

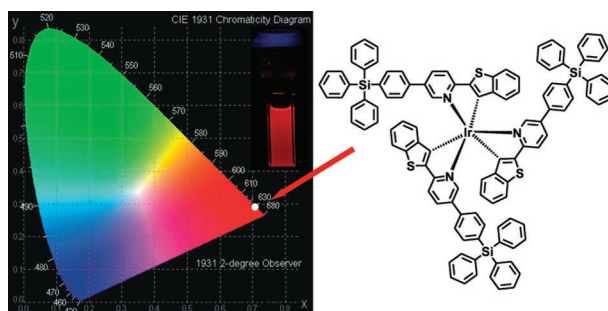
## A Deep Red Phosphorescent Ir(III) Complex for Use in Polymer Light-Emitting Diodes: Role of the Arylsilyl Substituents

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Here we report the synthesis and electrophosphorescence of a new deep-red phosphorescent Ir(III) complex with spatially embracing and thus solubilizing arylsilyl-substituted ligands, Ir(III) tris(2-(2'-benzo[*b*]-thienyl)-5-(4'-triphenylsilylphenyl)pyridinato-*N,C*<sup>3'</sup>). A poly(*N*-vinylcarbazole) (PVK) film doped with this Ir(III) complex exhibited excellent phase homogeneity and showed saturated red electrophosphorescence of 2.7% maximum external quantum efficiency, whose Commission Internationale de L'Éclairage coordinates were (0.69, 0.30).

### Introduction

Past works aimed at realizing large-area organic light-emitting diodes (OLEDs) have yielded promising results using solution processing with a fluorescent polymer-emitting layer.<sup>1</sup> However, the inherently low efficiency of fluorescent polymer devices has limited their practical applications. A potential approach to overcoming this problem is to use phosphorescent Ir(III) complexes, which greatly outperform inherently low efficiency of the fluorescence-based devices.<sup>2–8</sup>

One of key challenges in developing Ir(III) complexes suitable for use in emitting layers in OLEDs is achieving both saturated red emission and high processibility (solubility).<sup>9,10</sup> Generally, Ir(III) complexes are not sufficiently compatible to form

homogeneous molecular dispersions in polymer films. This poor solubility, in turn, restricts device efficiency and lifetime.<sup>11</sup> In this regard, macromolecular systems of (1) Ir(III) complexes covalently attached to polymer chains<sup>12a–c</sup> and (2) Ir(III)

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complexes embedded in hyperbranched structures<sup>12(d)</sup> have been enthusiastically studied with an aim of enhanced processibility.

A widely used approach to enhancing the solubility of Ir(III) complexes has been to attach solubilizing alkyl moieties or to introduce dendritic architectures.<sup>13</sup> However, the introduction of alkyl groups perturbs charge carrier transport and lowers the glass transition temperature ( $T_g$ ). Hence, sterically hindered all-aromatic substituents, which give rise to less side effects, are considered better solubilizing groups.<sup>10b</sup> As a successful example of this approach, we have found that the green electrophosphorescence from the well-known complex Ir(ppy)<sub>3</sub> (Ir(III) tris(2-phenylpyridinato-*N*, *C*<sup>2'</sup>)) can be improved remarkably by

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introducing tetraphenylsilyl group.<sup>14</sup> We found that compared to Ir(ppy)<sub>3</sub>, the modified Ir(ppy)<sub>3</sub> complex containing three identical 4-tetraphenylsilane-substituted ligands showed higher solubility and higher electrophosphorescence efficiency (32.8 cd/A) when doped in a poly(*N*-vinylcarbazole) (PVK) layer.

In addition to the improvement in solubility and phosphorescence efficiency that can be achieved by tetraphenylsilyl substitution, we wished to elucidate the phosphorescence color tuning effect of this type of substitution. Hence, in the present study, we sought to synthesize a saturated red-emitting Ir(III) complex with tetraphenylsilyl substitution and, additionally, to investigate the optical role of the tetraphenylsilyl substituents. To this end, we introduced a tetraphenylsilyl group into the 2-(2'-benzo[*b*]thienyl)pyridine ligand of the well-known red-emitting Ir(III) complex, btp<sub>2</sub>Ir(acac) (Ir(III) bis(2-(2'-benzo[*b*]thienyl)pyridinato-*N*, *C*<sup>3'</sup>) (acetylacetonato),<sup>5(a)</sup> **2**, in Scheme 1). To obtain deeper red phosphorescence than that of **2**, we attached a tetraphenylsilyl group to the 5-position of the pyridine ring (see Chart 1). This modification should extend the  $\pi$ -conjugation in the ligand structure, causing a red-shift in the phosphorescence emission.

This approach is supported by quantum chemical calculations based on density functional theory (DFT), which predict that the lowest unoccupied molecular orbital (LUMO) of **1** is stabilized by 0.095 eV compared to that of **2**. This stabilization is attributed to elongation of the region containing the LUMO electronic population, which is localized on the pyridine ring in **2**, but on both the pyridine ring as well as the additional phenyl ring of tetraphenylsilane in **1** (see Chart 1). We also find that energy levels of the molecular orbitals neighboring the frontier orbitals (i.e., a set of HOMO-1 and HOMO-2, and a set of LUMO+1 and LUMO+2) approach those of the highest occupied molecular orbital (HOMO) or LUMO (see bottom of Chart 1). Considering the fact that excitations between molecular orbitals other than HOMO and LUMO also significantly contribute effective transitions,<sup>15</sup> this prediction further supports stabilization of the phosphorescent state of **1**. Thus, tetraphenylsilyl introduction on the Ir(III) complex appears to lower the optical transition energy, making it possible to achieve deeper phosphorescence. These findings indicate that the introduction of structural motifs utilizing arylsilane substituents is a convenient way to achieve both enhanced processability and deep-red phosphorescence of Ir(III) complexes.

## Results and Discussion

The tetraphenylsilyl-substituted ligand **4** was synthesized by successive palladium-catalyzed Suzuki–Miyaura reactions. Specifically, lithiation of 1,4-dibromobenzene with *n*-BuLi (1.6 M in hexane) followed by substitution with a triphenylsilylchloride gave the bromine-terminated tetraphenylsilane in quantitative yield. Then, a further lithiation with *n*-BuLi and subsequent reaction with trimethylborate afforded the corresponding methyl boronate, which was further transformed to the corresponding boronic acid by treatment with aqueous 2 N HCl. Another part of the ligand, 2-(2'-benzo[*b*]thienyl)-5-bromopyridine, was easily obtained via Suzuki–Miyaura reaction of 5-bromo-2-iodopyridine and 2-benzo[*b*]thiopheneboronic acid. Exclusive coupling at the iodine of pyridine was observed, which was confirmed by mass spectrometry. Finally, the remaining bromine of the pyridine was coupled with triphenyl-

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## SCHEME 1. Synthesis of the Ir(III) Complex 1

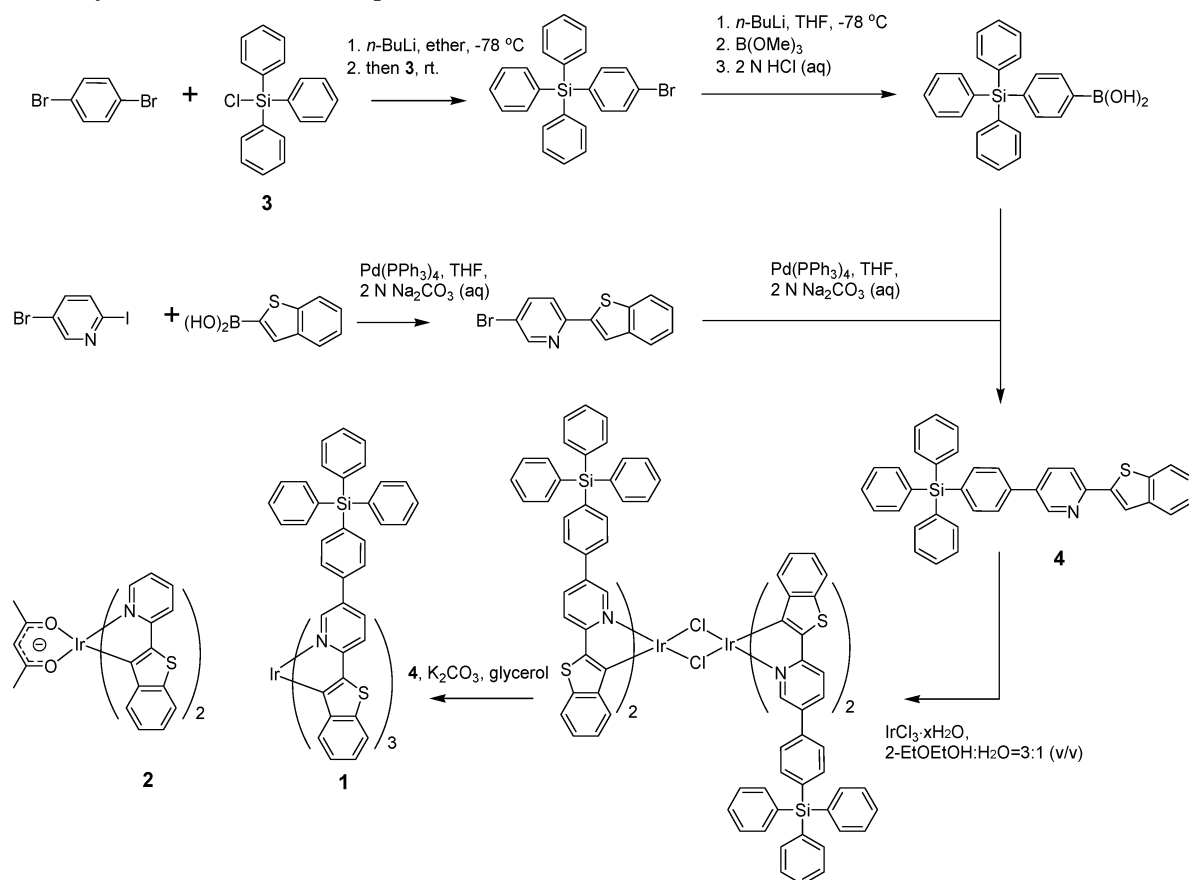
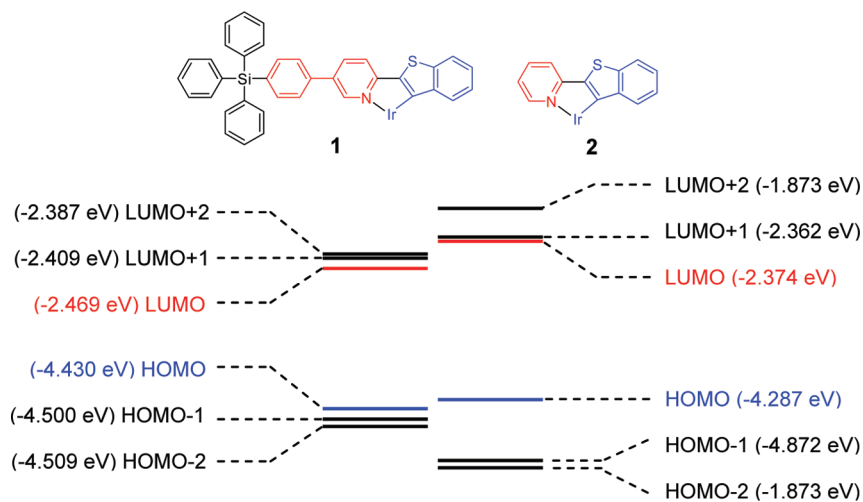


CHART 1. Top: Simplified Representation of the Spatial HOMO (blue) and LUMO (red) Positions of 1 and 2. Bottom: Their Respective Energy Level of Molecular Orbitals. See the Supporting Information for the Full Contour Plots

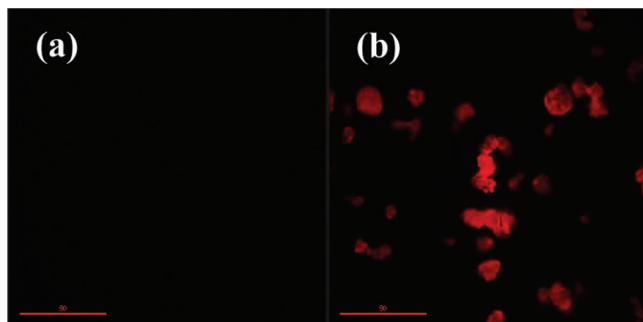


silylbenzeneboronic acid by further Suzuki–Miyaura reaction to give the chelating ligand **4** (2-(5-(4-(triphenylsilyl)phenyl)pyridyl)benzo[*b*]thiophene). Interestingly, a substantial amount (about 30%) of a homo-coupled adduct of the 4-triphenylsilylbenzeneboronic acids, 4,4'-bis(triphenylsilyl)biphenyl, was observed during the reaction.<sup>16</sup> The ligand **4** was thoroughly purified by silica gel column chromatography prior to the chelation reaction.

The Ir(III) complex was synthesized via the standard two-step procedure because direct formation of the tris-chelate from Ir(acac)<sub>3</sub> in the presence of excess ligand requires harsh reaction

conditions and generally gives low yields. Nonoyama reaction of the synthesized ligand **4** and IrCl<sub>3</sub>·xH<sub>2</sub>O in a mixed solvent system of 2-ethoxyethanol and water (3:1 by volume) gave the cyclometalated  $\mu$ -chloride-bridged Ir(III) dimer. Subsequently, the chloride of the  $\mu$ -chloride-bridged Ir(III) dimer was substituted by the additional chelating ligand **4** with the assistance of potassium carbonate in a thoroughly degassed glycerol at 240 °C. The crude product was purified by silica gel column chromatography followed by recrystallization in

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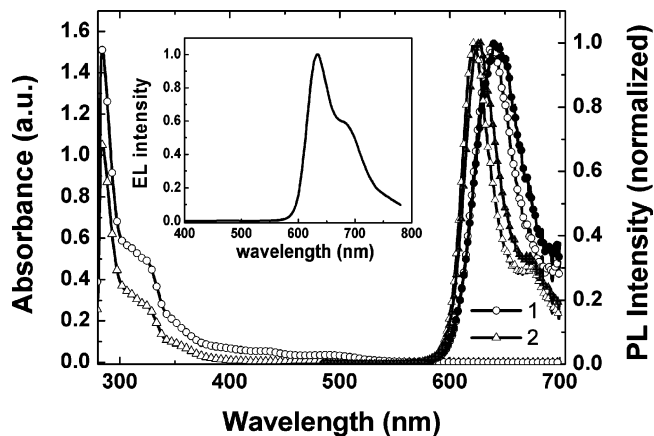


**FIGURE 1.** Image restoration microscope images of spin-coated PVK films doped with 60  $\mu\text{mol/g}$  of **1** (a) or **2** (b). Excitation wavelength was  $360 \pm 20$  nm from a 10 mW mercury lamp. The red color is pseudo color, and the length of scale bar corresponds to 90  $\mu\text{m}$ .

toluene to give the tris-chelate Ir(III) complex **1**, Ir(III) tris-(2-(2'-benzo[*b*]thienyl)-5-(4'-triphenylsilylphenyl)pyridinato-*N,C*<sup>3'</sup>), in 58% yield.

Compared to **2**, which lacks arylsilyl moieties, **1** exhibits much greater solubility in common organic solvents, indicating successful operation of the solubilizing triphenylsilyl group; for example, **1** and **2** showed solubilities of 71.8 mg/mL and 3.8 mg/mL in chlorobenzene, respectively. The high solubility of **1** was also evident in the polymer film state. When we spin-coated a chlorobenzene solution (5% w/w) containing Ir(III) complex/PVK (60  $\mu\text{mol/g}$ ) onto a glass substrate, we observed substantially different aggregate formation behavior after annealing under typical conditions (150 °C for 10 min), depending on whether **1** or **2** was used. Observation of the **1**/PVK film with an image restoration microscope (Figure 1a) revealed that it is homogeneous, with virtually no aggregates or crystals. In contrast, the image of the **2**/PVK film (Figure 1b) showed densely distributed luminescent spots of diameter 7–30  $\mu\text{m}$  range; given that even in the solid state, Ir(III) complexes are generally efficient phosphorescence emitters, these spots are attributed to aggregates or crystalline domains of **2**. The improved phase homogeneity of the **1**/PVK film compared to the **2**/PVK film is indicative of enhanced compatibility of **1** with the polymer host. Hence, in a polymer-emitting layer, **1** would be less prone to phase separation during long-term operation. Overall, the superior solubility and phase homogeneity of **1** are related to the structure of the arylsilyl moiety, and it is noteworthy that such improvements can be accomplished using an alkyl-free structure.

Another important issue in synthesizing **1** was to achieve deep red emission. As shown in Figure 2, the peak wavelengths of **1** are 640 and 646 nm in the solution and the film states, respectively, compared to 621 and 625 nm for **2** (Table 1). (The small red shift of the peak wavelength in the film state of **1** is likely due to a reduction of the dihedral angle between the phenyl and the pyridine rings.) The peak wavelengths of **1** are thus bathochromically shifted relative to those of **2** by ca. 20 nm, implying that the additional phenyl ring conjugated to the pyridine successfully yielded deeper red phosphorescence. Transformation of the phosphorescence spectra of the film states into Commission Internationale de L'Eclairage (CIE) coordinates gives  $(x, y) = (0.69, 0.31)$  for **1** compared to  $(0.68, 0.31)$  for **2**, confirming the deeper red emission of **1**. The absolute photoluminescence quantum yield was observed to be 17% from a poly(methyl methacrylate) film doped with **1** (7 wt % doped) compared to 11% for the corresponding film doped with **2**.<sup>17</sup>



**FIGURE 2.** Absorption and photoluminescence spectra of **1** in the solution state (10  $\mu\text{M}$  in Ar-saturated PhMe) (black open circles) and photoluminescence spectrum of **1** in the film state (PVK film doped by 7 wt % of **1**) (black filled circles). The corresponding spectra of **2** are shown for comparison (gray open triangles for the solution state and gray filled triangles for the film state). Inset: Electrophosphorescence spectrum of **1**.

This efficiency is satisfactory if we consider the very high purity of red phosphorescent color of the film.<sup>18</sup>

Finally, we constructed polymer light-emitting diodes employing **1** as a red phosphorescent emitter. A heterostructured polymer-based device was fabricated with the configuration of PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)) as a hole injection layer, an emitting layer of PVK codoped with PBD (2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) and **1** as electron transport and emitting components, respectively, BALq (bis-(2-methyl-8-quinolinolate)-4-(phenylphenolato) aluminum) as an exciton blocking layer, and LiF:Al as a cathode. PVK was selected as the polymer host because of its high hole mobility ( $\sim 10^{-5}$   $\text{cm}^2/\text{Vs}$ ),<sup>19</sup> high glass transition temperature, and good film forming property and because its HOMO and triplet state energy levels match those of **1**. When we consider the redox potentials of **1** measured by an electrochemical method, efficient hole and electron trapping inside the PVK was expected to give exclusive emission from **1**. Consistent with the excellent compatibility of **1** with PVK established above, a high-quality spin-coated **1**/PVK film was easily realized during device fabrication. From the device, saturated red electrophosphorescence was observed with a peak wavelength of 640 nm accompanied by a shoulder at 680 nm, giving a CIE coordinate of (0.69, 0.30) (Figure 3). A peak external quantum efficiency of 2.7% was recorded at a current density of 0.57  $\text{mA}/\text{cm}^2$ , and a luminance of 1018  $\text{cd}/\text{m}^2$  was observed at a current density of 132  $\text{mA}/\text{cm}^2$ . Considering the moderate absolute photoluminescence quantum yield of **1** (17%), this appreciable device efficiency demonstrates the beneficial role of the arylsilyl moiety.

(17) The poly(methyl methacrylate) host was used in order to exclude the energy transfer from the host. See the Supporting Information for experimental details.

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TABLE 1. Optical and Electrochemical Properties of Ir(III) Complexes

entry	$\lambda_{\text{abs}}$ (nm) (log $\epsilon$ ) <sup>a</sup>	$\lambda_{\text{p}}$ (nm) <sup>a</sup>	PLQY (%) <sup>b</sup>	$E_{\text{red}}$ (V) <sup>c</sup>	$E_{\text{ox}}$ (V) <sup>c</sup>	IP (eV) <sup>d</sup>	CIE coordinate (x, y) <sup>e</sup>
1	308 (4.75), 326 (4.69), 348 (4.32), 433 (3.74), 497 (3.54)	640 (sol), 646 (film)	17	-0.72, -1.35	1.55, 0.86 <sup>f</sup>	-5.36	(0.69, 0.30)
2	309 (4.52), 324 (4.44), 349 (3.98), 496 (3.00)	621 (sol), 625 (film)	11	-0.77, -1.36	1.40, 0.83	-5.33	(0.68, 0.31)

<sup>a</sup> Measured in Ar-saturated PhMe solutions (10  $\mu$ M). <sup>b</sup> Absolute photoluminescence quantum yield obtained with a system comprising an integrated sphere (see the Supporting Information for experimental details). PMMA films doped by the Ir(III) complex (7 wt %) were used for measurement. <sup>c</sup> Measured by cyclic voltammetry (Pt wires were used for a working and a counter electrodes, pseudo Ag wire for a reference electrode, and 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> for the electrolyte at a scan rate of 50 mV/s). <sup>d</sup> Ionization potentials calculated with the oxidation potential of Fc/Fc<sup>+</sup> as an internal standard. <sup>e</sup> Obtained with the electrophosphorescence spectra of the Ir(III) complexes. <sup>f</sup> Reversible wave.

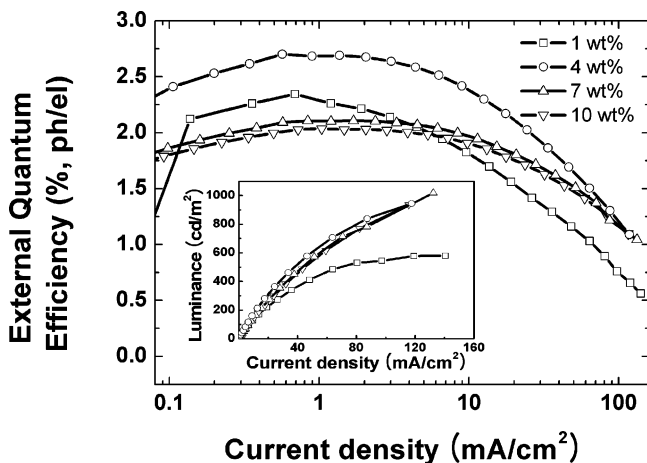


FIGURE 3. External quantum efficiency (% , photons/electron) versus current density (mA/cm<sup>2</sup>) of devices with a configuration of ITO/PSS: PEDOT/PVK:PBD (40 wt %):1 (x wt%)/BALq/LiF:Al. Inset: luminance (cd/m<sup>2</sup>) profiles against current density (mA/cm<sup>2</sup>).

In summary, we have designed and synthesized a new deep-red-emitting Ir(III) complex with excellent solubility and efficiency. Arylsilane-based alkyl-free substituents successfully facilitated both bathochromically shifted phosphorescence and higher phase homogeneity of the Ir(III) complex inside a PVK host. Polymer organic light-emitting devices based on the Ir(III) complex exhibited a peak electrophosphorescence wavelength of 640 nm along with a shoulder around 680 nm; which is deeper red (CIE (x, y) = (0.69, 0.30)) than for the original Ir(III) complex without a tetraphenylsilyl group at the ligand.

## Experimental Section

**Synthesis of 2-(2-Benzo[*b*]thienyl)-5-bromopyridine.** 5-Bromo-2-iodopyridine (10.0 g, 35.2 mmol), benzo[*b*]thiophene-2-ylboronic acid (6.21 g, 34.9 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.61 g, 1.40 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 200 mL of THF. After addition of 100 mL of aqueous 2 N sodium carbonate solution, the reaction mixture was heated at 80 °C for 1 day. The cooled crude mixture was poured onto water (200 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL  $\times$  three times) and dried over anhydrous magnesium sulfate. Finally, silica gel column chromatography (*n*-hexane:EtOAc = 5:1) gave a white powder (8.20 g, 28.3 mmol) in 81% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.34 (m, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.78 (m, 3H), 7.84 (m, 1H), 8.65 (d, *J* = 2.2 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  119.5, 120.8, 121.9, 122.8, 124.4, 124.8, 125.5, 139.3, 140.5, 140.9, 143.7, 150.9, 151.3. MS (FAB) *m/z* 289 (M<sup>+</sup>). Anal. Calcd for C<sub>13</sub>H<sub>8</sub>BrNS: C, 53.81; H, 2.78; N, 4.83; S, 11.05. Found: C, 53.86; H, 2.81; N, 4.85; S, 10.93.

**Synthesis of 2-(5-(4-Triphenylsilylphenyl)pyridyl)benzo[*b*]thiophene (4).** The same procedure for 2-(2-benzo[*b*]thienyl)-5-bromopyridine was applied to give white powder (4.10 g, 7.51 mmol) in 58% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.46 (m, 15H), 7.59–7.60 (m, 5H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.81 (m, 1H), 7.88 (m, 3H), 8.91 (d, *J* = 1.6 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  119.4, 122.8, 123.3, 124.3, 124.4, 128.1, 128.5, 132.5, 132.6, 133.1, 133.3, 134.3, 136.8, 137.7, 140.5, 140.9, 143.7. MS (FAB) *m/z* 546 (M<sup>+</sup>). Anal. Calcd for C<sub>37</sub>H<sub>27</sub>NSSi: C, 81.43; H, 4.99; N, 2.57; S, 5.88. Found: C, 81.39; H, 5.02; N, 2.69; S, 5.86.

**Synthesis of  $\mu$ -Chloride-Ir(III) Dimer.** The cyclometalating ligand **4** (3.00 g, 5.50 mmol) and iridium(III) chloride hydrate (0.41 g, 1.37 mmol) were solvated in the mixed solvent system of 2-EtOEtOH:water (30 mL:10 mL). After a thorough degassing procedure was performed, the temperature was maintained at 145 °C for 20 h. Red precipitates were observed when the reaction mixture was cooled down to room temperature. Filtration gave a red powder which was further washed with the mixed solvent system of acetone:EtOH:*n*-hexane (5 mL:5 mL:40 mL). Then, the filtrate was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and recrystallized to give red crystals (0.532 g, 0.221 mmol) in 68%. <sup>1</sup>H NMR (spectral shape was broad and structureless; splitting patterns were hard to assign. 500 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (m, 8H), 7.43 (m, 24H), 7.48 (m, 12H), 7.63 (m, 28H), 7.72 (s, 4H), 7.73 (s, 4H), 7.83 (m, 4H), 7.87–7.92 (m, 12H), 7.97 (m, 4H), 8.95 (s, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  119.2, 119.9, 122.3, 122.8, 123.0, 124.0, 124.2, 124.4, 124.8, 125.4, 125.6, 125.8, 126.5, 126.7, 126.8, 127.7, 128.1, 128.2, 128.3, 128.4, 128.7, 129.9, 130.0, 130.1, 131.3, 132.5, 133.3, 133.6, 134.1, 135.4, 135.7, 136.3, 136.6, 137.1, 137.4, 140.7, 141.0, 141.9, 143.0, 144.1, 144.5, 147.9, 148.1, 149.7, 152.3, 154.2, 162.9, 163.3, 165.1, 171.4, 175.2. MALDI-TOF-MS *m/z* 2634.50, calcd for C<sub>148</sub>H<sub>104</sub>Cl<sub>2</sub>Ir<sub>2</sub>N<sub>4</sub>S<sub>4</sub>Si<sub>4</sub> = 2632.49. Anal. Calcd for C<sub>148</sub>H<sub>104</sub>Cl<sub>2</sub>Ir<sub>2</sub>N<sub>4</sub>S<sub>4</sub>Si<sub>4</sub>: C, 67.48; H, 3.98; N, 2.13; S, 4.87. Found: C, 67.55; H, 4.01; N, 2.15; S, 4.95.

**Synthesis of Ir(III) Tris(2-(2-benzo[*b*]thienyl)-5-(4-triphenylsilylphenyl)pyridinato-*N,C*<sup>3</sup>) (1).** To a glycerol solution (10 mL) containing **4** (0.102 g, 0.208 mmol) and  $\mu$ -chloride-Ir(III) dimer (0.200 g, 0.0830 mmol) was delivered potassium carbonate (0.115 g, 0.830 mmol). Prior to raising the temperature, the reaction mixture was thoroughly degassed via repetitive vacuum-freeze-thaw technique. Then, refluxing at 220 °C was performed for 20 h. After being cooled down to room temperature, the reaction mixture was poured into water. The red precipitate was further washed with water (100 mL), MeOH (50 mL), and then ether (50 mL). A dark orange-colored powder was obtained after silica gel column purification with CH<sub>2</sub>Cl<sub>2</sub> eluent. Finally, recrystallization in PhMe gave the red phosphorescent product (0.131 g, 0.0790 mmol) in 48% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.34 (d, *J* = 8.1 Hz, 1H), 6.43 (d, *J* = 9.1 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.77–6.84 (m, 3H), 7.09–7.14 (m, 6H), 7.26 (d, *J* = 8.4, 2H), 7.34–7.47 (m, 36H), 7.52–7.54 (m, 16H), 7.62 (d, *J* = 6.6 Hz, 3H), 7.65 (m, 2H), 7.73 (d, *J* = 5.6, 2H), 7.80 (m, 2H), 8.02 (d, *J* = 1.6, 1H), 8.07 (d, *J* = 1.4 Hz, 1H), 8.38 (d, *J* = 1.6 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  118.2, 118.7, 119.2, 122.3, 122.8, 123.0, 124.0, 124.2, 125.3, 125.4, 125.6, 125.8, 126.5, 126.7, 126.8, 127.7, 128.1, 128.2, 128.3,

128.4, 128.7, 129.9, 130.0, 130.1, 131.3, 132.5, 133.3, 133.6, 134.1, 134.4, 134.5, 135.7, 136.3, 136.6, 137.1, 137.3, 137.4, 137.9, 138.0, 138.9, 142.1, 143.0, 144.1, 144.5, 147.9, 148.3, 148.4, 149.4, 153.0, 154.9, 162.9, 164.2, 165.6, 173.1, 177.2. MALDI-TOF-MS  $m/z$  1826.38, calcd for  $C_{111}H_{78}IrN_3S_3Si_3 = 1825.43$ . Anal. Calcd for  $C_{111}H_{78}IrN_3S_3Si_3$ : C, 72.99; H, 4.30; N, 2.30; S, 5.27. Found: C, 72.91; H, 4.30; N, 2.18; S, 5.29.

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**Supporting Information Available:** Copies of spectroscopic identification including  $^1H$ ,  $^{13}C$  NMR, and MALDI-TOF mass spectra, DFT calculation results, and electrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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