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Supporting Information

Bulky, Dendronized Iridium Complexes and their Photoluminescence

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Contents

Materials and methods

All chemicals and solvents were purchased from commercial sources and used as received except where noted. Reactions were all conducted under argon atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 250, AC 300, AMX 500, and AMX 700 NMR spectrometers. The solvents for NMRs were CD_2Cl_2 with the reference peak at 5.32 ppm (^{1}H) and 53.84 ppm (^{13}C) and THF-d_8 with the reference peak at 1.72 ppm (^{1}H) and 25.31 ppm (^{13}C). Field desorption (FD) mass spectra were recorded on a VG-Instruments ZAB 2-SE-FDP using 8 kV accelerating voltage. MALDI-TOF mass spectra were recorded by a Bruker Reflex II spectrometer with fullerene as the reference and dithranol as the matrix. High resolution-ESI mass spectra were recorded by an ESI Q-Tof Ultima 3 Micro Mass spectrometer from Waters. UV-Vis absorption spectra were measured by a Varian Cary 4000 UV/Vis spectrometer (Varian Inc. Palo Alto, USA) using quartz cells with path length of 1 cm. Fluorescence spectra were recorded with a SPEX Fluorolog 2 spectrometer. Cyclic voltammetry (CV) measurements were conducted on a computer-controlled GSTAT12 workstation using a three electrodes system in which a Pt wire, a silver wire, and a glassy carbon electrode were used as counter, reference and working electrode respectively. The measurements were conducted in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution under argon environment with a scan rate of 100mV/s at room temperature. The solvents were DCM for the oxidation part and THF for the reduction part. Ferrocene/Ferrocenium (Fc/Fc^+) worked as the internal reference throughout the measurements. The calculations of HOMO and LUMO using CV were based on the following equations:

$$\text{HOMO (eV)} = -E_{ox}^{onset} + E_{Fc}^{onset} - 4.80;$$

$$\text{LUMO (eV)} = -E_{red}^{onset} + E_{Fc}^{onset} - 4.80;$$

Where

E_{ox}^{onset} is the onset oxidation potential of the targeted molecule,

$E_{Fc/Fc+}^{onset}$ is the onset oxidation potential of ferrocene,

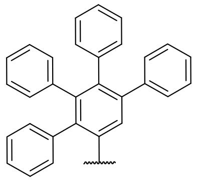
E_{red}^{onset} is the onset reduction potential of the targeted molecule compared to Ag/Ag^+ reference electrode.

PLQY of Ir complex **2** was measured with an integrating sphere integrated to HORIBA FL3C-111.

Phosphorescence lifetime was measured with an Edinburgh fluorescence spectrometer (FLS-980).

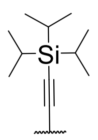
The X-ray intensity data was measured on a STOE IPDS-2T X-ray diffractometer system equipped with a Mo-target X-ray tube. The data frames were collected using the program X-AREA and processed using the program Integrate routine within X-AREA. The data were corrected for absorption based on the crystal faces using XRED-32. Structure solution and refinement were performed using SHELXT/SHELXL-2014. Crystal of compound **2** contains solvent molecules, one of CH_2Cl_2 could be refined, for another the refinement failed and the SQUEEZE option of PLATON was used.

The calculation of the van der Waals volumes[1] of pentaphenylene and TIPSE groups is according to the formula:
$V = \Sigma$ all atom volumes- $5.92N_B - 14.7R_A - 3.8R_{NR;}$
Where
N_B is the number of chemical bonds,
R_A is the number of aromatic rings,
R_{NA} is the number of nonaromatic rings.
The volume of C, H and Si atoms are 20.58, 7.24 and 38.79 respectively, according to the literature.
Therefore, $V_{pentaphenylene}$= 30×20.58+21×7.24-5.92×(34+21)-14.7×5=370.34 ($Å^3$);
V_{TIPSE}=11×20.58+21×7.24+ 1×38.79-5.92×32=227.77($Å^3$).



$C_{30}H_{21}$

Pentaphenylene



$C_{11}H_{21}Si$

TIPSE

Fabrications and characterizations of OLEDs:

Devices for Ir complex **2** were fabricated as follows. Firstly, the pre-cleaned ITO-coated glass substrates (15 Ω per square) were treated with ultraviolet-ozone for 40 min. Subsequently, a 40 nm PEDOT:PSS (Clevios AL4083) layer was deposited onto the substrates in air at a speed of 5000 rpm for 60 s, annealed at 120 °C for 1 h, and moved into a glove box filled with nitrogen. Then the chlorobenzene solution of Ir complex **2** was spin-coated onto the PEDOT:PSS layer at a speed of 1500 rpm for 60 s to form a 30 nm emissive layer. After transferred into a vacuum chamber, other layers including 8 nm TPCz, 42 nm TmPyPB, 1 nm LiF and 150 nm Al were successively evaporated under a base pressure ($< 4 \times 10^{-4}$ Pa). The current density-voltage-luminance characteristics were tested using a Keithley source measurement unit (Keithley 2400 and Keithley 2000) calibrated with a silicon photodiode. The EL spectra and CIE coordinates were measured on a CS2000 spectrometer. EQE were calculated from the EL spectrum, luminance, and current density, assuming a Lambertian emission distribution. All the measurements were performed at room temperature under ambient atmosphere.

Devices for dendrimer **D2** were fabricated on pre-patterned ITO substrates (Psiotec), which were mechanically cleaned with acetone and sonicated in isopropanol, followed by oxygen plasma treatment (Diener Femto). A 45 nm thick PEDOT:PSS film (Clevios AI4083) was spin coated on top and annealed for 10 min at 220 °C in air. CuSCN was deposited by inkjet printing from a proprietary solution (Inuru GmbH). The emissive layers were spin coated from 6 mg/ml solution in toluene to yield ca. 40 nm thick films. Ca (5 nm) and Al (200 nm) electrodes were deposited through a shadow mask at a base pressure of 10^{-6} mbar in a thermal evaporator to form multiple devices with an active area of 4 mm^2. The devices were encapsulated using a UV-curable epoxy (Ossila) and a glass cover slide. Current density/voltage/luminance characteristics were recorded using a Keithley 2450 source measurement unit, together with a Konica Minolta LS-160 luminance meter in a custom setup. Electroluminescence spectra were acquired using an Ocean Optics HR2000+ spectrometer run with Ocean View software.

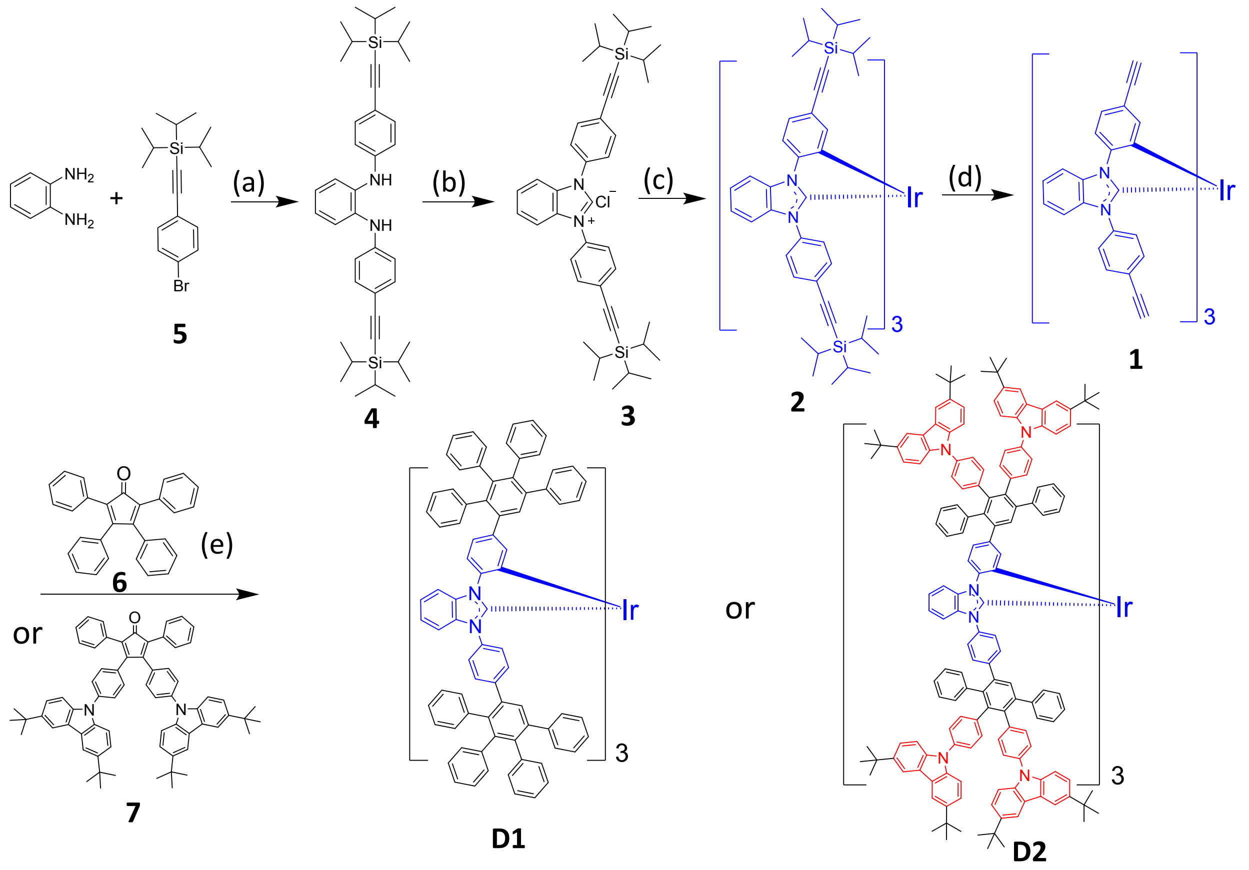
Methods of computation

First of all, we performed geometry optimizations of the designed complexes in gas phase both in the respective ground singlet (S_0) and first excited triplet (T_1) states. We used B3LYP exchange correlation functional along with 6-31G** basis sets for the lighter elements and LANL2DZ basis sets with compatible pseudopotential for the Ir atom as implemented in Gaussian 09 program suite.[2] A similar level of calculation is well explored for predicting the geometry and optoelectronic properties of different Ir-based OLED materials.[3-7] The previous theoretical calculations have demonstrated that the predicted T_1-S_0 energy gaps of the complexes are well matched with the experimental emission wave length.[4, 7] For calibrating the data, we adopted similar strategy and surprisingly, the computed T_1-S_0 energy gaps for fac-(dpbic)$_3$Ir (419 nm), Ir-complex 2 (432 nm) and dendrimer **D1** (448 nm) are in well agreement with the experimental emission wavelengths of 400, 440 and 462 nm, respectively. Analyzing the nature of the transition and orbital characteristics it is demonstrated that the T_1 state is the admixture of ^{3}MLCT and ^{3}LC characters (Table S4, and for example, for fac-(dpbic)$_3$Ir, as indicated in Figure S8). It is argued that appreciable amount of MLCT character is responsible for the emissive nature of the T_1 state. However, there exists a closely lying ^{3}MC state which is non-emissive in nature. For searching that state and computing the potential energy barrier for the conversion of ^{3}MLCT to ^{3}MC state, we performed relaxed potential energy surface (PES) scan along the longest metal-C (ligand) bond length, i.e., constrained geometry optimizations were done with different fixed Ir-C bond lengths. The energy difference between the highest point of the PES and the T_1 state is the barrier height (see Figure 6). The distinction between these two triplet states could easily be identified from the analysis of the frontier molecular orbitals of the relaxed states before and after the transition point. Secondly, we have calculated the vertical emission energy (T_1–S_0' energy gap, S_0' being the corresponding singlet state single point energy at the triplet geometry) for some specified Ir-C bond lengths in Table S3. It is revealed that the T_1–S_0' energy gap gradually decreases with increasing the Ir-C bond length, demonstrating the fact that the second triplet state is of MC character which involves $^3\text{MC}\rightarrow S_0$ radiationless decay.

Synthetic procedures

1-Bromo-4-[(triisopropylsilyl)ethynyl]benzene (**5**) [8], and tertbutyl-carbazole-functionalized-2,3,4,5-tetraphenylcyclopentadienone (**7**) [9] were synthesized according to the published procedures.

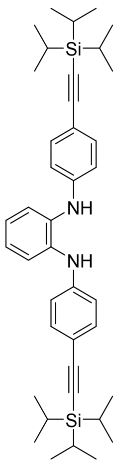
Scheme S1: Synthetic routes for the iridium complexes and polyphenylene dendrimers with iridium core.



* **Reagents and conditions:** (a) NaOtBu, $Pd_2(dba)_3$, 2,2′-bi(diphenylphosphino)-1,1′-dinaphthalene, toluene, 90 °C, 13 h, 89%; (b) triethyl orthoformate, conc. HCl, 80 °C, 14 h, 86%; (c) $IrCl_3 \cdot nH_2O$, Na_2CO_3, Ag_2CO_3, 2-ethoxylethanol, 145 °C, 20 h, 22%; (d) TBAF, THF, 0 °C, 1 h, 45%; (e) o-xylene, 140 °C, 24 h, 36% for **D1** and 150 °C, 48 h, 72% for **D2**.

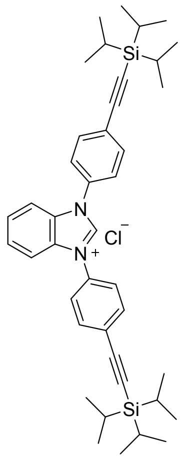
1,2-Di[(4-triisopropylsilylethynylphenyl)amino]benzene (4)

1,2-diaminobenzene (1.56 g, 14.43 mmol) and 1-bromo-4-[(triisopropylsilyl)ethynyl]benzene (9.75 g, 28.90 mmol) were placed in a 100 ml Schlenk flask. It was then transferred to a glove box, in which sodium tertbutoxide (4.16 g, 43.28 mmol) and 20 ml of toluene were added. In another flask, $Pd_2(dba)_3$ (295 mg, 0.289 mmol), 2,2'-bi(diphenylphosphino)-1,1'-dinaphthalene (864 mg, 1.39 mmol) and 20 ml of dry toluene were added sequentially to make it totally dissolved. Then the catalyst solution was added into the Schlenk flask. Then the mixture was heated at 90 °C and stirred for 13 hours. The



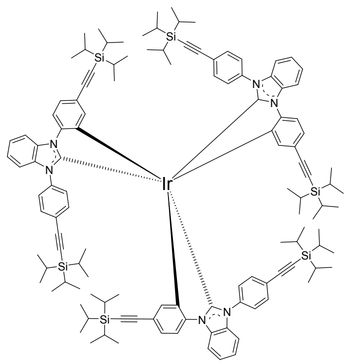
resulting mixture was quenched with aq. NH_4Cl solution and extracted with DCM and dilute NH_4Cl solution, followed by a silica gel flash column (DCM/hexane, 1/1). Eventually, 8.00 g of a white-brown solid was received after drying under reduced pressure (89.2%). ^{1}H NMR (300 MHz, CD_2Cl_2, 300 K) δ 7.41 – 7.26 (m, 6H), 7.04 (dd, *J* = 6.0, 3.2 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 4H), 5.78 (s, 2H), 1.11 (s, 42H). ^{13}C NMR (75 MHz, CD_2Cl_2, 300 K) δ 144.64, 134.69, 133.58, 124.19, 121.65, 116.34, 115.16, 107.92, 88.85, 18.87, 11.81. FD-Mass: calculated for $C_{40}H_{56}N_2Si_2$: 620.4 (100%), found: 621.7 $[M+H]^+$.

1,3-Di[(4-triisopropylsilylethynyl)phenyl]benzimidazolium chloride (**3**)



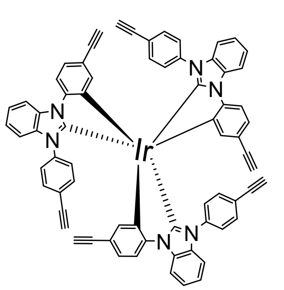
Compound **4** (7.26 g, 11.69 mmol) and 70 ml of triethyl orthoformate were placed in a Schlenk flask, stirred to make it dissolve. Then the system was degassed and added argon 3 times. Then conc. HCl (1.5 ml, 22.83 mmol) was added quickly. It was stirred at room temperature for 30 minutes. Then it was heated at 80 °C for 14 hours. After the mixture was cooled down, 40 ml of Et_2O was added to precipitate it. Then filtration was done to get 4.4 g of a white solid after drying (85.5%). ^{1}H NMR (250 MHz, DMSO-d_6, 298K) δ 10.62 (s, 1H), 8.06 – 7.76 (m, 12H), 1.14 (s, 42H). ^{13}C NMR (75 MHz, DMSO-d_6, 300K) δ 143.10, 133.65, 132.95, 131.07, 127.98, 125.89, 124.55, 113.88, 105.61, 93.08, 64.96, 18.55, 10.74. FD-Mass: calculated for $C_{41}H_{55}N_2Si_2$:631.4, found: 632.1 $[M+H]^+$.

Tris[1,3-bis(4-triisopropylsilylethynylphenyl)benzimidazolyl] iridium (**2**)



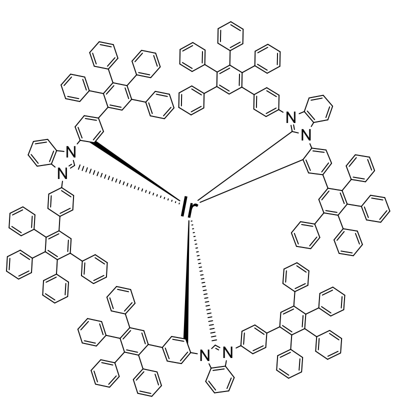
$IrCl_3.nH_2O$ (500 mg, 1.67 mmol), compound **3** (3.58 g, 5.36 mmol), Ag_2CO_3 (739 mg, 2.68 mmol), Na_2CO_3 (284 mg, 2.68 mmol) and 80 ml of 2-ethoxylethanol were added in a Schlenk flask. Then the mixture was degassed and added argon 3 times. It was stirred at 145 °C for 20 hours. After the mixture was cooled down, water was added to precipitate it. Then filtration was done to get pale-white-colored solid after drying. After that, the solid was further purified by recrystallization by hexane and 2 gram of light-yellow-colored solid product was obtained after drying under reduced pressure (57%). The obtained product could be used for next step reaction directly. To characterize the product, part of the product was further purified by a silica gel flash column (DCM/hexane, 1/4) to get 80 mg of a light-yellow solid after drying under reduced pressure (22%). ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K) δ 8.14 (d, J = 8.3 Hz, 3H), 7.88 (d, J = 8.2 Hz, 3H), 7.40 (dd, J = 8.2, 1.9 Hz, 3H), 7.40 (dd, J= 8.1, 1.8 Hz, 3H), 7.32 (dd, J=7.4, 7.4 Hz, 3H), 7.23 (dd, J = 8.2, 1.9 Hz, 3H), 7.06 (dd, J = 7.8, 7.6 Hz, 3H), 6.73 (d, J = 1.9 Hz, 3H), 6.52 (dd, J = 8.3, 3.7 Hz, 3H), 6.42 (dd, J = 8.2, 2.3 Hz, 3H), 6.28 (dd, J = 8.2, 1.9 Hz, 3H), 6.11 (dd, J = 8.1, 2.2 Hz, 3H), 1.11 (s, 63H), 1.04 (s, 63H). ^{13}C NMR (176 MHz, CD_2Cl_2, 300 K) δ 187.96, 148.74, 148.21, 140.82, 137.98, 137.55, 132.54, 132.12, 131.80, 128.90, 127.22, 126.14, 123.79, 123.61, 123.39, 119.72, 112.41, 111.22, 110.61, 110.08, 105.69, 92.53, 88.44, 18.88, 18.86, 11.85, 11.65. FD-Mass: calculated for $C_{123}H_{159}IrN_6Si_2$: 2082.1, found: 2082.2 $[M]^+$.

Tris[1,3-bis(4-ethynylphenyl)benzimidazolyl] iridium (2)



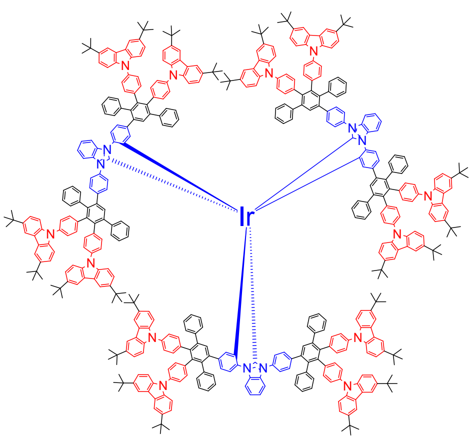
Compound **2** (1.66 g, 0.795 mmol) was added into a Schlenk flask. Then it was degassed and added argon 3 times. Then, 65 ml of THF was added to dissolve it and stirred under ice bath. Then TBAF (1.22 g, 4.66 mmol) dissolved in 20 ml of THF was added dropwise. Then the mixture was stirred for 1 hour at 0 °C. After that, THF was evaporated to get solid. Then a silica gel flash column was run (DCM/hexane, 4/1) to get 0.34 g of a light-yellow solid after drying under reduced pressure (37.4%). ^{1}H NMR (300 MHz, CD_2Cl_2, 300 K) δ 8.12 (d, J = 8.3 Hz, 3H), 7.91 (d, J = 8.2 Hz, 3H), 7.47 – 7.23 (m, 9H), 7.10 (t, J = 7.8 Hz, 3H), 6.72 (d, J = 2.0 Hz, 3H), 6.66 (dd, J = 8.2, 2.2 Hz, 3H), 6.54 (d, J = 8.1 Hz, 3H), 6.46 (dd, J = 8.1, 2.0 Hz, 3H), 6.14 (dd, J = 8.2, 2.3 Hz, 3H), 2.97 (s, 1H), 2.91 (s, 1H). ^{13}C NMR (63 MHz, CD_2Cl_2, 300 K) δ 187.49, 149.17, 148.30, 140.51, 137.88, 137.75, 132.55, 132.37, 131.97, 129.05, 127.06, 126.68, 124.12, 123.48, 122.51, 118.11, 112.61, 111.31, 110.71, 85.71, 82.06, 78.86, 75.75. FD-Mass: calculated for $C_{69}H_{39}IrN_6$: 1144.3 (100%), found: 1143.7 $[M-H]^+$.

Fac(dpbic)$_3$Ir-based polyphenylene dendrimer G1 (D1)



Compound **1** (5.8 mg, 5.07 µmol), 2,3,4,5-tetraphenylcyclopentadienone (20 mg, 52 µmol) and 0.5 ml of o-xylene were added into a Schlenk flask. Then the mixture was degassed and was added argon 3 times. Then, it was heated at 145 °C for 18 hours. After the mixture was cooled down, 10 ml of hexane was added to precipitate the product and filtration was done to get the solid. Then, the product was purified by silica gel flash column (DCM/hexane, 1/1 to 7/3) to get 6 mg of a white solid (36.1%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) δ 7.71 (d, J = 8.2 Hz, 3H), 7.40 (d, J = 8.2 Hz, 3H), 7.35 – 7.24 (m, 9H), 7.18 – 7.10 (m, 10H), 7.10 – 6.96 (m, 16H), 6.96 – 6.64 (m, 86H), 6.58 (s, 3H), 6.52 (dd, J = 8.1, 2.1 Hz, 3H), 6.44 – 6.21 (m, 22H), 6.02 (d, J = 8.0 Hz, 3H), 5.86 (s, 3H), 5.69 (d, J = 8.2 Hz, 3H). ^{13}C NMR (176 MHz, CD$_2$Cl$_2$, 300 K) δ 188.98, 147.48, 143.03, 142.35, 142.07, 141.75, 141.63, 141.30, 141.24, 141.10, 140.93, 140.75, 140.64, 140.45, 140.29, 140.12, 139.88, 139.81, 139.75, 138.59, 138.45, 138.19, 137.43, 135.89, 132.39, 132.10, 132.00, 131.82, 131.61, 130.52, 130.11, 129.90, 128.60, 127.87, 127.62, 127.23, 127.13, 127.05, 126.97, 126.92, 126.79, 126.68, 126.58, 126.26, 126.05, 125.84, 125.69, 125.37, 125.13, 123.53, 123.12, 122.15, 111.19, 110.81, 110.19. MALDI-TOF: calculated for $C_{237}H_{159}IrN_6$: 3283.2 (100%), found: 3283.2 [M]$^+$. HR-ESI-MS: calculated for $C_{237}H_{159}IrN_6$:3284.2412, found: 3284.2383 [M$^+$].

Fac(dpbic)$_3$Ir-based peripheral-carbazole polyphenylene dendrimer G1 (D2)



Compound **1** (36 mg, 31.5 µmol), compound **7** (300 mg, 319.4 µmol) and 7 ml of o-xylene were added into a Schlenk flask. Then it was degassed and added argon 3 times. Then, it was heated at 150 °C for 48 hours. After the mixture was cooled down, methanol was added to precipitate the product and filtration was done to get the solid. Then, the product was purified by silica gel flash column (DCM/hexane, 2/3) to get solid product. Then a GPC column (THF as eluent) was done to get 0.185g of a white solid (88.9%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K) δ 8.07 (m, 24H), 7.91 (d, J = 8.3 Hz, 3H), 7.59 (d, J = 8.2 Hz, 3H), 7.52 – 7.39 (m, 12H), 7.38 – 7.32 (m, 7H), 7.29 – 6.88 (m, 131H), 6.82 (s, 5H), 6.75 – 6.61 (m, 13H), 6.51 (m, 12H), 6.28 (d, J = 8.0 Hz, 3H), 6.16 (s, 3H), 5.95 (d, J = 8.1 Hz, 3H), 1.36 (m, 216H). ^{13}C NMR (214 MHz, CD$_2$Cl$_2$, 298 K) δ 149.08, 147.80, 143.44, 143.18, 143.14, 143.02, 142.98, 142.03, 141.84, 141.77, 141.43, 141.31, 141.11, 140.67, 140.64, 140.41, 140.33, 140.16, 139.99, 139.75, 139.65, 139.57, 139.54, 139.51, 139.27, 138.65, 138.39, 138.23, 137.46, 136.21, 136.18, 135.95, 135.85, 135.51, 133.54, 133.37, 133.33, 133.26, 132.60, 132.10, 131.94, 131.97, 130.79, 130.76, 130.53, 130.23, 129.95, 128.87, 128.22, 127.99, 127.51, 127.45, 127.37, 126.75, 126.32, 126.26, 125.82, 125.73, 125.70, 125.67, 125.62, 125.54, 125.42, 125.28, 123.94, 123.89, 123.84, 123.56, 123.52, 123.50, 123.45, 122.43, 116.59, 116.51, 111.54, 111.13, 110.42, 109.44, 109.41, 109.39, 109.34, 34.98, 34.95, 34.92, 32.16, 32.15. MALDI-TOF: calculated for $C_{477}H_{435}IrN_{18}$: 6612.4 (100%), found: 6611.4 $[M-H]^+$. HR-MALDI-TOF mass: calculated for $C_{477}H_{435}IrN_{18}$: 6612.4389, found: 6612.5690 $[M^+]$.

Single-crysal data

Table S1: Single-Crystal X-ray Diffraction Parameters and Crystal Data for Compound **2**

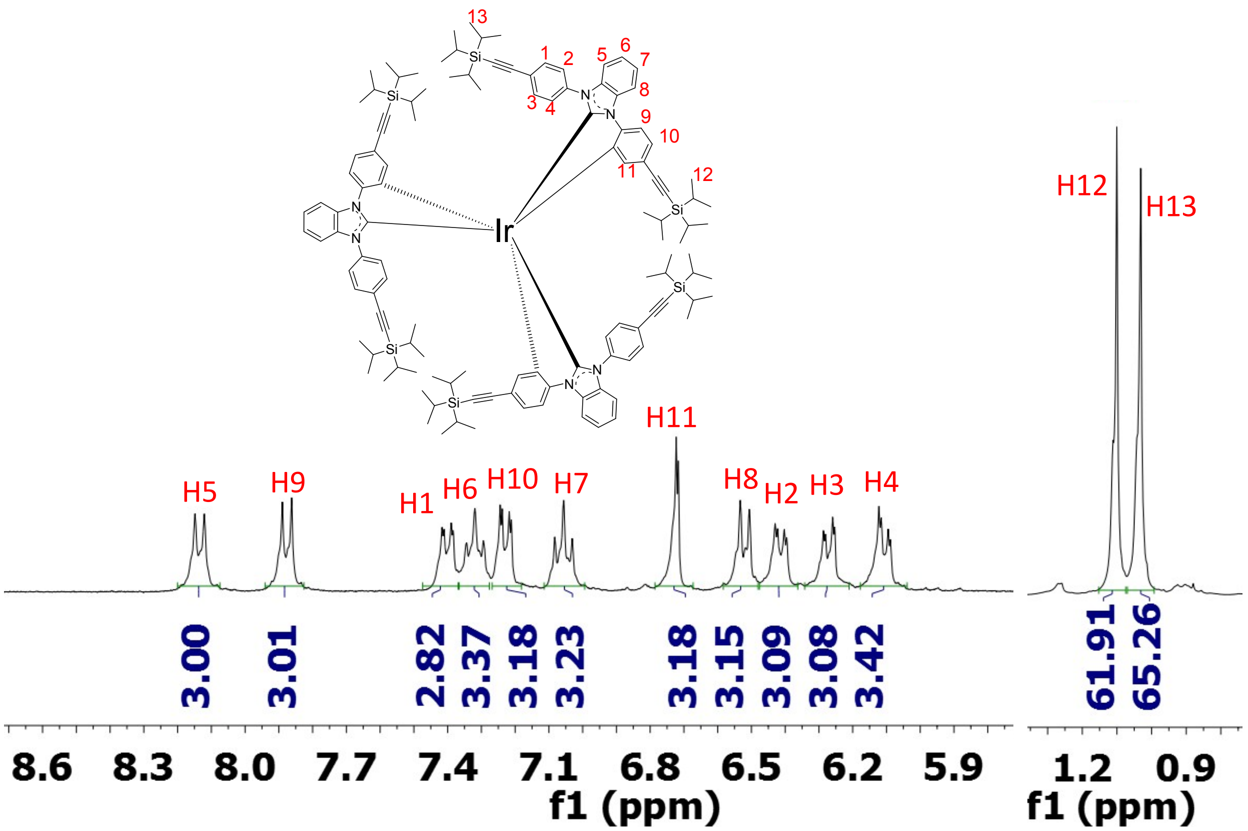
formula	$C_{123}H_{159}IrN_6Si_6$, CH_2Cl_2		
molecular weight	2167.22 gmol^{-1}		
absorption	μ = 1.222 mm^{-1} correction with 6 crystal faces		
transmission	T_{min} = 0.4957, T_{max} = 0.8321		
crystal size	0.16 x 0.20 x 0.96 mm^3 colourless block		
space group	P -1 (triclinic)		
lattice parameters	a = 13.9333(4)Å	α = 108.091(2)°	
(calculate from	b = 20.7812(6)Å	β = 101.797(2)°	
134269 reflections with	c = 23.3259(6)Å	γ = 94.351(2)°	
2.3° < θ < 28.2°)	V = 6213.7(3)Å^3	z = 2	F(000) = 2284
temperature	-153°C		
density	d_{xray} = 1.158 gcm^{-3}		
diffractometer	STOE IPDS 2T		
radiation	Mo-K_α Graphitmonochromator		
Scan – type	ω scans		
Scan – width	1°		
scan range	2° ≤ θ < 28.5°		
	$-18 \leq h \leq 18$ $-27 \leq k \leq 27$ $-30 \leq l \leq 30$		
number of reflections:			
measured	82904		
unique	30419 (R_{int} = 0.0333)		
observed	23140 ($|F|/\sigma(F) > 4.0$)		
wR2, R1, S	0.2308, 0.0783, 1.045		

Table S2: Bond length and torsion angle (between carbene and non-chelated phenyl plane) of compound **2** crystal and bond lengths of fac-$(pmb)_3$Ir crystal.[10]

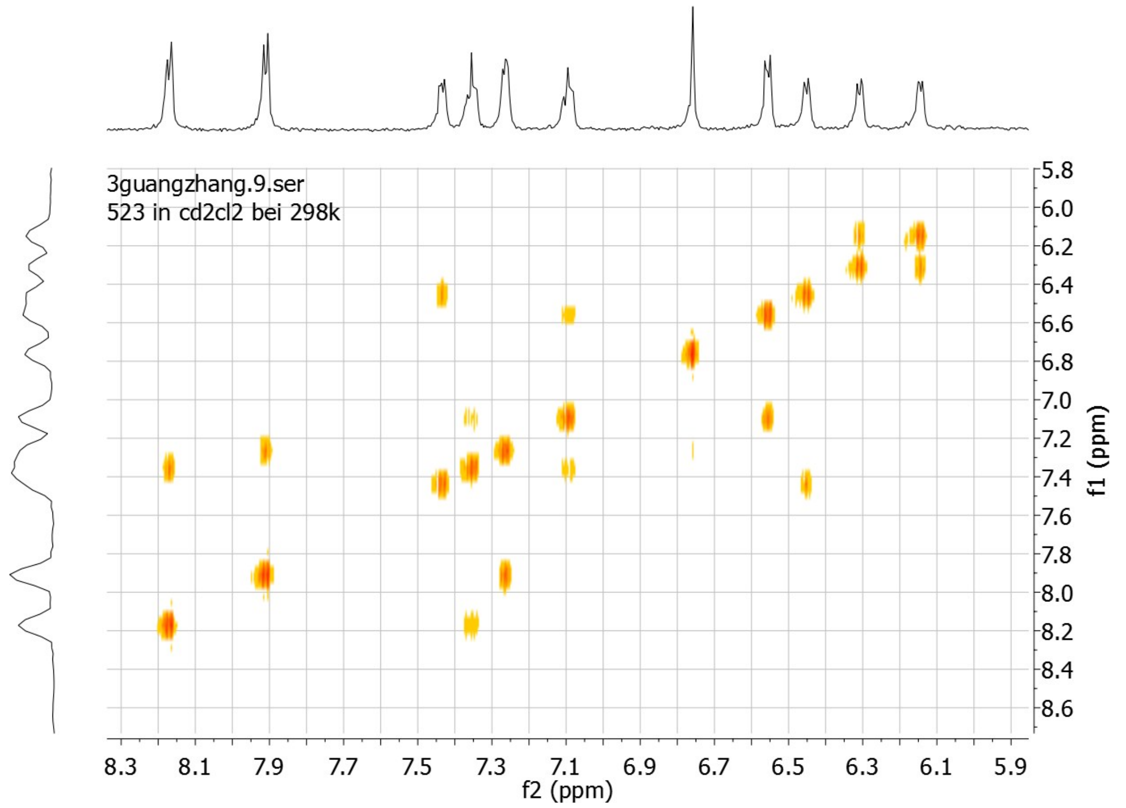
Compound 2	**Bond length (Å)**		**Torsion angle (degree)**
Ir-C$_{\text{carbene}}$1	2.045(7)	**Torsion 1**	54.76
Ir-C$_{\text{carbene}}$2	2.041(6)		
Ir-C$_{\text{carbene}}$3	2.065(5)	**Torsion 2**	69.94
Ir-C$_{\text{phenyl}}$4	2.096(6)		
Ir-C$_{\text{phenyl}}$5	2.081(6)	**Torsion 3**	69.17
Ir-C$_{\text{phenyl}}$6	2.091(6)		

Fac-(pmb)$_3$Ir	**Bond length (Å)**
Ir-C$_{\text{carbene}}$1	2.023
Ir-C$_{\text{carbene}}$2	2.022
Ir-C$_{\text{carbene}}$3	2.035
Ir-C$_{\text{phenyl}}$4	2.070
Ir-C$_{\text{phenyl}}$5	2.093
Ir-C$_{\text{phenyl}}$6	2.078

NMR data



13
1
2
5
6
7
8
3
4
9
10
11
12
Si
N
Ir
H5
H9
H1
H6
H10
H7
H11
H8
H2
H3
H4
H12
H13
3.00
3.01
2.82
3.37
3.18
3.23
3.18
3.15
3.09
3.08
3.42
61.91
65.26
8.6
8.3
8.0
7.7
7.4
7.1
6.8
6.5
6.2
5.9
f1 (ppm)
1.2
0.9
f1 (ppm)



3guangzhang.9.ser
523 in cd2cl2 bei 298k
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
f1 (ppm)
8.3
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
f2 (ppm)

Figure S1: ^{1}H NMR (top) and ^{1}H-^{1}H COSY (bottom) spectra of compound **2** (solvent: CD_2Cl_2). (According to the COSY, together with the proton environment in the molecule, the above proton correlations are partially correct because some protons' chemical shifts are not confirmed with these information; they are H1, H2, H3, H4 and H5, H6, H7, H8. But it is surprising that the difference in chemical shifts (between H1 and H3, and between H5 and H8) are so big.

Mass spectra

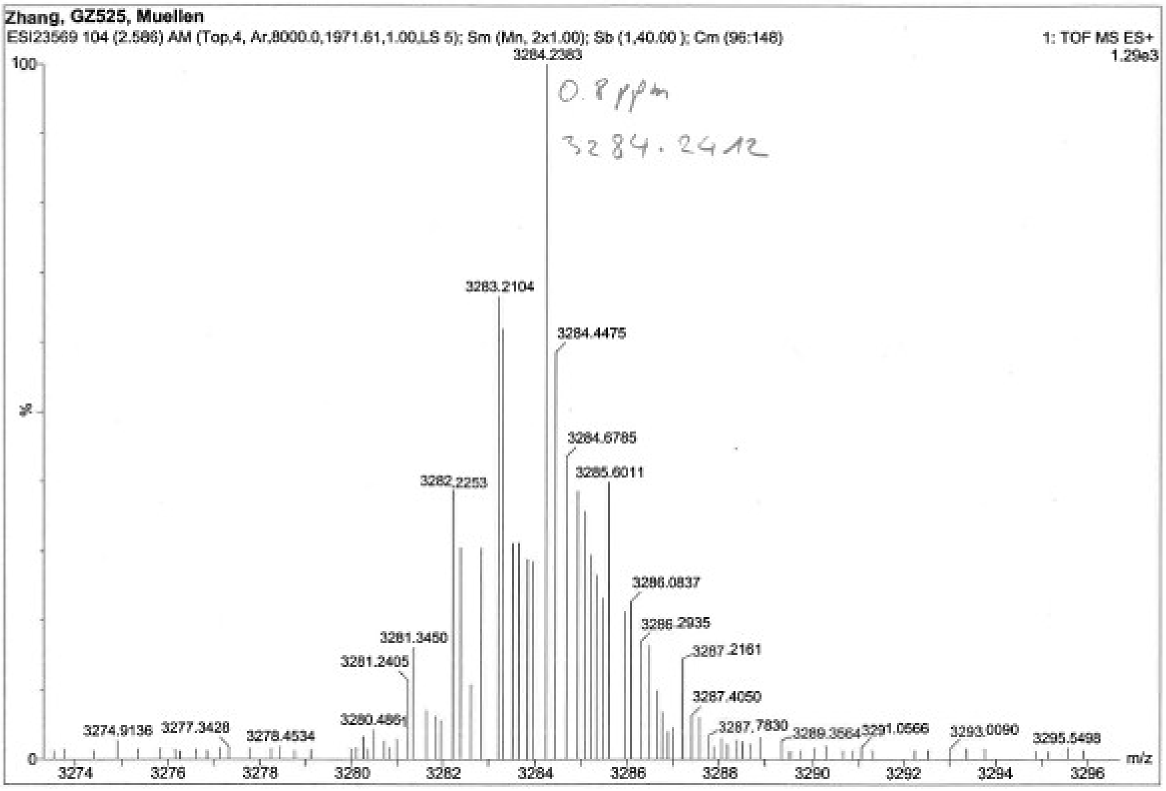


Figure S2: HR-ESI mass spectra of dendrimer **D1**[M^+].

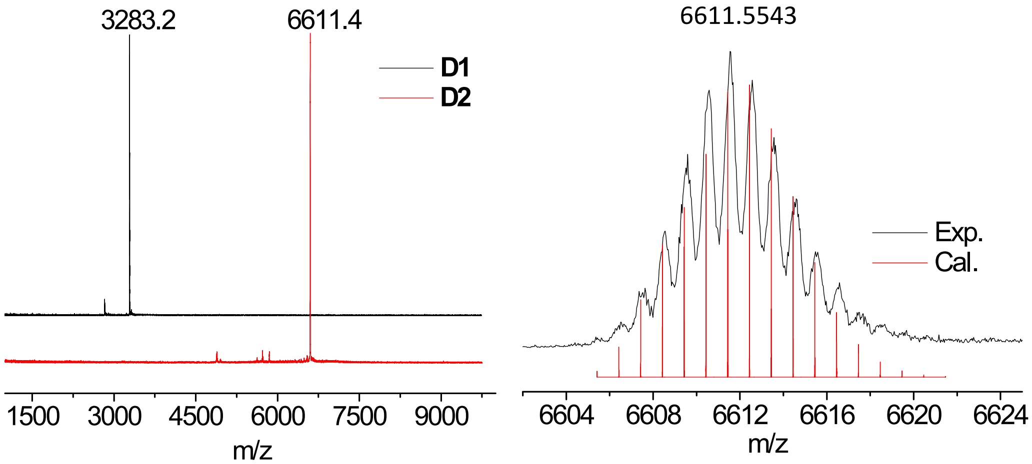


Figure S3: MALDI-TOF mass spectra of **D1** and **D2** (left) and HR-MALDI-TOF mass spectra of D2 (right).

UV-vis absorption and photoluminescence spectra

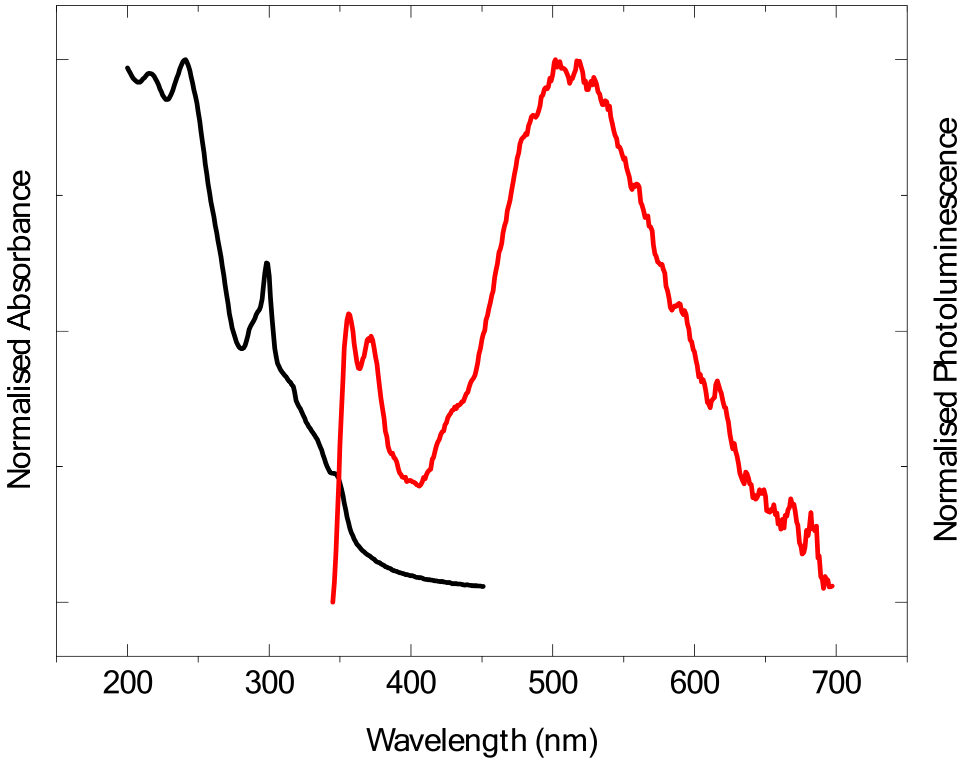


Figure S4: UV-vis absorption and photoluminescence spectra of dendrimer **D2** in thin films.

Curves of cyclic voltammetry

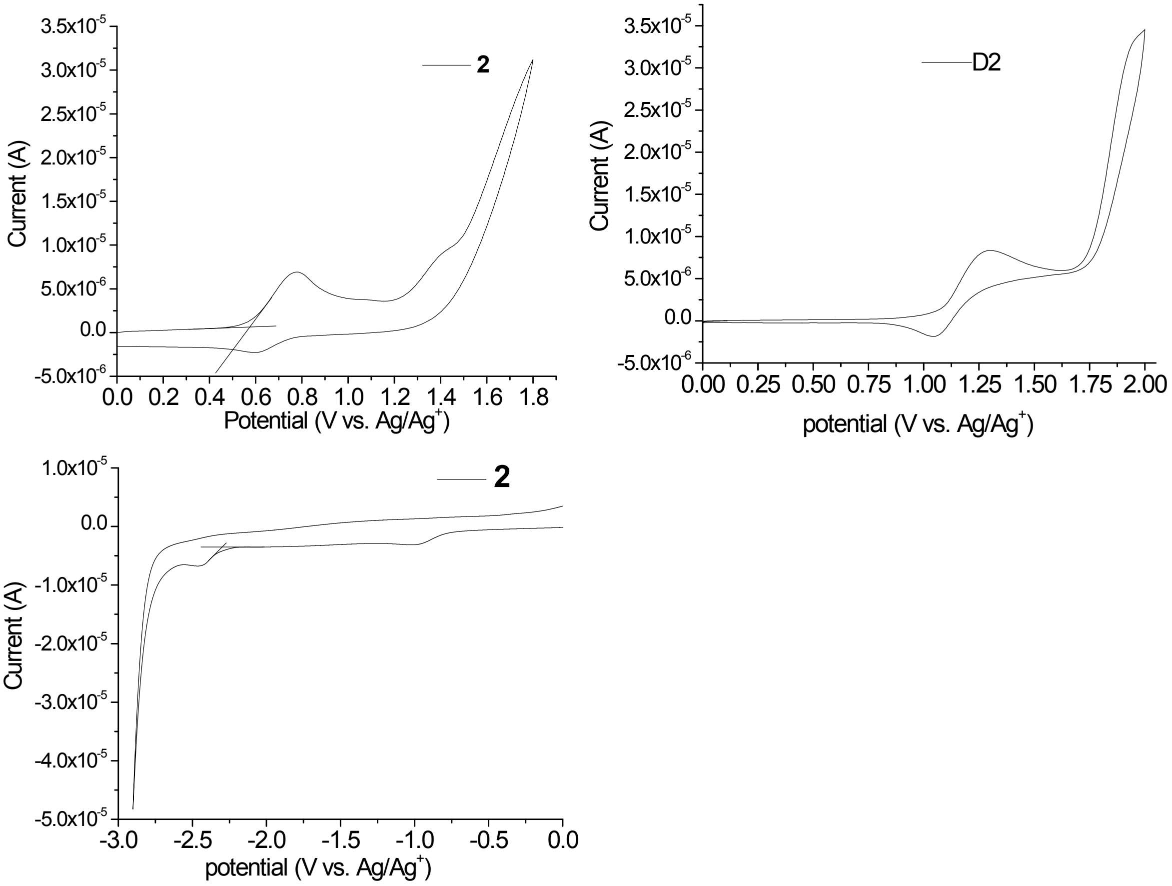


Figure S5: CV curves of compound **2** (left) and dendrimer **D2** (right) (reference: ferrocene).

Optimized molecular structures

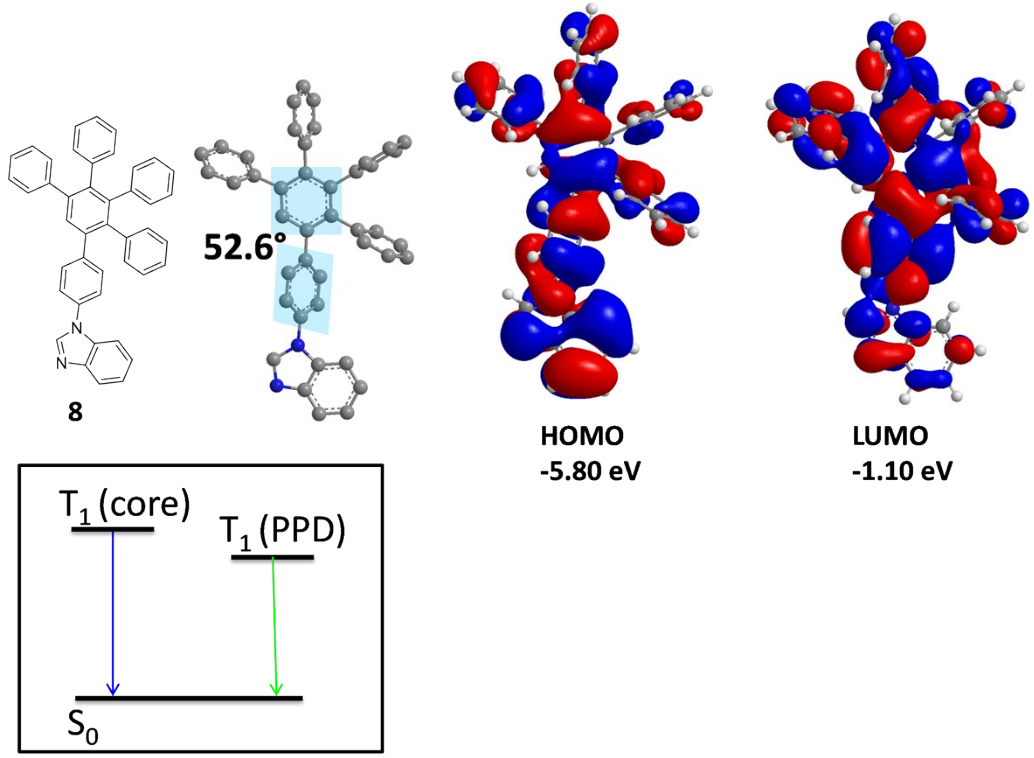


Figure S6: Optimized molecular structure and molecular orbital distributions of FMOs of compound **8 (**DFT, B3LYP, 6.31G method).

Photoluminescence decay

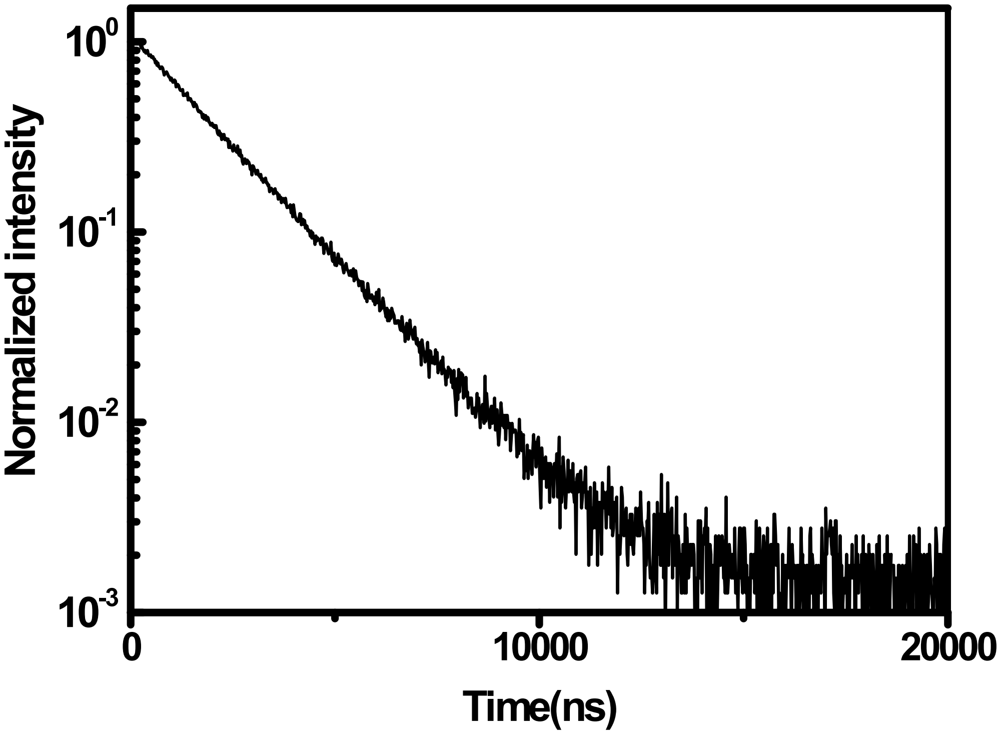


Figure S7: Photoluminescence decay of Ir complex **2** (measured at 298 K under N_2 in toluene with a concentration of 10^{-5} M).

Calculated transition and orbital characteristics

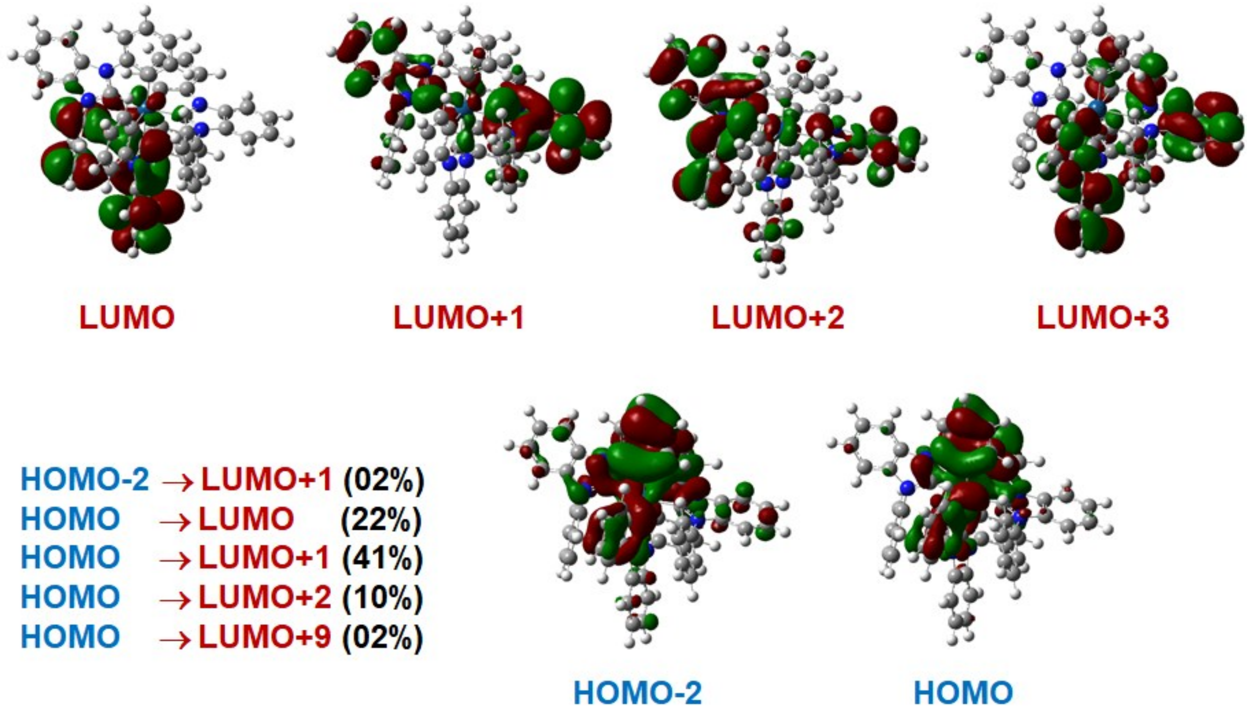


Figure S8: Calculated transition and orbital characteristics for the $\mathbf{T_1}$ state of fac-(dpbic)$_3$Ir. The main contributing transition orbitals are shown. It clearly reveals that the T_1 state is the admixture of ^{3}MLCT and ^{3}LC characters.

Table S3: Variation of T_1–S_0' energy gap for fac-(dpbic)$_3$Ir along the potential energy scan (for some selective Ir–C bond lengths). Shaded region is the transition point between radiative and nonradiative states.

Ir–C bond length (Å)	**T_1–S_0' energy gap (eV)**
2.15	2.42
2.55	2.32
2.75	1.57
3.15	0.64
3.65	0.18

Table S4: Excited state (T1) properties of the complexes obtained from TDDFT calculations.

Complex	Orbital contribution (in %)	Transition characteristics
Fac-(dpbic)$_3$Ir	HOMO → LUMO+1 (41) HOMO → LUMO (22) HOMO → LUMO+2 (10) HOMO-2 → LUMO+1 (2)	MLCT + LLCT
2	HOMO → LUMO+1 (53) HOMO → LUMO (13) HOMO-1 → LUMO (10) HOMO → LUMO+2 (6)	MLCT + LLCT
D1	HOMO → LUMO+1 (62) HOMO-1 → LUMO (12) HOMO → LUMO+1 (9) HOMO → LUMO+2 (2)	MLCT + LLCT

OLED performance

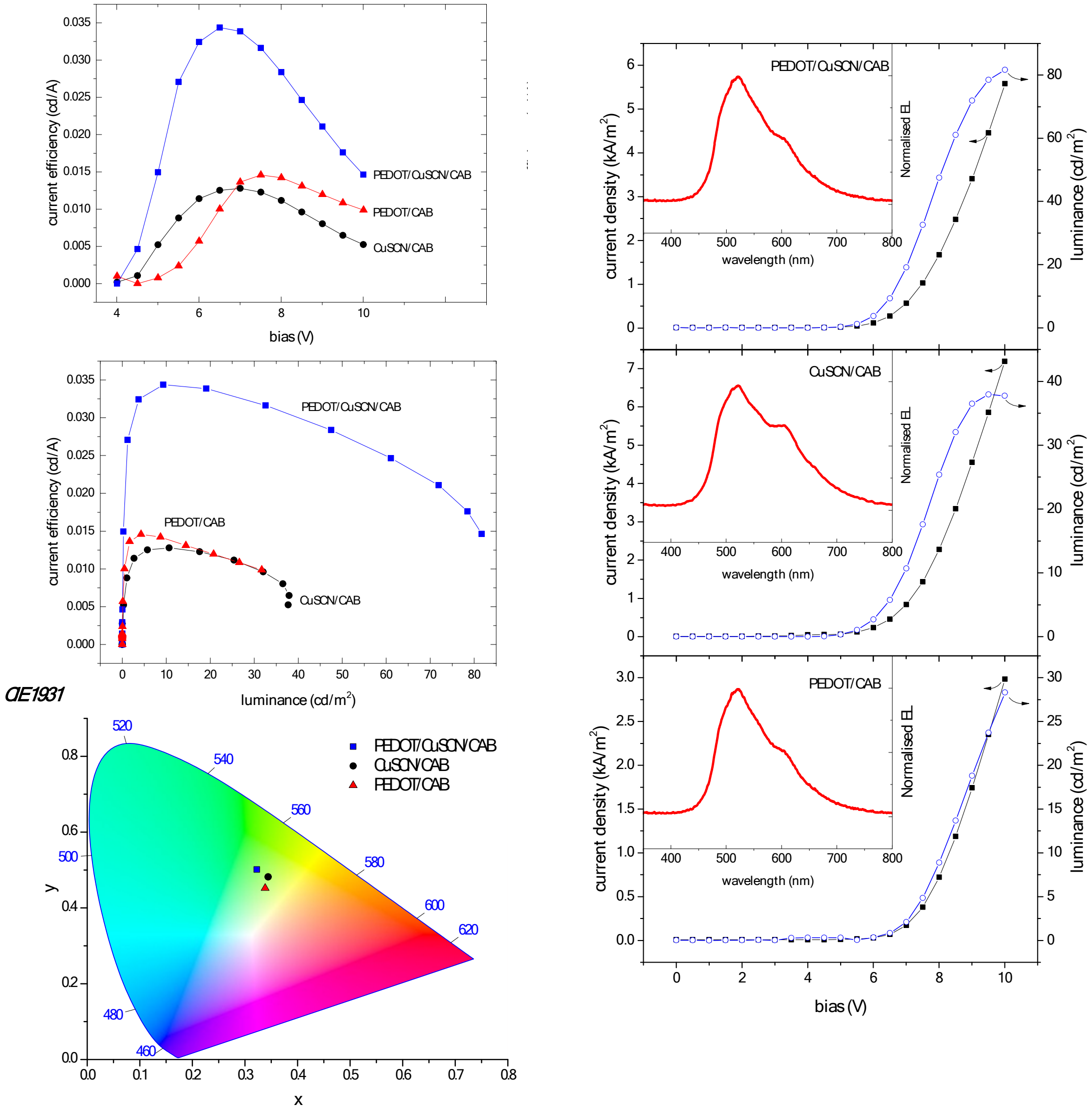


Figure S9: OLED performances of dendrimer **D2** in different device structures.

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