709	0.326	0.714
	O6	-0.302	-0.617	-0.303	-0.619
	Mg5	0.316	0.711	0.326	0.709
	Mg1	0.392	0.757	0.405	0.762
	O7	-0.396	-0.776	-0.395	-0.809
	Mg2	0.395	0.764	0.353	0.725
	O10	-0.462	-0.773	-0.462	-0.756
	O8	-0.397	-0.766	-0.390	-0.778
	Mg3	0.396	0.774	0.371	0.774
	O9	-0.396	-0.779	-0.394	-0.78
	Mg6	0.484	0.799	0.404	0.743
Naked [Bmim][OAc]	O1	-0.336	-0.39	-0.230	-0.344
	O2	-0.332	-0.403	-0.225	-0.342
	C4	0.126	0.175	0.192	0.235
	H1	0.0502	0.150	0.0675	0.152

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2 Y. L. Verma and R. K. Singh, Conformational States of Ionic Liquid 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide in Bulk and Confined Silica Nanopores Probed by Crystallization Kinetics Study, *J. Phys. Chem. C*, 2015, **119**, 24381–24392.

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