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Electronic Supplementary Information (ESI)

Triphenylpyrazine: Methyl substitute to achieve deep blue emitter

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1. General Information

THF was distilled with sodium and benzophenone under dry N₂ before using. All other chemicals and reagents were purchased from commercial sources and used as received without further purification. ¹H and ¹³C NMR spectra were measured on a VNMRS 500 spectrometer. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Absorption spectrum were tested on a Shimadzu UV-2600 spectrophotometer. Photoluminescence (PL) spectrum were measured on a Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields were charaterized using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus QY. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. The geometries were optimized using the (time dependent) density functional theory ((TD)DFT) method with M06-2X/6-31G (d, p) level performing on Gaussian 09 package. Thermogravimetric analysis (TGA) analysis was performed on a TA TGA Q5000 under dry nitrogen at a heating rate of 20 °C min⁻¹ and Differential scanning calorimetry (DSC) analysis was carried out on a DSC Q1000 under dry nitrogen at a heating rate of 10 °C min⁻¹. Cyclic voltammetry (CV) were performed on a BAS 100W Bioanalytical Systems, using a platinum wire as the auxiliary electrode, a glass carbon disk as the working electrode and Ag/Ag⁺ as the reference electrode, standardized for the redox couple ferricinium/ferrocene (Fc/Fc⁺).

2. Calculation



Fig. S1 (A) The optimized geometries of two compounds in S_0 states; (B) The HOMOs and LUMOs of two compounds in S_0 states.

			α_{a-b}	$lpha_{ ext{a-c}}$	α_{a-d}	$lpha_{ ext{a-e}}$	α_{d-Cz}
	TPP-3C	S_0	-41.34	-40.95	41.49	41.24	39.24
		\mathbf{S}_1	-38.34	-46.54	16.26	24.97	23.79
_	TrPP-3C	S_0	-36.29	-37.63	-33.41		38.81
		\mathbf{S}_1	-13.56	-23.95	-11.40		-31.82

Table S1. The variation of dihedral angel of two compounds in S_0 and S_1 states.

3. Synthesis and Characterization



Fig. S2 The synthesis route of target compounds.

The intermediate 1 and TPP-Br are prepared according the previous literature.^{1, 2}

9-phenyl-3-(4-(3,5,6-triphenylpyrazin-2-yl)phenyl)-9H-carbazole (*TPP-3C*): A mixture of intermediate TPP-Br (7 mmol, 3.25 g), (9-phenyl-9H-carbazol-3-yl)boronic acid (14 mmol, 4.02 g), Pd(PPh₃)₄ (0.35 mmol, 0.40 g) and K₂CO₃ (28 mmol, 3.90 g) was added in 100 mL two-neck bottle under nitrogen. After then, a mixed solvent system of THF/water (v/v = 7:3) 30 mL was injected into the bottle and the mixture was refluxed overnight under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane three times and the combined organic layers were washed with brine, and then dried over MgSO4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography, yield was 78%. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.43 (d, 1H), 8.21 (d, 1H), 7.77 – 7.69 (m, 7H), 7.68 – 7.59 (m, 8H), 7.55 – 7.47 (m, 2H), 7.44 (d, 2H), 7.41 – 7.29 (m, 10H). ¹³C NMR (126 MHz, CDCl₃) δ 149.0, 148.9, 148.8, 148.7, 142.3, 141.8, 141.0, 139.2, 139.11, 139.1, 137.9, 137.1, 132.8, 130.8, 130.4, 130.3, 129.0, 128.7, 128.6, 128.6, 128.0, 127.4, 127.2, 126.6, 125.6, 124.3, 123.8, 120.7, 120.6, 119.0, 110.5, 110.4. HRMS (C₄₆H₃₁N₃): *m/z* 625.2535 (M+, calcd 625.2518)

2-(4-bromophenyl)-3-methyl-5,6-diphenylpyrazine (**TrPP-Br**): **1** (2.29 g, 10 mmol), **2** (2.54 g, 12 mmol), CeCl₃ 7H₂O (0.37 g, 1 mmol) and NH₄OAc (3.08 g, 40 mmol) were dissolved in ethanol (50 mL) at two-neck bottle and the mixture was stirring at 60 °C for 4 h. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane three times and the combined organic layers were washed with brine, and then dried over MgSO4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography, white powder with yield of 24%. ¹H NMR (500 MHz, CDCl₃) δ 7.68 – 7.60 (m, 4H), 7.53 – 7.47 (m, 4H), 7.35 – 7.26 (m, 6H), 2.73 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 149.8, 149.5, 149.1, 148.1, 138.6, 138.5, 137.5, 131.6, 130.9, 129.8, 129.7, 128.6, 128.4, 128.3, 128.2, 123.1, 22.9. HRMS (C₂₃H₁₇N₂Br): *m/z* 400.0566 (M+, calcd 400.0575)

3-(4-(3-methyl-5,6-diphenylpyrazin-2-yl)phenyl)-9-phenyl-9H-carbazole (*TrPP-3C*): The synthetic method was analogous to that depicted for TPP-3C, white powder with yield of 76%. ¹H NMR (500 MHz, CDCl3) δ 8.43 (d, J = 1.6 Hz, 1H), 8.22 (d, J = 7.7 Hz, 1H), 7.89 – 7.83 (m, 4H), 7.73 (dd, J = 8.5, 1.8 Hz, 1H), 7.67 – 7.58 (m, 4H), 7.57 – 7.53 (m, 4H), 7.51 – 7.47 (m, 2H), 7.44 (d, J = 3.7 Hz, 2H), 7.36 – 7.27 (m, 7H), 2.85 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 150.7, 149.2, 149.1, 148.2, 142.4, 141.4, 140.6, 138.7, 138.4, 137.6, 136.6, 132.7, 130.0, 129.9, 129.8, 128.5, 128.4, 128.3, 128.2, 127.6, 127.2, 127.1, 126.2, 125.4, 124.0, 123.4, 120.4, 120.2, 118.9, 110.2, 110.0, 22.7. HRMS (C₄₁H₂₉N₃): *m/z* 563.2367 (M+, calcd 563.2361)



Fig. S3 The HRMS spectra of TrPP-Br.



Fig. S4 The HRMS spectra of TrPP-3C.



Fig. S5 The HRMS spectra of TPP-3C.



Fig. S6 The ¹H-NMR spectrum of TPP-3C in CD₂Cl₂.



Fig. S7 The ¹H-NMR spectrum of TrPP-Br in CDCl₃.



Fig. S8 The ¹H-NMR spectrum of TrPP-3C in CDCl₃.



Fig. S9 The 13 C-NMR spectrum of TPP-3C in CD₂Cl₂.



Fig. S10 The ¹³C-NMR spectrum of TrPP-Br in CDCl₃.



Fig. S11 The ¹³C-NMR spectrum of TrPP-3C in CDCl₃. (* the peak of ethyl acetate)

4. Characterization of photophysics properties



Fig. S12 The PL spectra of TPP-3C in THF/H₂O mixtures;

Table S2. Photophysical properties of two compounds in different solvents.

		TrPP-3C			TPP-3C	
	λ_{abs}	$\lambda_{\rm em}$	Φ	λ_{abs}	$\lambda_{\rm em}$	Φ
	(nm)	(nm)	(%)	(nm)	(nm)	(%)
Toluene	341	420	1.7	350	441	2.1
Ethyl Acetate	338	432	3.0	347	449	2.0
Dichloromethane	338	446	6.6	347	460	3.4
DMF	341	468	26.6	349	483	11.6



Fig. S13 The absorption spectra and PL spectra of TrPP-3C (A)(B) and TPP-3C (C)(D) in different solvents.



Fig. S14 The transient PL decay curve of TPP-3C and TrPP-3C in THF solution (A) and in film (B). (concentration: 10⁻⁵M).



Fig. S15 The TGA and DSC curve of TrPP-3C and TPP-3C.



Fig. S16 (A)(B) The oxidation part of the CV curve of in dichloromethane solution; (C)(D) the reduction part of the CV curve of in DMF solution.

Table S3 The value of T_{g} , T_{d} , HOMO and LUMO for two compounds

	T_{g} (°C)	$T_{\rm d}$ (°C)	HOMO (eV)	LUMO (eV)
TPP-3C	133	403	-5.53	-2.59
TrPP-3C	105	404	-5.54	-2.48

^a Determined by CV measurement and calculated using ferrocene HOMO and LUMO level: $E_{\text{HOMO}} = -(E_{\text{ox}} - E_{(1/2) \text{ Fc/Fc}^+} + 4.8) \text{ eV}, E_{\text{LUMO}} = -(E_{\text{red}} - E_{(1/2) \text{ Fc/Fc}^+} + 4.8) \text{ eV}, E_{(1/2) \text{ Fc/Fc}^+} = 0.42 \text{ eV}.$

4. Device fabrication and measurement

Devices with active areas of $4 \times 4 \text{ mm}^2$ were grown on patterned ITO glass substrates with a sheet resistance of 10 Ω sq⁻¹. Before OLED fabrication, the ITO glass substrates were cleaned with detergent and deionized water, dried in an oven at 120 °C for 1 hour, then treated with UV-ozone for 15 minutes, and finally loaded into a deposition chamber with a basic pressure of 1×10^{-4} Pa. The organic layers were fabricated by evaporating organic layers at a rate of 1-2 Å s⁻¹. A layer of Liq with 2 nm thickness was deposited at a rate of 0.1 Å s⁻¹, and finally Al was deposited at a rate of approximately 5.0 Å s⁻¹ as the cathode. The current–voltage– brightness characteristics and electroluminescence (EL) spectra were measured with a Keithley 2400 source meter and a Luminance Meter LS110, and electroluminescence (EL) spectra were measured with a Flame-S-VIS-NIR (Serial Number: FLMS03334).

Molecular Structure	$\lambda_{\rm EL}$ (nm)	CE(cd/A)	EQE(%)	CIE _{x,y}	Reference
	482	4.33	3.13	(0.21, 0.31)	3
Py(5,9)BTriPE	456	1.63	1.27	(0.16, 0.17)	4
	468	1.51	1.12	(0.16, 0.17)	5

Table S4 Some EL performances of the AIE emitters in past five years.

N N N N N N TPE-m-TPAI	476	5.74	3.10	(0.19, 0.28)	6
	451	2.76	/	(0.15, 0.15)	7
N-V-V-N pTPE-2mTPA	466	3.79	/	(0.17, 0.22)	8
	482	5.49	2.88	/	9
	444	3.21	2.46	(0.20, 0.15)	10
	461	5.21	3.89	(0.15, 0.14)	11

Reference

- 1. Y.-F. Liang, K. Wu, S. Song, X. Li, X. Huang and N. Jiao, Org. Lett., 2015, 17, 876-879.
- L. Pan, H. Wu, J. Liu, K. Xue, W. Luo, P. Chen, Z. Wang, A. Qin and B. Z. Tang, *Adv. Opt. Mater.*, 2019, 7, 1801673
- 3. A. Islam, D. Zhang, R. Peng, R. Yang, L. Hong, W. Song, Q. Wei, L. Duan and Z. Ge, *Chem. Asian J.*, 2017, **12**, 2189-2196.
- 4. X. Yang, Z. Zhao, H. Ran, J. Zhang, L. Chen, R. Han, X. Duan, H. Sun and J. -Y. Hu, *Dyes Pigm.*, 2020, 173, 107881
- X. Tang, L. Yao, H. Liu, F. Shen, S. Zhang, H. Zhang, P. Lu and Y. Ma, *Chem. Eur. J.*, 2014, 20, 7589-7592.

- 6. A. Islam, D. Zhang, Q. Guan, L. Hong, W. Song, J. Huang, R. Peng, L. Duan, Q. Wei and Z. Ge, *Dyes Pigm.*, 2018, **157**, 251-258.
- J. Huang, R. Tang, T. Zhang, Q. Li, G. Yu, S. Xie, Y. Liu, S. Ye, J. Qin and Z. Li, *Chem. Eur. J.*, 2014, 20, 5317-5326.
- 8. J. Huang, Y. Jiang, J. Yang, R. Tang, N. Xie, Q. Li, H. S. Kwok, B. Z. Tang and Z. Li, *J. Mater. Chem. C*, 2014, **2**, 2028-2036.
- M. Chen, H. Nie, B. Song, L. Li, J. Z. Sun, A. Qin and B. Z. Tang, J. Mater. Chem. C, 2016, 4, 2901-2908.
- Y. Cai, C. Shi, H. Zhang, B. Chen, K. Samedov, M. Chen, Z. Wang, Z. Zhao, X. Gui, D. Ma, A. Qin and B. Z. Tang, J. Mater. Chem. C, 2018, 6, 6534-6542.
- 11. X. Zhan, Z. Wu, Y. Lin, Y. Xie, Q. Peng, Q. Li, D. Ma and Z. Li, Chem. Sci., 2016, 7, 4355-4363.