

Influence of molecular spacing on the stability and efficiency of host-free sky-blue dendrimer organic light emitting diodes

Electronic Supplementary Information

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- 1. Additional OLED data**
- 2. MALDI-TOF of pristine materials**
- 3. Spectral mismatch correction integrating sphere**
- 4. Experimental for the synthesis of Ir(DDTri)₃**
- 5. Gel Permeation Chromatography (GPC)**
- 6. Thermal gravimetric analysis (TGA)**
- 7. Differential scanning calorimetry (DSC)**
- 8. Cyclic voltammetry**

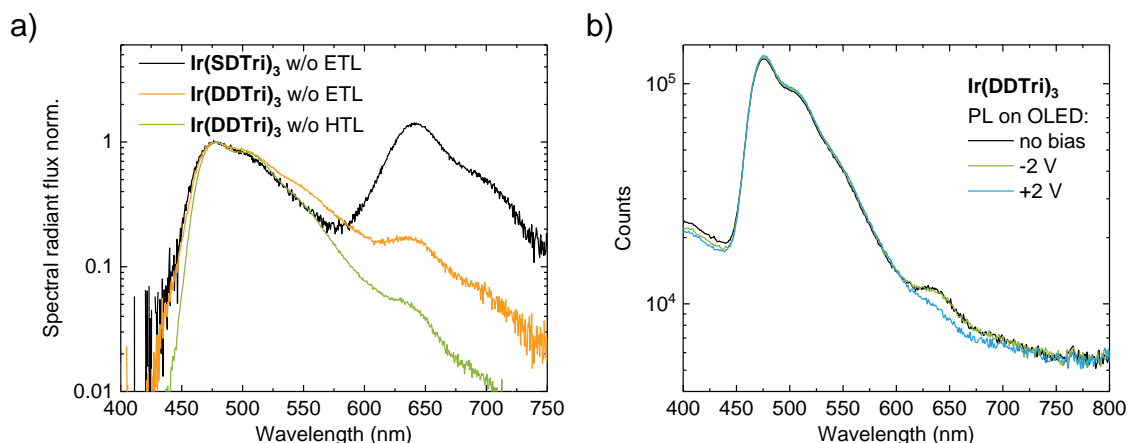


Figure S1: (a) Electroluminescence spectra of the **Ir(SDTri)₃** or **Ir(DDTri)₃** OLEDs without the ETL (ITO/PEDOT:PSS/EML/Liq/Al) and an **Ir(DDTri)₃** OLED without the HTL (ITO/EML/TmPyPB/Liq/Al). The electromer emission at 640 nm is visible in all cases, rendering interface effects between the emission layer and the transport layers as the origin of the emission unlikely. (b) Photoluminescence spectra (exc. 340 nm) of an OLED (ITO/PEDOT:PSS/**Ir(DDTri)₃**/TmPyPB/Liq/Al) after UV-irradiation and electrical operation (10 min, 0.5 mA/cm²). The emission at 640 nm can be suppressed by applying a forward bias.

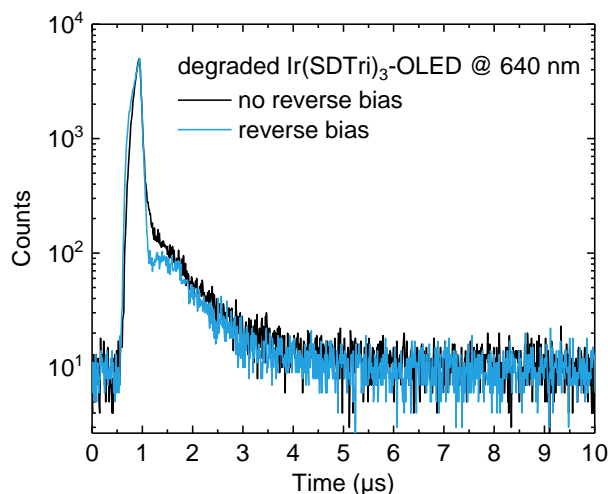


Figure S2: Transient EL of a degraded **Ir(SDTri)₃**-OLED. Forward pulse: A = +6 V, t = 0.5 μs. Reverse pulse directly after the forward pulse: A = -6 V, t = 0.5 μs. The transient EL magnitude is reduced by the reverse pulse, indicating trapped charge carriers as origin of the longer component.

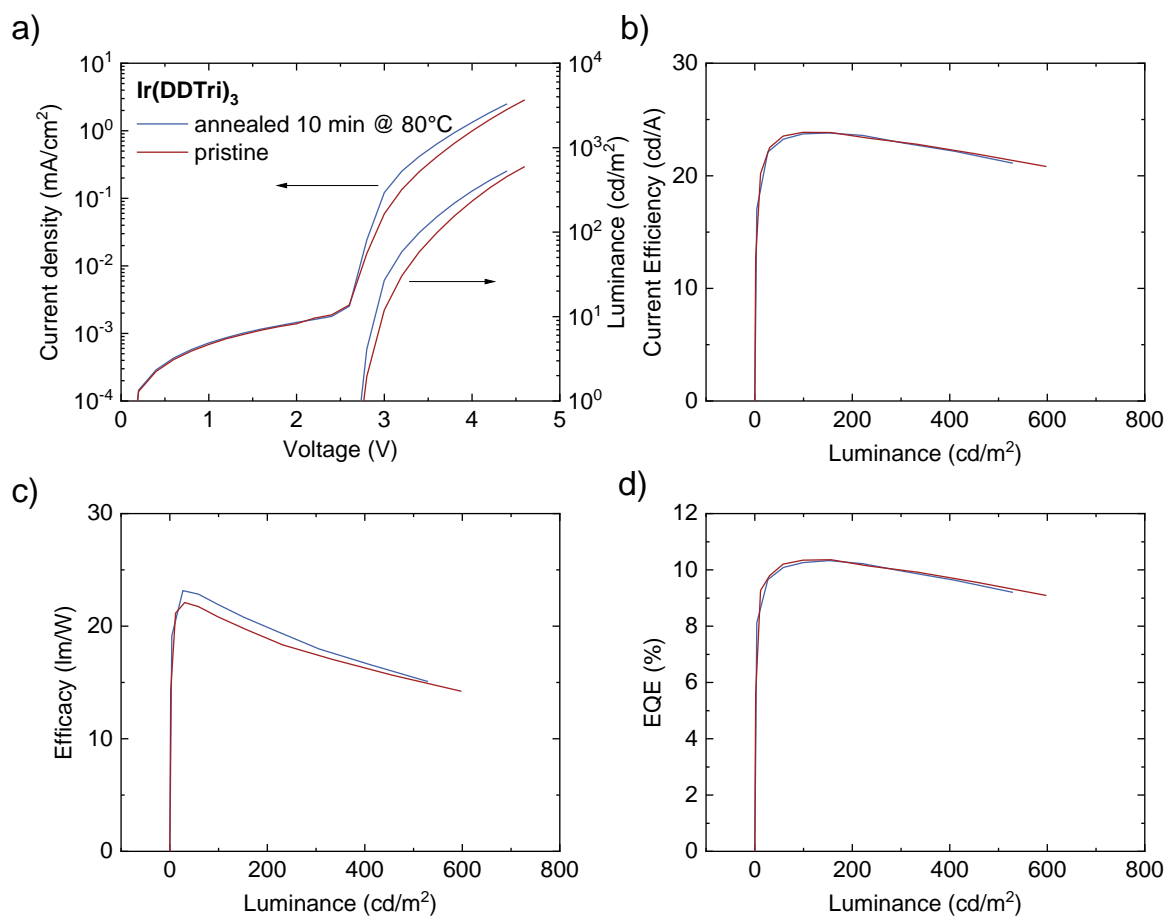


Figure S3: J - V - L characteristics and efficiencies of two OLEDs on the same substrate. The first OLED was measured directly after fabrication (red) and the second OLED after thermal annealing (blue). The EQE is not affected by the thermal annealing. The current through the thermally annealed device is enhanced, which might be caused by an increase of the mobility of TmPyPB due to enhanced stacking.

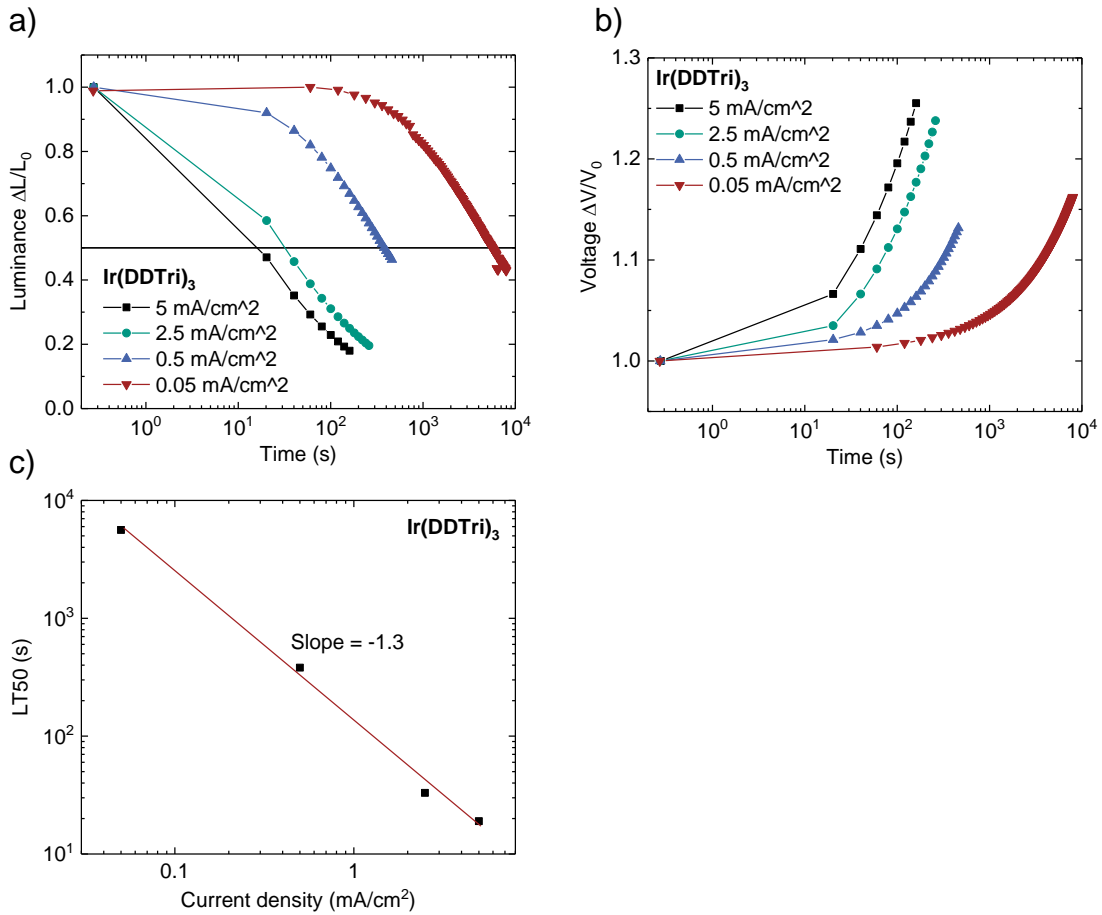


Figure S4: (a) Normalized luminance decay of Ir(DDTri)₃-OLEDs at different operation current densities. (b) Normalized voltage increase during constant current operation. (c) Double logarithmic plot of the decay time to reach 50% of the initial luminance (LT50) vs. current density. The power law follows a slope of -1.3, indicating that degradation is mostly caused by monomolecular processes.

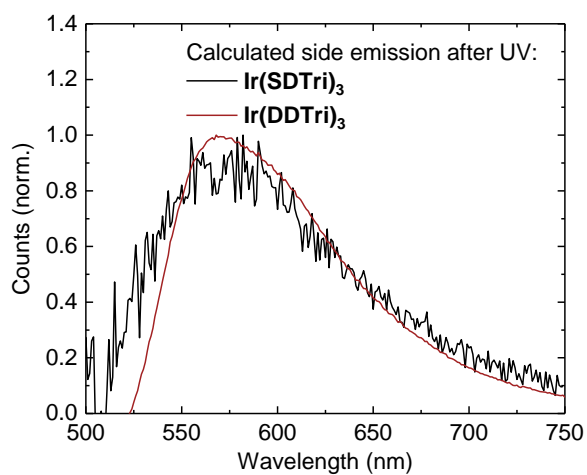


Figure S5: Calculated emission spectra of the secondary emission of dendrimer films on quartz that is caused by UV-degradation.

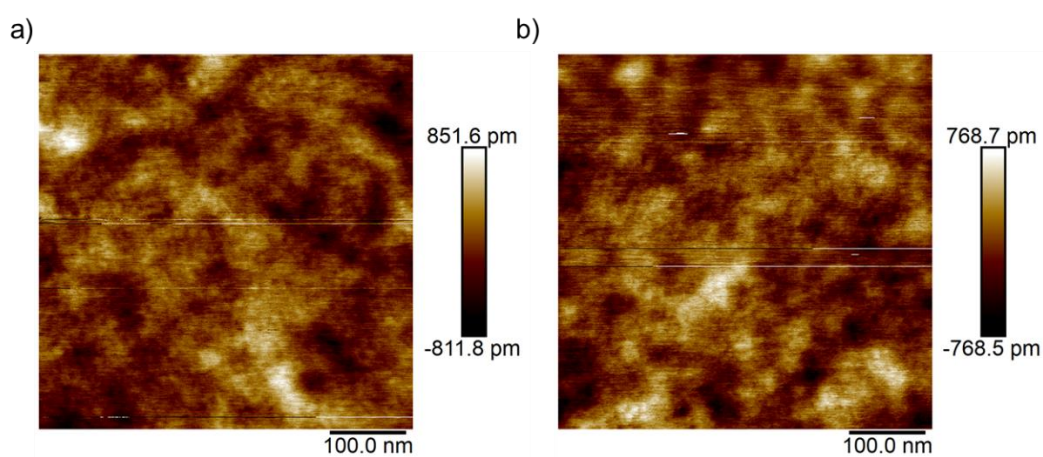


Figure S6: AFM-topography of $\text{Ir}(\text{DDTri})_3$ -films on quartz. Effectively, no difference is visible between (a) the pristine film and (b) the UV-treated film (400 nm, 100 mW/cm², 15 min). The peak-to-valley roughness is in the one-nanometer regime and no molecular aggregates were observed.

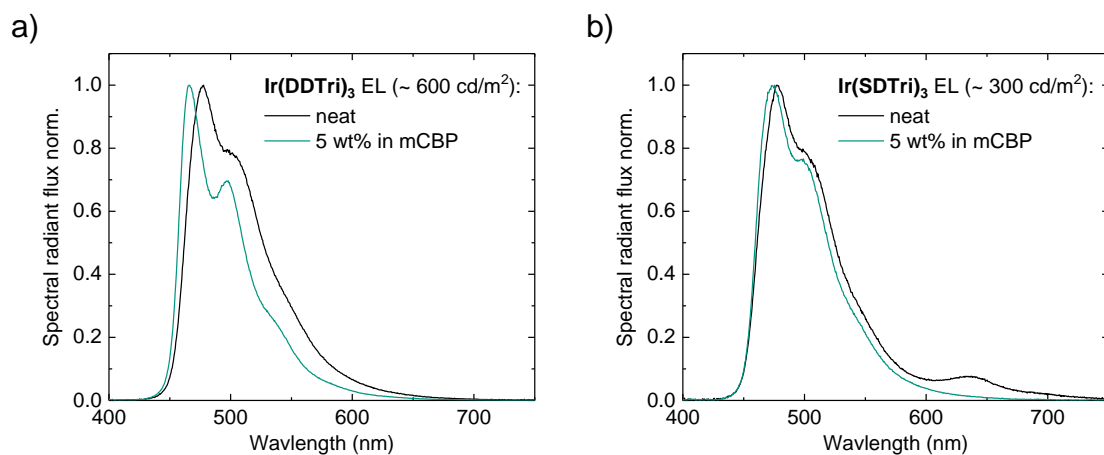


Figure S7: (a) Electroluminescence spectra of OLEDs comprising EMLs of either neat **Ir(DDTri)₃** or mCBP:**Ir(DDTri)₃** (5 wt%). The dispersion of **Ir(DDTri)₃** in mCBP suppresses emitter aggregation but causes a blue shift of the electroluminescence spectrum. (b) Dispersing **Ir(SDTri)₃** in mCBP has the same effect and suppresses the electromer during the initial *J-V-L* measurements at 640 nm.

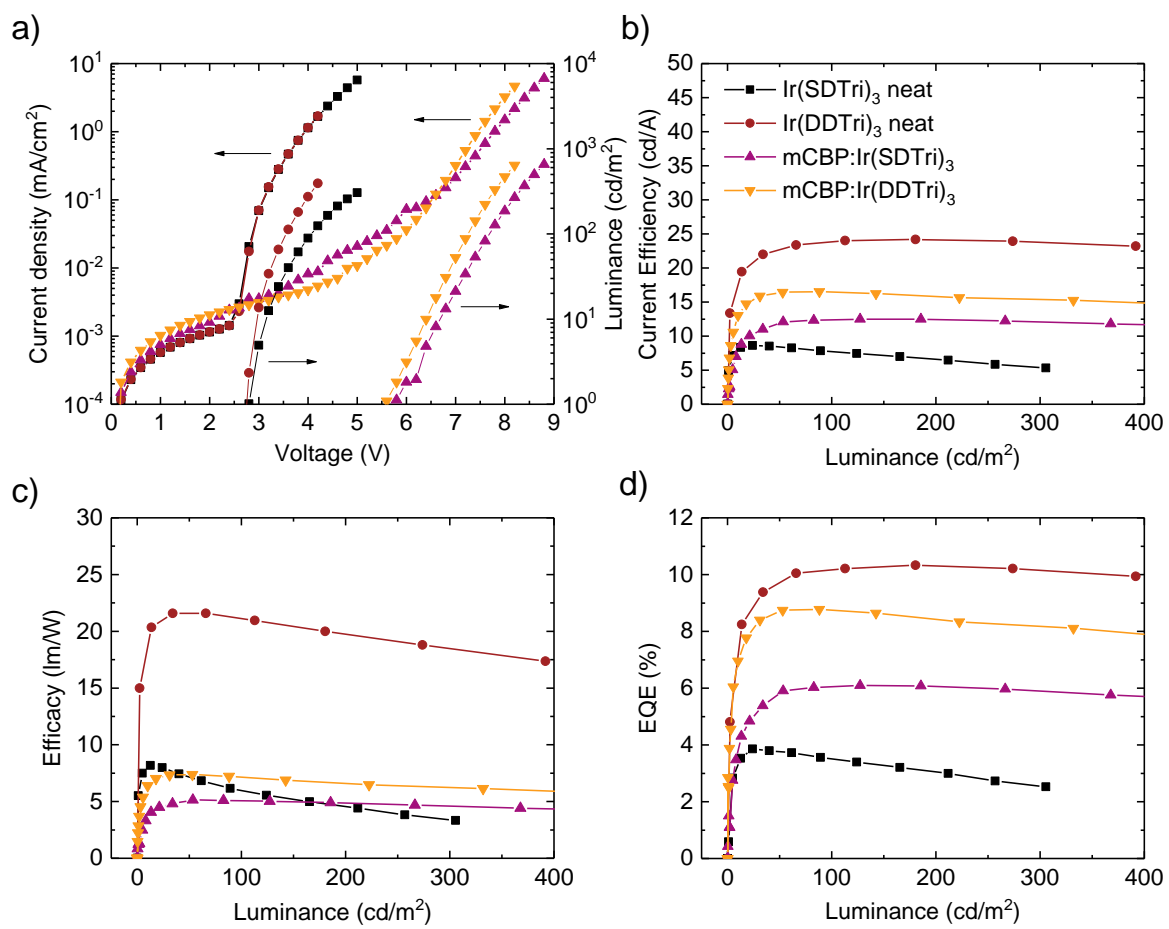


Figure S8: Comparison of host-free dendrimer OLEDs and OLEDs featuring the dendrimers immersed in an mCBP host (emitter concentration: 5 wt%).

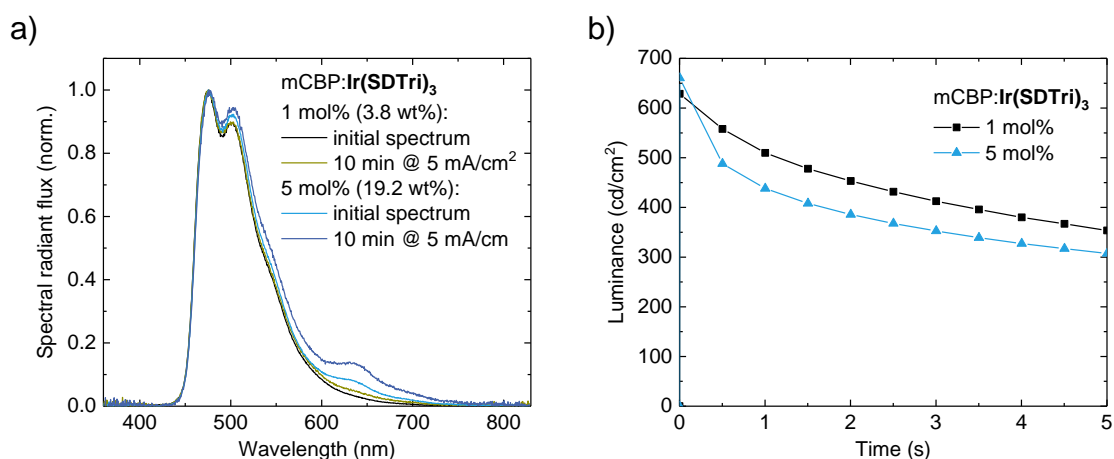


Figure S9: Lifetime measurements of mCBP:Ir(SDTri)₃-OLEDs with an ITO/PEDOT:PSS/EML/mCBP:Ir(SDTri)₃/BP4mPy/Liq/Al architecture. (a) Emission spectra of pristine and aged mCBP:Ir(SDTri)₃-OLEDs at 5 mA/cm². Reducing the concentration of Ir(SDTri)₃ in mCBP suppresses the electromer emission at 640 nm due to a reduced chance of emitter aggregation, supporting the conclusion of aggregation induced electromer formation. (b) This results in a higher OLED stability at a constant current density of 5 mA/cm². Compared to the host-free OLEDs the lifetime is greatly improved even at a 10-fold current density. The host-free Ir(SDTri)₃-OLED showed a shorter lifetime of LT50 = 2.5 min at an initial luminance of 40 cd/cm².

2. MALDI-TOF of pristine materials

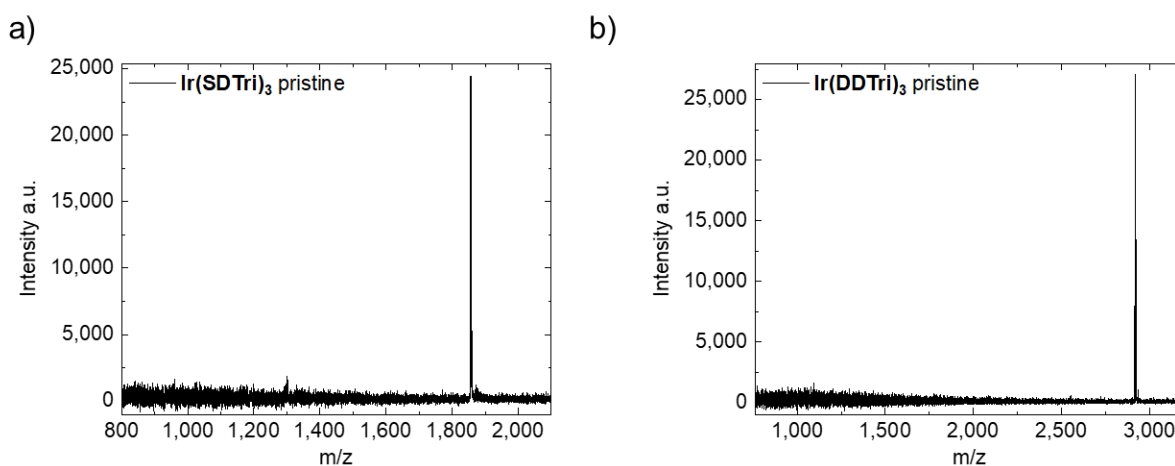


Figure S10: MALDI-ToF of pristine (a) Ir(SDTri)₃ and (b) Ir(DDTri)₃. The only visible peaks correspond to the molecular weight of the molecules, which lets us exclude molecular fragmentation during laser desorption when considering components of the film measured after the degradation experiments.

3. Spectral mismatch correction integrating sphere

$$\begin{aligned}
 \Phi_{DUT} &= \Phi_{Raw} SMCF_{DUT} \frac{\Phi_{Aux,N}}{\Phi_{Aux,DUT}} = \Phi_{Raw} \frac{\int X_{Aux,N} V(\lambda) \int X_{Aux,DUT} V(\lambda) \int X_{DUT,DUT} V(\lambda)}{\int X_{N,N} V(\lambda) \int X_{Aux,N} V(\lambda) \int X_{Aux,DUT} V(\lambda)} \frac{\Phi_{Aux,N}}{\Phi_{Aux,DUT}} \\
 &= \Phi_{Raw} \frac{\int X_{DUT,DUT} V(\lambda)}{\int X_{N,N} V(\lambda)} \frac{\int X_{Aux,DUT} V(\lambda)}{\int X_{Aux,N} V(\lambda)} \frac{\Phi_{Aux,N,Raw} SMCF_{Aux,N}}{\Phi_{Aux,DUT,Raw} SMCF_{Aux,DUT}} = \Phi_{Raw} SMCF_{DUT} \frac{\Phi_{Aux,N,Raw}}{\Phi_{Aux,DUT,Raw}} \left(\frac{\int X_{Aux,DUT} V(\lambda)}{\int X_{Aux,DUT} S_{DUT}} \right)^{-1} \frac{\int X_{Aux,N} V(\lambda)}{\int X_N V(\lambda)} \frac{\int X_{N,N} S_N}{\int X_N S_N} \\
 &= \Phi_{Raw} \frac{\int X_{DUT,DUT} V(\lambda)}{\int X_{N,N} V(\lambda)} \frac{\int X_{Aux,DUT} V(\lambda)}{\int X_{Aux,N} V(\lambda)} \frac{\Phi_{Aux,N,Raw}}{\Phi_{Aux,DUT,Raw}} \frac{\int X_{Aux,N} V(\lambda)}{\int X_{Aux,DUT} V(\lambda)} \frac{\int X_{N,N} S_N}{\int X_{Aux,DUT} \frac{X_{Aux,DUT}}{X_{Aux,N}} S_N}
 \end{aligned}$$

Φ_{Raw} : The luminous flux measured by the photometer after calibration.

$X_{A,B}$: Spectrum of lamp A with lamp B in the sphere.

S_N : Sensitivity of the Photometer with calibration standard in the sphere (can be calculated from the factory calibration (sphere open) with the aiding lamp).

S_{DUT} : Sensitivity of the Photometer with device under test (DUT) in the sphere.

4. Experimental for the synthesis of Ir(DDTri)₃

General methods

Dichloromethane, light petroleum spirits and ethyl acetate were distilled before use. Anhydrous tetrahydrofuran was either stirred over sodium before distillation or dried using a LC Technology SPBT-1 solvent purification system. Toluene was dried using a LC Technology SPBT-1 solvent purification system. Silica gel (230-400 mesh) used for column chromatography was purchased from Merck. Thin layer chromatography (TLC) was performed using aluminum backed silica gel 60 F254 plates from Merck. Size exclusion chromatography was performed with BioRad Laboratories Bio-Beads S-X1 Support, using toluene as eluent. Unless noted otherwise, all other reagents were used as received. NMR spectra were recorded using a Bruker Avance 300 MHz, Avance 500 MHz or Ascend 500 MHz spectrometer with chemical shifts (δ) reported in parts per million (ppm) and referenced to the residual solvent peak. Deuterated chloroform was referenced to 7.26 ppm and 77.16 ppm for proton and carbon NMRs, respectively. Deuterated dichloromethane was referenced to 5.32 ppm and 53.84 ppm for proton and carbon NMRs, respectively. Peak's multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplets (m), or doubled of doublets (dd). Coupling constants (J) are given in hertz (Hz) and are quoted to the nearest 0.5 Hz. PrH = *n*-propyl H, *t*-ButylH = *t*-butyl H, SPH = surface phenyl H, G1-BPH = first generation branching phenyl H, LPH = ligand phenyl H. FTIR spectra was performed on solid samples using a Perkin-Elmer Spectrum 100 FT-IR spectrometer with an ATR attachment. Melting points (Mp) were measured in a glass capillary on a Büchi B-545 melting point apparatus and are uncorrected. Elemental microanalyses were carried out on a Thermo Scientific FlashSmart CHNS/O Elemental Analyzer. Mass spectra (ESI, both LRMS and HRMS) were performed using Bruker micrOTOF-Q (quadrupole – Time of Flight) instrument with a Bruker ESI source (ESI-micrOTOF-Q). Accurate mass measurements were carried out with direct infusion of 10 nM to 10 μ M solutions of the sample in dichloromethane and with external calibration using an Agilent Tune Mix as the reference. UV-vis absorption measurements were recorded with a Cary Varian 5000 UV-vis-NIR spectrophotometer as a solution in dichloromethane distilled from calcium hydride. Photoluminescence spectra were recorded using an Edinburgh spectrofluorometer FS5. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris Diamond DSC. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer STA 6000 Simultaneous Thermal Analyser. The decomposition temperature (Td) is reported for a 5% decrease in sample mass corrected for the crucible. Electrochemistry was performed using a BAS Epsilon electrochemistry station, a standard three-electrode system, at room temperature using a solution comprising approximately 1 mM of the sample and 0.1 M tetra-*n*-butylammonium perchlorate (TBAP, Alfa Aesar, electrochemical grade) as the electrolyte in distilled dichloromethane (from calcium hydride) or distilled tetrahydrofuran (from lithium aluminium hydride) using a glassy

carbon working electrode, a platinum wire counter electrode, and a silver/silver nitrate solution in acetonitrile as the reference electrode at various scan rates between 50 and 200 mV s⁻¹ to obtain the optimal voltammograms. The glassy carbon electrode was polished between measurements with a polishing pad and rinsed with the appropriate solvent. The solutions were sparged with argon and measured under an argon atmosphere. Values were corrected against ferrocene as an external standard and expressed against the ferrocene/ferrocenium (Fc/Fc⁺) couple. Gel permeation chromatography (GPC) was carried out using an Agilent 1260 Infinity II system equipped with a variable wavelength detector set to 254 nm, two PLgel Mixed-E columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories, calibrated with polystyrene narrow standards (\bar{M}_p = 162 to 47,190 gmol⁻¹) and run in series in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran pumped at a rate of 0.5 mL min⁻¹ with the columns maintained at 40 °C. The PL spectra of the doubly dendronized dendrimer was measured in dilute solution (optical density of 0.1). The solution PLQYs were measured relative to quinine sulfate, which has a known absolute solution PLQY of 55%[ref]. Each complex was measured in carefully degassed toluene to avoid oxygen quenching of the excited state. Solutions were prepared by gradually increasing compound concentration until UV-vis showed an absorbance of 0.1 at the chosen excitation wavelength.

*Methyl 4,4''-di-tert-butyl-2'-methyl-[1,1':3',1''-terphenyl]-5'-carboxylate **3***

A mixture of methyl 3,5-dibromo-4-methylbenzoate (3.0 g, 9.7 mmol), 4-*t*-butylphenylboronic acid (3.8 g, 21 mmol) and sodium carbonate (6.3 g, 58 mmol) in toluene (40 mL), ethanol (20 mL) and water (10 mL) was deoxygenated with two cycles of freeze-pump-thaw, backfilling with argon. Tetrakis(triphenylphosphine)palladium(0) (2.3 g, 2.0 mmol) was added and reaction mixture was deoxygenated with one freeze-pump-thaw cycle, backfilling with argon. The reaction mixture was heated in an oil bath held at 95 °C for 16 h under argon. After being allowed to cool to room temperature, ethyl acetate (30 mL) was added, and the reaction mixture was filtered through a celite pad, which was then washed with ethyl acetate (10 mL). The filtrate was collected and washed with water (2 × 20 mL) and then brine (2 × 20 mL). The organic phase was dried over anhydrous sodium sulfate, filtered and the solvent removed. The residue was purified by column chromatography over silica using *n*-hexane/ethyl acetate mixtures (0-4%) as eluent to give **3** as a white solid (3.6 g, 90%). Mp. 168.9-169.4 °C; IR: $\bar{\nu}$ solid/cm⁻¹ 1720 (C=O); UV-Vis: $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 239 (log $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 4.57), 300sh (3.44). ¹H NMR (300 MHz, CDCl₃): 1.38 (18 H, s, *t*-butylH), 2.20 (3 H, s, PhCH₃), 3.88 (3 H, s, OCH₃), 7.30 and 7.46 (8 H, AA'BB', SPH), 7.90 (2 H, s, G1-BPH). ¹³C NMR (75 MHz, CD₂Cl₂) δ 19.1, 31.2, 34.6, 51.9, 125.2, 127.4, 129.0, 129.7, 138.7, 138.8, 143.2, 150.3, 167.0. HRMS (ESI-Orbitrap) for C₂₉H₃₄O₂ *m/z*: [M+H]⁺ calcd: 415.2632 (100%), 416.2665 (31%). Found: 415.2636 (100%), 416.2670 (31%).

[4,4''-Di-tert-butyl-2'-methyl-[1,1':3',1''-terphenyl]-5'-yl]methanol 4

3 (3.6 g, 8.7 mmol) was dissolved in tetrahydrofuran (40 mL) and the solution was slowly added to an ice bath cooled flask containing lithium aluminium hydride (0.50 g, 13 mmol) under argon. The reaction was then stirred for 3 h under argon at room temperature. The reaction mixture was then cooled in an ice bath before water (20 mL) was slowly and very carefully added to quench the excess lithium aluminium hydride. Hydrochloric acid (3 M, 20 mL) was added and then the mixture was extracted with ethyl acetate (60 mL). The organic phase was collected and washed with water (2 × 20 mL) and then brine (2 × 20 mL), dried over anhydrous sodium sulfate, filtered and the solvent removed. The residue was purified using column chromatography over silica with hexanes/ethyl acetate mixtures (0-20%) as eluent to give **4** (3.14 g, 93%) as a white crystalline solid. Mp. 95.8-96.4 °C. Anal. Calcd for C₂₈H₃₄O; C, 87.0; H, 8.9; Found: C, 86.7; H, 8.85. IR: $\bar{\nu}$ solid/cm⁻¹ = 3324 (OH); UV-Vis: λ_{\max} (CH₂Cl₂)/nm 243 (log ϵ /dm³mol⁻¹cm⁻¹ 4.57), 294sh (3.54). ¹H NMR (300 MHz, CD₂Cl₂): 1.36 (18 H, s, *t*-ButylH), 1.79 (1 H, t, J = 6.0 Hz, OH), 2.11 (3 H, s, PhCH₃), 4.66 (2 H, d, J = 6.0 Hz, CH₂), 7.19 (2 H, s, G1-BPH), 7.29 and 7.45 (8 H, AA'BB', SPH). ¹³C NMR (75 MHz, CD₂Cl₂) δ 18.5, 31.2, 34.5, 65.0, 125.1, 127.6, 129.0, 132.4, 138.3, 139.5, 143.1, 149.9. HRMS (ESI-Orbitrap) for C₂₈H₃₄O *m/z*: [M-OH]⁺ calcd: 369.2577 (100%), 370.2610 (30%). Found: 369.2582 (100%), 370.2610 (30%).

5'-[Bromomethyl]-4,4''-di-tert-butyl-2'-methyl-1,1':3',1''-terphenyl 5

Phosphorous tribromide (20 mL) was slowly added to **4** (4.8 g, 12 mmol) that had been cooled in an ice bath under argon. The reaction mixture was then heated in an oil bath held at 90 °C for 18 h under argon. The reaction mixture was cooled in an ice bath and water (20 mL) was slowly and very carefully added to quench the excess phosphorous tribromide. The mixture was extracted with dichloromethane (60 mL), and then the organic phase was washed with water (2 x 20 mL), brine (2 x 20 mL) and saturated aqueous sodium hydrogen carbonate (2 x 20 mL), dried over anhydrous sodium sulfate, filtered and the solvent removed to give **5** (5.0 g, 90%) as a white solid. Mp. 171.2-171.8 °C; UV-Vis: λ_{\max} (CH₂Cl₂)/nm 242 (log ϵ /dm³mol⁻¹cm⁻¹ 4.58). ¹H NMR (300 MHz, CDCl₃): 1.38 (18 H, s, *t*-ButylH), 2.15 (3 H, s, PhCH₃), 4.52 (2 H, s, CH₂), 7.27 (2 H, s, G1-BPH), 7.30 and 7.45 (8 H, AA'BB', SPH). ¹³C NMR (75 MHz, CD₂Cl₂) δ 18.6, 31.2, 33.8, 34.5, 125.2, 129.0, 129.5, 133.8, 135.0, 139.0, 143.4, 150.1. HRMS (ESI-Orbitrap) for C₂₈H₃₃Br *m/z*: [M-Br]⁺ calcd: 369.2577 (100%), 370.2610 (30%). Found: 369.2582 (100%), 370.2614 (30%).

5-[3-Bromophenyl]-1-[(4,4''-di-tert-butyl-2'-methyl-[1,1':3',1''-terphenyl]-5'-yl)methyl]-3-propyl-1H-1,2,4-triazole 10

Powdered potassium hydroxide (824 mg, 14.7 mmol) and tetra-*n*-butylammonium hydrogen sulfate (226 mg, 0.66 mmol) were added to a stirred solution of *tert*-butyl 2-[propan-2-ylidene]hydrazine-1-

carboxylate **6** (doi: 10.1055/s-2004-831336) (1.00 g, 6.00 mmol) in toluene (60 mL). The reaction mixture was heated in an oil bath held at 50 °C under argon for 10 min, then a solution of **5** (3.00 g, 6.66 mmol) in toluene (10 mL) was slowly added. The temperature was increased to 80 °C and the reaction mixture was stirred for 3 h under argon. The reaction mixture was allowed to cool to room temperature and the solvent removed. The residue was dissolved in dichloromethane (100 mL), washed with water (2 x 60 mL) and brine (2 x 60 mL), dried over anhydrous sodium sulphate, filtered, and the solvent removed to give crude **7** (≈3.60 g) as a colourless viscous liquid. The crude material was taken to the next step without further purification. The crude **7** (≈3.60 g) was dissolved in tetrahydrofuran (20 mL) and hydrochloric acid (3 M, 20 mL) was added. The reaction mixture was heated in an oil bath held at 95 °C for 18 h under argon. The mixture was then allowed to cool to room temperature and the solvent removed in vacuo to give crude **8** (≈2.60 g) as an off-white solid. The crude material was again taken to the next step without further purification. The crude **8** (≈2.60 g) was dissolved in dichloromethane (50 mL) and then **9** (doi.org/10.1021/cm061173b) (3.1 g, 10.30 mmol) was added. Triethylamine (3.6 mL, 26.0 mmol) was then added to the stirred reaction mixture over 10 min before being stirred at room temperature for 18 h under argon. The solvent was removed, and the residue was dissolved in ethyl acetate (50 mL), which was then washed with water (2 x 20 mL) and brine (2 x 20 mL), dried over anhydrous sodium sulphate, and filtered, and then the solvent was removed. The residue was first purified using column chromatography over silica, with *n*-hexane:dichloromethane mixtures (6:4 to 0:10) and then *n*-hexane:ethyl acetate mixtures (96:4 to 91:9) as eluent to give partially purified **10** as a colourless gum. The partially purified material was dissolved in *n*-hexane and placed in a freezer overnight. The solution was then decanted, and the solvent removed to give **10** (1.85 g, 44%, over three-steps) as an off-white solid. Mp. 89.1-89.8 °C. Anal. Calcd for C₃₉H₄₄BrN₃: C, 73.8; H, 7.0; N, 6.6. Found: C, 73.8; H, 7.0; N, 6.4. UV-Vis: λ_{max}(CH₂Cl₂)/nm 243 (log ε/dm³mol⁻¹cm⁻¹ 4.63). ¹H NMR (300 MHz, CD₂Cl₂): 0.95 (3 H, t, J = 7.5 Hz, PrH), 1.34 (18 H, s, *t*-ButylH), 1.69-1.82 (2 H, m, PrH), 2.09 (3 H, s, PhCH₃), 2.67 (2 H, t, J = 7.5 Hz, PrH), 5.35 (2 H, s, CH₂), 6.97 (2 H, s, G1-BPH), 7.23 and 7.42 (8 H, AA'BB', SPH), 7.32 (1H, dd, J= 8.0, 8.0 Hz, LPH), 7.52-7.55 (1 H, m, LPH), 7.57-7.61 (1 H, m, LPH), 7.77-7.78 (1 H, m, LPH). ¹³C NMR (125 MHz, CD₂Cl₂) δ 13.7, 18.5, 21.8, 30.3, 31.2, 34.5, 52.4, 122.8, 125.1, 127.2, 127.4, 129.0, 130.4, 130.6, 131.8, 132.9, 133.0, 133.2, 139.0, 143.5, 150.1, 153.8, 164.1. HRMS (ESI-Orbitrap) for C₃₉H₄₄BrN₃ *m/z*: [M+2H]⁺ calcd: 634.2791 (100%), 635.2825 (42%), 636.2771 (97%), 637.2804 (41%). Found: 634.2745 (100%), 635.2775 (41%), 636.2722 (99%), 637.2752 (41%).

5-[4''-(tert-butyl)-5'-(4-{tert-butyl}phenyl)-4'-methyl-[1,1':3',1''-terphenyl]-3-yl]-1-[(4,4''-di-tert-butyl-2'-methyl-[1,1':3',1''-terphenyl]-5'-yl)methyl]-3-propyl-1H-1,2,4-triazole **DDTri**

A mixture of **10** (1.0 g, 1.6 mmol), 2-[4,4''-di-*tert*-butyl-2'-methyl-[1,1':3',1''-terphenyl]-5'-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **11** (doi.org/10.1039/C8TC03491E) (989 mg, 2.05 mmol) and sodium carbonate (511 mg, 4.74 mmol) in toluene (20 mL), ethanol (10 mL) and water (7 mL) was deoxygenated with two cycles of freeze-pump-thaw, backfilling with argon. Tetrakis(triphenylphosphine)palladium(0) (182 mg, 0.16 mmol) was added and reaction mixture was deoxygenated with freeze-pump-thaw cycle, backfilling with argon. The mixture was then heated in an oil bath held at 95 °C for 18 h under argon before being allowed to cool to room temperature. The reaction mixture was diluted with ethyl acetate (60 mL), and the organic layer was washed with water (2 x 30 mL) and brine (2 x 30 mL) before being dried over anhydrous sodium sulfate, filtered and the solvent removed. The residue was purified using column chromatography over silica with *n*-hexane:dichloromethane mixtures (75:25 to 0:100) and then *n*-hexane:ethyl acetate mixtures (95:5 to 90:10) as eluent to give **DDTri** (890 mg, 62%) as an off-white solid. Mp. 165.9-166.3 °C. UV-Vis: $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 248 ($\log \epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 4.98). ^1H NMR (300 MHz, CDCl_3): 0.98 (3 H, t, $J = 7.5$ Hz, PrH), 1.34 (18 H, s, *t*-ButylH), 1.37 (18 H, s, *t*-ButylH), 1.77-1.89 (2 H, m, PrH), 2.06 (3 H, s, CH_3), 2.19 (3 H, s, CH_3), 2.75 (2 H, t, $J = 7.5$ Hz, PrH), 5.39 (2 H, s, CH_2), 6.96 (2 H, s, G1-BPH), 7.12 (4 H, 1/2AA'BB', SPH), 7.31 (4 H, 1/2AA'BB', SPH), 7.35 (4 H, 1/2AA'BB', SPH), 7.40-7.50 (7 H, m, BPH, SPH and LPH), 7.51-7.55 (1 H, m, LPH), 7.69-7.74 (1 H, m, LPH), 7.81-7.83 (1 H, m, LPH). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 14.2, 19.0, 19.1, 22.3, 30.9, 31.69, 31.71, 34.97, 35.01, 52.9, 125.5, 125.7, 127.7, 127.8, 128.0, 129.0, 129.5, 129.7, 133.3, 133.5, 134.1, 137.7, 139.6, 139.8, 141.9, 143.8, 144.1, 150.4, 150.5, 155.8, 164.5. HRMS (ESI-Orbitrap) for $\text{C}_{66}\text{H}_{75}\text{N}_3$ m/z : $[\text{M}+\text{H}]^+$ calcd: 910.6034 (100%), 911.6067 (71%), 912.6101 (25%). Found: 910.5968 (100%), 911.6002 (73%), 912.6034 (26%).

Fac-tris[5-(3-Bromophenyl)-1-({4,4''-di-*tert*-butyl-2'-methyl-[1,1':3',1''-terphenyl]-5'-yl)methyl)-3-propyl-1*H*-1,2,4-triazolyl]iridium(III) **13**

A mixture of **10** (400 mg, 0.63 mmol) and iridium(III) chloride hydrate (111 mg, 0.31 mmol) in 2-ethoxyethanol (6 mL) and water (2 mL) was deoxygenated by placing under vacuum and refilling with argon three times. The mixture was heated in an oil bath held at 126 °C under argon for 18 h before being allowed to cool to room temperature. The mixture was filtered and the isolated solid washed with methanol (3 x 10 mL) before drying in vacuo to afford **12** as a black solid (333 mg), which was taken through to the next step without further purification. A mixture of **12** (333 mg), **10** (900 mg, 1.42 mmol) and silver(I) triflate (71 mg, 0.27 mmol) was deoxygenated by placing under vacuum and refilling with argon three times. The mixture was heated in an oil bath held at 166 °C under argon for 18 h before being allowed to cool to room temperature. The residue was dissolved with dichloromethane (30 mL), filtered through a celite pad, which was then washed with dichloromethane (20 mL). The filtrate was collected, and the solvent was removed. The crude material was first purified in two steps;

first using chromatography over bio-beads using toluene as eluent, and then silica column chromatography using hexanes:ethyl acetate mixtures (95:5) as eluent to give **13** as a greenish yellow solid (295 mg, 45 %, over two-steps). Mp. 242.4-243.5 °C. Anal. Calcd for C₁₁₇H₁₂₉IrBr₃N₉: C, 67.1; H, 6.2; N, 6.0. Found: C, 67.3; H, 6.2; N, 5.9. UV-Vis. λ_{max}(CH₂Cl₂)/nm 244 (log ε/dm³mol⁻¹cm⁻¹ 5.20), 267sh (4.87), 280sh (4.56), 302 (4.22), 357 (4.09), 392sh (3.84), 414sh (3.57), 428sh (3.46), 457sh (2.99). ¹H NMR (500 MHz, CD₂Cl₂): 0.47 (9 H, t, J = 7.5 Hz, PrH), 1.03-1.11 (3 H, m, PrH), 1.20-1.29 (3 H, m, PrH), 1.34 (54 H, s, *t*-ButylH), 1.72-1.79 (3 H, m, PrH), 1.97-2.02 (3 H, m, PrH), 2.09 (9 H, s, CH₃), 5.67 (6 H, s, CH₂), 6.32 (3 H, d, J = 8.0 Hz, LPH), 6.63 (3 H, dd, J = 8.0, 2.0 Hz, LPH), 7.04 (6 H, s, G1-BPH), 7.22 and 7.40 (24 H, AA'BB', SPH), 7.57 (3 H, d, J = 2.0 Hz, LPH). HRMS (ESI-Orbitrap) for C₁₁₇H₁₂₉IrBr₃N₉ *m/z*: [M+H]⁺ calcd: 2088.7554 (10%), 2089.7528 (42%), 2090.7553 (50%), 2091.7534 (92%), 2092.7551 (92%), 2093.7542 (100%), 2094.7552 (81%), 2095.7555 (57%), 2096.7562 (34%), 2097.7577 (16%). Found: 2088.7556 (10%), 2089.7546 (37%), 2090.7573 (49%), 2091.7551 (86%), 2092.7561 (94%), 2093.7546 (100%), 2094.7549 (85%), 2095.7551 (62%), 2096.7559 (39%), 2097.7568 (19%).

Fac-tris[5-(4''-{*tert*-butyl}-5'-{4-[*tert*-butyl]phenyl}-4'-methyl-{1,1':3',1''-terphenyl}-3-yl)-1-({4,4''-di-*tert*-butyl-2'-methyl-[1,1':3',1''-terphenyl]-5'-yl)methyl)-3-propyl-1*H*-1,2,4-triazolyl]iridium(III)
Ir(DDTri)₃

A mixture of **13** (160 mg, 0.08 mmol), **11** (166 mg, 0.34 mmol) and sodium carbonate (74 mg, 0.69 mmol) in toluene (8 mL), ethanol (4 mL) and water (2 mL) were deoxygenated with two cycles of freeze-pump-thaw, backfilling with argon. Tetrakis(triphenylphosphine)palladium(0) (13 mg, 0.01 mmol) was added and reaction mixture was deoxygenated with one freeze-pump-thaw cycle, backfilling with argon. The mixture was heated in an oil bath held at 95 °C for 36 h under argon before been allowed to cool to room temperature. The mixture was diluted with ethyl acetate (30 mL), filtered through a celite pad, which was then washed with ethyl acetate (10 mL). The filtrate was collected and washed with water (2 × 10 mL) and then brine (2 × 10 mL) then dried over anhydrous sodium sulfate, filtered and the solvent removed. The residue was purified using chromatography over Biobeads with toluene as eluent to give **Ir(DDTri)₃** (110 mg, 49%) as a yellow powder. T_d (5%) = 383 °C: UV-Vis: λ_{max}(CH₂Cl₂)/nm 244 (log ε/dm³mol⁻¹cm⁻¹ 5.39), 269sh (5.10), 280sh (4.86), 331 (4.58), 358sh (4.26), 393sh (3.98), 423sh (3.58), 456sh (3.08). ¹H NMR (500 MHz, CD₂Cl₂): 0.44 (9 H, t, J = 7.5 Hz, PrH), 1.03-1.12 (3 H, m, PrH), 1.18 (54 H, s, *t*-ButylH), 1.20-1.32 (3 H, m, PrH), 1.27 (54 H, s, *t*-ButylH), 1.76-1.84 (3 H, m, PrH), 1.93 (9 H, s, CH₃), 1.97-2.06 (3 H, m, PrH), 2.09 (9 H, s, CH₃), 5.75 (6 H, s, CH₂), 6.57 (3 H, d, J = 8.0 Hz, LPH), 6.63 (3 H, dd, J = 8.0, 2.0 Hz, LPH), 7.02 (12 H, 1/2AA'BB', SPH), 7.06 (6 H, s, G1-BPH), 7.14 (12 H, 1/2AA'BB', SPH), 7.18 (12 H, 1/2AA'BB', SPH), 7.23 (6 H, s, GP-BPH), 7.31 (4 H, 1/2AA'BB', SPH), 7.74 (1 H, d, J = 2.0 Hz, LPH). HRMS (ESI-Orbitrap) for C₁₉₈H₂₂₂IrN₉ *m/z*: [M]⁺ calcd: 2916.7249 (18%), 2917.7282 (40%), 2918.7297 (75%), 2919.7319 (100%), 2920.7346 (92%), 2921.7376 (62%), 2922.7407 (32%),

2923.7439 (13%). Found: 2916.7251 (18%), 2917.7296 (40%), 2918.7303 (77%), 2919.7333 (100%), 2920.7356 (94%), 2921.7383 (63%), 2922.7455 (31%), 2923.7452 (13%). GPC: $\bar{M}_w = 2182$ Da; $\bar{M}_n = 2177$ Da; $\bar{D} = 1$. $E_{1/2}(\text{ox})$ (vs Fc/Fc^+) = 0.3 eV.

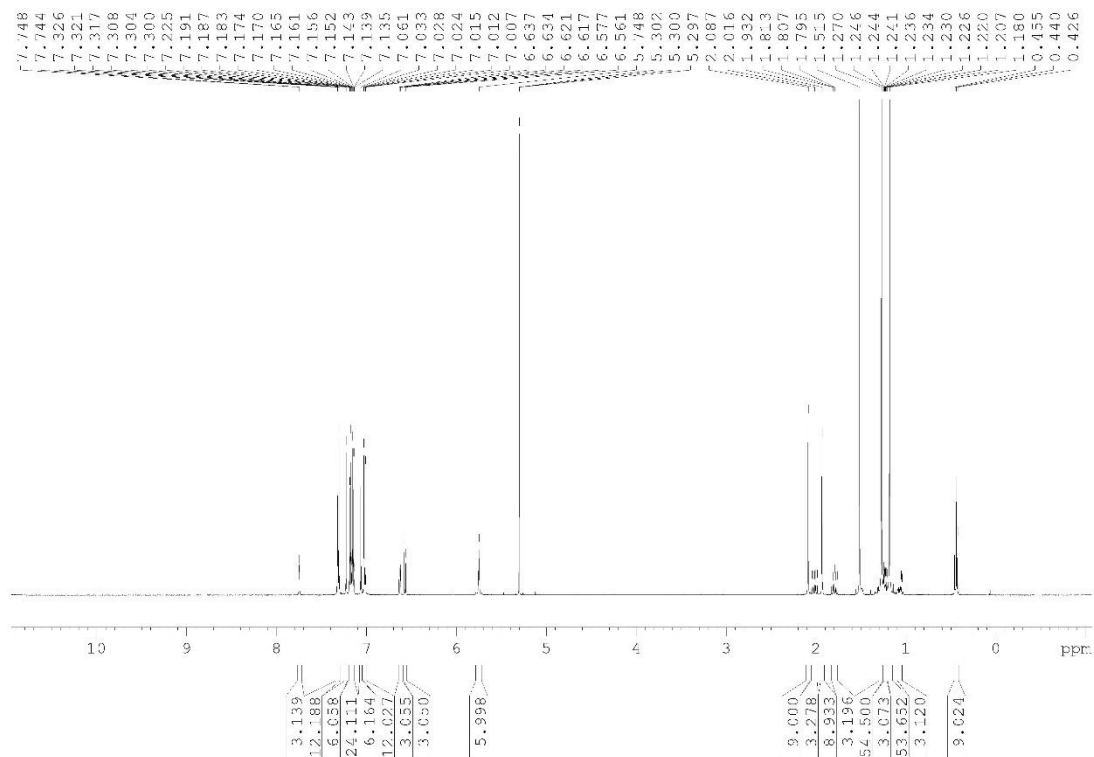


Figure S11: ^1H NMR spectrum of $\text{Ir}(\text{DDTri})_3$.

5. Gel Permeation Chromatography (GPC)

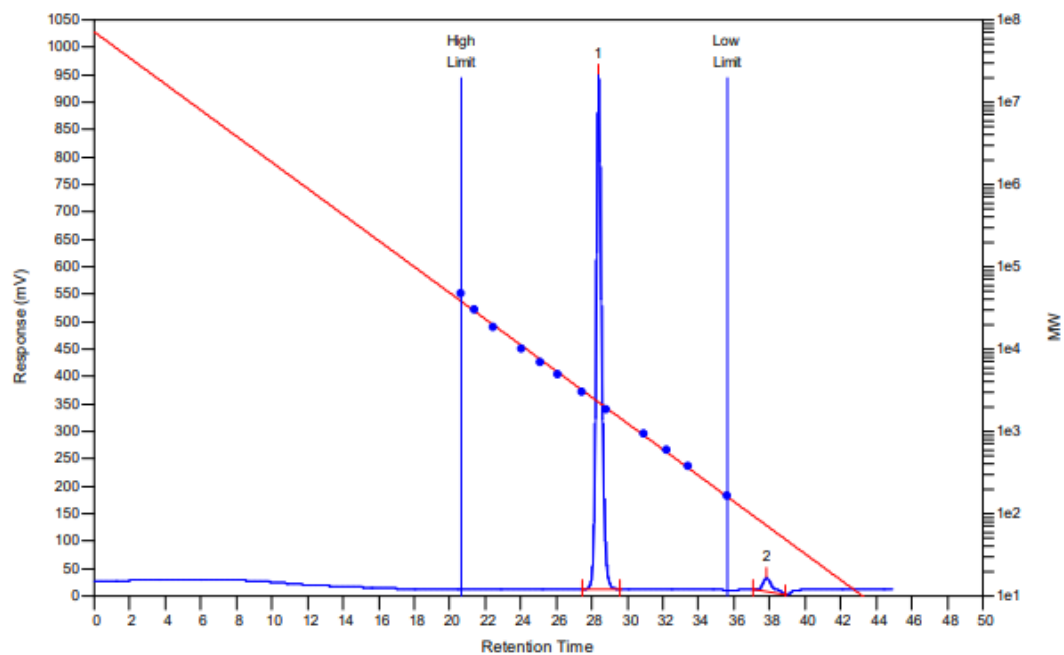


Figure S12: GPC trace of Ir(DDTri)₃.

6. Thermal gravimetric analysis (TGA)

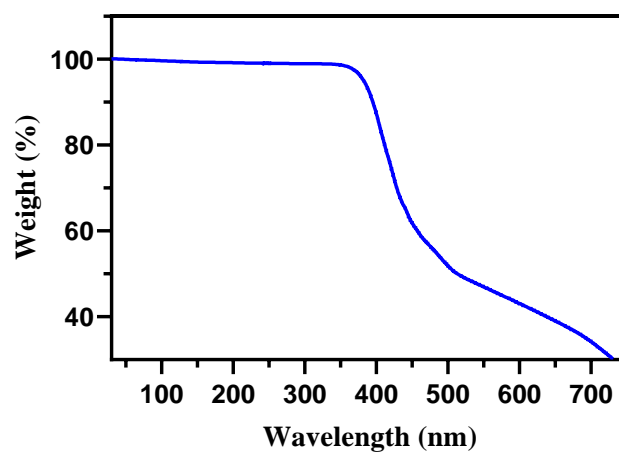


Figure S13: TGA trace for Ir(DDTri)₃. Observed at 30–800 °C at a rate of 10 °C/min under nitrogen

7. Differential scanning calorimetry (DSC)

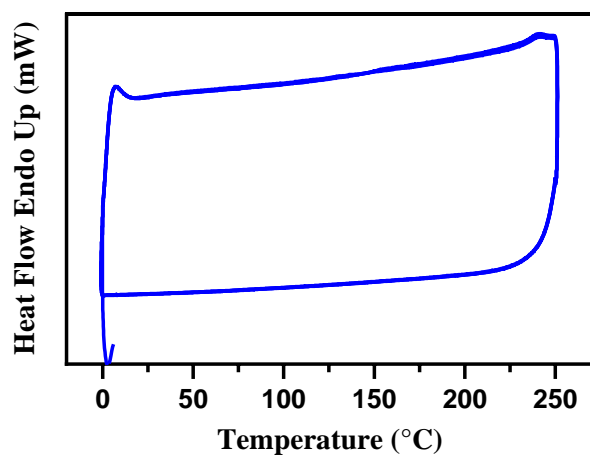


Figure S14: DSC trace for Ir(DDTri)₃. DSC thermograms at 200 °C/min to 300 °C/min heating rate (first scan) under nitrogen.

8. Cyclic voltammetry

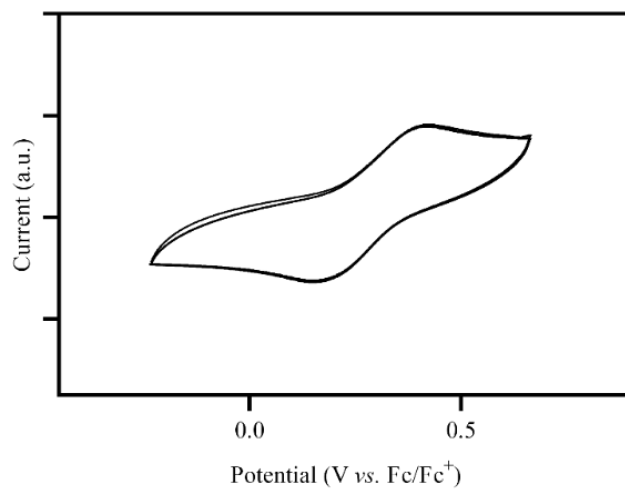


Figure S15: Oxidation cyclic voltammogram of Ir(DDTri)₃ referenced to the Fc/Fc⁺ couple.