Supplementary Information

**Figure S1.** Cyclic voltammetric scans of compounds at $10^{-3}$ M in acetonitrile:toluene (1:1 by volume) with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Both oxidation and reduction scans are reversible for all the three hybrids. The reduction potential of \textit{tBu-TPA} and the oxidation potential of \textit{TRZ} are beyond the CV measurement range.

**Figure S2.** Fluorescence spectra collected at 20 °C for (a) \textit{tBu-TPA-m-TRZ} and (b) \textit{tBu-TPA-L-TRZ} in toluene, chloroform, and DMF at $8.3 \times 10^{-6}$ M with photoexcitation at 277 nm.
Figure S3. DSC heating and cooling scans at ±20 °C/min of samples preheated to above their melting points followed by cooling down to –30 °C at –100 °C/min for (a) pure hybrids, and (b) hybrids doped with $\text{Ir(piq)}_3$ at 8 wt%. Symbols: $G$, glassy; $K$, crystalline; $I$, isotropic.

Synthesis and Characterization of Bipolar Hybrids

All starting chemicals, reagents, and solvents were used as received from commercial sources without further purification except toluene and tetrahydrofuran (THF) that had been distilled over sodium and benzophenone. Intermediates 2-(4-Bromophenyl)-4,6-diphenyl-1,3,5-triazine (4)\textsuperscript{1} and 2-chloro-4,6-biphenyl-1,3,5-triazine (10)\textsuperscript{2} were synthesized following literature procedures. All reactions were carried out under argon and anhydrous conditions unless noted otherwise.
Scheme S1. Synthesis of tBu-TPA-p-TRZ, tBu-TPA-m-TRZ and tBu-TPA-ℓ-TRZ.

4-Bromo-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, 2. To a solution of Pd2(dba)3 (0.25 g, 0.27 mmol), and dpff (0.23 g, 0.41 mmol) in toluene (50 ml) was added NaOtBu (2.36 g, 24.50 mmol) at 25 °C. The mixture was stirred for 15 min before adding 1,4-dibromobenzene (16.76 g, 71.06 mmol), and stirred for another 15 min. Bis(4-tert-butylphenyl)amine, 1 (5.00 g, 17.77 mmol), was added, and the reaction mixture was heated to 90 °C for 15 h. The reaction mixture was subsequently cooled to 25 °C and then poured into a large amount of water for extraction with toluene. The organic extracts were combined, washed with water and dried over MgSO4. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 9:1 (v/v) as the eluent to yield 2 (3.50 g, 45%) as a white powder. 1H NMR (400 MHz, CDCl3, 298K): δ (ppm) 7.30-7.23 (m, 6H), 7.01-6.96 (m, 4H), 6.95-6.89 (m, 2H), 1.30 (s, 18H).
4-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl-boronic acid, 3. To a solution of 2 (1.00 g, 2.30 mmol) in anhydrous THF (20 ml) was added n-BuLi (2.5 M in hexane, 1.19 ml, 3.00 mmol) at −78 °C. The reaction mixture was stirred for 3 h before tri-iso-propyl borate (1.05 ml, 4.60 mmol) was added in one portion. The mixture was warmed to room temperature, stirred overnight, and poured into a large amount of water for extraction with ether. The organic extracts were combined, washed with water and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate 2:1 (v/v) as the eluent to yield 3 (0.62 g, 67%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.98-7.96 (d, J = 8.0 Hz, 2H), 7.38-7.26 (m, 4H), 7.14-6.98 (m, 6H), 1.32 (s, 18H).

4-Allyl-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, 5. THF (50 ml) was added into a mixture of 2 (0.74 g, 1.70 mmol), allyltributyltin (3.37 g, 10.17 mmol), Pd(PPh₃)₄ (0.098 g, 0.085 mmol), and LiCl (0.14 g, 3.39 mmol). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO₄. After evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 8:1 (v/v) as the eluent to yield 5 (0.30 g, 45%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.25-7.22 (m, 2H), 7.22-7.20 (m, 2H), 7.08-6.96 (m, 8H), 6.08-5.90 (m, 1H), 5.15-5.00 (m, 2H), 3.34-3.32 (d, J = 8.0 Hz, 2H), 1.30 (s, 18H).

3-Bromo-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, 6. To a solution of Pd₂(dba)₃ (0.25 g, 0.27 mmol), and dppf (0.23 g, 0.41 mmol) in toluene (50 ml) was added NaOttBu (2.36 g, 24.50 mmol) at 25 °C. The mixture was stirred for 15 min followed by addition of 1,3-dibromobenzene (16.76 g, 71.06 mmol), and stirred for another 15 min. 1 (5.00 g, 17.77 mmol) was added, and the reaction mixture was heated to 90 °C for 15 h. The reaction mixture was subsequently cooled to 25 °C and poured into a large amount of water for extraction with toluene. The organic extracts were combined, washed with water and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 8:1 (v/v) as the eluent to yield 6 (5.56 g, 72%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.32-7.27 (m, 3H), 7.18-7.15 (m, 1H), 7.07-6.98 (m, 7H), 6.95-6.90 (m, 1H), 1.31 (s, 18H).
2-(3-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-
dioxaborolane, 7. n-BuLi (2.5 M in hexane, 5.50 ml, 13.75 mmol) was added dropwise into a
solution of 6 (4.0 g, 9.17 mmol) in THF (70 ml) at −78 °C, where the mixture was stirred for 3 h
before adding 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3.92 g, 21.08 mmol) in
one portion. The reaction mixture was allowed to warm up to room temperature over a period of
12 h, quenched with water, and then extracted with ether. The organic extracts were combined,
 washed with brine and water, and dried over MgSO4. Upon evaporating off the solvent, the crude
product was purified by column chromatography on silica gel with hexane/ethyl acetate 20:1
(v/v) as the eluent to yield 7 (3.15 g, 71%) as a white powder. 1H NMR (400 MHz, CDCl3,
298K): δ (ppm) 7.61-7.58 (m, 1H), 7.47-7.45 (d, J = 8.0 Hz 1H), 7.26-7.19 (m, 5H), 7.18-7.14
(m, 1H), 7.00-6.94 (m, 4H), 1.37-1.27 (m, 30H).

3-(3-Bromophenyl)-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, 8. Toluene (50 ml) and
H2O (30 ml) were added into a mixture of 7 (2.55 g, 5.27 mmol), 1,3-dibromobenzene (3.73 g,
15.82 mmol), Pd(PPh3)4 (0.22 g, 0.11 mmol), and Na2CO3 (6.36 g, 60 mmol). The reaction
mixture was stirred at 90 °C for 12 h, cooled to room temperature, and extracted with methylene
chloride. The organic extracts were combined, washed with water, and dried over MgSO4. Upon
 evaporating off the solvent, the crude product was purified by column chromatography on silica
gel with hexane/chloroform 7:1 (v/v) to yield 8 (2.20 g, 81%) as a white powder. 1H NMR (400
MHz, CDCl3, 298K): δ (ppm) 7.66-7.62 (m, 1H), 7.45-7.39 (m, 2H), 7.32-7.21 (m, 7H), 7.15-
7.10 (m, 1H), 7.08-7.01 (m, 5H), 1.31 (s, 18H).

2-(3-(3-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)phenyl)-4,4,5,5-tetramethyl-
[1,3,2]-dioxaborolane, 9. n-BuLi (2.5 M in hexane, 2.46 ml, 6.15 mmol) was added dropwise
into a solution of 8 (2.10 g, 4.10 mmol) in THF (40 ml) at −78 °C, where the mixture was stirred
for 3 h before adding 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (1.75 g, 9.42
mmol) in one portion. The reaction mixture was allowed to warm up to room temperature over a
period of 12 h, quenched with water, and then extracted with ether. The organic extracts were
combined, washed with brine and water, and dried over MgSO4. Upon evaporating off the
solvent, the crude product was purified by column chromatography on silica gel with
hexane/ethyl acetate 20:1 (v/v) as the eluent to yield 9 (1.70 g, 74%) as a white powder. \(^1\)H NMR (400 MHz, CDCl\(_3\), 298K): \(\delta\) (ppm) 7.95 (s, 1H), 7.76-7.74 (d, \(J = 8.0\) Hz, 1H), 7.62-7.57 (m, 1H), 7.43-7.33 (m, 2H), 7.32-7.18 (m, 6H), 7.09-6.98 (m, 5H), 1.37-1.27 (m, 30H).

2-(4-(4-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)phenyl)-4,6-diphenyl-1,3,5-triazine, \(tBu\)-TPA-\(p\)-TRZ. Toluene (15 ml) and H\(_2\)O (6 ml) were added into a mixture of 3 (0.48 g, 1.20 mmol), 4 (0.42 g, 1.08 mmol), Pd(PPh\(_3\))\(_4\) (0.028 g, 0.024 mmol), and Na\(_2\)CO\(_3\) (1.27 g, 12.00 mmol). The reaction mixture was stirred at 90 °C for 12 h, cooled to room temperature, and extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO\(_4\). Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane/chloroform 3:1 to 2:1 (v/v) to yield \(tBu\)-TPA-\(p\)-TRZ (0.51 g, 71%) as a yellow powder. \(^1\)H NMR (400 MHz, CDCl\(_3\), 298K): \(\delta\) (ppm) 8.83-8.78 (m, 6H), 7.79-7.77 (d, \(J = 8.0\) Hz, 2H), 7.62-7.56 (m, 8H), 7.31-7.29 (m, 4H), 7.17-7.15 (d, \(J = 8.0\) Hz, 2H), 7.10-7.08 (m, 4H), 1.33 (s, 18H). LDI TOF MS m/z ([M]\(^+\)): 664.3. Anal. calcd for C\(_{47}\)H\(_{44}\)N\(_4\) (%): C 84.90, H 6.67, N 8.43; found: C 84.64, H 6.56, N 8.33.

2-(3-(3-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)phenyl)-4,6-diphenyl-1,3,5-triazine, \(tBu\)-TPA-\(m\)-TRZ. Toluene (20 ml) and H\(_2\)O (12 ml) were added into a mixture of 9 (1.00 g, 1.79 mmol), 10 (0.48 g, 1.79 mmol), Pd(PPh\(_3\))\(_4\) (0.041 g, 0.036 mmol), and Na\(_2\)CO\(_3\) (2.54 g, 24.00 mmol). The reaction mixture was stirred at 90 °C for 40 h, cooled to room temperature, and then extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO\(_4\). Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane/chloroform 3:1 to 2:1 (v/v) as the eluent to yield \(tBu\)-TPA-\(m\)-TRZ (1.07 g, 90%) as a white powder. \(^1\)H NMR (400 MHz, CDCl\(_3\), 298K): \(\delta\) (ppm) 8.92 (s, 1 H), 8.79-8.77 (d, \(J = 8.0\) Hz, 4H), 8.73-8.71 (d, \(J = 8.0\) Hz, 1H), 7.73-7.71 (m, 1H), 7.66-7.56 (m, 7H), 7.43-7.28 (m, 7H), 7.13-7.08 (m, 5H), 1.29 (s, 18H). LDI TOF MS m/z ([M]\(^+\)): 664.0. Anal. calcd for C\(_{47}\)H\(_{44}\)N\(_4\) (%): C 84.90, H 6.67, N 8.43; found: C 84.83, H 6.71, N 8.43.

2-(4-(4-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)propyl)phenyl)-4,6-diphenyl-1,3,5-triazine, \(tBu\)-TPA-\(L\)-TRZ. 9-BBN (0.5 M in THF, 4.2 ml, 2.1 mmol) was added dropwise into a solution of 5 (0.28 g, 0.70 mmol) in THF (8 ml) at 0 °C. The mixture was stirred
at room temperature for 15 min and then at 35 °C for 3 h before transferring into a mixture of 4 (0.38 g, 0.99 mmol), Pd(PPh3)4 (0.016 g, 0.014 mmol), Na2CO3 (3.18 g, 30 mmol), H2O (15 ml) and Toluene (25 ml). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO4. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 3:1 (v/v) as the eluent to yield \(t\)Bu-TPA-\(L\)-TRZ (0.25 g, 50%) as a pale yellow powder. \(^1\)H NMR (400 MHz, CDCl3, 298K): \(\delta\) (ppm) 8.79-8.77 (d, \(J = 8.0 \) Hz, 4H), 8.71-8.69 (d, \(J = 8.0 \) Hz, 2H), 7.64-7.56 (m, 6H), 7.41-7.39 (d, \(J = 8.0 \) Hz, 2H), 7.26-7.21 (m, 4H), 7.08-6.98 (m, 8H), 2.84-2.76 (m, 2H), 2.69-2.61 (m, 2H), 2.08-2.00 (m, 2H), 1.30 (s, 18H). LDI TOF MS m/z ([M]+): 706.1. Anal. calcd for C50H50N4 (%): C 84.95, H 7.13, N 7.93; found: C 84.68, H 7.10, N 7.78.

Figure S4. Proton-NMR spectra of \(t\)Bu-TPA and TRZ in CDCl₃.
**Figure S5.** Proton-NMR spectrum of $\text{tBu-TPA}-p$-TRZ in CDCl$_3$. 
Figure S6. Proton-NMR spectrum of \( t\text{Bu}-\text{TPA-}m-\text{TRZ} \) in CDCl\(_3\).
Figure S7. Proton-NMR spectrum of tBu-TPA-2-TRZ in CDCl₃.

References
