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Supporting Information

for

Molecular Evolution of Host Materials by Regular Tuning N/P Ratio for High-Performance Phosphorescence Organic Light-Emitting Diodes

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Contents

1. Compound syntheses and characterization

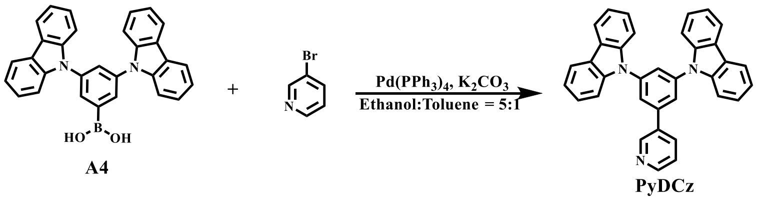
Intermediates A2, A3 and A4 were prepared following the literature methods.[1,2]

Synthesis of 2-bromo-5-(1H-triazol-1-yl)pyridine (A1). A mixture of 1,2,4-triazole (69 mg, 1 mmol), 2,5-dibromopyridine (237 mg, 1 mmol), CuI (95 mg, 0.5 mmol), 1,10-phenanthroline (90 mg, 0.5 mmol) and potassium carbonate (555 mg, 4 mmol) in dry N,N-dimethylformamide (DMF) (15 mL) was stirred and refluxed under N_2 atmosphere for 24 h. After removing the inorganic salts by filtering, evaporating the solvent under reduced pressure, the crude solid product was isolated by silica gel column chromatography using ethyl acetate/petroleum ether (1: 5) as eluent to afford pure white solid A1 (114 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.52 (d, J = 2.5 Hz, 1H), 8.11 (s, 1H), 8.01 (dd, J = 7.0, 2.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H). TOF-EI-MS (m/z): calcd for $C_7H_5BrN_4$ 223.9698; found, 223.9695 $[M]^+$.

Synthesis of 2-(3,5-Di(9H-carbazol-9-yl)-phenyl)-5-(1H-triazol-1-yl)pyridine (PyTzDCz). To a deoxygenated solution containing A1 (224 mg, 1 mmol), A3 (452 mg, 1mmol), toluene (15 mL), ethanol (3 mL), and aqueous sodium carbonate (2 M, 4 mL, 8 mmol) was added tetrakis(triphenylphosphino)palladium(0) (60 mg, 0.05 mmol) under nitrogen atmosphere. The reaction mixture was refluxed for 12 hours. After cooling to room temperature and diluted by water (10 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over anhydrous magnesium sulfate and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography over silica using ethyl acetate/petroleum ether as eluent, followed by recrystallization in chloroform/methanol to give white solid of the target compound (392 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.24 (s, 1H), 8.83 (d, *J* = 3.0 Hz, 1H), 8.21 (d, *J* = 9.5 Hz, 5H), 8.15 (s, 1H), 8.05 (d, *J* = 11.0 Hz, 1H), 7.94 (dd, *J* = 11.0, 2.5 Hz, 3H), 7.61 (d, *J* = 10.0 Hz, 4H), 7.48 (t, *J* = 9.5 Hz, 4H), 7.35 (t, *J* = 9.5 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.02, 149.26, 146.83, 141.65, 140.48, 140.24, 137.76, 134.43, 126.36, 124.94, 124.02, 123.81, 120.69, 120.64, 113.26, 109.57. TOF-MALDI-MS (*m*/*z*): calcd for $C_{37}H_{24}N_6$ 552.2062; found, 552.2060 $[M]^+$. Elemental analysis: C, 80.42; H, 4.38; N, 15.20. Found: C, 80.37; H, 4.41; N, 15.22.

2-(3-(9H-carbazol-9-yl)-phenyl)-5-(1H-triazol-1-yl)pyridine (PyTzSCz) was prepared from intermediate A2 (287 mg, 1 mmol) following the same method as PyTzDCz. White powder, yield: 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.24 (s, 1H), 8.76 (d, *J* = 2.5 Hz, 1H), 8.15 (m, 4H), 8.02 (d, *J* = 10.0 Hz, 1H), 7.83 (t, *J* = 2.0 Hz, 1H), 7.76 (d, *J* = 10.0 Hz, 1H), 7.71 (dt, *J* = 6.0, 2.0 Hz, 1H), 7.67 (dt, *J* = 6.0, 2.0 Hz, 1H), 7.44 (m, 4H), 7.33 (td, *J* = 8.0, 2.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.97, 148.88, 146.76, 141.59, 140.75, 138.84, 138.65, 137.66, 135.26, 130.87, 127.04, 126.12, 125.89, 125.54, 123.56, 120.47, 120.26, 113.09, 109.60. TOF-EI-MS (*m*/*z*): calcd. for $C_{25}H_{17}N_5$ 387.1484; found, 387.1476 $[M]^+$. Elemental analysis: C, 77.50; H, 4.42; N, 18.08. Found: C, 77.51; H, 4.40; N, 18.06.

Synthesis of 2-(3,5-di(9H-carbazol-9-yl)-phenyl)-pyridine (PyDCz). Intermediate A4 (453 mg, 1mmol), 3-bromopyridine (158 mg, 1 mmol), tetrakis-(triphenylphosphino)palladium(0) (57 mg, 0.05 mmol), toluene (10 mL), ethanol (2 mL), and aqueous K_2CO_3 solution (2 M, 2.5 mL, 4 mmol) was mixed and refluxed at 80 °C overnight under a nitrogen atmosphere overnight. After adding 20 mL of water to the cooled mixture, the organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layer was evaporated under reduced pressure after dried over with anhydrous $MgSO_4$. The crude product was isolated by silica gel column chromatography using ethyl acetate /petroleum ether (1:7) as eluent and further purified by repeated recrystallization in methanol/chloroform to afford pure PyDCz as white solid with a yield of 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.37 (s, 2H), 8.17 (d, J = 7.5 Hz, 4H), 7.86 (d, J = 14 Hz, 3H), 7.61 (d, J = 8.0 Hz, 4H), 7.46 (t, J = 7.5 Hz, 4H), 7.32 (t, J = 7.5 Hz, 5H). TOF-EI-MS (*m*/*z*): calcd for $C_{35}H_{23}N_3$ 485.1892; found, 485.1887 $[M]^+$. Elemental analysis: C, 86.57; H, 4.77; N, 8.66. Found: C, 86.60; H, 4.75; N, 8.65.



Scheme S1. Chemical structure and synthetic route of PyDCz.

References

1 W. Li, J. Li, D. Liu, D. Li, F. Wang, *ACS Appl. Mater. Interfaces* 2016, **8**, 21497;.

2 A. Suzuki, *Chem. Commun.*, 2005, 4759.

2. Supplementary figures

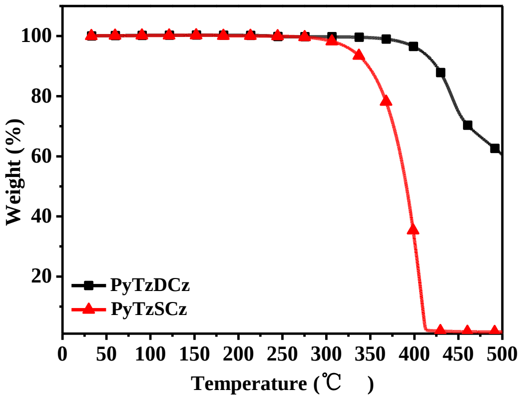


Fig. S1 TGA thermograms of PyTzDCz and PyTzSCz recorded at a heating rate of 10 ℃ min^{-1}.

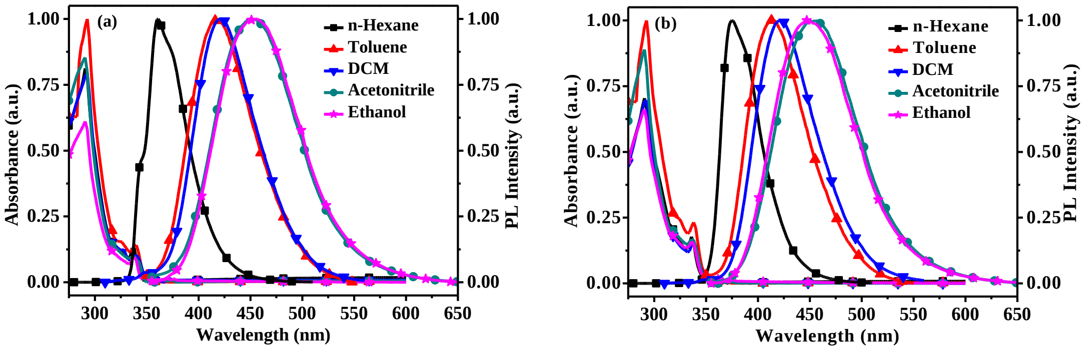


Fig. S2 The UV-vis absorption and fluorescence spectra of (a) PyTzDCz and (b) PyTzSCz in various solvents with different polarities (n-hexane, toluene, DCM, acetonitrile and ethanol).

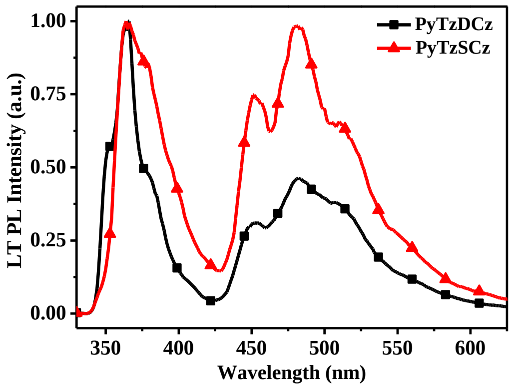


Fig. S3 LT PL spectra of PyTzDCz and PyTzSCz in frozen 2-MeTHF matrix at 77 K.

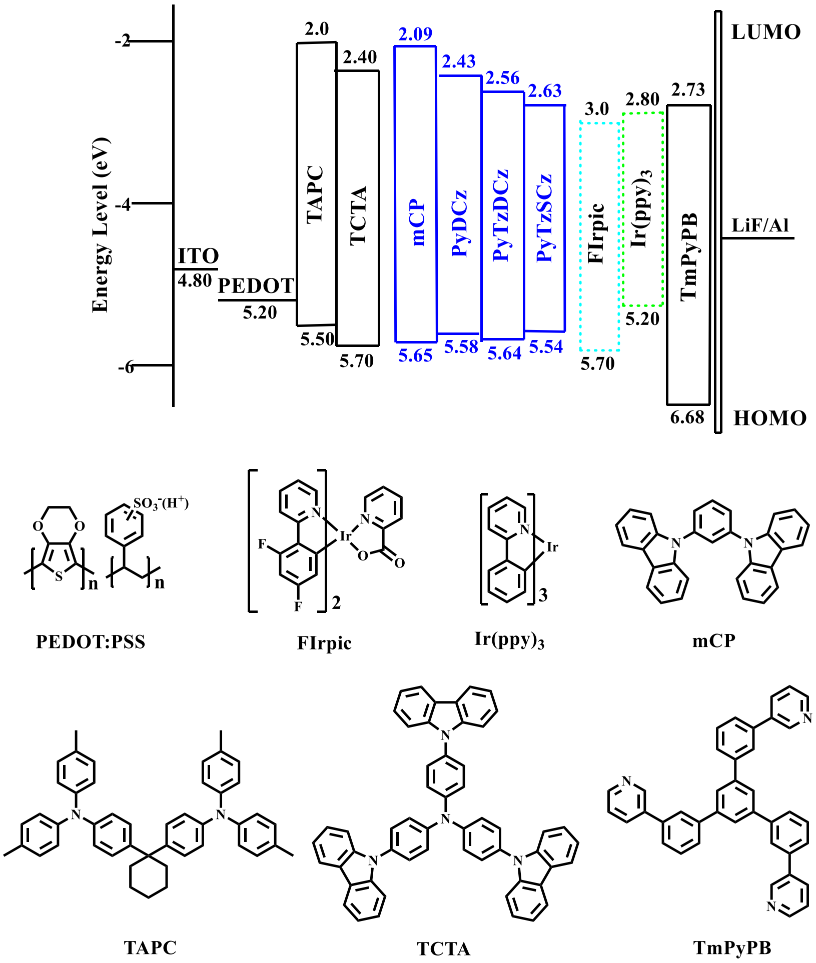


Fig. S4 Chemical structures and energy level diagram for the single carrier devices and blue, green PhOLEDs.

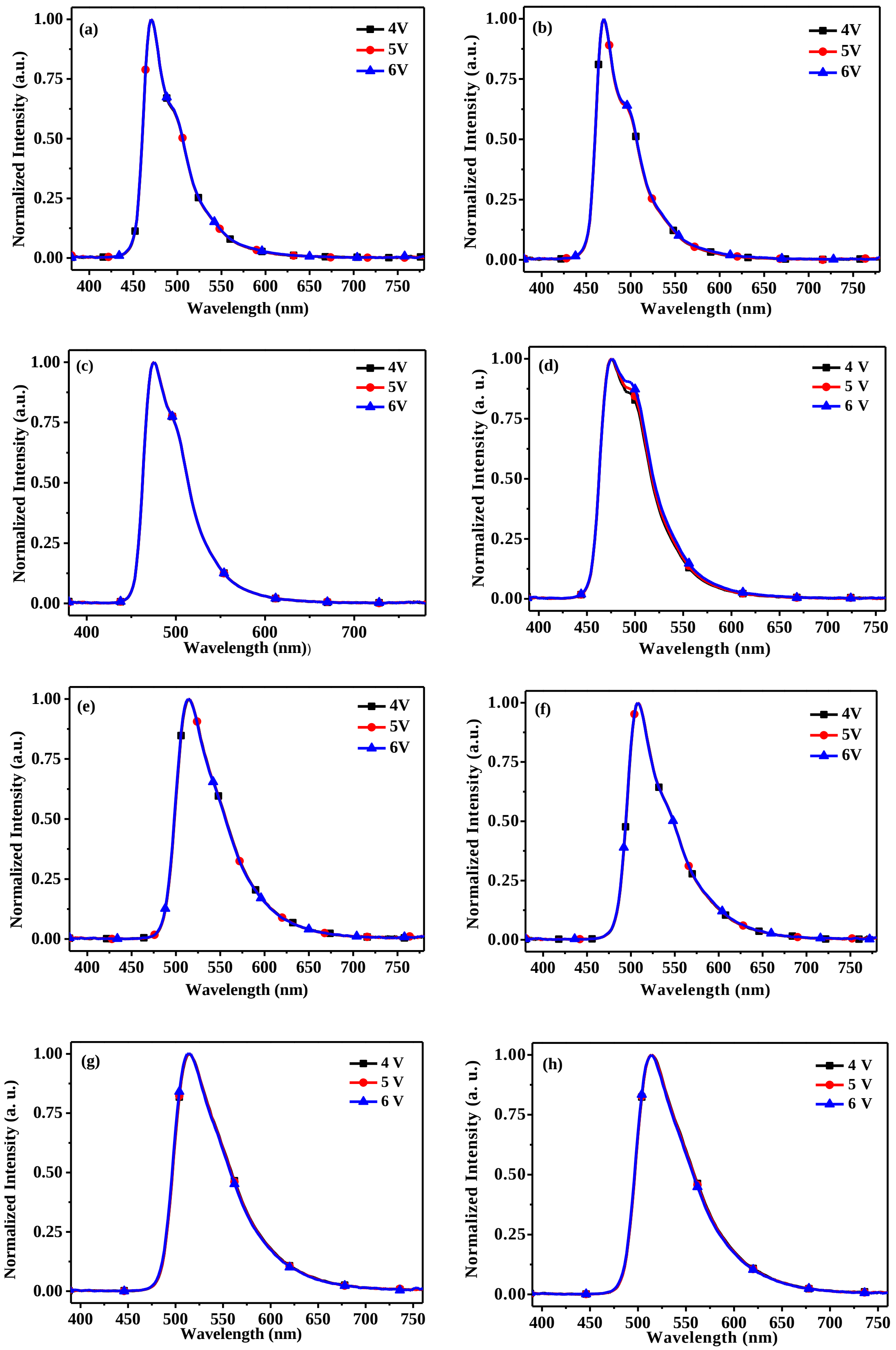


Fig. S5 EL spectra of blue devices B1 (a), B2 (b), B3 (c) and B4 (d), and of green devices G1 (e), G2 (f), G3 (g) and G4 (h) at various operating voltages.

Table S1 Summary of the turn-on voltage and power efficiency for FIrpic PhOLEDs.

Host	V_{on} (V)	$\eta_{\mathrm{p,\ max}}$ (lm/W)	reference
PyTzSCz	**2.6**	**48.1**	**This work**
PyTzDCz	**2.7**	**43.9**	
POAPF	3.0	35.4	Adv. Funct. Mater. 2009, 19, 2834–2843
BCPO	2.8	40.6	Adv. Mater. 2010, 22, 2468–2471
p-BISiTPA	3.5	26.1	Adv. Funct. Mater. 2011, 21, 1168–1178
m-BISiTPA	3.1	21.0	
p-OXDSiTPA	3.7	31.4	
m-OXDSiTP	3.3	20.3	
CSPO	3.4	9.1	Adv. Funct. Mater. 2012, 22, 2830–2836
pDCSPO	3.6	7.7	
DCSPO	3.6	9.9	
pTCSPO	4.0	5.1	
TCSPO	3.6	9.4	
9TPAFSPO	--	26.5	Adv. Mater. 2012, 24, 509–514
9CzFSPO	--	35.6	
9PhCzFSPO	--	34.3	
SitCz	2.9	36.5	Adv. Mater. 2012, 24, 2911–2915
pPCB2CZ	3.1	32.6	ACS Appl. Mater. Interfaces 2014, 6, 19808−19815
mPCB2CZ	3.7	31.3	
26DCzPPy	3.5	22.8	
mCP-BPBI	7.6	2.0	ACS Appl. Mater. Interfaces 2015, 7, 7303−7314
CP-QPBI	4.6	3.9	
o-CzCN	4.5	21.42	J. Mater. Chem. C, 2015, 3, 12529--12538
m-CzCN	3.8	24.50	
p-CzCN	3.5	13.40	
o-CzDPz	4.2	29.4	ACS Appl. Mater. Interfaces 2015, 7, 26206−26216
m-CzDPz	3.8	30.3	
3-CzDPz	3.6	28.9	
*m*CPDPz	3.7	22.4	
POSTF	--	50.5	Adv. Funct. Mater. 2015, 25, 645–650
ICDP	3.0	14.0	Adv. Funct. Mater. 2015, 25, 5548–5556
4ICPPy	3.0	24.0	
4ICDPy	3.2	34.5	
o-CzPyPz	4.1	30.4	ACS Appl. Mater. Interfaces 2016, 8, 22382−22391
m-CzPyPz	3.9	30.9	
p-CzPyPz	3.1	45.1	
m-PyPOmCP	3.5	43.6	Chem. Sci., 2016,7, 6706-6714
p-PyPOmCP	3.5	37.2	

SAF-3-DMB	3.2	42.6	ACS Appl. Mater. Interfaces 2016, 8, 20230−20236
DTzSCz	3.0	19.5	J. Mater. Chem. C, 2016, 4, 7260--7268
DTzDCz	2.9	15.5	
STzDCz	3.1	39.5	
m-BPyCz	2.9	42.4	ACS Appl. Mater. Interfaces 2017, 9, 37888−37897
p-BPyCz	2.8	40.4	
m-POPyCz	3.0	46.5	
p-POPyCz	3.0	45.2	
o-CzTP	3.3	40.5	ACS Appl. Mater. Interfaces 2018, 10, 5714−5722
m-CzTP	4.5	27.4	