

Efficient Solid Emitters with Aggregation-Induced Emission and Intramolecular Charge Transfer Characteristics: Molecular Design, Synthesis, Photophysical Behaviors, and OLED Application

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Synthetic Procedures and Characterization Data

Synthesis of 2-(4-bromophenyl)-3,3-diphenylacrylonitrile (3). Into a 500 mL, three-necked, round-bottom flask equipped with a condenser were placed 8.1 g of benzophenone (**2**), 2.2 g of 60% NaH, and 80 mL of benzene under nitrogen. The mixture was reflux for 10 min, then 9.4 g of 4-bromobenzonitrile (**1**) in 150 mL of benzene was added dropwise over 60 min while maintaining reflux. Evolving H_2 was observed at the oil bubbler and the reaction was lasted for another 20 h. Upon cooling to room temperature, 100 mL of water was added to the mixture. The organic layer was collected and washed with brine three times. The organic phase was then dried over anhydrous Na_2SO_4 and concen-

trated under vacuum. Addition of methanol gives pale yellow crystals in 86.3% yield. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.43 (m, 5H), 7.34 (d, 2H), 7.29 (m, 1H), 7.22 (t, 2H), 7.14 (d, 2H), 7.01 (d, 2H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 158.41, 140.12, 138.72, 133.80, 131.70, 131.25, 130.67, 130.09, 129.87, 129.26, 128.49, 128.44, 122.55, 119.71, 110.43.

Synthesis of 2-(4-pinacolatoboronphenyl)-3,3-diphenylacrylonitrile (5). Into a 100 mL one-necked round-bottom flask were placed 2.16 g of **3** (6 mmol), 1.68 g of bis(pinacolato)diborane (**4**, 6.6 mmol), 1.77 g of KOAc (18 mmol), and 114 mg of Pd(dppf)Cl_2 (0.156 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen for three times. Then 40 mL of dimethylacetamide (DMA) was injected. Before heating the mixture, the sealing rubber plug was secured with copper wire. Then the mixture was heated to 80 °C under stirring for 2 h. Upon cooling to room temperature, the mixture was diluted with 30 mL of benzene and washed with water and brine, then dried over anhydrous Na_2SO_4 . The resulting filtrate was concentrated under vacuum, then diluted with methanol to afford an off white powder in 70.6% yield. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.63 (d, 2H), 7.44, 7.43 (m, 5H), 7.27 (m, emerged with the solvent peak), 7.18 (t, 2H), 7.00 (d, 2H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 158.27, 140.40, 138.98, 137.48, 134.76, 130.76, 129.93, 128.93, 128.44, 128.29, 120.04, 115.43, 111.57, 83.97, 24.86. HRMS (MALDI-TOF, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{BNO}_2$, 408.2135; found 408.2175.

Synthesis of $N^4, N^4, N^{4'}, N^{4'}$ -tetraphenylbiphenyl-4,4'-diamine (8, DTPA). Into a 500 mL, two-necked, round-bottom flask equipped with a condenser were placed 4.06 g of diphenylamine (**6**, 24 mmol), 4.06 g of 4,4'-diiodobiphenyl (**7**, 10 mmol), 5.53 g of K_2CO_3 (40 mmol), 2.54 g of copper powder (40 mmol), and 0.5 mL of 18-crown-6. After the flask was vacuumized and flushed with nitrogen for three times, 200 mL of DMF was injected. The resulting mixture was stirred and heated to reflux for 24 h. Upon cooling to room temperature, 300 mL of water was added to the mixture. Then the mixture was extracted with dichloromethane (DCM) for three times (3×150 mL) and the collected organic layer was washed by brine twice (2×150 mL). After being dried over anhydrous Na_2SO_4 , the crude product was

condensed and purified on a silica-gel column using chloroform/hexanes (1:9 by volume) as eluent. White solid; yield 83.5%. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.43 (d, 4H), 7.28, 7.26, and 7.24 (t, emerged with solvent peak), 7.13 and 7.11 (m, 12 H), 7.02 (t, 4H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 147.72, 146.73, 134.74, 129.23, 127.28, 124.29, 124.07, 122.80.

Synthesis of N^4,N^4,N^4,N^4 -tetrakis(4-iodophenyl)-[1,1'-biphenyl]-4,4'-diamine (9). Into a 250 mL, two-necked, round-bottom flask equipped with a condenser were placed 977.2 mg of **8** (2 mmol), 879.8 mg of potassium iodide (KI, 5.25 mmol), 1.13 g of potassium iodate (KIO_3 , 5.25 mmol), and 100 mL of acetic acid. The mixture was heated to 80 °C under stirring. With increasing reaction time, large amount of solid was precipitated out of the solution. Then 50 mL of THF was added and the mixture was further heated to 100 °C to obtain a clear and homogenous mixture. After reaction for 12 h, the mixture was cooled to room temperature. Then the mixture was poured into large amount of water. The precipitates were collected through vacuum filtration, and washed consecutively with water, 1 M bicarbonate, sodium thiosulfate, and water. The crude product was purified on a silica-gel column using chloroform/hexanes (1:4 by volume) as eluent. Light yellow solid; yield 78.2%. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.53 (d, 8H), 7.44 (d, 4H), 7.11 (d, 4 H), 6.87 (d, 8H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 146.94, 145.78, 138.32, 135.62, 127.68, 125.90, 124.72, 86.01. HRMS (MALDI-TOF, m/z): M^+ calcd for $\text{C}_{36}\text{H}_{24}\text{I}_4\text{N}_2$, 991.8118; found 991.8166.

Synthesis of TPA3TPAN. Into a 50 mL, two-necked, round-bottom flask were added 207.7 mg of **10** (0.33 mmol), 488.8 mg of **5** (1.2 mmol), and 21.4 mg $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.03 mmol). The flask was evacuated under vacuum and then flushed with dry nitrogen three times. 20 mL of THF and 3 mL of 2 M sodium carbonate solution were injected into the flask and the mixture was refluxed for 2 days and then slowly cooled to room temperature. The solution was poured into water and extracted with DCM. The collected organic layer was washed with water and brine twice, and then dried over anhydrous Na_2SO_4 . After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography using chloroform/hexanes (gradually changed from 1:4~1:1 by volume) as eluent. A yellow solid

was obtained in 73.2% yield. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.50, 7.48, 7.46, 7.44, 7.42, 7.33, 7.31, 7.27, 7.23, 7.21, 7.19, 7.17, 7.07, 7.05. ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 157.52, 146.96, 140.47, 140.17, 139.19, 134.53, 133.40, 130.79, 130.16, 129.95, 129.89, 129.02, 128.46, 128.33, 127.78, 126.45, 124.44, 111.27. HRMS (MALDI-TOF, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{81}\text{H}_{54}\text{N}_4$, 1083.4427; found, 1083.4620.

Synthesis of DTPA4TPAN. The experimental procedure for DTPA4TPAN is similar to that for the synthesis of TPA3TPAN described above. A yellow solid was obtained in 65.6% yield. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.52, 7.50, 7.48, 7.46, 7.44, 7.34, 7.32, 7.30, 7.28, 7.24, 7.22, 7.20, 7.18, 7.07, 7.06. ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 157.51, 141.09, 140.46, 139.18, 133.36, 131.44, 130.79, 130.08, 129.95, 129.88, 129.00, 128.91, 128.44, 128.32, 126.47, 126.04, 125.50, 120.14, 111.23. HRMS (MALDI-TOF, m/z): M^+ calcd for $\text{C}_{120}\text{H}_{80}\text{N}_6$, 1605.6478; found, 1605.6542.

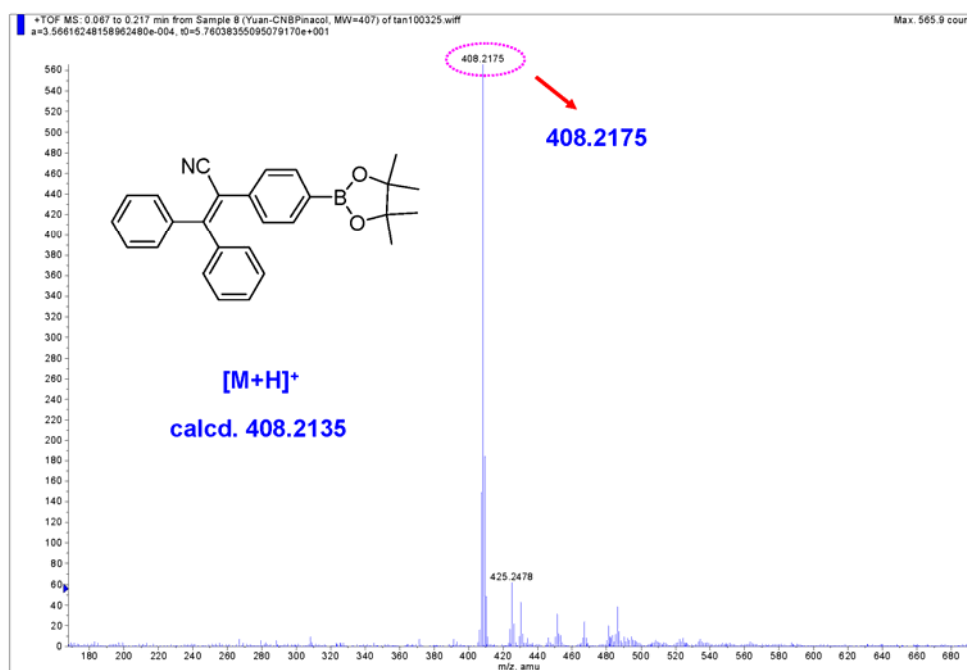


Figure S1. MALDI-TOF mass spectrum of compound **5**.

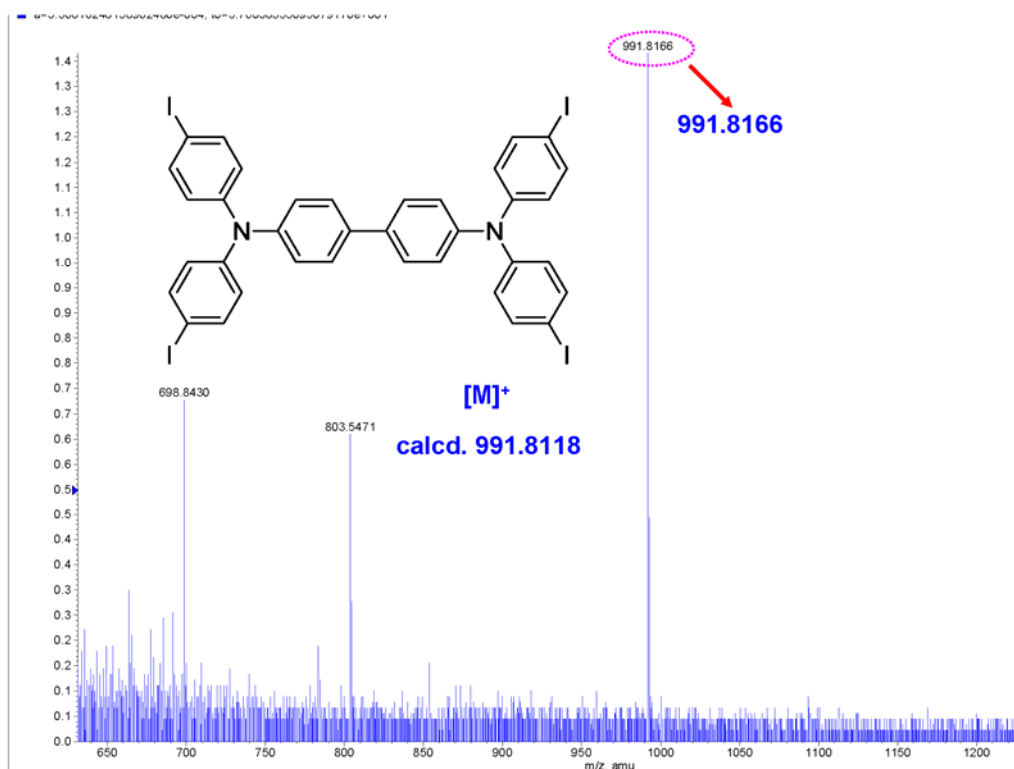


Figure S2. MALDI-TOF mass spectrum of compound **9**.

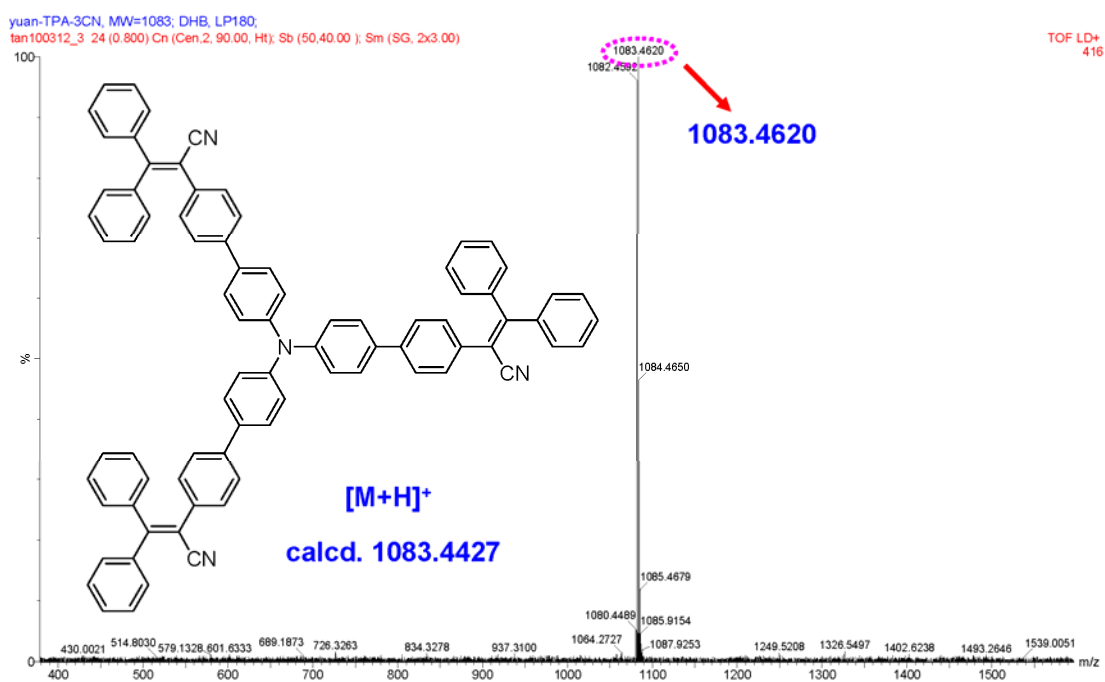


Figure S3. MALDI-TOF mass spectrum of TPA3TPAN.

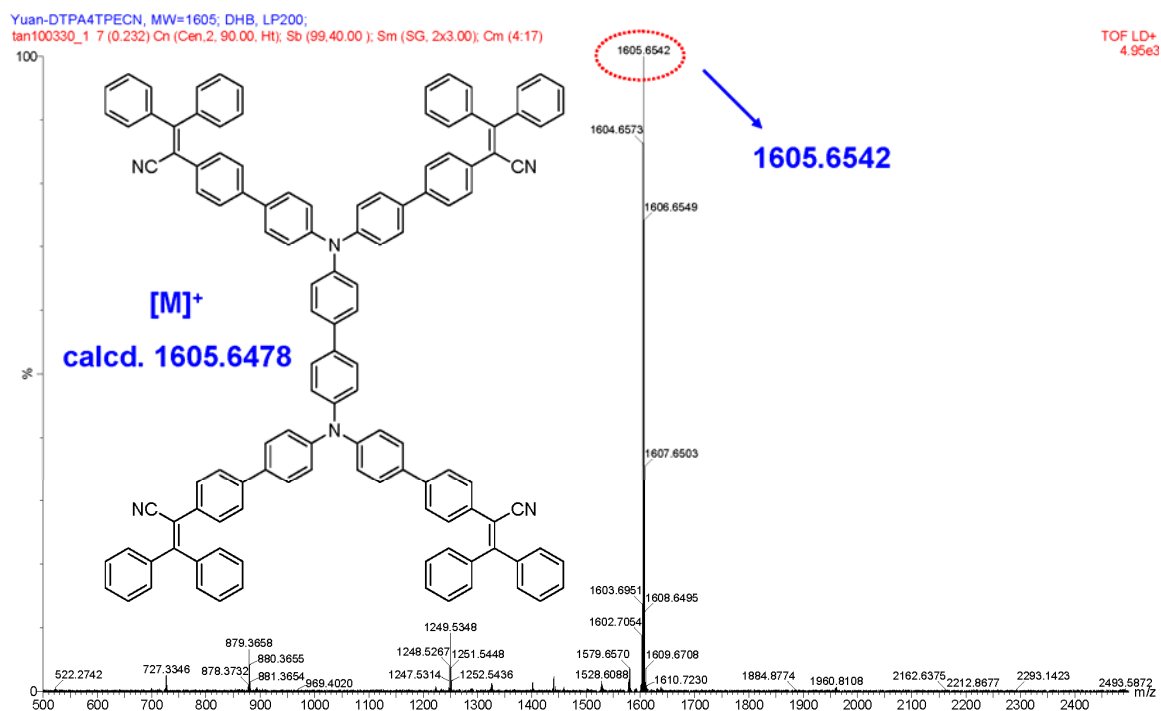


Figure S4. MALDI-TOF mass spectrum of DTPA4TPAN.

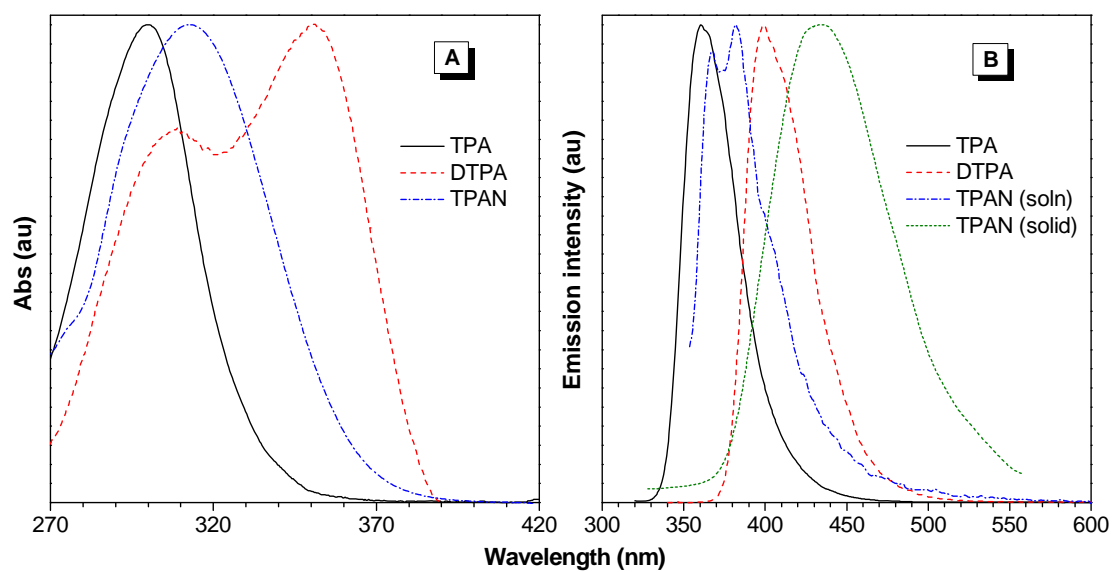


Figure S5. Normalized (A) absorption and (B) emission spectra of TPA, DTPA, and TPAN in THF and as crystalline solid powders. Concentration (μM): 20 (TPAN), 50 (TPA, DTPA).

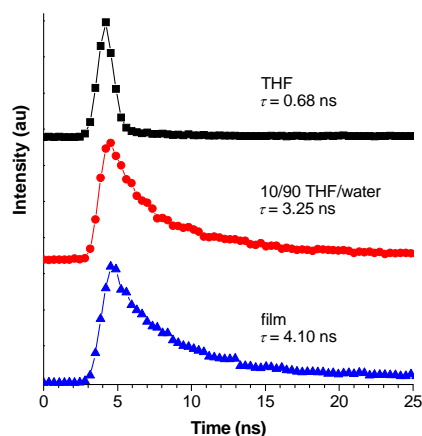


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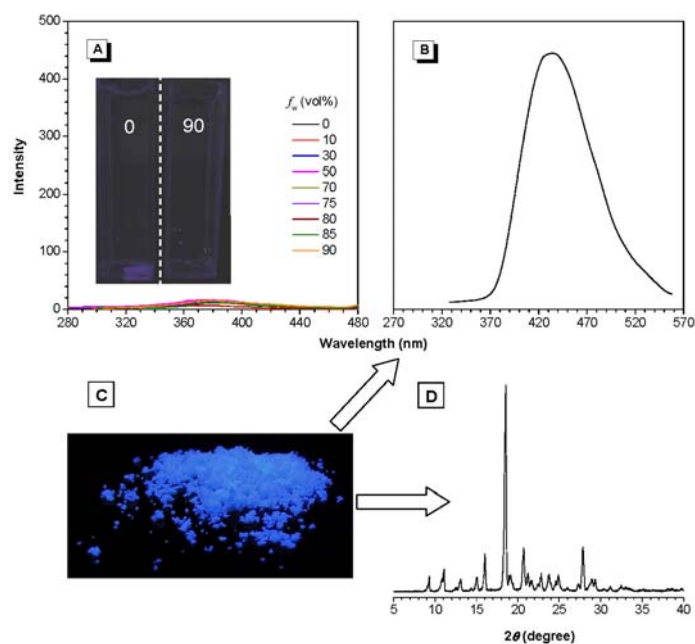


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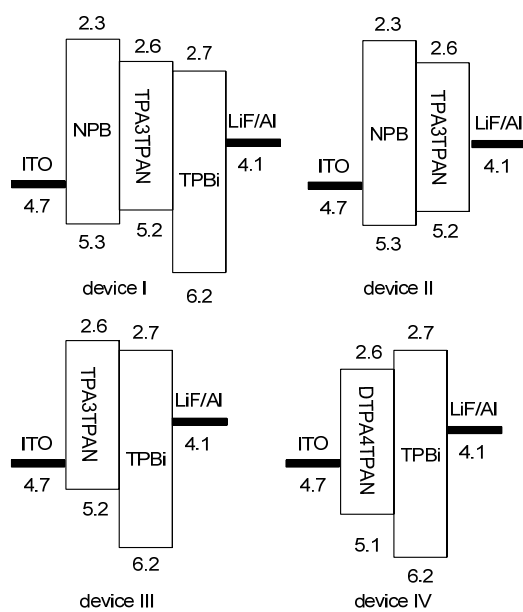


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