Electronic Supplementary Information

De novo design of D-σ-A molecules as universal hosts for monochrome and white phosphorescence organic light-emitting diodes

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General information

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Mass analyses were performed on an Applied Biosystems API-2000 liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) Triple-Q mass spectrometer with electrospray ionization source. Thermal weight change analysis was recorded on a thermal gravimetric analyzer (TGA Q50, TA Instruments). Temperature for 5% weight loss is used as the decomposition temperature. Glass transition temperatures were determined with a Perkin-Elmer DSC 7 differential scanning calorimetric at a heating rate of 10 °C minute$^{-1}$ under a nitrogen atmosphere. UV-vis absorption spectra were acquired with an Agilent 8453 spectrophotometer. Photoluminescence spectra were measured on a Hitachi F-4500 Fluorescence spectrophotometer. Cyclic voltammetry was scanned on a CHI600 voltammetric analyzer equipped with a three-electrode system (platinum disk: working electrode, platinum wire: auxiliary electrode, Ag/AgCl: reference electrode). Ferrocene with an absolute highest occupied molecular orbital level of -4.80 eV was used as an internal standard. Nitrogen-saturated 0.1 mol L$^{-1}$ tetrabutylammonium hexafluorophosphate CH$_2$Cl$_2$ (oxidation scan) or DMF (reduction scan) solution was used as the supporting electrolyte.

Synthesis detail

$^1$H-benzo[4,5]imidazo[1,2-a]indol-11-one (BIO) was prepared according to the literature.$^1$

![Scheme S1 Synthesis of BII-BCz and BII-TPA.](image)
11,11-bis(9-phenyl-9H-carbazol-3-yl)-11H-benzo[4,5]imidazo[1,2-a]indole (BII-BCz): BIO (2 mmol, 0.44 g), 9-phenyl-9H-carbazole (40 mmol, 9.7 g) and methanesulfonic acid (1 mL) were mixed in a two-neck flask. The mixture was heated to 170 °C under a N₂ atmosphere. After 10 h reaction, the resulting mixture was cooled to room temperature, and then extracted with CH₂Cl₂. The extracted solution was washed with saturated NaHCO₃ aq., and dried by anhydrous MgSO₄. After evaporation of the solvent, the residue was purified via column chromatography. First, petroleum ether (PE) was used as eluent to separate the excessive non-polar triphenylamine, and then CH₂Cl₂/PE mixture (1:1, v/v) was used as eluent to give a white solid (0.86 g, 62.5%). ¹H NMR (400 MHz, DMSO-d₆) δ [ppm]: 8.19 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 1.8 Hz, 2H), 8.08 (d, J = 7.8 Hz, 1H), 8.03 (d, J = 7.8 Hz, 2H), 7.87 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.64 – 7.58 (m, 4H), 7.59 – 7.54 (m, 5H), 7.51 – 7.43 (m, 4H), 7.42 – 7.27 (m, 9H), 7.18 – 7.14 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ [ppm]: 165.23, 145.86, 141.55, 141.20, 140.05, 137.55, 134.73, 129.79, 129.60, 128.53, 127.68, 127.41, 126.97, 126.78, 125.94, 124.57, 123.23, 123.19, 122.68, 121.00, 120.53, 119.86, 119.83, 111.19, 110.67, 110.07, 109.73, 58.74. MS (ESI): m/z = 689.4 [M + H]⁺.

4,4’-(11H-benzo[4,5]imidazo[1,2-a]indole-11,11-diyl)bis(N,N-diphenylaniline) (BII-TPA): Prepared as white powder (yield: 71.2%) in a similar manner as BII-BCz by using triphenylamine as the starting materials. ¹H NMR (400 MHz, DMSO-d₆) δ [ppm]: 8.21 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.34 – 7.19 (m, 12H), 7.10 – 6.90 (m, 17H). ¹³C NMR (151 MHz, CDCl₃) δ [ppm]: 163.63, 147.43, 146.90, 146.34, 139.57, 136.61, 135.73, 129.54, 128.94, 127.43, 124.83, 124.07, 123.41, 123.20, 122.73, 120.10, 111.76, 111.58, 56.59. MS (ESI): m/z = 693.6 [M + H]⁺.

Device fabrication and measurement

Pre-cleaned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω/□ were used as transparent anodes. Before use, the substrates were treated a 20 min UV-ozone bath, and then immediately transferred into a deposition chamber with vacuum better than 10⁻⁷ Torr. Current density-voltage characteristics and electroluminescence spectra were recorded
with a Keithley 237 power source and a Spectrascan PR650 photometer, respectively. Device measurement was performed under an ambient condition.

**Thermal properties**

![Thermal properties graph](image)

**Fig. S1** TGA and DSC (inset) measurements of the new hosts.

**Absorption and PL spectra of films**

![Absorption and PL spectra graph](image)

**Fig. S2** Absorption and PL spectra of BII-BCz and BII-TPA in 30-nm films prepared on quartz substrates by thermal evaporation.
Solvent-dependent PL spectra

![Fig. S3 PL spectra of BII-BCz and BII-TPA measured in different solvents (~10^{-6} mol L^{-1})](image)

Optimal molecular configurations

<table>
<thead>
<tr>
<th>Structure</th>
<th>Configuration</th>
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<tbody>
<tr>
<td></td>
<td>Side view 1</td>
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<tr>
<td><img src="image" alt="BII-BCz structure" /></td>
<td><img src="image" alt="BII-BCz side view 1" /></td>
</tr>
<tr>
<td><img src="image" alt="BII-TPA structure" /></td>
<td><img src="image" alt="BII-TPA side view 1" /></td>
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**Fig. S4** Energy minimized molecular configurations of BII-BCz and BII-TPA.
Absorption of dopants and PL of hosts

Fig. S5 Absorption spectra of the phosphorescence dopants (dash lines) and PL spectra of the hosts (solid lines) in CH$_2$Cl$_2$.

Cyclic voltammetry

Fig. S6 Cyclic voltammetry of the new compounds; the HOMO/LUMO levels are estimated to be -2.03/-5.70 eV and -2.05/-5.34 eV for BII-BCz and BII-TPA, respectively.
**EL spectra of monochrome devices**

![EL spectra graph](image)

**Fig. S7** EL spectra of the monochrome devices; solid and dash lines are for the BII-BCz and the BII-TPA based devices, respectively.

**Transient decay PL spectra**

![Transient decay PL spectra graph](image)

**Fig. S8** Transient decay PL spectra of the host:10 wt% Flrpic doped films (30 nm) prepared on quartz substrates.
**J-V-L** characteristics of monochrome devices

**Fig. S9** J-V-L characteristics of the devices based on (a) Flrpic, (b) Ir(ppy)$_2$(acac), (c) PO-01, (d) Ir(2-phq)$_3$ and (e) Ir(piq)$_2$(acac) as dopants, respectively.
Single carrier-only devices

Fig. S10 $J-V$ characteristics of (a) hole-only devices (HOD) and (b) electron-only devices (EOD). HOD: ITO/MoO$_3$ (10 nm)/BII-BCz or BII-TPA (50 nm)/MoO$_3$ (10 nm)/Al; EOD: ITO/TmPyPB (10 nm)/BII-BCz or BII-TPA (50 nm)/TmPyPB (10 nm)/LiF (1 nm)/Al.

EL spectra of white OLEDs

Fig. S11 Voltage-dependent EL spectra of the D-EML white OLEDs based on BII-BCz, with a PO-01 concentration of (a) 0.6 wt%, (b) 1.0 wt% and (c) 2.0 wt%, respectively. (d) Plots of the yellow to blue emission intensity as a function of voltage.
**Fig. S12** Voltage-dependent EL spectra of the D-EML white OLEDs based on BII-TPA, with a PO-01 concentration of (a) 0.6 wt%, (b) 1.0 wt% and (c) 2.0 wt%, respectively. (d) Plots of the yellow to blue emission intensity as a function of voltage.

**Reference**