Tailoring the Emission of Fluorinated-Bipyridine-Chelated Iridium Complexes

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\textbf{Synthetic procedures}

Compound 21 was prepared the same as the published procedure.\textsuperscript{[1]}

\textbf{Scheme S1}: Synthetic routes for the iridium complexes and polyphenylene dendrimers with iridium complex core. *
* Reagents and conditions: (a) (1) n-BuLi, Et₂O, -78 °C, 1 h, (2) TMSCl, rt, 12 h, 82%; (b) compound 9, Pd(PPh₃)₄, K₂CO₃, THF, water, 85°C, 24 h, 50%; (c) IrCl₃·nH₂O, 2-ethoxylethanol, 140 °C, 24 h, 48%; (d) compound 7, AgSO₃CF₃, K₂CO₃, mesitylene, 170 °C, 24 h, 53%; (e) UV light, THF, 12 h; (f) (1) isopropylamine, THF, n-BuLi, 0 °C, 30 min for making fresh LDA, (2) LDA, THF, -78 °C, 1 h, (3) triisopropylborate, rt, 12 h, 1M HCl (aq), 100%; (g) Pd(PPh₃)₄,
K₂CO₃, THF, water, 80 °C, 24 h, 39% for 16, 34% for 17; (h) Pd(PPh₃)₂Cl₂, PPh₃, CuI, triethylamine, (triisopropylsilyl)acetylene, 80 °C, 24 h, 85% for 14 and 96% for 15; (k) IrCl₃·nH₂O, 2-ethoxylethanol, 140 °C, 24 h, 57% for 12, 24% for 13; (i) compound 14 or 15, K₂CO₃, AgSO₃CF₃, 1,3,5-trimethylbenzene, 170 °C, 24 h, 25% for 2, 20% for 3; (l) TBAF, THF, r.t, 46%; (m) o-xylene, 150 °C, 48 h, 55%; (n) UV light, THF, 12 h, r.t, 83%.

2-Bromo-5-trimethylsilylpyridine (8)

![2-Bromo-5-trimethylsilylpyridine](image)

In a Schlenk flask was added 2,5-dibromopyridine (5.00 g, 21.11 mmol), degassed and added argon 3 times. Then 200 ml of diethyl ether was added. The mixture was stirred at -78 °C in dry ice bath, followed by addition of 1.6 M n-BuLi (20.05 mmol, 12.53 ml). The mixture was stirred for 1h. Then TMSCl (4.00 ml, 31.66 mmol) was added. The mixture was stirred at room temperature overnight followed by quenching with dilute HCl solution and extraction with DCM. Finally the condensed organic crude material was purified by distillation at 170 °C under vacuum to get 4.00 gram of colorless liquid (82%). ¹H NMR(250 MHz, CD₂Cl₂, 292 K) δ 8.40 (d, 1H), 7.65 (dd, 1H), 7.46 (dd, 1H), 0.24 (s, 9H). ¹³C NMR (75 MHz, CD₂Cl₂, 298 K) δ 154.67, 143.87, 143.49, 134.74, 127.91, -1.38.

(2,6-Difluoro-3-pyridinyl)boronic acid (9)

(1) Synthesis of LDA: In a Schlenk flask was added diisopropylamine (13.8 ml, 98.8 mmol) and 10 ml of dry THF. It was stirred in ice bath. Then 1.6 M n-butyllithium in hexane (58.7 ml, 93.9 mmol) was added slowly. The mixture was stirred at this temperature for 30 min and ready for use.

(2) In another Schlenk flask was added 2,6-difluoropyridine (9.4 ml, 103.8 mmol) and 30 ml of dry THF. The mixture was stirred at dry ice bath. Then LDA was added into the mixture slowly. The mixture was continually stirred for another 2 hours, followed by addition of triisopropylborate (34.2 ml, 148.2 mmol). The mixture was stirred at room temperature overnight. Then it was quenched by 1 M aqus. HCl and purified by extraction using ethyl acetate. Finally 15.70 g yellow-colored solid was received after drying under reduced pressure (100%). The spectral data were consistent with those published.[²]

2,6-Difluoro-5'-trimethylsilyl-3,2'-bipyridine (7)

S3
In a 100 ml round bottom flask were added compound 8 (2.00 g, 8.69 mmol), compound 9 (1.70 g, 10.69 mmol), K$_2$CO$_3$ (2.40 g, 17.38 mmol), 60 ml of THF and 5 ml of water sequentially. Then the mixture was degassed and added argon for 3 times, followed by the addition of Pd (PPh$_3$)$_4$ (502 mg, 434 mmol). The mixture was then stirred at 85 °C for 24 hours. Then it was extracted by DCM and purified by a silica gel flash column (1/49, Ethyl acetate/DCM). Eventually, 1.2 g of a light yellow solid was received after drying under reduced pressure (50%). $^1$H NMR (250 MHz, CD$_2$Cl$_2$, 292 K) δ 8.78 (dd, 1H), 8.70 (dt, 1H), 7.92 (dd, 1H), 7.81 (ddd, 1H), 6.99 (ddd, 1H). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$, 298 K) δ 154.44, 150.81, 146.46, 142.40, 135.28, 123.37, 107.46, 107.00, -1.30. FD-Mass: calculated for C$_{13}$H$_{14}$F$_2$N$_2$Si: 264.1, found:263.7 [M]$^+$. 

[2,6-Difluoro-5'-trimethylsilyl-3,2'-bipyridinyl)$_2$Ir(μ-Cl)$_2$] (6)

In a Schlenk flask was added compound 7 (0.25g, 0.946 mmol), IrCl$_3$.nH$_2$O (277 mg, 0.927 mmol) and 10 ml of 2-ethyoxylethanol. The mixture was stirred at 140 °C under argon for 24 hours. Then water was added to precipitate the product, followed by centrifuge to get the solid. Eventually, 0.67g of a yellow solid was received after drying under reduced pressure (47.8%). It was directly used for next step without further purification. FD-Mass: calculated for C$_{52}$H$_{52}$Cl$_2$F$_8$Ir$_2$N$_8$Si$_4$: 1506.2, found: 1506.7 [M]$^+$. 

Mer(2,6-difluoro-5'-trimethylsilyl-3,2'-bipyridinyl)$_3$Ir (5)

In a round bottom flask were added compound 6 (0.67 g, 0.44 mmol), compound 7 (0.235 g, 0.89 mmol), K$_2$CO$_3$ (0.31 g, 2.22 mmol) and 16 ml of mesitylene. The mixture was degassed and added argon 3 times, followed by addition of silver trifluoromethanesulfonate (0.24 g, 0.92 mmol). The mixture was heated at 170 °C for 20 hours. Then it was extracted by DCM and purified by a silica gel flash column (DCM). Eventually, 0.46 g of a yellow solid was received after drying under reduced pressure (53%). $^1$H NMR (250 MHz, CD$_2$Cl$_2$, 292 K) δ 8.33 (dt, 1H), 8.20 (ddt, 2H), 8.00 (m, 3H), 7.84 (ddd, 1H), 7.33 (dd, 1H), 6.45 (t, 1H), 5.95 (t, 1H), 5.74 (t, 1H), 0.13 (s, 9H), 0.11 (s, 9H), 0.04 (s, 9H). $^{19}$F NMR (471
MHz, CD$_2$Cl$_2$, 298 K) δ -68.56, -69.19, -69.63, -72.54, -72.73, -73.15. FD-Mass: calculated for C$_{39}$H$_{39}$F$_6$IrN$_6$Si$_3$: 982.2, found: 980.6.

Fac(2,6-difluoro-5'-trimethylsilyl-3,2'-bipyridinyl)$_3$Ir (4)

In a quartz tube were mixed compound 5 (0.282 g, 0.287 mmol) and 15 ml of THF. The tube was degassed and added argon 3 times. Then the sealed tube was put in a photochemical reactor and shined for 12 hours while the solution was stirred. After that, extraction was done using DCM and water. It was purified by a silica gel flash column (ethyl acetate/hexane, 2/3). Eventually, 0.254 g light-yellow-colored solid was received after drying under reduced pressure (90%).$^1$H NMR (250 MHz, CD$_2$Cl$_2$, 300 K) δ 8.29 (d, $J = 8.2$ Hz, 1H), 7.95 (d, $J = 8.2$ Hz, 1H), 7.33 (s, 1H), 6.34 (s, 1H), 0.07 (s, 8H).$^{19}$F NMR (471 MHz, DMSO-d$_6$, 298 K) δ -68.62, -72.25. MALDI-TOF: Calculated for C$_{39}$H$_{39}$F$_6$IrN$_6$Si$_3$: 982.2, found: 980.6 [M-H]$^+$.  

2,6-Difluoro-5'-bromo-3,2'-bipyridine (16)

In a 250 ml round bottom flask were added compound 9 (3.00 g, 18.9 mmol), 2-iodo-5-bromo-pyridine (6.43 g, 22.7 mmol), K$_2$CO$_3$ (5.22 g, 37.7 mmol), 150 ml of THF and 50 ml of water. The mixture was degassed and added argon 3 times. Then, Pd(PPh$_3$)$_4$ (436 mg, 0.38 mmol) was added. The mixture was stirred at 80 °C for 24 hours. Then extraction was done with DCM and water. It was purified by a silica gel flash column (DCM). Eventually, 2.00 g white-colored solid was received after drying under reduced pressure. $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) δ 8.77 (d, 1H), 8.68 (dd, 1H), 7.95 (dd, 1H), 7.77 (dd, 1H), 7.00 (dd, 1H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 298 K) δ -68.50, -69.53. FD-Mass: calculated for C$_{19}$H$_{15}$BrF$_2$N$_2$: 270.0 (100%), found: 270.3 [M]$^+$.  

2,6-Difluoro-5'-triisopropylsilylthynyl-3,2'-bipyridine (14)

In a Schlenk flask was added compound 16 (1.71 g, 6.31 mmol), PPh$_3$ (165 mg, 0.63 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (221 mg, 0.31 mmol), Cul (60 mg, 0.31 mmol) and 80 ml of triethylamine. The mixture was bubbled argon for 10 min. Then (triisopropyl)acetylene (1.6 ml, 6.94 mmol) was added by cannula. The mixture was stirred at 80 °C for 24 hours. Then the mixture was
extracted with DCM and water. It was purified by a silica gel flash column (DCM). Eventually, 2.0 g orange sticky liquid was received after drying under reduced pressure (85 %). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) δ 8.77 (d, 1H), 8.71 (dd, 1H), 7.88-7.81 (m, 2H), 7.00 (dd, 1H), 1.15 (s, 21H). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$, 300 K) δ 152.98, 149.49, 149.40, 146.59, 146.54, 146.48, 146.43, 139.93, 123.31, 123.16, 120.26, 107.62, 107.54, 107.16, 107.09, 103.59, 96.46, 18.76, 11.64. FD-Mass: calculated for C$_{21}$H$_{26}$F$_2$N$_2$Si: 372.2(100%), found: 372.0 [M$^+$].

$[(2,6$-Difluoro-$5'$-triisopropylsilyl)ethynyl-$3,2'$-bipyridinyl)$_2$Ir($\mu$-Cl)$_2$] (12)

In a round bottom flask were added IrCl$_3$ (0.718 g, 2.40 mmol), compound 14 (1.84 g, 4.93 mmol) and 24 ml of 2-ethoxylethanol. The mixture was degassed and was added argon 3 times and stirred at 140 °C for 24 hours. Then water was added to precipitate it. After filtration and washing with water, 1.34 g of a yellow-brown solid was received after drying under reduced pressure (57.5%). It was directly used for next step without further purification. But it can do be purified by silica gel flash column (DCM). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) δ 9.11 (d, 4H), 8.25 (dd, 4H), 8.06 (dd, 4H), 1.20 (s, 84H). FD-Mass: calculated for C$_{84}$H$_{100}$C$_{12}$F$_8$Ir$_2$N$_8$Si$_4$: 1938.6 (100%), found: 1942.2.

Mer($2,6$-difluoro-$5'$-triisopropylsilyl)ethynyl-$3,2'$-bipyridinyl)$_3$Ir (2)

In a round bottom flask were added compound 12 (1.20 g, 0.62 mmol), compound 14 (0.46 g, 1.24 mmol), K$_2$CO$_3$ (0.43 g, 3.09 mmol), Silver trifluoromethanesulfonate (0.33 g, 1.28 mmol) and 24 ml of 1,3,5-trimethylbenzene. The reactor was degassed and added argon 3 times and stirred at 170 °C for 24 hours. The resulting mixture was extracted with DCM and water. It was purified by a silica gel flash column (DCM) and a GPC column afterwards. Eventually, 0.49 g of a yellow solid was received after drying under reduced pressure (25%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) δ 8.33 (dd, 1H), 8.23 (dd, 1H), 8.16 (dd, 1H), 8.00 (d, 1H), 7.95 (d, 1H), 7.87 (dd,1H), 7.82 (dd, 1H), 7.77 (dd, 1H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 298 K) δ -67.62, -68.35, -68.98, -71.21, -71.52, -71.86. FD-Mass: calculated for C$_{63}$H$_{75}$F$_6$Ir$_6$N$_6$Si$_3$: 1306.5 (100%), found: 1305.4 [M-H$^+$].
**Mer(2,6-difluoro-5'-ethynyl-3,2'-bipyridinyl)$_3$Ir (22)**

In a round bottom flask were added compound 2 (420 mg, 0.32 mmol), tetrabutylammonium fluoride (0.25 g, 0.96 mmol) and 50 ml of THF. The reactor was degassed and added argon 3 times and stirred at room temperature overnight. Then it was extracted with DCM and water for several times to remove TBAF. Then it was purified by a silica gel flash column (Ethyl acetate/ hexane, 45/55). Eventually, 120 mg of a light yellow solid was received after drying under reduced pressure (46%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) $\delta$ 8.39 (dd, 1H), 8.27 (ddd, 1H), 7.99 (d, 1H), 7.98 (s, 1H), 7.96 (d, 1H), 7.89 (dd, 1H), 7.86 (dd, 1H), 6.33 (t, 1H), 5.97 (t, 1H), 5.71 (t, 1H), 3.33 (s, 1H), 3.30 (s, 1H), 3.28 (s, 1H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ @66.93, @67.67, @68.48, @70.62, -71.07, -71.37. FDMass: calculated for C$_{36}$H$_{15}$F$_6$IrN$_6$: 838.1 (100%), found: 836.8 [M-H]$^+$. 

**Mer(dfpypy)$_3$Ir-based-5'-dendronized, peripheral-carbazole polyphenylene dendrimer G1 (20)**

In a round bottom flask were added compound 22 (68 mg, 0.081 mmol), compound 21 (0.27 g, 0.28 mmol) and 12 ml of o-xylene. The reactor was degassed and added argon 3 times. Then it was heated at 150 °C for 24 hours. After that, the mixture was purified by a silica gel flash column (DCM/Hexane, 1/1~4/1). The product was further purified by a GPC column. Eventually, 160 mg yellow-colored solid was received after drying under reduced pressure (55%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) $\delta$ 8.25 (m, 2H), 8.09-8.06 (m, 12H), 8.03 (d, 2H), 7.93 (dd, 1H), 7.72 (dd, 1H), 7.58 (dd, 3H), 7.45 (d, 2H), 7.36-6.72 (m, 79H), 5.98(t, 1H), 5.74 (t, 1H), 5.19 (t, 1H), 1.41-1.34 (m, 108H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ -68.02, -68.86, -70.32, -71.36, -71.81, -72.72. MALDI-TOF: Calculated for C$_{240}$H$_{213}$F$_6$IrN$_{12}$: 3571.6 (100%), found: 3571.1 [M]$^+$. 

**Fac(dfpy))$_3$Ir-based-5'-dendronized, peripheral-carbazole polyphenylene dendrimer G1 (1)**
In a quartz tube were added 120 mg meridional dendrimer (20), and 20 ml of THF. The tube was degassed and added argon 3 times. Then the sealed tube was put in photochemical reactor and shined for 12 hours while the solution was stirred. After that, extraction was done using DCM and water. It was purified by a silica gel flash column (DCM). Eventually, 100 mg yellow-colored solid was received after drying under reduced pressure (83%).

\[^1^H\] NMR (300 MHz, CD$_2$Cl$_2$, 300 K) $\delta$ 8.13 (d, 3H), 8.07 (d, 6H), 7.32-6.65 (m, 84H), 7.52 (d, 3H), 5.91 (t, 3H), 1.36 (s, 54H), 1.30 (s, 54H).

\[^{19}F\] NMR (470 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ -68.98, -72.98. MALDI-TOF: calculated for C$_{240}$H$_{213}$F$_6$IrN$_{12}$: 3571.6 (100%), found: 3572.3 [M+H]$^+$. HR-MALDI-TOF: calculated for C$_{240}$H$_{213}$F$_6$IrN$_{12}$: 3571.6637, found: 3571.6842 [M$^+$].

2-Iodo-4-bromopyridine (19)

2-amino-4-bromopyridine (4.00 g, 23.12 mmol), CuI (4.40 g, 23.12 mmol), iodine (5.87 g, 23.12 mmol) and tertbutylnitrite (8.25 ml, 69.36 mmol) were added into a 50 ml two-neck Schlenk flask sequentially. After that, 25 ml of diiodomethane was added. The system was heated at 50 °C for 12 hours with one outlet connecting with reflux tube and open for nitrogen going and the other opening sealed. After that, extraction was done with K$_2$CO$_3$ and Na$_2$S$_2$O$_3$ solution. After that, a silica gel flash column was done with DCM as eluent. Eventually, 4.00 g of a light-yellow solid was received after drying under reduced pressure. \[^1^H\] NMR (300 MHz, DMSO-d$_6$, 298 K) $\delta$ 8.25 (d, J = 5.3 Hz, 1H), 8.19 (d, J = 1.8 Hz, 1H), 7.72 (dd, J = 5.3, 1.8 Hz, 1H). \[^{13}C\] NMR (75 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ 151.45, 137.70, 133.31, 127.03, 118.17.

2,6-Difluoro-4'-bromo-3,2'-bipyridine (17)

In a 250 ml round bottom flask were added compound 9 (1.27 g, 7.99 mmol), 2-iodo-4-bromo-pyridine (19) (2.50 g, 8.79 mmol), K$_2$CO$_3$ (2.21 g, 15.99 mmol), 50 ml of THF and 20 ml of water. The mixture was degassed and added argon 3 times. Then, Pd(PPh$_3$)$_4$ (318 mg, 0.27 mmol) was added. The mixture was stirred at 80 °C for 24 hours. Then extraction was done with DCM and water. It was purified by a
silica gel flash column (DCM). Eventually, 0.738 g of a yellow solid was received after drying under reduced pressure (34%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) δ 8.69 (dt, $J = 9.7, 8.0$ Hz, 1H), 8.53 (dd, $J = 5.2, 0.6$ Hz, 1H), 8.05 (td, $J = 1.7, 0.6$ Hz, 1H), 7.51 (dd, $J = 5.3, 1.8$ Hz, 1H), 7.01 (ddd, $J = 8.3, 3.0, 0.9$ Hz, 1H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 298 K) δ @68.08, @69.52. FD-Mass: calculated for C$_{10}$H$_5$BrF$_2$N$_2$: 270.0 (100%), found: 270.2 [M$^+$].

2,6-Difluoro-4'-triisopropylsilylethynyl-3,2'-bipyridine (15)

In a Schlenk flask were added compound 17 (0.10 g, 0.369 mmol), PPh$_3$ (9 mg, 36.9 µmol), Pd(PPh$_3$)$_2$Cl$_2$ (13 mg, 18.4 µmol), CuI (10 mg, 52.6 µmol) and 5 ml of triethylamine. The mixture was bubbled argon for 10 min. Then (triisopropyl)acetylene (74 mg, 0.406 mmol) was added by syringe. The mixture was stirred at 80 °C for 24 hours. Then the mixture was extracted with DCM and water. It was purified by a silica gel flash column (DCM). Eventually, 131 mg of a yellow sticky liquid was received after drying under reduced pressure (96 %). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) δ 8.73–8.58 (m, 1H), 7.86 (dt, $J = 2.3, 1.2$ Hz, 1H), 7.34 (dd, $J = 5.0, 1.5$ Hz, 1H), 7.05–6.92 (m, 1H), 1.15 (s, 21H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 298 K) δ -68.79, -69.83. FD-Mass: calculated for C$_{21}$H$_{26}$F$_2$N$_2$Si: 372.2(100%), found: 372.3 [M$^+$].

[(2,6-Difluoro-4'-triisopropylsilylethynyl-3,2'-bipyridinyl)$_2$Ir(µ-Cl)$_2$] (13)

In a round bottom flask were added IrCl$_3$ (19 mg, 63.6 µmol), compound 15 (50 mg, 0.134 mmol) and 1 ml of 2-ethoxylethanol. The mixture was degassed and added argon 3 times and stirred at 140 °C for 24 hours. Then water was added to precipitate it. After filtration and washing with water, 30 mg of a yellow-brown solid was received after drying under reduced pressure (24.4%). It was directly used for next step without further purification. FD-Mass: calculated for C$_{84}$H$_{100}$C$_{12}$F$_8$Ir$_2$N$_8$Si$_4$: 1938.6 (100%), found: 1941.1.

Mer(2,6-difluoro-4'-triisopropylsilylethynyl-3,2'-bipyridinyl)$_3$Ir (3)
In a round bottom flask was added compound 13 (30 mg, 0.015 mmol), compound 15 (11 mg, 0.031 mmol), K$_2$CO$_3$ (10 mg, 0.077 mmol), Silver trifluoromethanesulfonate (8 mg, 0.032 mmol) and 1 ml of 1,3,5-trimethylbenzene. The reactor was degassed and added argon 3 times and stirred at 170 °C for 24 hours. The resulting mixture was extracted with DCM and water. It was purified by a silica gel flash column (DCM) and a GPC column afterwards. Eventually, 4 mg of a yellow solid was received after drying under reduced pressure (20%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300 K) δ 8.34 (s, 1H), 8.28 – 8.19 (m, 2H), 7.85 (d, J = 6.1 Hz, 1H), 7.82 – 7.75 (d, J = 5.7 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.08 (dd, J = 5.8, 1.7 Hz, 1H), 6.95 (ddd, J = 6.3, 5.1, 1.8 Hz, 3H), 6.31 (t, J = 2.8 Hz, 1H), 6.00 (t, J = 2.7 Hz, 1H), 5.81 (t, J = 2.0 Hz, 1H), 1.13 (s, 6H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, 298 K) -67.80, -68.39, -69.09, -71.64, -72.10, -72.22. FD-Mass: calculated for C$_{63}$H$_{75}$F$_6$IrN$_6$Si$_3$: 1306.5 (100%), found: 1305.9 [M]$.^+$
Figure S1: $^1$H NMR (250 MHz) and $^{19}$F NMR (471 MHz) (inset) spectra of compound 5 (top) and compound 4 (bottom) (solvent: CD$_2$Cl$_2$, except the $^{19}$F NMR of compound 4 using DMSO-d$_6$).
Figure S2: $^1$H-$^1$H COSY spectra of compound 16 (left) and $^1$H NMR (300 MHz) spectra of compound 14 (top right) and 12 (bottom right) (solvent: CD$_2$Cl$_2$).

Figure S3: MALDI-TOF mass (left) and HRMS (right) spectra of dendrimer 1.
Table S1: Single-Crystal X-ray Diffraction Parameters and Crystal Data for compounds 4 and 5.

| Parameter                     | Compound 4                                      | Compound 5                                      |
|-------------------------------|-------------------------------------------------|-------------------------------------------------|
| formula                       | C_{39}H_{39}F_{6}IrN_{6}Si_{3}, 1.25(CH_{2}Cl_{2}) | C_{39}H_{39}F_{6}IrN_{6}Si_{3}                  |
| molecular weight /gmol⁻¹      | 1088.39                                         | 982.23                                          |
| absorption /µ mm⁻¹            | 3.108                                           | 3.28                                            |
| transmission T_{min}, T_{max} | 0.4957, 0.7679                                   | 0.6032, 0.7456                                  |
| crystal size /mm³             | 0.16 x 0.20 x 0.96                              | 0.07 x 0.2 x 0.2                                |
| space group                   | P 2₁/n monoclinic                               | F ddd orthorhombic                              |
| lattice parameters /Å, °      | a = 13.5973(4)                                  | a = 24.169(14)                                  |
|                               | b = 24.1687(9)                                  | b = 25.884(14)                                  |
|                               | c = 14.5358(5)                                  | c = 54.40(3)                                    |
|                               | ß = 99.195(2)                                   |                                                 |
| Volume V /Å³, z, F(000)       | 4715.7(3), 4, 2162                              | 34032(57), 32, 15616                            |
| temperature /K                | 193                                             | 173                                             |
| scan range θ /°               | 2, 28                                           | 2,28                                            |
| number of reflections:        |                                                 |                                                 |
| measured                      | 28524                                           | 57061                                           |
| unique                        | 11348 (R_{int} = 0.0333)                        | 9778, (R_{int} = 0.0684)                        |
| refined parameters            | 551                                             | 504                                             |
| observed (|F|/σ(F) > 4.0)               | 8940                                           | 7026                                           |
| wR2, R1, S                    | 0.0732, 0.0306, 1.055                           | 0.0848, 0.0349, 1.011                           |

Table S2: Selected bond lengths of compound 4 and 5 in single crystals.  

| Bonds | Bond length (Å) |
|-------|-----------------|
|       | Compound 4      | Compound 5      |
| Ir-N1 | 2.128(3)        | 2.070(3)        |
| Ir-N2 | 2.126(3)        | 2.161(3)        |
| Ir-N3 | 2.120(3)        | 2.060(3)        |
| Ir-C1 | 2.000(3)        | 2.076(4)        |
| Ir-C2 | 2.004(4)        | 2.089(4)        |
| Ir-C3 | 2.000(4)        | 2.006(4)        |

*the atom numbers are consistent with Figure 2 in the main text.*
**Figure S4:** Close contacts in compounds 4 (top) and 5 (bottom) and crystal packing of compound 4 (middle).
**Figure S5:** Photoluminescence spectra of compounds 1-5 at 77 K (measured in 2-methylTHF solution).
**Figure S6:** Frontier molecular orbitals and electron-density distributions of phenyl-pyridine-based molecules (calculated using DFT, B3LYP, 6.31G method). (It shows that the energy gaps of the triphenylene and pentaphenylene containing materials have reduced compared with phenyl pyridine and it shows considerable contributions of the triphenylene and pentaphenylene to the HOMO level of the material, thus reducing the energy gap).
Figure S7: CV curves of compounds 1-5.
Figure S8: Emission spectra of thin film of dendrimer 1.

Reference

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