

## Supporting information

### Isomer dependent molecular packing and carrier mobility of N-phenylcarbazole–phenanthro[9,10-*d*]imidazole based materials as hosts for efficient electrophosphorescence devices

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#### General Information

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on Bruker AVANCE III 500 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra was recorded on a Thermo Fisher ITQ1100 GC/MS mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. The UV-Vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer. Phosphorescent spectra at low temperature (77 K) were recorded by Ocean Optics QE Pro with a 365 nm Ocean Optics LLS excitation source. The absolute fluorescence quantum yields of solutions and films were measured on Edinburgh FLS920 steady state fluorimeter utilizing an integrating sphere (excited at 340 nm). Differential scanning calorimetric (DSC) measurements were performed on a NETZSCH DSC204 instrument at a heating rate of  $10\text{ K min}^{-1}$  under a nitrogen atmosphere. Thermogravimetric analyses (TGA) were performed on a TA Q500 thermogravimeter by measuring their weight loss while heating at a rate of  $10\text{ K min}^{-1}$  from 30 to  $700\text{ }^\circ\text{C}$  under nitrogen. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station, using platinum disk as working electrode, platinum wire as auxiliary electrode and a porous glass wick  $\text{Ag}/\text{Ag}^+$  as pseudo reference electrode with ferrocene/ferrocenium as the internal standard. The oxidation and reduction potentials were measured in  $\text{CH}_2\text{Cl}_2$  and THF solution containing 0.1 M of  $n\text{-Bu}_4\text{NPF}_6$  as a supporting electrolyte at a scan rate of  $50\text{ mV s}^{-1}$ .

**Single Crystal Structure:** X-ray diffraction data of were collected at 100 K in a dry stream of nitrogen using Mo K $\alpha$  radiation generated by microfocus tube on a Bruker D8 VENTURE with a PHOTON III CCD detector. Data reduction and absorption correction were performed with Bruker APEX3 software suite. The structure was solved employing dual-space algorithm with SHELXT and refined against F<sup>2</sup> with SHELXL,<sup>S1, S2</sup> and ShelXle were used to visualize assist these processes.<sup>S3</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding on the parent Carbon atom. CCDC 1893407 and 1893408 contain the supplementary crystallographic data for PI33PPCz and PI22PPCz, respectively; these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Theoretical Calculation method:** All calculations were carried out using B3LYP method including Grimme's dispersion correction with 6-311G(d,p) basis set as implemented in the Gaussian 09 D.01 software package.<sup>S4-S8</sup> Vibrational frequency calculations were used to confirm that the optimized structures were minima of corresponding potential energy surface, as characterized by all real vibrational frequencies. For ground states, the optimization followed the restricted Kohn-Sham (KS) DFT process, while for triplet states, unrestricted KS ground state calculations were performed. The calculation results were visualized with VMD 1.9.3.<sup>S9</sup>

Here, the hopping model<sup>S10, S11</sup> was selected to describe the mechanism of the carrier transport. All the compounds were investigated at 300 K. The charge transport mechanism of the hopping model can be described as a nonadiabatic electron-transfer reaction from a charged molecule to an adjacent neutral one involving the self-exchange charge. The hopping rate could be described by Marcus theory:<sup>S12, S13</sup>

$$k = V^2 \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda}} \exp\left(-\frac{\lambda}{4k_B T}\right)$$

where  $T$  is the absolute temperature,  $k_B$  is Boltzmann and  $\hbar$  is Planck constants,  $\lambda$  and  $V$  represent reorganization energy and transfer integral, respectively. The large transfer rate can

be attributed to the minimal reorganization and the maximal transfer integral.

The reorganization energy consists of contributions from the external and inner reorganization energy.<sup>S14, S15</sup> The external reorganization energy that is due to the polarization of the medium can be neglected.<sup>S16, S17</sup> And the inner reorganization is caused by the change of the internal nuclear coordinates from the reactant to the product, and the value can be evaluated from adiabatic potential energy surface.<sup>S18</sup>

$$\lambda = \lambda_{\text{rel}}^{(1)} + \lambda_{\text{rel}}^{(2)} = \left[ E^0(M^c) - E^0(M^0) \right] + \left[ E^c(M^0) - E^c(M^c) \right]$$

Here,  $E^0(M^0)$  is the energy of the neutral state with the optimized geometry of neutral molecule,  $E^c(M^c)$  is the energy of the charged states with the optimized charged geometry,  $E^c(M^0)$  is the charged states with the optimized geometry of the neutral molecule, and  $E^0(M^c)$  is the neutral state with the optimized charged geometry. The equilibrium structures of the neutral and ionic species were optimized at B3LYP level with 6-31G(d,p) basis set.

The transfer integral represents the strength of electronic coupling between the two adjacent neighboring molecules. It was obtained from the site-energy corrected method<sup>S19</sup> at the PW91/TZP level using ADF.<sup>S20-S22</sup>

The drift mobility  $\mu$  can be evaluated from the Einstein relation:

$$\mu = \frac{e}{k_B T} D$$

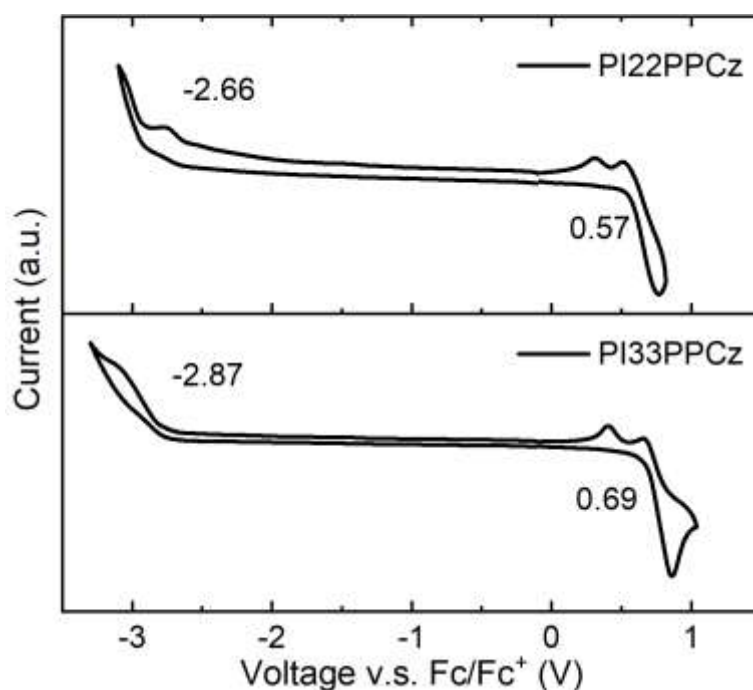
where  $e$  is the electronic charge and  $D$  is the diffusion coefficient, which is related to the charge-transfer rate  $k$  as summing over all possible hops. The diffusion coefficient can be approximately evaluated as

$$D = \frac{1}{2n} \sum_i d_i^2 k_i P_i$$

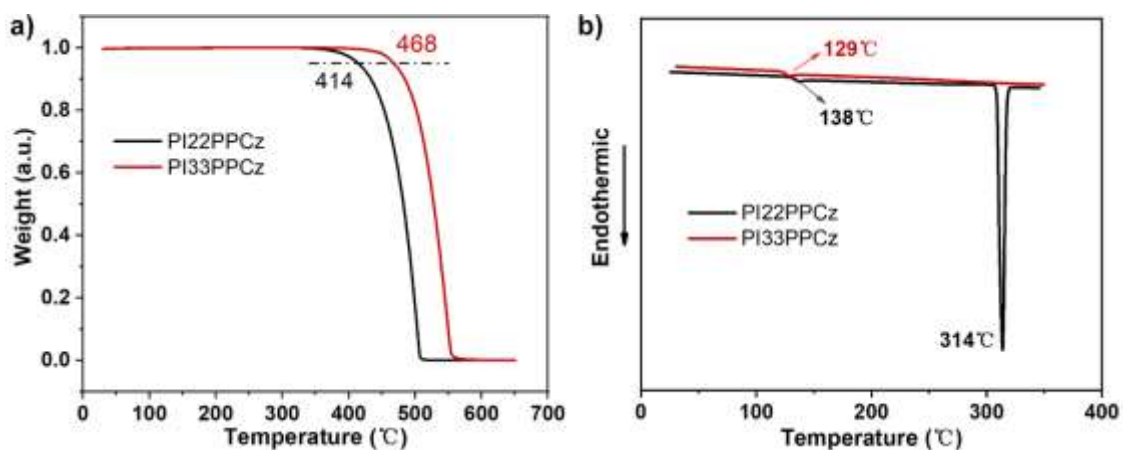
where  $n = 3$  is the dimensionality,  $k_i$  is the hopping rate due to charge carrier to the  $i$ th neighbor, and  $d_i$  is the center mass distance to neighbor  $i$ .  $P_i$  is the relative probability for charge carrier to a particular  $i$ th neighbor.

$$P_i = k_i / \sum_i k_i$$

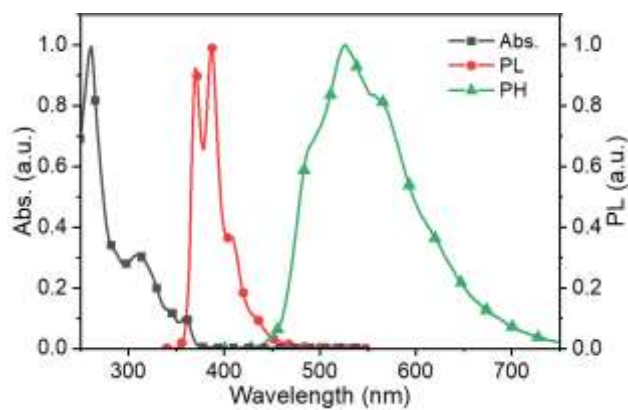
**Device Fabrication and Characterization.** Glass substrates pre-coated with indium tin oxide (ITO) with a sheet resistance of 15  $\Omega$  per square were cleaned sequentially in ultrasonic bath of detergent, deionized water, acetone and isopropyl alcohol, then treated with plasma for 5 min. Organic layers were deposited onto the ITO-coated glass substrates by thermal evaporation under high vacuum ( $<6 \times 10^{-4}$  Pa). Cathode was patterned using a shadow mask with an array of 2.0 mm  $\times$  2.0 mm openings. Deposition rates are 1  $\text{\AA s}^{-1}$  for organic materials, 0.1  $\text{\AA s}^{-1}$  for LiF, and 5  $\text{\AA s}^{-1}$  for Al, respectively. All OLEDs are characterized in the atmosphere and at room temperature. Electroluminescence (EL) spectra and luminance intensities (L) were recorded by Photo Research PR655. The current density (J) and driving voltage (V) characteristics were measured by Keithley 2400 simultaneously. External quantum efficiencies (EQE) were calculated from the current density, luminance and EL spectrum, assuming a Lambertian distribution.



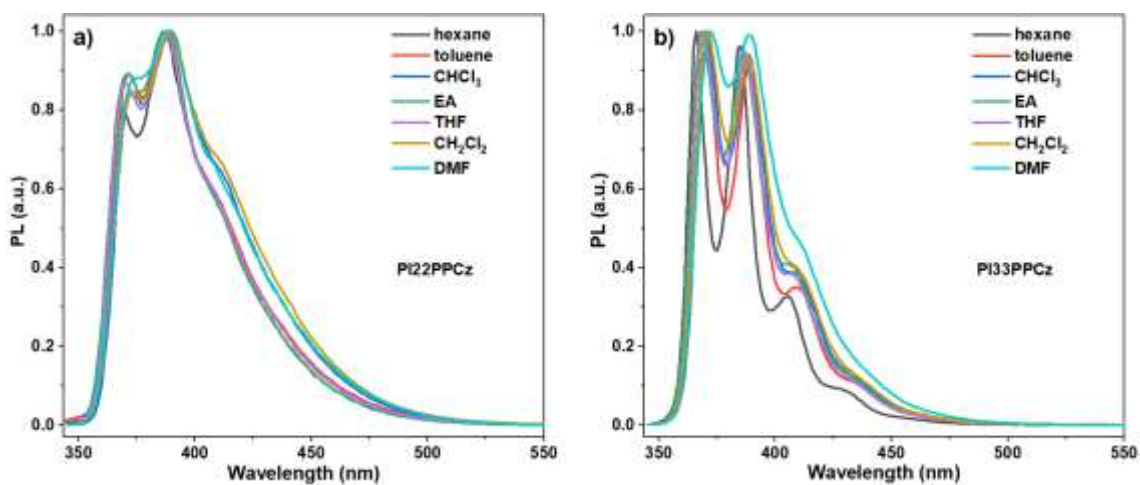
**Fig. S1** Cyclic voltammetry using ferrocene as reference.



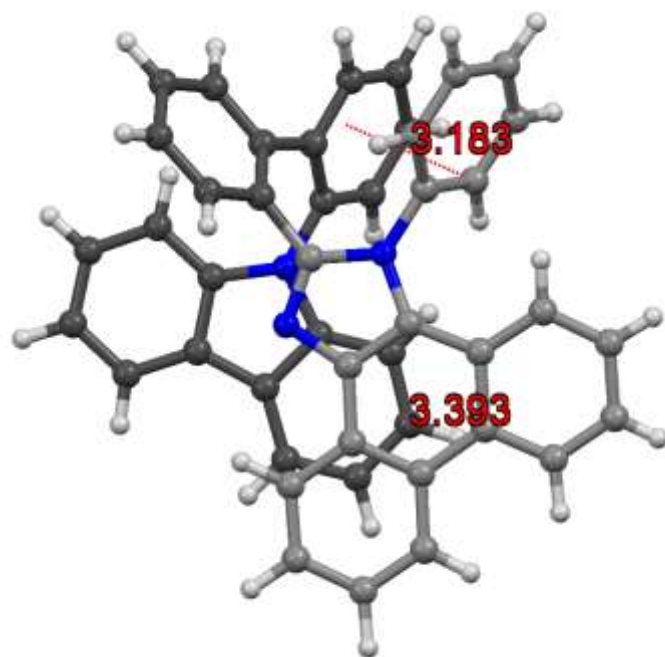
**Fig. S2** a) Thermogravimetric analysis (TGA) and b) differential scanning calorimetry (DSC) of **PI22PPCz** and **PI33PPCz**.



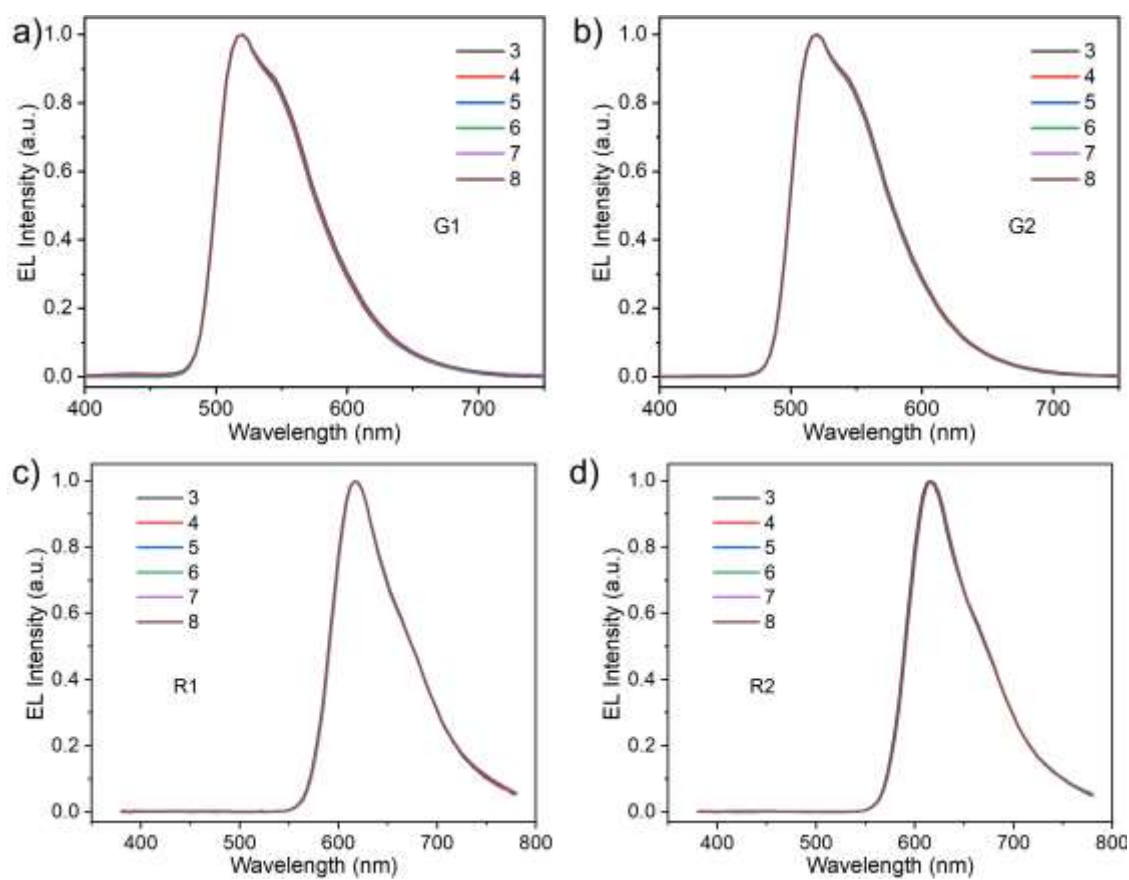
**Fig. S3** UV-Visible absorption spectra, fluorescence spectra and phosphorescence spectra in toluene solution ( $\sim 10^{-5}$  mol L $^{-1}$ ) of PI.



**Fig. S4** Solvatochromism PL spectra of **PI22PPCz** and **PI33PPCz** measured in different dilute solvents ( $\sim 10^{-5}$  mol L $^{-1}$ ).

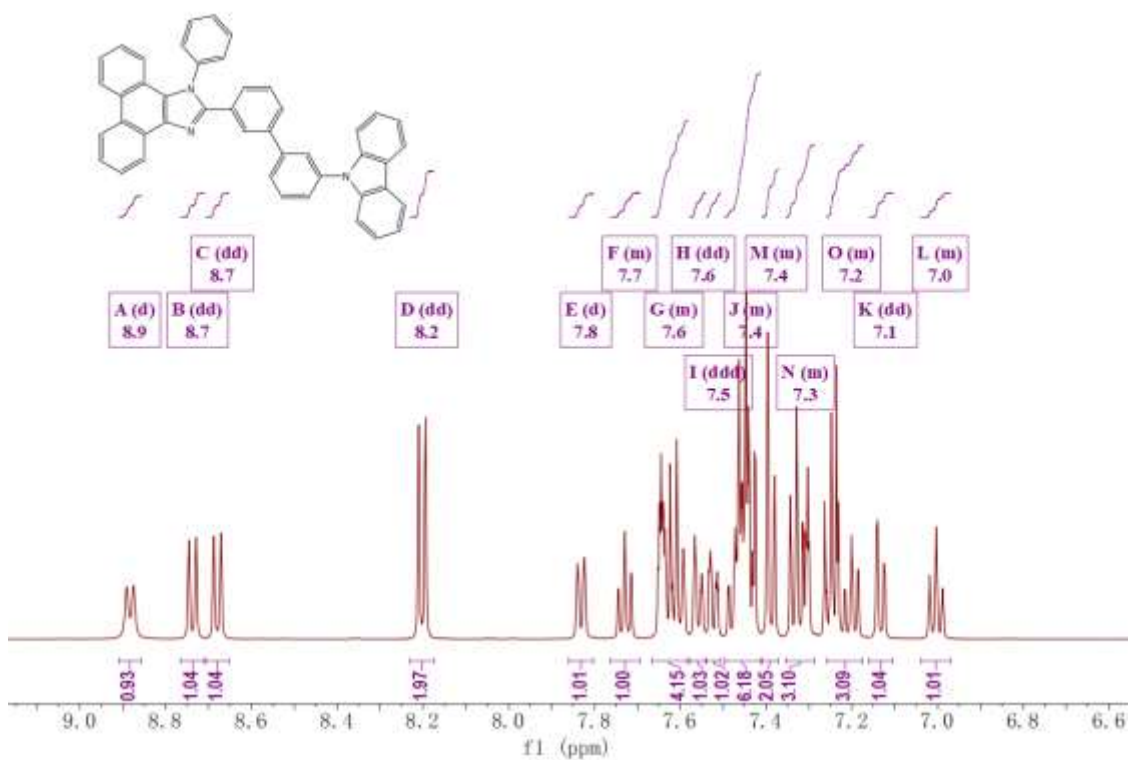


**Fig. S5** Intramolecular  $\pi$ - $\pi$  interactions for **PI22PPCz** molecule. The upper part is drawn in lighter color for easy identification.



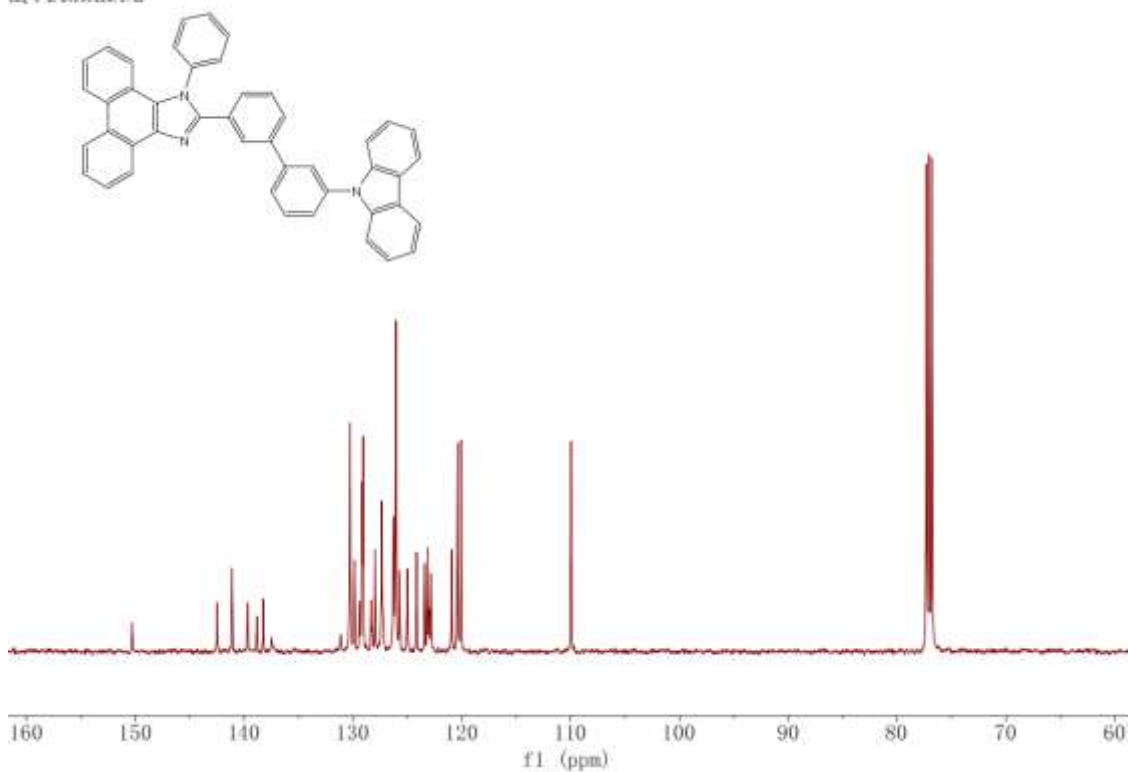
**Fig. S6** Electroluminescence spectrum of G1 a), G2 b), R1 c) and R2 d) at different driving voltages.

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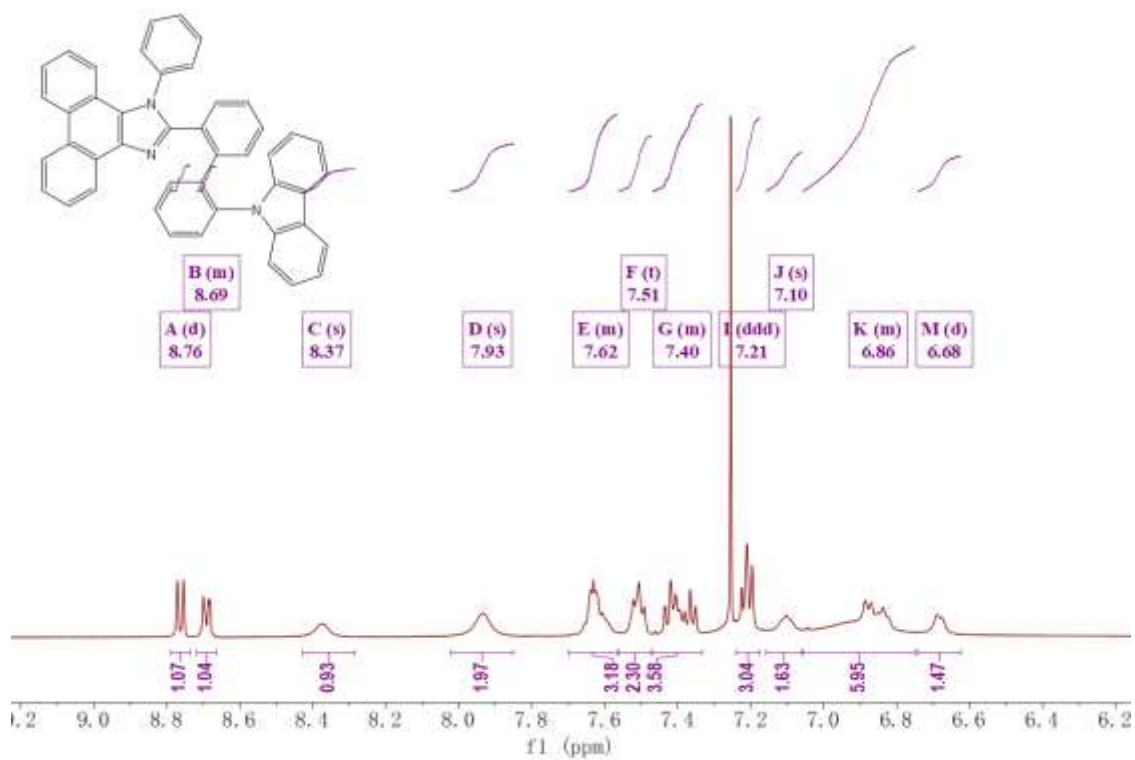
**Fig. S7**  $^1\text{H}$  NMR of PI33PPCz.

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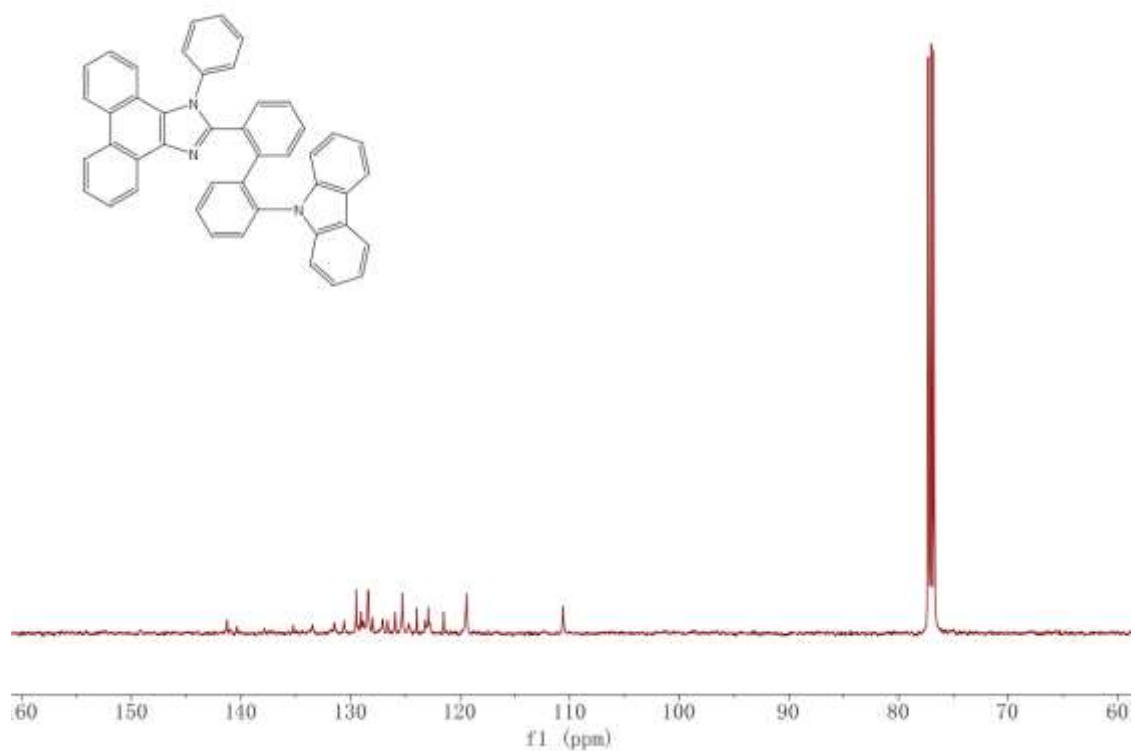
**Fig. S8**  $^{13}\text{C}$  NMR of PI33PPCz.

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**Fig. S9**  $^1\text{H}$  NMR of PI22PPCz.

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**Fig. S10**  $^{13}\text{C}$  NMR of PI22PPCz.



**Table S1.** Crystal data and structure refinement for **PI22PPCz**.

CCDC Deposition Number	1893408	
Empirical formula	C <sub>45</sub> H <sub>29</sub> N <sub>3</sub>	
Formula weight	611.71	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub> /n	
Unit cell dimensions	a = 10.052(2) Å	α = 90°.
	b = 14.186(3) Å	β = 91.84(3)°.
	c = 21.411(4) Å	γ = 90°.
Volume	3051.6(11) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.331 Mg/m <sup>3</sup>	
Absorption coefficient	0.078 mm <sup>-1</sup>	
F(000)	1280	
Crystal size	0.390 x 0.350 x 0.330 mm <sup>3</sup>	
Theta range for data collection	3.026 to 27.483°.	
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -26 ≤ l ≤ 27	
Reflections collected	26281	
Independent reflections	6815 [R(int) = 0.0897]	
Completeness to theta = 25.242°	97.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6815 / 0 / 549	
Goodness-of-fit on F <sup>2</sup>	1.069	
Final R indices [I > 2σ(I)]	R1 = 0.0663, wR2 = 0.1424	
R indices (all data)	R1 = 0.1310, wR2 = 0.1672	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.200 and -0.221 e.Å <sup>-3</sup>	

**Table S2.** Crystal data and structure refinement for **PI33PPCz**.

CCDC Deposition Number	1893407	
Empirical formula	C <sub>45</sub> H <sub>29</sub> N <sub>3</sub>	
Formula weight	611.71	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 12.5354(8) Å	α = 90°.
	b = 14.1497(9) Å	β = 90°.
	c = 35.992(2) Å	γ = 90°.
Volume	6383.9(7) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.273 Mg/m <sup>3</sup>	
Absorption coefficient	0.074 mm <sup>-1</sup>	
F(000)	2560	
Crystal size	0.350 x 0.290 x 0.200 mm <sup>3</sup>	
Theta range for data collection	1.980 to 26.048°.	
Index ranges	-13 ≤ h ≤ 15, -17 ≤ k ≤ 17, -44 ≤ l ≤ 44	
Reflections collected	38493	
Independent reflections	6307 [R(int) = 0.0746]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6307 / 0 / 433	
Goodness-of-fit on F <sup>2</sup>	1.070	
Final R indices [I > 2σ(I)]	R1 = 0.0558, wR2 = 0.0978	
R indices (all data)	R1 = 0.0876, wR2 = 0.1094	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.191 and -0.152 e.Å <sup>-3</sup>	

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