**Supporting Information**

# Triazine-dibenzofuran-Based n-Type Host Materials for High-Efficiency and Long-Lifetime Green Phosphorescent Organic Light-Emitting Diodes

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**Synthesis and Characterisations**

**2-(biphenyl-4-yl)-4,6-bis(dibenzo[*b*,*d*]furan-1-yl)-1,3,5-triazine (DBT1)**

2-([1,1'-biphenyl]-4-yl)-4,6-dichloro-1,3,5-triazine (7.0 g, 23.2 mmol), dibenzo[*b*,*d*]furan-1-ylboronic acid (20.5 g, 69.6 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol), $K_2CO_3$ (9.6 g, 69.6 mmol) were dissolved in 1,4-dioxane/$H_2O$ (100 mL/20 mL) in a 250-mL single-neck round-bottom flask. The mixture was stirred at reflux for 24 h and cooled to room temperature. This was followed by filtration, and subsequently the crude product was purified by recrystallisation, to obtain **DBT1** as a white powder (10.1 g, yield: 77 %). $^1$H NMR (300 MHz, $CDCl_3$, $\delta$): 8.90 (d, 2H, $J$ = 8.7 Hz), 8.73 (dd, 2H, $J$ = 8.1 and 0.6 Hz), 8.52 (dd, 2H, $J$ = 7.8 and 1.2 Hz), 7.85 (t, 4H, $J$ = 9.1 Hz), 7.74 (d, 2H, $J$ = 7.7 Hz), 7.67 (t, 4H, $J$ = 8.0 Hz), 7.54−7.48 (m, 4H), 7.44 (d, 1H, $J$ = 7.2 Hz), 7.20 (td, 2H, $J$ = 7.5 and 1.2 Hz);$^{13}$C NMR (75 MHz, $CDCl_3$, $\delta$): 207.2, 173.6, 171.6, 157.3, 157.1, 145.8, 140.3, 134.7, 133.1, 130.3, 129.1, 128.3, 128.2, 127.7, 127.4, 127.0, 126.7, 126.5, 123.7, 122.5, 115.3, 111.6. HRMS: calculated for $C_{39}H_{23}N_3O_2$: 565.1790, Found: 565.1799. Elemental analysis: calculated for $C_{39}H_{23}N_3O_2$: C, 82.82; H, 4.10; N, 7.43; O, 5.66, Found: C, 82.83; H, 4.11; N, 7.42.

**2-(biphenyl-4-yl)-4,6-bis(dibenzo[*b*,*d*]furan-2-yl)-1,3,5-triazine (DBT2)**

2-([1,1'-biphenyl]-4-yl)-4,6-dichloro-1,3,5-triazine (7.0 g, 23.2 mmol), dibenzo[*b*,*d*]furan-2-ylboronic acid (20.5 g, 69.6 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol), $K_2CO_3$ (9.6 g, 69.6 mmol) were dissolved in 1,4-dioxane/$H_2O$ (100 mL/20 mL) in a 250-mL single-neck round-bottom flask. The mixture was stirred at reflux for 12 h and cooled to room temperature. This was followed by filtration, and subsequently the crude product was purified by recrystallisation, to obtain **DBT2** as a white powder (10.5 g, yield: 80 %). $^1$H NMR (300 MHz, $CDCl_3$, $\delta$): 9.46 (d, 2H, $J$ = 1.5 Hz), 9.04 (dd, 2H, $J$ = 8.7 and 1.8 Hz), 8.94 (d, 2H, $J$ = 8.7 Hz), 8.22 (d, 2H, $J$ = 7.2 Hz), 7.88 (d, 2H, $J$ = 8.7 Hz), 7.79 (d, 2H, $J$ = 9.3 Hz), 7.76 (d, 2H, $J$ = 6.9 Hz), 7.66 (d,

2H, $J$ = 7.8 Hz), 7.58−7.55 (m, 4H), 7.46 (td, 3H, $J$ = 7.5 and 0.9 Hz); $^{13}$C NMR is not available due to the low solubility. HRMS: calculated for $C_{39}H_{23}N_3O_2$: 565.1790, Found: 565.1798. Elemental analysis: calculated for $C_{39}H_{23}N_3O_2$: C, 82.82; H, 4.10; N, 7.43; O, 5.66, Found: C, 82.81; H, 4.12; N, 7.41.

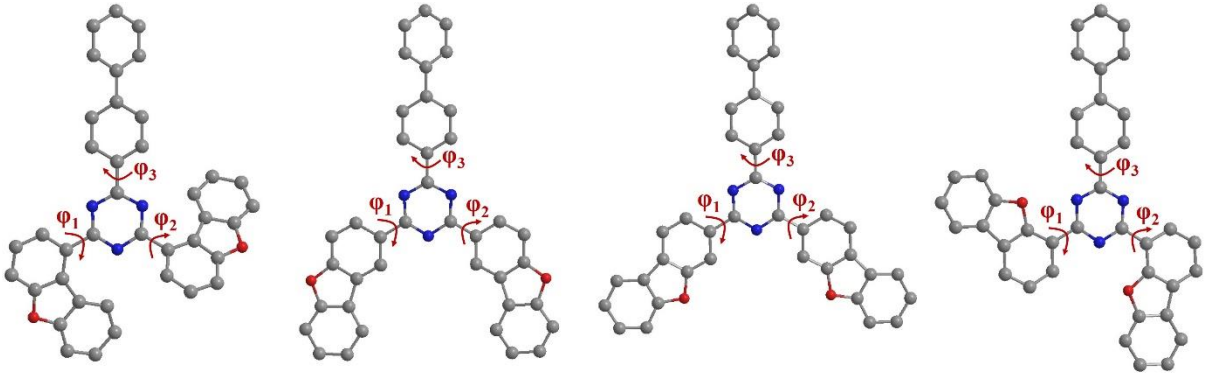
**2-(biphenyl-4-yl)-4,6-bis(dibenzo[*b*,*d*]furan-3-yl)-1,3,5-triazine (DBT3)**

2-([1,1'-biphenyl]-4-yl)-4,6-dichloro-1,3,5-triazine (7.0 g, 23.2 mmol), dibenzo[*b*,*d*]furan-3-ylboronic acid (20.5 g, 69.6 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol), $K_2CO_3$ (9.6 g, 69.6 mmol) were dissolved in 1,4-dioxane/$H_2O$ (100 mL/20 mL) in a 250-mL single-neck round-bottom flask. The mixture was stirred at reflux for 24 h and cooled to room temperature. This was followed by filtration, and subsequently the crude product was purified by recrystallisation, to obtain **DBT3** as a white powder (9.8 g, yield: 75 %). $^1$H NMR (300 MHz, $CDCl_3$, $\delta$): 9.06 (d, 2H, $J$ = 0.9 Hz), 8.93−8.86 (m, 4H), 8.15 (d, 2H, $J$ = 8.7 Hz), 8.07 (d, 2H, $J$ = 6.9 Hz), 7.85 (d, 2H, $J$ = 8.4 Hz), 7.74 (d, 2H, $J$ = 7.8 Hz), 7.67 (d, 2H, $J$ = 8.1 Hz), 7.58−7.50 (m, 4H), 7.46−7.39 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, $\delta$): 171.6, 157.6, 156.6, 135.6, 135.2, 130.5, 129.7, 129.1, 128.4, 128.2, 127.7, 127.5, 127.4, 123.9, 123.8, 123.2, 121.5, 121.7, 117.2, 112.5, 112.2. HRMS: calculated for $C_{39}H_{23}N_3O_2$: 565.1790, Found: 565.1799. Elemental analysis: calculated for $C_{39}H_{23}N_3O_2$: C, 82.82; H, 4.10; N, 7.43; O, 5.66, Found: C, 82.83; H, 4.11; N, 7.42.

**2-(biphenyl-4-yl)-4,6-bis(dibenzo[*b*,*d*]furan-4-yl)-1,3,5-triazine (DBT4)**

2-([1,1'-biphenyl]-4-yl)-4,6-dichloro-1,3,5-triazine (7.0 g, 23.2 mmol), dibenzo[*b*,*d*]furan-4-ylboronic acid (20.5 g, 69.6 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol), $K_2CO_3$ (9.6 g, 69.6 mmol) were dissolved in 1,4-dioxane/$H_2O$ (100 mL/20 mL) in a 250-mL single-neck round-bottom flask. The mixture was stirred at reflux for 24 h and cooled to room temperature. This was followed by filtration, and subsequently the crude product was purified by recrystallisation, to

obtain **DBT4** as a white powder (9.5 g, Yield: 72 %). $^{1}$H NMR (300 MHz, $CDCl_3$, $\delta$): 9.06 (d, 2H, $J$ = 8.4 Hz), 8.96 (dd, 2H, $J$ = 7.8 and 1.5), 8.26 (dd, 2H, $J$ = 7.5 and 1.2), 8.07 (d, 2H, $J$ = 7.8), 7.91 (d, 2H, $J$ = 8.4), 7.82 (d, 2H, $J$ = 8.4), 7.77 (d, 2H, $J$ = 7.2), 7.63 (t, 2H, $J$ = 7.8), 7.55−7.51 (m, 4H), 7.47−7.42 (m, 3H); $^{13}$C NMR is not available due to the low solubility. HRMS: calculated for $C_{39}H_{23}N_3O_2$: 565.1790, Found: 565.1798. Elemental analysis: calculated for $C_{39}H_{23}N_3O_2$: C, 82.82; H, 4.10; N, 7.43; O, 5.66, Found: C, 82.81; H, 4.11; N, 7.41.




DBT1 DBT2 DBT3 DBT4

| | DBT1 | DBT2 | DBT3 | DBT4 |
|---|---|---|---|---|
| $\varphi_1$ | 22.9° | 0.1° | 0.0° | 0.4° |
| $\varphi_2$ | 28.2° | 0.1° | 0.0° | 0.1° |
| $\varphi_3$ | 8.8° | 0.2° | 0.2° | 0.1° |

**Figure S1.** Optimised structures and dihedral angles for **DBT1**–**DBT4** using *Gaussian16* program.

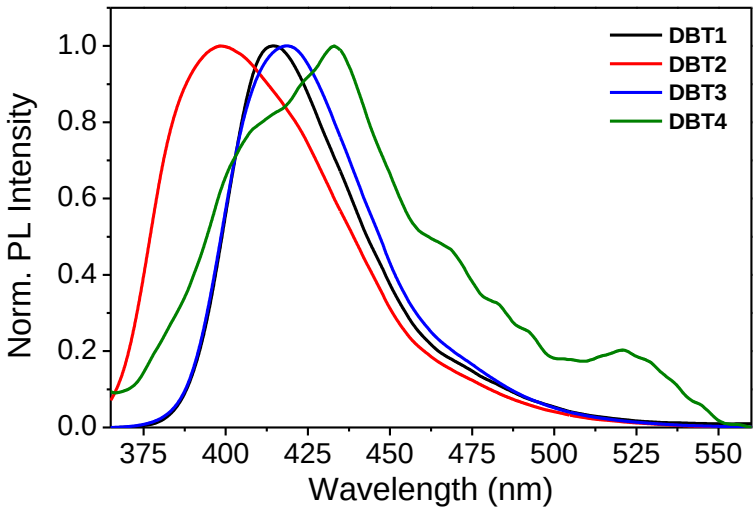



**Figure S2.** PL spectra of **DBT1**–**DBT4** in film state.

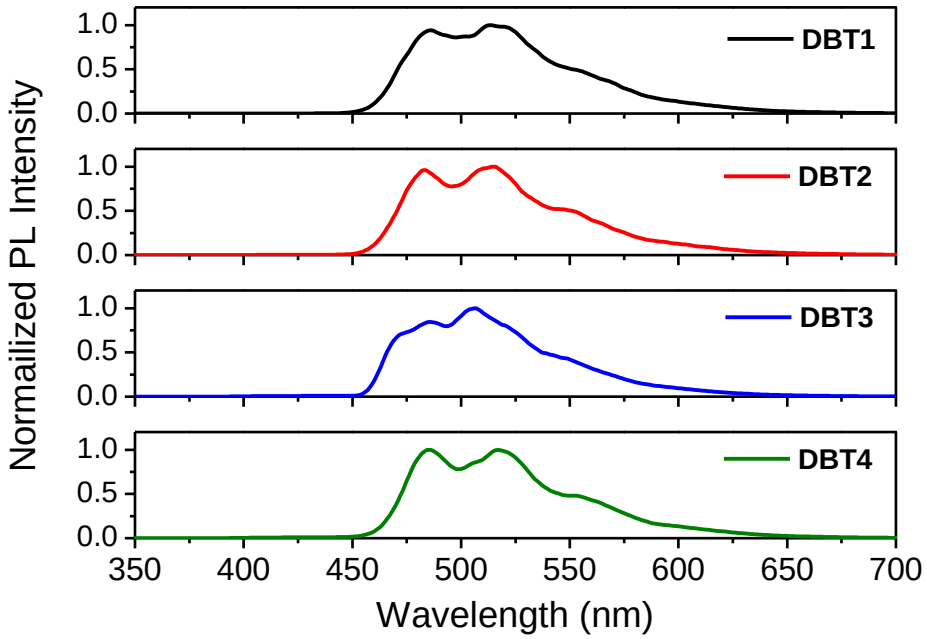



**Figure S3.** Photoluminescence spectra of **DBT1**–**DBT4** in 2-MeTHF at 77 K.

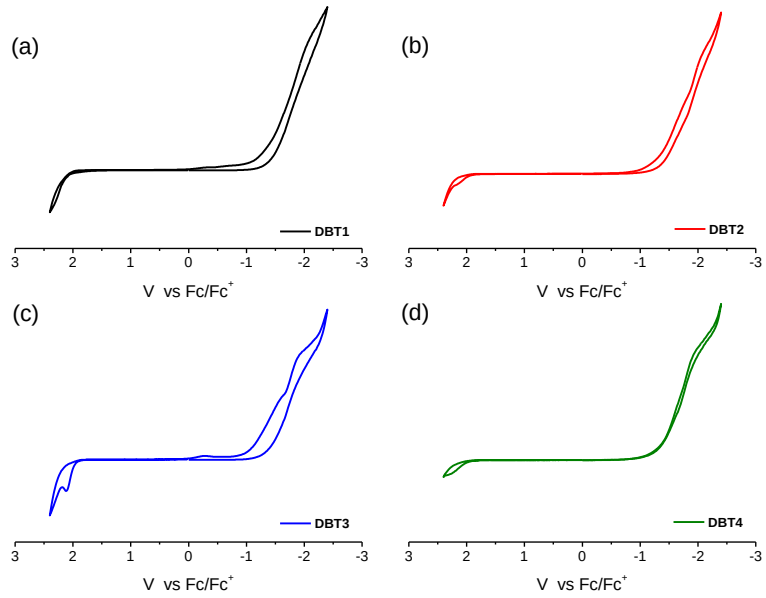



**Figure S4.** CV curves of **DBT1**-**DBT4** in dichloromethane solution containing 0.1 M *n*-$Bu_4PF_6$ as an electrolyte, at a scan rate of 0.1 V $s^{-1}$.

**Table S1.** Photophysical properties of the materials used in device.

| Materials | Abs. (nm) | Em. (nm) | HOMO (eV) | LUMO (eV) | Band gap (eV) | $T_1$ (eV) |
|---|---|---|---|---|---|---|
| **HAT-CN** | – | – | –9.0 | –5.1 | 3.9 | – |
| **BPBPA** | 353 | 414 | –5.5 | –2.4 | 3.1 | 2.39 |
| **3DF** | 355 | 440 | –5.1 | –2.0 | 3.1 | 2.46 |
| **BPCz** | 253 | 407 | –5.3 | –1.9 | 3.4 | 2.71 |
| **Ir(mdp)$_3$** | 292 | 527 | –4.9 | –2.6 | 2.3 | 2.35 |
| **LG201** | – | – | –5.6 | –2.6 | 3.0 | < 2.00 |

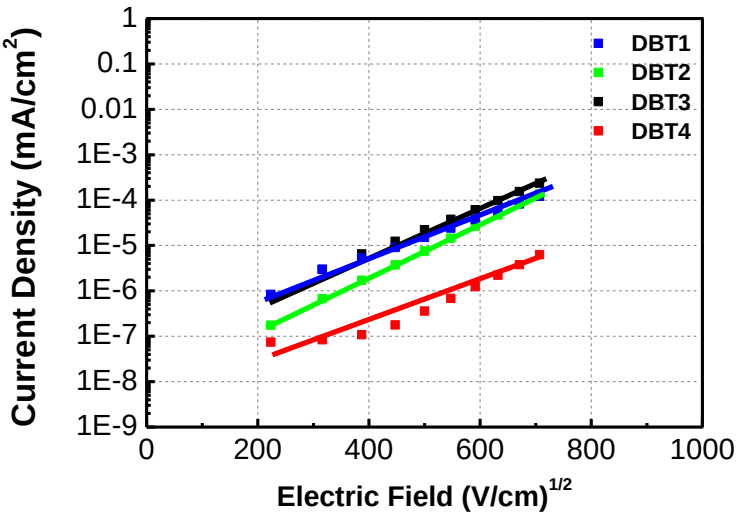



**Figure S5.** Electrical measurements on single-carrier devices. The devices were fabricated with the following structure: ITO/Mg(150 Å)/Host(2000 Å)/Yb/Mg(200 Å). The J–V characteristics were fitted to SCLC with field-dependent mobility. $J = (9/8)_{\varepsilon_0\varepsilon_r}(E^2/L)_{\mu_0}\exp(0.89)\beta\sqrt{E}$, where $J$ is the current density; $\varepsilon_0\varepsilon_r$ is the dielectric constant; $E$ is the electric field; $L$ is the film thickness; $\mu_0$ is the zero-field carrier mobility; $\beta$ is the Poole–Frenkel factor. The values of $\mu_0$ and $\beta$ were calculated by assuming that $\varepsilon_r$ is equal to 3. The field-dependent mobility was calculated using the Poole–Frenkel equation: $\mu(\mathrm{E}) = \mu_0 \exp(\beta\sqrt{E})$.

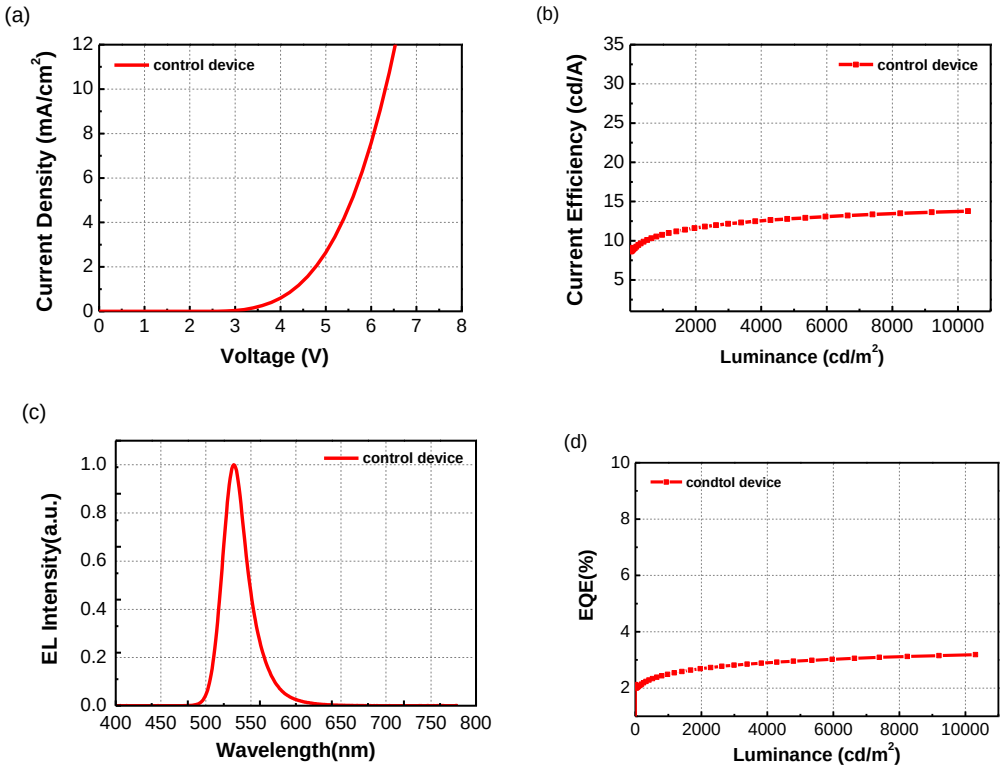



**Figure S6.** Device performance of **control device**. (a) Current density–voltage, (b) current efficiency–luminance, (c) EL spectrum, and (d) EQE–luminance.

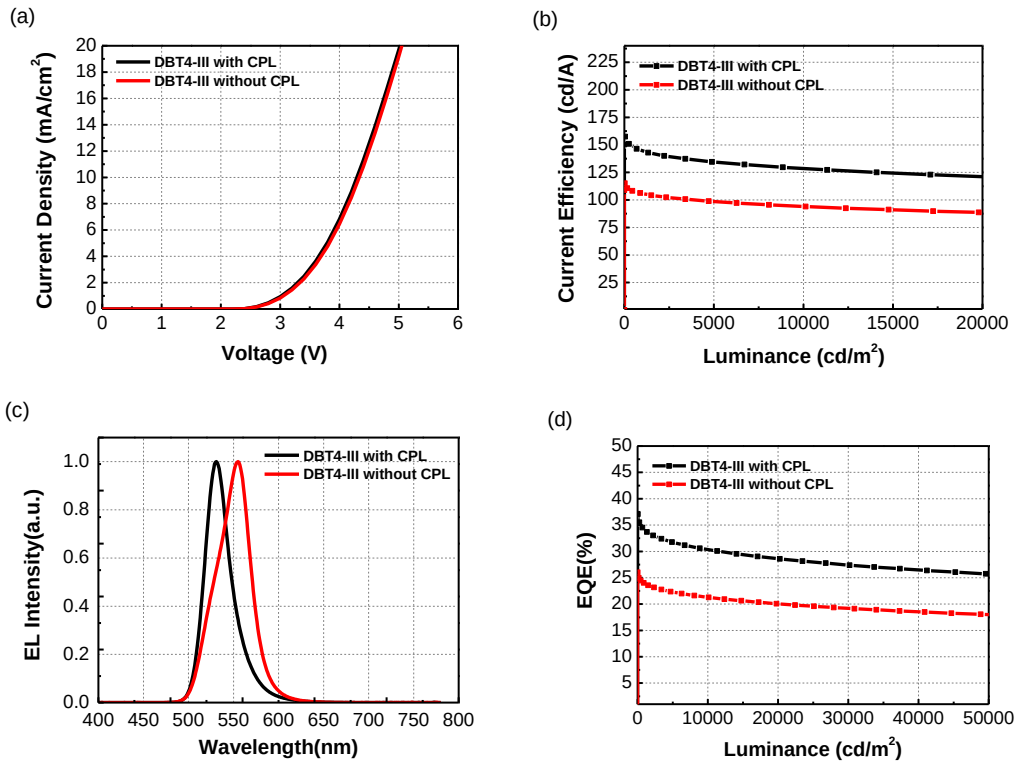



**Figure S7.** Comparison of device performances of **DBT4-III with and without CPL**. (a) Current density–voltage, (b) current efficiency–luminance, (c) EL spectrum, and (d) EQE–luminance.