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# Highly efficient phosphorescent materials based on Ir(III) complexesgrafted on polyhedral oligomeric silsesquioxane core

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Abstract: A new iridium(III) complex containing coumarin derivative as the cyclometalated ligand (L) and a carbazole-functionalized  $\beta$ -diketonate (Cz-acac-allyl) as the ancillary ligand, namely, Ir(III) bis(3-(pyridin-2-yl)coumarinato-*N*, *C*<sup>4</sup>)(1-(9-butyl-9*H*-carbazol-3-yl)hept-6-ene-1,3-dionato-*O*, *O*) [Ir(L)<sub>2</sub>(Cz-acac-allyl)], was firstly synthesized as the emissive iridium(III) complex. Then three new phosphorescent polyhedral oligomeric silsesquioxane (POSS) materials, consisting of the emissive Ir(III) complex and carbazole moieties covalently attached to a polyhedral oligomeric silsesquioxane (POSS) core were successfully synthesized by hydrosilylation reaction in the presence of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt-dvs) as the catalyst. These phosphorescent POSS materials offer many advantages including amorphous properties, good thermal stabilities, and good solubility in common solvents, and high purity via column chromatography. The photoluminescence spectra of the POSS materials in solutions and in the solid states indicate a reduction in the degrees of interactions among Ir(III) complex units and concentration quenching due

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to the bulky POSS core. Solution processed light-emitting devices based on these phosphorescent POSS materials exhibit maximum external quantum efficiency (EQE) of 9.77%.

**Keywords**: Iridium complex; POSS; Carbazole; β-diketone; Photoluminescence; Electroluminescence

### 1. Introduction

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Phosphorescent heavy-metal complexes are widely used in organic light-emitting diodes (OLEDs) <sup>[1-4]</sup>, light-emitting electrochemical cells <sup>[5-7]</sup>, chemosensors <sup>[8-10]</sup>, biological labeling and bioimaging [11-13], which successfully overcome low luminescent efficiency of traditional fluorescent materials because they can fully utilize both singlet and triplet excitons through the strong spinorbital coupling of heavy-metal ions and the internal quantum efficiency of phosphorescent emitters can theoretically approach 100%. Among phosphorescent heavy-metal complexes, cyclometalated iridium complexes are the most promising emitting materials due to their high quantum efficiency, brightness, color diversity and short excited-state lifetime. In the past decades, considerable efforts have been devoted to the exploitation of novel Ir(III) complexes for highly efficient OLEDs. However, the Ir(III) complexes used as electroluminescent (EL) materials are suffering from selfquenching in solid state due to interaction and aggregation with its neighboring complexes. Thus, as the EL materials they are always doped in the host materials at appropriate concentration to fabricate OLEDs with reasonable, luminant efficiency. Unfortunately, this method usually leads to the phase separation during the device manufacturing process by the vacuum deposition. Alternative feasible approach is to introduce the steric hindrance or bulky side groups into Ir(III) complexes to suppress the emission quenching and enhance the device performance <sup>[14-16]</sup>

Recently, polyhedral oligomeric silsesquioxanes (POSS) derivatives have attracted a great deal of attention in the materials field because of their unique nanoscale cage-shaped structures and good solubility in organic solvents. POSS derivatives are three-dimensional, structurelly well-difined cage

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molecules which can provide huge stretching space for chromophoric groups, which are regarded as organic-inorganic hybrid materials at a molecular level and used for the development of high performance materials in medical, aerospace, microelectronics and so on <sup>[17-21]</sup>. Polyhedral oligomeric silsesquioxane has eight hydrogen atoms linked with silicon atoms at the corner of the Si<sub>8</sub>O<sub>12</sub> core, the introduction of chromophoric groups onto the corner of POSS greatly improved the quantum efficiency by suppressing  $\pi$ - $\pi$  aggregation of chromophoric groups and effectively inhibiting the aggregation-caused quenching (ACQ) effect. Furthermore, the incorporation of POSS core into luminescent materials produces nanocomposites with improved properties such as increases in glass transition temperature, thermal stability, mechanical strength, oxidation resistance and ease of processing. On the other hand, POSS materials attaching the carrier-transporting moieties and/or chromophores can provide the advantages of both small molecule and polymer light-emitting materials including high purity and solution processability. Since the first use of POSS as central cores for solution processed hybrid hole transport materials in OLEDs that enhanced brightness and efficiencies as compared to the devices that used traditional hole transport materials <sup>[22]</sup>, the POSS functionalized light emitting materials were widely used in OLEDs <sup>[20, 23-26]</sup>. In previous research, the Heeger group pioneered the use of POSS-based light emitting polymers in which POSS cores as endcappers were attached at the chain ends of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4phenylenevinylene] (MEH-PPV) and poly(9,9'-dioctylfluorene) <sup>[23]</sup>. The electroluminescent device made from the POSS-capped MEH-PPV polymer was found to exhibit higher brightness (1320 cd/m<sup>2</sup> at 3.5V) and external quantum efficiency (EQE) ( $\eta_{ext} = 2.2\%$ ) than the POSS-free MEH-PPV (230 cd/m<sup>2</sup> at 3.5 V and  $\eta_{ext} = 1.5\%$ ). The enhanced device properties may be attributed to reduced aggregation caused by the bulky POSS end groups and improved adhesion of the polymer to the ITO coated glass substrate. Jabbour et al. <sup>[24]</sup> and Shim et al. <sup>[25]</sup> synthesized POSS materials containing eight chromophore groups and reported that they enhanced the EL properties and quantum efficiencies of the host through energy transfer. Besides, Jabbour et al. <sup>[26,27]</sup> reported a group of Ir-

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complexes anchored POSS macromolecules and platinum-complexes-anchored polyhedral oligomeric silsesquioxane materials. The devices based on hole-transporting and Ir-complex moieties dualfunctionalized POSS materials and platinum-complexes-anchored POSS materials exhibited encouraging efficiency, which was significantly higher than that of the analogous devices with a physical blend of the platinum-complexes and a polymer matrix, indicating that POSS core was necessary to improve the efficiencies of the devices. Recently, we have succeeded in the synthesis and electroluminescence of two new POSS-based organic-inorganic hybrid materials, the devices based on these POSS materials exhibit maximum external quantum efficiency (EQE) of 7.82% and a maximum luminance of 21285 cd/m<sup>2</sup> <sup>[28]</sup>. These previous researches indicated that the light-emitting devices fabricated with the POSS-functionalized materials showed much improved brightness and quantum efficiency in comparison with devices fabricated with the corresponding parent materials. Developing new organic-inorganic hybrid materials based on POSS is of interest both for scientific knowledge and applications.

Previously, we have reported the phosphorescent OLEDs (PhOLEDs) based on the cyclometalated Ir(III) coumarin complexes <sup>[29-31]</sup>, in which 3-(pyridin-2-yl)coumarin was used as the cyclometalated ligand and the  $\beta$ -diketone derivatives were used as the ancillary monoanionic ligand, respectively. The research results indicated that the device performance can be improved by modifying the ancillary ligand. Especially, a carbazole-functionalized  $\beta$ -diketonate as the ancillary ligand, the PhOLEDs possess better performance as compared with those fabricated by similar complexes containing acac or TTA as the ancillary ligand <sup>[29]</sup>. Encouraged by the advantages of the carbazole-functionalized  $\beta$ -diketonate ligands and POSS-based light-emitting materials, in this paper, we used a carbazole-functionalized  $\beta$ -diketonate (Cz-acac-allyl) as the ancillary ligand to synthesize a new iridium(III) coumarin complex, Ir(L)<sub>2</sub>(Cz-acac-allyl), which was as an emissive iridium complex. Then three new Ir(III) complex-functionalized POSS meterials, 7Cz-Ir(L)<sub>2</sub>(Cz-acac)-POSS (POSS-1), 6Cz-2Ir(L)<sub>2</sub>(Cz-acac)-POSS (POSS-2) and 5Cz-3Ir(L)<sub>2</sub>(Cz-acac)-POSS (POSS-3) (Fig. 1),

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were successfully synthesized and characterized. The photophysical and electrochemical properties and thermal stabilities of these POSS materials were investigated. Furthermore, solution processed light-emitting devices based on POSS-1 and POSS-2 materials were fabricated to investigate the electroluminescence properties of the POSS materials.

The synthetic routes of the Ir(III) complex-functionalized POSS meterials were shown in Scheme 1.

### 2. Experimental

### 2.1 Materials and methods

Carbazole, potassium tert-butoxide and allyl bromide were bought from Alfa Aesar. 4-Pentenoic acid was obtained from Energy Chemical (China). Platinum complex (platinum-1,3divinyl-1,1,3,3-tetramethyldisiloxane, Pt-dvs, 2 wt% Pt in xylene) was purchased from Aldrich, USA. Octakis(dimethylsiloxy)silsesquioxane ( $Q_8M_8^H$ ) containing eight hydro-silane groups was purchased from the Hybrid Plastics Co., USA. 8-Hydroxyquinolinolato-lithium (Liq), 4,4'-Bis(9carbazolyl)biphenyl (CBP) and 1,3,5-Tri(N-phenylbenzimidazol-2-yl)benzene (TPBi) were purchased from Electro-Light Technology Corp., Beijing. Toluene was dried by distillation before use in the hydrosilylation reaction. All other chemicals were analytical grade reagent.

The cyclometalated coumarin ligand (3-(pyridine-2-yl)coumarin, **L**) and the cyclometalated Ir(III)  $\mu$ -chlorobridged dimmer ((L)<sub>2</sub>Ir( $\mu$ -Cl)<sub>2</sub>Ir(L)<sub>2</sub>) were prepared as previously described <sup>[32]</sup>. 9-allyl-9*H*-carbazole (Cz-allyl) and 3-Acetyl-9-butyl-carbazole were synthesized as previously described <sup>[28,29]</sup>.

<sup>1</sup>H NMR spectra were obtained on Unity Varian-500MHz. IR spectra (400 – 4000 cm<sup>-1</sup>) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental analysis instrument. Mass spectrum was obtained from a Thermo Scientific Orbitrap Elite mass spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris system. UV-vis absorption and photoluminescent spectra were recorded on a Shimadzu UV-2550 spectrometer and on a Perkin-Elmer LS-55 spectrometer, respectively.

### 2.2 Synthesis and characterization of Ir(L)<sub>2</sub>(Cz-acac-allyl) and the POSS materials

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**Butyl pent-4-enoate**: In a 250 mL flask equipped with a reflux condenser and a water segregater was placed NaHSO<sub>4</sub>•H<sub>2</sub>O (0.2 g, 1.45 mmol), 4-pentenoic acid (10 g, 0.1 mol) and butyl alcohol (15 g, 0.2 mol) and cyclohexane (20 mL). The reaction mixture was stirred at 110 °C for 5 h. After cooling, the reaction mixture was poured into water (100 mL), and neutralization with saturated aqueous sodium bicarbonate to pH 6 followed by extration with ethyl acetate (100 mL  $\times$  3) was performed. The obtained organic layer was dried over anhydrous magnesium sulfate and concentrated, collecting 13.51 g (86.48% yield) of colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ , ppm): 5.87-5.77 (m, 1H), 5.08-4.98 (m, 2H), 4.08 (t, J = 6.8 Hz, 2H), 2.42-2.35 (m, 4H), 1.64-1.57 (m, 2H), 1.43-1.36 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H).

**1-(9-butyl-9***H***-carbazol-3-yl)hept-6-ene-1,3-dione (Cz-acac-allyl)**: To a solution of butyl pent-4-enoate (9.185 g, 58.76 mmol) in anhydrous toluene (50 mL) was added t-BuOK (13.19 g, 117.55 mmol). The mixture was stirred at room temperature for 1 h. A solution of 3-acetyl-9-butyl-carbazole (5.23 g, 19.71 mmol) in 20 mL of anhydrous toluene was added dropwise over 5 min, and then stirring overnight at 40 °C. The mixture was poured into cooled water (150 mL), and then acidified with dilute hydrochloric acid to pH 5. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL), and the combined organic phase was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with a mixture of ethyl acetate/petroleum ether (1:20, v/v) as eluent to obtain Cz-acac-allyl as a yellow solid (3.72 g, 54.3%). <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$ : 15.71 (s, 1H), 8.69 (s, 1H), 8.15 (d, J = 7.2 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 6.8 Hz, 1H), 7.42 (t, J = 9.2 Hz, 2H), 7.29 (d, J = 6.4 Hz, 1H), 6.32 (s, 1H), 5.95-5.74 (m, 1H), 5.15-4.97 (m, 2H), 4.32 (t, J = 6.4 Hz, 2H), 2.55 (t, J = 6.0 Hz, 2H),

2.49 (t, J = 5.2 Hz, 2H), 1.86-1.82 (m, 2H), 1.41-1.38 (m, 2H), 0.95 (t, J = 6.8 Hz, 3H). <sup>13</sup> C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 193.0, 185.7, 143.0, 141.0, 137.1, 126.4, 125.8, 125.0, 123.0, 122.9, 120.6, 120.3, 119.8, 115.5, 109.2, 108.5, 95.4, 43.1, 37.9, 31.1, 29.9, 20.5, 13.9. Anal. Calc. for C<sub>23</sub>H<sub>25</sub>NO<sub>2</sub>: C 79.51, H 7.25, N 4.03; Found C 79.62, H 7.21, N 4.07 %.

 $Ir(L)_2(Cz-acac-allyl)$ : The cyclometalated Ir(III)  $\mu$ -chlorobridged dimmer  $((L)_2Ir(\mu-Cl)_2Ir(L)_2)$ (1.20 g, 0.89 mmol), Cz-acac-allyl (1.60 g, 4.60 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (1.00 g, 7.24 mmol) were refluxed in dichloroethane under nitrogen atmosphere for 24 h. After cooling, a small quantity of water was added. The mixture was extracted with dichloromethane (100 mL  $\times$  3). The organic phase was washed with water (2  $\times$  100 mL) and dried over anhydrous MgSO<sub>4</sub>. After filtering, the filtrate was evaporated to dryness under reduced pressure. The crude was purified by chromatography on silica gel using petroleum ether/acetone (15:1, v/v) as the eluent to give yellow powdery Ir(L)<sub>2</sub>(Cz-acac-allyl) in 77.5% yield (1.36 g). <sup>1</sup>H NMR(CDCl<sub>3</sub>,  $\delta$ , ppm): 9.17 (d, 2H, J = 8.0 Hz, Aryl-H), 8.38 (s, 1H, Aryl-H), 8.15-8.08 (m, 3H, Aryl-H), 7.91-7.82 (m, 2H, Aryl-H), 7.77 (d, 1H, J = 7.2 Hz, Aryl-H), 7.48 (t, 1H, J = 7.6 Hz, Aryl-H), 7.39 (d, 1H, J = 8.4 Hz, Aryl-H), 7.27 (d, 6H, J = 6.8 Hz, Aryl-H), 6.99 (t, 2H, J = 8.8 Hz, Aryl-H), 6.67 (d, 2H, J = 6.8 Hz, Aryl-H), 6.23 (d, 2H, J = 5.2 Hz, Aryl-H), 5.97 (s, 1H), 5.58-5.52 (m, 1H,  $-CH=CH_2$ ), 4.85 (t, 2H, J = 17.6 Hz, -CH=CH<sub>2</sub>), 4.28 (t, 2H, J = 6.2 Hz, -N-CH<sub>2</sub>-), 2.26 (t, 2H, J = 7.2 Hz), 2.11-2.04 (m, 2H), 1.81 (t, 2H, J = 7.2 Hz, 1.38-1.32 (m, 2H), 0.92 (t, J = 6.8 Hz, 3H). Anal. Calc. for  $C_{51}H_{40}IrN_{3}O_{6}$  (%): C, 62.31; H, 4.10; N, 4.27. Found: C, 62.56; H, 3.97; N, 4.32. ESI-MS: Calcd for  $[C_{51}H_{40}IrN_{3}O_{6} + H]^{+}$ , 984.12; Found, 984.34.

**POSS Materials:** A round bottom flask (100 mL) was charged with octakis(dimethylsiloxy)silsesquioxane (0.92 g, 0.90 mmol),  $Ir(L)_2(Cz$ -acac-allyl) (0.89 g, 0.90 mmol) and anhydrous toluene (30 mL). The solution was degassed with argon for 5 min and then 5 drops of a solution of platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt-dvs) (2 wt% Pt in xylene) were added, and the reaction mixture was stirred at room temperature under positive argon pressure for 4 h.

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Then Cz-allyl (1.87 g, 9.02 mmol) was introduced, and the reaction mixture was allowed to stir at room temperature overnight. The toluene was evaporated in vacuo and the crude product was isolated by chromatography on silica gel using dichloromethane/ethyl acetate/petroleum ether (1:1:20, v/v/v) as the eluent to yield pure fractions of POSS-1, POSS-2 and POSS-3, which were isolated separately in 26.2%, 14.7% and 6.4% yields, respectively.

**POSS-1**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 9.12 (t, 2H, J = 7.6 Hz, Aryl-H), 8.34 (s, 1H, Aryl-H), 8.06-8.00 (m, 16H, Aryl-H), 7.71 (dd, 3H, J = 7.6 Hz, Aryl-H), 7.42 (t, 2H, J = 8.0 Hz, Aryl-H), 7.37-7.32 (m, 16H, Aryl-H), 7.24-7.22 (m, 17H, Aryl-H), 7.15-7.10 (m, 16H, Aryl-H), 6.81-6.76 (m, 2H, Aryl-H), 6.63 (t, 2H, J = 7.8 Hz, Aryl-H), 6.19 (t, 2H, J = 7.8 Hz, Aryl-H), 5.88 (s, 1H), 4.18 (t, 2H, J = 7.2 Hz, -N-CH<sub>2</sub>-), 4.10-4.02 (m, 14H,-N-CH<sub>2</sub>-), 2.03 (t, 2H, J = 8.0 Hz, -CH<sub>2</sub>-), 1.82-1.72 (m, 18H, -CH<sub>2</sub>-), 1.32-1.28 (m, 4H, -CH<sub>2</sub>-), 1.13-1.06 (m, 3H, -CH<sub>3</sub>), 0.57-0.41 (m, 16H, -CH<sub>2</sub>-Si), 0.06-(-0.05) (m, 48H, Si-CH<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 3058, 2963, 2924, 2875, 1693, 1603, 1542, 1475, 1352, 1330, 1263, 1230, 1168, 1089, 800, 560, 471. ESI-MS: Calcd for [C<sub>172</sub>H<sub>187</sub>IrN<sub>10</sub>O<sub>26</sub>Si<sub>16</sub> + H]<sup>+</sup>, 3452.97; Found, 3452.98.

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**POSS-2:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 9.13 (t, 4H, J = 7.6 Hz, Aryl-H), 8.36 (s, 2H, Aryl-H), 8.07-7.99 (m, 18H, Aryl-H), 7.72-7.68 (m, 6H, Aryl-H), 7.43-7.40 (m, 4H, Aryl-H), 7.35-7.31(m, 14H, Aryl-H), 7.28-7.18 (m, 20H, Aryl-H), 7.16-7.11 (m, 14H, Aryl-H), 6.85-6.76 (m, 4H, Aryl-H), 6.64 (t, 4H, J = 7.2 Hz, Aryl-H), 6.21 (t, 4H, J = 6.8 Hz, Aryl-H), 5.90 (s, 2H), 4.18 (t, 4H, J = 7.6 Hz, -N-CH<sub>2</sub>-), 4.14-4.01 (m, 12H,-N-CH<sub>2</sub>-), 2.03 (t, 4H, J = 7.6 Hz, -CH<sub>2</sub>-), 1.81-1.74 (m, 18H, -CH<sub>2</sub>-), 1.32-1.23 (m, 10H, -CH<sub>2</sub>-), 1.14-1.07 (m, 6H, -CH<sub>3</sub>), 0.63-0.42 (m, 16H, -CH<sub>2</sub>-Si), 0.08-(-0.06) (m, 48H, Si-CH<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 3058, 2963, 2924, 2875, 1693, 1597, 1542, 1514, 1469, 1408, 1352, 1330, 1258, 1230, 1157, 1089, 845, 800, 750, 560, 471. ESI-MS: Calcd for [C<sub>208</sub>H<sub>214</sub>Ir<sub>2</sub>N<sub>12</sub>O<sub>32</sub>Si<sub>16</sub> + H]<sup>+</sup>, 4228.80; Found, 4229.12.

**POSS-3:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 9.12 (t, 6H, J = 7.6 Hz, Aryl-H), 8.35 (s, 3H, Aryl-H), 8.06-7.97 (m, 18H, Aryl-H), 7.71-7.67 (m, 9H, Aryl-H), 7.44-7.39 (m, 3H, Aryl-H), 7.34-

7.30(m, 15H, Aryl-H), 7.28-7.17 (m, 22H, Aryl-H), 7.15-7.08 (m, 15H, Aryl-H), 6.82-6.77 (m, 6H, Aryl-H), 6.64 (t, 6H, J = 7.2 Hz, Aryl-H), 6.19 (t, 6H, J = 6.8 Hz, Aryl-H), 5.89 (s, 3H), 4.19-4.15 (m, 6H, -N-CH<sub>2</sub>-), 4.12-3.99 (m, 10H,-N-CH<sub>2</sub>-), 2.06-1.99 (m, 6H, -CH<sub>2</sub>-), 1.81-1.74 (m, 18H, -CH<sub>2</sub>-), 1.31-1.23 (m, 16H, -CH<sub>2</sub>-), 1.13-1.07 (m, 9H, -CH<sub>3</sub>), 0.61-0.39 (m, 16H, -CH<sub>2</sub>-Si), 0.07-(-0.09) (m, 48H, Si-CH<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 3047, 2958, 2925, 2875, 1693, 1603, 1547, 1519, 1464, 1402, 1352, 1325, 1263, 1229, 1163, 1089, 845, 800, 744, 722, 549, 471. ESI-MS: Calcd for  $[C_{244}H_{241}Ir_3N_{14}O_{38}Si_{16} + H]^+$ , 5004.62; Found, 5004.27.

### 2.3 Crystallography

The diffraction data were collected with a Bruker Smart Apex CCD area detector with graphitemonochromatized Mo-K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 293(2) K. The structure was solved by using the program SHELXL and Fourier difference techniques, and refined by full-matrix least-squares method on  $F^2$ . All hydrogen atoms were added theoretically.

### 2.4 OLEDs fabrication and characterization

The multilayer OLEDs with a device architecture of ITO/PEDOT:PSS (30 nm)/CBP: POSS materials (x wt %, 50 nm)/TPBi (50 nm)/Liq (2 nm)/Al(150 nm) were fabricated. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) was spin-coated onto precleaned and O<sub>2</sub>-plasma-treated indium tin oxide (ITO) substrates, yielding layers ca. 45 nm thick. PEDOT:PSS layers were heated at 180 °C for 10 min to remove residual water. Blends of POSS materials + 4,4'-Bis(9-carbazolyl)biphenyl (CBP) in chlorobenzene solution was spin-coated on top of the PEDOT:PSS layers, yielding films ca. 50 nm thick. The samples were then dried at 80 °C for 30 min. A TPBi hole/exciton-blocking layer was deposited via thermal evaporation at a rate of ~ 2 Å s<sup>-1</sup>. A cathode consisting of an ultrathin Liq interfacial layer with a nominal thickness of 2 nm and an Al layer ca. 150 nm thick was deposited by thermal evaporation. The deposition rates for Liq and Al were ~ 1 and 10 Å s<sup>-1</sup>, respectively. The active area of the devices was 12 mm<sup>2</sup>. The EL spectra and Commission Internationale de L'Eclairage (CIE) coordinates were measured on a Hitachi MPF-4

fluorescence spectrometer. The characterization of brightness-current-voltage (B–I–V) were measured with a 3645 DC power supply combined with a 1980A spot photometer and were recorded simultaneously. All measurements were done in the air at room temperature without any encapsulation.

### 3. Results and discussion

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### 3.1 Synthesis and characterization of the POSS materials

The synthesis of the phosphorescent Ir(III) complex  $[Ir(L)_2(Cz-acac-allyl)]$  from Scheme 1 began first with preparing the ancillary ligand, 1-(9-butyl-9H-carbazol-3-yl)hept-6-ene-1,3-dione (Cz-acac-allyl), which has a terminal alkene group for later attachment to POSS core. The ancillary ligand Cz-acac-allyl was successfully synthesized via three steps including N-alkylation reaction of carbazole, Friedel-crafts acylation of carbazole ring and Claisen condensation reaction. This method leads to medium yield of the target product (41%). The ancillary ligand was then reacted with the chlorobridged dimer complex based on the cyclometalated coumarin ligand (3-(pyridine-2yl)coumarin) and anhydrous K<sub>2</sub>CO<sub>3</sub> in refluxing dichloroethane under nitrogen atmosphere to obtain Ir(L)<sub>2</sub>(Cz-acac-allyl) complex. The ancillary ligand and the Ir(III) complex were characterized using <sup>1</sup>H NMR, MS, elemental analysis and X-ray crystallograpgy.

Yellow columnar crystal of the Ir(III) complex  $[Ir(L)_2(Cz-acac-allyl)]$  was obtained by the evaporation of the ethyl acetate solution. The crystallographic data of  $Ir(L)_2(Cz-acac-allyl)$  are shown in Table 1. The selected bond lengths and bond angles of  $Ir(L)_2(Cz-acac-allyl)$  are listed in Table 2.

The crystal structure of the complex  $Ir(L)_2(Cz\text{-acac-allyl})$  is given in Fig. 2. The crystal of  $Ir(L)_2(Cz\text{-acac-allyl})$  belongs to the monoclinic space group P2(1)/n, a = 10.0465(6) Å, b = 30.8172(15) Å, c = 13.9390(11) Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 98.719(2)^\circ$ , U = 4265.7(5) Å<sup>3</sup>, Z = 4,  $D_c = 1.531$  g/cm<sup>3</sup>,  $\mu = 6.503$  mm<sup>-1</sup>. It is shown that the iridium(III) ion in  $Ir(L)_2(Cz\text{-acac-allyl})$  is

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hexacoordinated by two C atoms and two N atoms from 3-(pyridin-2-yl)coumarin ligands and two O atoms from Cz-acac-allyl ligand, displaying a distorted octahedral coordination geometry. Two C atoms and two N atoms from the 3-(pyridin-2-yl)coumarin ligands exhibit *cis-C-C* and *trans-N,N* chelate mode, and two O atoms from Cz-acac-allyl ligand locate *cis-O-O* chelate disposition. The Ir-C bonds (1.989(10) and 2.006(11) Å) are shorter than the Ir-N bonds (2.016(9) and 2.030(9) Å). In the  $\beta$ -diketone chelate ring of the complex, the average distances for the carbon–carbon (C17–C18 and C18–C19) bonds of 1.404 Å and the average distances for the carbon–oxygen (C17–O1 and C19–O2) bonds of 1.270 Å lie between the single- and double-bond distances, indicating that the delocalized  $\pi$  bond formed when Cz-acac-allyl ligand coordinated to Ir atom. Two Ir-O bonds are 2.104(6) and 2.126(7) Å, respectively. In addition, the dihedral angle between the plane defined by the carbazole ring and the plane defined by the  $\beta$ -diketone chelate ring (Ir1/O1/O2/C17/C18/C19) is 19.37°. Compared with the free Cz-acac-allyl ligand, it is twisted slightly due to the steric hindrance.

The hole-transporting and Ir(III) complex unit functionalized POSS materials were obtained via hydrosilylation reaction in the presence of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Ptdvs) as the catalyst. The POSS materials were synthesized in a stepwise mode by sequentially reacting the Ir(III) complex Ir(L)<sub>2</sub>(Cz-acac-allyl) with octakis(dimethylsiloxy)silsesquioxane ( $Q_8M_8^H$ ) in a 1:1 ratio, and followed by reaction with excess Cz-allyl. There are several different amount of new products finding in the reaction system, but only three products (POSS-1, POSS-2 and POSS-3) were larger and easily isolated from the reaction mixture chromatographically. The other products' amount was very small, so we did not separate them. The POSS materials (POSS-1, POSS-2 and POSS-3) were found to be completely soluble in common organic solvents (toluene, chlorobenzene, THF, chloroform, dichloromethane and acetone), and homogeneous thin films of these POSS materials were fabricated easily by spin-coating onto the quartz glasses and indium tin oxide (ITO) substrates.

These POSS materials were characterized using <sup>1</sup>H NMR, MS, FT-IR and X-ray diffraction (XRD) analysis. The resonance of Si-H protons in  $Q_8M_8^{H}$  is located at 4.7 ppm. For Cz-allyl, two doublets (with fine coupling) and the quartet resonance proton resonance peaks from the allyl group are located at 5.03, 5.15 and 5.99 ppm with a relative molar ratio of 1:1:1, corresponding to iso-, *trans*- and substituted vinyl protons. The resonance of methylene (-CH<sub>2</sub>-Cz) is observed at 4.90 ppm. The peaks from the terminal alkene group of Ir(L)<sub>2</sub>(Cz-acac-allyl) are observed at ca. 4.85 and 5.54 ppm with a relative molar ratio of 2:1. In <sup>1</sup>H NMR spectra of the POSS materials, the peaks for the vinyl groups of Cz-allyl (5.03, 5.15 and 5.99 ppm) and Ir(L)<sub>2</sub>(Cz-acac-allyl) (4.85 and 5.54 ppm) and Si-H protons (4.7 ppm) disappeared, supporting the complete hydrosilylation reaction and the vinyl groups of Cz-allyl and Ir(L)<sub>2</sub>(Cz-acac-allyl) underwent hydrosilylation of the Si-H bonds of Q<sub>8</sub>M<sub>8</sub><sup>H</sup>.

The FT-IR spectra of  $Q_8M_8^{H}$ , POSS-1 and POSS-2 are shown in Fig. 3. The strong absorption peak around 1098 cm<sup>-1</sup> for  $Q_8M_8^{H}$ , POSS-1 and POSS-2 represented the vibrations of the siloxane Si-O-Si groups, and it is a general feature of POSS derivatives. In POSS-1 and POSS-2, the characteristic stretching vibration of the Si-H groups (2147 cm<sup>-1</sup>) disappeared completely, indicating that the hydrosilylation occurred to completion. The characteristic stretching vibration bands of -CH<sub>3</sub> and -CH<sub>2</sub>- are clearly observed at 2800 – 2900 cm<sup>-1</sup>. The FT-IR spectrum of POSS-3 was similar to that of POSS-1 and POSS-2.

The thermogravimetric analyses (TGA) were performed in flowing drying nitrogen atmosphere at the heating rate of 10 °C/min. The result of TGA measurements of the POSS materials are shown in Fig. 4. The POSS materials display good thermal stability up to 345 °C. With increasing temperature, the POSS materials begin to decompose at 347 °C accompanied by a sharp weight loss in their TGA curves, indicating that the POSS materials meet with the thermal stability requirement of fabrication of OLED luminescence application. For the POSS materials, the final residues should mainly be iridium oxide (Ir<sub>2</sub>O<sub>3</sub>) and silicon oxide (SiO<sub>2</sub>) in the thermal decomposition processes.

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Because the POSS materials have different quantities of carbazole moieties and Ir(III) complex units, the results of TGA measurements of them display different weight losses.

Figure 5 presents the X-ray diffraction (XRD) patterns of Cz-allyl,  $Ir(L)_2(Cz$ -acac-allyl) and the POSS materials. Cz-allyl and  $Ir(L)_2(Cz$ -acac-allyl) exhibit several sharp XRD peaks because of their crystallinity, suggesting that Cz-allyl and  $Ir(L)_2(Cz$ -acac-allyl) show the crystal morphology. Interestingly, the attachment of Cz-allyl and  $Ir(L)_2(Cz$ -acac-allyl) to the POSS core led to the disappearance of these sharp peaks, which were replaced by two broad amorphous halos appearing at ca. 8.5° and 20°, indicating that the crystalline Cz-allyl and  $Ir(L)_2(Cz$ -acac-allyl) became amorphous state after their attachments to the POSS cage.

### 3.2 Electrochemical, optical and electroluminescence properties of the POSS materials

The UV-vis absorption and photoluminescence spectra of  $Ir(L)_2(Cz-acac-allyl)$  and the POSS materials were measured in diluted dichloromethane solutions, as shown in Fig. 6. The absorption spectrum of the complex  $Ir(L)_2(Cz-acac-allyl)$  exhibits two intense absorption bands at about 227 and 271 nm, and three weak absorption bands at 341, 410 and 446 nm, respectively, in which the absorption bands below 360 nm could be ascribed to spin-allowed  $\pi$ - $\pi$ \* transitions of the ligands and the bands at the longer wavelength (410 and 446 nm) can be assigned to both spin-orbit coupling enhanced  ${}^3(\pi \rightarrow \pi^*)$  and spin-forbidden  ${}^3MLCT$  transitions [<sup>33-35</sup>].

The absorption spectra of POSS-1, POSS-2 and POSS-3 approximately resemble each other, which can be described as two components: an intense absorption region in high energy region ranging from 230 to 360 nm and a weak absorption region in low energy region ranging from 360 to 480 nm. In intense absorption region, there are six visible absorption peaks at 236 (242), 264, 284, 295, 334 and 347 nm, which can be attributed to the  $\pi \rightarrow \pi^*$  transitions of the ligands. In weak absorption region, there are three absorption peaks at 380, 418 and 440 nm, in which the band around 380 nm can be assigned to the spin-allowed metal-to-ligand charge transfer <sup>1</sup>MLCT (metal-ligandcharge-transfer) and the latter bands (418 and 440 nm) can be assigned to both spin-orbit coupling enhanced  ${}^{3}(\pi \rightarrow \pi^{*})$  and spin-forbidden  ${}^{3}MLCT$  transitions.

As shown in Fig. 6, the photoluminescence spectra of  $Ir(L)_2(Cz-acac-allyl)$  and the POSS materials strongly resemble each other, they all exhibit a strong green emission with a maximum main peak at 530 nm and a shoulder peak at 570 nm.

The luminescence quantum yields of the POSS materials in the solid states were measured in order to study their optical characteristics. The quantum yields of POSS-1, POSS-2 and POSS-3 at room temperature were measured to be 47.49%, 18.98% and 18.41% in the solid states by an absolute method using the Edinburgh Instruments (FLS920) integrating sphere excited at 380 nm with the Xe lamp. The result indicates that the luminescence quantum yields of the POSS materials decrease as the Ir(III) complex unit content on the POSS materials increases, which can be attributed to the interactions among the Ir(III) complex units and the concentration quenching. The lifetime decays of POSS-1, POSS-2 and POSS-3 were measured to be 9.27, 9.85 and 9.92 µs, respectively, by a time-correlated single photon counting spectrometer using Edinburgh Instruments (FLS920) with a microsecond flashlamp as the excitation source (repetition rate 90 Hz) at room temperature.

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Cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of the POSS materials. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the POSS materials were calculated from their cyclic voltammetry measurements and their extrapolated UV-Vis absorption edges. The POSS materials were dissolved in dichloromethane with tetra-*n*-butylammonium tetrafluoroborate (0.1 mol/L) as the electrolyte. A platinum working electrode and a saturated Ag/AgCl reference electrode were used. Ferrocene was used for potential calibration. As shown in Fig. 7, the potentials for oxidation of the POSS materials were observed to be 0.88, 0.86 and 0.87 V, respectively. At the same condition, the oxidation peak and the reductive peak of ferrocene were observed at 0.55 and 0.34 V, respectively, then the  $E_{1/2}$  (Fc/Fc<sup>+</sup>) is 0.445 V. Thus the HOMO energy levels of POSS-1, POSS-2 and POSS-3

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were determined to be -5.24, -5.22 and -5.23 eV regarding the energy level of ferrocene/ferrocenium as -4.80 eV <sup>[37]</sup>. The optical band edge of the POSS materials was estimated to be about 464 nm, which corresponds to 2.67 eV. Then the LUMO energy levels of POSS-1, POSS-2 and POSS-3 are calculated to be -2.57, -2.55 and -2.56 eV, respectively. Table 3 summarizes the photophysical, thermal and electrochemical properties of the POSS materials.

Due to the amount of POSS-3 was too little to investigate its electroluminescence (EL) property, POSS-1 and POSS-2 were selected as the light-emitting materials in the paper. The light-emitting devices with the architecture of ITO/PEDOT:PSS (30 nm)/CBP: POSS materials (x wt %, 50 nm)/TPBi (50 nm)/Liq (2 nm)/Al(150 nm) have been made and fabricated. The emitting layers are consisted of host materials CBP and dopants of the POSS materials at different concentrations (x wt%), and prepared by solution-processable method. TPBi was used as the electron transport and hole/exciton-blocking material. Liq was used as the electron-injection layer. CBP and the POSS materials were dissolved in 1,2-dichlorobenzene, and their concentrations were prepared to be 10 and 5 mg/mL, respectively. The mixture solutions with different volume ratios (3:2, 1:1, 2:3 and 1:2) between CBP and the POSS materials were used to fabricate the emitting layers (spin speed: 1000 rpm/min). The doped concentrations of the POSS materials were about 25 wt%, 33.33 wt%, 42.86 wt% and 50 wt%, respectively.

The electroluminescence (EL) spectra of the devices based on POSS-1 with different dopant concentrations and at different voltages are shown in Fig. 8. The doped devices of POSS-1 exhibit green emissions with a maximum main peak at 530 nm and a shoulder peak at 570 nm, it was found that the EL spectra of POSS-1 resemble closely its PL spectrum in dichloromethane solution, and the EL spectra of the devices were independent of the different dopant concentrations and the different driving voltages. The Commission Internationale de L'Eclairage (CIE) coordinates of the devices based on POSS-1 is (0.41, 0.57). The EL spectra of the doped devices based on POSS-2 were identical with that of the devices based of POSS-1.

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The luminance vs. the driving voltage and the current efficiency vs. the driving voltage Published on 29 July 2016. Downloaded by Northern Illinois University on 05/08/2016 09:21:00

characteristics of the devices fabricated with different POSS-1 doping concentrations in CBP host are shown in Fig. 9. Table 4 summarized the performances of the devices based on the POSS materials. As shown in Fig. 9, the maximum brightness of 8311, 10940, 10160 and 10725 cd/m<sup>2</sup> were observed in the devices with 25 wt%, 33.33 wt%, 42.86 wt% and 50 wt% doping concentrations, respectively. The maximum luminous efficiencies of 9.56, 35.24, 29.38 and 28.51 cd/A were obtained in the devices with different doping concentrations. By comparing the device performances of the different doping concentrations, the devices based on POSS-1 with 33.33 wt% doping concentration showed the best EL performance. The maximum current efficiency of 35.24 cd/A at 6.1 V and maximum brightness of 10940 cd/m<sup>2</sup> at 12.2 V have been observed in the device, and the maximum external quantum efficiency (EQE) was 9.77%. For POSS-2 material, the EL performances of the devices with the different doping concentrations varying from 25 wt%, 33.33 wt%, 42.86 wt% and 50 wt% were also investigated.

Figure 10 displays the luminance vs. the driving voltage and the current efficiency vs. the current density characteristics of the devices with various POSS-2 doping concentrations in CBP host. The performances of the devices based on POSS-2 are summarized in Table 4. The device with 25 wt% doping concentration exhibited the best EL performance. The device had a maximum brightness of 12390 cd/m<sup>2</sup> at 10.7 V and a maximum current efficiency of 30.52 cd/A at 1.57 mA/cm<sup>2</sup> and a maximum external quantum efficiency (EQE) of 8.46%.

As shown in Table 4, the EL performances of the devices fabricated from POSS-1 are substantially higher than that of the devices based on POSS-2, indicating that concentration quenching leads to the reduction in device efficiency with increasing amounts of the Ir(III) complex units on the POSS core. The device efficiency increases as the Ir(III) complex unit content on the POSS materials decreases, which can be attributed to reduced interactions among the Ir(III) complex

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units and diminished concentration quenching. Similar phenomenon was found in our previous work <sup>[28]</sup>.

### 4. Conclusion

We reported the synthesis, photophysics, electrochemical characterization and thermal stabilities of three inorganic/organic hybrid materials, 7Cz-Ir(L)<sub>2</sub>(Cz-acac)-POSS (POSS-1), 6Cz-2Ir(L)<sub>2</sub>(Cz-acac)-POSS (POSS-2) and 5Cz-3Ir(L)<sub>2</sub>(Cz-acac)-POSS (POSS-3), consisting of an emissive Ir(III) complex and carbazole moieties covalently attached to a polyhedral oligometric silsesquioxane (POSS) core. Attachment of Ir(III) complex on the POSS core has no significant effects on the photophysical properties of the POSS materials, and the POSS materials have high thermal stability and exhibit strong green emission with a main peak (530 nm) and a shoulder peak (570 nm). Solution processed light-emitting devices with a configuration of ITO/PEDOT:PSS (30 nm)/CBP: POSS materials (x wt %, 50 nm)/TPBi (50 nm)/Liq (2 nm)/Al(150 nm) exhibited higher brightness and higher external quantum efficiency, in which POSS-1 and POSS-2 were used as the emitting materials. At the doping concentration of 33.33 wt%, the devices fabricated from POSS-1 material exhibited green emission with a maximum luminance of 10940 cd/m<sup>2</sup> at 12.2 V and a maximum current efficiency of 35.24 cd/A at 6.1 V and a maximum external quantum efficiency (EQE) of 9.77%. When the doping concentration was 25 wt%, the devices based on POSS-2 material showed a maximum brightness of 12390 cd/m<sup>2</sup> at 10.7 V and a maximum current efficiency of 30.52 cd/A at 1.57 mA/cm<sup>2</sup> and a maximum external quantum efficiency (EQE) of 8.46%. Compared the device performances of POSS-1 and POSS-2 materials, it is found that the device efficiency increases as the Ir(III) complex unit content on the POSS materials decreases, which can be attributed to reduced interactions among the Ir(III) complex units and diminished concentration quenching.

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### Supplementary material

CCDC 1472276 contains the supplementary crystallographic data for the complex  $Ir(L)_2(Cz$ acac-allyl) in this paper. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Legends:

Fig. 1 The molecular structures of the POSS materials used in this study.

Scheme 1. Synthetic routes to the ancillary ligand and the POSS materials.

Fig. 2 Crystal structure of the Ir(III) complex [Ir(L)<sub>2</sub>(Cz-acac-allyl)].

Fig. 3 The FT-IR spectra of Q<sub>8</sub>M<sub>8</sub><sup>H</sup>, POSS-1 and POSS-2.

Fig. 4 Thermogravimetric analyses (TGA) of the POSS materials.

Fig. 5 The X-ray diffraction (XRD) patterns of Cz-allyl, Ir(L)<sub>2</sub>(Cz-acac-allyl) and the POSS materials. (a: Ir(L)<sub>2</sub>(Cz-acac-allyl); b: Cz-allyl; c: POSS-3; d: POSS-2; e: POSS-1)

Fig. 6 UV-vis absorption and photoluminescence spectra of  $Ir(L)_2(Cz-acac-allyl)$  and the POSS materials in diluted dichloromethane solutions (C =  $1.0 \times 10^{-5}$  mol/L,  $\lambda_{ex} = 430$  nm).

Fig. 7 Cyclic voltammograms of ferrocene and the POSS materials (scan rate: 10 mV s1, solvent: dichloromethane).

Fig. 8 EL spectra of POSS-1 at different doped concentrations and different voltages (inset). Device configuration: ITO/PEDOT:PSS (30 nm)/CBP: POSS-1 (x wt%, 50 nm)/TPBi (50 nm)/Liq (2 nm)/Al(150 nm).

Fig. 9 The luminance vs. voltage (a) and current efficiency vs. voltage (b) curves of the doped devices with different POSS-1 concentrations. Device configuration: ITO/PEDOT:PSS (30 nm)/CBP: POSS-1 (x wt%, 50 nm)/TPBi (50 nm)/Liq (2 nm)/Al(150 nm).

Fig. 10 The luminance vs. voltage (a) and current efficiency vs. current density (b) curves of the

doped devices with different POSS-2 concentrations. Device configuration: ITO/PEDOT:PSS (30

nm)/CBP: POSS-2 (x wt%, 50 nm)/TPBi (50 nm)/Liq (2 nm)/Al(150 nm).

Table 1. Crystallographic data for Ir(L)<sub>2</sub>(Cz-acac-allyl).

Table 2. Selected bond lengths and bond angles for Ir(L)<sub>2</sub>(Cz-acac-allyl).

Table 3. Photophysical, thermal and electrochemical properties of the POSS materials.

Table 4. EL performances of the POSS materials.

POSS materials:





Scheme 1













Fig. 7



### **Dalton Transactions**



Fig. 9



Fig. 10

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Table 1. Crystallographic data for Ir(L)<sub>2</sub>(Cz-acac-allyl)

Compound	Ir(L) <sub>2</sub> (Cz-acac-allyl)
Empirical formula	C <sub>51</sub> H <sub>40</sub> IrN <sub>3</sub> O <sub>6</sub>
Formula weight	983.06
Temperature (K)	293(2)
Wavelength (Å)	1.54178
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	
a (Å)	10.0465(6)
b (Å)	30.8172(15)
c (Å)	13.9390(11)
α (°)	90
β (°)	98.719(2)
γ (°)	90
Volume (Å <sup>3</sup> ), Z	4265.7(5), 4
Density (calculated) (g/cm <sup>3</sup> )	1.531
Absorption coefficient (mm <sup>-1</sup> )	6.503
F (000)	1968
Crystal size (mm)	$0.21\times0.17\times0.08$
$\theta$ range for data collected (°)	2.87 to 66.20
Limiting indices	$-8 \le h \le 11$
	$-36 \le k \le 33$
	$-16 \le l \le 16$
Reflections collected	15544
Independent reflections	7448 ( $R_{int} = 0.0934$ )
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	0.6242 and 0.3421
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	7448 / 0 / 551
Goodness-of-fit on F <sup>2</sup>	1.054
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0620, wR_2 = 0.1080$
R indices (all data)	$R_1 = 0.1136$ , $wR_2 = 0.1278$
Largest diff. Peak and hole (eÅ <sup>-3</sup> )	1.161 and -0.894

Bond length (Å)				
Ir(1)–N(2)	2.016(9)	Ir(1)–N(3)	2.030(9)	
Ir(1)–O(1)	2.104(6)	Ir(1)–O(2)	2.126(7)	
Ir(1)–C(40)	1.989(10)	Ir(1)–C(26)	2.006(11)	
C(17)–C(18)	1.418(12)	C(18)–C(19)	1.389(13)	
O(1)–C(17)	1.293(11)	O(2)–C(19)	1.246(12)	
C(22)–C(23)	1.299(19)			
Bond angles (°)				
C(26)–Ir(1)–N(2)	80.7(4)	C(26)–Ir(1)–N(3)	102.6(4)	
C(26)–Ir(1)–O(1)	89.5(3)	C(26)–Ir(1)–O(2)	173.3(4)	
C(26)–Ir(1)–C(40)	95.3(4)	N(2)–Ir(1)–N(3)	174.7(4)	
N(2)–Ir(1)–O(1)	81.2(3)	N(2)–Ir(1)–O(2)	92.6(3)	
N(2)-Ir(1)-C(40)	103.9(4)	O(1)–Ir(1)–O(2)	88.9(2)	
O(1)–Ir(1)–N(3)	94.6(3)	O(1)–Ir(1)–C(40)	173.5(4)	
O(2)–Ir(1)–N(3)	84.0(3)	O(2)–Ir(1)–C(40)	86.8(3)	
N(3)-Ir(1)-C(40)	80.1(4)			

Table 2. Selected bond lengths and bond angles for Ir(L)<sub>2</sub>(Cz-acac-allyl)

Material	UV-vis (nm)	PL (nm)	$T_d$	τ (us)	$\Phi_{\rm f}$	$E_{OX}$ (V)	HOMO (eV)	LUMO (eV)
POSS-1	236, 264, 284, 295, 334, 347, 380, 418, 440	530, 570	347	9.27	47.49	0.88	-5.24	-2.57
POSS-2	236, 264, 284, 295, 334, 347, 380, 418, 440	530, 570	347	9.85	18.98	0.86	-5.22	-2.55
POSS-3	242, 264, 284, 295, 334, 347, 380, 418, 440	530, 570	347	9.92	18.41	0.87	-5.23	-2.56

Table 3. Photophysical, thermal and electrochemical properties of the POSS materials

Table 4. EL performances of the POSS materials

POSS materials	Concentration	$L_{max} (cd/m^2)$	LE <sub>max</sub> (cd/A)	EQE <sub>max</sub> (%)
POSS-1	25 wt%	8311@14.8 V	9.56@8.4 V	2.65
	33.33 wt%	10940@12.2 V	35.24@6.1 V	9.77
	42.86 wt%	10390@14.1 V	29.38@6.5 V	8.14
	50 wt%	10160@12.2 V	28.51@6.5 V	7.90
POSS-2	25 wt%	12390@10.7 V	30.52@1.57 mA/cm <sup>2</sup>	8.46
	33.33 wt%	12050@10 V	26.86@2.72 mA/cm <sup>2</sup>	7.44
	42.86 wt%	11350@10.2 V	25.10@3.37 mA/cm <sup>2</sup>	6.96
	50 wt%	11240@10.2 V	23.26@0.96 mA/cm <sup>2</sup>	6.45

## A table of contents entry

Three hybrid materials contained POSS core were synthesized and characterized, in

which two materials were used for light-emitting devices.

