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Supporting Information

Each Performs Own Functions on Luminescence: Phenyl Substituted Effect in Tetraphenylpyrazine

Haozhong Wu, Xiaojuan Song, Bing Zhang, Zhiming Wang,* Tian Zhang,* Anjun Qin and Ben Zhong Tang

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 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. Single crystal X-ray diffraction intensity data were collected on a Bruker–Nonices Smart Apex CCD diffractometer with graphite monochromated CuK α radiation. Photoluminescence (PL) spectra 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. Thermogravimetric analysis (TGA) analysis was performed on a TA TGA Q5000 under dry nitrogen at a heating rate of 20 °C min⁻¹. Differential scanning calorimetry (DSC) analysis was 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 ferricenium/ferrocene (Fc/Fc⁺).

2. Computational Methodology

The solution phase and aggregation effect were taken into account through the polarizable continuum model (PCM) and the combined quantum mechanics/molecular mechanics (QM/MM) approach as implemented in the B.01 version of the Gaussian 16 package. ^[R1] The computational clusters for both 23-B3C and 25-B3C were built from the X-ray crystal structure, including 72 molecules (3600 atoms). The two-layer ONIOM ^[R2] method was used for QM/MM simulations, where the centroid molecule was chosen as QM region (high layer) and the remaining molecules were treated as MM region (low layer). The geometry optimizations were performed on the QM region using at (TD)-DFT level while the MM region was kept frozen. The PBE0 ^[R3] functional together with 6-31G(d) basis set was employed for all QM calculations. The Amber force field ^[R4] was used for the MM expressions. The electrostatic embedding scheme ^[R5] was adopted in the QM/MM

calculations, incorporating the MM partial charges into the effective Hamiltonian of the QM part. The normal mode analyses were done with the help of the DUSHIN program. ^[R6] Under the harmonic oscillator approximation, the reorganization energy λ_j of each normal mode is defined as its energy $\frac{h\omega_j}{m}$ multiplied by

Huang-Rhys factor S_j , $\lambda_j = hS_j\omega_j = \frac{1}{2}D_j^2\omega_j^2$. D_j is the displacement along each normal mode between two electronic states. The summation over all normal modes is the total reorganization energy λ . **3. Supporting Data**





9-phenyl-3-(pyrazin-2-yl)-9H-carbazole (3C): A mixture of 2-bromopyrazine (1) (4 mmol, 0.64 g), (9-phenyl-9H-carbazol-3-yl)boronic acid (2) (5.2 mmol, 1.51 g), Pd(PPh₃)₄ (0.2 mmol, 0.23 g) and K₂CO₃ (12 mmol, 1.66 g) was added in 100 mL two-neck bottle under nitrogen. After then, a mixed solvent system of toluene, ethanol and water (v/v/v = 8:1:1) 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 72%. ¹H NMR (500 MHz, CDCl₃) δ 9.15 (d, *J* = 1.4 Hz, 1H), 8.83 (d, *J* = 1.5 Hz, 1H), 8.63 (dd, *J* = 2.4, 1.6 Hz, 1H), 8.46 (d, *J* = 2.5 Hz, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.59 (tdd, *J* = 8.3, 7.1, 1.5 Hz, 4H), 7.52 – 7.38 (m, 4H), 7.33 (ddd, *J* = 7.9, 6.5, 1.6 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 153.5, 144.0, 142.1, 142.0, 141.9, 141.5, 137.3, 130.0, 128.3, 127.8, 127.1, 126.5, 124.8, 124.1, 123.4, 120.6, 120.50, 119.2, 110.3, 110.1. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₂₂H₁₅N₃; 321.1266. found, 321.1245.

9-phenyl-3-(3-phenylpyrazin-2-yl)-9H-carbazole (23-B3C): A mixture of 2,3-dibromopyrazine (3) (5 mmol, 1.19 g), phenylboronic acid (4) (6.5 mmol, 0.79 g), (9-phenyl-9H-carbazol-3-yl)boronic acid (2) (5.5 mmol, 1.61 g), Pd(PPh₃)₄ (0.5 mmol, 0.58 g) and K₂CO₃ (30 mmol, 4.14 g) was added in 100 mL two-neck bottle under nitrogen. After then, a mixed solvent system of toluene, ethanol and water (v/v/v = 8:1:1) 70 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 26%. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.68 – 8.57 (m, 2H), 8.37 (d, *J* = 1.4 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.49 (m, 6H), 7.46 (ddd, *J* = 6.9, 2.8, 1.4 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.32 – 7.23 (m, 5H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 154.5, 153.9, 143.3, 142.7, 142.6, 142.2, 140.6, 138.6, 131.7, 131.2, 131.0, 129.7, 129.5, 129.2, 129.0, 128.2, 127.6, 124.6, 124.6, 123.3, 121.6, 121.6, 111.3, 110.6 HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₂₈H₁₉N₃; 397.1579. found, 397.1584.

9-phenyl-3-(5-phenylpyrazin-2-yl)-9H-carbazole (25-B3C): A mixture of 2,5-dibromopyrazine (5) (5 mmol, 1.19 g), phenylboronic acid (4) (6.5 mmol, 0.79 g), (9-phenyl-9H-carbazol-3-yl)boronic acid (2) (5.5 mmol, 1.61 g), Pd(PPh₃)₄ (0.5 mmol, 0.58 g) and K₂CO₃ (30 mmol, 4.14 g) was added in 100 mL two-neck bottle under nitrogen. After then, a mixed solvent system of toluene, ethanol and water (v/v/v = 8:1:1) 70 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 31%. ¹H NMR (400 MHz, CD₂Cl₂) δ 9.22 (d, *J* = 1.5 Hz, 1H), 9.10 (d, *J* = 1.5 Hz, 1H), 8.93 (dd, *J* = 1.8, 0.5 Hz, 1H), 8.27 (dt, *J* = 7.8, 1.0 Hz, 1H), 8.18 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.15 – 8.08 (m, 2H), 7.69 – 7.58 (m, 4H), 7.58 – 7.39 (m, 7H), 7.35 (ddd, *J* = 8.0, 6.1, 2.0 Hz, 1H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 152.5, 150.9, 143.2, 142.9, 142.3, 142.2, 138.6, 137.9, 131.3, 130.8, 130.3, 129.6, 129.1, 128.3, 127.9, 127.8, 126.1, 125.3, 124.7, 121.8, 121.8, 120.2, 111.6, 111.4. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₂₈H₁₉N₃; 397.1579. found, 397.1602.

9-phenyl-3-(6-phenylpyrazin-2-yl)-9H-carbazole (**26-B3C**): A mixture of 2,6-dibromopyrazine (**6**) (5 mmol, 1.19 g), phenylboronic acid (**4**) (6.5 mmol, 0.79 g), (9-phenyl-9H-carbazol-3-yl)boronic acid (**2**) (5.5 mmol, 1.61 g), Pd(PPh₃)₄ (0.5 mmol, 0.58 g) and K₂CO₃ (30 mmol, 4.14 g) was added in 100 mL two-neck bottle under nitrogen. After then, a mixed solvent system of toluene, ethanol and water (v/v/v = 8:1:1) 70 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 35%. ¹H NMR (400 MHz, CD₂Cl₂) δ 9.11 (s, 1H), 9.02 – 8.91 (m, 2H), 8.34 – 8.19 (m, 4H), 7.71 – 7.42 (m, 11H), 7.36 (s, 1H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 153.6, 152.8, 143.3, 142.9, 140.7, 139.9, 138.6, 138.1, 131.3, 131.2, 130.3, 129.8, 129.1, 128.4, 127.8, 126.4, 125.3, 124.7, 121.8, 121.8, 120.5, 111.6, 111.4. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₂₈H₁₉N₃; 397.1579. found, 397.1609.

9-phenyl-3-(phenylethynyl)-9H-carbazole (9): A mixture of 3-bromo-9-phenyl-9H-carbazole (7) (5 mmol, 1.60 g), CuI (0.1 mmol, 19 mg), Pd(PPh₃)₄ (0.05 mmol, 58 mg) and was added in 100 mL two-neck bottle under nitrogen. After then, the liquid reactant phenylacetylene ($\boldsymbol{8}$) (7.5 mmol, 0.82 mL), trimethylamine and THF was injected into the bottle and the mixture was

refluxed overnight under nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and solid was dissolved into dichloromethane and washed with brine and water, successively. And then, the organic solution was dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography, yield is 82%. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.34 (d, *J* = 0.8 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.59 – 7.54 (m, 5H), 7.52 – 7.47 (m, 1H), 7.45 – 7.29 (m, 7H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 142.0, 141.1, 137.8, 131.9, 130.6, 130.0, 129.0, 128.5, 128.4, 127.6, 127.1, 124.4, 124.3, 124.0, 123.4, 121.0, 114.9, 110.6, 110.5, 91.0, 88.3. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₂₆H₁₇N; 343.1361. found, 343.1349.

1-phenyl-2-(9-phenyl-9H-carbazol-3-yl)ethane-1,2-dione (10): An aqueous solution of KMnO₄ (15 mmol, 2.37 g), NaHCO₃ (5.5 mmol, 0.46 g) and tetraethylammonium bromide (2.5 mmol, 0.35 g) was added into a solution of *9* (5 mmol, 1.71 g) in dichloromethane. The mixture was rapidly stirred at room temperature for 24 h. The Na₂S₂O₃ saturated aqueous solution and 1M HCl were added into the mixture successively until the solution became clear. The organic layer was separated and washed with brine and water, and dried over MgSO₄. Evaporation of the solvent afforded nearly pure compound, yield is 93%. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.76 (d, *J* = 1.3 Hz, 1H), 8.18 (t, *J* = 7.8 Hz, 1H), 8.04 (td, *J* = 8.5, 1.5 Hz, 3H), 7.70 – 7.63 (m, 3H), 7.58 – 7.52 (m, 5H), 7.50 – 7.32 (m, 4H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 195.7, 194.5, 144.9, 142.3, 136.8, 135.0, 133.8, 130.5, 130.2, 129.3, 128.7, 127.9, 127.4, 127.4, 125.6, 124.1, 123.8, 123.5, 121.6, 121.0, 110.8, 110.5. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₂₆H₁₇NO₂; 375.1259. found, 375.1340.

9-phenyl-3-(3,5,6-triphenylpyrazin-2-yl)-9H-carbazole (TP-3C): A mixture of *10* (2 mmol, 0.75 g), 1,2-diphenylethane 1,2-diamine (2.6 mmol, 0.55 g) and glacial acetic acid (15 mL) were added in 100 mL two-neck bottle and then refluxed under air for 3 h. After cooling down, the solid product was filtrated and washed with methanol. The crude product was purified by column chromatography, yield is 65%. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.50 (dd, *J* = 1.7, 0.6 Hz, 1H), 8.05 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.70 – 7.55 (m, 11H), 7.49 (d, *J* = 7.1 Hz, 1H), 7.44 – 7.23 (m, 13H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 150.5, 149.9, 149.8, 149.3, 142.6, 142.3, 140.3, 140.0, 140.0, 138.6, 131.4, 131.2, 131.2, 131.2, 131.2, 129.9, 129.8, 129.8, 129.5, 129.4, 129.0, 128.3, 127.5, 124.7, 124.7, 123.4, 121.6, 121.6, 111.3, 110.6. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₄₀H₂₇N₃; 549.2205. found, 549.2172.

Crystal data for 23-B3C (CCDC 1976103): C₂₈H₁₉N₃, $M_w = 397.46$, Monoclinic, *P*21/C, a = 9.10690(10) Å, b = 23.4059(3) Å, c = 9.80850(10) Å, $a = 90^\circ$, $\beta = 101.0980(10)^\circ$, $\gamma = 90^\circ$, V = 2051.63(4) Å³, Z = 4, Dc = 1.287 g cm⁻³, $\mu = 0.594$ mm⁻¹ (CuK α , $\lambda = 1.54184$), F(000) = 832, T = 109.99(15) K, $2\theta_{max} = 67.079^\circ$ (98.3%), 18754 measured reflections, 3665 independent reflections ($R_{int} = 0.0167$), GOF on $F^2 = 1.081$, $R_1 = 0.0382$, $wR_2 = 0.0933$ (all data), $\Delta e 0.190$ and -0.284 eÅ⁻³.

Crystal data for 25-B3C (CCDC 1976104): C₂₈H₁₉N₃, $M_w = 397.46$, Triclinic, *P*-1, a = 9.8929(2) Å, b = 13.4587(4) Å, c = 15.4233(5) Å, $a = 69.319(3)^\circ$, $\beta = 88.055(2)^\circ$, $\gamma = 88.148(2)^\circ$, V = 1919.66(10) Å³, Z = 4, Dc = 1.375 g cm⁻³, $\mu = 0.635$ mm⁻¹ (CuK α , $\lambda = 1.54184$), F(000) = 832, T = 149.99(10) K, $2\theta_{max} = 67.076^\circ$ (100%), 9918 measured reflections, 6740 independent reflections ($R_{int} = 0.0183$), GOF on $F^2 = 1.051$, $R_1 = 0.0387$, $wR_2 = 0.1009$ (all data), $\Delta e 0.216$ and -0.398 eÅ⁻³.



Fig. S3. The ¹³C-NMR of 3C in CDCl₃.



Fig. S5. The ¹³C-NMR of 23-B3C in CD₂Cl₂.





Fig. S9. The ¹³C-NMR of 26-B3C in CD₂Cl₂.



Fig. S10. The ¹H-NMR of immediate 9 in CD₂Cl₂.



Fig. S11. The ¹³C-NMR of immediate 9 in CD₂Cl₂.



Fig. S12. The ¹H-NMR of immediate 10 in CD₂Cl₂.







Fig. S16. PL spectra of (A)3C, (B) 23-B3C, (C) 25-B3C, (D) 26-B3C and (E) TP-3C in THF/water mixtures with different water fractions; concentration: 10^{-5} M; (F) Change in relative emission intensity (I/I_0) versus the water fraction of the THF/water mixtures of five compounds. I_0 is the emission intensity in pure THF; The transient PL decay curve of 3C, 25-B3C, 26-B3C and TP-3C in THF (G) and film states (H); (I)The transient PL decay curve of 23-B3C in THF and film states.



Fig. S17. The NTOs of 3C, 26-B3C and TP-3C in THF solution.



Fig. S18. Projection of the reorganization energy onto mode relaxations for 3C, 23-B3C, 25-B3C, 26-B3C and TP-3C in solution.

Table S1 Reorganization energies of low-frequency (LF, < 200 cm⁻¹) and high-frequency (HF, 1400–1800 cm⁻¹) modes and the related contributions to the total reorganization energies (λ) obtained by normal mode analyses for 3C, 23-B3C, 25-B3C, 26-B3C and TP-3C in solution and 23-B3C and 25-B3C in solid.

	$\lambda_{\rm LF}~({ m meV})$	$\lambda_{ m HF}(m meV)$	λ (meV)	$\lambda_{ m LF}$ / λ	$\lambda_{ m HF}$ / λ
			THF solution		
3C	35	86	219	0.16	0.39
23-B3C	218	155	529	0.41	0.29
25-B3C	46	104	239	0.19	0.44
26-B3C	48	90	240	0.20	0.38
TP-3C	120	116	406	0.30	0.29
			crystal		
23-B3C	46	145	329	0.14	0.44
25-B3C	51	76	208	0.25	0.37

Table S2. The selected dihedral angle of 3C, 26-B3C and TP-3C in THF solution.

	3C		26-1	B3C	TP-3C			
	$\alpha_{1-2-3-4}$	a3-2-5-6	$\alpha_{1-2-3-4}$	$\alpha_{3-2-5-6}$	$\alpha_{1-2-3-4}$	a3-2-5-6	$\alpha_{5-2-3-7}$	
S0	-2.02	158.92	-3.61	157.20	-16.59	147.58	-18.89	
S 1	0.50	-177.97	-1.78	175.93	-30.63	165.71	-34.10	
Δ	-2.52	-23.11	-1.83	-18.73	14.04	-18.13	15.21	



Toluene, reflux







H₂N

H₂N

17

ΝH₂

16







14

14

0

O[']

1,2-bis(4-(9,9-dimethyl-9H-fluoren-2-yl)phenyl)ethane-1,2-dione (14): A mixture of 1,2-bis(4-bromophenyl)ethane-1,2dione (12) (10 mmol, 3.66 g), (9,9-dimethyl-9H-fluoren-2-yl)boronic acid (13) (30 mmol, 7.14 g), Pd(PPh₃)₄ (0.5 mmol, 0.58 g) and K₂CO₃ (60 mmol, 8.28 g) was added in 100 mL two-neck bottle under nitrogen. After then, a mixed solvent system of toluene, ethanol and water (v/v/v = 8:1:1) 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 68%.¹H NMR (500 MHz, CD₂Cl₂) δ 8.10 (d, *J* = 8.3 Hz, 4H), 7.85 (dd, *J* = 10.9, 8.2 Hz, 6H), 7.81 – 7.73 (m, 4H), 7.66 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.40 – 7.30 (m, 4H), 1.54 (d, *J* = 8.7 Hz, 12H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 194.65, 155.00, 154.53, 148.31, 140.31, 138.83, 138.79, 132.02, 130.88, 128.18, 127.98, 127.54, 126.91, 123.13, 122.07, 120.91, 120.71, 47.41, 27.34. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₄₄H₃₄O₂; 594.2559. found, 594.2540

2,3-bis(4-(9,9-dimethyl-9H-fluoren-2-yl)phenyl)pyrazine (**P-2PF**): A mixture of **14** (1 mmol, 0.59 g), ethane-1,2-diamine (**15**) (3 mmol, 0.2 mL) and glacial acetic acid (15 mL) were added in 100 mL two-neck bottle and then refluxed under air for 3 h. After cooling down, the solid product was filtrated and washed with methanol. The crude product was purified by column chromatography, yield is 63%. ¹H NMR (400 MHz, CDCl₃) δ 8.65 (s, 2H), 7.85 – 7.58 (m, 16H), 7.48 – 7.40 (m, 2H), 7.39 – 7.29 (m, 4H), 1.53 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.36, 153.93, 152.45, 142.03, 141.81, 139.38, 138.89, 138.74, 137.39, 130.18, 127.40, 127.08, 126.16, 122.65, 121.24, 120.37, 120.15, 46.99, 27.23. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₄₆H₃₂N₂; 616.2878. found, 616.2859.

2,3-bis(4-(9,9-dimethyl-9H-fluoren-2-yl)phenyl)-5,6,7,8-tetrahydroquinoxaline (**HP-2PF**): A mixture of **14** (0.8 mmol, 0.48 g), cyclohexane-1,2-diamine (**16**) (1.2 mmol, 0.15 mL) and glacial acetic acid (15 mL) were added in 100 mL two-neck bottle and then refluxed under air for 3 h. After cooling down, the solid product was filtrated and washed with methanol. The crude product was purified by column chromatography, yield is 67%. ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.71 (m, 4H), 7.62 (ddd, J = 22.0, 10.6, 4.8 Hz, 12H), 7.46 – 7.41 (m, 2H), 7.37 – 7.29 (m, 4H), 3.10 (s, 4H), 2.02 (s, 4H), 1.54 (d, J = 9.8 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.31, 153.92, 150.58, 149.17, 141.20, 139.67, 138.80, 138.71, 137.94, 130.15, 127.33, 127.03, 126.13, 122.63, 121.22, 120.33, 120.11, 46.98, 31.92, 27.24, 22.90. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₅₀H₄₂N₂; 670.3348. found, 670.3370.

2,3-bis(4-(9,9-dimethyl-9H-fluoren-2-yl)phenyl)quinoxaline (**PP-2PF**): A mixture of **14** (1 mmol, 0.59 g), benzene-1,2-diamine (**17**) (1.5 mmol, 0.16 g) and glacial acetic acid (15 mL) were added in 100 mL two-neck bottle and then refluxed under air for 3 h. After cooling down, the solid product was filtrated and washed with methanol. The crude product was purified by column chromatography, yield is 78%. ¹H NMR (400 MHz, CDCl₃) δ 8.26 – 8.17 (m, 2H), 7.83 – 7.67 (m, 16H), 7.63 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.38 – 7.29 (m, 4H), 1.54 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.37, 153.94, 153.11, 141.94, 141.32, 139.45, 138.92, 138.74, 137.94, 130.42, 130.00, 129.25, 127.41, 127.09, 126.21, 122.65, 121.28, 120.39, 120.16, 47.00, 27.25. HRMS (MALDI-TOF): *m/z* [M+] calcd. for C₅₀H₃₈N₂; 666.3035. found, 666.3058.









Table S3. The selected dihedral angles of three P-2PF derivatives



		α ₁₋₂₋₃₋₄	α ₃₋₂₋₅₋₆	a2-3-7-8	α5-2-3-7
	S_0	8.89	-143.20	-143.51	12.78
P-2PF	\mathbf{S}_1	25.80	-166.59	-165.70	35.30
	Δ	16.91	-23.39	-22.19	22.52
	S ₀	8.42	-143.17	-143.64	12.37
HP-2PF	\mathbf{S}_1	26.04	-165.94	-167.25	35.33
	Δ	17.62	-22.77	-23.61	22.96
	S_0	7.29	-142.50	-142.39	11.66
PP-2PF	\mathbf{S}_1	10.61	-151.54	-151.54	18.53
	Δ	3.32	-9.04	-9.15	6.87



Fig. S28. The NTOs (transition ratios up to 95%) of three P-2PF derivatives.



Fig. S29. The absorption spectra (A) and PL spectra (B) of three P-2PF derivatives.



Fig. S30. The transient PL spectrum of three P-2PF derivatives in (A) THF solution (10-5M) and (B) film states.

$\lambda_{abs}{}^a$	$\lambda_{ m abs}{}^a$	$\lambda_{\mathrm{em}}{}^{b}(\mathrm{nm})$			Φ^c		τ^{d} (ns)		$k_{\rm r}^{e} (10^7 {\rm s}^{-1})$		_	$k_{\rm nr}^{f}(10^7 {\rm s}^{-1})$		
Compound	(nm)	soln	FWHM	film	FWHM	 soln	film	soln	film	soln	film	_	soln	film
P-2PF	322	441	84	442	80	0.022	0.186	0.58	0.86	3.79	21.6		169	94.6
HP-2PF	330	443	88	438	81	0.021	0.157	0.48	0.79	4.38	19.9		204	107
PP-2PF	316	440	68	447	63	0.155	0.419	0.83	0.96	18.7	43.7		102	60.5



^a Maximum absorption wavelength, concentration: 10⁻⁵ M; ^b Maximum emission wavelength, soln: THF solution, film: neat film, FWHM: full width at half maximum ^c absolute fluorescence quantum efficiency; ^d fluorescence lifetime; ^e $\alpha_{AIE} = \Phi$ (film)/ Φ (soln); ^f $k_r = \Phi/\tau$; ^g $k_{nr} = (1-\Phi)/\tau$.



Fig. S31. The curve of thermogravimetric analysis (A) and differential scanning calorimetry (B) for 25-B3C, 26-B3C and TP-3C.



Fig. S32. The cyclic voltammetry curve of (A) 25-B3C, (B) 26-B3C and (C) TP-3C in dichloromethane solution (oxidation section).

Table S5 The value of T_g , T_d , HOMO, LUMO and E_{gap} for 25-B3C, 26-B3C and TP-3C.

	T_{g} (°C)	$T_{\rm d}$ (°C)	HOMO (eV)	LUMO (eV)	$E_{gap}(eV)$
25-B3C	60	343	-5.59	-2.42	3.17
26-B3C	60	315	-5.54	-2.29	3.25
TP-3C	119	386	-5.55	-2.40	3.15

^a Determined by CV measurement and calculated using ferrocene HOMO level: $E_{\text{HOMO}} = -(E_{\text{ox}} - E_{(1/2) \text{ Fc/Fc}}^{+} + 4.8) \text{ eV}, E_{(1/2) \text{ Fc/Fc}}^{+} = 0.42 \text{ eV}.$ ^b Calculated from the formula: $E_{\text{HOMO}} = E_{\text{LUMO}} + E_{\text{gap}}$.^c Calculated from 1240/ λ_{edge} .

3.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).

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