Electronic Supplementary Information (ESI):

Conjugated Polymers with Cationic Iridium(III) Complexes in the Side-chain for Flash Memory Devices Utilizing Switchable Through-space Charge Transfer

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Synthesis and Characterization of Materials

Materials. All reagents, unless otherwise specified, were obtained from Sigma-Aldrich, Acros, and Alfa and used as received. The solvents (THF, toluene) were purified by routine procedures and distilled under dry N₂ before use. All manipulations involving air-sensitive reagents were performed in an atmosphere of dry N₂.

Synthesis. 2-(4-Bromophenyl)quinoline (3), 2-(4-((dimesitylboryl)phenyl)-quinoline (4), 2,7-dibromo-9-octyl-9H-fluorene (6), M2, M3, M5, and M6 were prepared according to the literature procedures.[1-3] All other reagents were used as received from commercial suppliers.

Synthesis of 1-(4-bromobuty1)-N-2-(pyridin-2-yl)benzimidazole (1): A mixture of 2-(2-pyridyl)benzimidazole (0.59 g, 3 mmol) and KOH (0.87 g, 15 mmol) was stirred in [Bmim]BF₄⁻ (5 mL) at room temperature. 1,4-dibromobutane was added to the mixture after 5 minutes. The reaction mixture was stirred at room temperature for 6 h. After the reaction was complete, the product was extracted with Et₂O (3 × 20 mL). The combined ethereal phases were evaporated under reduced pressure, and the crude product was purified by column chromatography on silical by using ethyl acetate/petroleum ether (1:3) as eluent to yield colorless oil in 60% yield. ¹H NMR (400 MHz, CDCl₃, δ): 1.84 (m, 2H), 1.99 (m, 2H), 3.32 (t, J = 6.8, 2H), 4.76 (t, J = 6.8, 2H), 7.26-7.37 (m, 3H), 7.37 (m, 1H), 7.77 (m, 2H), 8.38 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ): 28.05, 29.34, 32.63,
Synthesis of 3,6-dibromo-9-[N-[2-(pyridin-2-yl)benzimidazole]-butyl]carbazole (2): In a two neck flask, a mixture of 1 (1.11 g, 3.36 mmol), 3,6-dibromo-9H-carbazole (1.64 g, 5.05 mmol), and KOH (3.78 g, 67.3 mmol) were refluxed in DMSO (70 mL) under nitrogen atmosphere for 24 h. After being cooled to room temperature, the reaction mixture was extracted with CH$_2$Cl$_2$, dried over anhydrous Na$_2$SO$_4$, and then concentrated. The crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:2) as the eluent to give a white solid in 50% yield. $^1$H NMR (400 MHz, CDCl$_3$, δ): 1.93 (m, 4H), 4.22 (t, J = 6.4 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 7.31 (m, 4H), 7.51 (dd, J = 8.8, J = 2.0 Hz, 2H), 7.82 (m, 2H), 8.12 (d, J = 1.6 Hz, 2H), 8.38 (m, 1H), 8.49 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, δ): 26.06, 27.77, 42.98, 45.02, 110.05, 110.40, 112.26, 120.40, 122.84, 123.46, 123.59, 123.62, 123.96, 124.80, 129.25, 136.61, 136.61, 139.30, 142.71, 145.58, 149.76, 150.60.

Synthesis of M1: M1 was synthesized through a standard two-step procedure. IrCl$_3$. 3H$_2$O (1 mmol) and 4 (2.5 mmol) were heated at reflux in a mixture of 2-ethoxyethanol and water (3:1 v/v) under N$_2$ atmosphere. After being cooled to room temperature, the red solid was filtered to give crude dichloro-bridged diiridium complex [Ir(Bpq)$_2$Cl]$_2$. A red solution of [Ir(Bpq)$_2$Cl]$_2$ (0.034 mmol) and 2 (0.0748 mmol) in MeOH (5 mL) and CH$_2$Cl$_2$ (10 mL) was refluxed under an inert atmosphere of N$_2$ for 4 h. The solution was then cooled down to room temperature and a 10-fold excess of potassium hexafluorophosphate was added. The mixture was stirred for 10 h at room temperature. The suspension was then filtered and evaporated to dryness. The crude product was purified with column chromatography on silica gel with CH$_2$Cl$_2$/acetone (60:1) as the eluent to afford an red solid in 45% yield. $^1$H NMR (400 MHz, CDCl$_3$, δ): 1.58 (s, 12H), 1.64 (s, 12H), 1.85 (m, 4H), 2.18 (s, 6H), 2.26 (s, 6H), 3.75 (m, 4H), 6.16 (s, 1H), 6.30 (s, 1H), 6.43 (s, 4H), 6.50-6.55 (m, 5H), 6.61 (d, J = 8.4 Hz, 1H), 6.67 (m, 1H), 6.78 (m, 2H), 6.95 (m, 2H), 7.08 (t, J = 8.0 Hz, 1H), 7.18-7.30 (m, 9H), 7.36 (m, 2H), 7.51-7.57 (m, 2H), 7.67 (d, J 8.8 Hz, 1H), 7.73 (d, J
$= 8.0\text{ Hz, }1\text{H}),\ 7.81\ (d,\ J = 8.0\text{ Hz, }1\text{H}),\ 7.94\ (m,\ 2\text{H}),\ 8.01\ (d,\ J = 1.6\text{ Hz, }1\text{H}),\ 8.19\ (m,\ 3\text{H});^{13}\text{C NMR (100 MHz, CDCl}_3,\ \delta):\ 21.23,\ 21.31,\ 22.84,\ 25.62,\ 67.98,\ 110.47,\ 112.00,\ 122.86,\ 123.13,\ 124.06,\ 125.01,\ 125.30,\ 125.38,\ 126.47,\ 126.69,\ 127.26,\ 127.55,\ 127.63,\ 127.68,\ 128.39,\ 128.60,\ 129.17,\ 129.87,\ 130.01,\ 130.53,\ 130.73,\ 136.00,\ 137.91,\ 138.51,\ 138.79,\ 140.10,\ 146.82,\ 146.78,\ 147.31,\ 148.36,\ 149.37,\ 151.64,\ 169.22,\ 169.65;\ \text{ESI-MS: } m/z\ 1671.33\ [M-\text{PF}_6]^+.$

**Synthesis of 1-(6-bromohexyl)-N-2-(pyridin-2-yl)-1H-benzo[d]imidazole (5).**

KOH (2.86 g, 51 mmol) and 2-(2-pyridyl)benzimidazole (2 g, 10.2 mmol) were added to ionic liquid (20 mL), and the mixture was stirred magnetically for 5 min. Then, 1,6-dibromohexane (8 mL, 51 mmol) was introduced in a single portion, the stirring was continued for 5 h. After the reaction was complete, the product was extracted with Et$_2$O (3 × 20 mL). The combined ethereal phases were evaporated under reduced pressure, and the crude product was purified by column chromatography on silica by using ethyl acetate/petroleum ether (1:3) as eluent to yield colorless oil product (2.2 g, 60 %). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 1.35-1.51 (m, 4H), 1.79-1.92 (m, 4H), 3.38 (t, $J = 6.8$ Hz, 2H), 4.84 (t, $J = 6.8$ Hz, 2H), 7.30-7.37 (m, 3H), 7.44-7.46 (m, 1H), 7.83-7.87 (m, 2H), 8.41 (d, $J = 8.0$ Hz, 1H), 8.69 (d, $J = 4.8$ Hz, 1H); $^{13}$C (100 MHz, CDCl$_3$, $\delta$): 26.07, 27.81, 29.94, 32.64, 33.88, 45.36, 110.28, 120.23, 122.68, 123.40, 123.88, 124.82, 136.69, 136.94, 142.71, 148.76, 149.94, 150.79.

**Synthesis of 1-(6-(2,7-dibromo-9-octyl-fluoren-9-yl)hexyl)-2-(pyridin-2-yl)-benzoimidazole (7).**

5 (1.4 g, 4.0 mmol), 2,7-dibromo-9-octyl-9H-fluorene (4.0 mmol) and KOH (20 mmol) were added to DMSO (10 mL). The solution was stirred at 60 ºC for 5 h. The mixture was poured into H$_2$O (40 mL), and then was extracted three times with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica by using ethyl acetate/petroleum ether (1:3) as eluent to yield a white solid (74%). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 0.55 (m, 4H), 0.83 (t, $J = 7.2$ Hz, 3H), 1.04-1.23 (m, 14H), 1.71 (m, 2H), 1.87 (m, 4H), 4.73 (t, $J = 7.6$ Hz, 2H), 7.52-7.29 (m, 10H), 7.85-7.80 (m, 2H),
Synthesis of M4. A mixture of 2-ethoxyethanol and water (3:1, v/v) was added to a flask containing IrCl$_3$•3H$_2$O (1 mmol) and 4 (2.5 mmol). The mixture was refluxed for 24 h. After cooling, the orange solid precipitate was filtered to give crude cyclometalated iridium(III) chloro-bridged dimer. The solution of cyclometalated iridium(III) chloro-bridged dimer (0.079 mmol) and 7 (0.158 mmol) in CH$_2$Cl$_2$/MeOH (30 mL, 2:1 (v/v)) was heated to reflux. After 4 h, the red solution was cooled to room temperature and then a 10-fold excess of potassium hexafluorophosphate was added. The suspension was stirred for 2 h and then was filtered to remove insoluble inorganic salts. The solution was evaporated to dryness under reduced pressure. It was chromatographed by using CH$_2$Cl$_2$/acetone (50:1) to afford an orange-red solid in 70% yield. $^1$H NMR (400 MHz, CDCl$_3$, δ): 0.40-0.70 (m, 4H), 0.83 (t, $J$ = 7.2 Hz, 3H), 1.04-1.25 (m, 14H), 1.63(s, 24H), 1.74-1.90 (m, 6H), 2.23-2.26 (m, 12H), 4.34-4.64 (m, 2H), 6.26 (s, 1H), 6.30 (s, 1H), 6.55-6.47 (m, 9H), 6.69 (t, $J$ = 8.0 Hz, 1H), 6.83 (t, $J$ = 8.0 Hz, 1H), 6.98 (m, 2H), 7.14-7.39 (m, 9H), 7.45-7.63 (m, 8H), 7.71 (m, 2H), 7.83(d, $J$ = 8.0 Hz, 1H), 7.95 (m, 2H), 8.15-8.27 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, δ): 14.20, 14.25, 21.42, 21.44, 22.73, 22.79, 22.83, 22.96, 23.02, 23.63, 23.68, 25.55, 29.27, 29.29, 29.42, 29.49, 29.79, 29.83, 29.92, 31.72, 31.88, 32.06, 39.94, 40.35, 45.60, 55.74, 111.83, 116.68, 117.26, 118.08, 121.34, 121.37, 121.71, 121.77, 124.35, 124.86, 125.09, 125.41, 125.49, 125.64, 126.03, 126.34, 126.43, 126.75, 127.51, 127.59, 127.70, 127.79, 127.82, 128.64, 128.70, 129.91, 130.20, 130.41, 130.43, 130.68, 130.88, 136.27, 137.99, 138.06, 138.36, 138.76, 139.14, 139.23, 139.42, 140.28, 140.56, 141.71, 142.02, 144.04, 147.17, 147.22, 147.53, 148.59, 148.84, 149.57, 151.02, 151.49, 152.57, 152.67, 169.36, 169.91.

Synthesis of iamP5. To a mixture of 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) (M6) (1 equiv), dibromo compound (1 equiv), including the
9,9-dioctyl-2,7-dibromofluorene (M5) and Ir complex monomer (M4), tetrabutylammonium bromide, and 4.0 mol% Pd(PPh₃)₄, was added to a degassed mixture of toluene ([monomer] = 0.25 M) and aqueous 2 M potassium carbonate (3:2 in volume). The mixture was vigorously stirred at 85–90 °C for 72 h and then bromobenzene was added. After the mixture was cooled to room temperature, it was washed with water. The solution was concentrated and then it was slowly add dropwise to a mixture of methanol and deionized water (220 mL, 10:1 v/v). A fibrous solid was obtained by filtration. The solid was dissolved in THF and then the solution was evaporated. The concentrated solution obtained was dropped slowly into methanol (250 mL) again. And this procedure was repeated twice. The fibrous solid was filtered and was then washed with acetone in a Soxhlet apparatus for 3 days to remove oligomers and catalyst residues. The resulting polymer was collected and dried under vacuum. Yields: 55%.

**1H NMR (400 MHz, CDCl₃, δ):** 0.63-0.89 (m, 10H), 1.05-1.28 (m, 20H), 2.12 (m, 4H), 7.67-7.85 (m, 6H); **13C NMR (100 MHz, CDCl₃, δ):** 14.31, 22.84, 24.14, 29.46, 30.18, 30.28, 32.03, 40.62, 55.57, 120.21, 121.72, 126.39, 140.26, 140.72, 152.04.

**The synthesis of iamP4 is similar to iamP5.**

**1H NMR (400 MHz, CDCl₃, δ):** 0.86 (m, 3H) 1.23-1.44 (m, 6H), 1.87 (m, 2H), 4.28 (m, 2 H), 7.45 (m, 2H), 7.74-7.91 (m, 2H), 8.42-8.55 (m, 2H); **13C NMR (100 MHz, CDCl₃, δ):** 14.19, 22.70, 27.13, 29.20, 31.74, 43.36, 109.15, 119.09, 123.81, 125.58, 133.34, 140.10.
**Scheme S1.** The synthetic route of monomer M4. Reagents and conditions: i) KOH, [Bmim]BF$_4$, 20 °C, 5-6 h; ii) KOH, DMSO, 60 °C, 6 h; iii) IrCl$_3$•H$_2$O, 2-ethoxyethanol/H$_2$O = 3/1, 110 °C, 24 h; iv) CH$_2$Cl$_2$/CH$_3$OH = 2:1, 40 °C, 4 h; v) KPF$_6$, room temperature, 2 h.

**Scheme S2.** The synthetic route of polymer iamP5. Reagents and conditions: i) Pd(PPh$_3$)$_4$, 2 M K$_2$CO$_3$ (aq), toluene, 90 °C, 72h.
Fig. S1 (a) Chemical structure and the typical I-V characteristics of an Al/polycarbazole/ITO device. (b) Chemical structure and the typical I-V characteristics of an Al/polyfluorene/ITO device.

References

