Inorganic Chemistry

pubs.acs.org/IC

Synthesis and Optoelectronic Properties of Cationic Iridium(III) Complexes with *o*-Carborane-Based 2-Phenyl Benzothiazole Ligands

Zi-Jian Yao,* Yong-Xu Jin, Wei Deng, and Zhen-Jiang Liu*

 Cite This: Inorg. Chem. 2021, 60, 2756–2763
 Read Online

 ACCESS |
 Image: Metrics & More
 Image: Article Recommendations
 Image: Supporting Information

 ABSTRACT: A series of cationic cyclometalated iridium(III)
 Image: Chem. 2021, 60, 2756–2763
 Image: Chem. 2021, 60, 2756–2763

ABSTRACT: A series of cationic cyclometalated iridium(III) complexes with *o*-carborane cage on the main ligand of 2-phenylbenzothiazole were synthesized. The prepared iridium complexes (C1–C6) were fully characterized by UV–vis, NMR, and FT-IR spectra. The exact molecular structure of complex C1 was further studied by single crystal X-ray diffraction analysis. The different substitution position of *o*-carborane on the 2-phenylbenzothiazole ring lead to obvious differences in the emission properties of the synthesized complexes. The *o*-carboranyl unit results in a bathochromic shift of 10 nm in the fluorescence



emission spectrum of C2. In addition, the presence of an *o*-carborane fragment promoted the strong fluorescence intensity of C1 and C4, which can be used as a tool to effectively boost the intensity of fluorescence properties. The emission fluorescent behavior of iridium(III) complexes can be facilely tuned by structural variations in the main ligands of these materials.

INTRODUCTION

Over the past several years, the development and application of the iridium(III) cyclometalated complexes, as luminescent materials, have attracted the interest of many researchers.^{1–3} Iridium(III) coordination compounds have been proven to exhibit good light and thermal stability, a wide range of tunable emission colors, and high quantum yields.^{4–6} They have been thoroughly used in organic light emitting diodes (OLEDs),⁷ luminescent probes,⁸ cell imaging,⁹ and chemosensing.¹⁰ The structure of ligands in iridium(III) complexes strongly affect their photophysical properties.^{11,12} Therefore, the electronic properties and performance of iridium(III) complexes are directly affected by the nature, structure, and position of the introduced ligand substituents.^{13,14} Thus, the design and construction of new ligands with unique structures are attractive.

o-Carborane (1,2-C₂B₁₀H₁₂) has a three-dimensional geometric cage-like rigid structure with a large volume group, $^{13-18}$ providing a unique steric hindrance, $^{19-24}$ hindering intermolecular interactions, reducing self-quenching, and potential concentration quenching 25 with high chemical and thermal stability. $^{26-30}$ The strong electron-withdrawing behavior of the cage in combination with its steric effects strongly affects the photoluminescence (PL) characteristics of this compound. 31 Therefore, chemical functionalization of carborane has been the focus of intense research by introducing new carboranyl groups into the ligands of cyclometalated iridium(III) complexes. $^{32-42}$

Up to now, several cyclometalated iridium(III) complexes with the 2-phenylbenzothiazole ligand were reported.⁴³ However, no research is performed to introduce *o*-carborane functionalization on the 2-phenylbenzothiazole ligand ring. Herein, we prompted to synthesize a new carborane-modified C^N ligand (2-phenylbenzothiazole ligand) and tried to introduce the carborane fragment into different positions of 2-phenylbenzothiazole ligands to achieve a new type of iridium(III) complexes (C1–C6). 2,2-Bipyridine and phenan-throline are used as the auxiliary ligands, and the structure and photoelectric properties of the prepared complexes are fully characterized. The experimental results show that introduction of a rigid and large carboryl group into the 2-phenylbenzothiazole ligand can improve the quantum efficiency of the generated cationic $C_{,N}$ -chelate iridium(III) complex.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cationic Iridium Complexes with Functionalized o-Carobrane Ligands. The *o*-carborane-modified 2-phenylbenzothiazole ligands (L1–L3) were prepared through reported synthetic methods from $B_{10}H_{10}(Et_4N)_2$ (see SI), as cheap, commercially available, stable, and nontoxic starting materials in a good yield.^{44,45} The *o*-carborane-functionalized iridium(III) complexes (C1–C6) were prepared through the reaction of the *o*-carboranemodified 2-phenylbenzothiazole ligands with iridium chlorides

Received: December 11, 2020 Published: January 22, 2021



Article

Scheme 1. Synthetic Routes of Iridium(III) Complexes C1-C6



to give the dimeric iridium intermediate $[(Cb-btz)_2Ir(\mu-Cl)]_2(Cb = o$ -carborane, btz = 2-phenyl benzothiazole). The prepared dimer was then reacted with the corresponding N^N ligands to yield the corresponding hexafluorophosphate salts after the addition of KPF₆ (Scheme 1). The detailed synthesis method of these compounds is described in the Experimental Section.⁴⁶

The generation of *o*-carborane functionalized iridium(III) complexes **C1–C6** was supported by ¹H NMR and FT-IR spectroscopic techniques. The ¹H NMR spectra of these iridium complexes exhibited one proton signal at δ 5.00 ppm, which is the typical signal of *o*-carboranyl C–H protons. Meanwhile, a broad B–H proton signal in the high-field range of δ 3.00–1.00 ppm for **C1–C6** also suggested the presence of an *o*-carborane cage, as confirmed by similar previous reports.⁴⁷ Observation of a characteristic absorption band at about 2570 cm⁻¹ in the FT-IR spectra of **C1–C6** further confirmed the presence of an *o*-carborane fragment in these complexes (see Figure S1).

In order to clearly elucidate the chemical structure of the target complexes, a suitable single crystal of complex C1 was prepared from the saturated Et_2O solution by slow evaporation of the DCM solution. The molecular structure of C1 was determined via X-ray diffraction analysis (Figure 1 and detailed



Figure 1. X-ray crystal structure of C1. All hydrogen atoms and PF_6^- anions are omitted for clarity. Selected bond lengths (Å) and angles (deg) for C1: Ir(1)–C(1), 2.018(2); Ir(1)–N(1), 2.061(2); Ir(1)–N(2), 2.145(2); N(1)–C(7), 1.322(3); N(1)–C(13), 1.397(3); N(2)–C(20), 1.332(3); N(2)–C(16), 1.363(3); C(1)–C(2), 1.398(4); C(1)–C(6), 1.415(4); C(10)–C(14), 1.505(3); C(14)–C(15), 1.642(4); C(1)–Ir(1)–N(1), 79.93(9); C(7)–N(1)–C(13), 111.3(2); C(2)–C(10)–C(6), 116.4(2); C(20)–N(2)–C(16), 118.0(2); C(9)–C(10)–C(11), 120.1(2); C(10)–C(14)–C(15), 119.1(2).

crystallographic data in Table S1). The iridium center of C1 adopted a distorted octahedral geometry. The introduction of *o*-carborane increased the molecular structure volume, and the generated large cage occupied a relatively large space. It is believed that inhibition of metal interactions can effectively enhance the optical physical properties of the complex, as previously reported in analogous iridium(III) complexes with the cyclometalated C^N ligands.^{48,49}

Photophysical Properties of Cationic Cyclometalated Iridium Complexes. The UV–vis absorption and photoluminescence measurements were implemented in water- and oxygen-free CH_2Cl_2 solution for all iridium complexes (C1– C6), and their detailed photophysical data were summarized in Table 1. All synthesized complexes exhibited similar absorption

 Table 1. Photophysical and Electrochemical Data of o

 Carborane-Functionalized Iridium(III) Complexes C1–C6^a

complex	λ_{em}^{a} (nm)	$\Phi_{ ext{PL}}{}^{a}$	$\begin{array}{c} E_{\mathrm{onset}}^{\mathrm{ox}} & \mathrm{ev} \\ \mathrm{(eV)} \end{array}$	$(eV)^{E_g^b}$	HOMO/LUMO ^c (eV)
C1	527.0	0.17	-0.70	2.54	-4.10/-1.56
C2	535.0	0.14	-0.77	2.62	-4.03/-1.41
C3	525.0	0.19	-0.72	2.63	-4.08/-1.45
C4	528.0	0.21	-0.76	2.56	-4.04/-1.48
C5	534.0	0.21	-0.72	2.63	-4.08/-1.45
C6	526.0	0.26	-0.78	2.57	-4.02/-1.45
^a In degassed CH ₂ Cl ₂ at 298 K. ^b In degassed CH ₂ CN at 298 K					

"In degassed CH₂Cl₂ at 298 K. "In degassed CH₃CN at 298 K. "HOMO (eV) = $-e(E_{onset}^{ox} + 4.8), E_g = 1240/\lambda, LUMO (eV) = E_g + HOMO.$

curves. The main strong absorption peaks below 360 nm were principally ascribed to the π - π * transitions in the carboranebased ligands. Additionally, weak absorption peaks in the range of 360–480 nm were assigned to the ligand-to-ligand (LLCT) and metal-to-ligand (MLCT) charge transfers, which are referenced in similar previous reports describing photophysical characteristics of iridium(III) complexes (Figure 2).⁴⁹

As indicated in Figure 3, C1 and C4, C2 and C5, and C3 and C6 have similar largest emission peaks (λ_{max}) at 528, 526, and 534 nm, respectively. The emission profiles of the photoluminescent iridium complexes C2 and C5 were redshifted (λ_{max} 535 and 534 nm, respectively) compared to that of the other complexes, maybe due to the substitution position of the relatively strong electron-withdrawing carborane in the L2 ligand. This observation demonstrated that changing the ocarboranylation position on the ancillary ligand can obviously tune the phosphorescence efficiency of the cationic cyclometalated iridium(III) complexes.⁵⁰



Figure 2. UV-vis absorption spectra of o-carborane-functionalized iridium complexes C1-C6 in the degassed CH_2Cl_2 (5.0 × 10⁻⁵ M, 298 K).



Figure 3. Emission spectra of o-carborane-functionalized iridium complexes C1–C6 in the degassed CH₂Cl₂ (5.0×10^{-5} M, λ_{em} 365 nm, 298 K).

Figure 4 shows the emission spectra of C2 and C4 in various solvents to study the solvent effects, as is disclosed in recent papers. Obviously, the intensity of fluorescence emission was changed with solvent polarity; however, C2 and C4 complexes

displayed little discoloration. The MLCT transitions in iridium(III) complexes have shown that the solvatochromic effects would be related to the molecular dipole moments. Therefore, **C2** and **C4** complexes were less affected by the



Figure 4. Emission spectra of C2 and C4 complexes in various degassed solvents: DCM, THF, CH₃Cl, acetone, CH₃CN, MeOH (1.0×10^{-5} M, λ_{ex} 365 nm, 298 K).



Figure 5. Emission spectra of C2 and C4 complexes at different O₂ concentrations (0 and 21%) in the degassed CH₃OH at 298 K (2.5×10^{-5} M, λ_{ex} 365 nm).

polarity changes. The *o*-carborane fragment on the 2phenylbenzothiazole ligand induces a powerful electronwithdrawing environment, which caused a small change in the molecular dipole moment of these complexes.

Ensuring adequate oxygen is very important to diagnosis and treatment evaluations. It is rather remarkable that the fluorescence intensities of both C2 and C4 are very sensitive to the changes of oxygen concentration from 0 to 21%, though the emission color of these complexes remained relatively stable (Figure 5). In the absence of O_2 , the light intensities of C2 and C4 were brighter. This means that these complexes have the potential to monitor a lower level of endocellular oxygen concentration.

Electrochemical Properties of the Iridium Complexes. The electrochemical properties of the cationic *o*-carboranebased iridium(III) complexes were investigated by cyclic voltammetry (CV) using n-Bu₄NPF₆ (0.1 M), as the supporting electrolyte in the degassed CH₃CN solution. All complexes showed reversible oxidation waves with potentials in the range of 0.4–0.8 V. CV curves are recorded in Figure 6, and their redox potentials are summarized in Table 1. Oxidation potentials are almost the same for all of the cationic



Figure 6. Cyclic voltammograms of iridium(III) complexes C1–C6 at a scan rate of 100 mV s⁻¹.

o-carborane-based cyclometalated iridium(III) complexes, consistent with the energy gaps and emissive wavelengths.

Inorganic Chemistry

CONCLUSIONS

In summary, a series of particular emissive fluorescent iridium(III) complexes containing *o*-carborane modified 2phenyl benzothiazole ligands has been prepared. The emission spectra of the prepared iridium(III) complexes were thoroughly affected by introducing *o*-carborane on different positions of 2-phenyl benzothiazole and resulted in a bathochromic shift of 10 nm. The fluorescence intensity of the prepared complexes is also affected by the inclusion of *o*carborane at different positions of 2-phenyl benzothiazole. Additionally, all iridium complexes showed reversible oxidation waves with potentials in the range of 0.4–0.8 V. The design and photophysical properties of *o*-carborane-functionalized fluorescent materials will be deeply investigated in the near future.

EXPERIMENTAL SECTION

General Data. All reactions were performed under an atmosphere of nitrogen using standard Schlenk and glovebox techniques unless otherwise noted. Chemicals were purchased from commercial sources without further purification. All solvents were treated with a molecular sieve to remove water. Toluene was freshly distilled on CaH₂. ¹H and ¹³C NMR spectra were recorded on a Bruker DMX-500 spectrometer. UV-vis absorption spectra were attained using a UV 765 spectrophotometer by using a 1 cm path length quartz cuvette. FT-IR spectra were measured with the Nicolet FT-IR spectrophotometer by using KBr. Fluorescence measurements were carried out on a Lenguang Technology F97 fluorescence spectrophotometer. $B_{10}H_{12}(Et_2S)_2$ and intermediate compounds were synthesized by a modified reported method (see Scheme S1). Some impurities in ¹H NMR spectra in the range of 0.80-1.70 ppm of the ligands and iridium complexes are assigned to the solvent (petroleum ether) and H₂O peaks.

Synthesis of L1 (2-Phenyl-6-carboranylbenzothiazole). In a 100 mL Schlenk tube, a mixture of 6-ethynyl-2-phenyl-benzothiazole (1.3 g, 5.5 mmol) and the carborane precursor $B_{10}H_{12}(Et_2S)_2$ (2.2 g, 5.7 mmol) was mixed in dry toluene (25 mL). The mixture was heated to 120 °C for 72 h under a nitrogen atmosphere. After cooling to room temperature, the reaction progress was monitored by TLC. Then, the solvent was evaporated to dryness under reduced pressure, and the residue was purified by silica gel column chromatography using PE/EA 1:10 (v/v) as an eluent. Drying in a vacuum afforded L1 as a white solid with 46% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.08 (s, 3H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.53 (s, 3H), 4.04 (s, carborane-CH, 1H), 3.34–1.69 (br, 10H, BH).

Synthesis of L2 (2-(4-Carboborylphenyl) Benzothiazole). The compound was prepared in a manner similar to the synthesis of L1 using 2-(4-ethynylphenyl) benzothiazole (1.3 g, 5.5 mmol) and the carborane precursor $B_{10}H_{12}$ (Et₂S)₂(2.2 g, 5.7 mmol) in dry toluene (25 mL). The white solid L2 was attained in 64% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.09 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 7.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 2H), 7.53 (td, J = 8.0 Hz, 1 Hz, 1H), 7.43 (td, J = 8.0 Hz, 1 Hz, 1H), 4.02 (s, carborane CH, 1H), 3.23–1.72 (br, 10H, BH).

Synthesis of L3 (2-(3-Carboborylphenyl) Benzothiazole). This compound was prepared in a manner similar to the synthesis of L1 using 2-(3-ethynylphenyl) benzothiazole (1.3 g, 5.5 mmol) and the carborane precursor $B_{10}H_{12}$ (Et₂S)₂ (2.2 g, 5.7 mmol) in dry toluene (25 mL). The light yellow solid L3 was attained in 42% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.24 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 4.14 (s, carborane-CH, 1H), 3.01–1.80 (br, 10H, BH).

Synthesis of Iridium Complex C1. In a 100 mL Schlenk tube, a mixture of L1 (0.8 g, 2.30 mmol) and $IrCl_3 \cdot 3H_2O$ (0.4 g, 1.14 mmol) was dissolved in a mixed solvent including 2-ethoxyethanol (30 mL) and H_2O (10 mL). The mixture was stirred at 120 °C for 8 h under

nitrogen and, then, filtered to remove the solvent. The insoluble inorganic salt was washed with water and ether. Thereafter, the resulting solid was achieved by the evaporation of solvent under reduced pressure. Finally, the chlorine-bridged iridium dimer complex precursor $[(Cb-btz)_2Ir(\mu-Cl)]_2$ was attained. Then, the complex precursor (0.5 mg, 0.27 mmol) was reacted with 1,10-phenanthroline (0.107 g, 0.54 mmol) in THF (15 mL). Thereafter, the reaction solution was stirred at 80 °C for 16 h under nitrogen and cooled to room temperature, and KPF₆ was added in 10-fold excess. This mixture was stirred for 2 h, then, evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with elution by 1:3 PE/EA (v/v) to give C1 as an orange-red solid with 32% yield. ¹H NMR (500 MHz, $(CD_3)_2CO$): δ 8.95 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 5.0 Hz, 1H), 8.46 (s, 1H), 8.38 (s, 1H), 8.14 (dd, J = 5.0 Hz, 2.5 Hz, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 9.0 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.55 (d, J = 7.5 Hz, 1H), 5.91 (d, J = 9.0 Hz, 1H), 5.04 (s, 1H, carborane-CH), 2.81–1.80 (br, 10H, BH). ¹³C NMR (125 MHz, (CD₃)₂CO): 184.46, 152.04, 150.51, 150.09, 147.58, 140.31, 139.65, 133.47, 132.41, 131.45, 130.96, 128.60, 127.44, 127.30, 123.90, 123.56, 117.09, 75.93 (B-C), 61.15 (B-C). IR (KBr): v 2570 cm⁻¹ (B-H). Elemental analysis calcd (%) for C₄₂H₄₄B₂₀N₄S₂IrPF₆: C 41.27, H 3.63, N 4.58. Found: C 41.35, H 3.69, N 4.62.

Synthesis of Iridium Complex C2. This complex was prepared in a manner similar to that of C1. Then, a mixture of the corresponding precursor complex (0.5 mg, 0.27 mmol) and 1,10phenanthroline (0.107 g, 0.54 mmol) was prepared, and KPF₆ in THF (15 mL) was added in 10-fold excess to this mixture to afford an orange-red solid of C2 with 30% yield. ¹H NMR (500 MHz, $(CD_3)_2CO$: δ 8.97 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 5.0 Hz, 1H), 8.39 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.15 (m, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.5 Hz, 1H), 6.69 (s, 1H), 6.12 (d, J = 8.5 Hz, 1H), 4.84 (s, 1H, carborane-CH), 2.86-1.47 (br, 10H, BH). ¹³C NMR (125 MHz, (CD₃)₂CO): 180.62, 152.08, 149.39, 149.14, 147.64, 142.52, 139.72, 139.53, 135.92, 133.08, 132.13, 131.56, 128.62, 128.44, 127.45, 126.66, 126.63, 124.23, 122.31, 117.75, 76.45 (B-C), 60.76 (B-C). IR (KBr): v 2559 cm⁻¹ (B-H). Elemental analysis calcd (%) for C42H44B20N4S2IrPF6: C 41.27, H 3.63, N 4.58, Found: C 41.39, H 3.66, N 4.67.

Synthesis of Iridium Complex C3. This complex was prepared in a manner similar to that of C1. A mixture of the corresponding precursor complex (0.5 mg, 0.27 mmol) and 1,10-phenanthroline (0.107 g, 0.54 mmol) was prepared, and KPF₆ in THF (15 mL) was added in 10-fold excess to this mixture to afford an orange solid of C3 with 27% yield. ¹H NMR (500 MHz, $(CD_3)_2CO$): δ 8.95 (d, J = 8.5 Hz, 1H), 8.63 (s, 1H), 8.36 (s, 1H), 8.26 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.63 (d, J = 6.0 Hz, 1H), 6.02 (d, J = 8.5 Hz, 1H), 5.23 (s, 1H, carborane-CH), 2.87-1.81 (br, 10H, BH). ¹³C NMR (125 MHz, (CD₃)₂CO): 180.77, 152.14, 151.80, 148.94, 147.48, 141.63, 139.79, 134.17, 131.83, 131.47, 131.02, 128.89, 128.58, 128.24, 127.46, 126.57, 125.09, 124.21, 117.46, 77.04 (B-C), 61.24 (B-C). IR (KBr): v 2570 cm⁻¹ (B-H). Elemental analysis calcd (%) for $C_{42}H_{44}B_{20}N_4S_2IrPF_6$: C 41.27, H 3.63, N 4.58. Found: C 41.21, H 3.70, N 4.67.

Synthesis of Iridium Complex C4. This complex was prepared in a manner similar to that of **C1**. A mixture of the corresponding precursor complex (0.5 mg, 0.27 mmol) and 2,2'-bipyridine (0.084 g, 0.54 mmol) was prepared, and KPF₆ in THF (15 mL) was added in 10-fold excess to this mixture to afford an orange-red solid of **C4** with 29% yield. ¹H NMR (500 MHz, (CD₃)₂CO): δ 8.84 (d, J = 8.0 Hz, 1H), 8.56 (s, 1H), 8.35 (t, J = 7.5 Hz, 1H), 8.27 (d, J = 5 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.80 (t, J = 6.5 Hz, 1H), 7.45 (dd, J = 9.0 Hz, 1.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.95 (t, J = 7.0 Hz, 1H), 6.44 (d, J = 7.5 Hz, 1H), 6.24 (d, J = 9.0 Hz, 1H), 5.16 (s, 1H, carborane–CH), 3.01–1.63 (br, 10H, BH). ¹³C NMR (125 MHz, (CD₃)₂CO): 184.32, 156.58, 151.32, 151.03, 150.04, 140.51, 140.06, 133.18, 132.68, 132.50, 131.13, 129.12, 127.57, 127.45, 124.84, 127.06, 123.47, 117.33, 76.01 (B–C), 61.24 (B–C). IR (KBr): v2569 cm⁻¹ (B–H). Elemental analysis calcd (%) for $C_{40}H_{44}B_{20}N_4S_2IrPF_6:$ C 40.09, H 3.70, N 4.68. Found: C 40.16, H 3.61, N 4.77.

Synthesis of Iridium Complex C5. This complex was prepared in a manner similar to that of C1. A mixture of the corresponding precursor complex (0.5 mg, 0.27 mmol) and 2,2'-bipyridine (0.084 g, 0.54 mmol) was prepared, and KPF₆ in THF (15 mL) was added in 10-fold excess to this mixture to afford an orange-red solid of C5 with 34% yield. ¹H NMR (500 MHz, (CD₃)₂CO): δ 8.88 (d, J = 8.0 Hz, 1H), 8.36 (t, J = 8.0 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 5.0Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.39 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 6.56 (s, 1H), 6.45 (d, J = 8.5 Hz, 1H), 4.84 (s, 1H, carborane-CH), 2.80–1.46 (br, 1H, BH). ¹³C NMR (125 MHz, (CD₃)₂CO): 180.47, 156.72, 151.26, 149.88, 149.10, 142.29, 140.53, 135.96, 132.77, 132.23, 129.11, 128.64, 126.59, 125.00, 124.36, 122.13, 117.98, 76.36 (B-C), 60.64 (B-C). IR (KBr): v 2570 cm⁻¹ (B-H). Elemental analysis calcd (%) for C40H44B20N4S2IrPF6: C 40.09, H 3.70, N 4.68. Found: C 40.00, H 3.76, N 4.79.

Synthesis of Iridium Complex C6. This complex was prepared in a manner similar to that of C1. A mixture of the corresponding precursor complex (0.5 mg, 0.27 mmol) and 2,2'-bipyridine (0.084 g, 0.54 mmol) was prepared, and KPF₆ in THF (15 mL) was added in 10-fold excess to this mixture to afford an orange-red solid of C6 with 36% yield. ¹H NMR (500 MHz, (CD₃)₂CO): δ 8.83 (d, J = 8.5 Hz, 1H), 8.33 (t, J = 7.5 Hz, 1H), 8.23 (d, J = 5.0 Hz, 1H), 8.21 (s, 1H), 8.20 (d, J = 5.0 Hz, 1H), 7.75 (t, J = 6.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.19 (dd, J = 8.5 Hz, 2.0 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 6.34 (d, J = 8.5 Hz, 1H), 5.20 (s, 1H, carborane-CH) 2.82–1.70 (br, 1H, BH). ¹³C NMR (125 MHz, (CD₃)₂CO): 180.62, 156.53, 152.59, 150.96, 148.90, 141.38, 140.64, 133.90, 131.95, 130.97, 129.12, 128.47, 126.70, 125.05, 124.93, 124.35, 117.75, 76.94 (B-C), 61.13 (B-C). IR (KBr): v 2581 cm⁻¹ (B-H). Elemental analysis calcd (%) for $C_{40}H_{44}B_{20}N_4S_2IrPF_6$: C 40.09, H 3.70, N 4.68. Found: C 40.02, H 3.75, N 4.60.

X-ray Crystallography. Diffraction data of C1 were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromated Mo Ka radiation (λ 0.71073 Å). All data were collected at room temperature, and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL).⁵⁰ SADABS⁵¹ absorption corrections were applied to the data. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were located at the calculated positions. All calculations were performed using the Bruker program Smart.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03625.

A synthesis scheme for the carborane-functionalized 2phenyl benzothiazole ligands (L1–L3) and the intermediate compound $B_{10}H_{12}(Et_2S)_2$; ¹H NMR spectra of L1–L3, ¹H and ¹³C NMR spectra of complexes C1–C6; FT-IR spectra of complexes C1–C6 (PDF)

Accession Codes

CCDC 2047084 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Zi-Jian Yao – School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China; Key Lab of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China; • orcid.org/ 0000-0003-1833-1142; Phone: +86-21-60877231; Email: zjyao@sit.edu.cn; Fax: +86-21-60873335

Zhen-Jiang Liu – School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China; orcid.org/0000-0001-6850-9485; Email: zjliu@sit.edu.cn

Authors

- Yong-Xu Jin School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China
- Wei Deng School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c03625

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 21601125), the Chenguang Scholar of Shanghai Municipal Education Commission (No. 16CG64), the Shanghai Gaofeng & Gaoyuan Project for University Academic Program Development, the research funding of Shanghai Institute of Technology (ZQ2020-10 and XTCX2020-24).

REFERENCES

(1) Ma, D.-L.; Lin, S.; Wang, W.; Yang, C.; Leung, C.-H. Luminescent chemosensors by using cyclometallated iridium(III) complexes and their applications. *Chem. Sci.* **2017**, *8*, 878–889.

(2) Sun, L.; Chen, Y.; Kuang, S.; Li, G.; Guan, R.; Liu, J.; Ji, L.; Chao, H. Iridium(III) Anthraquinone Complexes as Two-Photon Phosphorescence Probes for Mitochondria Imaging and Tracking under Hypoxia. *Chem. - Eur. J.* **2016**, *22*, 8955–8965.

(3) Van Nghia, N.; Park, S.; An, Y.; Lee, J.; Jung, J.; Yoo, S.; Lee, M. H. Impact of the number of o-carboranyl ligands on the photophysical and electroluminescent properties of iridium(III) cyclometalates. *J. Mater. Chem. C* **2017**, *5*, 3024–3034.

(4) Wang, W.; Mao, Z.; Wang, M.; Liu, L.-J.; Kwong, D. W. J.; Leung, C.-H.; Ma, D.-L. A long lifetime luminescent iridium(III) complex chemosensor for the selective switch-on detection of Al³⁺ ions. *Chem. Commun.* **2016**, *52*, 3611–3614.

(5) Shi, C.; Tu, D.; Yu, Q.; Liang, H.; Liu, Y.; Li, Z.; Yan, H.; Zhao, Q.; Huang, W. Carboranes Tuning the Phosphorescence of Iridium Tetrazolate Complexes. *Chem. - Eur. J.* **2014**, *20*, 16550–16557.

(6) Kim, T.; Kim, H.; Lee, K. M.; Lee, Y. S.; Lee, M. H. Phosphorescence Color Tuning of Cyclometallated Iridium Complexes by o-Carborane Substitution. *Inorg. Chem.* 2013, *52*, 160–168.
(7) Bin Mohd Yusoff, A. R.; Huckaba, A. J.; Nazeeruddin, M. K. Phosphorescent Neutral Iridium (III) Complexes for Organic Light-Emitting Diodes. *Top. Curr. Chem.* 2017, *375*, 39.

(8) Wang, W.; Lu, L.; Wu, K.-J.; Liu, J.; Leung, C.-H.; Wong, C.-Y.; Ma, D.-L. Long-lived iridium(III) complexes as luminescent probes for the detection of periodate in living cells. *Sens. Actuators, B* **2019**, 288, 392–398.

(9) Liu, S.; Wei, L.; Guo, S.; Jiang, J.; Zhang, P.; Han, J.; Ma, Y.; Zhao, Q. Anionic iridium(III) complexes and their conjugated polymer soft salts for time-resolved luminescent detection of intracellular oxygen levels. *Sens. Actuators, B* **2018**, *262*, 436–443.

(10) Liu, J.-B.; Wang, W.; Li, G.; Wang, R.-X.; Leung, C.-H.; Ma, D.-L. Luminescent Iridium(III) Chemosensor for Tandem Detection of F^- and Al^{3+} . ACS Omega **2017**, 2, 9150–9155.

(11) Kim, H. U.; Sohn, S.; Choi, W.; Kim, M.; Ryu, S. U.; Park, T.; Jung, S.; Bejoymohandas, K. S. Substituents engineered deep-red to near-infrared phosphorescence from tris-heteroleptic iridium(iii) complexes for solution processable red-NIR organic light-emitting diodes. J. Mater. Chem. C 2018, 6, 10640–10658.

(12) (a) Axtell, J. C.; Kirlikovali, K. O.; Djurovich, P. I.; Jung, D.; Nguyen, V. T.; Munekiyo, B.; Royappa, A. T.; Rheingold, A. L.; Spokoyny, A. M. Blue Phosphorescent Zwitterionic Iridium(III) Complexes Featuring Weakly Coordinating nido-Carborane-Based Ligands. J. Am. Chem. Soc. 2016, 138, 15758–15765. (b) Wang, Y.-S.; Feng, T.; Wang, Y.-Y.; Hahn, F. E.; Han, Y.-F. Homo- and Heteroligand Poly-NHC Metal Assemblies: Synthesis by Narcissistic and Social Self-Sorting. Angew. Chem., Int. Ed. 2018, 57, 15767– 15771.

(13) Bae, H. J.; Chung, J.; Kim, H.; Park, J.; Lee, K. M.; Koh, T.-W.; Lee, Y. S.; Yoo, S.; Do, Y.; Lee, M. H. Deep Red Phosphorescence of Cyclometallated Iridium Complexes by o-Carborane Substitution. *Inorg. Chem.* **2014**, *53*, 128–138.

(14) Nishino, K.; Yamamoto, H.; Tanaka, K.; Chujo, Y. Development of Solid-State Emissive Materials Based on Multifunctional o-Carborane–Pyrene Dyads. *Org. Lett.* **2016**, *18*, 4064–4067.

(15) Dash, B. P.; Satapathy, R.; Gaillard, E. R.; Maguire, J. A.; Hosmane, N. S. Synthesis and Properties of Carborane-Appended C_3 -Symmetrical Extended π Systems. *J. Am. Chem. Soc.* **2010**, *132*, 6578–6587.

(16) (a) Guo, J.; Liu, D.; Zhang, J.; Zhang, J.; Miao, Q.; Xie, Z. o-Carborane functionalized pentacenes: synthesis, molecular packing and ambipolar organic thin-film transistors. *Chem. Commun.* **2015**, *51*, 12004–12007. (b) Wang, L.-J.; Li, X.; Bai, S.; Wang, Y.-Y.; Han, Y.-F. Self-Assembly, Structural Transformation, and Guest-Binding Properties of Supramolecular Assemblies with Triangular Metal-Metal Bonded Units. J. Am. Chem. Soc. **2020**, *142*, 2524–2531.

(17) Bregadze, V. I. Dicarba-closo-dodecaboranes $C_2B_{10}H_{12}$ and their derivatives. *Chem. Rev.* **1992**, *92*, 209–223.

(18) Zhao, D.; Xie, Z. Recent advances in the chemistry of carborynes. *Coord. Chem. Rev.* **2016**, *314*, 14–33.

(19) Wee, K.-R.; Han, W.-S.; Cho, D. W.; Kwon, S.; Pac, C.; Kang, S. O. Carborane Photochemistry Triggered by Aryl Substitution: Carborane-Based Dyads with Phenyl Carbazoles. *Angew. Chem., Int. Ed.* **2012**, *51*, 2677–2680.

(20) Shi, C.; Sun, H.; Tang, X.; Lv, W.; Yan, H.; Zhao, Q.; Wang, J.; Huang, W. Variable Photophysical Properties of Phosphorescent Iridium(III) Complexes Triggered by closo- and nido-Carborane Substitution. *Angew. Chem., Int. Ed.* **2013**, *52*, 13434–13438.

(21) Kokado, K.; Chujo, Y. Multicolor Tuning of Aggregation-Induced Emission through Substituent Variation of Diphenyl-ocarborane. J. Org. Chem. 2011, 76, 316–319.

(22) Kokado, K.; Tominaga, M.; Chujo, Y. Aromatic Ring-Fused Carborane-Based Luminescent π -Conjugated Polymers. *Macromol. Rapid Commun.* **2010**, *31*, 1389–1394.

(23) Kim, S.-Y.; Cho, Y.-J.; Jin, G. F.; Han, W.-S.; Son, H.-J.; Cho, D. W.; Kang, S. O. Intriguing emission properties of triphenylamine–carborane systems. *Phys. Chem. Chem. Phys.* **2015**, *17*, 15679–15682.

(24) Kober, E. M.; Sullivan, B. P.; Meyer, T. J. Solvent dependence of metal-to-ligand charge-transfer transitions. Evidence for initial electron localization in MLCT excited states of 2,2'-bipyridine complexes of ruthenium(II) and osmium(II). *Inorg. Chem.* **1984**, 23, 2098–2104.

(25) Yao, Z.-J.; Yu, W.-B.; Lin, Y.-J.; Huang, S.-L.; Li, Z.-H.; Jin, G.-X. Iridium-Mediated Regioselective B-H/C-H Activation of Carborane Cage: A Facile Synthetic Route to Metallacycles with a Carborane Backbone. J. Am. Chem. Soc. **2014**, 136, 2825–2832.

(26) Xiong, L. Q.; Zhao, Q.; Chen, H. L.; Wu, Y. B.; Dong, Z. S.; Zhou, Z. G.; Li, F. Y. Phosphorescence Imaging of Homocysteine and Cysteine in Living Cells Based on a Cationic Iridium(III) Complex. *Inorg. Chem.* **2010**, *49*, 6402–6408. (27) Li, X.; Yin, Y. H.; Yan, H.; Lu, C. S.; Zhao, Q. Novel phosphorescent cationic iridium(III) complexes with o-carboranylation on the ancillary N-N ligand. *Dalton Trans.* **2017**, *46*, 10082–10089.

(28) Zhao, Q.; Liu, S.; Shi, M.; Wang, C.; Yu, M.; Li, L.; Li, F.; Yi, T.; Huang, C. Series of New Cationic Iridium(III) Complexes with Tunable Emission Wavelength and Excited State Properties: Structures, Theoretical Calculations, and Photophysical and Electro-chemical Properties. *Inorg. Chem.* **2006**, *45*, 6152–6160.

(29) Shi, C.; Sun, H.; Jiang, Q.; Zhao, Q.; Wang, J.; Huang, W.; Yan, H. Carborane tuning of photophysical properties of phosphorescent iridium(III) complexes. *Chem. Commun.* **2013**, *49*, 4746–4748.

(30) Lee, Y. H.; Park, J.; Jo, S.-J.; Kim, M.; Lee, J.; Lee, S. U.; Lee, M. H. Manipulation of Phosphorescence Efficiency of Cyclometallated Iridium Complexes by Substituted o-Carboranes. *Chem.* -*Eur. J.* **2015**, *21*, 2052–2016.

(31) Nghia, N. V.; Oh, J.; Jung, J.; Lee, M. H. Deboronation-Induced Turn-on Phosphorescent Sensing of Fluorides by Iridium-(III) Cyclometalates with o-Carborane. *Organometallics* **2017**, *36*, 2573–2580.

(32) (a) Wilson, J. S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Younus, M.; Khan, M. S.; Raithby, P. R.; Kohler, A.; Friend, R. H. The Energy Gap Law for Triplet States in Pt-Containing Conjugated Polymers and Monomers. J. Am. Chem. Soc. 2001, 123, 9412–9417.
(b) Ma, L.-L.; An, Y.-Y.; Sun, L.-Y.; Wang, Y.-Y.; Hahn, F. E.; Han, Y.-F. Supramolecular Control of Photocycloadditions in Solution: In Situ Stereoselective Synthesis and Release of Cyclobutanes. Angew. Chem., Int. Ed. 2019, 58, 3986–3991.

(33) Dash, B. P.; Satapathy, R.; Maguire, J. A.; Hosmane, N. S. Polyhedral boron clusters in materials science. *New J. Chem.* **2011**, *35*, 1955–1972.

(34) Caspar, J. V.; Meyer, T. J. Photochemistry of MLCT excited states. Effect of nonchromophoric ligand variations on photophysical properties in the series cis-Ru(bpy) $_{2}L_{2}^{2+}$. *Inorg. Chem.* **1983**, *22*, 2444–2453.

(35) Ferrer-Ugalde, A.; González-Campo, A.; Viñas, C.; Rodríguez-Romero, J.; Santillan, R.; Farfán, N.; Sillanpää, R.; Sousa-Pedrares, A.; Núñez, R.; Teixidor, F. Fluorescence of New o-Carborane Compounds with Different Fluorophores: Can it be Tuned. *Chem.* -*Eur. J.* **2014**, *20*, 9940–9951.

(36) Teixidor, F.; Núñez, R.; Viñas, C.; Sillanpää, R.; Kivekäs, R. The Distinct Effect of the o-Carboranyl Fragment: Its Influence on the I-I Distance in R₃PI₂ Complexes. *Angew. Chem., Int. Ed.* **2000**, *39*, 4290–4292.

(37) Núñez, R.; Farràs, P.; Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R. A Discrete P-I-I-P Assembly: The Large Influence of Weak Interactions on the ³¹P NMR Spectra of Phosphane–Diiodine Complexes. *Angew. Chem., Int. Ed.* **2006**, *45*, 1270–1272.

(38) Lee, Y. H.; Park, J.; Lee, J.; Lee, S. U.; Lee, M. H. Iridium Cyclometalates with Tethered o-Carboranes: Impact of Restricted Rotation of o-Carborane on Phosphorescence Efficiency. *J. Am. Chem. Soc.* **2015**, *137*, 8018–8021.

(39) Li, X.; Tong, X.; Yan, H.; Lu, C.; Zhao, Q.; Huang, W. A Convenient Approach To Synthesize o-Carborane-Functionalized Phosphorescent Iridium(III) Complexes for Endocellular Hypoxia Imaging. *Chem. - Eur. J.* **2016**, *22*, 17282–17290.

(40) Chen, L. Q.; You, H.; Yang, C. L.; Ma, D.; Qin, J. G. Novel, highly efficient blue-emitting heteroleptic iridium(III) complexes based on fluorinated 1,3,4-oxadiazole: tuning to blue by dithiolate ancillary ligands. *Chem. Commun.* **2007**, *13*, 1352–1354.

(41) Wilde, A. P.; Watts, R. J. Solvent effects on metal-to-ligand charge-transfer bands in ortho-metalated complexes of iridium(III): estimates of transition dipole moments. *J. Phys. Chem.* **1991**, *95*, 622–629.

(42) Li, X.; Yan, H.; Zhao, Q. Carboranes as a Tool to Tune Phosphorescence. *Chem. - Eur. J.* 2016, 22, 1888–1898.

(43) Kapturkiewicz, A.; Chen, T.-M.; Laskar, I. R.; Nowacki, J. Electrochemiluminescence studies of the cyclometallated iridium(III)

complexes with substituted 2-phenylbenzothiazole ligands. *Electro*chem. Commun. 2004, 6, 827-831.

(44) Shi, X.; Guo, J.; Liu, J.; Ye, M.; Xu, Q. Unexpectedly Simple Synthesis of Benzazoles by tBuONa-Catalyzed Direct Aerobic Oxidative Cyclocondensation of o-Thio/Hydroxy/Aminoanilines with Alcohols under Air. *Chem. - Eur. J.* **2015**, *21*, 9988–9993.

(45) Toppino, A.; Genady, A. R.; El-Zaria, M. E.; Reeve, J.; Mostofian, F.; Kent, J.; Valliant, J. F. High Yielding Preparation of Dicarba-closo-dodecaboranes Using a Silver(I) Mediated Dehydrogenative Alkyne-Insertion Reaction. *Inorg. Chem.* **2013**, *52*, 8743– 8749.

(46) Sinha, S.; Mandal, S.; Gupta, P. Cyclometallated iridium(III) complexes of (aryl)ethenyl functionalized 2,2'-bipyridine: synthesis, photophysical properties and trans-cis isomerization behavior. *RSC Adv.* **2015**, *5*, 99529–99539.

(47) Galliamova, L. A.; Varaksin, M. V.; Chupakhin, O. N.; Slepukhin, P. A.; Charushin, V. N. Heterocyclic and Open-Chain Carboranes via Transition-Metal-Free C–H Functionalization of Mono- and Diazine-N-oxides. *Organometallics* **2015**, *34*, 5285–5290.

(48) Li, X.; Tong, X.; Yin, Y.; Yan, H.; Lu, C.; Huang, W.; Zhao, Q. Using highly emissive and environmentally sensitive o-carborane-functionalized metallophosphors to monitor mitochondrial polarity. *Chem. Sci.* **2017**, *8*, 5930–5940.

(49) Li, X.; Yin, Y.; Gao, P.; Li, W.; Yan, H.; Lu, C.; Zhao, Q. A novel phosphorescent iridium(III) complex bearing a donor-acceptor-type o-carboranylated ligand for endocellular hypoxia imaging. *Dalton Trans.* **2017**, *46*, 13802–13810.

(50) Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; Universität Göttingen: Germany, 1997.

(51) Sheldrick, G. M. SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998.