Supplementary Information

Substituent effect of 2-R-*o*-carborane on the photophysical properties of iridium(III) cyclometalates

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Contents

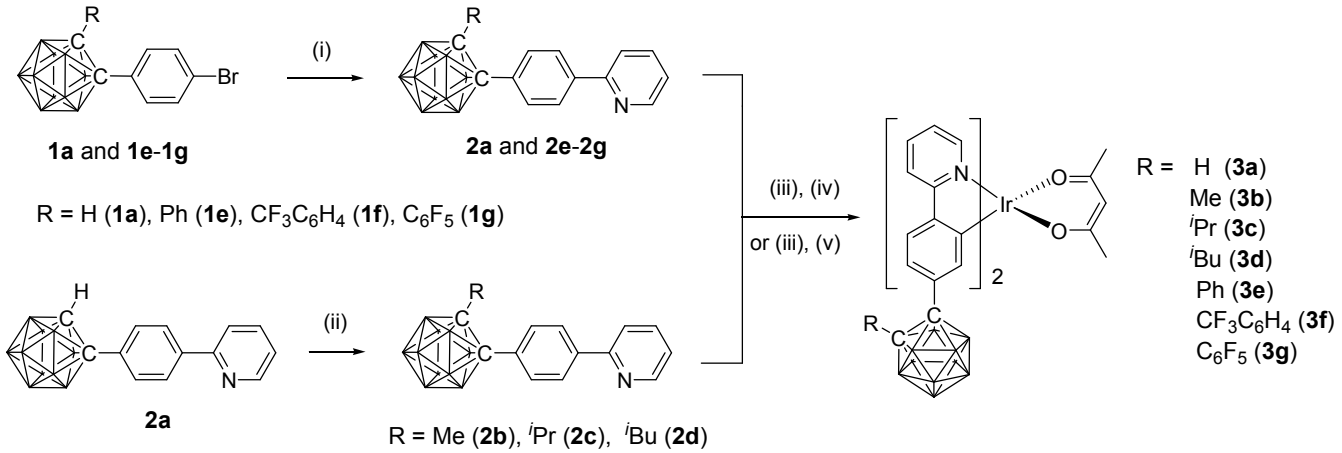
1. Experimental

1.1. General Considerations

All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous grade solvents (Aldrich) were dried over activated molecular sieves (5Å). Spectrophotometric-grade tetrahydrofuran (THF) and toluene were used as received from Aldrich. Commercial reagents were used without further purification after purchasing from Aldrich (2-bromopyridine, *n*-BuLi (2.5 M solution in *n*-hexane), NaH (60% dispersion in mineral oil), copper(I) iodide, diisopropylamine (*i*-Pr_2NH), sodium carbonate, diethyl sulfide, methyl iodide, and 2,4-pentanedione (acacH)), Alfa Aesar (1-(trifluoromethyl)-4-iodobenzene, 1,2,3,4,5-pentafluoro-6-iodobenzene, ethynyl(trimethyl)silane, and phenylacetylene), TCI (1-bromo-4-iodobenzene, Me_3SnCl), Strem Chemicals (iridium(III) chloride hydrate, $Pd(PPh_3)_4$), and Katchem (decaborane, $B_{10}H_{14}$). 1-Bromo-4-ethynylbenzene,[1] 1-bromo-4-(2-phenylethynyl)benzene,[2] 2-(trimethylstannyl)pyridine,[3] 1-(4-bromophenyl)-2-H-1,2-*closo*-carborane (**1a**),[4] 2-{*p*-(2-H-1,2-carboran-1-yl)phenyl}pyridine (**2a**),[5] 2-{*p*-(2-Me-1,2-carboran-1-yl)phenyl}pyridine (**2b**),[4] [4-(2-HCB)ppy]$_2$Ir(acac) (**3a**),[5] [4-(2-MeCB)ppy]$_2$Ir(acac)] (**3b**),[4] and Ir(ppy)$_2$(acac) (**4**)[6] were synthesized according to the reported procedures.

1. 2. Synthesis

The ligands (**2c**–**2g**) and their iridium(III) complexes, [4-(2-RCBppy)]$_2$Ir(acac) (**3c**–**3g**) were prepared as shown in Scheme S1. Full experimental details are given below.



Scheme S1. Conditions: (i) 2-(trimethylstannyl)pyridine, $Pd(PPh_3)_4$, toluene, 110 °C, 12 h. (ii) NaH, RI (R = Me, *i*Pr, *i*Bu), DMF, rt. (iii) $IrCl_3 \cdot 3H_2O$, 2-ethoxyethanol, 110 °C, 1 d. (iv) 2,4-pentanedione, Na_2CO_3, CH_3CN, reflux, 1 d for **3a–3d**. (v) AgOTf, CH_3CN, rt, 6 h, and then 2,4-pentanedione, Et_3N, toluene, reflux, o/n for **3e–3g**.

Bromo-4-(2-(4-(trifluoromethyl)phenyl)ethynyl)benzene. To a Schlenk flask charged with 1-bromo-4-ethynylbenzene (1.18 g, 6.52 mmol), 1-(trifluoromethyl)-4-iodobenzene (1.77 g, 6.52 mmol), $Pd(PPh_3)_4$ (0.091 g, 0.13 mmol), and CuI (0.12 g, 0.65 mmol), degassed anhydrous diisopropylamine (*i*-Pr_2NH, 50 mL) was added under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 12 h. The resulting solution was concentrated under reduced pressure and purified by silica gel column chromatography using *n*-hexane as eluent to give a white powder (1.75 g, 82%). ^1H NMR ($CDCl_3$): δ 7.59 (s, 4H), 7.50 (dt, J = 6.7, 2.0 Hz, 2H), 7.41 (dt, J = 8.6, 2.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 133.1, 131.8, 131.7, 130.3, 129.9, 126.7, 125.3, 123.1, 121.4 (Ar–*C*), 90.6, 89.0 (ethynyl–*C*).

1-(2-(4-Bromophenyl)ethynyl)-2,3,4,5,6-pentafluorobenzene. This compound was prepared in a manner analogous to the synthesis of 1-bromo-4-(2-(4-(trifluoromethyl)phenyl)ethynyl)benzene using 1-bromo-4-ethynylbenzene (2.79 g, 15.4 mmol), 1,2,3,4,5-pentafluoro-6-iodobenzene (2.05 mL, 15.4 mmol), $Pd(PPh_3)_4$ (0.22 g, 0.31 mmol), and CuI (0.29g, 1.54 mmol) in the presence of *i*-Pr_2NH (50 mL) to give a white powder (2.56 g, 48%). ^1H NMR ($CDCl_3$): δ. 7.52 (d, J = 7.5 Hz, 2H), 7.43 (d, J = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 133.2, 131.8, 124.2, 120.4, 118.0, 115.7 (Ar–*C*), 100.2 (ethynyl–*C*).

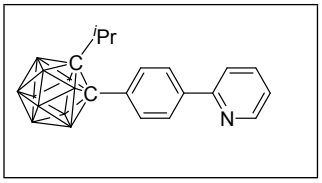
1-(4-Bromophenyl)-2-phenyl-1,2-*closo*-carborane (1e). A solution of decaborane ($B_{10}H_{14}$, 0.47 g, 3.8 mmol) and diethyl sulfide (Et_2S, 1.04 mL, 11.4 mmol) in toluene (30 mL) was stirred at room temperature for 0.5 h and then 1-bromo-4-(2-phenylethynyl)benzene (0.82 g, 3.21 mmol) in toluene (10 mL) was added to this solution. The mixture was refluxed for 3 days under nitrogen atmosphere. After cooling to room temperature, the resulting solution was concentrated under reduced pressure and purified by silica gel column chromatography using CH_2Cl_2/*n*-hexane (1:20, v/v) as eluent to give a white powder of **1e** (0.9 g, 74%). ^1H NMR ($CDCl_3$): δ 7.41 (m, 4H), 7.21 (t, J = 1.2Hz, 1H), 7.14 (m, 4H), 4.15–1.2 (br, 10H, B–*H*). ^{13}C NMR ($CDCl_3$): δ 132.0, 131.4, 130.5, 130.4, 129.7, 128.4, 125.0 (Ar–*C*), 85.2, 84.0 (CB–*C*). ^{11}B NMR ($CDCl_3$): δ –2.4, –9.3, –10.4, –11.5.

1-(4-Bromophenyl)-2-(4-trifluoromethyl)phenyl-1,2-*closo*-carborane (1f). This compound was prepared in a manner analogous to the synthesis of **1e** using 1-bromo-4-(2-(4-(trifluoromethyl)phenyl)ethynyl)benzene (1.40 g, 4.03 mmol), decaborane (0.59 g, 4.84 mmol), and Et_2S (1.30 mL, 12.0 mmol), affording a white powder of **1f** (1.30 g, 82%). ^1H NMR ($CDCl_3$): δ 7.55 (m, J = 7.5 Hz, 4H), 7.40 (m, J = 7.4 Hz, 4H), 4.3–1.4 (br, 10H, B–*H*). ^{13}C NMR ($CDCl_3$): δ 134.0, 132.5, 131.9, 131.7, 131.0, 129.3, 125.5, 125.0, 121.4 (Ar–*C*), 84.2, 83.3 (CB–*C*). ^{11}B NMR ($CDCl_3$): δ –1.9,

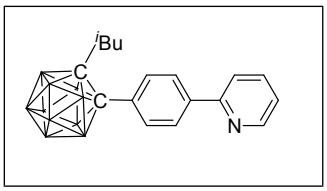
–9.9.

1-(4-Bromophenyl)-2-(2,3,4,5,6-pentafluorophenyl)-1,2-*closo*-carborane (1g). This compound was prepared in a manner analogous to the synthesis of **2e** using 1-(2-(4-bromophenyl)ethynyl)-2,3,4,5,6-pentafluorobenzene (0.55 g, 1.58 mmol), decaborane (0.23 g, 1.72 mmol), and Et_2S (0.51 mL, 4.73 mmol), affording a white powder of **1g** (0.44 g, 60%). ^{1}H NMR ($CDCl_3$): δ 7.41 (m, J = 7.4 Hz, 4H), 4.3–1.4 (br, 10H, B–*H*). ^{13}C NMR ($CDCl_3$): δ 132.1, 131.8, 129.6 , 126.0 (Ar–*C*), 85.6, 74.8 (CB–*C*). ^{11}B NMR ($CDCl_3$): δ 0.9, –3.0, –9.0.

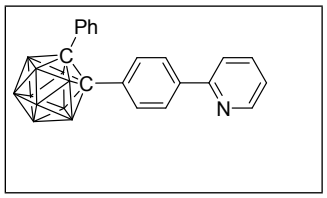
2-{*p*-(2-Isopropyl-1,2-carboran-1-yl)phenyl}pyridine (2c). Sodium hydride (60% dispersion in mineral oil, 0.041 g, 1.02 mmol) was suspended in dry DMF (5 mL). After cooling down to –20 °C, a solution of **2a** (0.10 g, 0.34 mmol) in DMF (5 mL) was added slowly to the suspension. The mixture was stirred at room temperature for 1 h, and then 2-iodopropane (0.10 mL, 1.02 mmol) was added at –20 °C, and further stirred at room temperature overnight. The reaction was quenched by saturated aqueous NH_4Cl solution, and extracted with diethyl ether (30 mL × 3). The organic layer was washed with water (30 mL × 3) and dried over $MgSO_4$. After filtration, the filtrate was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/*n*-hexane (1:4, v/v) as eluent. Drying *in vacuo* afforded a white powder of **2c** (0.11 g, 97%).^{1}H NMR ($CDCl_3$): δ 8.71 (dq, J = 4.8, 0.8 Hz, 1H), 7.98 (d, J = 8.5 Hz 2H), 7.79 (m, 4H), 7.30 (m, 1H), 4.3–1.4 (br, 10H, B–*H*), 1.72 (heptet, J = 7.0 Hz, 1H, –C*H*(CH_3)$_2$), 1.04 (d, J = 6.9, 6H, –C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 156.0, 150.2, 141.8, 137.2, 131.8, 131.5, 127.5, 123.2, 121.0 (Ar–*C*), 89.2, 85.3 (CB–*C*), 31.6, 24.2 (isopropyl–*C*). ^{11}B NMR ($CDCl_3$): δ –2.9, –3.8, –9.8, –11.6. HR EI-MS: *m/z* calcd for $C_{16}H_{25}B_{10}N$, 339.2990; found, 339.2998.



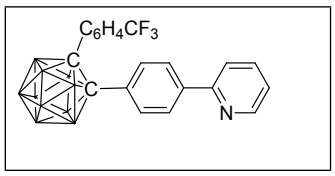
2-{*p*-(2-Isobutyl-1,2-carboran-1-yl)phenyl}pyridine (2d). This compound was prepared in a manner analogous to the synthesis of **2c** using **2a** (1.00 g, 3.36 mmol) and 1-iodo-2-methylpropane (0.12 g, 5.04 mmol) to give a colorless oil of **2d** (0.74 g, 62%). ^{1}H NMR ($CDCl_3$): δ 8.71 (dq, J = 4.8, 1.2 Hz, 1H), 8.02 (dt, J = 8.7, 1.8 Hz, 2H), 7.74 (m, 2H), 7.27 (m, 1H), 3.9–1.4 (br, 10H, B–*H*), 1.78 (m, 3H, –C*H*C*H*$_2$CH$_3$), 0.80 (d, J = 6.3 Hz, 6H, –C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 155.6, 149.8, 141.3, 137.0, 131.6, 131.2, 127.2, 122.9, 120.7 (Ar–*C*), 83.8, 82.6 (CB–*C*), 43.6, 28.3, 23.2 (isobutyl–*C*). ^{11}B NMR ($CDCl_3$): δ –3.4, –10.1. HR EI-MS: *m/z* calcd for $C_{17}H_{27}B_{10}N$, 353.3147; found, 353.3155.



2-{*p*-(2-Phenyl-1,2-carboran-1-yl)phenyl}pyridine (2e). A mixture of **1e** (2.64 g, 7.03 mmol), 2-(trimethylstannyl)pyridine (1.87 g, 7.73 mmol), and $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol) in dry toluene (30 mL) was refluxed for 12 h under nitrogen atmosphere. After cooling down to room temperature, the solvent was evaporated off under reduced pressure and the residue was purified by column chromatography on silica gel using ethylacetate/*n*-hexane (1:9, v/v) as eluent to give a white powder of **2e** (1.49 g, 57%). ^{1}H NMR ($CDCl_3$): δ 8.70 (d, J = 4.4 Hz, 1H), 8.10 (s, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.80 (td, J = 7.7, 1.4 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.51 (m, 2H), 7.47 (dd, J = 8.0, 1.7 Hz, 1H), 7.28 (m, 5H), 4.3–1.4 (br, 10H, B–*H*). ^{13}C NMR ($CDCl_3$): δ 156.9, 150.8, 140.5, 137.9, 132.1, 131.7, 131.6, 131.5, 131.2, 130.3, 129.6, 129.5, 129.3, 123.6, 121.4 (Ar–*C*), 86.3, 86,0 (CB–*C*). ^{11}B NMR ($CDCl_3$): δ –2.4, –9.3, –10.3. HR EI-MS: *m/z* calcd for $C_{19}H_{23}B_{10}N$, 373.2834; found, 373.2843.



2-{*p*-(2-(4-(Trifluoromethyl)phenyl)-1,2-carboran-1-yl)phenyl}pyridine (2f). This compound was prepared in a manner analogous to the synthesis of **2e** using **1f** (1.00, 2.26 mmol), 2-(trimethylstannyl)pyridine (0.60 g, 2.49 mmol), and $Pd(PPh_3)_4$ (0.050 g, 0.045 mmol) to give a white powder of **2f** (0.69 g, 65%). ^{1}H NMR ($CDCl_3$): δ 8.63 (dq, J = 4.0, 0.9, Hz, 1H), 7.81 (dt, J = 10.9, 1.9 Hz, 2H), 7.72 (td, J = 7.9, 1.8 Hz, 1H), 7.56 (m, 5H), 7.40 (d, J = 8.4 Hz, 2H), 7.25 (m, 1H), 4.1–1.3 (br, 10H, B–*H*). ^{13}C NMR ($CDCl_3$): δ 155.3, 149.8, 137.0, 134.2, 132.4, 131.0, 130.9, 130.7, 126.8, 125.4, 125.3, 122.9, 120.7(Ar–*C*), 84.9, 83.4 (CB–*C*). ^{11}B NMR ($CDCl_3$): δ –2.0, –9.9. HR EI-MS: *m/z* calcd for $C_{20}H_{22}B_{10}F_3N$, 441.2708; found, 441.2717.



2-{*p*-(2-(2,3,4,5,6-Pentafluorophenyl)-1,2-carboran-1-yl)phenyl}pyridine (2g). This compound was prepared in a manner analogous to the synthesis of **2e** using **1g** (0.44 g, 0.97 mmol), 2-(trimethylstannyl)pyridine (0.27 g, 1.03 mmol), and $Pd(PPh_3)_4$ (0.022 g, 0.020 mmol) to give a white powder of **2g** (0.20 g, 46%). ^{1}H NMR ($CDCl_3$): δ 8.65 (dq, J = 4.0, 0.9, Hz, 1H), 7.86 (dt, J = 6.8, 2.2 Hz, 2H), 7.74 (td, J = 7.9, 1.8 Hz, 1H), 7.68 (m, 2H), 7.24 (m, 1H), 4.7–1.4 (br, 10H, B–*H*). ^{13}C NMR ($CDCl_3$): δ 155.2, 149.8, 141.6, 137.0, 130.8, 130.7, 127.1, 123.0, 120.8 (Ar–*C*), 86.5, 74.9 (CB–*C*). ^{11}B NMR ($CDCl_3$): δ 0.8, –3.2, –9.1. HR EI-MS: *m/z* calcd for $C_{19}H_{18}B_{10}F_5N$, 463.2363; found, 463.2372.

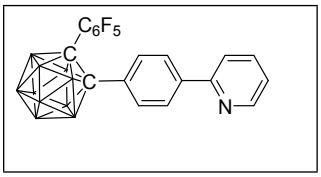


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Table S1. Crystallographic data and parameters for **3c–3g**.

	3c	**3d**	**3e**·(CH_2Cl_2)	**3f**·(C_6H_{14})	**3g**
formula	$C_{37}H_{55}B_{20}IrN_2O_2$	$C_{39}H_{59}B_{20}IrN_2O_2$	$C_{44}H_{53}B_{20}Cl_2IrN_2O_2$	$C_{51}H_{63}B_{20}F_6IrN_2O_2$	$C_{43}H_{41}B_{20}F_{10}IrN_2O_2$
formula weight	968.23	996.30	1121.18	1258.43	1216.18
crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
space group	*C*2/*c*	*Pbcn*	*C*2/*c*	*P-1*	*P-1*
a (Å)	12.5230(2)	23.771(5)	26.5068(5)	13.744(5)	11.0264(5)
b (Å)	25.7041(4)	13.231(3)	13.0602(3)	14.295(5)	12.8256(7)
c (Å)	15.0564(3)	14.707(3)	15.2624(3)	16.525(6)	18.9683(10)
α (°)	90	90	90.00	99.553(18)	78.772(4)
β (°)	112.8670(10)	90	104.8820(10)	108.392(16)	74.603(4)
γ (°)	90	90	90.00	95.195(18)	86.356(4)
V (Å^3)	4465.65(13)	4625.6(16)	5106.37(18)	3002.4(18)	2536.5(2)
Z	4	4	4	2	2
ρ_{calc} (g cm^{-3})	1.440	1.431	1.458	1.392	1.592
μ (mm^{-1})	3.027	2.804	2.760	2.283	2.710
F(000)	1936	2000	2232	1260	1192
T (K)	100(2)	100(2)	100(2)	100(2)	296(2)
hkl range	−14 → +14, −30 → +30, −17 → +17	−29 → +29, −16 → +16, −18 → +18	−41 → +36, −20 → +20, −24 → +24	−16 → +15, −16 → +16, −19 → +19	−11→ +13, −13 → +15, −22 → +22
measd reflns	31835	30874	40992	30634	21469
unique reflns [R_{int}]	3815 [0.0284]	4732 [0.0952]	10784 [0.0239]	10433 [0.0586]	8712 [0.1061]
reflns used for refinement	3815	4732	10784	10433	8712
refined parameters	314	294	346	742	693
R1[a] (I > 2σ(I))	0.0177	0.0416	0.0199	0.0551	0.0735
wR2[b] all data	0.0394	0.1295	0.0487	0.1477	0.1990
GOF on F^2	1.044	1.040	1.043	1.030	1.015
ρ_{fin} (max/min) (e Å^{-3})	0.500/–0.352	2.910/–2.033	0.975/–0.699	1.861/–0.742	1.774/–1.910

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

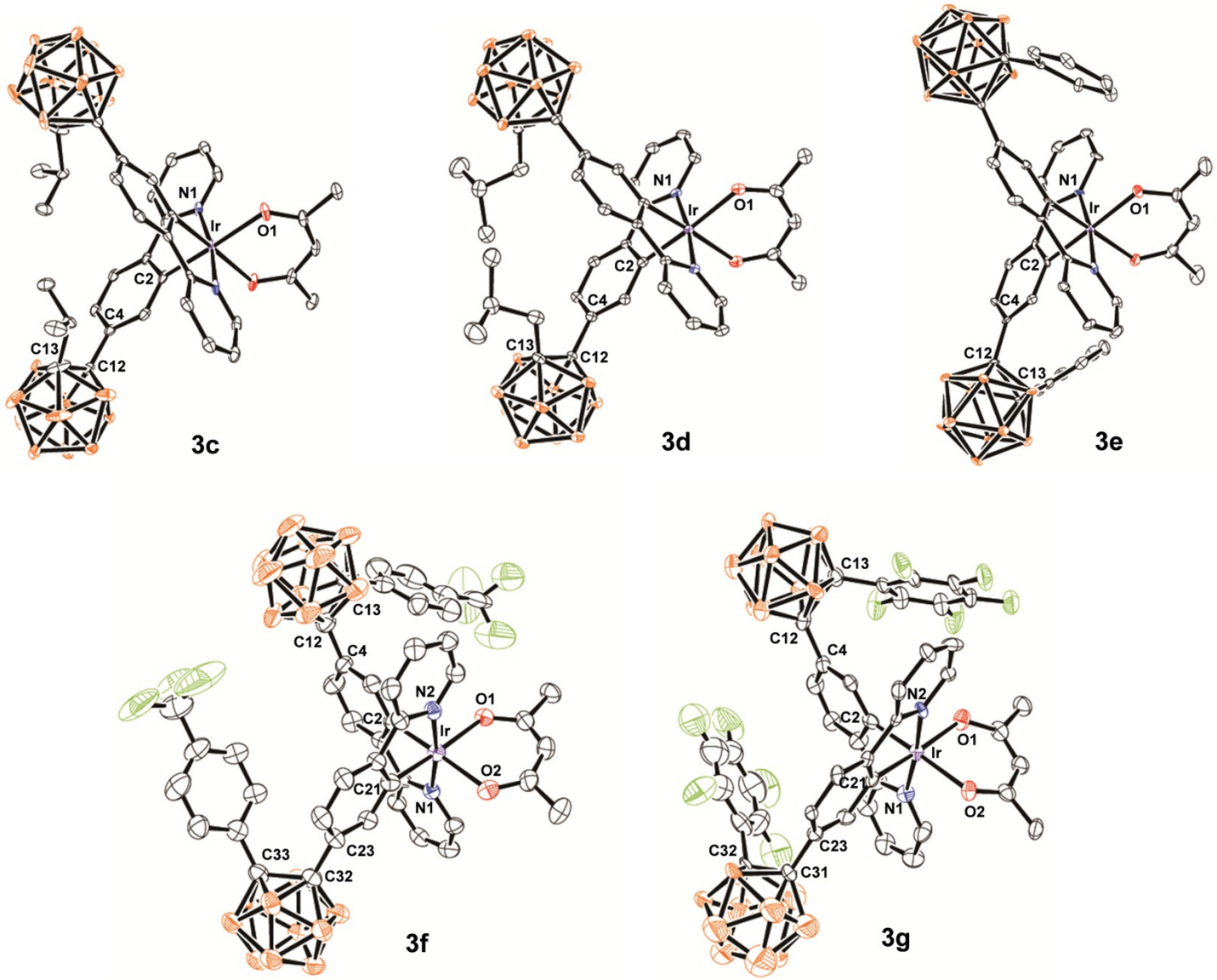

Figure S1. Crystal structures of **3c**–**3g** (40% thermal ellipsoids) with atom labels. H atoms and solvent molecules are omitted for clarity. Color code: gray = carbon, purple = iridium; green = fluorine; red = oxygen; orange = boron; blue = nitrogen atom.

Table S2. Selected bond lengths (Å) and angles (deg) for **3c–3g**.

Compound	**3c**	**3d**	**3e**		**3f**	**3g**
			Lengths (Å)			
Ir–O(1)	2.1485(15)	2.1657(18)	2.1349(9)	Ir–O(1)	2.139(5)	2.131(9)
				Ir–O(2)	2.161(5)	2.143(8)
Ir–N(1)	2.0383(19)	2.041(2)	2.0302(11)	Ir–N(1)	2.057(6)	2.040(11)
				Ir–N(2)	2.035(6)	2.021(10)
Ir–C(2)	1.990(2)	1.995(3)	1.9832(11)	Ir–C(2)	1.972(7)	1.989(14)
				Ir–C(21)	1.978(7)	2.000(13)
C_{Ph}(CB1)–C_R(CB1)[a]	1.715(3)	1.724(4)	1.7213(16)	C_{Ph}(CB1)–C_R(CB1)[a]	1.709(11)	1.717(19)
				C_{Ph}(CB2)–C_R(CB2)[a]	1.706(11)	1.693(19)
			Angles (°)			
C(2)–Ir–C(2)	89.78(12)	86.34(14)	91.99(6)	C(2)–Ir–C(21)	87.9(3)	91.4(5)
C(2)–Ir–N(1)	80.72(9)	81.07(9)	80.93(4)	C(2)–Ir–N(1)	80.8(3)	80.2(5)
				C(21)–Ir–N(2)	81.2(3)	80.6(4)
N(1)–Ir–N(1)	171.17(10)	173.12(11)	173.06(5)	N(2)–Ir–N(1)	172.0(2)	174.6(4)
C(2)–Ir–O(1)	176.37(8)	174.69(8)	176.15(4)	C(21)–Ir–O(1)	176.0(2)	175.4(4)
				C(2)–Ir–O(2)	175.5(2)	172.3(4)
O(1)–Ir–O(1)	88.60(9)	86.61(10)	88.88(5)	O(1)–Ir–O(2)	88.1(2)	88.5(3)

[a] CB denotes *o*-carborane. C_{Ph} and C_R correspond to the cage carbon atoms attached to the phenyl and R group, respectively.

2. Photophysical data

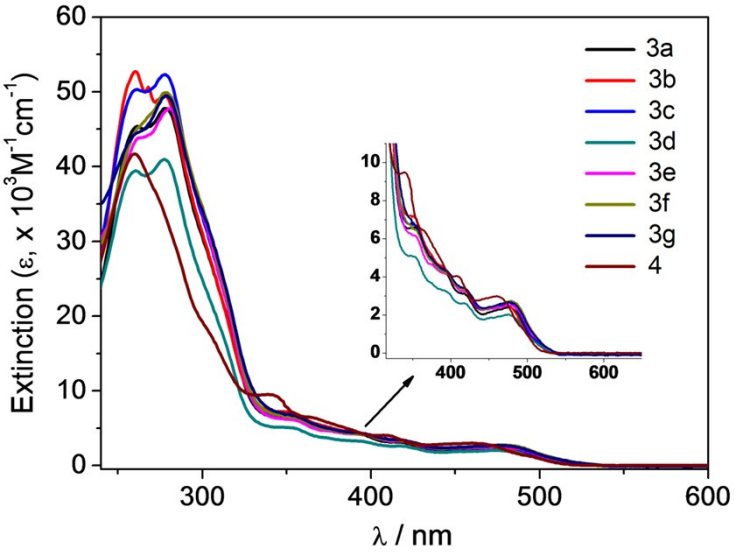

Figure S2. UV/Vis absorption spectra of **3a–3g** and **4** in THF at 298 K.

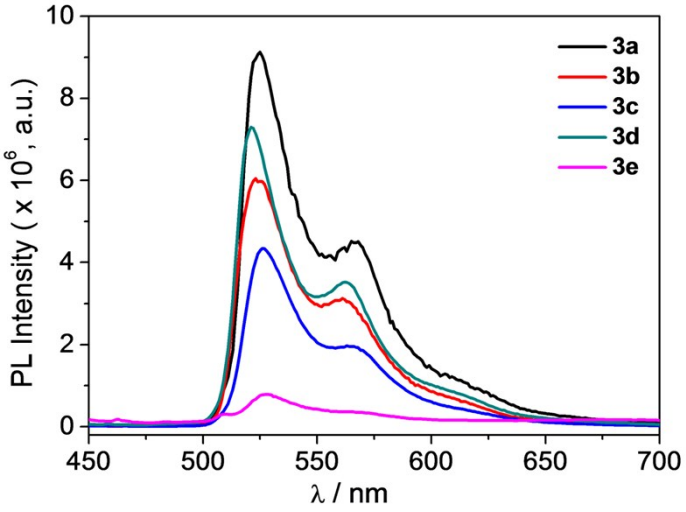

Figure S3. PL spectra of **3a**–**3e** in toluene at 77 K.

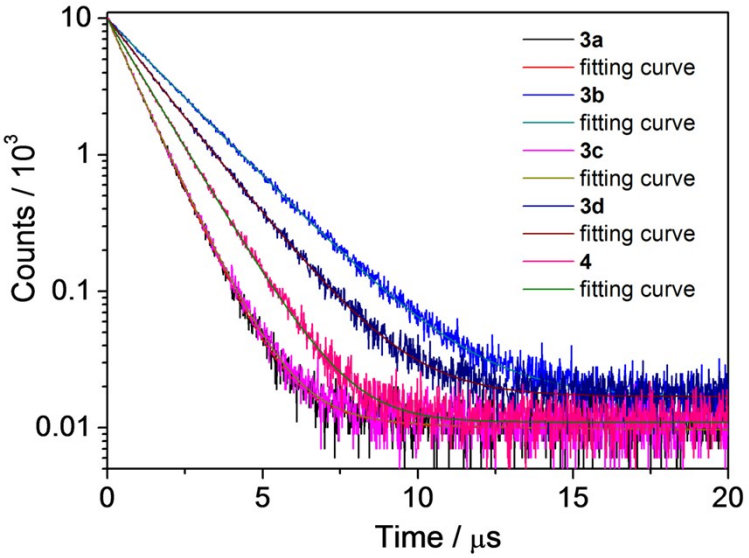

Figure S4. Emission decay curves of **3a**–**3d** and **4** in toluene at 298 K.