Tuning Intramolecular Conformation and Packing Mode of Host Materials through Noncovalent Interactions for High-Efficiency Blue Electrophosphorescence

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1. Synthesis and characterization

Materials

2,5-Dibromopyridine, 2,5-dibromopyrimidine, 2,5-dibromopyrazine and 9H-carbazole were purchased from Energy Chemical Corp. and used as received without purification. Copper power and potassium carbonate were obtained from commercial suppliers.

Measurements and Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ultra Shield Plus AV400 spectrometer (\(^1\)HNMR 400 MHz and \(^{13}\)C NMR 100 MHz) with CDCl\(_3\) as the solvents and tetramethylsilane (TMS) as the internal standard. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was measured utilizing a Shimadzu AXIMA-CFR mass spectrometer. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer.

\[\text{Scheme S1. Synthetic route of PyDCz, PymDCz and PyaDCz.}\]

9, 9'-((Pyridine-2, 5-diyl)bis(9H-carbazole)) (PyDCz):

To a 250 mL round-bottom flask charged with 2,5-dibromopyridine (3 g, 12.8 mmol), 9H-carbazole (6.5 g, 38.9 mmol), copper power (1.12 g, 11.3 mmol) and potassium carbonate (15.7 g, 113 mmol) was injected 40 mL nitrobenzene (PhNO\(_2\)) using a syringe under an argon atmosphere. The resulted mixture was allowed to be stirred at 180°C for 48 h. After the completion of the reaction, the mixture was extracted with dichloromethane (DCM) for three times (3×50 mL).\(^1\) The organic phase was separated, collected, dried, and concentrated under
reduced pressure. The crude solid product was further purified by column chromatography on silica gel with PE/CH$_2$Cl$_2$ (v:v = 2:1) as the eluent to afford a white solid (yield: 90%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 8.99 (d, $J$ = 2.6 Hz, 1H), 8.32–8.10 (m, 5H), 8.03 (d, $J$ = 8.3 Hz, 2H), 7.92 (d, $J$ = 8.5 Hz, 1H), 7.61–7.44 (m, 6H), 7.44–7.33 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 150.55, 148.01, 140.73, 139.45, 136.84, 131.83, 126.43, 126.40, 124.59, 123.79, 121.38, 120.72, 120.62, 120.35, 119.35, 111.34, 109.39. MALDI-TOF-MS. Calcd for C$_{29}$H$_{19}$N$_3$: 409.158 found: 409.662. Elemental analysis calcd. for C$_{29}$H$_{19}$N$_3$: C 85.06%, H 4.68%, N 10.26%; Found: C 84.74%, H 4.38%, N 10.37%.

9, 9'-((Pyrimidine-2, 5-diyl)bis(9H-carbazole) (PymDCz):

PymDCz was prepared under the identical synthetic conditions described in the preparation of PyDCz using 2,5-dibromopyrimidine (3 g, 12.7 mmol), 9H-carbazole (6.5 g, 38.9 mmol), copper powder (1.12 g, 11.3 mmol) and potassium carbonate (15.7 g, 113 mmol) (yield: 85%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 9.08 (s, 2H), 8.99 (d, $J$ = 8.4 Hz, 2H), 8.20 (d, $J$ = 7.8 Hz, 2H), 8.12 (d, $J$ = 7.1 Hz, 2H), 7.61–7.34 (m, 10H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 157.61, 156.48, 140.81, 139.14, 127.77, 126.87, 126.55, 126.12, 123.86, 122.83, 120.94, 120.72, 119.67, 116.64, 109.13. MALDI-TOF-MS. Calcd for C$_{28}$H$_{18}$N$_4$: 410.153 found: 410.626. Elemental analysis calcd. for C$_{28}$H$_{18}$N$_4$: C 81.93%, H 4.42%, N 13.65%; Found: C 81.62%, H 4.05%, N 13.76%.

2, 5-Di(9H-carbazol-9-yl)pyrazine (PyaDCz):

PyaDCz was prepared under the identical synthetic conditions described in the preparation of PyDCz using 2,5-dibromopyrazine (3 g, 12.7 mmol), 9H-carbazole (6.5 g, 38.9 mmol), copper powder (1.12 g, 11.3 mmol) and potassium carbonate (15.7 g, 113 mmol) (Yield: 92%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 9.12 (s, 2H), 8.17 (ddd, $J$ = 7.7, 1.2, 0.7 Hz, 4H), 7.99 (d, $J$ = 8.3 Hz, 4H), 7.53 (ddd, $J$ = 8.4, 7.2, 1.3 Hz, 4H), 7.46–7.36 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 145.38, 139.21, 138.85, 126.67, 124.81, 121.87, 120.51, 111.07. MALDI-TOF-MS. Calcd for C$_{28}$H$_{18}$N$_4$: 410.153 found: 410.608. Elemental analysis calcd. for C$_{28}$H$_{18}$N$_4$: C 81.93%, H 4.42%, N 13.65%; Found: C 81.91%, H 4.05%, N 13.74%. 
Figure S1. $^1$H NMR spectrum of PyDCz in CDCl$_3$.

Figure S2. $^{13}$C NMR spectrum of PyDCz in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of PymDCz in CDCl$_3$.

Figure S4. $^{13}$C NMR spectrum of PymDCz in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of PyaDCz in CDCl$_3$.

Figure S6. $^{13}$C NMR spectrum of PyaDCz in CDCl$_3$. 
2. Single crystal and NCI analysis

Single crystals of PyDCz, PymDCz and PyaDCz were grown by slow evaporation of combined dichloromethane and petroleum ether solutions at room temperature. X-ray crystallography was carried out on a Bruker SMART APEX-II CCD diffractometer with graphite monochromated Mo-Kα radiation at 296 K. The crystal structures were analyzed by Mercury 1.4 software and the structure data were summarized in Table S1. The CIF files of the single crystals were also attached. Nonbonding covalent interaction analysis (NCI) were adopted to investigate the intramolecular interactions using Multiwfn version 3.3 software based on the optimized molecular structures at the ground state (S₀). NCI isosurface plots were performed with color scaling that the dark blue color represents an attractive interaction, while dark red color represents repulsive interactions. Plotted isosurfaces were demonstrated with reduced density gradient (RDG) of 0.5 and -0.5 < sign(λ₂)ρ < 0.5, where sign(λ₂) means the sign of the second largest eigenvalue of Hessian and ρ represents the electron density.²

**Figure S7.** Chemical structures, single crystal structures and packing modes of PyDCz, PymDCz and PyaDCz (distance in Å).
Figure S8. Plots of reduced density gradient (RDG) versus the electron density ($\rho$) multiplied by the sign of the second Hessian eigenvalue ($\lambda_2$) with front (left) and side (right) view of low-gradient (RDG < 0.5 a.u.) RDG maps of (a, d) PyDCz, (b, e) PymDCz, (c, f) PyaDCz. Isovalue of RDG is set to 0.5, while that of sign($\lambda_2$)$\rho$ on the surface is represented by filling color according to color bar at the bottom from blue to red (from -0.05 to 0.05 a.u.).
Table S1. Crystallographic data for PyDCz, PymDCz and PyaDCz single crystals.

| Compound | PyDCz | PymDCz | PyaDCz |
|----------|-------|--------|--------|
| Empirical formula | C_{29}H_{19}N_{3} | C_{28}H_{18}N_{4} | C_{28}H_{18}N_{4} |
| Formula weight (g mol\(^{-1}\)) | 409.47 | 410.46 | 410.46 |
| Crystal color | colorless | colorless | light yellow |
| Wavelength, (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic |
| Space group | P 21/c | P 21 21 21 | P 1 21/n 1 |
| a, (Å) | 15.140(2) | 10.7559(8) | 15.160(13) |
| b, (Å) | 3.9030(5) | 13.2279(10) | 3.840(3) |
| c, (Å) | 18.3188(17) | 14.0925(11) | 18.267(16) |
| α, (deg.) | 90 | 90 | 90 |
| β, (deg.) | 115.026(8) | 90 | 113.337(19) |
| γ, (deg.) | 90 | 90 | 90 |
| volume, (Å\(^3\)) | 980.9(2) | 2005.1(3) | 976.4(15) |
| Z | 2 | 4 | 2 |
| Density, (g cm\(^{-3}\)) | 1.386 | 1.360 | 1.396 |
| h\(_{max}\), k\(_{max}\), l\(_{max}\) | 18, 4, 22 | 18, 21, 22 | 21, 5, 21 |
| CCDC NO. | 1903050 | 1902873 | 1903049 |
3. Thermal properties

Thermogravimetric analysis (TGA) was performed to study the thermal properties on a Shimadzu DTG-60H thermogravimetric analyses at a heating rate of 10°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A instrument under a heating rate of 10°C/min and a nitrogen flow rate of 20 cm³/min.

Figure S9. (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) curves of PyDCz, PymDCz and PyaDCz.
4. Optical properties

UV-vis absorption spectra were obtained using a Jasco V-750 spectrophotometer. Fluorescence and phosphorescence spectrums were measured using an Edinburg LFS980 fluorescence spectrophotometer. The time-resolved phosphorescence spectra of the compounds were collected at 77 K in 2-methylfuran with a 5 ms delay time after excitation at 320 nm using a microsecond flash lamp.

![Normalized PL spectra of (a) PyDCz, (b) PymDCz and (c) PyaDCz in different solvents of hexane, dichloromethane (DCM), acetonitrile (MeCN) and methanol (MeOH).](image-url)

**Figure S10.** Normalized PL spectra of (a) PyDCz, (b) PymDCz and (c) PyaDCz in different solvents of hexane, dichloromethane (DCM), acetonitrile (MeCN) and methanol (MeOH).
5. Theoretical calculations

Density functional theory (DFT) computations were carried out using Gaussian 09 program package for structure optimizations and vibrational analyses. The ground state ($S_0$) geometries of the molecules were optimized by the Becker's three-parameter exchange functional along with the Lee-Yang Parr's correlation functional (B3LYP) with 6-31G(d) basis sets; the optimized stationary point was further characterized by harmonic vibrational frequency analysis to ensure that real local minima were reached. The lowest triplet excited state ($T_1$) geometries were optimized by time-dependent DFT (TD-DFT) of TD-B3LYP/6-31G(d). The triplet energy (adiabatic $S_0 \rightarrow T_1$ excitation) was calculated by the difference of the total energy of the $S_0$ and $T_1$ states. The charge (hole and electron) mobilities of hosts of PyDCz, PymDCz and PyaDCz are assessed by using the incoherent hopping model, which assumes a charge transport process between two adjacent molecules in $M^\pm + M \rightarrow M + M^\pm$, where $M$ is a neutral molecule interacting with the neighboring cationic or anionic molecule ($M^\pm$) to transfer the charge between them. Therefore, the hole (h) or...
electron (e) reorganization energy ($\lambda_{be}$), in principle, can be calculated in Equations S1 and S2.

$$\lambda_h = \lambda_\ast + \lambda_1 = [E^+(M) - E^+(M')] + [E(M') - E(M)]$$

$$= [E^+(M) - E(M)] - [E^+(M') - E(M')] = \text{IP}_v - \text{HEP} \quad (S1)$$

$$\lambda_e = \lambda_\ast + \lambda_2 = [E(M)-E(M')] + [E(M') - E(M)]$$

$$= [E(M') - E(M)] - [E(M) - E(M')] = \text{EEP} - \text{EA}_v \quad (S2)$$

where $\lambda_\ast$ is the relaxation energy of a neutral molecule (M) that captured a hole going toward the optimum geometry on the potential energy surface of a cation (M$^+$); $\lambda_1$ is the relaxation energy from a cation (M$^+$) extracting a hole going toward the M optimum geometry on the potential energy surface of M; $E^+$ (M) and $E^+$ (M$^+$) are the total energies of the cation species under the optimum geometry of M and M$^+$, respectively; $E(M^+)$ and $E(M)$ represent the total energies of the neutral molecule under the optimum geometry of M$^+$ and M, respectively; IP$_v$ and EA$_v$ are the vertical ionization potential and electron affinity of the molecule, respectively; HEP and EEP are the hole and electron extraction potentials, respectively. The sum of $\lambda_\ast$ and $\lambda_1$ is the hole reorganization energy $\lambda_h$. Similarly, in the electron transport process, the sum of $\lambda_\ast$ and $\lambda_2$ is the hole reorganization energy ($\lambda_e = \lambda_\ast + \lambda_2$), where $\lambda_\ast$ is the relaxation energy of a neutral molecule (M) that captured an electron going toward the optimum geometry on the potential energy surface of an anion (M$^-$) and $\lambda_2$ is the relaxation energy from an anion (M$^-$) extracting an electron going toward the M optimum geometry on the potential energy surface of M.

**Table S2** Vertical ionization potential (IP$_v$), vertical electronic affinity (EA$_v$), extraction potentials (HEP for hole, EEP for electron), and reorganization energies ($\lambda_h$ for hole, $\lambda_e$ for electron) of PyDCz, PymDCz and PyaDCz (in eV).

| Compound | IP$_v$ | HEP | EA$_v$ | EEP | $\lambda_h$ | $\lambda_e$ |
|----------|--------|-----|--------|-----|-------------|-------------|
| PyDCz    | 6.55   | 6.41| -0.19  | 0.09| 0.14        | 0.28        |
| PymDCz   | 6.66   | 6.51| -0.06  | 0.56| 0.15        | 0.62        |
| PyaDCz   | 6.59   | 6.46| 0.20   | 0.80| 0.13        | 0.60        |
6. Electrochemical properties

Electrochemical properties were investigated by cyclic voltammetry (CV) measurements, which were carried out at room temperature on a CHI660E system in a typical three-electrode cell with a working electrode (glass carbon), a reference electrode (Ag/Ag\(^+\)), and a counter electrode (Pt wire) in an acetonitrile solution of \(n\)-Bu\(_4\)NPF\(_6\) (0.1 M) at a sweeping rate of 100 mV/s. The thin solid film of the compound was solution deposited on the surface of the glass carbon working electrode for the CV measurements and the CV curves were calibrated using ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple (4.8 eV below the vacuum level) as the internal standard. The highest occupied molecular orbital (HOMO) energy level (\(E_{\text{HOMO}}\)) was calculated according to: 
\[
E_{\text{HOMO}} = -e (E_{\text{ox onset}} + 4.80 \text{ V})
\]
where \(E_{\text{ox onset}}\) is the onset potential of the oxidation wave. The lowest unoccupied molecular orbital (LUMO) energy level (\(E_{\text{LUMO}}\)) was deduced by: 
\[
E_{\text{LUMO}} = E_{\text{HOMO}} + E_g
\]
where \(E_g\) is the optical bandgap.\(^4\)

Figure S12. Cyclic voltammograms of PyDCz, PymDCz and PyaDCz.
Figure S13. Natural transition orbitals (NTOs) describing the optimized molecular structures at lowest triplet ($T_1$) excited state of the host materials of PyDCz, PymDCz and PyaDCz.

7. Device fabrication and characterization

PhOLEDs using molecules of PyDCz, PymDCz and PyaDCz as host materials were investigated. Iridium(III) [bis(4,6-difluorophenyl)-pyridinato-N,C$^2$] picolinate (FIrpic) is selected as the blue emitter. In a general procedure, ITO-coated glass substrates were etched, patterned, and washed with detergent, deionized water, acetone, and ethanol in turn. After ultraviolet (UV)-ozone treating for 4 min, a 30 nm PEDOT: PSS was spin coated on the ITO substrate and dried at 120°C in a vacuum oven for 15 min. The other organic layers were deposited by high-vacuum ($\approx 4\times10^{-4}$ Pa) thermal evaporation with a rate of 0.1–0.2 nm s$^{-1}$. The layer thickness and the deposition rate were monitored in situ by an oscillating quartz thickness monitor. The devices without encapsulation were measured immediately after fabrication under ambient atmosphere at room temperature. Electroluminescent (EL) spectra of the devices were measured by a PR655 spectra scan spectrometer. The luminance-voltage and current-voltage characteristics were recorded using an optical power meter and a Keithley 2602 voltage current source. And the external quantum efficiency (EQE) was calculated by the following Equation S3.

$$EQE = \frac{\pi e n_{\text{cd/A}} \int \lambda p(\lambda) d\lambda}{h c K_m \int p(\lambda) \Phi(\lambda) d\lambda}$$  \hspace{1cm} \text{(S3)}$$

where is the current efficiency (cd/A); $h$ is the Planck constant; $c$ is the speed of light in vacuum; $\lambda$ is the wavelength (nm); $e$ is the electron charge; $p(\lambda)$ is the electroluminescent intensity; $\Phi(\lambda)$ is the luminous efficiency; $K_m$ is a constant of 683 lm/W.
The single-carrier transporting devices were fabricated with the configuration of ITO/PEDOT: PSS (35 nm)/host (100 nm)/MoO$_3$ (10 nm)/Al for hole-only devices and ITO/LiF (1 nm)/host (100 nm)/LiF (1 nm)/Al for electron-only devices, respectively.$^5$

**Scheme S2.** Molecular structures of the materials used in the blue PhOLED devices.
Figure S14. (a) PL spectra of the composite films with 10 wt% Flrpic and host molecules of PyDCz, PymDCz and PyaDCz, respectively and (b) PL spectra of PyaDCz and PyaDCz: 10 wt% Flrpic film and electroluminescent (EL) spectra of PyaDCz-hosted blue PhOLED with different Flrpic concentrations of 10 wt%, 15 wt% and 20 wt%, respectively.
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