Supporting information

for

Different Electronic Structures and Spectroscopic Properties of Cationic [M(ppy)$_2$(N$^\wedge$N)]$^+$ (M=Rh, Ir; N$^\wedge$N= Hcmbpy, H$_2$dcbpy), A DFT Study

Submitted to journal- **Phys. Chem. Chem. Phys.** by:

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Table S1. Partial molecular orbital compositions (%) for **Rh1** in the ground state.

MO	energy (eV)	Rh	compositions (%)				bond type
			ppy	bpy	COOH	CH$_3$	
150a	-3.7827	$2.2/1.7\,p_z$	1.0	91.8	1.7	3.3	π^*(bpy)
149a	-3.9457	$4.9/2.4\,d_{x^2-y^2}$	86.1	8.8			π^*(ppy)
148a	-4.0091	$4.9/2.4\,d_{yz}$	92.1	4.9			π^*(ppy)
147a	-4.4553			89.5	9.6		π^*(bpy)
146a(L)	-5.1228	$2.6/1.5\,d_{yz}$		86.4	10.1		π^*(bpy)
HOMO-LUMO gap (3.0281eV)							
145a(H)	-8.1509	$30.4/4.2\,d_{xy}+5.2\,d_{xz}+8.9\,d_{x^2-y^2}+9.0\,d_{z^2}$	67.6	2.0			d (Rh)+π(ppy)
144a	-8.5095	1.6	96.7	1.6			π(ppy)
143a	-8.7387	$5.5/2.8\,d_{x^2-y^2}+2.2\,d_{z^2}$	93.8				π(ppy)
142a	-8.8298	$3.0/2.4\,d_{yz}$	95.1	1.8			π(ppy)
141a	-9.2590	$61.1/37.1\,d_{xy}+10.7\,d_{xz}+10.1\,d_{x^2-y^2}$	34.2	4.4			d (Rh)+π(ppy)

TableS2. Partial molecular orbital compositions (%) for **Ir2** in the ground state.

| MO | energy (eV) | Ir | compositions (%) | | | | bond type |
			ppy	bpy	COOH	CH$_3$	
150a	-3.8999	3.9/1.4 d_{z^2}	54.7	36.0	4.0	1.3	π^*(ppy)+π^*(bpy)
149a	-3.9500	4.8/1.5 $d_{x^2-y^2}$	24.0	65.9	3.3	1.9	π^*(ppy)+π^*(bpy)
148a	-4.0009	4.7/2.6 d_{yz}	80.4	4.7			π^*(ppy)
147a	-4.5696			88.7	11.2		π^*(bpy)
146a(L)	-5.2510	4.1/2.7 d_{yz}		82.6	10.0		π^*(bpy)
HOMO-LUMO gap (2.5875eV)							
145a(H)	-7.8385	34.0/4.7 d_{xy} +6.1 d_{xz} +9.4 $d_{x^2-y^2}$ +10.1 d_{z^2}	63.2	2.7			d (Ir)+π(ppy)
144a	-8.4470	4.0/1.6 d_{yz}	94.2	1.7			π(ppy)
143a	-8.6222	14.4/5.7 d_{xy} +4.7 $d_{x^2-y^2}$ +3.1 d_{z^2}	85.4	1.1			π(ppy)
142a	-8.7381	10.5/7.8 d_{yz}	87.7	1.7			π(ppy)
141a	-8.9087	50.1/31.5 d_{xy} +8.3 d_{xz} +7.1 $d_{x^2-y^2}$	46.4	3.6			d (Ir)+π(ppy)

Table S3 Partial molecular orbital compositions (%) for **Rh3** in the ground state.

MO	energy (eV)	Rh	compositions (%) ppy	bpy	COOH	bond type
157a	-4.0273	$4.8/2.5\,d_{yz}$	92.5	2.6		π^*(ppy)
156b	-4.0991	$5.1/1.8\,d_{xz}+1.7\,d_{yz}$	92.0	3.9		π^*(ppy)
155b	-4.5500			91.2	7.6	π^*(ppy)
154a	-4.7497		2.8	73.0	26.4	π^*(bpy)
153b(L)	-5.3957	$3.0/2.2\,d_{xz}$	3.8	81.8	11.4	π^*(bpy)
HOMO-LUMO gap (2.8636eV)						
152a(H)	-8.2593	$29.7/22.1\,d_{xy}+4.4\,d_{x^2-y^2}+3.0\,d_{z^2}$	68.3	2.0		d (Rh)+π(ppy)
151b	-8.5980	$1.6/0.8\,d_{yz}$	96.8	1.6		π(ppy)
150a	-8.8271	$5.3/2.8\,d_{xy}+1.6\,d_{x^2-y^2}$	94.1	0.6		π(ppy)
149b	-8.9185	$2.6/1.9\,d_{xz}$	95.7	1.7		π(ppy)
148a	-9.3896	$61.7/53.9\,d_{z^2}+7.2\,d_{x^2-y^2}$	34.8	3.5		d (Rh)+π(ppy)

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TableS4. Partial molecular orbital compositions (%) for **Ir4** in the ground state.

MO	energy (eV)	Ir	ppy	bpy	COOH	bond type
			compositions (%)			
157a	-4.0189	$5.7/2.2\,d_{xy}+1.3\,d_{z^2}$	91.5	2.8		$\pi^*(\mathrm{ppy})$
156b	-4.0989	$5.0/2.7\,d_{xz}$	91.1	3.9		$\pi^*(\mathrm{ppy})$
155b	-4.6480	1.4		93.2	7.8	$\pi^*(\mathrm{bpy})$
154a	-4.8670	1.2		74.2	25.3	$\pi^*(\mathrm{bpy})$
153b(L)	-5.5155	$4.9/4.1\,d_{xz}$	3.5	81.2	10.4	$\pi^*(\mathrm{bpy})$
HOMO-LUMO gap (2.4468eV)						
152a(H)	-7.9623	$33.2/24.3\,d_{xy}+4.7\,d_{x^2-y^2}+3.9\,d_{z^2}$	64.2	2.6		$\mathrm{d\,(Ir)}+\pi(\mathrm{ppy})$
151b	-8.5455	$3.4/2.6\,d_{xz}$	94.9	1.7		$\pi(\mathrm{ppy})$
150a	-8.7264	$11.1/6.2\,d_{z^2}+3.2\,d_{x^2-y^2}+1.6\,d_{xy}$	87.6	1.3		$\mathrm{d\,(Ir)}+\pi(\mathrm{ppy})$
149b	-8.8434	$7.0/6.6\,d_{xz}$	91.7	1.3		$\pi(\mathrm{ppy})$
148a	-9.0516	$53.9/45.6\,d_{z^2}+7.8\,d_{x^2-y^2}$	43.1	3.0		$\mathrm{d\,(Ir)}+\pi(\mathrm{ppy})$

Table S5. Single-electron transitions according to TDDFT calculations for the absorption of the complexes in acetonitrile

	state	energy (eV)	major contribution	character	exptl[20]
Ir2	T_1	583/2.12	HOMO→LUMO(100%)	d (Ir)+π(ppy)→π*(bpy)/MLCT/LLCT	
	T_2	452/2.75	HOMO-2→LUMO(47%)	d (Ir)+π(ppy)→π*(bpy)/MLCT/LLCT	467
			HOMO-4→LUMO(35%)	d (Ir)+π(ppy)→π*(bpy)/MLCT/LLCT	
	T_3	445/2.78	HOMO→LUMO+2(65%)	d (Ir)+π(ppy)→π*(ppy)/MLCT/ILCT	
	T_4	440/2.82	HOMO-1→LUMO(65%)	π(ppy)→π*(ppy)/LLCT	
	T_5	437/2.84	HOMO→LUMO+3(35%)	d (Ir)+π(ppy)→π*(ppy)/MLCT/ILCT	
			HOMO-1→LUMO+2(22%)	d (Ir)+π(ppy)+π(bpy)→π*(ppy)/MLCT/ILCT/LLCT	
Ir4	T_1	681/1.82	HOMO→LUMO(100%)	d (Ir)+π(ppy)→π*(bpy)/MLCT/LLCT	
	T_2	536/2.31	HOMO-6→LUMO(48%)	(Ir)+π(ppy)+π(bpy)→π*(bpy)/MLCT/ILCT/LLCT	
			HOMO-4→LUMO(28%)	d (Ir)+π(ppy)→π*(bpy)/MLCT/LLCT	
	T_3	486/2.55	HOMO-1→LUMO(48%)	π(ppy)→π*(ppy)/LLCT	
	T_4	459/2.70	HOMO-2→LUMO(50%)	d (Ir)+π(ppy)→π*(bpy)/MLCT/LLCT	457
			HOMO-6→LUMO(43%)	(Ir)+π(ppy)+π(bpy)→π*(bpy)/MLCT/ILCT/LLCT	
	T_5	457/2.71	HOMO-1→LUMO(49%)	π(ppy)→π*(ppy)/LLCT	
			HOMO-3→LUMO(33%)	π(ppy)→π*(ppy)/LLCT	

Table S6. Partial molecular orbital compositions (%) of the complexes in the excited states under the TDDFT calculations.

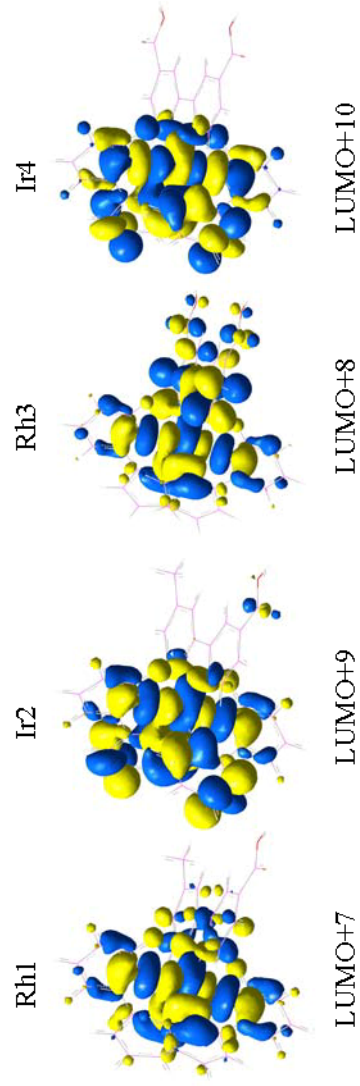| MO		energy	composition (%)					bond type
		(eV)	M(M=Rh or Ir)	ppy	bpy	COOH	CH$_3$	
Rh1	146 (H)	-5.67	6.8	14.9	71.4	6.1	0.8	π^*(ppy+bpy)
	145 (H-1)	-9.03	3.2	5.1	90.5	1.1		π^*(bpy)
Ir2	146(H)	-5.70	3.2	3.1	86.6	5.7	1.1	π^*(bpy)
	145(H-1)	-8.95	33.2	52.4	14.3			d(Ir)+π(ppy+bpy)
Rh3	153(H)	-5.70	3.2	5.3	83.1	8.4		π^*(bpy)
	152(H-1)	-9.09	0.6	0.3	98.1	1.0		π(bpy)
Ir4	153(H)	-5.98	3.4	3.1	85.8	7.6		π^*(bpy)
	152(H-1)	-9.07	30.8	62.9	4.7			d(Ir) + π(ppy)

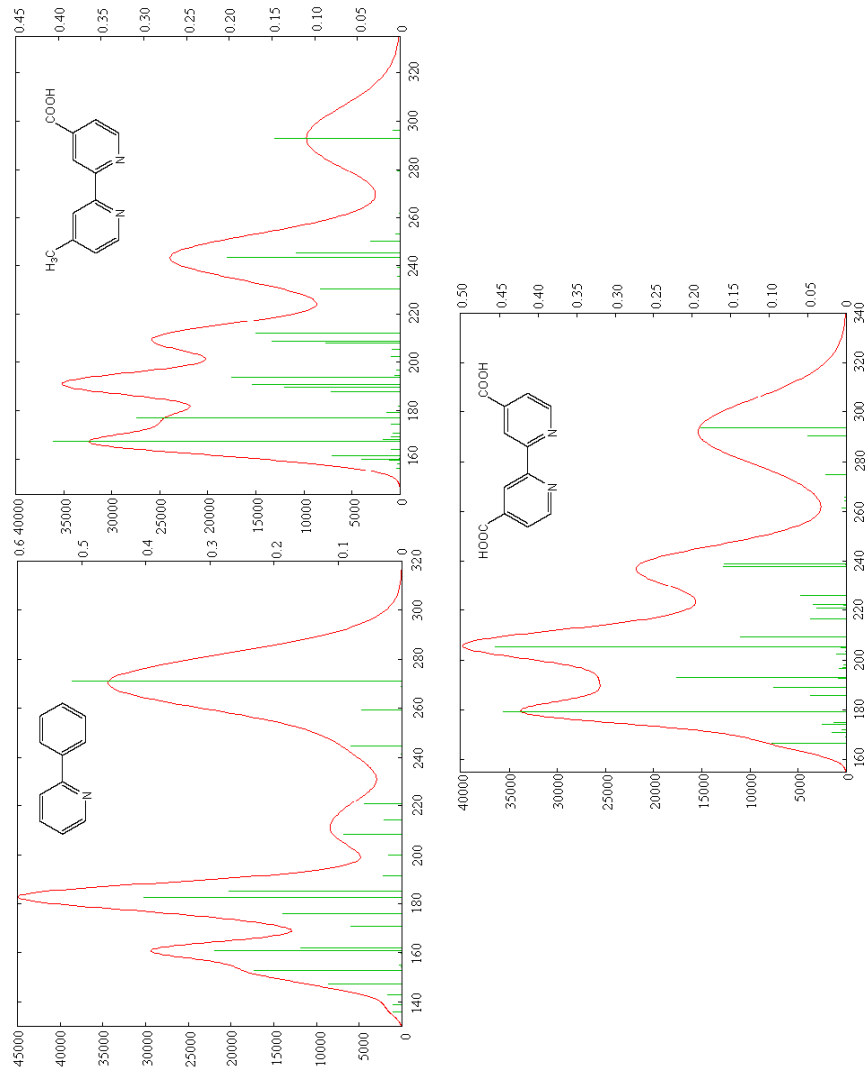**Fig. S1** The calculated d(M, M=Rh or Ir)-based e_g^*-like orbital of the complexes.

Fig.S2 The simulated absorption spectra of isolated ligands in acetonitrile media.