Supporting Information for

Tuning the NLO response of bis-cyclometalatediridium(III) complexes by modifying ligands: Experimental and structural DFT analysis

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Table S1 The crystal structure data of complex **IRC-1**

Compound	$[Ir(OXD)_2(Phbd)]^+(PF_6^-)$
Formula	$C_{46}H_{31}F_6IrN_7O_2P$
Formula weight	1050.95g/mol
Crystal System Space group	Monoclinic C 12/c 1 (15)
a/Å	32.804(5) Å
b/Å	12.6273(15) Å
c/Å	27.092(4) Å
V/Å3	9444.88(200)
Z	8
$D_{calcd.}$[g cm^{-3}]	1.47808 g/cm^3

Table S2 Selected Bond Lengths in Å for **IRC-1.**

Atom	Atom	Length/Å
Ir1	N1	2.057(7)
Ir1	N4	2.002(7)
Ir1	N8	2.161(9)
Ir1	N9	2.081(10)
Ir1	C46	2.229(10)
Ir1	C45	1.970(9)
N1	Ir2	2.003(7)
N4	Ir2	2.043(7)
C46	Ir2	1.911(10)
C45	Ir2	2.117(10)
N8	Ir2	2.073(9)
N9	Ir2	2.407(10)

Table S3 Selected Bond Angles for **IRC-1**.

Atom	Atom	Atom	Angle/°
N1	Ir1	N8	94.8(3)
N1	Ir1	N9	93.3(3)
N1	Ir1	C46	88.8(3)
N4	Ir1	N1	164.3(3)
N4	Ir1	N8	90.1(3)
N4	Ir1	N9	102.4(3)
N4	Ir1	C46	75.7(3)
N8	Ir1	N9	77.7(4)
N8	Ir1	C46	97.9(4)
N9	Ir1	C46	175.3(4)
C45	Ir1	N1	79.6(3)
C45	Ir1	N4	95.7(3)
C45	Ir1	N8	174.2(4)
C45	Ir1	N9	101.2(4)
C45	Ir1	C46	83.3(4)
N1	Ir2	N4	167.1(3)
N1	Ir2	C45	77.4(3)
N1	Ir2	N8	99.3(3)
N1	Ir2	N9	85.5(3)
N4	Ir2	C45	90.1(3)
N4	Ir2	N8	91.5(3)
N4	Ir2	N9	90.9(3)
C46	Ir2	N1	100.1(3)
C46	Ir2	N4	82.2(3)
C46	Ir2	C45	87.8(4)
C46	Ir2	N8	112.3(4)
C46	Ir2	N9	171.(4)
N8	Ir2	C45	159.8(4)
N9	Ir2	C45	87.3(3)
N9	Ir2	N8	72.5(4)

Table S4 Selected bond lengths and bond angles of studied complexes **IRC-1** and **IRC-2**

Bond	**IRC-1**		**IRC-2**	
	Exp	B3LYP	Exp	B3LYP
Ir-C1	2.026	2.12674		2.12670
Ir-C2	2.092	2.12440		2.12597
Ir-N1	2.227	2.08440		2.08450
Ir-N2	2.119	2.08142		2.08137
Ir-N3	2.119	2.05591		2.05435
Ir-N4	2.227	2.06898		2.06958
C1-Ir-C2	46.172	173.51169		173.65357
N1-Ir-N2	4.945	87.19010		87.30301
N3-Ir-N4	53.915	78.94646		78.89915

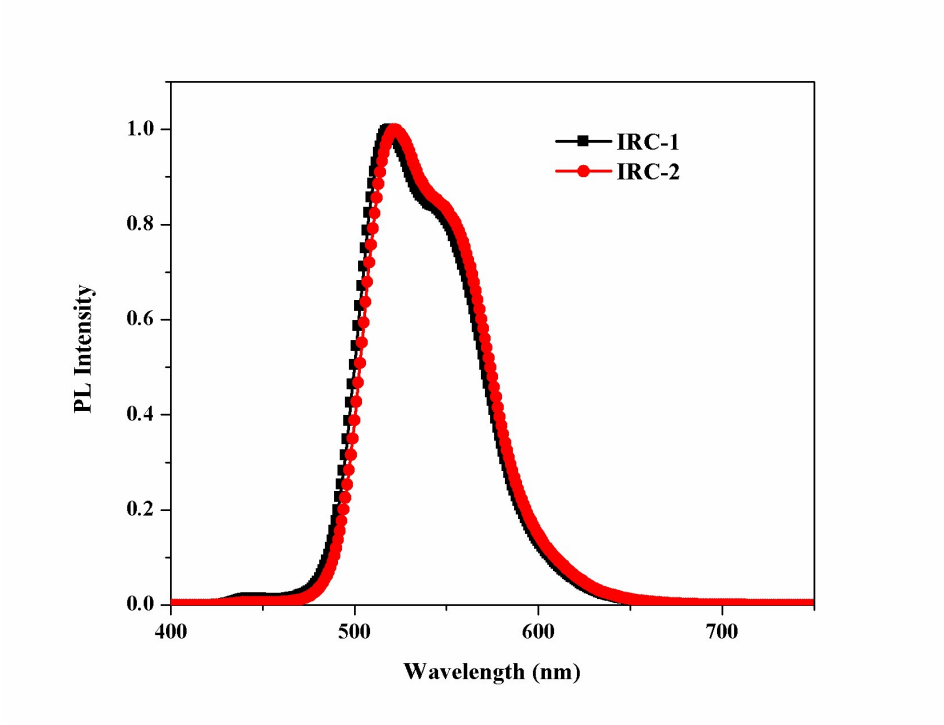


Fig S1 Electronic emission spectra of **IRC-1**and **IRC-2** in CH_2Cl_2 solution.

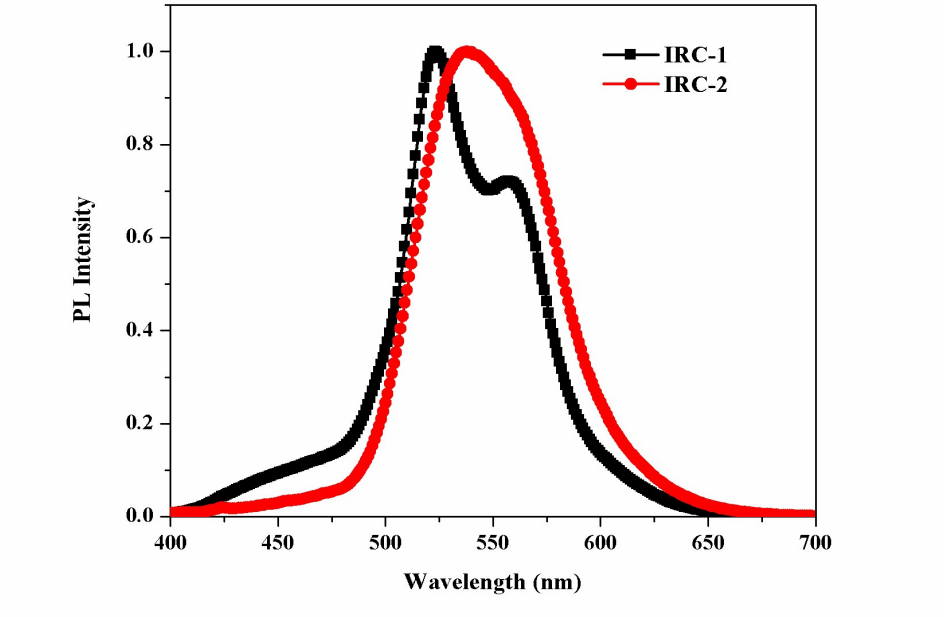


Fig S2 Emission spectra of **IRC-1**and **IRC-2** in neat thin films at room temperature.

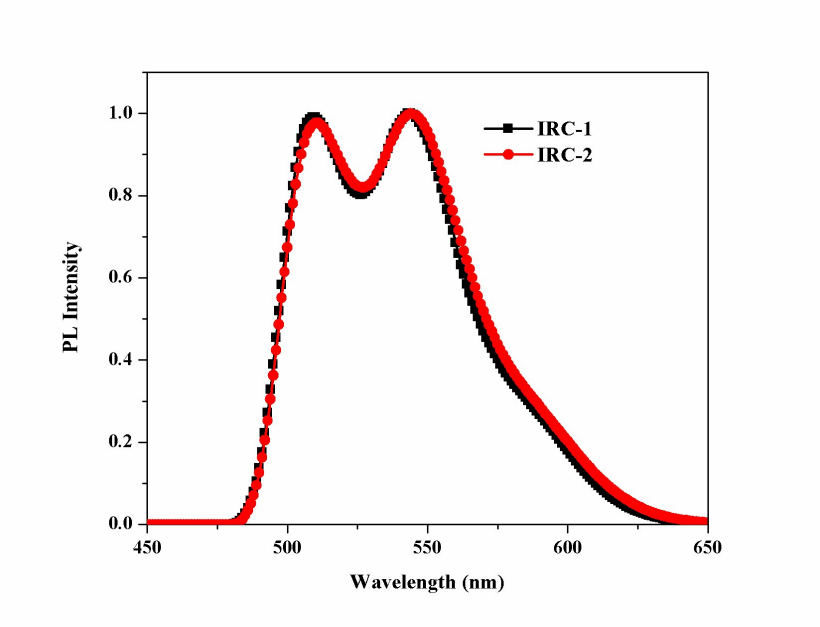


Fig S3 PL spectra of **IRC-1**and **IRC-2** at low temperature 77 K

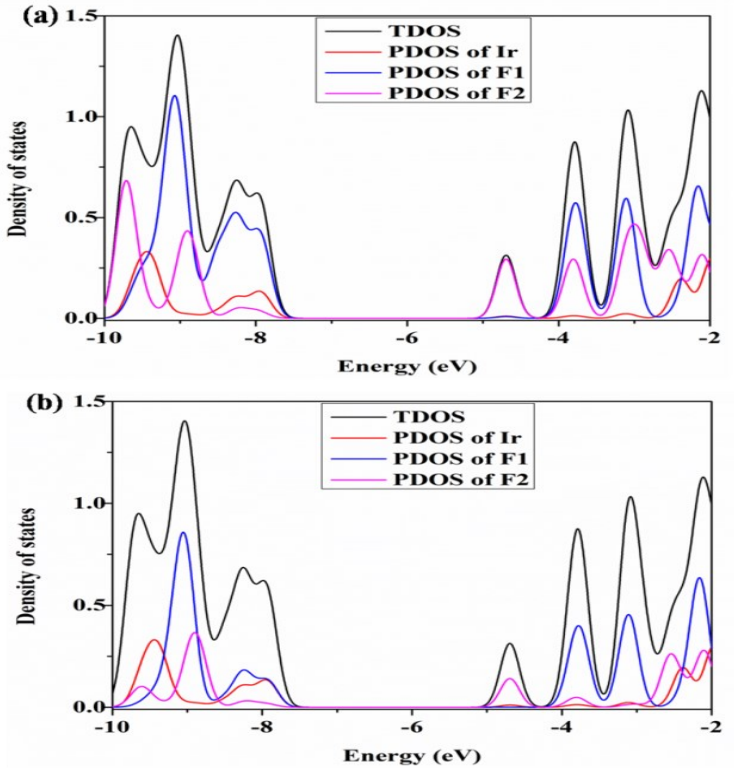


Fig S4 Partial and total density of states (PDOS and TDOS) obtained at B3LYP/6-31G*/SDD level for studied complexes **IRC-1** and **IRC-2**.

Table S5 Frontier molecular orbital analysis of complexes **IRC-1** and **IRC-2**.

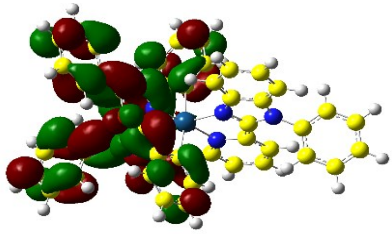
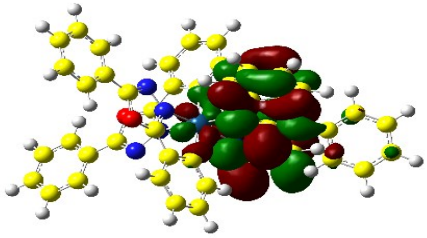
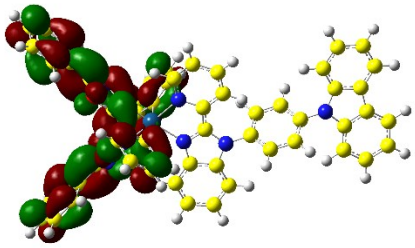
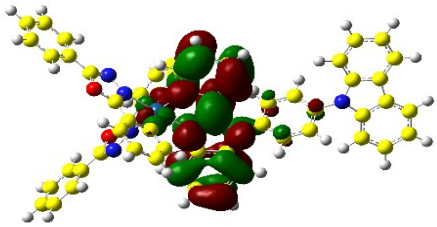
Complexes	HOMO	LUMO
IRC-1		
IRC-2		

Table S6 The HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_{gap}) in eV at B3LYP/ 6-31G** level of theory

Complex	E_{HOMO}	E_{LUMO}	$^*E_{gap}$
IRC-1	-0.19711	-0.06731	3.53
IRC-2	-0.11447	-0.06751	1.27

$^*E_{gap} = E_{HOMO} - E_{LUMO}$

Supplementary spectrum data

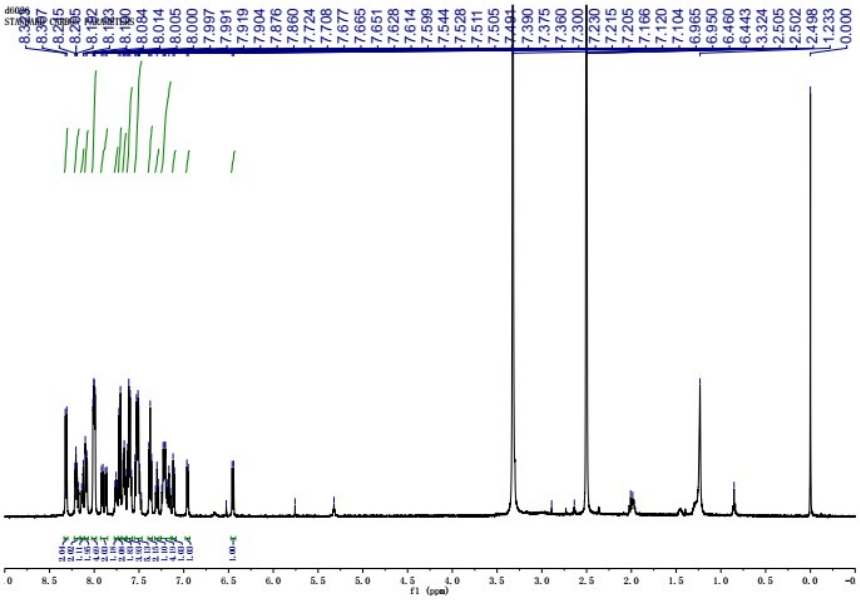


Fig. S5 ^{1}H-NMR spectrum of **IRC-1** in DMSO-d_6

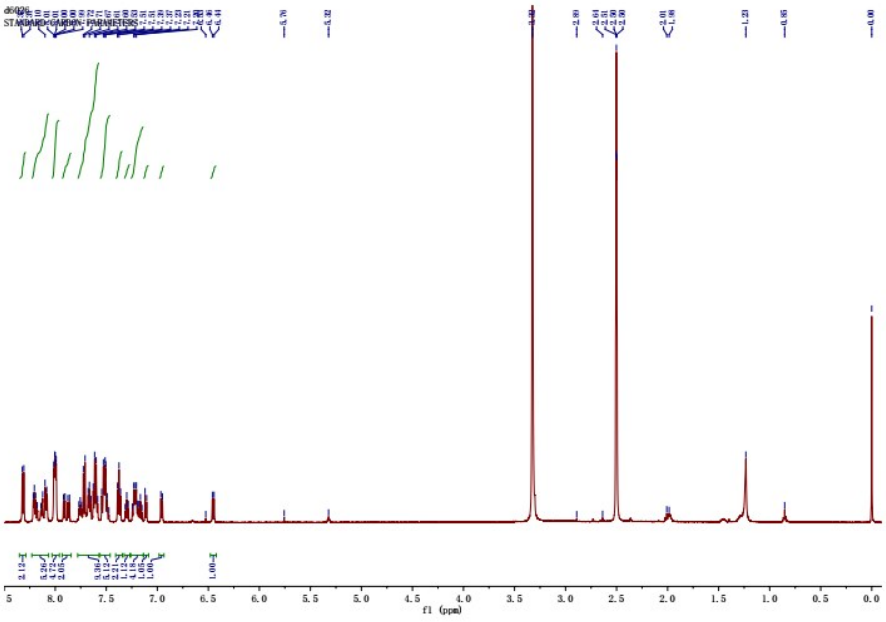


Fig. S6 ^{1}H-NMR spectrum of **IRC-2** in DMSO-d_6

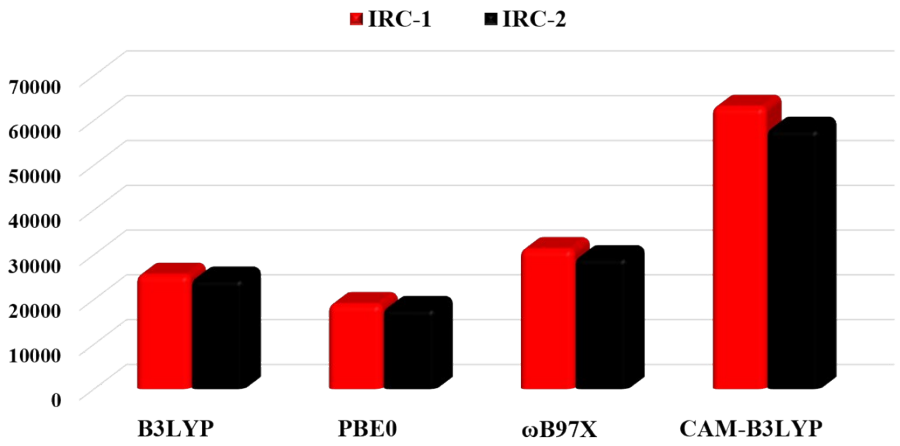


Fig. S7 The graphical representation of calculated first hyperpolarizability (β_{tot}) at different level of theory