Supporting information

Highly efficient near infrared organic solid fluorophore based on naphthothiadiazole derivatives with aggregation-induced emission enhancement for non-doped electroluminescent device

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Experimental Methods

All reagents were purchased from Aldrich and TCI companies. They were used without further purification. Solvents were dried by using standard procedures.

¹H-NMR and ¹³C-NMR spectra were recorded on Bruker Avance-600 or 500 spectrometers. A Bruker microflex MALDI-TOF mass spectrometer was used to obtain the high-resolution mass spectra of the samples. Differential scanning calorimetry (DSC) was performed using PerkinElmer DSC-8500 thermal analyzer at a heating rate of 10 °C min⁻¹ under N₂ flow. Thermalgravimetric (TGA) was recorded by TGA/DSC1 Mettler Toledo at a heating rate of 10 $^{\circ}$ C min⁻¹ under N₂ flow. UV-visible absorption spectra were obtained in CH₂Cl₂ on a Perkin-Elmer UV Lambda 1050 spectrometer. Photoluminescence and lifetime were measured by steady state, fluorescence and phosphorescence lifetime spectrometer FLS980 Edinburgh Instruments. Absolute quantum yield ($\Phi_{\rm F}$) was measured by integrating sphere on an Edinburgh FLS980 fluorospectrophotometer. Photoelectron spectroscopy (AC-2) was measured by Riken-Keiki ultraviolet photoelectron spectrometer AC-2 in air. Cyclic voltammetry (CV) measurements were performed on an Autolab potentiostat PGSTAT 101 equipped with platinum counter electrode, glassy carbon working electrode, Ag/AgCl reference electrode and n-Bu₄NPF₆ as a supporting electrolyte in CH₂Cl₂ under Ar atmosphere at a scan rate of 50 mV s⁻¹. The concentration of analytical materials and the electrolyte were 10⁻³ and 0.1 M, respectively. Melting points were measured using a Krüss KSP1N melting point meter and are uncorrected.

The quantum chemical calculations were performed with Gaussian 09 program package using density functional theory (DFT).¹ The HOMO and LUMO distributions of the complexes were calculated by DFT B3LYP/6-31G (d) for the main-group atoms.

OLED devices using **TPE3HN** and **TPE4HN** as EML with non-doped configurations of ITO/PEDOT: PSS (40nm)/NPB (30 nm)/**TPE3HN** or **TPE4HN** (50 nm)/TPBi (35 nm)/LiF (0.5 nm): AI (150 nm), were fabricated and characterized as followed. The patterned indium tin oxide (ITO) glass substrate with a sheet resistance $12 \Omega \text{ sq}^{-1}$. was thoroughly cleaned by successive ultrasonic treatment in Liquinox detergent, deionized water, acetone, and isopropanol and brew with nitrogen for drying. The cleaned ITO was then treated by UV ozone for 30 min before deposited the hole injection layer (HTL) layer. A 40 nm thick poly(3,4-ethylenedioxythiophene): poly(4-styrene sulfonate) (PEDOT:PSS, CLEVIOSTM P VP AI 4083) hole injection layer was spin-coated on top of UV ozone treated ITO from a 1.2 wt% aqueous dispersion at a spin speed of 5000 rpm for 30 s and dried at 120 °C for 15 min. Subsequently, the 30 nm thick N,N'-Di(1-

naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) hole transport layer was deposited on top of PEDOT: PSS layer by thermal evaporation at the evaporation rate of 1 Å/s from low temperature evaporator sources in Kurt J. Lasker mini SPECTROS 100 thin film deposition system under a base pressure of 5 x 10^{-6} bar. The film thickness was monitored by quartz oscillator thickness sensor. Thin films of **TPE3HN** or **TPE4HN** as EML were deposited on top of NPB layer with 50 nm thick. The 35 nm thick 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-Hbenzimidazole) (TPBi) electron transport layer (ETL) was A 0.5 nm thick LiF and a 150 nm thick aluminium layers were the subsequently deposited through a shadow mask on the top of ETL film without braking vacuum to form an active diode area of 4 mm². Current density-voltageradiance (*J-V-R*) characteristics were measured simultaneous using a Keithley 2400 source meter and a Hamamatsu Photonics PMA-12 multi-channel analyser. The absolute external quantum efficiency (EQE) of OLED devices was obtained by Hamamatsu Photonics C9920-12 External Quantum Efficiency Measurement System utilizing an integrating sphere. All the measurements were performed under ambient atmosphere at room temperature. Hole only device with configuration of ITO/MoO₃/**TPEHN** (100nm)/MoO₃/Al was also fabricated.

Materials synthesis and characterisation



Scheme S1 Synthetic route to **TPE3HN** and **TPE4HN**: *Reagents and conditions:* (i) Br_2 , glacial acetic acid, R.T., 8 h. (ii) anhydride pyridine, thionylaniline, chlorotromethylsilane, 80 °C, overnight (iii) 2M Na_2CO_3 (aq), Pd(PPh_3)_4, THF, 3-hexylthiophene-2-boronic acid pinacol ester or 4-hexylthiophene-2-boronic acid pinacol ester, reflux, 48 h. (iv) N-Bromosuccinimide, THF, 8 h. (v) KOAc, Pd(dppf)Cl₂, bis(pinacolato)diboron, reflux, overnight (vi) 2M Na_2CO_3 (aq), Pd(PPh_3)_4, THF, reflux, 48 h.

<u>1,4-Dibromonaphthalene-2,3-diamine</u> (2). Naphthalene-2,3-diamine (5g, 31.6 mmol) was dissolved in glacial acetic acid 200 ml and then bromine solution was added by dropwise into the reaction. The mixture was stirred for 6 hours at room temperature. After that the water was poured into the completed reaction and filter the product by using filter paper. The product (2) of 98% yield as a white solid. APCI/Q-TOF (m/z) calcd for (M⁺) $C_{10}H_8Br_2N_2$: 315.9034; found 316.9536.

<u>4,9-Dibromonaphtho[2,3-c][1,2,5]thiadiazole</u> (3). Compound (2) (1g, 3.16 mmol), anhydride pyridine (15ml), thionylaniline (0.75 ml) and chlorotrimetylsilane (4 ml) were stirred at 80°c for 24 hours. When the reaction was completed, methanol was poured into the reaction in order to recrystallize the product. Then the compound 3 was obtained as orange solid. ¹H NMR (600 MHz, CDCl₃) δ ppm: 8.44 (d, J = 7.62 Hz, 2H), 7.61 (d, J = 7.92 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ ppm: 150.52, 133.73, 133.29, 132.35, 131.62, 129.63, 129.51, 128.71, 127.89 and 112.65. APCI/Q-TOF (m/z) calcd for (M⁺) C₁₀H₄Br₂N₂S: 343.8441; found 344.8982.

<u>4,9-Bis(3-hexylthiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole</u> (4a). Compound (3) (1g, 2.91 mmol), 3-hexylthiophene-2-boronic acid pinacol ester (1.88 g, 6.39 mmol) and Pd(PPh₃)₄ (168 mg) were dissolved in THF 40 ml. Then 2M Na₂CO₃ (14.5 ml) was added into the mixture. The mixture was degassed under N₂ for 3 times. The reaction was stirred at reflux under N₂ for overnight. After the completion of reaction, the reaction was poured into water and extracted with DCM. The combined organic phases were washed with water followed by dried with sodium sulfate anhydrous. The product (4a) cannot be purified by column chromatography, so they must be set to next step (bromination) and purify after that.

<u>4,9-Bis(4-hexylthiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole (4b)</u>. Compound (3) (1g, 2.91 mmol), 3-hexylthiophene-2-boronic acid pinacol ester (1.88 g, 6.39 mmol) and Pd(PPh₃)₄ (168 mg) were dissolved in THF 40 ml. Then 2M Na₂CO₃ (14.5 ml) was added into the mixture. The mixture was degassed under N₂ for 3 times. The reaction was stirred at reflux under N₂ for overnight. After the completion of reaction, the reaction was poured into water and extracted with DCM. The combined organic phases were washed with water followed by dried with sodium sulfate anhydrous. The product (4b) of 70% yield as a dark orange solid was obtained by silica gel column chromatography eluting with mixture of dichloromethane and hexane (1:3). ¹H NMR (600 MHz, CDCl₃) δ ppm: 8.32 (dd, J = 3.18, 7.02 Hz, 2H), 7.42 (dd, J = 3.06, 7.08 Hz, 2H), 7.29 (s, 2H), 2.77 (t, J = 7.62 Hz, 4H), 1.78-1.73 (m, 4H), 1.46-1.42 (m, 4H), 1.36-1.35 (m, 8H) and 0.93-0.90 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ ppm: 151.67, 143.45, 136.03, 132.87, 131.80, 127.09, 126.79, 123.85, 122.56, 31.73, 30.61, 30.44, 29.12, 22.64 and 14.09. APCl/Q-TOF (m/z) calcd for (M⁺) C₃₀H₃₄N₂S₃: 518.1884; found 519.1947.

<u>4,9-Bis(5-bromo-3-hexylthiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole (5a)</u>. Compound (4a) (390 mg, 0.75 mmol) was dissolved in THF 10 ml. Then N-bromosuccinimide (334 mg, 1.88 mmol) solution in THF was added by dropwise into the reaction. The reaction was stirred at room temperature for 8 hours. After the completion of reaction, the reaction was poured into water and extracted with DCM. The combined organic phases were washed with water followed by dried with sodium sulfate anhydrous. The product (5a) of 67% yield as an orange solid was obtained by silica gel column chromatography eluting with mixture of dichloromethane and hexane (1:4). ¹H NMR (600 MHz, CDCl₃) δ ppm: 7.98 (s, 2H), 7.44 (s, 2H), 7.17 (s, 2H), 2.27 (t, J = 7.56 Hz, 4H), 1.43-1.42 (m, 4H), 1.03-0.95 (m, 12H) and 0.70-0.67 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ ppm: 152.06, 143.96, 143.68, 133.80, 131.60, 127.36, 126.91, 122.80, 113.42, 31.35, 29.94, 29.16, 28.69, 22.34 and 13.93. APCI/Q-TOF (m/z) calcd for (M⁺) C₃₂H₃₂Br₂N₂S₃: 676.0074; found 677.1341.

<u>4,9-Bis(5-bromo-4-hexylthiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole</u> (5b). The synthesis procedure for compound (4b) (1.7 g, 3.28 mmol) was same as that of compound (5a). The product (5b) of 99% yield as a red solid was obtained by silica gel column chromatography eluting with mixture

of dichloromethane and hexane (1:4). ¹H NMR (600 MHz, CDCl₃) δ ppm: 8.33 (dd, J = 3.12, 6.99 Hz, 2H), 7.45 (dd, J = 3.06, 7.05 Hz, 2H), 7.16 (s, 2H), 2.71 (t, J = 7.56 Hz, 4H), 1.72-1.68 (m, 4H), 1.44-1.43 (m, 4H), 1.35-1.34 (m, 8H) and 0.92-0.90 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ ppm: 151.36, 142.37, 135.87, 132.79, 131.54, 127.20, 126.82, 123.08, 111.84, 31.64, 29.71, 29.70, 29.00, 22.62 and 14.07. APCl/Q-TOF (m/z) calcd for (M⁺) C₃₀H₃₂N₂S₃Br₂: 676.0074; found 676.1133.

4.4.5.5-Tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (7). 1-(4-Bromophenyl)-1,2,2-triphenylethylene (1g, 2.43 mmol), KOAc (2.86g, 29.17 mmol), Pd(dppf)Cl₂ (100mg, 0.12 mmol) and Bis(pinacolato)diboron (1.23g, 4.86 mmol) were dissolved in dry toluene (30 ml). The mixture was degassed under N₂ for 3 times. The reaction mixture was stirred at reflux under N₂ for 24 hours. After the reaction was completed, the water was poured into the reaction and then they were extracted with DCM. The product (7) of 71% yield as a white solid was obtained by silica gel column chromatography eluting with mixture of dichloromethane and hexane (1:1). ¹H NMR (600 MHz, CDCl₃) δ ppm: 7.53 (d, J = 7.80 Hz, 2H), 7.09-7.07 (m, 9H), 7.04-7.00 (m, 8H) and 1.31 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ ppm: 147.00, 143.71, 141.39, 134.09, 131.36, 131.32, 130.69, 127.73, 127.63, 126.52, 126.45, 83.69 and 24.88. APCI/Q-TOF (m/z) calcd for (M⁺) C₃₂H₃₁BO₂: 458.2417; found 459.3385.

4,9-Bis(3-hexyl-5-(4-(1,2,2-triphenylvinyl)phenyl)thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole (TPE3HN). The synthesis procedure for compound (5a) (200 mg, 0.30 mmol) and compound (7) (312mg, 0.68 mmol) was same as that of compound (4a). The product TPE3HN of 68% yield as a red solid was obtained by silica gel column chromatography eluting with mixture of dichloromethane and hexane (1:4). ¹H NMR (600 MHz, CDCl₃) δ ppm: 8.04-8.01 (m, 2H), 7.44 (d, J = 7.80 Hz, 4H), 7.42-7.40 (m, 2H), 7.38 (d, J = 4.62 Hz, 2H), 7.15-7.04 (m, 34H), 2.34-2.29 (m, 4H), 1.50-1.44 (m, 4H), 1.09-0.94 (m, 12H) and 0.72-0.66 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ ppm: 152.21, 144.99, 144.88, 144.31, 144.04, 143.70, 143.57, 143.19, 141.27, 140.47, 133.79, 133.74, 132.25, 131.89, 131.43, 131.37, 129.63, 129.49, 127.83, 127.72, 127.66, 127.19, 127.16, 126.99, 126.59, 126.54, 126.47, 124.86, 124.84, 124.70, 124.66, 123.57, 31.43, 31.32, 30.12, 30.00, 29.39, 29.37, 28.80, 28.73, 22.38, 22.35, 13.97 and 13.89. APCl/Q-TOF (m/z) calcd for (M⁺) C₈₂H₇₀N₂S₃: 1,178.4701; found 1,179.5161.

4,9-Bis(3-hexyl-5-(4-(1,2,2-triphenylvinyl)phenyl)thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole (TPE4HN). The synthesis procedure for compound (5b) (200 mg, 0.30 mmol) and compound (7) (312mg, 0.68 mmol) was same as that of compound (4a). The product TPE4HN of 75% yield as a dark purple solid was obtained by silica gel column chromatography eluting with mixture of dichloromethane and hexane (1:5). ¹H NMR (600 MHz, CDCl3) δ ppm: 8.45 (dd, J = 3.18, 7.02 Hz, 2H), 7.44 (dd, J = 3.12, 7.08 Hz, 2H), 7.33 (s, 2H), 7.33 (d, J = 8.04 Hz, 4H), 7.15-7.05 (m, 34H), 2.77 (t, J = 7.74 Hz, 4H), 1.71-1.66 (m, 4H), 1.40-1.28 (m, 12H) and 0.90 (t, J = 7.08 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ ppm: 151.55, 143.70, 143.69, 143.57, 142.95, 141.42, 140.66, 140.54, 138.92, 134.26, 133.40, 132.78, 132.49, 131.53, 131.46, 131.40, 131.36, 128.44, 127.76, 127.22, 126.83, 126.59, 126.55, 126.49, 123.49, 31.65, 30.86, 29.26, 29.04, 22.66 and 14.10. APCI/Q-TOF (m/z) calcd for (M⁺) C₈₂H₇₀N₂S₃: 1,178.4701; found 1,179.5399.



Fig. S2 ¹³C NMR (151 MHz, CDCl₃) of compound TPE3HN



Fig. S4 ¹³C NMR (151 MHz, CDCl₃) of compound TPE4HN



Fig. S5 Q-TOF (APCI) of compounds TPE3HN (top) and TPE4HN (bottom)



 ^{13}C NMR (151 MHz, CDCl_3) of compound $\boldsymbol{3}$



 ^{13}C NMR (151 MHz, CDCl₃) of compound 4b



¹³C NMR (151 MHz, CDCl₃) of compound **5a**



 ^{13}C NMR (151 MHz, CDCl_3) of compound 5b



 ^{13}C NMR (151 MHz, CDCl₃) of compound 7



Fig. S7 Photoluminescence spectra of compound a) TPE3HN and b) TPE4HN in different solvents







Fig. S8 Photoluminescence spectra measured in a water-THF mixture at 2.5 x 10⁻⁶ M and photo in water-THF mixture under black light of **a**) **TPE3HN** and **b**) **TPE4HN** at various water fractions



Fig. S9 a) TGA and b) DSC (1st heating scan and 2nd heating scan) traces of TPE3HN and TPE4HN measured at heating rate of 10 °C min⁻¹ under N_2 flow



Fig. S10 CV plots of **TPE3HN** and **TPE4HN** measured in CH_2Cl_2 containing n-Bu₄NPF₆ as a supporting electrolyte at a scan rate of 50 mV s⁻¹ under Ar flow



Fig. S11 Photoemission yield spectroscopy in air (PYSA) spectra of compounds a) TPE3HN and b) TPE4HN



Fig. S12 AFM images of the evaporated thin films of a) TPE3HN and b) TPE4HN



Fig. S13 Electroluminescence spectra of compound a) TPE3HN and b) TPE4HN at different applied voltages.

Reference

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