Supplementary Information

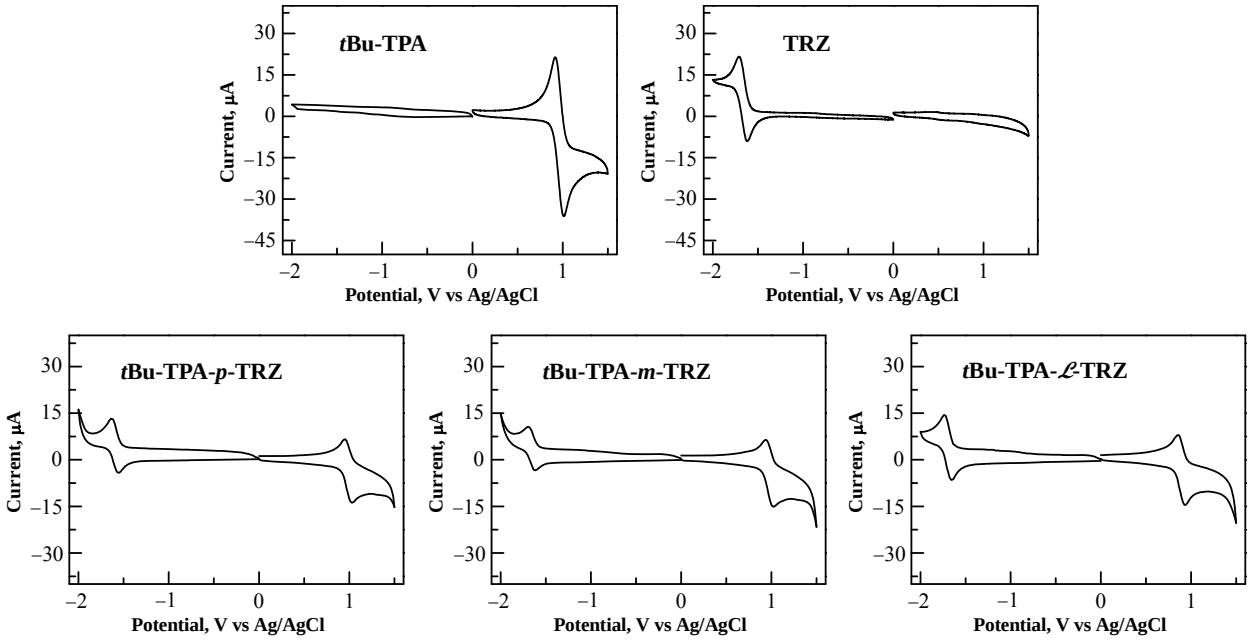


Figure S1. Cyclic voltammetric scans of compounds at 10^{-3} M in acetonitrile:toluene (1:1 by volume) with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Both oxidation and reduction scans are reversible for all the three hybrids. The reduction potential of ***t*Bu-TPA** and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

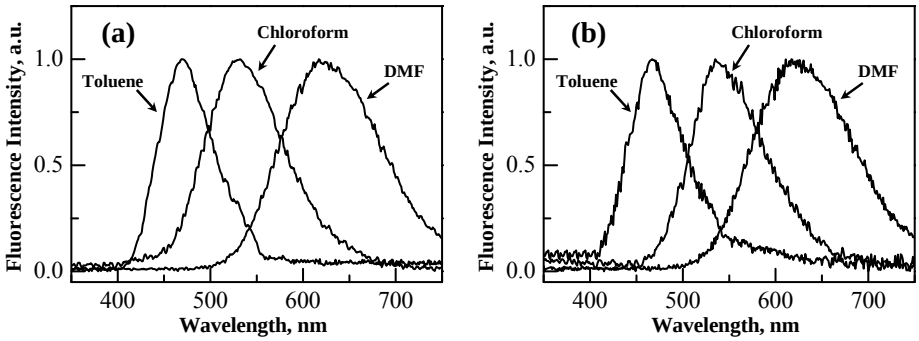


Figure S2. Fluorescence spectra collected at 20 °C for (a) ***t*Bu-TPA-*m*-TRZ** and (b) ***t*Bu-TPA-ℒ-TRZ** in toluene, chloroform, and DMF at 8.3×10^{-6} M with photoexcitation at 277 nm.

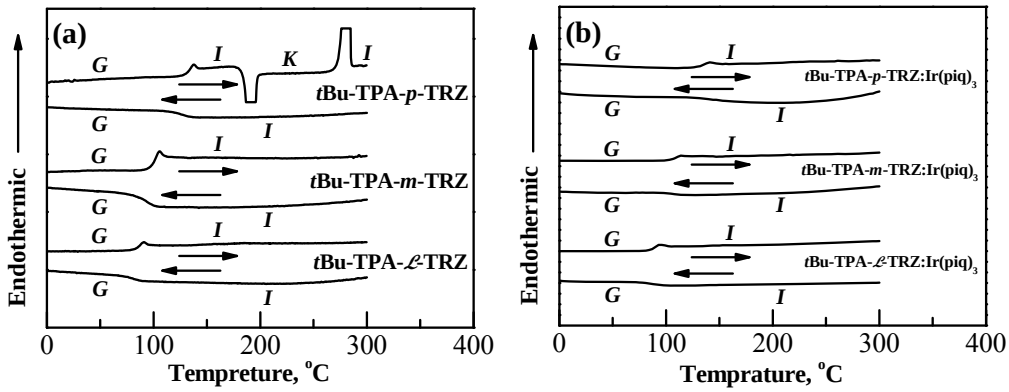
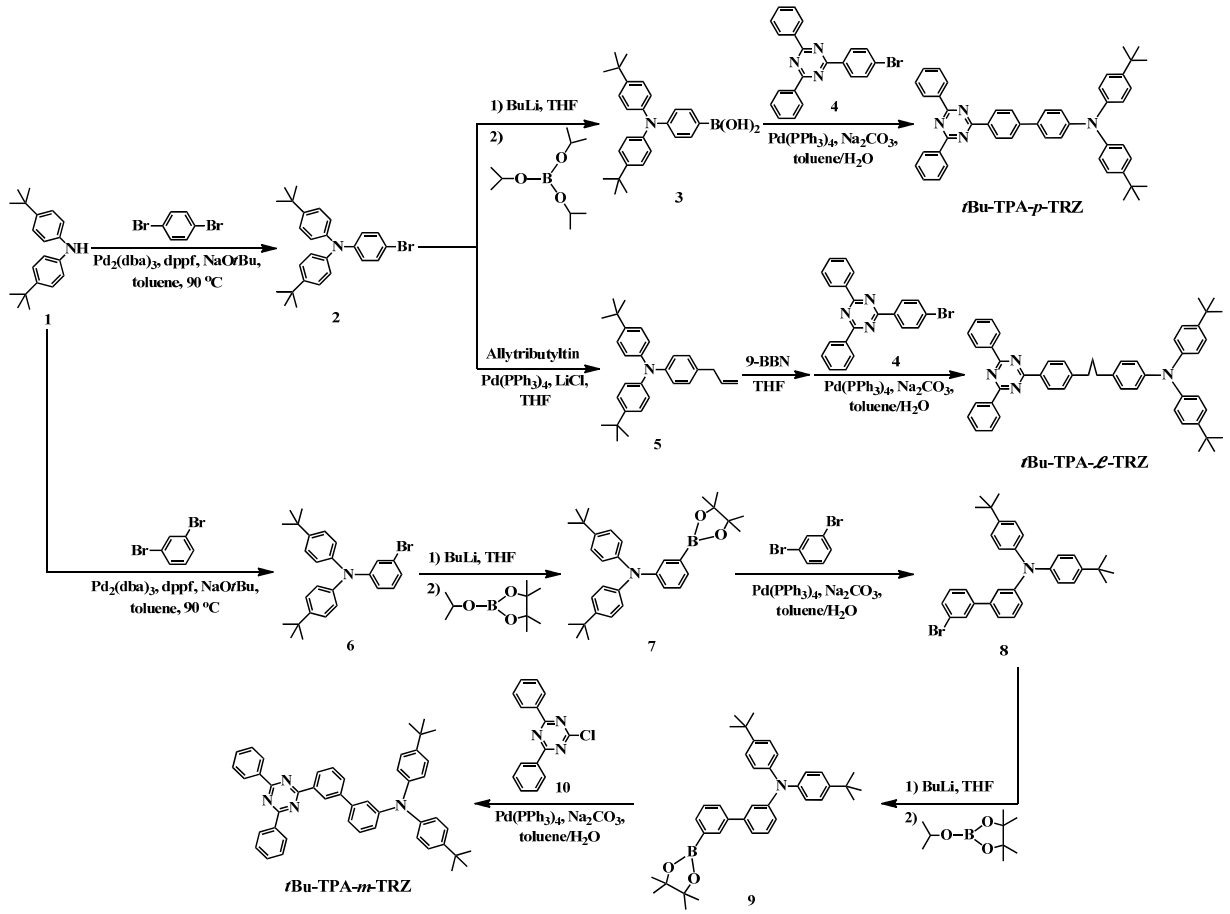


Figure S3. DSC heating and cooling scans at ±20 °C/min of samples preheated to above their melting points followed by cooling down to –30 °C at –100 °C/min for (a) pure hybrids, and (b) hybrids doped with **Ir(piq)$_3$** at 8 wt%. Symbols: *G*, glassy; *K*, crystalline; *I*, isotropic.

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**)[1] and 2-chloro-4,6-biphenyl-1,3,5-triazine (**10**)[2] were synthesized following literature procedures. All reactions were carried out under argon and anhydrous conditions unless noted otherwise.



Scheme S1. Synthesis of ***t*Bu-TPA-*p*-TRZ**, ***t*Bu-TPA-*m*-TRZ** and ***t*Bu-TPA-*ℓ*-TRZ**.

4-Bromo-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, **2**. To a solution of $Pd_2(dba)_3$ (0.25 g, 0.27 mmol), and dppf (0.23 g, 0.41 mmol) in toluene (50 ml) was added NaO*t*Bu (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 $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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 $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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), $Pd(PPh_3)_4$ (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 $MgSO_4$. 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** (0.30g, 45%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$, 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 $Pd_2(dba)_3$ (0.25 g, 0.27 mmol), and dppf (0.23 g, 0.41 mmol) in toluene (50 ml) was added NaO*t*Bu (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 $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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 $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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 H_2O (30 ml) were added into a mixture of **7** (2.55 g, 5.27 mmol), 1,3-dibromobenzene (3.73 g, 15.82 mmol), $Pd(PPh_3)_4$ (0.22 g, 0.11 mmol), and Na_2CO_3 (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 $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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 $MgSO_4$. 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): δ (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-dimethylehtyl)phenyl)amino)phenyl)phenyl)-4,6-diphenyl-1,3,5-triazine, ***t*Bu-TPA-*p*-TRZ**. Toluene (15 ml) and H_2O (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_2CO_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 ***t*Bu-TPA-*p*-TRZ** (0.51 g, 71%) as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (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-dimethylehtyl)phenyl)amino)phenyl)phenyl)-4,6-diphenyl-1,3,5-triazine, ***t*Bu-TPA-*m*-TRZ**. Toluene (20 ml) and H_2O (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_2CO_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 ***t*Bu-TPA-*m*-TRZ** (1.07 g, 90%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (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-(3-(4-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)propyl)phenyl)-4,6-diphenyl-1,3,5-triazine, ***t*Bu-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 ^{o}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), $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol), Na_2CO_3 (3.18 g, 30 mmol), H_2O (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 $MgSO_4$. 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-*Δ*-TRZ** (0.25 g, 50%) as a pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (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 $C_{50}H_{50}N_4$ (%): C 84.95, H 7.13, N 7.93; found: C 84.68, H 7.10, N 7.78.

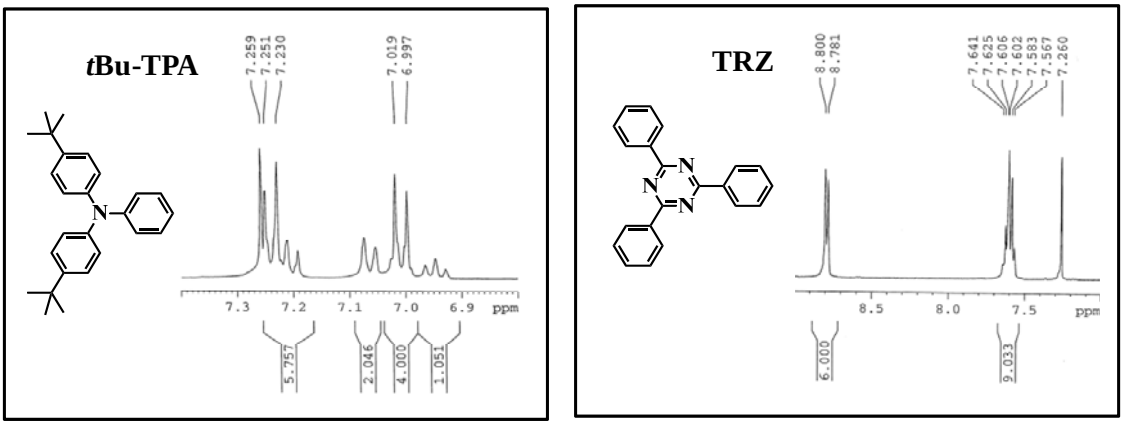


Figure S4. Proton-NMR spectra of ***t*Bu-TPA** and **TRZ** in $CDCl_3$.

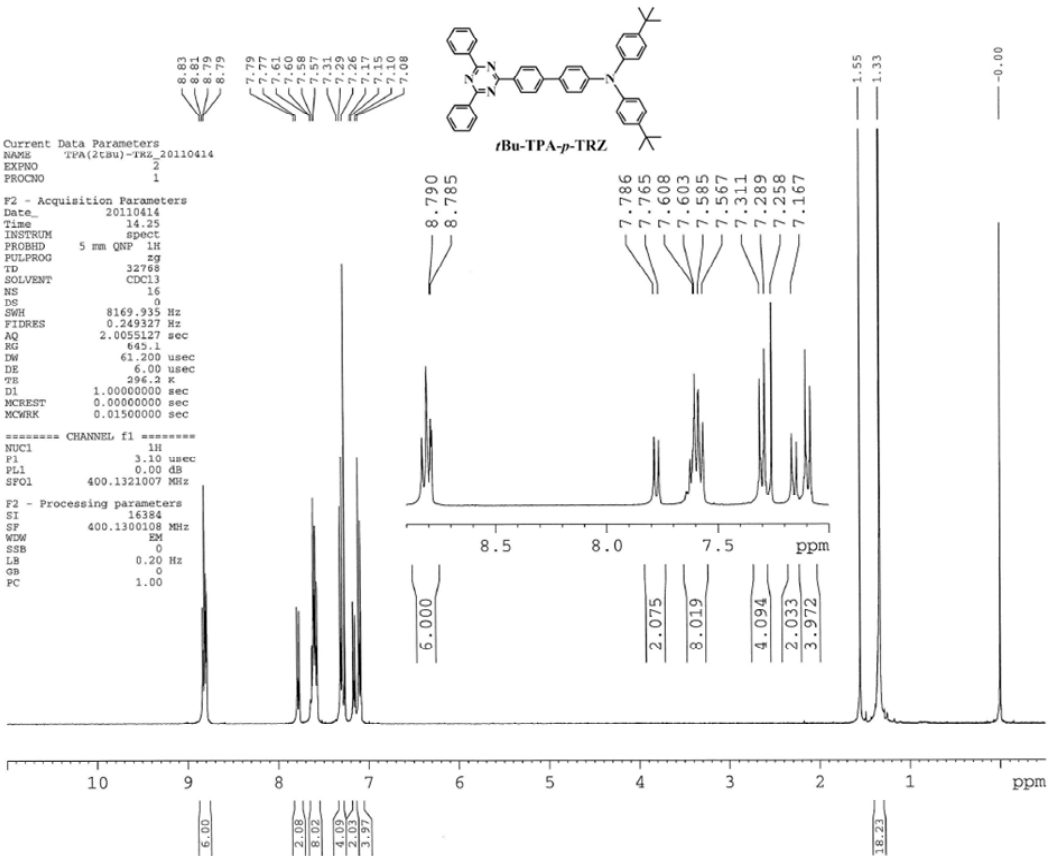


Figure S5. Proton-NMR spectrum of ***t*Bu-TPA-*p*-TRZ** in $CDCl_3$.

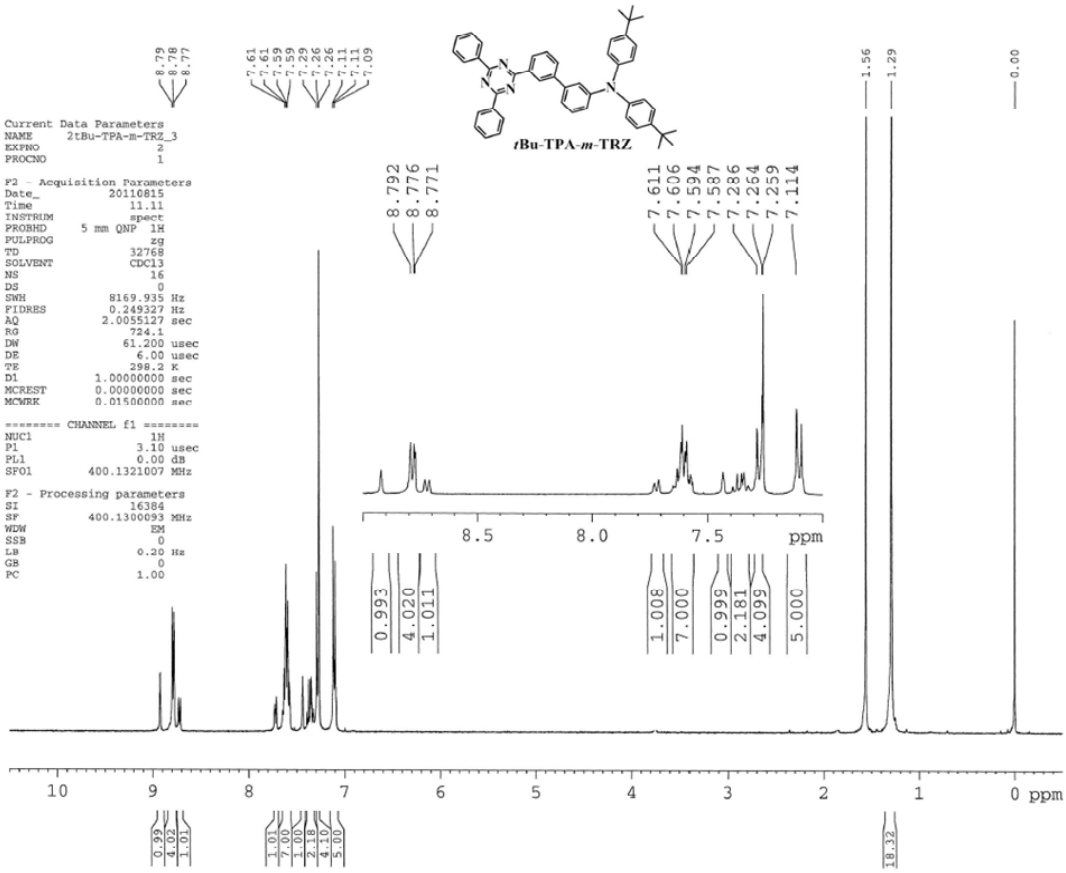


Figure S6. Proton-NMR spectrum of ***t*Bu-TPA-*m*-TRZ** in $CDCl_3$.

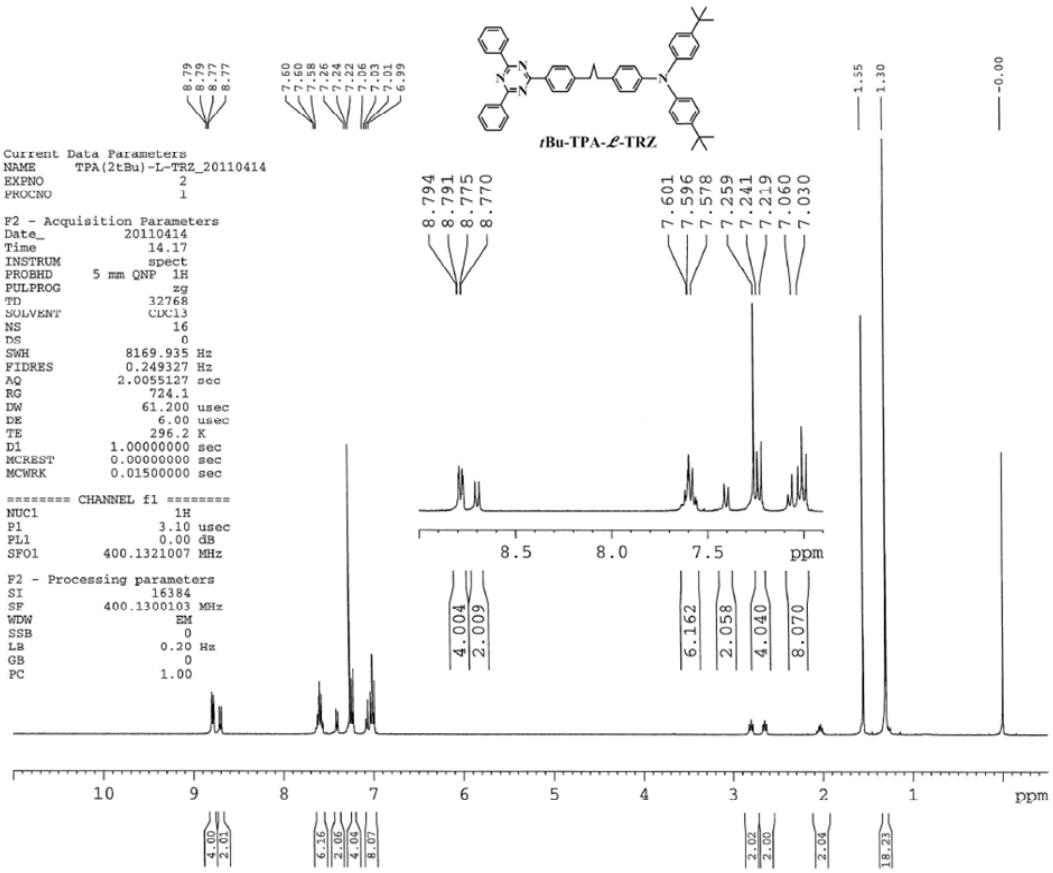


Figure S7. Proton-NMR spectrum of ***t*Bu-TPA-ℒ-TRZ** in $CDCl_3$.

References

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