Electronic Supplementary Information (ESI)

Synthesis, X-ray structure, photophysical properties and theoretical studies of novel six-membered cyclometalated iridium(III) complexes: Revisiting Ir(pnbi)$_2$(acac)

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Table S1. X-ray crystallographic data for $Ir(pnbi)_2(tmehd)\cdot CH_2Cl_2$ and $Ir(nbi)_2(acac)$

	$Ir(pnbi)_2(tmehd)\cdot CH_2Cl_2$	$Ir(nbi)_2(acac)$
chemical formula	$C_{66}H_{55}Cl_2IrN_4O_2$	$C_{51}H_{37}IrN_4O_2$
fw	1199.24	930.10
temperature , K	173(2)	93(2)
cryst color, habit	brown, block	orange, prism
dimensions of crystal	0.28 × 0.12 × 0.10	0.097 × 0.088 × 0.084
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	15.1126(19)	20.490(5)
b, Å	20.493(3)	13.025(3)
c, Å	18.690(2)	15.824(4)
α, deg		
β, deg	99.009(2)	105.930(3)
γ, deg		
V, Å^3	5716.7(13)	4061(2)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.393	1.521
μ, cm^{-1}	24.76	33.435
range of trans. factors	0.640-0.790	0.644-0.755
no. rflns measured	31999	33031
no. unique rflns	13036	9291
R_{int}	0.0606	0.1159
no. rflns used	9984	7858
no. params refined	713	525
R [$I > 2\ \sigma(I)$]	0.0366	0.0913
R_w [$I > 2\ \sigma(I)$]	0.0953	0.1660
GOF [$I > 2\ \sigma(I)$]	1.010	1.140

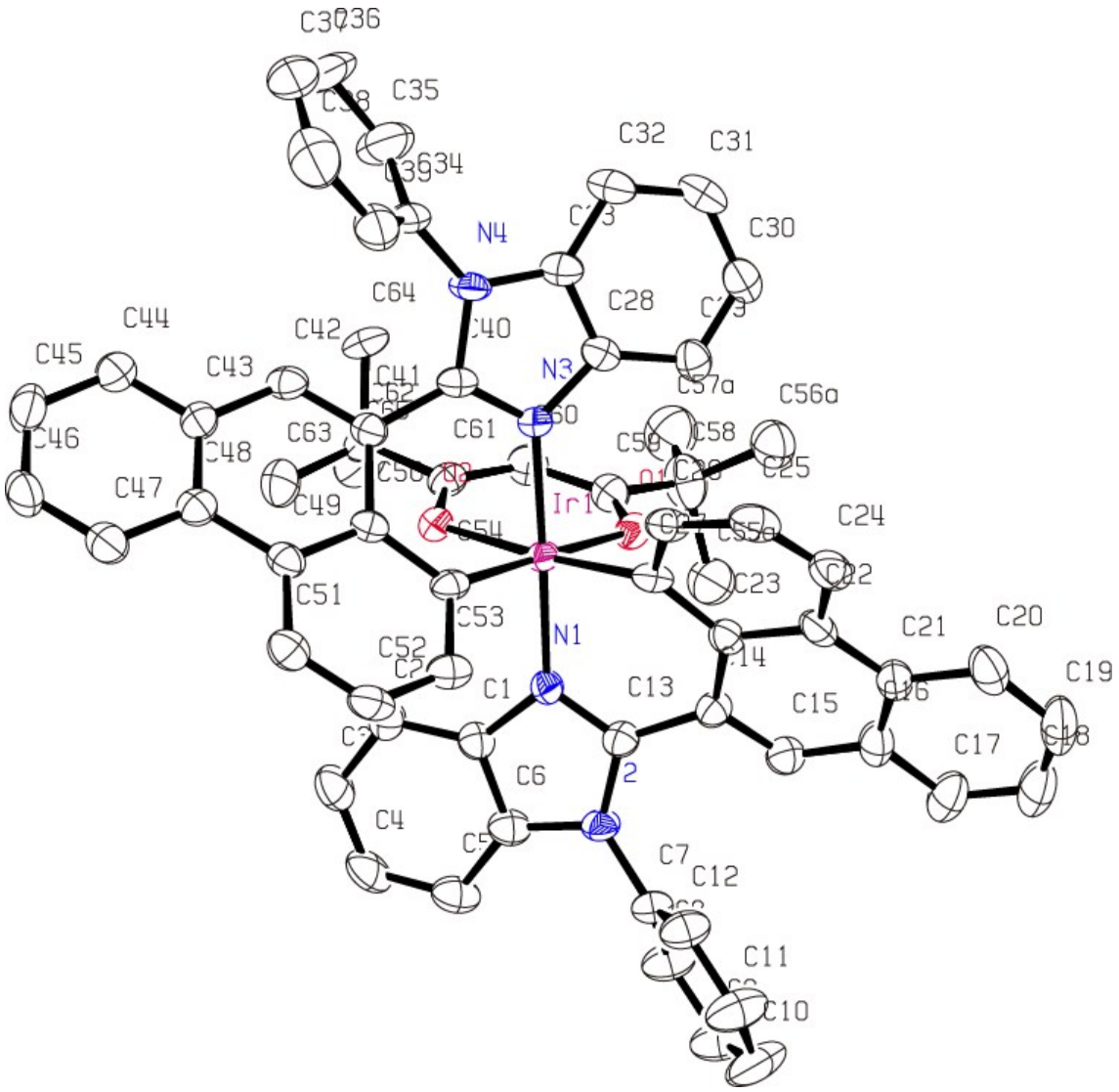


Figure S1. Crystal structure of $Ir(pnbi)_2(tmehd)$ with thermal ellipsoids at 50 % probability; all hydrogen atoms omitted for clarity.

Table S2a. Bond lengths (Å) for $Ir(pnbi)_2(tmehd)$

atom-atom	distance	atom-atom	distance
C(1)-C(2)	1.398(5)	C(27)-Ir(1)	2.006(4)
C(1)-N(1)	1.399(4)	C(28)-N(3)	1.393(4)
C(1)-C(6)	1.389(5)	C(28)-C(33)	1.381(5)
C(2)-C(3)	1.384(5)	C(28)-C(29)	1.399(5)
C(3)-C(4)	1.396(6)	C(29)-C(30)	1.382(5)
C(4)-C(5)	1.380(6)	C(30)-C(31)	1.404(6)
C(5)-C(6)	1.381(5)	C(31)-C(32)	1.380(6)
C(6)-N(2)	1.403(5)	C(32)-C(33)	1.405(5)
C(7)-C(12)	1.375(5)	C(33)-N(4)	1.381(5)
C(7)-C(8)	1.386(5)	C(34)-C(35)	1.374(6)
C(7)-N(2)	1.445(5)	C(34)-C(39)	1.383(6)
C(8)-C(9)	1.400(6)	C(34)-N(4)	1.435(5)
C(9)-C(10)	1.320(7)	C(35)-C(36)	1.392(7)
C(10)-C(11)	1.413(7)	C(36)-C(37)	1.381(9)
C(11)-C(12)	1.375(6)	C(37)-C(38)	1.377(9)
C(13)-N(1)	1.322(4)	C(38)-C(39)	1.391(6)
C(13)-N(2)	1.378(4)	C(40)-N(3)	1.326(5)
C(13)-C(14)	1.468(5)	C(40)-N(4)	1.381(4)
C(14)-C(15)	1.368(5)	C(40)-C(41)	1.466(5)
C(14)-C(23)	1.451(5)	C(41)-C(42)	1.348(5)
C(15)-C(16)	1.415(5)	C(41)-C(50)	1.466(5)
C(16)-C(17)	1.410(6)	C(42)-C(43)	1.422(5)
C(16)-C(21)	1.410(5)	C(43)-C(44)	1.408(5)
C(17)-C(18)	1.376(7)	C(43)-C(48)	1.411(5)
C(18)-C(19)	1.373(6)	C(44)-C(45)	1.382(5)
C(19)-C(20)	1.384(6)	C(45)-C(46)	1.383(6)
C(20)-C(21)	1.412(5)	C(46)-C(47)	1.382(6)
C(21)-C(22)	1.460(6)	C(47)-C(48)	1.407(5)
C(22)-C(24)	1.398(5)	C(48)-C(49)	1.455(5)
C(22)-C(23)	1.429(5)	C(49)-C(50)	1.420(5)
C(23)-C(27)	1.429(5)	C(49)-C(51)	1.404(5)
C(24)-C(25)	1.359(6)	C(50)-C(54)	1.438(5)
C(25)-C(26)	1.387(5)	C(51)-C(52)	1.377(5)
C(26)-C(27)	1.393(5)	C(52)-C(53)	1.385(5)

C(53)-C(54)	1.399(5)	C(61)-O(2)	1.280(4)
C(54)-Ir(1)	2.005(4)	C(61)-C(62)	1.535(5)
C(58)-C(57B)	1.458(8)	C(62)-C(65)	1.519(6)
C(58)-C(57A)	1.481(7)	C(62)-C(63)	1.521(6)
C(58)-C(59)	1.547(5)	C(62)-C(64)	1.554(6)
C(58)-C(56A)	1.565(7)	Cl(1)-C(66)	1.749(8)
C(58)-C(56B)	1.552(7)	Ir(1)-N(1) 2.021(3)	
C(58)-C(55B)	1.611(8)	Ir(1)-N(3) 2.022(3)	
C(58)-C(55A)	1.606(7)	Ir(1)-O(1) 2.142(2)	
C(59)-O(1)	1.264(4)	Ir(1)-O(2) 2.144(2)	
C(59)-C(60)	1.392(6)	Cl(2)-C(66)	1.604(9)
C(60)-C(61)	1.395(5)		

Table S2b. Bond angles (°) for $Ir(pnbi)_2(tmehd)$

atom-atom-atom	angle	atom-atom-atom	angle
C(2)-C(1)-N(1)	130.4(4)	C(16)-C(21)-C(22)	119.6(4)
C(2)-C(1)-C(6)	121.0(4)	C(24)-C(22)-C(23)	118.4(4)
N(1)-C(1)-C(6)	108.7(3)	C(24)-C(22)-C(21)	121.4(4)
C(1)-C(2)-C(3)	116.3(4)	C(23)-C(22)-C(21)	120.1(4)
C(4)-C(3)-C(2)	121.9(4)	C(27)-C(23)-C(22)	120.6(3)
C(3)-C(4)-C(5)	121.8(4)	C(27)-C(23)-C(14)	122.0(3)
C(4)-C(5)-C(6)	116.3(4)	C(22)-C(23)-C(14)	117.4(3)
C(5)-C(6)-N(2)	131.6(4)	C(25)-C(24)-C(22)	120.6(4)
C(5)-C(6)-C(1)	122.6(4)	C(24)-C(25)-C(26)	120.5(4)
N(2)-C(6)-C(1)	105.8(3)	C(25)-C(26)-C(27)	122.9(4)
C(12)-C(7)-C(8)	121.0(4)	C(26)-C(27)-C(23)	115.6(3)
C(12)-C(7)-N(2)	119.5(3)	C(26)-C(27)-Ir(1)	121.3(3)
C(8)-C(7)-N(2)	119.5(4)	C(23)-C(27)-Ir(1)	122.6(3)
C(7)-C(8)-C(9)	118.8(4)	N(3)-C(28)-C(33)	108.7(3)
C(10)-C(9)-C(8)	120.9(4)	N(3)-C(28)-C(29)	130.1(4)
C(9)-C(10)-C(11)	120.4(5)	C(33)-C(28)-C(29)	121.2(3)
C(12)-C(11)-C(10)	119.9(5)	C(30)-C(29)-C(28)	117.1(4)
C(7)-C(12)-C(11)	119.0(4)	C(29)-C(30)-C(31)	121.6(4)
N(1)-C(13)-N(2)	110.5(3)	C(32)-C(31)-C(30)	121.5(4)
N(1)-C(13)-C(14)	126.1(3)	C(31)-C(32)-C(33)	116.6(4)
N(2)-C(13)-C(14)	123.4(3)	N(4)-C(33)-C(28)	106.4(3)
C(15)-C(14)-C(23)	120.7(3)	N(4)-C(33)-C(32)	131.6(4)
C(15)-C(14)-C(13)	119.1(3)	C(28)-C(33)-C(32)	122.0(4)
C(23)-C(14)-C(13)	119.7(3)	C(35)-C(34)-C(39)	121.3(4)
C(14)-C(15)-C(16)	122.6(4)	C(35)-C(34)-N(4)	118.4(4)
C(15)-C(16)-C(17)	120.8(4)	C(39)-C(34)-N(4)	120.3(4)
C(15)-C(16)-C(21)	118.9(4)	C(34)-C(35)-C(36)	119.6(6)
C(17)-C(16)-C(21)	120.1(4)	C(37)-C(36)-C(35)	118.9(6)
C(18)-C(17)-C(16)	120.7(5)	C(36)-C(37)-C(38)	121.7(5)
C(17)-C(18)-C(19)	119.7(5)	C(39)-C(38)-C(37)	119.1(5)
C(18)-C(19)-C(20)	120.8(4)	C(38)-C(39)-C(34)	119.3(5)
C(19)-C(20)-C(21)	121.3(5)	N(3)-C(40)-N(4)	110.0(3)
C(20)-C(21)-C(16)	117.2(4)	N(3)-C(40)-C(41)	125.6(3)
C(20)-C(21)-C(22)	123.2(4)	N(4)-C(40)-C(41)	124.4(3)

C(42)-C(41)-C(50)	120.1(4)	C(59)-C(58)-C(55A)	104.9(4)
C(42)-C(41)-C(40)	120.3(4)	C(56A)-C(58)-C(55A)	103.3(5)
C(50)-C(41)-C(40)	119.3(3)	O(1)-C(59)-C(60)	125.9(4)
C(41)-C(42)-C(43)	122.9(4)	O(1)-C(59)-C(58)	114.5(3)
C(44)-C(43)-C(48)	119.8(4)	C(60)-C(59)-C(58)	119.6(4)
C(44)-C(43)-C(42)	121.4(4)	C(59)-C(60)-C(61)	129.0(4)
C(48)-C(43)-C(42)	118.7(3)	O(2)-C(61)-C(60)	124.8(4)
C(43)-C(44)-C(45)	120.7(4)	O(2)-C(61)-C(62)	115.0(3)
C(46)-C(45)-C(44)	119.7(4)	C(60)-C(61)-C(62)	120.1(4)
C(45)-C(46)-C(47)	120.7(4)	C(65)-C(62)-C(61)	112.9(3)
C(46)-C(47)-C(48)	121.1(4)	C(65)-C(62)-C(63)	107.9(4)
C(47)-C(48)-C(43)	118.1(3)	C(61)-C(62)-C(63)	111.0(3)
C(47)-C(48)-C(49)	122.8(4)	C(65)-C(62)-C(64)	110.4(4)
C(43)-C(48)-C(49)	119.0(4)	C(61)-C(62)-C(64)	105.2(3)
C(50)-C(49)-C(51)	118.2(3)	C(63)-C(62)-C(64)	109.5(4)
C(50)-C(49)-C(48)	120.3(3)	C(54)-Ir(1)-C(27)	92.90(15)
C(51)-C(49)-C(48)	121.5(4)	C(54)-Ir(1)-N(1)	91.10(13)
C(49)-C(50)-C(54)	121.1(3)	C(27)-Ir(1)-N(1)	89.27(13)
C(49)-C(50)-C(41)	116.9(3)	C(54)-Ir(1)-N(3)	88.81(13)
C(54)-C(50)-C(41)	122.0(3)	C(27)-Ir(1)-N(3)	92.47(13)
C(52)-C(51)-C(49)	120.7(4)	N(1)-Ir(1)-N(3)	178.26(11)
C(51)-C(52)-C(53)	120.3(4)	C(54)-Ir(1)-O(1)	176.33(11)
C(52)-C(53)-C(54)	122.8(4)	C(27)-Ir(1)-O(1)	89.97(13)
C(53)-C(54)-C(50)	115.8(3)	N(1)-Ir(1)-O(1)	86.65(11)
C(53)-C(54)-Ir(1)	122.6(3)	N(3)-Ir(1)-O(1)	93.35(11)
C(50)-C(54)-Ir(1)	121.0(3)	C(54)-Ir(1)-O(2)	90.05(12)
C(57B)-C(58)-C(59)	114.0(6)	C(27)-Ir(1)-O(2)	175.48(12)
C(57A)-C(58)-C(59)	119.1(5)	N(1)-Ir(1)-O(2)	94.10(11)
C(57A)-C(58)-C(56A)	109.8(6)	N(3)-Ir(1)-O(2)	84.16(11)
C(59)-C(58)-C(56A)	110.1(4)	O(1)-Ir(1)-O(2)	87.23(10)
C(57B)-C(58)-C(56B)	118.5(8)	C(13)-N(1)-C(1)	107.5(3)
C(59)-C(58)-C(56B)	108.3(5)	C(13)-N(1)-Ir(1)	124.2(2)
C(57B)-C(58)-C(55B)	108.9(8)	C(1)-N(1)-Ir(1)	128.1(2)
C(59)-C(58)-C(55B)	102.7(5)	C(13)-N(2)-C(6)	107.5(3)
C(56B)-C(58)-C(55B)	102.8(6)	C(13)-N(2)-C(7)	127.8(3)
C(57A)-C(58)-C(55A)	108.3(6)	C(6)-N(2)-C(7)	122.2(3)

C(40)-N(3)-C(28)	107.2(3)
C(40)-N(3)-Ir(1)	123.1(2)
C(28)-N(3)-Ir(1)	129.5(3)
C(33)-N(4)-C(40)	107.7(3)
C(33)-N(4)-C(34)	123.1(3)
C(40)-N(4)-C(34)	128.2(3)
C(59)-O(1)-Ir(1)	125.2(2)
C(61)-O(2)-Ir(1)	124.4(2)
Cl(2)-C(66)-Cl(1)	116.4(6)

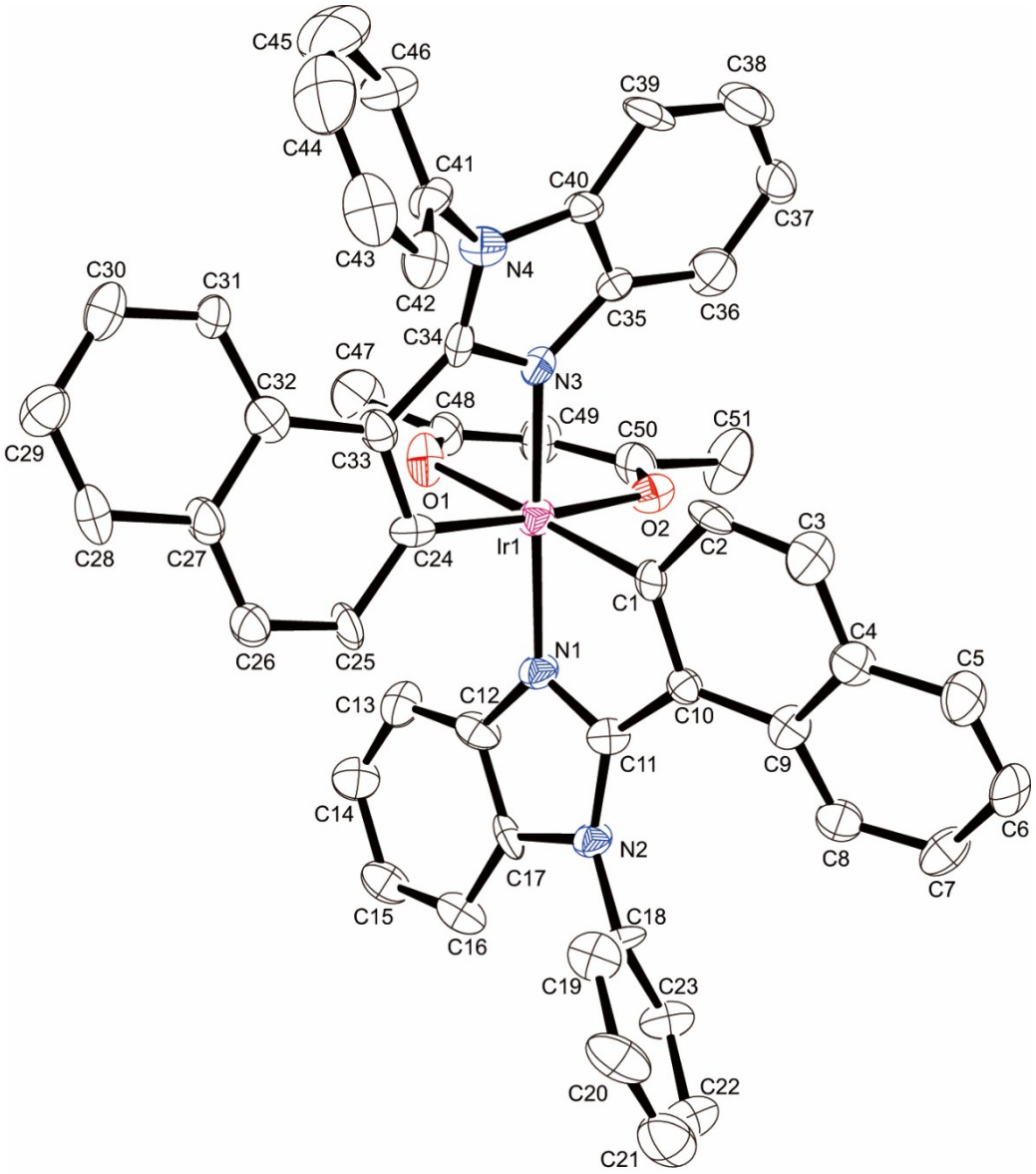


Figure S2. Crystal structure of $Ir(nbi)_2(acac)$ with thermal ellipsoids at 50 % probability; all hydrogen atoms omitted for clarity.

Table S3a. Bond lengths (Å) for $Ir(nbi)_2(acac)$

atom	atom	distance	atom	atom	distance
Ir1	O1	2.114(7)	Ir1	O2	2.100(8)
Ir1	N1	2.033(7)	Ir1	N3	2.032(8)
Ir1	C1	1.993(10)	Ir1	C24	2.005(11)
O1	C48	1.285(15)	O2	C50	1.282(14)
N1	C11	1.344(12)	N1	C12	1.375(12)
N2	C11	1.380(12)	N2	C17	1.407(13)
N2	C18	1.450(13)	N3	C34	1.351(15)
N3	C35	1.374(13)	N4	C34	1.376(12)
N4	C40	1.405(14)	N4	C41	1.442(14)
C1	C2	1.442(13)	C1	C10	1.393(12)
C2	C3	1.376(14)	C3	C4	1.422(14)
C4	C5	1.415(15)	C4	C9	1.427(13)
C5	C6	1.352(15)	C6	C7	1.425(14)
C7	C8	1.370(15)	C8	C9	1.404(13)
C9	C10	1.438(13)	C10	C11	1.451(13)
C12	C13	1.383(14)	C12	C17	1.407(13)
C13	C14	1.369(15)	C14	C15	1.418(14)
C15	C16	1.377(16)	C16	C17	1.373(14)
C18	C19	1.385(17)	C18	C23	1.389(14)
C19	C20	1.374(16)	C20	C21	1.372(18)
C21	C22	1.37(2)	C22	C23	1.380(16)
C24	C25	1.428(15)	C24	C33	1.404(12)
C25	C26	1.358(17)	C26	C27	1.427(13)
C27	C28	1.417(18)	C27	C32	1.434(15)
C28	C29	1.376(14)	C29	C30	1.397(17)
C30	C31	1.362(17)	C31	C32	1.401(13)
C32	C33	1.458(16)	C33	C34	1.450(15)
C35	C36	1.394(18)	C35	C40	1.404(14)
C36	C37	1.400(15)	C37	C38	1.388(17)
C38	C39	1.371(19)	C39	C40	1.396(14)
C41	C42	1.368(17)	C41	C46	1.383(14)
C42	C43	1.379(18)	C43	C44	1.392(18)
C44	C45	1.36(3)	C45	C46	1.405(19)
C47	C48	1.528(15)	C48	C49	1.379(18)
C49	C50	1.403(16)	C50	C51	1.508(19)
C2	H2	0.950	C3	H3	0.950

C5	H5	0.950	C6	H6	0.950
C7	H7	0.950	C8	H8	0.950
C13	H13	0.950	C14	H14	0.950
C15	H15	0.950	C16	H16	0.950
C19	H19	0.950	C20	H20	0.950
C21	H21	0.950	C22	H22	0.950
C23	H23	0.950	C25	H25	0.950
C26	H26	0.950	C28	H28	0.950
C29	H29	0.950	C30	H30	0.950
C31	H31	0.950	C36	H36	0.950
C37	H37	0.950	C38	H38	0.950
C39	H39	0.950	C42	H42	0.950
C43	H43	0.950	C44	H44	0.950
C45	H45	0.950	C46	H46	0.950
C47	H47A	0.980	C47	H47B	0.980
C47	H47C	0.980	C49	H49	0.950
C51	H51A	0.980	C51	H51B	0.980
C51	H51C	0.980			

Table 3b. Bond angles (°) for $Ir(nbi)_2(acac)$

atom	atom	atom	angle	atom	atom	atom	angle
O1	Ir1	O2	88.2(3)	O1	Ir1	N1	98.7(3)
O1	Ir1	N3	87.2(3)	O1	Ir1	C1	175.5(4)
O1	Ir1	C24	87.4(4)	O2	Ir1	N1	85.7(3)
O2	Ir1	N3	97.7(3)	O2	Ir1	C1	88.5(4)
O2	Ir1	C24	175.0(3)	N1	Ir1	N3	173.3(4)
N1	Ir1	C1	78.1(4)	N1	Ir1	C24	97.2(4)
N3	Ir1	C1	96.2(4)	N3	Ir1	C24	79.8(4)
C1	Ir1	C24	96.1(4)	Ir1	O1	C48	126.0(7)
Ir1	O2	C50	126.9(7)	Ir1	N1	C11	115.8(6)
Ir1	N1	C12	135.6(7)	C11	N1	C12	108.0(8)
C11	N2	C17	107.8(8)	C11	N2	C18	127.5(8)
C17	N2	C18	120.0(8)	Ir1	N3	C34	115.1(7)
Ir1	N3	C35	134.9(7)	C34	N3	C35	107.7(8)
C34	N4	C40	107.1(9)	C34	N4	C41	129.0(10)
C40	N4	C41	122.7(8)	Ir1	C1	C2	123.2(6)
Ir1	C1	C10	118.5(7)	C2	C1	C10	117.9(9)
C1	C2	C3	120.5(8)	C2	C3	C4	121.3(9)
C3	C4	C5	121.3(9)	C3	C4	C9	119.3(9)
C5	C4	C9	118.9(9)	C4	C5	C6	122.6(10)
C5	C6	C7	118.5(10)	C6	C7	C8	120.2(9)
C7	C8	C9	122.3(9)	C4	C9	C8	117.5(9)
C4	C9	C10	117.9(8)	C8	C9	C10	124.5(9)
C1	C10	C9	121.6(8)	C1	C10	C11	109.8(8)
C9	C10	C11	128.1(8)	N1	C11	N2	109.8(8)
N1	C11	C10	116.3(8)	N2	C11	C10	133.9(9)
N1	C12	C13	131.9(9)	N1	C12	C17	109.1(9)
C13	C12	C17	119.0(9)	C12	C13	C14	119.7(9)
C13	C14	C15	119.7(11)	C14	C15	C16	121.8(10)
C15	C16	C17	116.9(9)	N2	C17	C12	105.3(8)
N2	C17	C16	131.8(9)	C12	C17	C16	122.8(10)
N2	C18	C19	120.0(8)	N2	C18	C23	119.1(10)
C19	C18	C23	120.9(10)	C18	C19	C20	119.0(10)
C19	C20	C21	121.0(13)	C20	C21	C22	119.5(11)
C21	C22	C23	121.2(11)	C18	C23	C22	118.4(11)
Ir1	C24	C25	126.4(7)	Ir1	C24	C33	115.0(8)
C25	C24	C33	118.1(10)	C24	C25	C26	122.5(9)

C25	C26	C27	119.9(10)	C26	C27	C28	120.9(10)
C26	C27	C32	120.7(11)	C28	C27	C32	118.4(9)
C27	C28	C29	121.2(11)	C28	C29	C30	119.3(12)
C29	C30	C31	120.9(10)	C30	C31	C32	121.5(10)
C27	C32	C31	118.2(11)	C27	C32	C33	116.7(9)
C31	C32	C33	124.8(10)	C24	C33	C32	121.1(9)
C24	C33	C34	112.5(10)	C32	C33	C34	126.4(8)
N3	C34	N4	110.3(9)	N3	C34	C33	115.6(8)
N4	C34	C33	133.3(10)	N3	C35	C36	131.2(9)
N3	C35	C40	108.8(10)	C36	C35	C40	119.9(9)
C35	C36	C37	117.7(11)	C36	C37	C38	121.0(12)
C37	C38	C39	122.2(11)	C38	C39	C40	117.1(10)
N4	C40	C35	106.2(8)	N4	C40	C39	131.8(10)
C35	C40	C39	122.0(11)	N4	C41	C42	121.0(9)
N4	C41	C46	117.4(10)	C42	C41	C46	121.5(10)
C41	C42	C43	119.3(10)	C42	C43	C44	119.2(13)
C43	C44	C45	122.4(14)	C44	C45	C46	118.0(12)
C41	C46	C45	119.6(12)	O1	C48	C47	117.3(11)
O1	C48	C49	125.2(10)	C47	C48	C49	117.5(11)
C48	C49	C50	129.2(11)	O2	C50	C49	124.2(11)
O2	C50	C51	115.8(10)	C49	C50	C51	120.0(11)
C1	C2	H2	119.7	C3	C2	H2	119.7
C2	C3	H3	119.3	C4	C3	H3	119.3
C4	C5	H5	118.7	C6	C5	H5	118.7
C5	C6	H6	120.8	C7	C6	H6	120.8
C6	C7	H7	119.9	C8	C7	H7	119.9
C7	C8	H8	118.9	C9	C8	H8	118.9
C12	C13	H13	120.1	C14	C13	H13	120.1
C13	C14	H14	120.1	C15	C14	H14	120.1
C14	C15	H15	119.1	C16	C15	H15	119.1
C15	C16	H16	121.6	C17	C16	H16	121.6
C18	C19	H19	120.5	C20	C19	H19	120.5
C19	C20	H20	119.5	C21	C20	H20	119.5
C20	C21	H21	120.3	C22	C21	H21	120.3
C21	C22	H22	119.4	C23	C22	H22	119.4
C18	C23	H23	120.8	C22	C23	H23	120.8
C24	C25	H25	118.8	C26	C25	H25	118.8
C25	C26	H26	120.1	C27	C26	H26	120.1

C27	C28	H28	119.4	C29	C28	H28	119.4
C28	C29	H29	120.3	C30	C29	H29	120.3
C29	C30	H30	119.6	C31	C30	H30	119.5
C30	C31	H31	119.2	C32	C31	H31	119.2
C35	C36	H36	121.1	C37	C36	H36	121.1
C36	C37	H37	119.5	C38	C37	H37	119.5
C37	C38	H38	118.9	C39	C38	H38	118.9
C38	C39	H39	121.5	C40	C39	H39	121.5
C41	C42	H42	120.4	C43	C42	H42	120.4
C42	C43	H43	120.4	C44	C43	H43	120.4
C43	C44	H44	118.8	C45	C44	H44	118.8
C44	C45	H45	121.0	C46	C45	H45	121.0
C41	C46	H46	120.2	C45	C46	H46	120.2
C48	C47	H47A	109.5	C48	C47	H47B	109.5
C48	C47	H47C	109.5	H47A	C47	H47B	109.5
H47A	C47	H47C	109.5	H47B	C47	H47C	109.5
C48	C49	H49	115.4	C50	C49	H49	115.4
C50	C51	H51A	109.5	C50	C51	H51B	109.5
C50	C51	H51C	109.5	H51A	C51	H51B	109.5
H51A	C51	H51C	109.5	H51B	C51	H51C	109.5

2. ^{1}H NMR spectra of the ligand pnbi and its Ir complexes

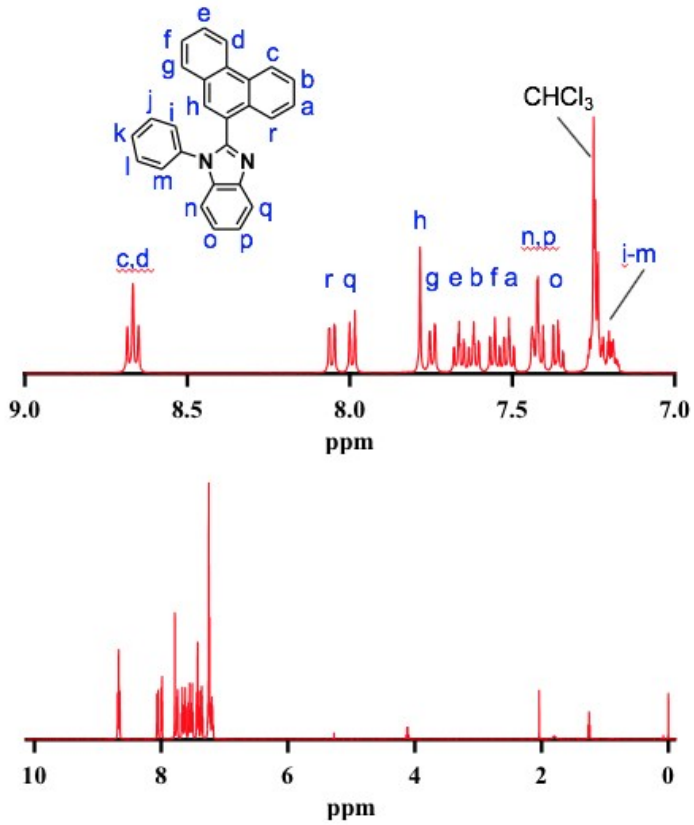


Figure S3. ^{1}H NMR (500 MHz) spectrum of the ligand pnbi ligand in $CDCl_3$.

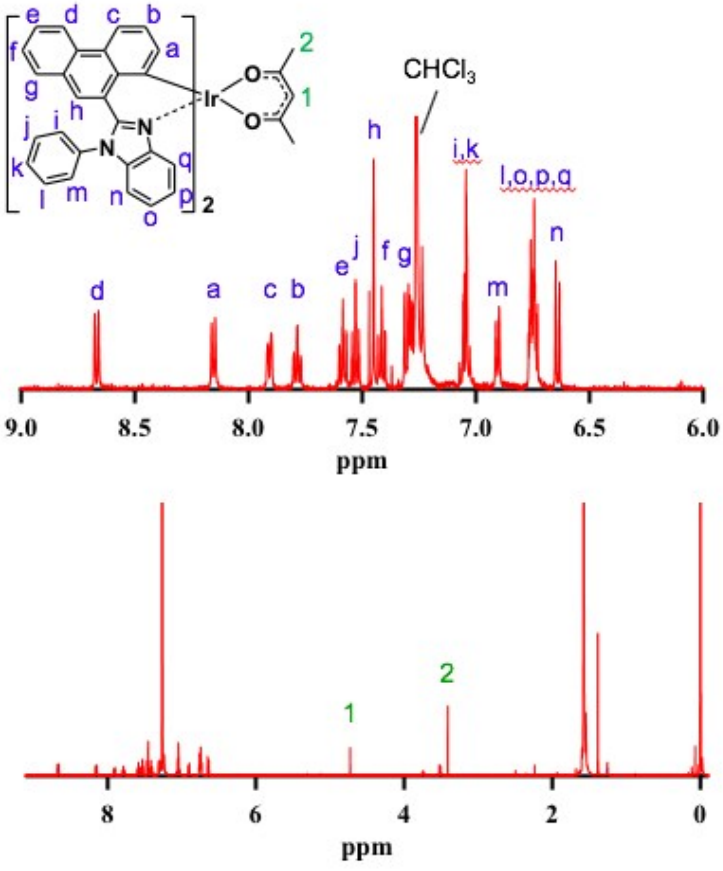


Figure S4. ^{1}H NMR (500 MHz) spectrum of $Ir(pnbi)_2(acac)$ in $CDCl_3$.

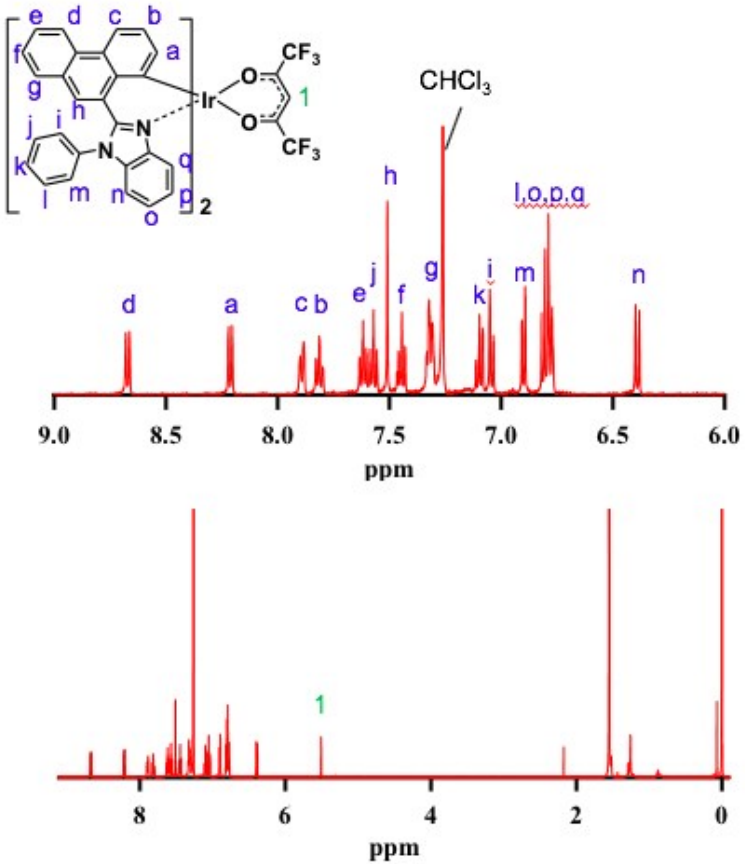


Figure S5. ^{1}H NMR (500 MHz) spectrum of $Ir(pnbi)_2(hfpd)$ in $CDCl_3$.

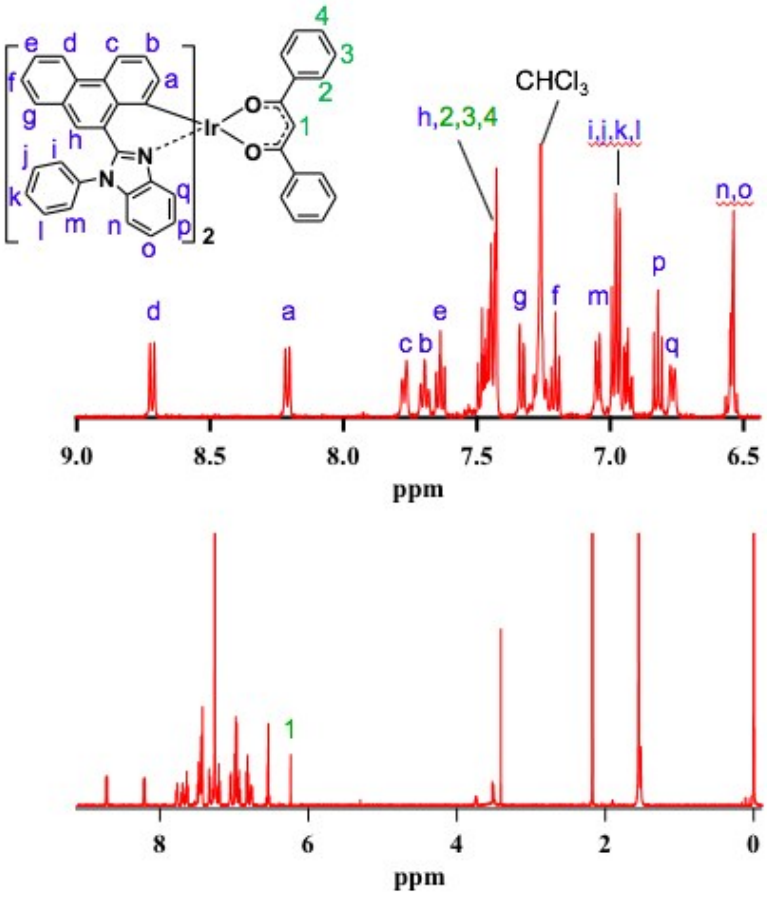


Figure S6. ^{1}H NMR (500 MHz) spectrum of Ir(pnbi)$_2$(dppd) in $CDCl_3$.

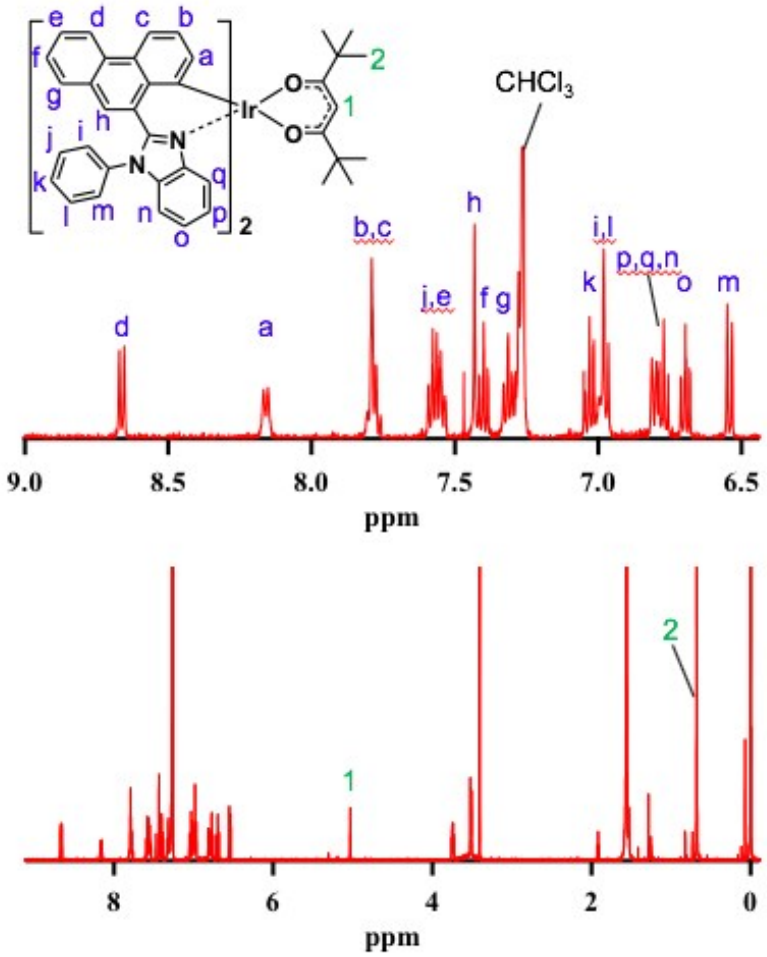


Figure S7. ^{1}H NMR (500 MHz) spectrum of Ir(pnbi)$_2$(tmehd) in $CDCl_3$.

3. ESI-TOF-MS spectra of Ir complexes

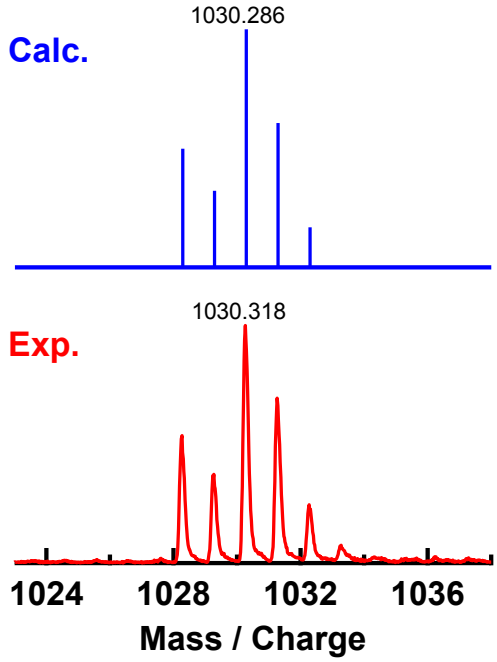


Figure S8 ESI-TOF-MS spectrum of Ir(pnbi)$_2$(acac): *m/z* 1030.318 (calcd for $[C_{59}H_{41}IrN_4O_2]^+$, : 1030.286).

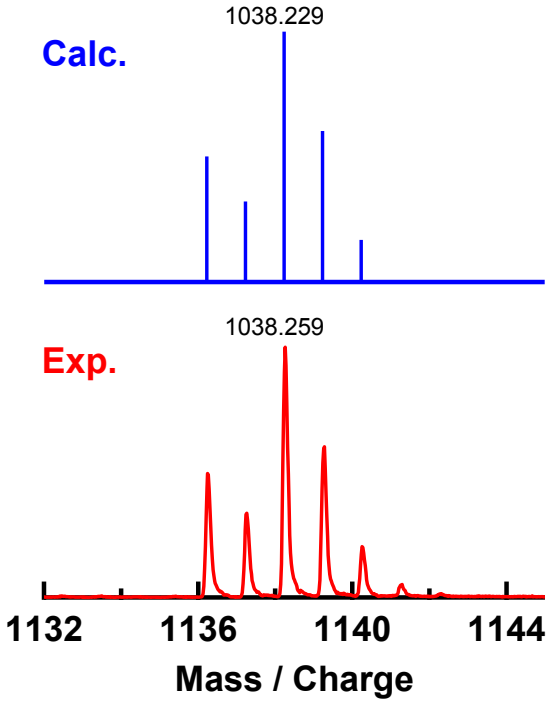
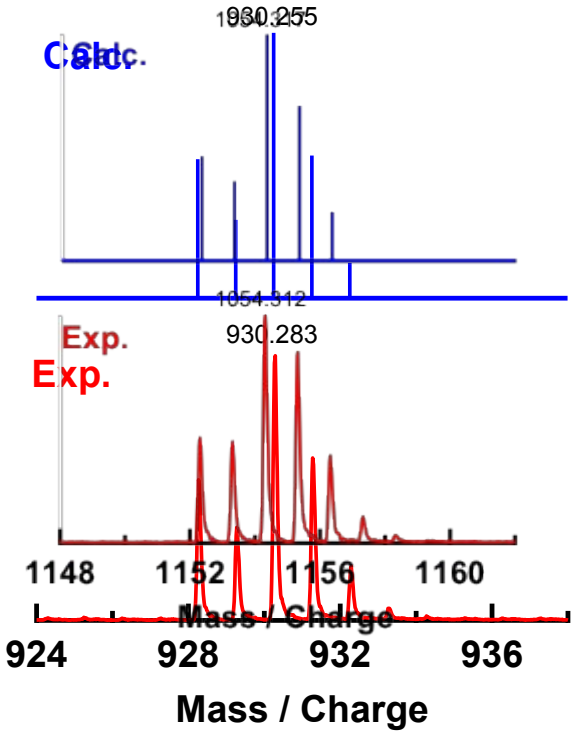


Figure S9 ESI-TOF-MS spectrum of Ir(pnbi)$_2$(hfpd): *m/z* 1038.259 (calcd for $[C_{59}H_{35}IrN_4O_2]^+$, : 1038.229).



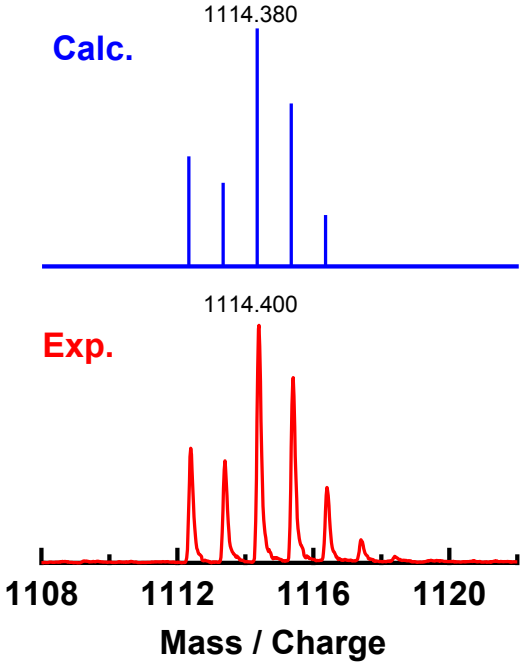


Figure S10 ESI-TOF-MS spectrum of Ir(pnbi)$_2$(dppd): *m/z* 1054.312 (calcd for $[C_{69}H_{45}IrN_4O_2]^+$, : 1054.317).

Figure S11. ESI-TOF-MS spectra Ir(pnbi)$_2$(tmehd): *m/z* 1114.400 (calcd for $[C_{69}H_{45}IrN_4O_2]^+$, : 1114.380).

Figure S12 ESI-TOF-MS spectrum of Ir(nbi)$_2$(acac): *m/z* 930.283 (calcd for $[C_{69}H_{45}IrN_4O_2]^+$, : 930.255).

4. Electrochemical data

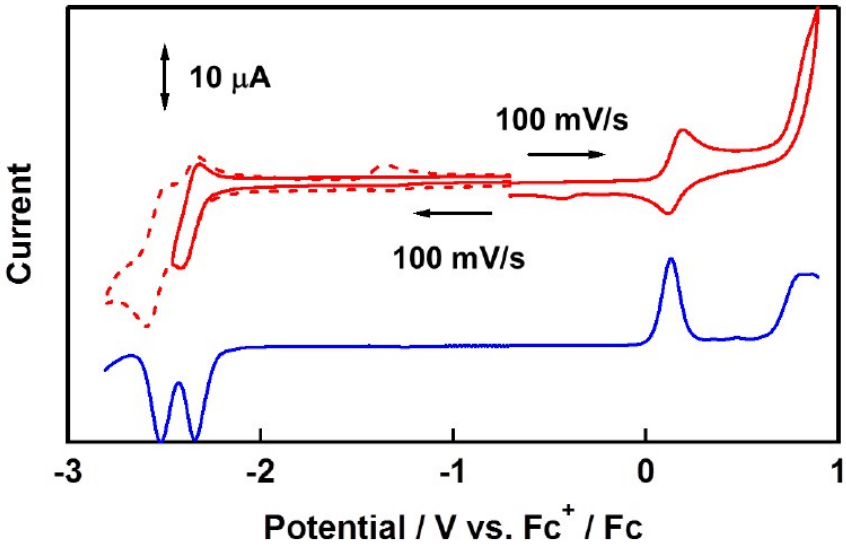


Figure S13. Cyclic and differenfial pulse voltammograms of $Ir(pnbi)_2(acac)$ in DMF (0.1 M $[TBA][PF_6]$) at a glassy carbon electrode.

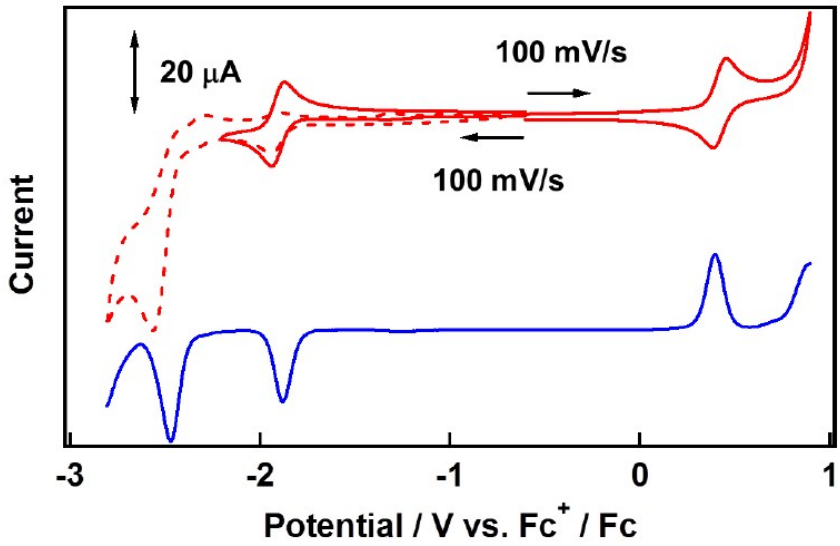
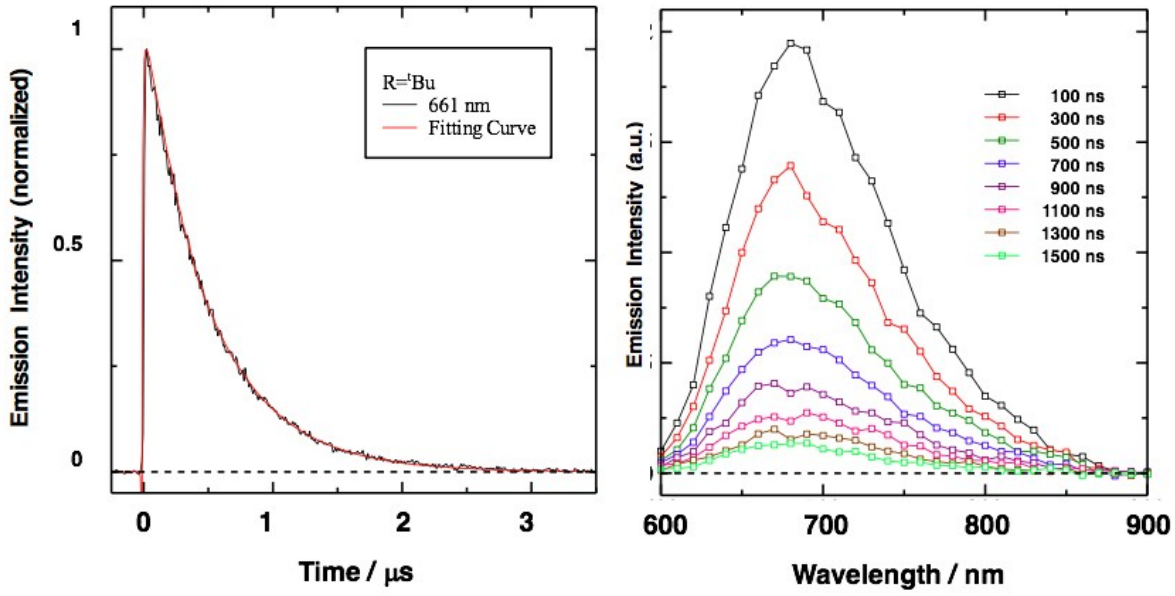


Figure S14. Cyclic and differenfial pulse voltammograms of $Ir(pnbi)_2(hfpd)$ in DMF (0.1 M $[TBA][PF_6]$) at a glassy carbon electrode.

5. Photophysical data of $Ir(pnbi)_2(tmehd)$
Room temperature



77 K

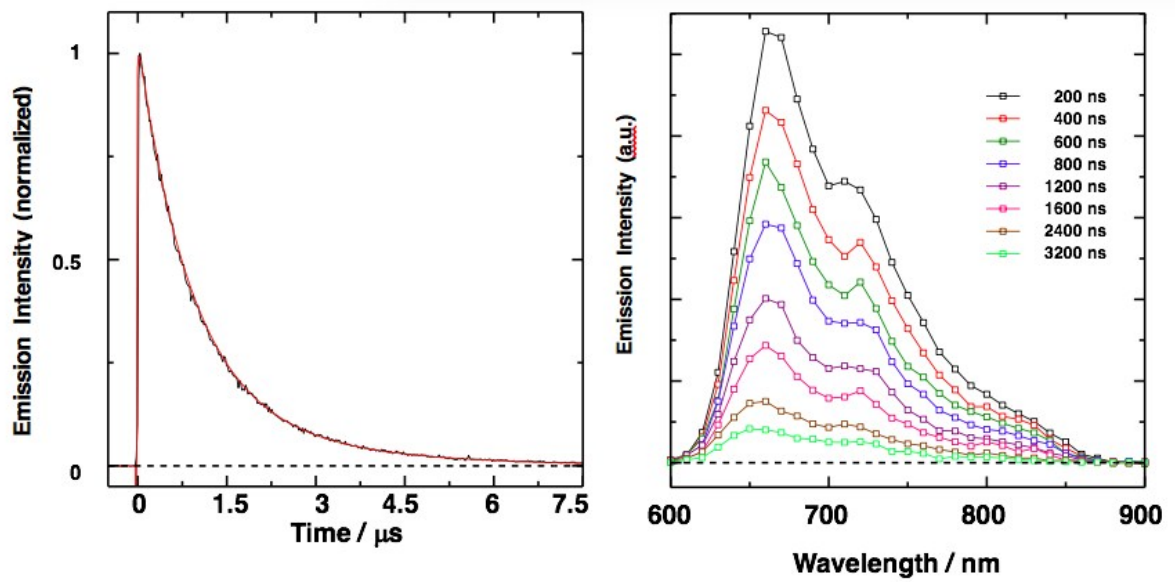


Figure S15. Emission decay curves and time-resolved emission spectra of $Ir(pnbi)_2(tmehd)$ in CH_2Cl_2 at room temperature and 77 K.

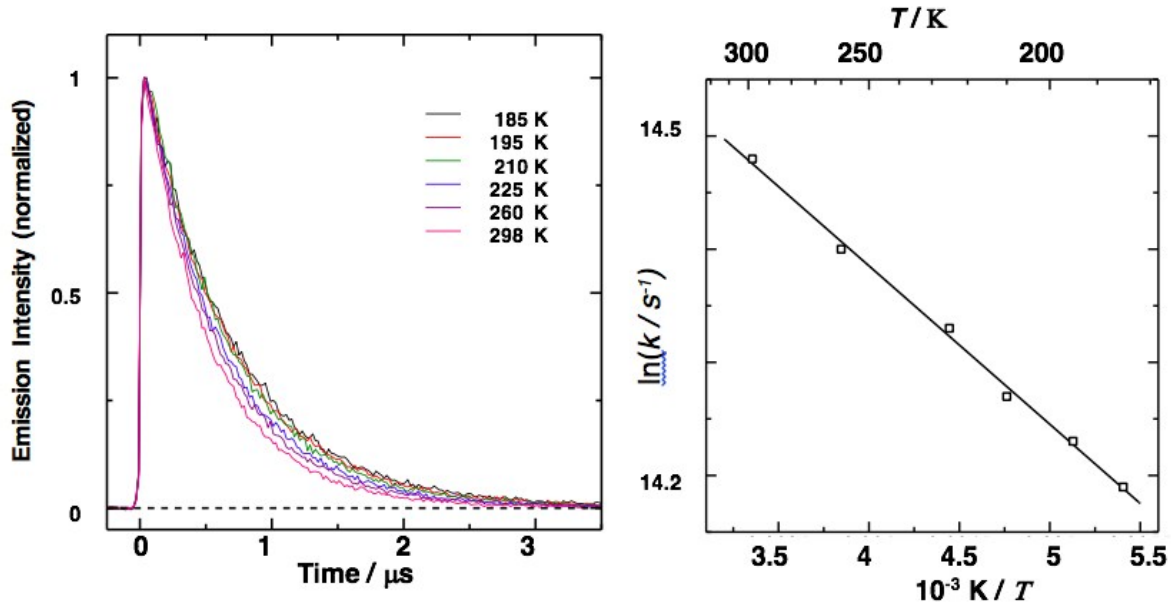


Figure S16. Temperature dependence of the emission decay curves and their Arrhenius plots.

Table S4. Temperature dependence of the emission lifetime and calculated radiative decay constants of $Ir(pnbi)_2(tmehd)$ in CH_2Cl_2.

T / K	*τ* / ns	10^{-6} *k* / s^{-1}
185	688	1.45
195	661	1.51
210	635	1.58
225	598	1.67
260	557	1.79
298	515	1.94

Table S5. Emission lifetime of the Ir-cyclometalated complexes in toluene at room temperature.

Complex	Lifetime, τ ns
$Ir(pnbi)_2(acac)$	557 (2370)[a]
$Ir(pnbi)_2(dppd)$	297
$Ir(pnbi)_2(tmehd)$	580

[a] Reported in ref. 22.

6. DFT calculations of the Ir(pndi)$_2$(acac) complex with two different Ir-(N^C) ring structures: a five-membered or a six-membered structure.

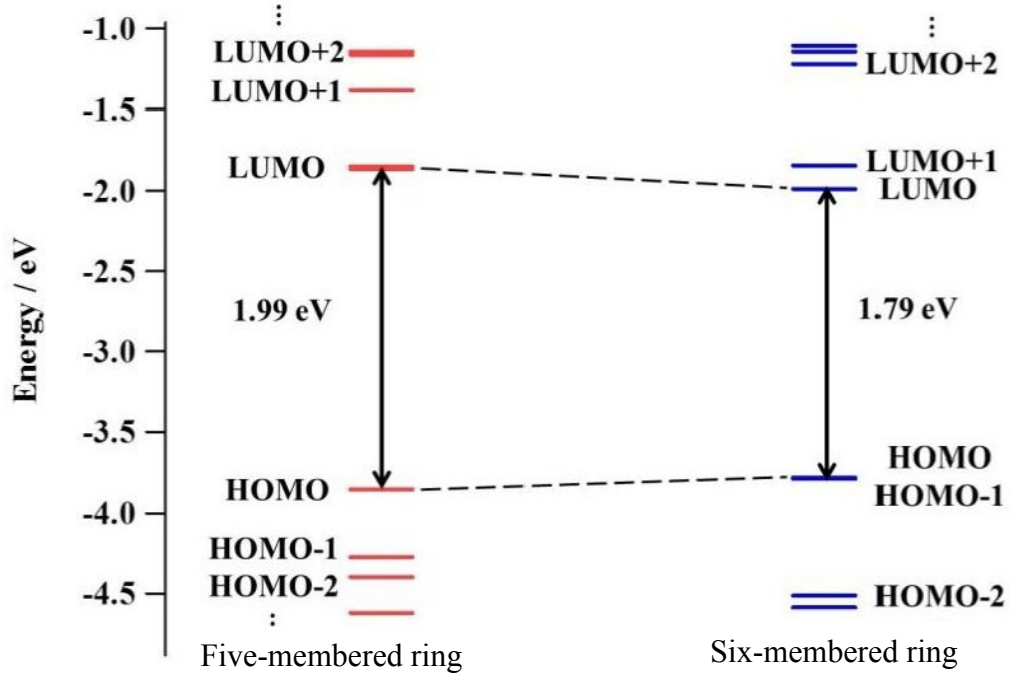


Figure S17. Dependence of the MO levels of Ir(pndi)$_2$(acac) on the ring size, including the solvent effect: five-membered ring (left) and six-membered ring structure (right).

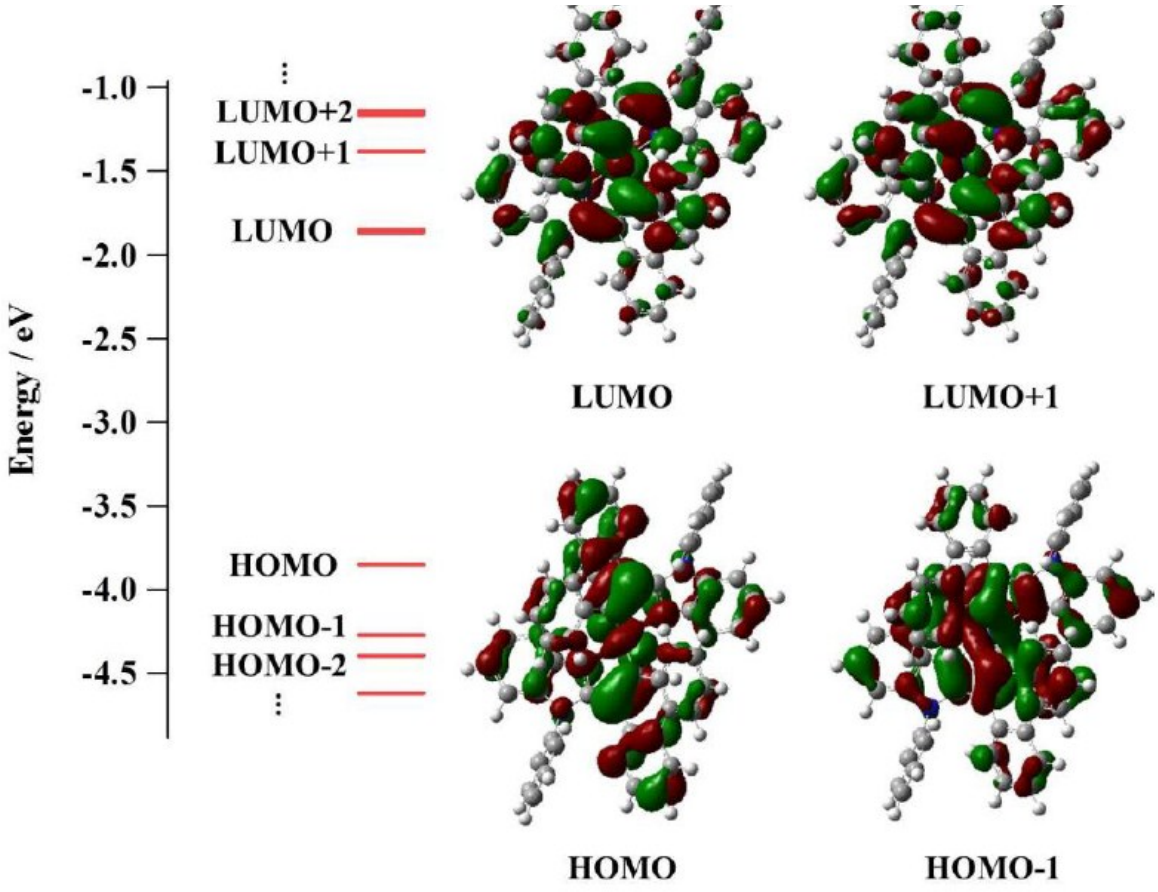
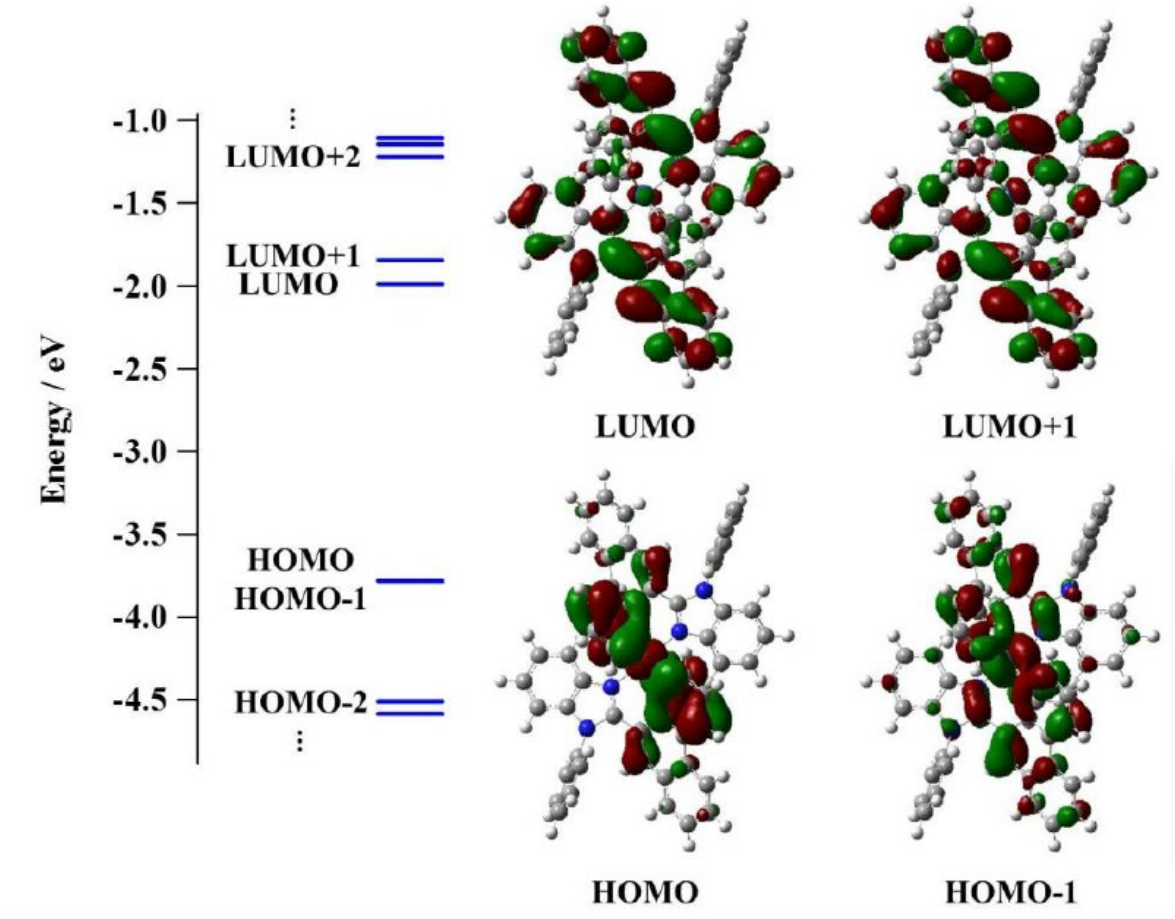


Figure S18. Frontier MOs of Ir(pndi)$_2$(acac) with five-membered Ir(C^N) ring structures.


Energy / eV
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
LUMO+2
LUMO+1
LUMO
HOMO
HOMO-1
HOMO-2
LUMO
LUMO+1
HOMO
HOMO-1