# **Electronic Supplementary Information**

# Rational design of high efficiency green to deep red/nearinfrared emitting materials based on isomeric donoracceptor chromophores

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## 1. General considerations for characterization

Instrument: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. MALDI-TOF mass spectrometric measurements were performed on a Bruker Bifiex III MALDI-TOF spectrometer. Thermogravimetric analysis (TGA) was conducted under a dry nitrogen gas flow at a heating rate of 10 °C min<sup>-1</sup> on a Perkin-Elmer TGA 7. UV-Vis absorption spectra were recorded on a HP-8453 UV-visible system. Cyclic voltammetry was carried out on a CHI660A electrochemical work station in a three-electrode cell dipped in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution under nitrogen protection at a scan rate of 100 mV/s and room temperature (RT). In this three-electrode cell, a platinum rod, platinum wire and Ag/AgCl electrode were used as a working electrode, counter electrode and reference electrode, respectively. Steady state fluorescence spectra, fluorescence lifetime, and quantum efficiency were measured with Edinburgh fluorescence spectrometer (FLS980) with an integrating sphere. Lifetime in the time range from 0 ns to 150 ns was measured using picosecond pulsed diode laser under the excitation at 375 nm. The DFT calculations were performed with the Gaussian09 series of programs using the B3LYP hybrid functional and 6-31G(d, p) basis set.

# 2. Device fabrication and characterization

The layers of HATCN (20 nm)/TAPC (40 nm)/EML (30 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (100 nm) were successively deposited on the pre-cleaned ITO glass substrates at a pressure of less than  $10^{-4}$  Torr. The active area of devices was 2 mm × 2

mm. The EL spectra of devices were measured by fiber optic spectrometer (Ocean Optics USB 2000) in the normal direction. The *J-V-L* curves were investigated by a dual-channel Keithley 2614B source measure unit and a PIN-25D silicon photodiode. All the measurements were conducted at room temperature under ambient condition.

## **3.** Experimental section

Synthesis of TPA-BT-Q: To a mixture of 5 (0.147 g, 2.38 mmol), 6 (0.588 g, 2.86 mmol), and tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.165 g) was added a degassed mixture of toluene (50 mL), anhydrous ethanol (10 mL) and 2 M potassium carbonate aqueous solution (9 mL). The mixture was refluxed for 23 h under the protection of nitrogen. After being cooled to room temperature, the mixture was poured into water (100 mL). It was extracted with dichloromethane (DCM) ( $3 \times 120$  mL) and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent was removed off by rotary evaporation and the residue was passed through a flash silica gel column with DCM as the eluent to give a red solid (0.941 g, yield 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.73 (d, J = 3.8 Hz, 1H), 7.97 (d, J = 12.6 Hz, 1H), 7.91 (d, J = 6.8 Hz, 3H), 7.83 (dd, J = 15.8, 6.4 Hz, 3H), 7.74 (t, J = 7.6 Hz, 1H), 7.55 - 7.47(m, 1H), 7.32 (d, J = 6.7 Hz, 4H), 7.21 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 4H), 1.34 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 31.47, 34.38, 121.01, 121.78, 124.72, 126.20, 126.54, 127.12, 127.35, 127.65, 129.65, 130.00, 130.44, 131.28, 134.84, 136.82, 142.26, 144.66, 146.37, 148.77, 153.71, 154.78, 157.34. MALDI-MS (m/z) calcd for C<sub>41</sub>H<sub>38</sub>N<sub>4</sub>S [M]<sup>+</sup>: 618.83. Found: 619.11.

Synthesis of 9: To a mixture of 7 (1.860 g, 10.50 mmol), 8 (3.502 g, 12.11 mmol), and

tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.504 g) was added a degassed mixture of toluene (80 mL), anhydrous ethanol (20 mL) and 2 M potassium carbonate aqueous solution (10 mL). The mixture was refluxed for 8 h under the protection of nitrogen. After being cooled to room temperature, the mixture was poured into water (120 mL). It was extracted with DCM (3 × 150 mL) and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent was removed off by rotary evaporation and the residue was passed through a flash silica gel column with petroleum ether (PE)/DCM ( $\nu/\nu$ , 2:1) as the eluent to give a red solid (2.155 g, yield 58%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.96 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.98 (t, J = 8.2 Hz, 2H), 7.90 (d, J = 7.0 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 156.28, 155.12, 150.82, 145.62, 134.02, 133.21, 131.16, 130.85, 130.76, 129.50, 128.61, 126.95, 126.29, 125.30, 125.22, 125.04, 124.98, 110.25. MALDI-MS (m/z) calcd for C<sub>15</sub>H<sub>8</sub>BrN<sub>3</sub>S [M+H]<sup>+</sup>: 343.21. Found: 343.97.

Synthesis of TPA-pyT-N-naph: The ligand TPA-pyT-N-naph was synthesized by the similar synthetic procedure for TPA-BT-Q with compounds 1 (1.203 g, 2.55 mmol) and 9 (0.793 g, 2.32 mmol) as starting materials and obtained as a crimson solid with a yield of 61% (0.875 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.04 (d, J = 8.2 Hz, 2H), 7.95 (t, J = 9.2 Hz, 4H), 7.66 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 4H), 7.22 (t, J = 8.2 Hz, 3H), 7.15 (d, J = 8.6 Hz, 4H), 1.34 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 156.24, 153.56, 151.25, 149.18, 146.65, 144.49, 141.41, 134.22, 134.07, 131.51, 130.29, 129.87, 129.26, 128.54, 127.30, 126.73, 126.46, 126.28, 126.14, 125.64, 125.06, 124.91, 121.66, 34.41, 31.48. MALDI-MS (*m/z*) calcd for C<sub>41</sub>H<sub>38</sub>N<sub>4</sub>S [M]<sup>+</sup>: 618.28. Found: 618.29.

Synthesis of 10: The compound 10 was synthesized by the similar synthetic procedure for 9 with compounds 1 (2.655 g, 5.50 mmol) and 8 (1.95 g, 6.60 mmol) as the starting materials and obtained as a red solid with a yield of 77% (2.414 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.73 (s, 1H), 8.47 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.6 Hz, 4H), 7.13 (dd, J = 8.6, 3.8 Hz, 6H), 1.33 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 150.97, 146.31, 144.67, 135.77, 126.35, 126.10, 125.30, 124.61, 121.00, 120.37, 83.46, 34.34, 31.48. ESI-MS (*m/z*) calcd for C<sub>31</sub>H<sub>31</sub>BrN<sub>4</sub>S [M]<sup>+</sup>: 571.57. Found: 571.65.

Synthesis of TPA-N-pyT-naph: The ligand TPA-N-pyT-Nnaph was synthesized by the similar synthetic procedure for **TPA-BT-Q** with compounds **7** (0.166 g, 0.96 mmol) and **10** (0.459 g, 0.80 mmol) as the starting materials and obtained as a crimson solid with a yield of 52% (0.251 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.72 (s, 1H), 8.58 (d, *J* = 8.8 Hz, 2H), 7.98 (dd, *J* = 13.6, 8.2 Hz, 2H), 7.69–7.59 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45–7.37 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 4H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 4H), 1.34 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 158.21, 152.58, 150.62, 149.36, 147.02, 145.02, 144.20, 133.90, 132.66, 132.05, 131.02, 129.26, 128.58, 128.51, 126.36, 126.31, 126.14, 125.78, 125.50, 125.44, 125.24, 120.65, 34.44, 31.47. MALDI-MS (*m/z*) calcd for C<sub>41</sub>H<sub>38</sub>N<sub>4</sub>S [M]<sup>+</sup>: 618.28. Found: 618.29.

**Synthesis of 11:** The compound **11** was synthesized by the similar synthetic procedure for **9** with compounds **2** (5.36 g, 18.2 mmol) and **7** (2.85 g, 16.6 mmol) as the starting materials and obtained as a yellow solid with a yield of 55% (3.104 g). <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.03–7.92 (m, 3H), 7.64–7.54 (m, 3H), 7.51 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 154.39, 153.46, 134.60, 133.80, 133.63, 132.04, 131.69, 130.78, 129.21, 128.57, 127.98, 126.37, 126.13, 125.64, 125.31, 113.63. MALDI-MS (m/z) calcd for C<sub>16</sub>H<sub>9</sub>BrN<sub>2</sub>S [M+H]<sup>+</sup>: 341.23. Found: 341.05.

Synthesis of 13: To a mixture of 11 (0.341 g, 1.00 mmol), 12 (0.447 g, 1.00 mmol), and tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.116 g) was added a degassed mixture of toluene (10 mL). The mixture was refluxed for 15 h under the protection of nitrogen. After the mixture was cooled to room temperature, the solvent was removed off by rotary evaporation and the residue was passed through a flash silica gel column with petroleum ether (PE)/DCM ( $\nu/\nu$ , 1.5:1) as the eluent to give a red solid (0.220 g, yield 53%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.86 (d, J = 4.0 Hz, 1H), 8.76 (s, 1H), 8.64 (d, J = 4.4 Hz, 1H), 8.05 (d, J = 4.4 Hz, 1H), 7.98 (m, 2H), 7.68 (d, J = 5.4 Hz, 1H), 7.58 (m, 3H), 7.48 (d, J = 6.8 Hz, 1H), 7.28 (d, J = 6.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 155.54, 155.42, 152.97, 152.85, 152.41, 150.81, 139.28, 135.29, 135.07, 133.84, 131.82, 131.73, 130.69, 130.06, 129.35, 129.10, 128.55, 128.45, 128.02, 126.29, 126.08, 126.06, 125.83, 125.33, 120.31. MALDI-MS (m/z) calcd for C<sub>21</sub>H<sub>12</sub>BrN<sub>3</sub>S [M+H]<sup>+</sup>: 418.99. Found: 418.99.

**Synthesis of DPA-py-N-BT-naph:** To a mixture of **13** (0.437 g, 1.05 mmol), **14** (0.281 g, 1.00 mmol), palladium acetate (Pd(OAc)<sub>2</sub>, 3 mg), RuPhos (9 mg) and sodium *tert*-butoxide (0.115 g, 1.20 mmol) was added a degassed mixture of toluene (5 mL). The mixture was refluxed for 16 h under the protection of nitrogen. After being cooled to

room temperature, the mixture was poured into water (50 mL). It was extracted with DCM (3 × 80 mL) and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent was removed off by rotary evaporation and the residue was passed through a flash silica gel column with petroleum ether (PE)/DCM ( $\nu/\nu$ , 1.5:1) as the eluent to give a yellow solid (0.358 g, yield 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.64 (d, J = 8.0 Hz, 2H), 8.50 (m, 2H), 7.94 (d, J = 12.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.78 (m, 3H), 7.57 (d, J = 4.8 Hz, 1H), 7.50 (m, 1H), 7.73 (m, 5H), 7.15 (d, J = 8.0 Hz, 4H), 1.34 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 155.59, 153.03, 147.25, 144.25, 143.67, 135.63, 133.84, 133.39, 131.94, 130.89, 128.87, 128.48, 128.08, 127.99, 127.82, 126.53, 126.17, 125.97, 125.33, 124.93, 124.64, 34.45, 31.43. MALDI-MS (m/z) calcd for C<sub>41</sub>H<sub>38</sub>N<sub>4</sub>S [M]<sup>+</sup>: 618.28. Found: 618.29.



Fig. S1. Synthetic routes of TPA-BT-Q, TPA-pyT-N-naph, TPA-N-pyT-naph and DPA-py-N-BT-naph



Fig. S2. Thermogravimetric analysis for TPA-BT-Q, TPA-pyT-N-naph, TPA-N-pyT-naph, and DPA-py-N-BT-naph.



**Fig. S3**. Cyclic voltammograms for isomers in chloroform solution with a scan rate of 100 mV s<sup>-1</sup> using 0.1 mol/L Bu<sub>4</sub>NPF<sub>6</sub> and ferrocene as the electrolyte and internal standard, respectively.



**Fig. S4.** Cyclic voltammograms for isomers in ethyl acetate solution with a scan rate of 100 mV s<sup>-1</sup> using 0.1 mol/L Bu<sub>4</sub>NPF<sub>6</sub> and ferrocene as the electrolyte and internal standard, respectively.



Fig. S5. UV-vis absorption spectra of TPA-BT-Q, TPA-pyT-N-naph, TPA-N-pyT-naph and DPA-py-N-BT-naph in neat films



Fig. S6. PL spectra of TPA-BT-Q, TPA-pyT-N-naph, TPA-N-pyT-naph and DPApy-N-BT-naph in PMMA films



**Fig. S7**. Lippert-Mataga plots of **TPA-BT-Q** (a), **TPA-pyT-N-naph** (b), **TPA-N-pyT-naph** (c) and **DPA-py-N-BT-naph** (d).



Fig. S8. Lifetime measurements of TPA-BT-Q (a), TPA-pyT-N-naph (b), TPA-N-

## pyT-naph (c) and DPA-py-N-BT-naph (d) in different solvents



Fig. S9. Lifetime measurements of TPA-BT-Q, TPA-pyT-N-naph, TPA-N-pyT-naph and DPA-py-N-BT-naph in neat films (a) and 8 wt% doped in PMMA films (b)



**Fig. S10**. Electroluminescence (EL) spectra (a), current density-voltage-luminance (J-V-L) (b), current efficiency-current density (CE-J) (c), power efficiency-current density (PE-J) (d) and external quantum efficiency-current density (EQE-J) (e) curves for **TPA-N-pyT-naph** based non-doped devices with configuration of ITO/HATCN (20 nm)/TAPC (40 nm)/**TPA-N-pyT-naph** (30 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (100 nm)



**Fig. S11**. Electroluminescence (EL) spectra (a), current density-voltage-luminance (J-V-L) (b), current efficiency-current density (CE-J) (c), power efficiency-current density (PE-J) (d) and external quantum efficiency-current density (EQE-J) (e) curves for **TPA-N-pyT-naph** based doped devices with configuration of ITO/HATCN (20 nm)/TAPC (40 nm)/**TPA-N-pyT-naph**:AlQ<sub>3</sub> (8 wt%, 30 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (100 nm)



**Fig. S12**. Electroluminescence (EL) spectra (a), current density-voltage-luminance (J-V-L) (b), current efficiency-current density (CE-J) (c), power efficiency-current density (PE-J) (d) and external quantum efficiency-current density (EQE-J) (e) curves for **TPA-N-pyT-naph** based doped devices with configuration of ITO/HATCN (20 nm)/TAPC (40 nm)/**TPA-N-pyT-naph**: *m*CP (8 wt%, 30 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (100 nm)



**Fig. S13**. Emission spectra of Xenon lamp and TPA-BT-Q:AlQ<sub>3</sub> + TPA-BT-Q:*m*CP composed film.



**Fig. S14**. Emission spectra of Xenon lamp and TPA-pyT-N-naph:AlQ<sub>3</sub> + TPA-pyT-N-naph:*m*CP composed film.



**Fig. S15**. Emission spectra of Xenon lamp and TPA-N-pyT-naph:AlQ<sub>3</sub> + TPA-N-pyT-naph:*m*CP composed film.



**Fig. S16**. Emission spectra of Xenon lamp and DPA-py-N-BT-naph:AlQ<sub>3</sub> + DPA-py-N-BT-naph:*m*CP composed film.







Fig. S18. <sup>13</sup>C NMR spectrum of 9



Fig. S19. <sup>1</sup>H NMR spectrum of 10



Fig. S20. <sup>13</sup>C NMR spectrum of 10







Fig. S22. <sup>13</sup>C NMR spectrum of 11







Fig. S24. <sup>13</sup>C NMR spectrum of 13



Fig. S25. <sup>1</sup>H NMR spectrum of TPA-BT-Q



Fig. S26. <sup>13</sup>C NMR spectrum of TPA-BT-Q



Fig. S27. <sup>1</sup>H NMR spectrum of TPA-pyT-N-naph



Fig. S28. <sup>13</sup>C NMR spectrum of TPA-pyT-N-naph



Fig. S29. <sup>1</sup>H NMR spectrum of TPA-N-pyT-naph



Fig. S30. <sup>13</sup>C NMR spectrum of TPA-N-pyT-naph



Fig. S31. <sup>1</sup>H NMR spectrum of DPA-py-N-BT-naph



Fig. S32. <sup>13</sup>C NMR spectrum of DPA-py-N-BT-naph



Fig. S33. MALDI-TOF mass spectrum of TPA-BT-Q



Fig. S34. MALDI-TOF mass spectrum of TPA-pyT-N-naph



Fig. S35. MALDI-TOF mass spectrum of TPA-N-pyT-N-naph



Fig. S36. MALDI-TOF mass spectrum of DPA-py-N-BT-naph