

Supporting Information

Five-Coordinate Iridium(III) Complex with $\Delta\Delta$ Chirality

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1. NMR and MS spectra of [Ir(2-Bubzq)₂Cl]

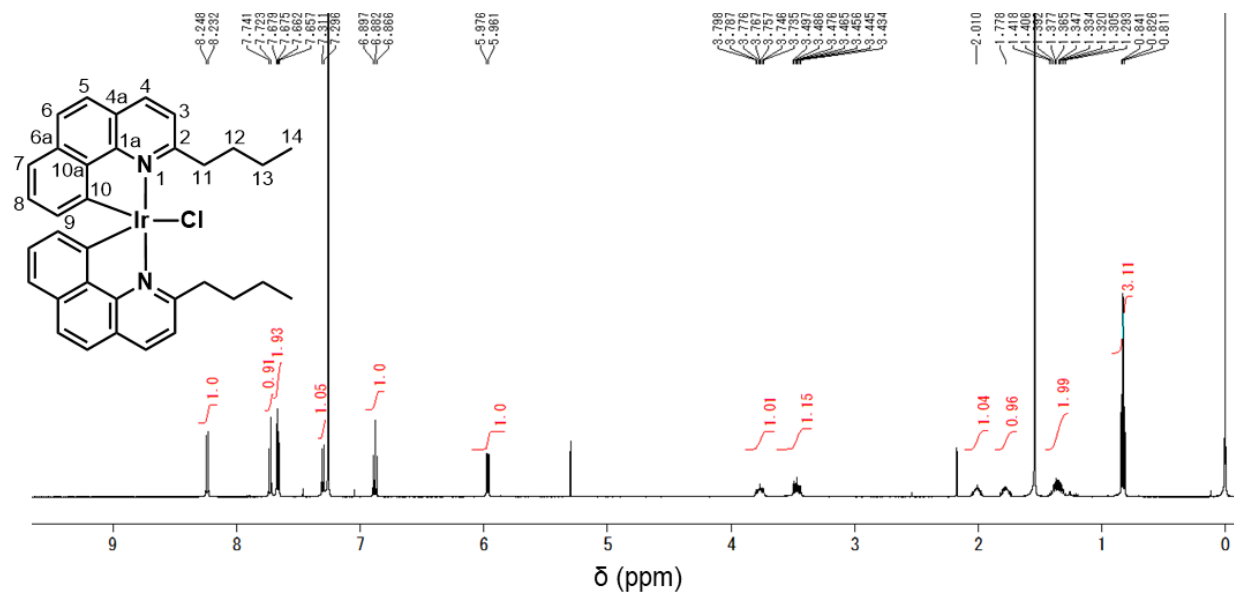


Figure S1. ¹H NMR spectrum of [Ir(2-Bubzq)₂Cl] in CDCl₃ (500 MHz, 27 °C).

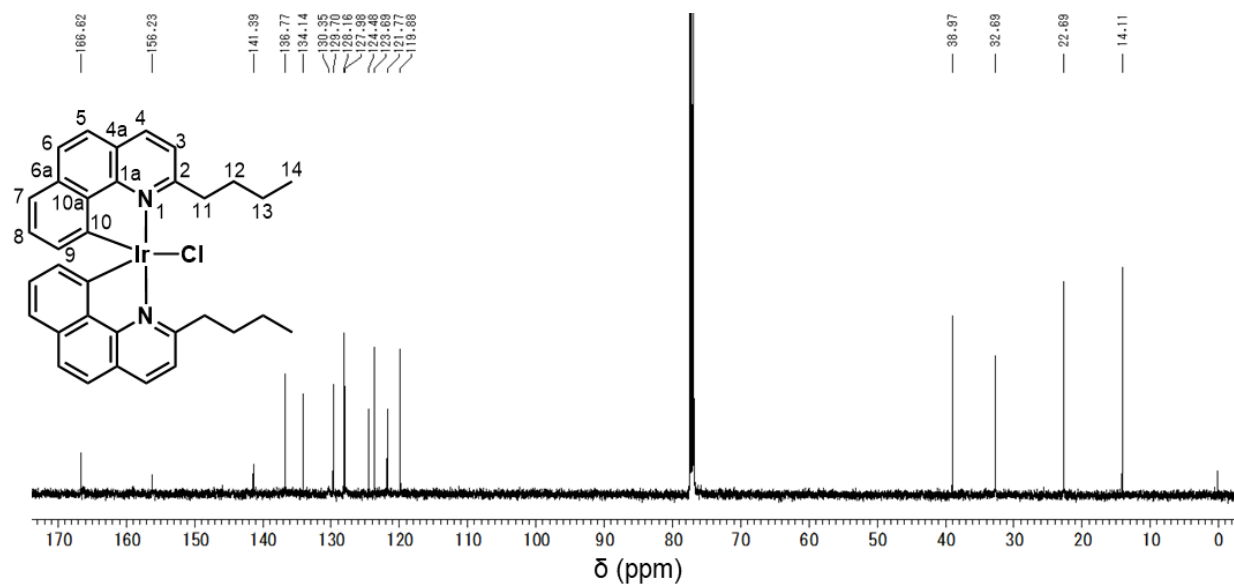


Figure S2. ¹³C NMR spectrum [Ir(2-Bubzq)₂Cl] in CDCl₃ (126 MHz, 27 °C).

[Mass Spectrum]
Data : 20180914001 Date : 14-Sep-2018 13:49
Instrument : MS7000
Sample : Ir-dimer Bu-bzq
Note : Matrix:NBA
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 1.50 min Scan# : (10,38) Temp : 3276.7 deg.C
BP : m/z 154 Int. : 563.00 (5903505)
Output m/z range : 50 to 2000 Cut Level : 0.00 %

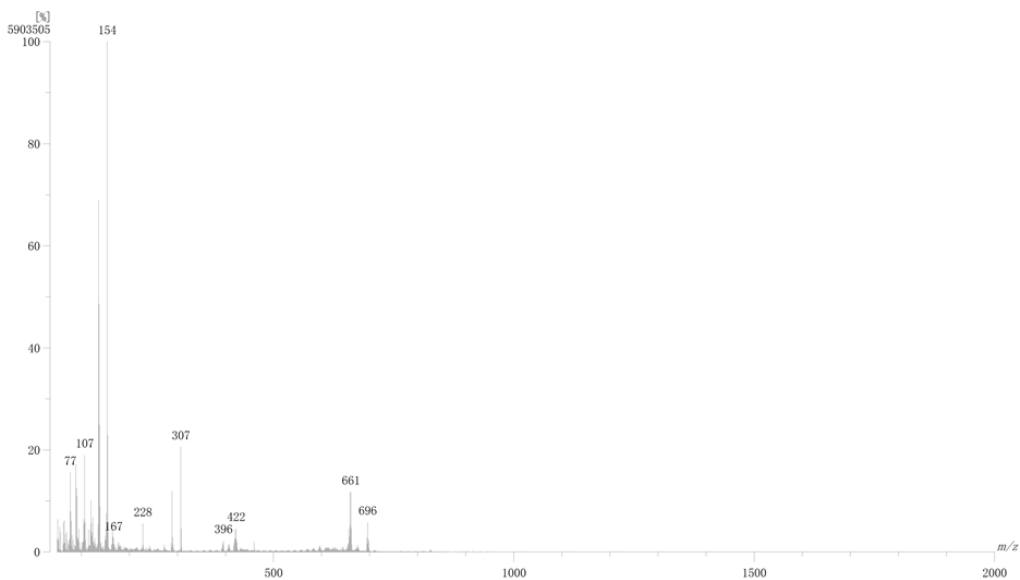


Figure S3. LRMS spectrum of $[\text{Ir}(2\text{-Bubzq})_2\text{Cl}]$ (FAB^+ , 3-nitrobenzyl alcohol (3-NBA) as a matrix).

2. X-ray analysis data

2.1 X-Ray analysis of [Ir(2-Bubzq)₂Cl]

Table S1. Selected bond distances (Å) and angles (deg) of [Ir(2-Bubzq)₂Cl].

<u>Distance (Å)</u>			
Ir1 – C10	1.975 (4)	Ir1 – N1	2.057 (3)
Ir1 – C30	2.001 (4)	Ir1 – N2	2.112 (3)
Ir1 – Cl1	2.4341 (10)		
<u>Angle (deg)</u>			
C30—Ir1—N21	81.26 (16)	N21—Ir1—Cl1	102.27 (10)
C30—Ir1—N1	91.07 (15)	N1—Ir1—Cl1	86.68 (9)
C10—Ir1—N21	92.65 (15)	C10—Ir1—Cl1	119.21 (12)
C10—Ir1—N1	82.37 (15)	C30—Ir1—Cl1	152.28 (11)
C10—Ir1—C30	87.75 (16)		

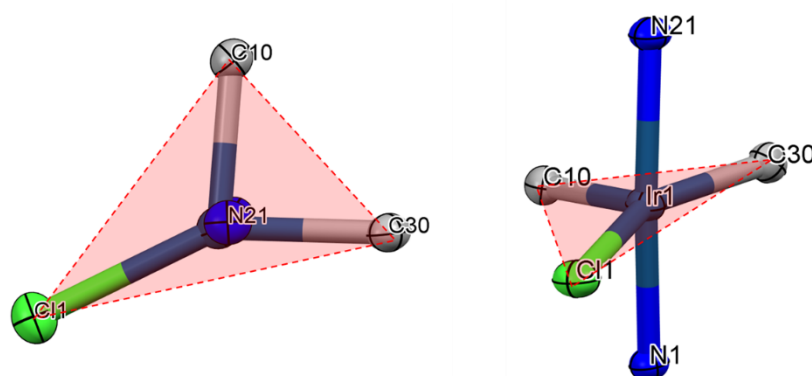


Figure S4. The distorted square pyramidal structure is deduced from the X-ray analysis: (left) the top view and (right) the side view. The space between C30 and Cl1 looks like a vacant coordination site.

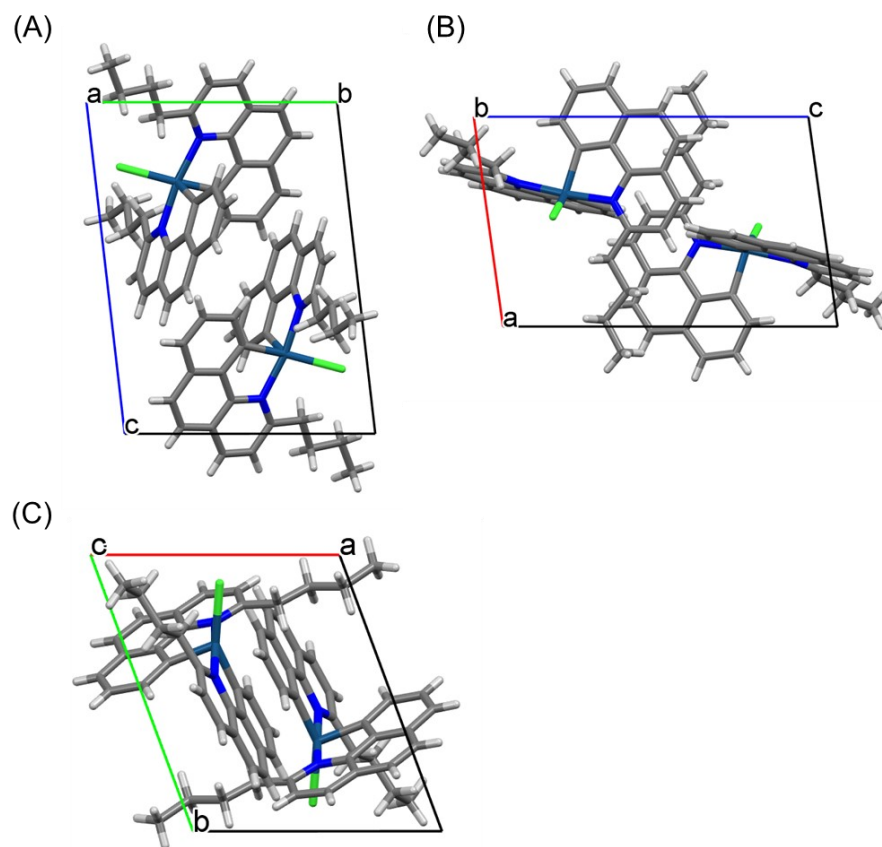


Figure S5. Crystal structures of $[\text{Ir}(\text{2-Bubzq})_2\text{Cl}]$ viewed along (A) the *a* axis, (B) the *b* axis, and (C) the *c* axis, respectively.

Table S2. Structure information of [Ir(2-Bubzq)₂Cl].

Compound	[Ir(2-Bubzq) ₂ Cl]
Recrystallization solvent	Dichloromethane
Formula	C ₃₄ H ₃₂ IrN ₂ Cl
FW	696.29
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> [Å]	9.4178 (6)
<i>b</i> [Å]	11.1107 (8)
<i>c</i> [Å]	14.0254 (6)
α [deg]	79.931 (4)
β [deg]	79.001 (4)
γ [deg]	68.307 (6)
<i>V</i> [Å ³]	1329.82 (15)
<i>Z</i>	2
μ [mm ⁻¹]	10.84
Crystal size	0.16 × 0.10 × 0.06
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.029, 0.074, 1.07
wR_2	0.074 (all data)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13583, 5254, 4941
No. of parameters	345
CCDC No.	1974083

2.2 The τ value of $[\text{Ir}(2\text{-Bubzq})_2\text{Cl}]$

To distinguish whether the geometry of the coordination center is SP or TBP, τ value is defined by Addison *et al.* which is the parameters as $(\beta - \alpha)/60$, where β and α ($\beta > \alpha$) are the two greatest bond angles of the coordination center.^{S1} The τ is zero for an ideal SP geometry, while it is unity for an ideal TBP geometry. As the τ of $[\text{Ir}(2\text{-Bubzq})_2\text{Cl}]$ is 0.31, the iridium ion is in between SP and TBP geometry. The previously reported bis-chelated five-coordinate iridium complex has $\tau = 0.65$,^{S2} which means that these structures are classified in between SP and TBP like $[\text{Ir}(2\text{-Bubzq})_2\text{Cl}]$.

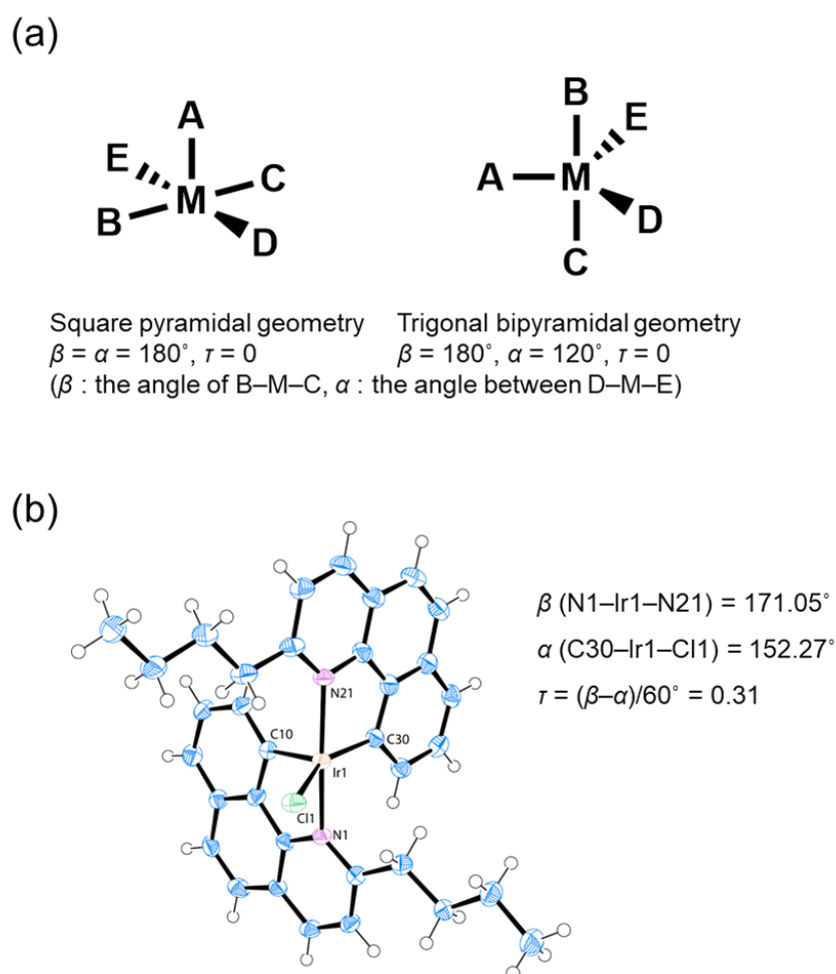


Figure S6. (a) Schematic diagram of the extreme values of τ in a square pyramidal and trigonal bipyramidal geometry. The τ value defined as $(\beta - \alpha)/60$, where β and α ($\beta > \alpha$) are the two greatest bond angles of the coordination center. (b) The molecular structure of $[\text{Ir}(2\text{-Bubzq})_2\text{Cl}]$ with atom numbering and the τ value.

3. Optical resolution of [Ir(2-Bubzq)₂Cl]

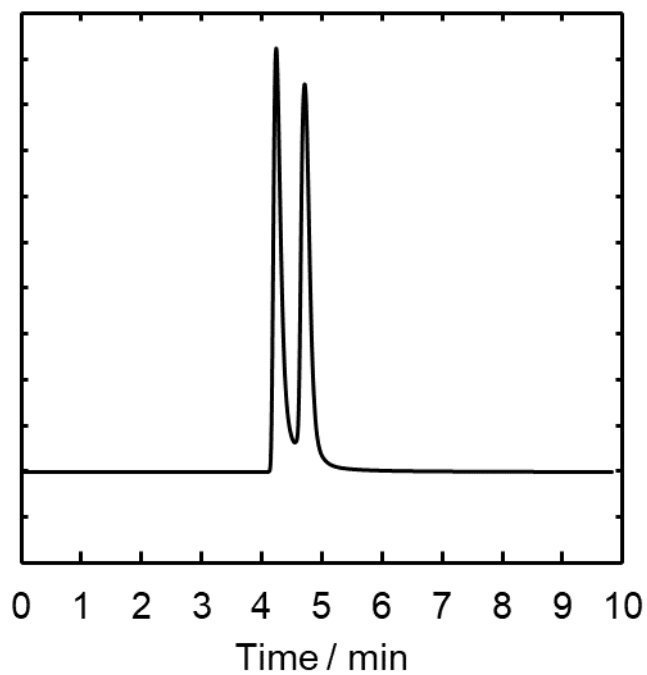


Figure S7. The HPLC chromatogram of [Ir(2-Bubzq)₂Cl] was eluted on a 4 mm (i.d.) × 25 cm chiral column (IG Daicel, Japan) at a flow rate of 0.75 ml/min. The eluent was dichloromethane. The monitoring wavelength was 511 nm. The vertical axis is the intensity in terms of arbitrary unit.

4. Thermal stability of [Ir(2-Bubzq)₂Cl]

The thermal stability of the enantiomers of [Ir(2-Bubzq)₂Cl] was examined by heating the toluene solution (3.2 mM) at 70 °C for 8 h. No racemization was confirmed by the measurement of ECD and HPLC.

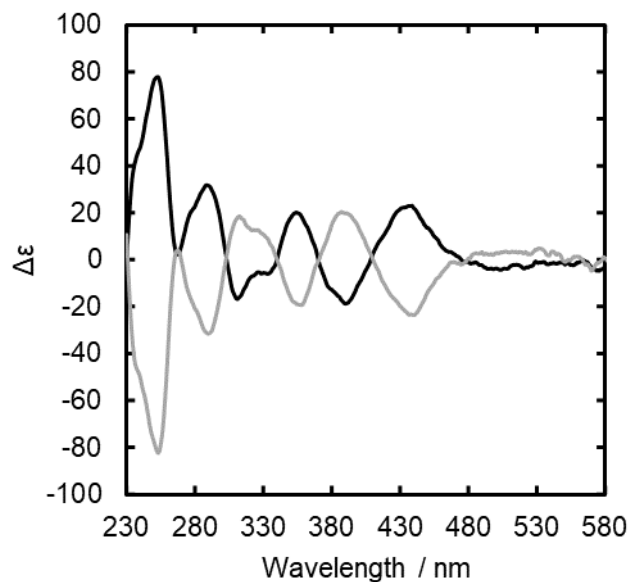


Figure S8. The ECD spectra in dichloromethane of [Ir(2-Bubzq)₂Cl] obtained by the heating experiment. The black and grey curves indicate the fractions collected at 1st and 2nd elution peaks, respectively.

5. Experimental and calculated VCD and IR data of [Ir(2-Bubzq)₂Cl]

Table S3. Assignment of VCD and IR peaks of enantiopure [Ir(2-Bubzq)₂Cl] in CHCl₃

NO	Exp. First peak (optical resolution) / cm ⁻¹	Calc. C ₂ symmetry Λ / cm ⁻¹	assignment
1	1628 (-)	1636 (-) B	bzq (C-C) stretching
2	1594 (+)	1611 (+) A	bzq(C-C-C) stretching
3	1565/1554 (-)	1587 (-) B	bzq(C-C-C) stretching
4	1509 (+)	1519 (+) A	bzq(C-C-C) stretching, C-H (bzq)
5	1502 (-)	1515 (-) B	bzq(C-C-C) stretching, C-H (bzq)
6	1431 (+)	1434 (+) A	bzq(C-C-C) stretching, C-H (bzq), butyl (C-C) bending
7	1382 (+)	1391 (+) A	butyl (CH ₃) bending, butyl (C-C-C) stretching butyl (CH ₂) bending
8	1375 (-)	1389 (-) B	butyl (CH ₃) bending, butyl (C-C-C) stretching butyl (CH ₂) bending (in-phase)
9	1303 (+)	1337 (+) B	butyl (CH ₂) bending (out of phase), bzq(C-C-C) stretching
10	1214 (+)	1226 (+) B	bzq and butyl CH bending
11	1197/1190 (-/+)	1194 (+) B	bzq C-H bending
12	1140 (-)	1152 (-) B	bzq C-H bending
13	1117 (+)	1118 (+) A	bzq CH bending
14	1107 (-)	1112 (-) B	butyl CH bending
15	1099(+)	1106 (+) A	butyl C-C-C bending
16	1036 (-)	1038 (-) B	butyl C-C -C bending, bzq C-C bending

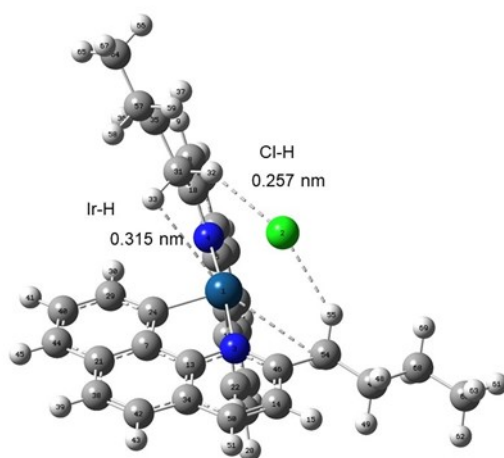


Figure S9. The optimized structure of Λ -[Ir(2-Bubzq)₂Cl] in CHCl₃ medium. The complex was assumed to take C_2 symmetry.

6. X-ray analysis of $[\text{Ir}(\text{2-Bubzq})_2(\text{EtOH})\text{Cl}]$

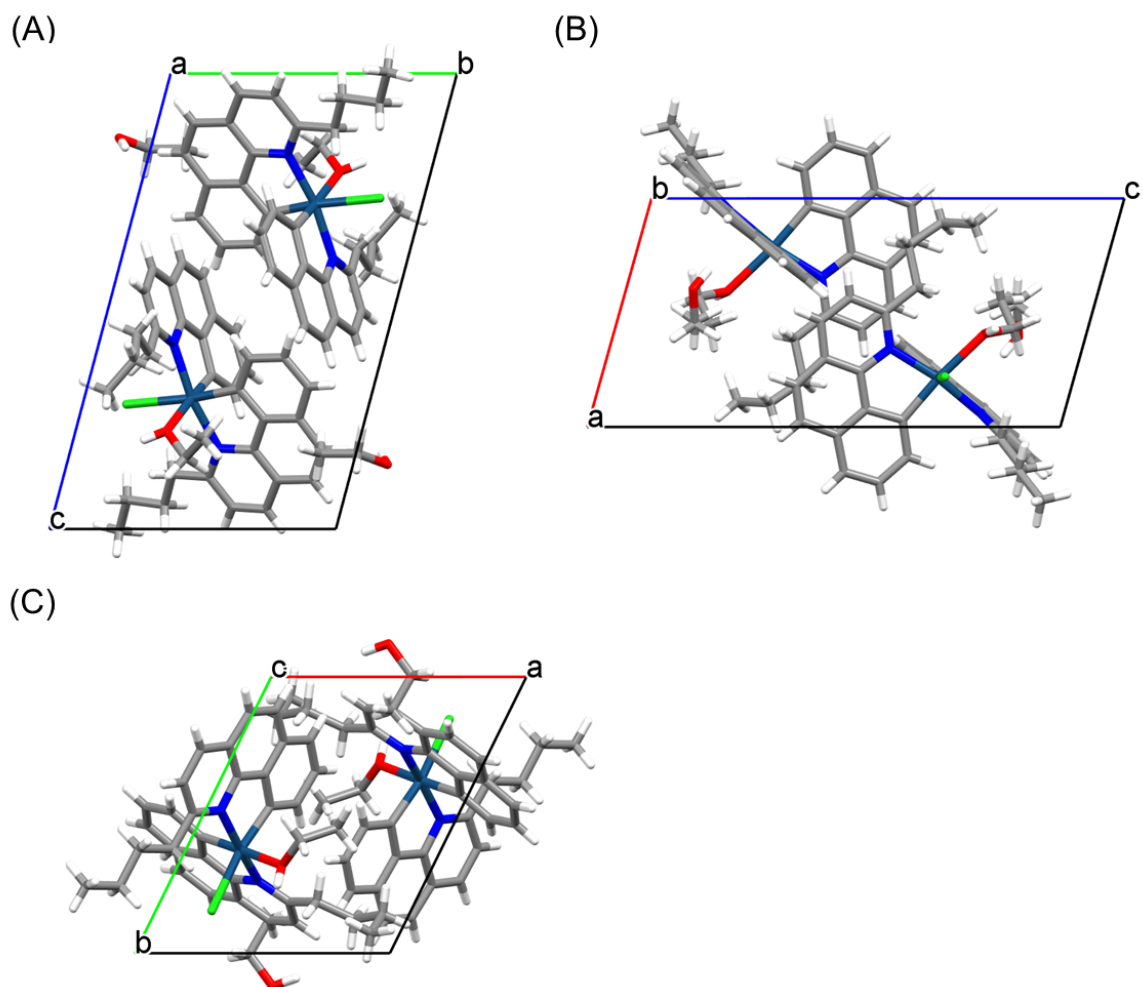


Figure S10. Crystal structures of $[\text{Ir}(\text{2-Bubzq})_2(\text{EtOH})\text{Cl}]$ viewed along (A) the a axis, (B) the b axis, and (C) the c axis, respectively.

Table S4. Structure information of [Ir(2-Bubzq)₂(EtOH)Cl].

Compound	[Ir(2-Bubzq) ₂ (EtOH)Cl]
Recrystallization solvent	Ethanol
Formula	C ₃₆ H ₃₈ IrN ₂ OCl, EtOH
FW	788.40
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> [Å]	9.3674 (4)
<i>b</i> [Å]	11.2876 (5)
<i>c</i> [Å]	17.3082 (6)
α [deg]	99.175 (3)
β [deg]	100.384 (3)
γ [deg]	113.623 (4)
<i>V</i> [Å ³]	1593.84 (12)
<i>Z</i>	2
μ [mm ⁻¹]	4.310
Crystal size	0.04 × 0.04 × 0.02
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.039, 0.072, 1.05
wR_2	0.072 (all data)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14272, 7672, 6817
No. of parameters	408
CCDC No.	2085213

7. Solvent effects of [Ir(2-Bubzq)₂Cl]

7.1 Experimental and calculated UV-vis spectra of [Ir(2-Bubzq)₂Cl]

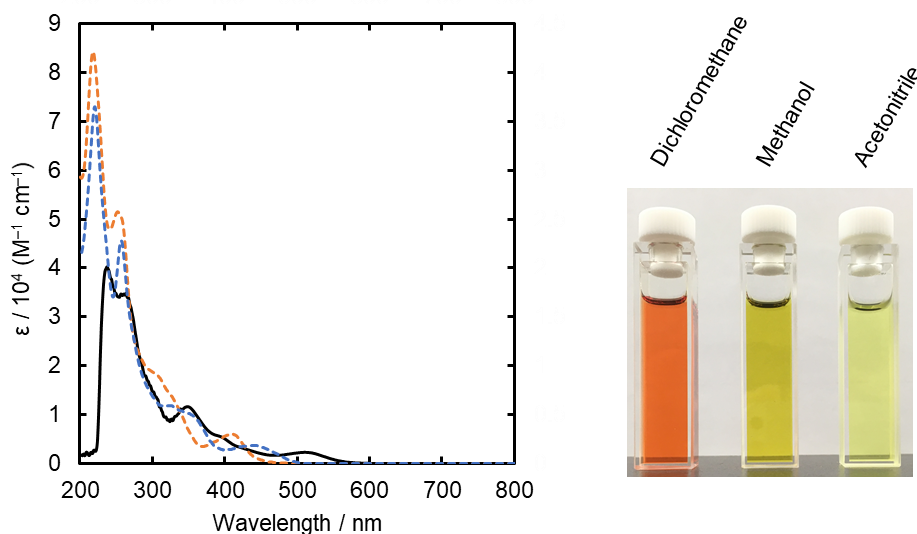


Figure S11. The experimental UV-vis spectra of [Ir(2-Bubzq)₂Cl] in dichloromethane (5.9×10^{-5} M), methanol (4.4×10^{-5} M), and acetonitrile (5.0×10^{-5} M). The black solid, blue dotted and orange dotted lines indicated dichloromethane, methanol, and acetonitrile, respectively.

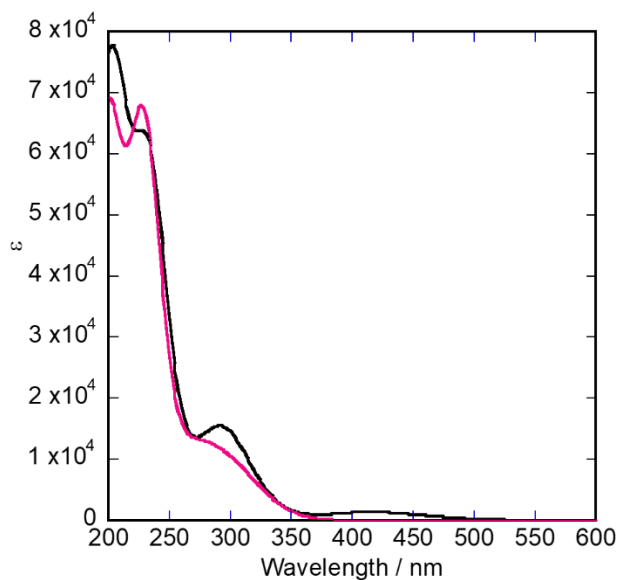


Figure S12. Calculated UV-vis spectra by TDDFT using the LC-BLYP functional. The black and red show dichloromethane and ethanol solvent, respectively. At the spectral edge of 410 nm, the HOMO-LUMO transition is assigned in CH₂Cl₂ solvent. The calculated UV-vis spectrum in ethanol is calculated as a six-coordination with an ethanol molecule.

7.2 The experimental and calculated VCD and IR spectra of [Ir(2-Bubzq)₂Cl]

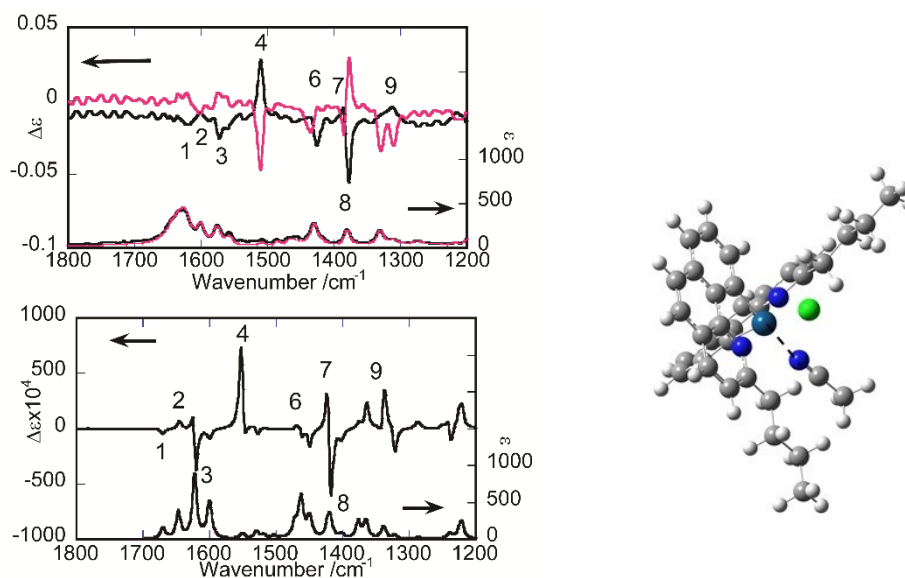


Figure S13. (Upper left) The observed IR (lower) and VCD (upper) spectra of enantiopure [Ir(2-Bubzq)₂Cl] in CD₃CN. The black and red curves indicate the optically resolved 1st and 2nd elution peaks, respectively. The baseline correction was performed for the VCD and IR spectra by subtracting the solvent contribution. (Lower left) the DFT calculation of IR and VCD spectra for an enantiopure six-coordinate Ir(III) complex, Λ -[Ir(2-Bubzq)₂(CH₃CN)Cl], in CH₃CN medium. The scale factor was not included in the calculation. The numbers indicate assignments in VCD bands. (Right) The optimized structure of Λ -[Ir(2-Bubzq)₂(CH₃CN)Cl].

8. Reaction with carbon monoxide

8.1 Reaction of [Ir(2-Bubzq)₂Cl] with carbon monoxide

A solution of [Ir(2-Bubzq)₂Cl] (29.0 μmol) in CH₂Cl₂ was bubbled by carbon monoxide (CO) for 1 minute. After removal of volatile materials by evaporation under reduced pressure, the residue was washed by *n*-hexane. [Ir(2-Bubzq)₂(CO)Cl] was obtained as a white solid (28.8 μmol, Yield 99%). ¹H NMR (500 MHz; CDCl₃) 0.98 (3H, t, *J* = 7.5 Hz), 1.02 (3H, t, *J* = 7.5 Hz), 1.62 (4H, m), 1.96 (2H, m), 2.06 (1H, m), 2.12 (1H, m), 3.67 (2H, m), 4.12 (1H, m), 4.24 (1H, m), 6.00 (1H, d, *J* = 7.5 Hz), 6.15 (1H, d, *J* = 7.5 Hz), 6.95 (1H, t, *J* = 7.5 Hz), 6.98 (1H, t, *J* = 7.5 Hz), 7.31 (1H, d, *J* = 7.5 Hz), 7.35 (1H, d, *J* = 7.5 Hz), 7.54 (1H, d, *J* = 8.5 Hz), 7.63 (1H, d, *J* = 8.5 Hz), 7.65 (1H, d, *J* = 8.5 Hz), 7.69 (2H, d, *J* = 8.5 Hz), 7.71 (1H, d, *J* = 8.5 Hz), 8.26 (1H, d, *J* = 8.5 Hz), 8.35 (1H, d, *J* = 8.5 Hz); ¹³C NMR (126 Hz, CD₂Cl₂) 14.16, 14.30, 22.62, 22.70, 32.37, 33.81, 40.32, 44.19, 121.38, 122.36, 122.44, 124.11, 124.15, 124.54, 126.20, 126.52, 127.74, 127.91, 128.70, 129.08, 129.11, 129.15, 134.54, 134.66, 135.92, 138.69, 138.73, 141.80, 141.99, 157.94, 158.40, 161.98, 163.62, 170.65, 176.82; LRMS(FAB⁺, 3-NBA), *m/z* = 696 (M–CO).

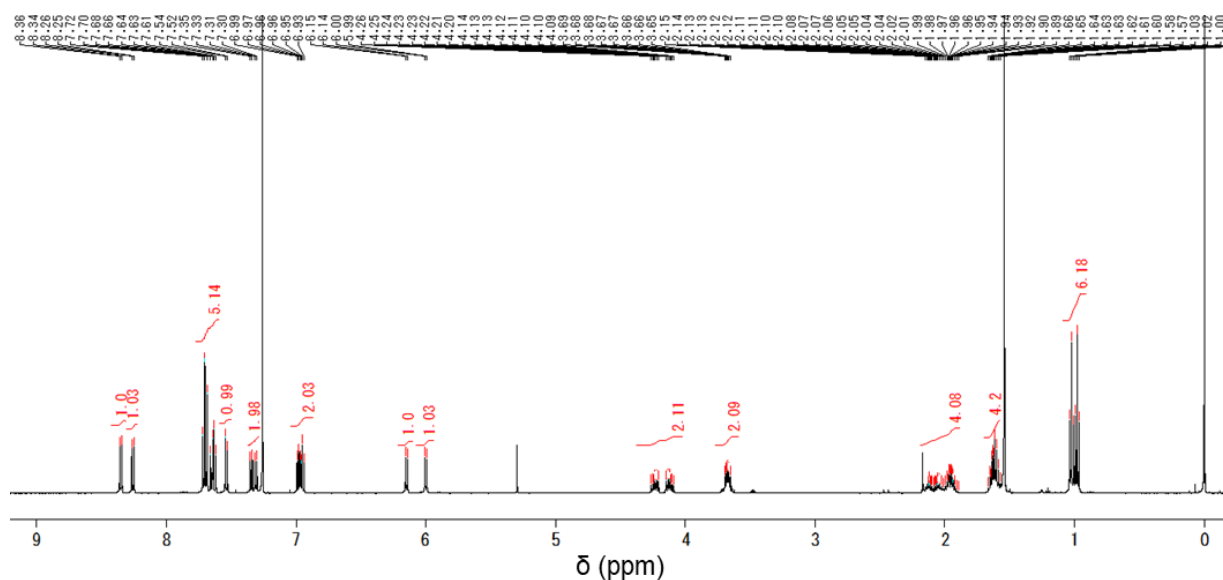


Figure S14. ¹H NMR spectrum of [Ir(2-Bubzq)₂(CO)Cl] in CDCl₃ (500 MHz, 27 °C).

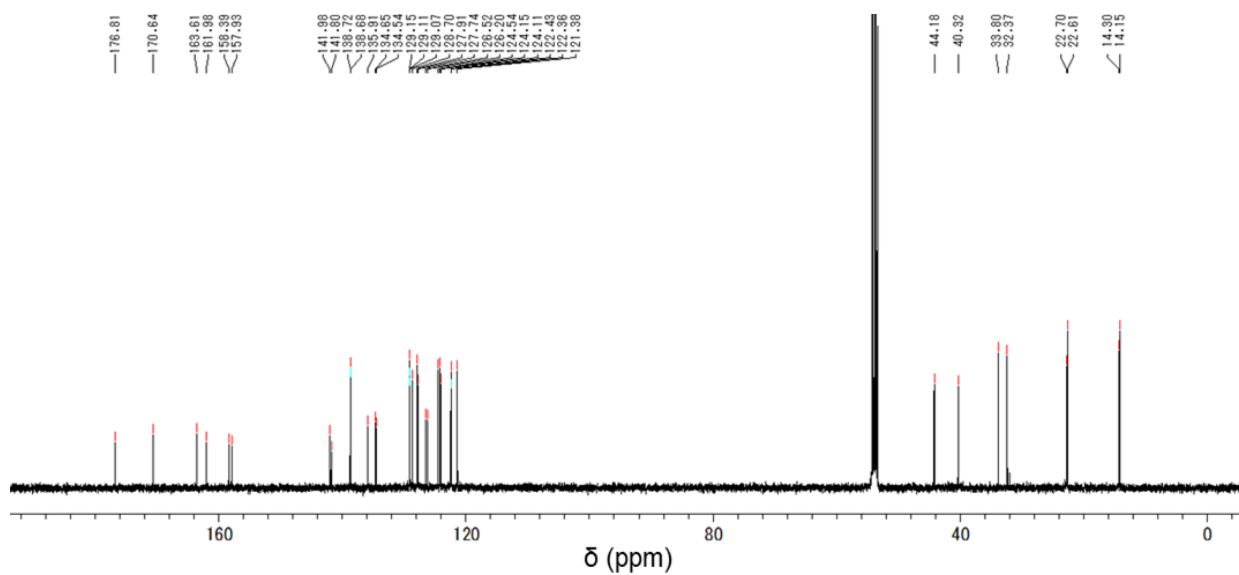


Figure S15. ^{13}C NMR spectrum of $[\text{Ir}(\text{2-Bubzq})_2(\text{CO})\text{Cl}]$ in CD_2Cl_2 (126 MHz, 27 °C).

[Mass Spectrum]
 Data : Ir-Co001 Date : 03-Jul-2019 08:46
 Instrument : MS700D
 Sample : Ir-Co
 Note : Matrix:3NBA
 Inlet : Direct Ion Mode : FAB+
 Spectrum Type : Normal Ion [MF-Linear]
 RT : 0.14 min Scan# : (2,15) Temp : 3276.7 deg.C
 BP : m/z 661.3717 Int. : 3264.82 (34234080)
 Output m/z range : 50 to 903 Cut Level : 0.00 %

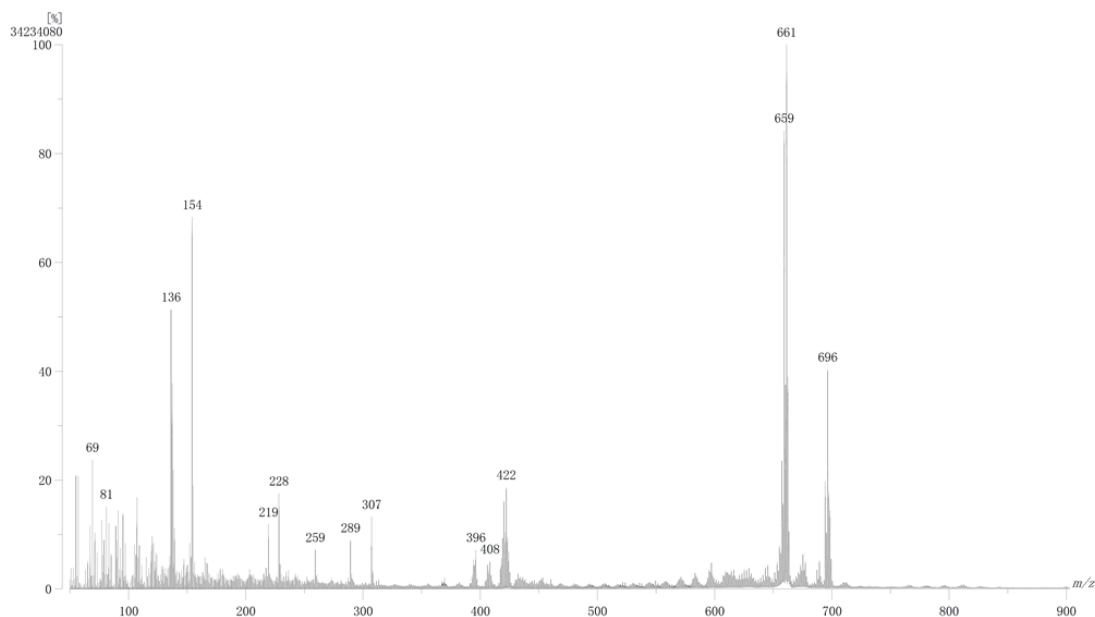


Figure S16. LRMS spectrum of $[\text{Ir}(\text{2-Bubzq})_2(\text{CO})\text{Cl}]$ (FAB^+ , 3-nitrobenzyl alcohol (3-NBA) as a matrix).

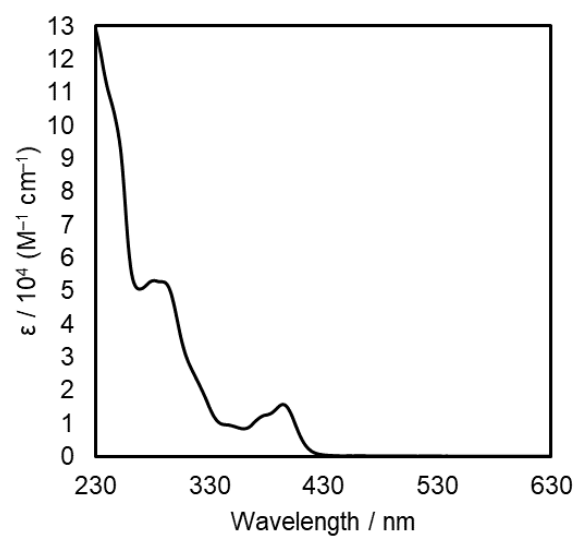
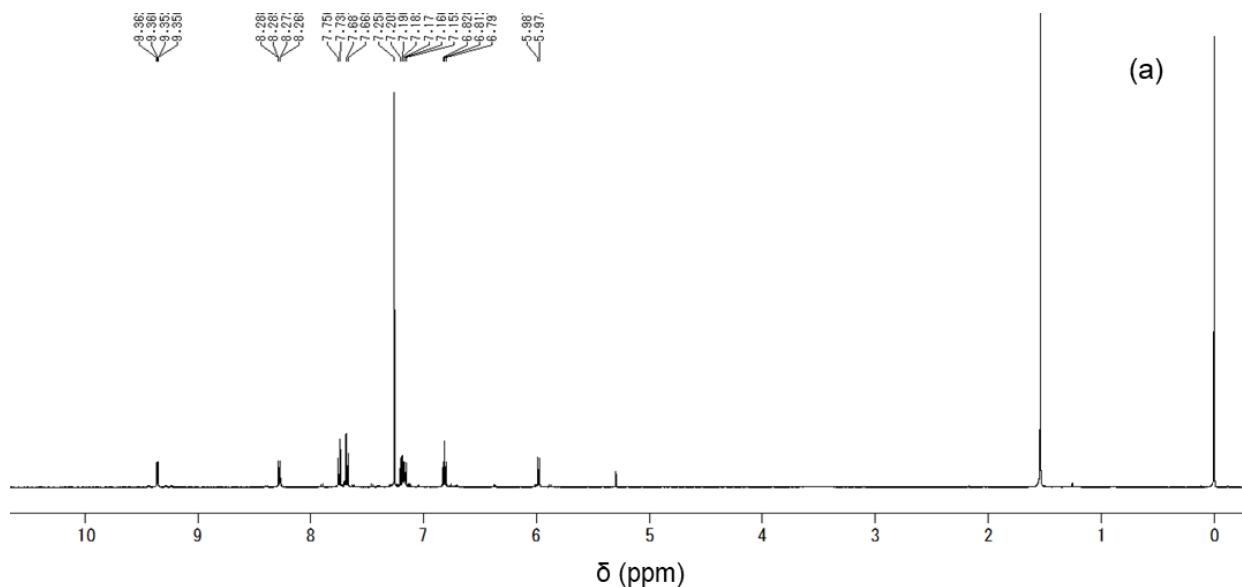


Figure S17. UV-vis spectrum of [Ir(2-Bubzq)₂(CO)Cl] in CH₂Cl₂.

8.2 Reaction of [Ir(bzq)₂Cl]₂ with carbon monoxide

A solution of [Ir(bzq)₂Cl]₂ in CH₂Cl₂ (7.2 μmol) was bubbled by CO for 1 hour. After removal of volatile materials by evaporation under reduced pressure, the residue was analysed by ¹H NMR. The integrated ratio of the ¹H NMR spectrum showed that 60% of [Ir(bzq)₂Cl]₂ reacted with CO and afforded a new complex. After CO bubbling another 4h, the reaction was completed and [Ir(bzq)₂(CO)Cl] was obtained as a white solid (13.7 μmol, Yield 95%). These results are in agreement with the previous report that [Ir(ppy)₂Cl]₂ (ppyH = 2-phenylpyridine), an analog of [Ir(bzq)₂Cl]₂, reacts with CO 5 h to give the carbonyl complex [Ir(ppy)₂(CO)Cl] quantitatively.^{S3} ¹H NMR (400 MHz; CDCl₃) 5.93 (1H, d, *J* = 7.5 Hz), 6.35 (1H, d, *J* = 7.5 Hz), 7.06 (1H, dd, *J* = 5.0, 7.5 Hz), 7.08 (1H, dd, *J* = 5.0, 7.5 Hz), 7.38 (1H, d, *J* = 8.0 Hz), 7.41 (1H, d, *J* = 8.0 Hz), 7.64 (1H, d, *J* = 5.0 Hz), 7.66 (1H, d, *J* = 5.0 Hz), 7.72 (1H, d, *J* = 9.0 Hz), 7.77 (1H, d, *J* = 8.0 Hz), 7.78 (1H, d, *J* = 8.0 Hz), 7.81 (1H, d, *J* = 9.0 Hz), 8.43 (1H, d, *J* = 8.0 Hz), 8.47 (1H, d, *J* = 8.0 Hz), 9.49 (1H, d, *J* = 5.0 Hz), 10.12 (1H, d, *J* = 5.0 Hz); ¹³C NMR (126 Hz, CDCl₃) 121.29, 121.96, 122.19, 122.79, 123.26, 123.69, 127.49, 127.66, 128.16, 128.45, 129.70, 129.94 (2C), 130.60, 134.22, 134.41, 136.87, 137.31, 137.54, 140.26, 140.84, 150.65, 151.75, 157.13, 157.29, 162.00, 172.94; LRMS(FAB⁺, 3-NBA), *m/z* = 613 (M+1).



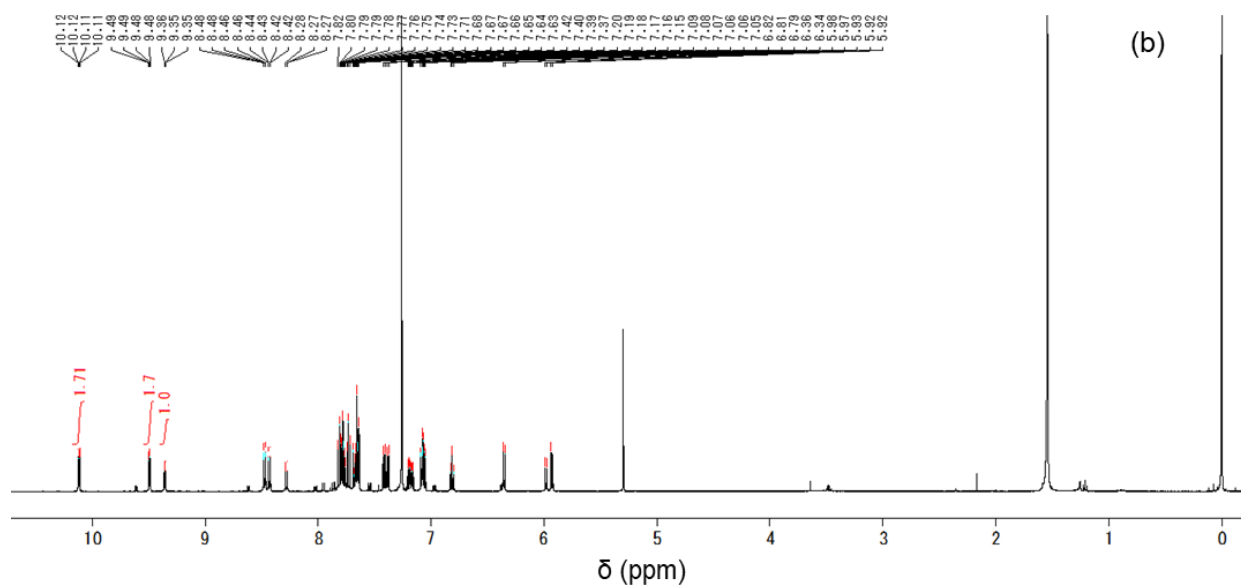


Figure S18. ¹H NMR spectra of (a) [Ir(bzq)₂Cl]₂ and (b) the residue of the reaction between [Ir(bzq)₂Cl]₂ and carbon monoxide in CDCl₃ (500 MHz, 27 °C).

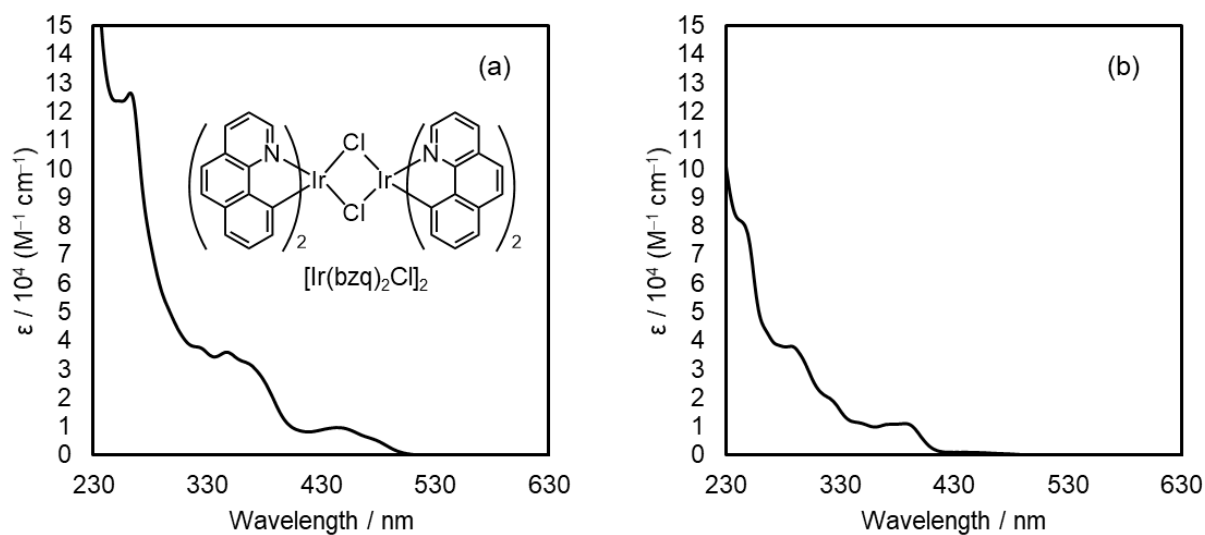


Figure S19. UV-vis spectra of (a) [Ir(bzq)₂Cl]₂ and (b) the residue of the reaction between [Ir(bzq)₂Cl]₂ and carbon monoxide in CH₂Cl₂.

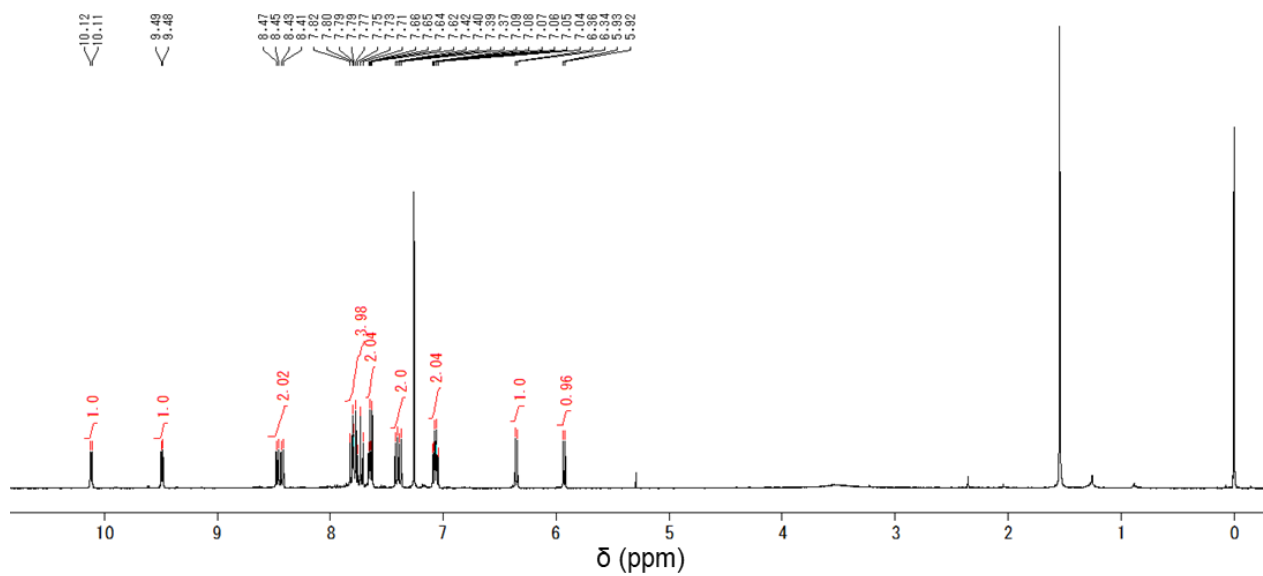


Figure S20. ^1H NMR spectrum of $[\text{Ir}(\text{bzq})_2(\text{CO})\text{Cl}]$ in CDCl_3 (400 MHz, 27 °C).

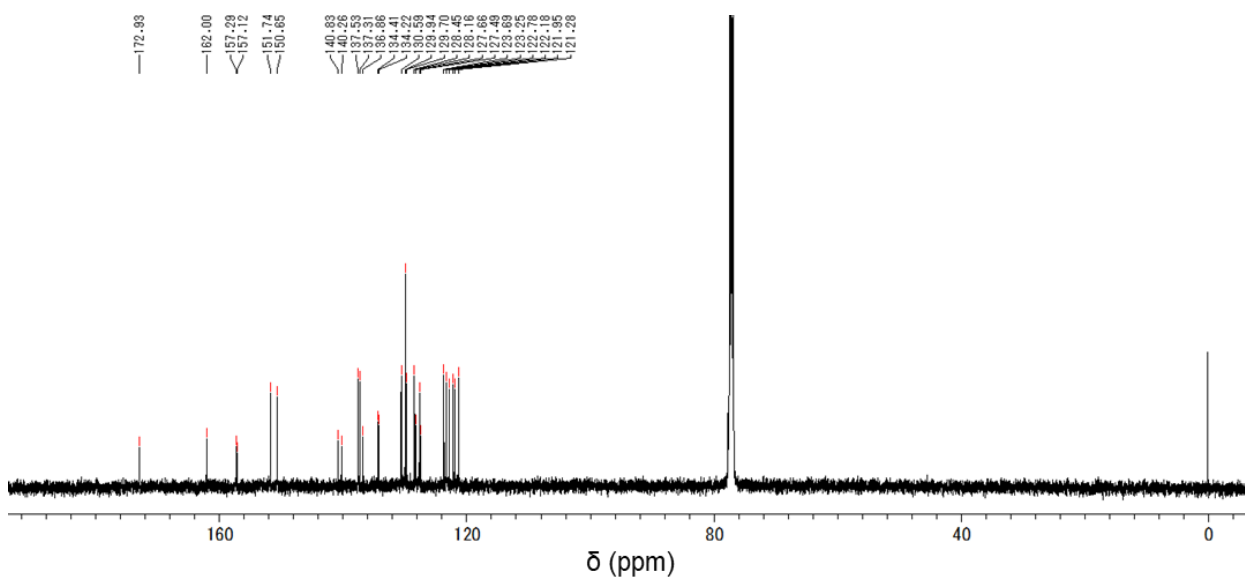


Figure S21. ^{13}C NMR spectrum of $[\text{Ir}(\text{bzq})_2(\text{CO})\text{Cl}]$ in CDCl_3 (126 MHz, 27 °C).

[Mass Spectrum]
Data : takimoto006 Date : 14-Jul-2021 15:26
Instrument : MS700D
Sample : Ir bzq CO
Note : Matrix:NBA
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.00 min Scan# : (1,22) Temp : 3276.7 deg.C
BP : m/z 154.2311 Int. : 35193.44 (369029584)
Output m/z range : 50 to 2000 Cut Level : 0.00 %

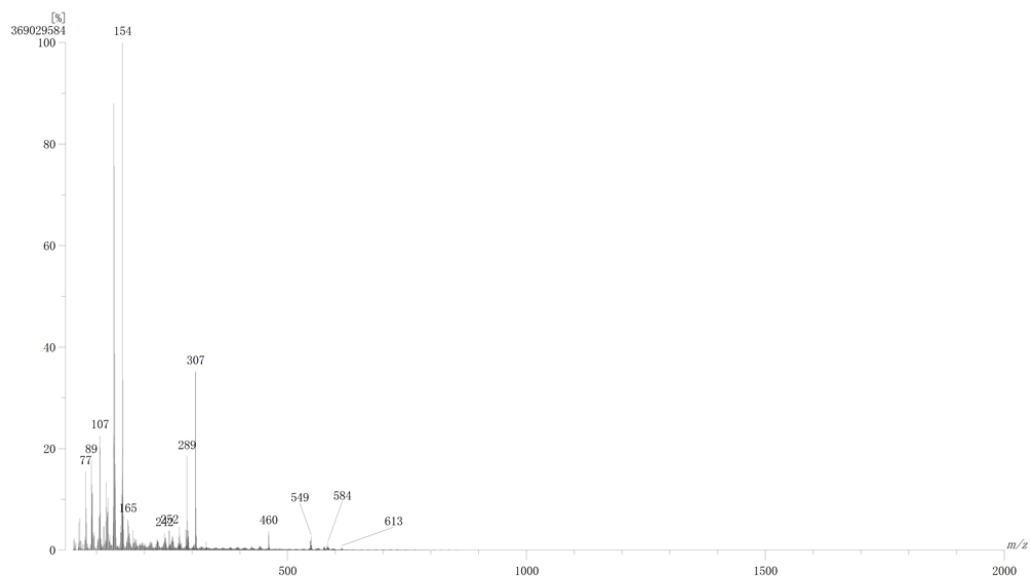


Figure S22. LRMS spectrum of $[\text{Ir}(\text{bzq})_2(\text{CO})\text{Cl}]$ (FAB^+ , 3-nitrobenzyl alcohol (3-NBA) as a matrix).

8.3 X-Ray analysis of $[\text{Ir}(\text{2-Bubzq})_2(\text{CO})\text{Cl}]$

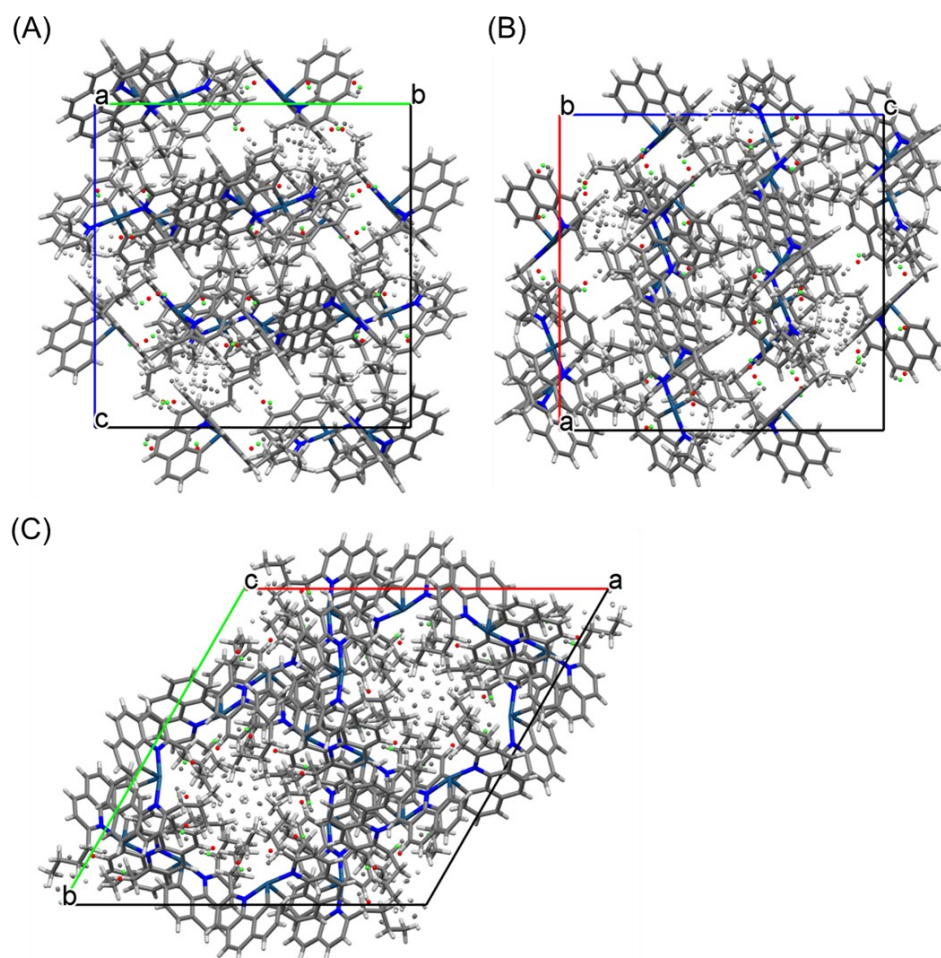


Figure S23. Crystal structures of $[\text{Ir}(\text{2-Bubzq})_2(\text{CO})\text{Cl}]$ viewed along (A) the a axis, (B) the b axis, and (C) the c axis, respectively.

Table S5. Structure information of [Ir(2-Bubzq)₂(CO)Cl].

Compound	[Ir(2-Bubzq) ₂ (CO)Cl]
Recrystallization solvent	Dichloromethane/ <i>n</i> -Hexane
Formula	C ₃₅ H ₃₂ IrN ₂ OCl
FW	724.27
Crystal system	Trigonal
Space group	<i>R</i> -3
<i>a</i> [Å]	26.0164 (6)
<i>b</i> [Å]	26.0164 (6)
<i>c</i> [Å]	23.1213 (4)
α [deg]	90
β [deg]	90
γ [deg]	120
<i>V</i> [Å ³]	13553.1 (7)
<i>Z</i>	18
μ [mm ⁻¹]	4.552
Crystal size	0.07 × 0.07 × 0.06
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.051, 0.108, 1.07
wR_2	0.108 (all data)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29087, 7270, 6174
No. of parameters	417
CCDC No.	2071813

8.4 ECD spectra of $[\text{Ir}(\text{2-Bubzq})_2(\text{CO})\text{Cl}]$

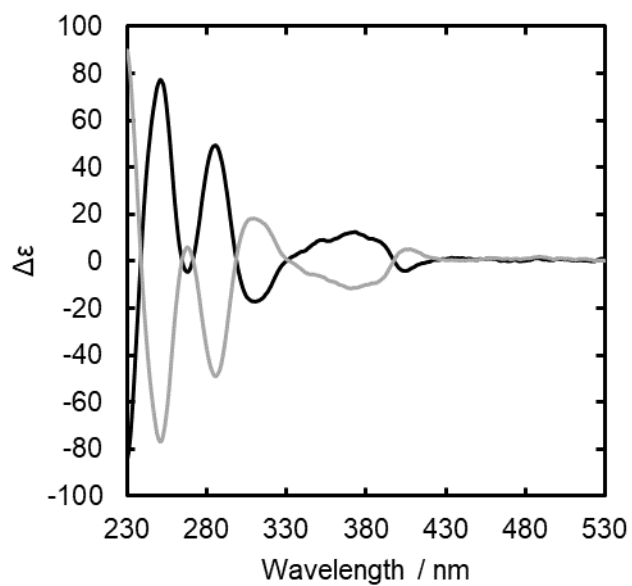


Figure S24. The ECD spectra of $[\text{Ir}(\text{2-Bubzq})_2(\text{CO})\text{Cl}]$ in dichloromethane. The solid and grey lines correspond to the CO adducts of Λ - and Δ - $[\text{Ir}(\text{2-Bubzq})_2\text{Cl}]$, respectively.

9. Reaction with 1,10-phenanthroline

9.1 Reaction of racemic [Ir(2-Bubzq)₂Cl] with 1,10-phenanthroline

[Ir(2-Bubzq)₂Cl] (15.9 μmol) and 1,10-phenanthroline (phen) (17.2 μmol) were dissolved in 2 mL of dichloromethane. After removal of volatile materials by evaporation under reduced pressure, the residue was washed by *n*-hexane to remove the unreacted phen. The product was obtained as a yellow solid (15.9 μmol, Yield 100%). ¹H NMR (500 MHz; CD₃OD) 0.22 (2H, m, H13a), 0.42 (6H, t, *J* = 7.5 Hz, H14), 0.50 (2H, m, H12a), 0.59 (2H, m, H13b), 1.13 (2H, m, H12b), 1.80 (2H, m, H11a), 2.61 (2H, m, H11b), 6.48 (2H, d, *J* = 7.5 Hz, H9), 7.16 (2H, t, *J* = 7.5 Hz, H8), 7.35 (2H, d, *J* = 8.5 Hz, H3), 7.59 (2H, d, *J* = 7.5 Hz, H7), 7.67 (2H, dd, *J* = 5.5, 8.5 Hz, H2'), 7.79 (2H, d, *J* = 9.0 Hz, H5), 7.93 (2H, dd, *J* = 1.5, 5.5 Hz, H1'), 7.95 (2H, d, *J* = 9.0 Hz, H6), 8.28 (2H, s, H4'), 8.33 (2H, d, *J* = 8.5 Hz, H4), 8.69 (2H, d, *J* = 1.5, 8.5 Hz, H3'); ¹³C NMR (126 Hz, CD₃OD) 13.86, 23.26, 32.90, 39.17, 121.98, 122.64, 125.34, 127.41, 127.80, 129.50, 130.00, 130.05, 131.45, 132.75, 136.41, 139.61, 139.67, 143.75, 145.10, 148.80, 150.86, 159.02, 167.09; LRMS(FAB⁺, 3-NBA), *m/z* = 841 (M-Cl).

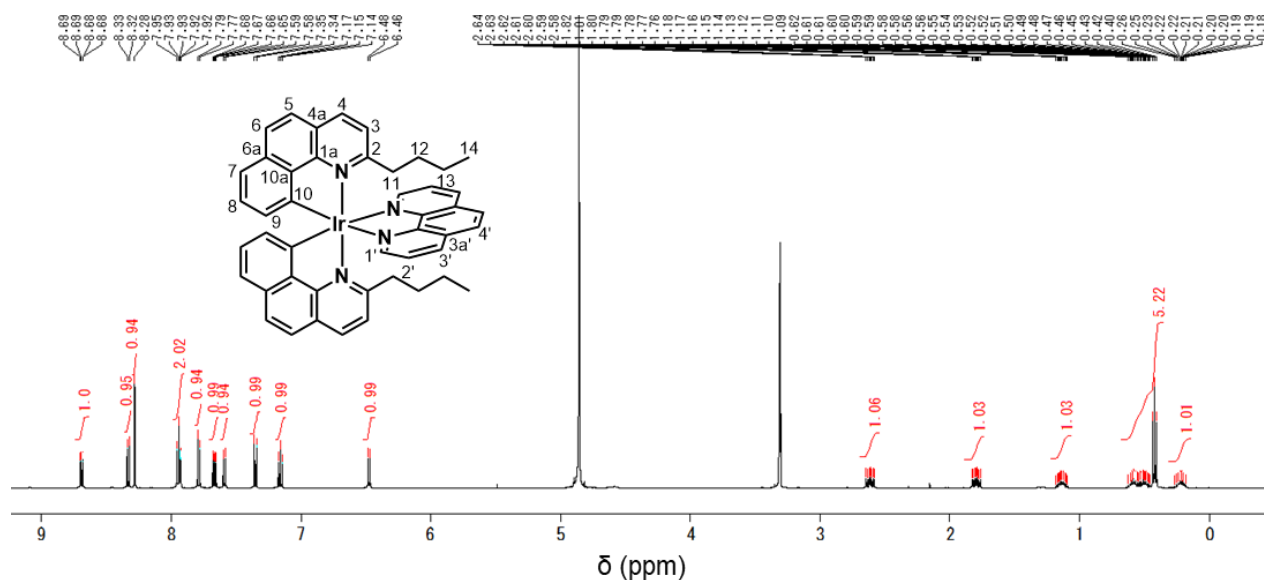


Figure S25. ¹H NMR spectrum of [Ir(2-Bubzq)₂(phen)]Cl in CD₃OD (500 MHz, 27 °C).

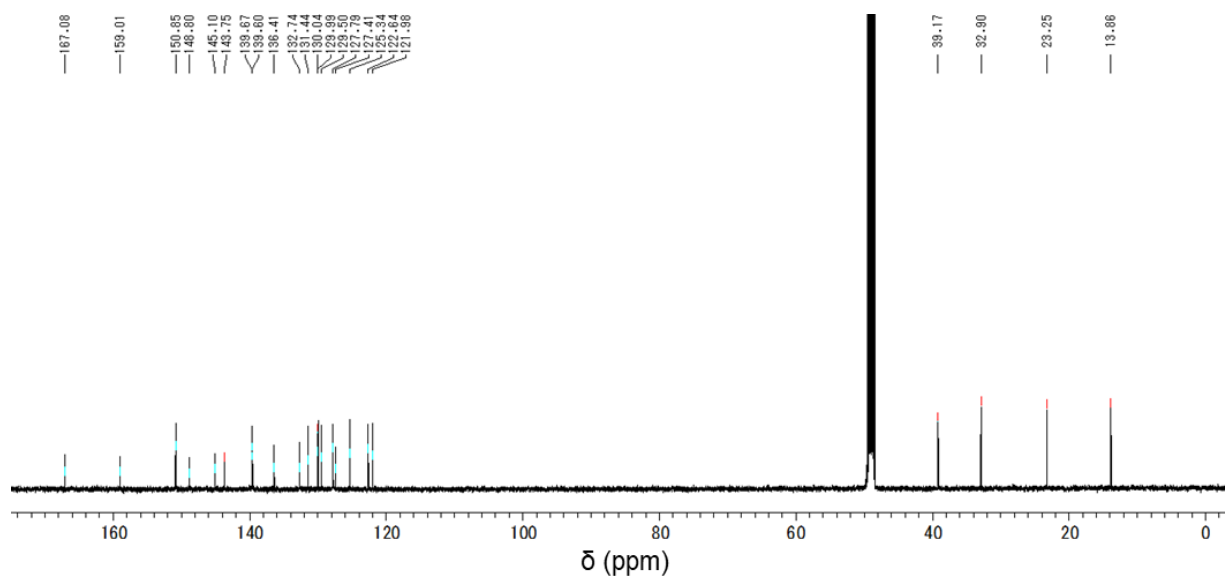


Figure S26. ^{13}C NMR spectrum of $[\text{Ir}(\text{2-Bubzq})_2(\text{phen})]\text{Cl}$ in CD_3OD (126 MHz, 27 °C).

[Mass Spectrum]
 Data : 20210526001 Date : 26-May-2021 09:37
 Instrument : MS700D
 Sample : Ir-Bubzq phen
 Note : Matrix:NBA
 Inlet : Direct Ion Mode : FAB+
 Spectrum Type : Normal Ion [MF-Linear]
 RT : 0.60 min Scan# : (5,8) Temp : 3276.7 deg.C
 BP : m/z 841.1522 Int. : 2009.59 (21072064)
 Output m/z range : 50 to 1028 Cut Level : 0.00 %

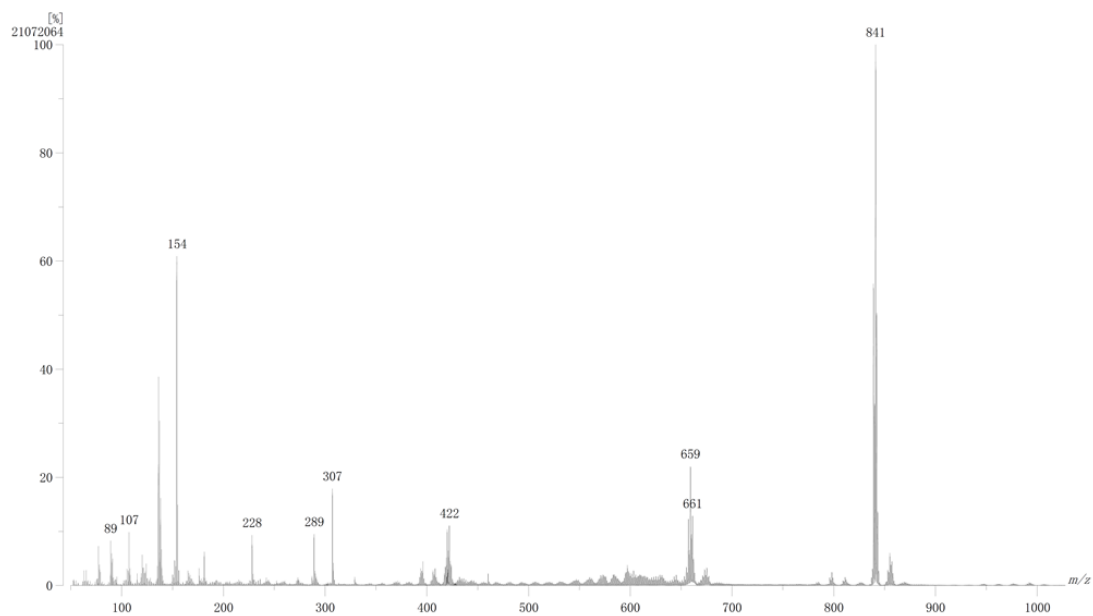


Figure S27. LRMS spectrum of $[\text{Ir}(\text{2-Bubzq})_2(\text{phen})]\text{Cl}$ (FAB^+ , 3-nitrobenzyl alcohol (3-NBA) as a matrix).

9.2 X-Ray analysis of racemic $[\text{Ir}(2\text{-Bubzq})_2(\text{phen})]\text{Cl}$

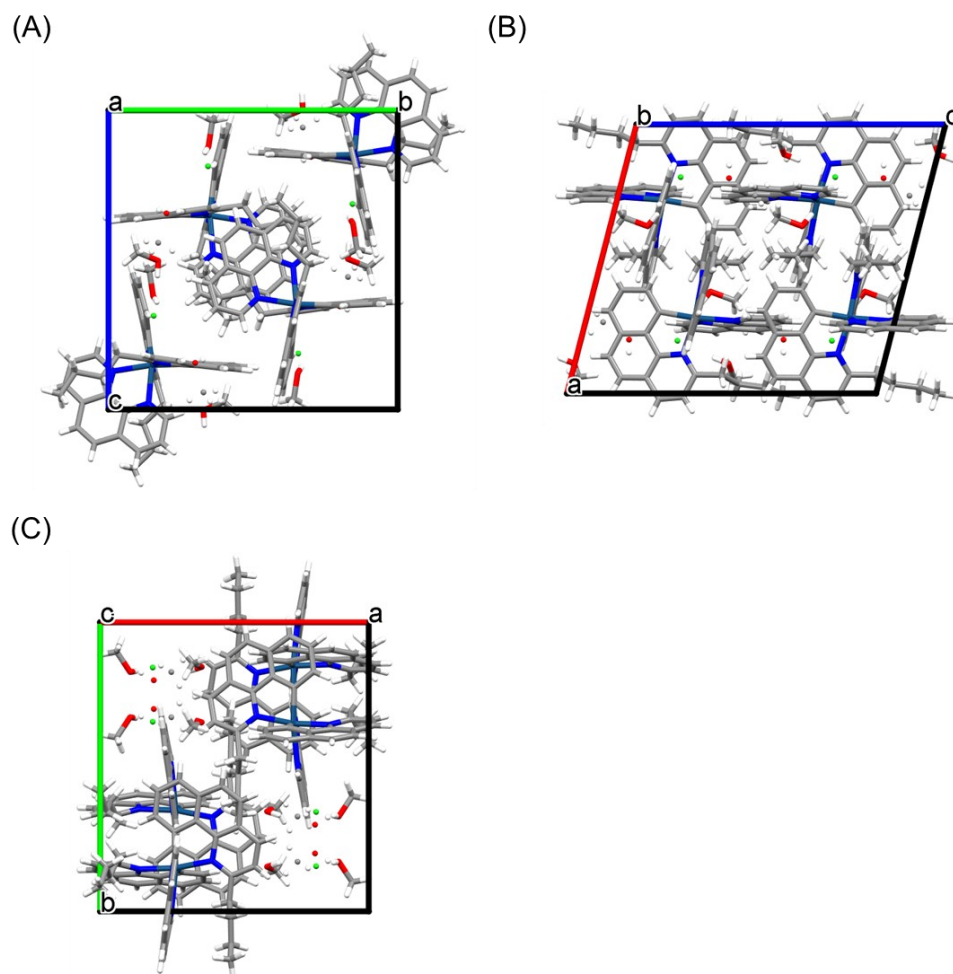


Figure S28. Crystal structures of $[\text{Ir}(2\text{-Bubzq})_2(\text{phen})]\text{Cl}$ viewed along (A) the *a* axis, (B) the *b* axis, and (C) the *c* axis, respectively.

Table S6. Structure information of racemic [Ir(2-Bubzq)₂(phen)]Cl.

Compound	[Ir(2-Bubzq) ₂ (phen)]Cl
Recrystallization solvent	Methanol/diethyl ether
Formula	C ₄₆ H ₄₀ IrN ₄ Cl, 1.31(MeOH), C _{0.69} H _{3.07} O _{0.69}
FW	940.89
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	15.3729 (4)
<i>b</i> [Å]	16.0231 (3)
<i>c</i> [Å]	17.1143 (4)
α [deg]	90
β [deg]	104.488 (3)
γ [deg]	90
<i>V</i> [Å ³]	4081.56 (17)
<i>Z</i>	4
μ [mm ⁻¹]	3.381
Crystal size	0.1 × 0.08 × 0.02
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.044, 0.080, 1.10
wR_2	0.080 (all data)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	68718, 9849, 8091
No. of parameters	532
CCDC No.	2099501

9.3 Comparison of the ECD spectra of Λ -[Ir(2-Bubzq)₂(phen)]Cl and Λ -[Ir(bzq)₂(phen)]ClO₄

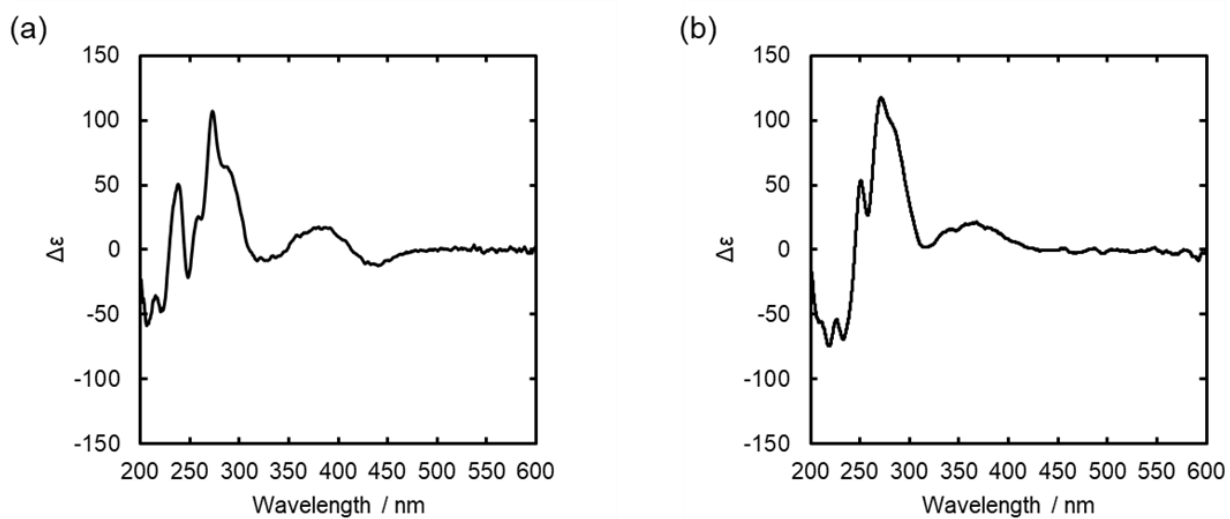


Figure S29. The ECD spectra of (a) Λ -[Ir(2-Bubzq)₂(phen)]Cl and (b) Λ -[Ir(bzq)₂(phen)]ClO₄^{S4} in methanol.

10. References

- (S1) A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn, G. C. Verschoor *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
- (S2) M. J. Auburn, R. D. Holmes-Smith, S. R. Stobart, P. K. Bakshi, T. S. Cameron *Organometallics* **1996**, *15*, 13, 3032.
- (S3) W. J. Finkenzeller, P. Stöbel, H. Yersin, *Chem. Phys. Lett.* **2004**, *397*, 289.
- (S4) K. Takimoto, K. Tamura, Y. Watanabe, A. Yamagishi and H. Sato, *New J. Chem.* **2018**, *42*, 4818.