

# Iridium Cyclometalates with Tethered *o*-Carboranes: Impact of Restricted Rotation of *o*-Carborane on Phosphorescence Efficiency

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## Supporting Information

**ABSTRACT:** Iridium(III) cyclometalates (**1c** and **2c**) in which the two carborane units on the 4- or 5-positions of 2-phenylpyridine (ppy) ligands were tethered by an alkylene linker were prepared to investigate the effect of free rotation of *o*-carborane on phosphorescence efficiency. In comparison with the unlinked complex, tethering the *o*-carboranes to the 5-positions of ppy ligands (**2c**) enhanced phosphorescence efficiency by over 30-fold in polar medium ( $\Phi_{\text{PL}} = 0.37$  vs 0.011 in THF), while restricting the rotation of *o*-carborane at the 4-positions (**1c**) negatively affected the phosphorescence efficiency. The different effects of restricted rotation of *o*-carborane on phosphorescence efficiency were likely a result of the different variations of the carboranyl C–C bond distances in the excited state.

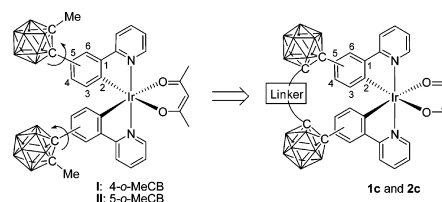
Due to their excellent photophysical properties and high stability, iridium(III) cyclometalates have been widely used as highly efficient phosphorescent emitters in organic light-emitting diodes (OLEDs) and solid-state lighting.<sup>1</sup> The successful utilization of iridium(III) cyclometalates in such applications is mainly attributed to the facile control of the emissive lowest-lying triplet excited states (<sup>3</sup>MLCT and <sup>3</sup> $\pi\pi^*$ ) by modifying the electronic structure of the cyclometalating (C<sup>^</sup>N) ligand.<sup>2,3</sup> This allowed to develop a variety of color-tunable emitters with a high phosphorescence efficiency.<sup>4</sup>

As a novel substituent on the cyclometalating ligand (C<sup>^</sup>N), *o*-carborane (1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>)<sup>5</sup> attracts growing interest because it may serve not only as a steric auxiliary to suppress quenching of solid state emission but also offer an electronic effect to alter the band gap and phosphorescence efficiency.<sup>6–11</sup> Recent studies of *o*-carborane containing phosphorescent iridium(III) cyclometalates have shown that incorporating *o*-carborane in the C<sup>^</sup>N ligand can lead to unusual emission band shifts<sup>8–12</sup> or tuning of phosphorescence efficiency depending on the substitution position in the C<sup>^</sup>N ligand and the type of 2-substituent on *o*-carborane.<sup>6</sup> Although these results originated from the involvement of *o*-carborane in controlling the triplet excited states by the unique inductive and conjugation effects of *o*-carborane,<sup>13</sup> the emissive properties of the complexes were significantly sensitive to the polarity of the medium, leading to emission quenching in polar media.<sup>6,9,11</sup> The main cause of emission quenching has been suggested to be the variable nature of carboranyl C–C bonds<sup>9,14,15</sup> and the rotational mobility of *o*-

carborane<sup>16</sup> during electronic transition. However, clear evidence has not been disclosed yet to support this hypothesis. Moreover, overcoming the adverse effects of *o*-carborane on phosphorescence efficiency in polar medium remains a challenge, though the solid-state emission properties of complexes are still promising as an efficient phosphorescent emitter in OLEDs.<sup>6,8,11</sup>

To tackle this issue, we designed a new type of *o*-carborane containing iridium(III) cyclometalate (**1c** and **2c**) in which the two carborane units on the 4- or 5-positions of the 2-phenylpyridine (ppy) ligands are covalently tethered by an alkylene linker to restrict free rotation of the *o*-carborane (Chart 1). Herein, the photophysical properties of **1c** and **2c** were

Chart 1

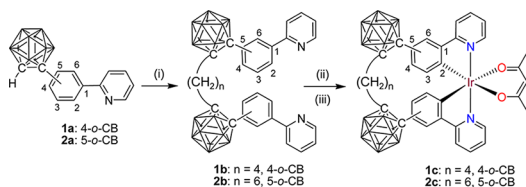


investigated and compared with the properties of the corresponding unlinked complexes (**I** and **II**) to see the effect of restricted rotation of *o*-carborane on phosphorescence efficiency. We find that in combination with the substitution position, rotation of *o*-carborane plays a crucial role in controlling phosphorescence efficiency.

Alkylene-linked bis-*o*-carboranyl C<sup>^</sup>N ligands **1b** and **2b** were prepared by deprotonation of 4- or 5-*o*-carborane-substituted 2-phenylpyridine (**1a** and **2a**) with NaH followed by the reaction with 1,4-diiodobutane or 1,6-dibromohexane, respectively, in DMF (Scheme 1). The cyclometalation reactions of iridium(III) chloride with ligands **1b** and **2b** yielded dimeric [(C<sup>^</sup>N)<sub>2</sub>Ir( $\mu$ -Cl)<sub>2</sub>Ir(C<sup>^</sup>N)<sub>2</sub>] complexes. The dimers were further treated with acacH under mild basic conditions,<sup>11,18</sup> producing the iridium(III) cyclometalates with alkylene-linked *o*-carboranyl C<sup>^</sup>N ligands, [R-(*m*-CBppy)<sub>2</sub>]Ir(acac) (R = 1,4-butanediyl, *m* = 4 (**1c**); R = 1,6-hexanediyl, *m* = 5 (**2c**); CB = *o*-carboran-1-yl; ppy = 2-phenylpyridinato-C<sup>2</sup>,N; acac = acetylacetonate). Complex formation was characterized by NMR spectroscopy, elemental

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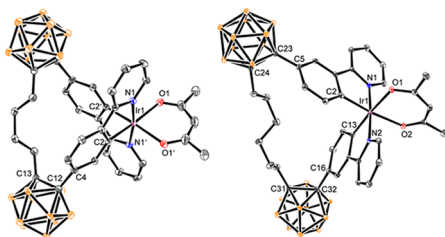
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Scheme 1. Synthesis of **1c** and **2c**<sup>a</sup>

<sup>a</sup>Legend: (i) NaH, 1,4-diiodobutane or 1,6-dibromohexane, DMF. (ii) IrCl<sub>3</sub>·3H<sub>2</sub>O, 2-ethoxyethanol, 110 °C, 1 d. (iii) 2,4-Pentanedione, Na<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN, 80 °C, 1 d.

analysis, and X-ray diffraction. The broad aliphatic proton resonances in the <sup>1</sup>H NMR spectra of **1c** and **2c** are consistent with the rigid nature of the alkyne-linked bis-*o*-carboranyl C<sup>N</sup> ligands in the complexes.

The crystal structures of both complexes revealed that two *o*-carborane cages on the phenyl rings of ppy moieties were linked through an alkyne bridge to form a tetradentate C<sup>N</sup> chelation to the Ir atom (Figure 1). The structural analyses showed that the

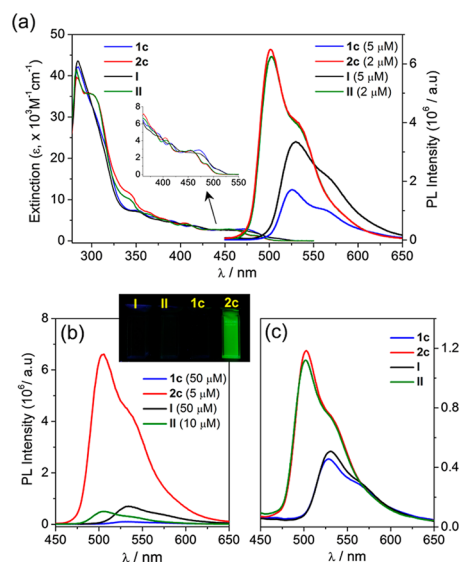


**Figure 1.** Crystal structures of **1c** (left) and **2c** (right) (40% thermal ellipsoids). H atoms and solvent molecules are omitted for clarity. C<sub>cage</sub>–C<sub>cage</sub> bond distances (Å): 1.705(6) for **1c**; 1.704(8), 1.706(6) for **2c** (cf., 1.696(9) for **I**; 1.694(5), 1.704(5) for **II**).

carboranyl C–C bonds (C<sub>cage</sub>–C<sub>cage</sub>) in **1c** and **2c** had almost identical bond distances of 1.705 Å, which is comparable to that of the corresponding unlinked complexes **I** and **II**. The torsion angles ( $\psi = \angle(\text{C}_{\text{Ph}}-\text{C}_{\text{Ph}}-\text{C}_{\text{cage}}-\text{C}_{\text{cage}})$ ) of 74–88° indicate that the carboranyl C–C bond remains nearly perpendicular to the phenyl ring of the ppy in **1c** and **2c**, indicating the existence of  $\pi(\text{ppy})-\sigma^*(\text{C}-\text{C})$  interactions.<sup>15</sup>

To investigate the photophysical properties of complexes **1c** and **2c**, UV/vis absorption and photoluminescence (PL) experiments were carried out in toluene (Figure 2 and Table 1). The spectra of unlinked complexes **I** and **II** were also compared. The linked complexes featured low-energy absorption bands attributable to the MLCT transition in the region of  $\lambda = 405\text{--}416$  nm (<sup>1</sup>MLCT,  $\epsilon \approx 3700\text{--}4300$  M<sup>-1</sup> cm<sup>-1</sup>) and 455–473 nm (<sup>3</sup>MLCT,  $\epsilon \approx 2800\text{--}2900$  M<sup>-1</sup> cm<sup>-1</sup>), which were similar to those in the corresponding unlinked complex. The MLCT absorption of 4-carborane substituted **1c** and **I** was red-shifted with respect to that of (ppy)<sub>2</sub>Ir(acac) complex (**3**), while the 5-substituted **2c** and **II** were blue-shifted, similar to previous reports.<sup>6,11</sup> The almost invariant absorption features between the linked and unlinked complexes suggest that the effects of the 2-alkylene linker on the electronic transition are negligible.

The PL spectra of **1c** and **2c** in toluene showed emission peak positions comparable to those of **I** and **II** at both room temperature and 77 K (Figures 2a and S4 and Table 1). The emission lifetimes ( $\tau$ ) of 1.19 and 1.32  $\mu\text{s}$  for **1c** and **2c**, respectively, confirmed the phosphorescence origin of the emission. The shape of the phosphorescence bands also



**Figure 2.** (a) UV/vis absorption ( $5 \times 10^{-5}$  M) and PL spectra ( $\lambda_{\text{exc}} = 380\text{--}390$  nm) of **1c**, **2c** and **I**, **II** in toluene at 298 K. PL spectra of **1c**, **2c** and **I**, **II** (b) in THF and (c) in PMMA film (4 wt % Ir) at 298 K ( $\lambda_{\text{exc}} = 380\text{--}390$  nm). The picture shows the emission of THF solution (5  $\mu\text{M}$  for all) under UV illumination.

resembled that of **I–II** and **3**, indicating that the phosphorescence in **1c** and **2c** was mainly <sup>3</sup>MLCT in nature.<sup>3</sup> All of the complexes (**1c–2c** and **I–II**) exhibited intense green emission at 298 K, although the 4-carborane substituted **1c** and **I** were less emissive than the 5-substituted **2c** and **II**.<sup>11</sup> In particular, the quantum efficiency of complex **2c** with tethered carboranes at the 5-position of the ppy ligand was very high ( $\Phi_{\text{PL}} = 0.96$ ) and apparently higher than those of the unlinked **II** ( $\Phi_{\text{PL}} = 0.83$ ) and parent **3** ( $\Phi_{\text{PL}} = 0.77$ ). In contrast, complex **1c** ( $\Phi_{\text{PL}} = 0.24$ ) with the tethered carboranes at the 4-position had a lower quantum efficiency than that of **I** ( $\Phi_{\text{PL}} = 0.47$ ). These results indicate that restricting carborane rotation may enhance or reduce the quantum efficiency of the complex depending on the substitution position of the carborane unit. To gain more insight into the effect of tethered carboranes on quantum efficiency, PL spectra of all complexes were obtained in THF and in a rigid matrix (Figure 2b,c). Remarkably, **2c** had a high quantum efficiency ( $\Phi_{\text{PL}} = 0.37$ ) in THF, which was enhanced over 30-fold compared with that of **II** ( $\Phi_{\text{PL}} = 0.011$ ). In a PMMA film, however, the quantum efficiency of **II** ( $\Phi_{\text{PL}} = 0.32$ ) was comparable to that of **2c** ( $\Phi_{\text{PL}} = 0.36$ ) probably due to rigidity of **II** in the film state. In contrast, the linked **1c** was still less emissive than the unlinked **I** in THF, although both **1c** and **I** were poorly emissive ( $\Phi_{\text{PL}} < 0.01$ ). In the PMMA film, both complexes showed comparable and largely increased quantum efficiency ( $\Phi_{\text{PL}} = 0.16\text{--}0.17$ ). These findings indicate that while restricting the free rotation of carborane units on the 5-position of the ppy ligand efficiently reduces nonradiative decay processes, even in a polar solvent, restricting rotation at the 4-position has little influence on quantum efficiency. The comparable quantum efficiency of each pair of the linked and unlinked complexes in a PMMA film further implies the significance of rotational effect of carborane on phosphorescence efficiency.

To elucidate the effect of restricted rotation of *o*-carborane and the dependence of the position of the carborane substitution on phosphorescence efficiency, the structures of the ground state ( $S_0$ ) and lowest triplet excited state ( $T_1$ ) of all complexes were optimized in different media, followed by TD-DFT calculations

Table 1. Photophysical Data for 1c–2c and I–II

compd	$\lambda_{\text{abs}}$ (nm) for MLCT ( $\epsilon \times 10^{-3}$ (M <sup>-1</sup> cm <sup>-1</sup> )) <sup>a</sup>	$\lambda_{\text{em}}$ (nm) in toluene		$\lambda_{\text{em}}$ (nm) in THF	$\lambda_{\text{em}}$ (nm) in PMMA	$\Phi_{\text{PL}}$			$\tau$ ( $\mu\text{s}$ )
		298 K <sup>b</sup>	77 K <sup>b</sup>	298 K <sup>c</sup>	298 K <sup>d</sup>	toluene <sup>b,e</sup>	THF <sup>c,e</sup>	PMMA <sup>d,f</sup>	toluene <sup>b</sup>
1c	415 (3.7), 472 (2.9)	526	517	531	530	0.24	<0.01	0.16	1.19
2c	405 (4.3), 455 (2.8)	502	490	504	503	0.96	0.37	0.36	1.32
I	416 (3.6), 473 (2.4)	529	521	534	531	0.47	<0.01	0.17	1.88
II <sup>g</sup>	407 (3.9), 456 (2.8)	503	492	506	503	0.83	0.011	0.32 <sup>i</sup>	1.22
3 <sup>g,h</sup>	412 (4.2), 465 (3.2)	516	504	519	517	0.77	0.77	0.30 <sup>i</sup>	1.48

<sup>a</sup>In degassed toluene ( $5.0 \times 10^{-5}$  M). <sup>b</sup>In  $5.0 \times 10^{-6}$  M for 1c and I;  $2.0 \times 10^{-6}$  M for 2c and II. <sup>c</sup>In  $5.0 \times 10^{-5}$  M for 1c and I;  $1.0 \times 10^{-5}$  M for 2c and II. <sup>d</sup>Spin-coated PMMA film doped with Ir<sup>III</sup> complexes (4 wt %). <sup>e</sup>fac-Ir(ppy)<sub>3</sub> as a standard ( $\Phi_{\text{PL}} = 0.97$ ). <sup>f</sup>Absolute PLQY. <sup>g</sup>From ref 6. <sup>h</sup>3:(ppy)<sub>2</sub>Ir(acac). <sup>i</sup>This work.

(Figures 3 and S7–S10 and Tables S5–S16). Unlike the fixed conformations of 1c and 2c, the geometries of complexes I and II

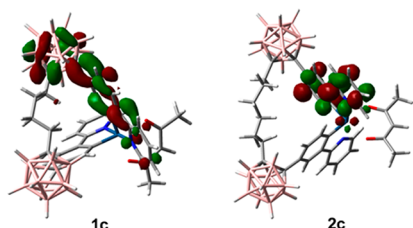


Figure 3. LUMOs of 1c and 2c at the lowest triplet excited state ( $T_1$ ) structures from DFT calculations (isovalue = 0.04).

were optimized at three different conformations according to the orientation of two methyl (Me) groups to consider free rotation of carborane units in solution (Table S17). The optimized conformations were I–I, I–O, and O–O, where I denotes a Me-inside orientation and O denotes a Me-outside orientation.

**1. Molecular Orbital Analysis.** The lowest-energy absorption ( $S_0$ – $S_1$ ) and phosphorescence ( $S_0$ – $T_1$ ) processes mainly involved HOMO–LUMO transition in the linked complexes 1c and 2c. The computed transition energy of 2c was higher than that of 1c ( $\lambda_{\text{abs}} = 419$  nm vs 435 nm and  $\lambda_{\text{em}} = 462$  nm vs 488 nm in THF), which is in accordance with the experimentally observed absorption and phosphorescence wavelengths. The transition energies of 1c and 2c were virtually the same as those of the corresponding unlinked complexes, I and II, indicating that the alkylene linker in 1c and 2c has little effect on the transition energy. The molecular orbital (MO) distributions of the complexes with and without the alkylene linker were similar in both the  $S_0$  and  $T_1$  states, which in turn supports the similarity of absorption and phosphorescence band shapes and wavelengths. Importantly, the contributions of the carborane cages to LUMOs had apparent differences depending on the position of the carborane substitution in the  $T_1$  structure. In the 4-carborane substituted 1c and I, the LUMO was delocalized over the ligand with a major contribution from carborane cages (ca. 60%). The carborane contributed little to the LUMO of the 5-substituted 2c and II (ca. 2%) (Figure 3). These orbital features are consistent with the red-shift of phosphorescence caused by 4-carborane substitution (the conjugation effect) and the blue-shift caused by 5-substitution (the inductive effect) with respect to 3.<sup>11</sup>

**2. Effect of Restricted Rotation of o-Carborane.** To examine the rotational effect of carborane cages on the emission properties, C–C bond variations between the  $S_0$  and  $T_1$  states ( $\Delta(\text{C–C})_{T_1-S_0}$ ) of I and II were investigated at every carborane cage rotation ( $30^\circ$ ) starting from the I–O conformation to I–I

and to O–O (Figure 4). The three conformations of each complex had similar MO energies and carborane contributions to

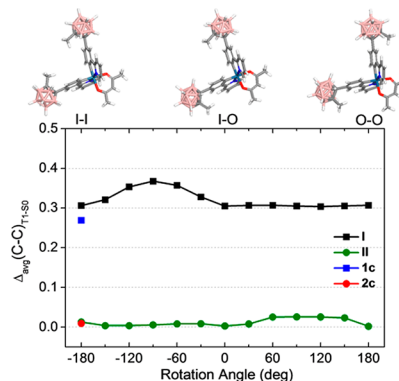


Figure 4. Computed average variations in the  $\text{C}_{\text{cage}}\text{–}\text{C}_{\text{cage}}$  bond distances between the  $S_0$  and  $T_1$  state structures ( $\Delta_{\text{avg}}(\text{C–C})_{T_1-S_0}$ , Å) of I and II in THF upon rotation of the carborane cages.

MOs (Tables S18–S19). The computational results show that the 4-carborane substituted I undergoes large C–C bond variations ( $\Delta_{\text{avg}}(\text{C–C})_{T_1-S_0} > 0.30$  Å) irrespective of the Me orientation of the carboranes. In particular, the C–C bond in a carborane cage where the LUMO is majorly delocalized in the  $T_1$  state was elongated to 0.73 Å (Figure S11 and Table S20). This feature suggests that the  $T_1$  excited state of I may undergo facile nonradiative decay due to the high elasticity of the C–C bond in THF. Likewise, the tethered complex 1c, which resembles the I–I conformation of I, also exhibited large variation ( $\Delta_{\text{avg}}(\text{C–C})_{T_1-S_0} = 0.28$  Å). Although the variation in I fluctuated upon carborane rotation from I–O to I–I, the high level of C–C bond variation seemed to govern the excited state properties of both 1c and I because the quantum efficiency of I was slightly higher than that of 1c.

However, the 5-carborane substituted complexes 2c and II with little LUMO contribution by carborane in the  $T_1$  structure showed very small C–C bond variation ( $\Delta_{\text{avg}}(\text{C–C})_{T_1-S_0} < \text{ca. } 0.01$  Å) in all three conformations (Figure 4). This feature is quite different from that of the 4-substituted 1c and I, thus indicating that the  $T_1$  excited states of 2c and II have high structural stability for efficient phosphorescence. However, upon rotation of carborane, II underwent substantial fluctuation in the C–C bond ( $\Delta(\text{C–C})_{T_1-S_0}$ ) ranging from 0.00 to 0.03 Å (Figure S11 and Table S20). This relatively large variation in the  $T_1$  excited states of II might be responsible for the low quantum efficiency of II in THF. Nevertheless, II is intrinsically more emissive than 1c and I due to the small C–C bond variations. Finally, the variations in all complexes increased with increased

solvent polarity (gas < toluene < THF), which is in parallel with the decreasing order of experimental quantum efficiencies (Figure S12).<sup>6,9</sup>

In summary, iridium(III) cyclometalates (**1c** and **2c**) with *o*-carboranes tethered by an alkylene linker were prepared and characterized. High phosphorescence efficiency was attained even in polar medium ( $\Phi_{\text{PL}} = 0.37$  in THF) by tethering the *o*-carboranes to the 5-positions of the ppy ligands (**2c**). Restricting rotation of the *o*-carborane at the 4-positions (**1c**) had little effect on the enhancement of phosphorescence efficiency. Variations in the carboranyl C–C bond distances of the excited states differed for the 4- and 5-substituted systems, which might be responsible for the different effects of restricted rotation of *o*-carborane on phosphorescence efficiency.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental and computational details. Crystallographic data for **1c** and **2c** in cif format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04576.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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