Electronic Supporting Information（ESI）

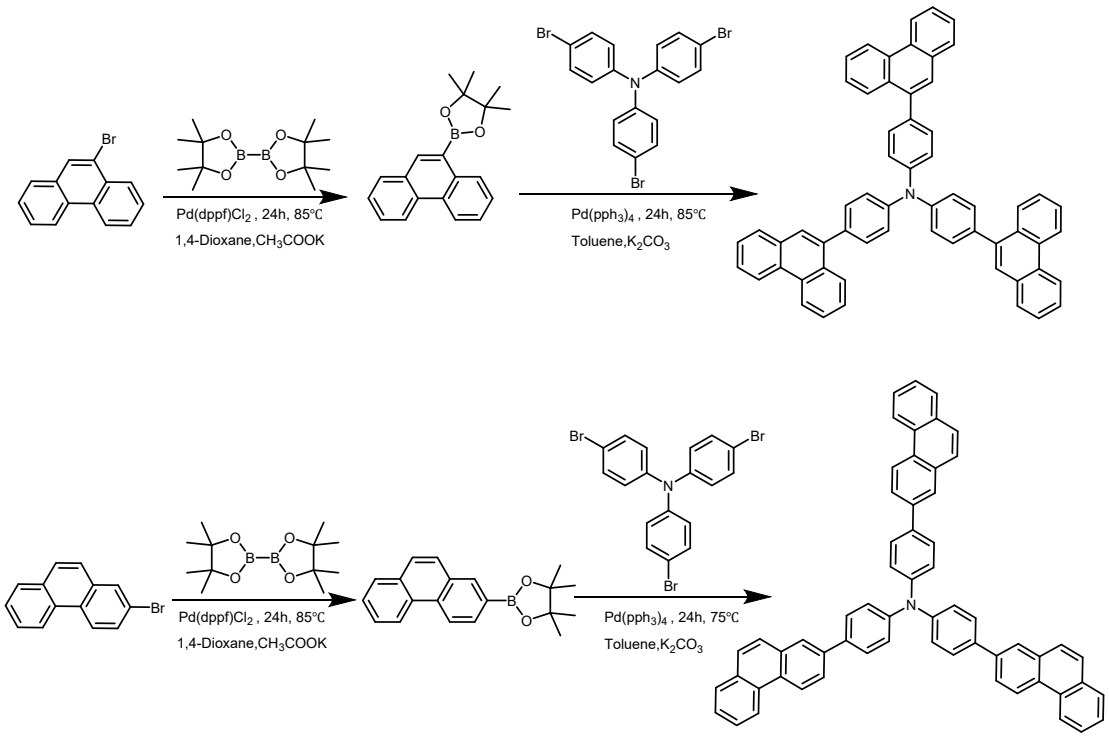
Manipulating Excited States of Non-Doped Deep Blue Emitter by Adjusting the Intramolecular Torsion Angle

Ling Lin, Mingke Li, Yulong Li, Youran Lin, Yu Huang, Yue Yu,* Lei Ying and Yuguang Ma*

Institute of Polymer Optoelectronic Materials and Devices, Guangdong Basic Research Center of Excellence for Energy and Information Polymer Materials, State Key Laboratory, of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China.

Email: yuyue924@scut.edu.cn; ygma@scut.edu.cn

1. Material and Synthesis



Scheme S1. Synthetic route of TPA-1PN and TPA-4PN.

4,4,5,5-tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane.

Under N_2 atmosphere, 9-bromophenanthrene (2.57g, 10mmol), bis(pinacolato)diboron (3.8g, 15mmol), potassium acetate (2.95g, 30mmol), and the catalyst Pd(dppf)Cl_2 (0.21g, 3mmol) were sequentially added to a 100 mL flask containing anhydrous 1,4-dioxane. The reaction was carried out at 85°C for 24 hours. The reaction mixture was first extracted with dichloromethane, and the organic phase was dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography to give a pale white solid (2.37 g, yield 78%).

Tris(4-(phenanthren-9-yl)phenyl)amine (TPA-1PN).

9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenanthrene (1.82 g, 6 mmol) and Tris(4-bromophenyl)amine (0.96g, 2 mmol) were added to the Na_2CO_3(2.0 M L^{-1}) and toluene (toluene/water was at a 3:2 ratio), and Pd(PPh_3)$_4$ (0.35 g, 0.3 mmol) acted as a catalyst. The reaction was carried out at 85°C for 24 hours. The reaction mixture was first extracted with dichloromethane, and the organic phase was dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography to give a pale white solid (0.65 g, yield 42%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (dd, *J* = 31.1, 8.3 Hz, 3H), 8.18 (dd, *J* = 37.9, 8.4 Hz, 3H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.69 – 7.58 (m, 12H), 7.47 (ddd, *J* = 29.8, 16.2, 6.3 Hz, 12H), 7.39 – 7.33 (m, 4H), 6.85 (d, *J* = 8.2 Hz,

3H).MALDI-TOF-MS(m/s): calcd for $C_{60}H_{39}N$, 773.98;found,773.02.

4,4,5,5-tetramethyl-2-(phenanthren-2-yl)-1,3,2-dioxaborolane.

The procedure above was followed to prepare 4,4,5,5-tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane from 2-bromophenanthrene (2.57 g, 10 mmol) to afford a white solid (1.8 g, yield 58%)

Tris(4-(phenanthren-2-yl)phenyl)amine. (TPA-4PN).

The procedure above was followed to prepare TPA-PA from4,4,5,5-tetramethyl-2-(phenanthren-2-yl)-1,3,2-dioxaborolane (0.9 g, 3 mmol) using tris(4-bromophenyl) amine (0.48 g, 1 mmol) and $Pd(PPh_3)_4$ (0.18 g, 0.015 mmol) to act as a catalyst. The reaction was carried out at 85°C for 24 hours. The reaction mixture was first extracted with dichloromethane, and the organic phase was dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography to give a pale white solid (0.29 g, yield 38%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (dd, *J* = 18.4, 8.4 Hz, 6H), 8.13 (s, 3H), 7.93 (dd, *J* = 15.4, 8.2 Hz, 6H), 7.79 (dt, *J* = 17.9, 8.8 Hz, 11H), 7.65 (dt, *J* = 28.2, 7.3 Hz, 7H), 7.37 (d, *J* = 8.1 Hz, 6H). MALDI-TOF-MS(m/s): calcd for $C_{60}H_{39}N$, 773.98; found,773.02.

2. Supporting figures and tables

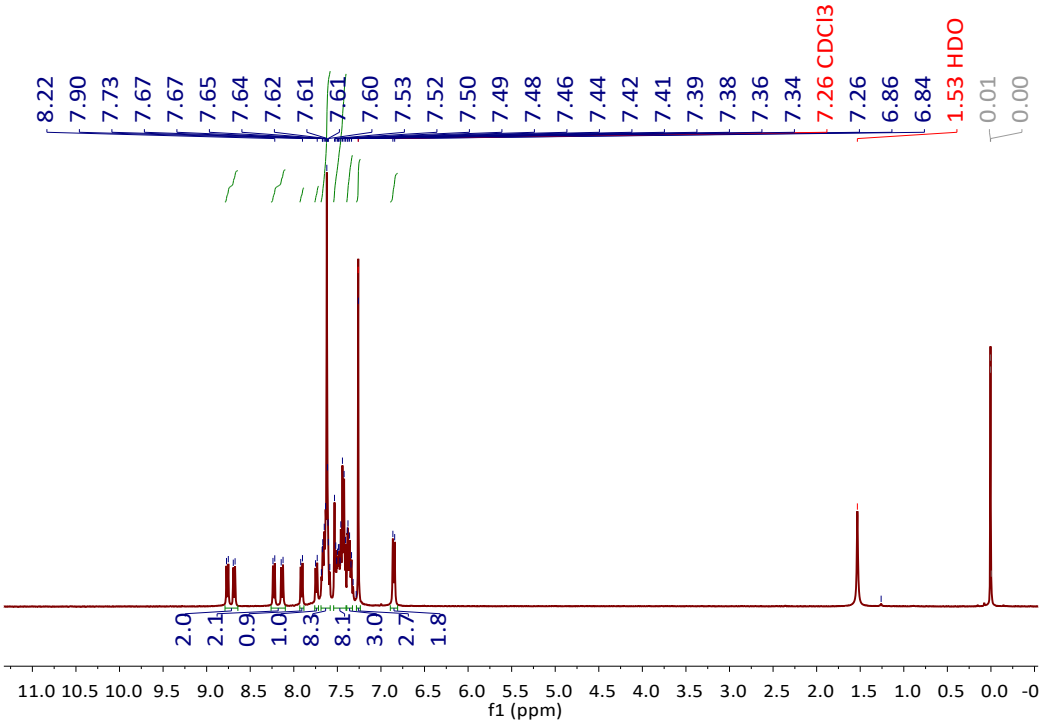


Figure S1 ^{1}H NMR of **TPA-1PN** in $CDCl_3$.

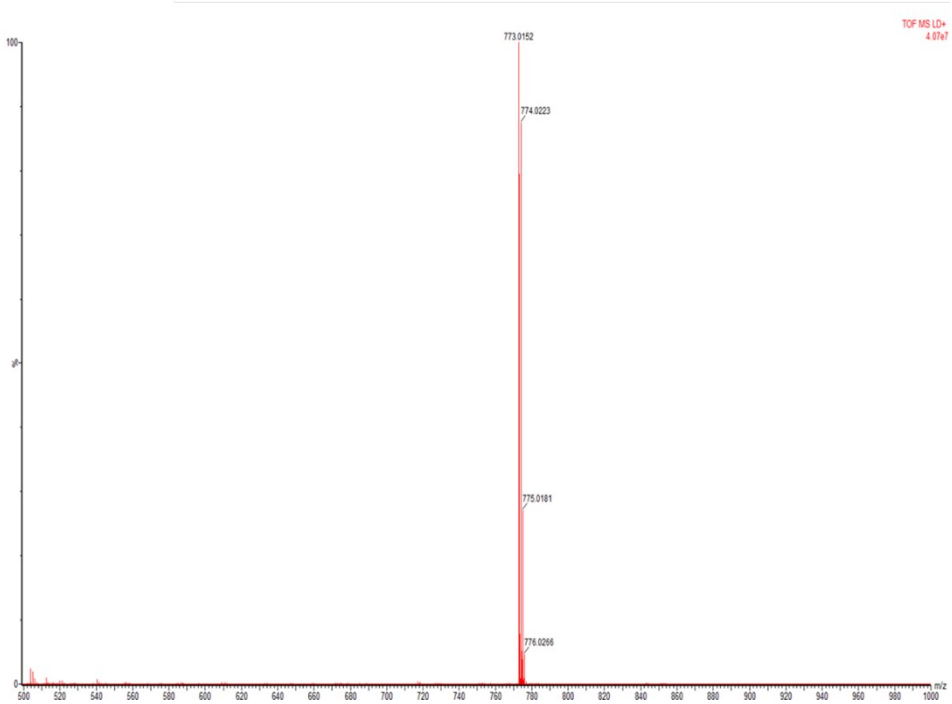


Figure S2 The high resolution ESI mass spectrum of **TPA-1PN**.

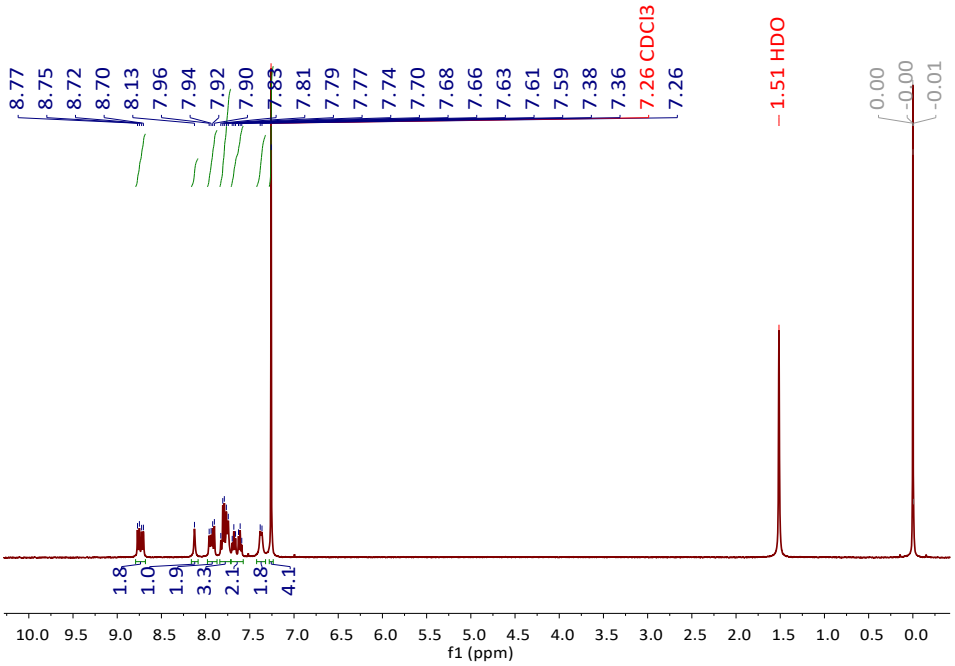


Figure S3 ^{1}H NMR of **TPA-4PN** in $CDCl_3$.

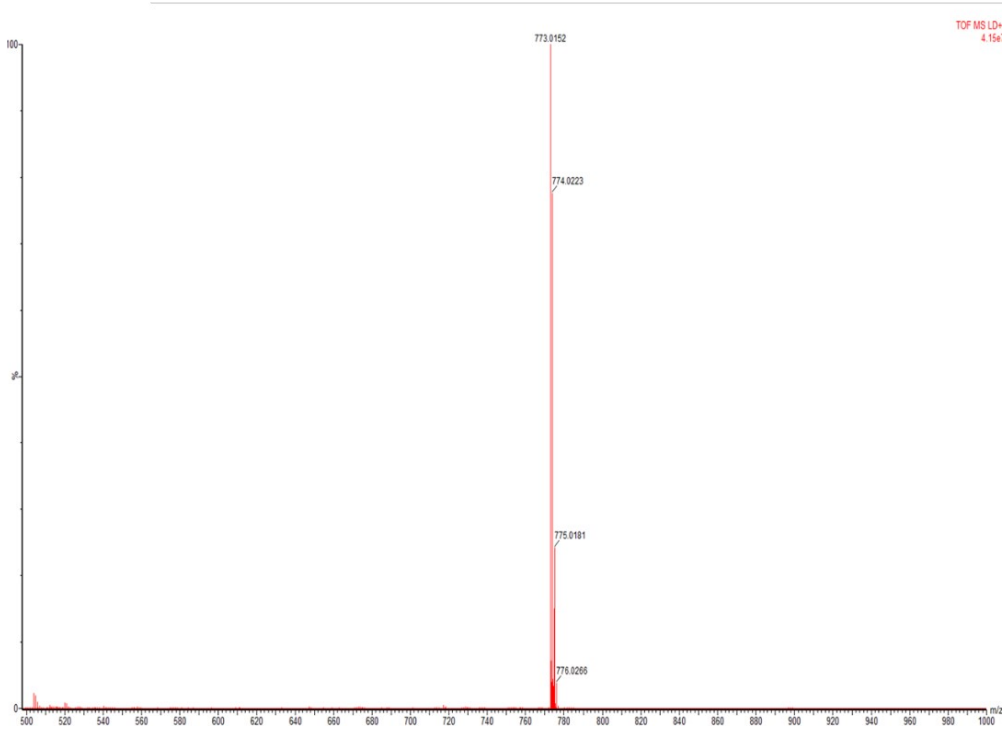


Figure S4 The high resolution ESI mass spectrum of **TPA-4PN**.

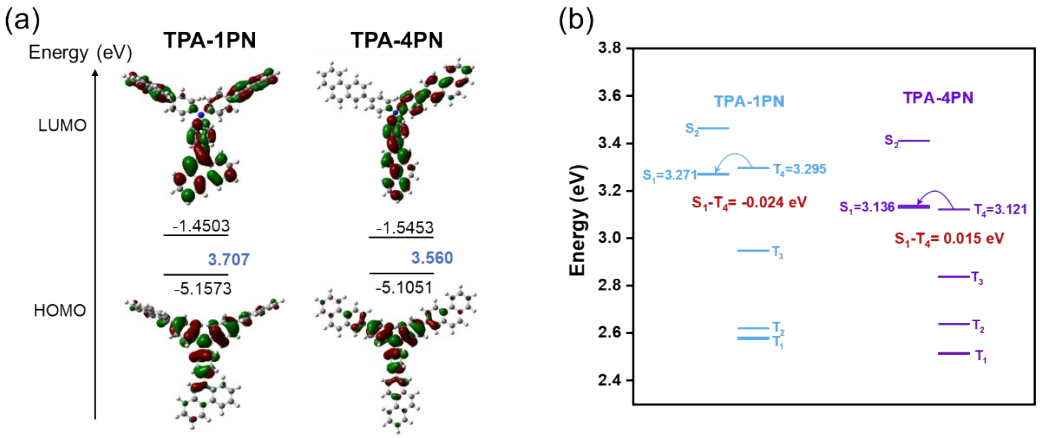


Figure S5 (a) Molecular geometries (b) Energy levels of the singlet/triplet excited states.

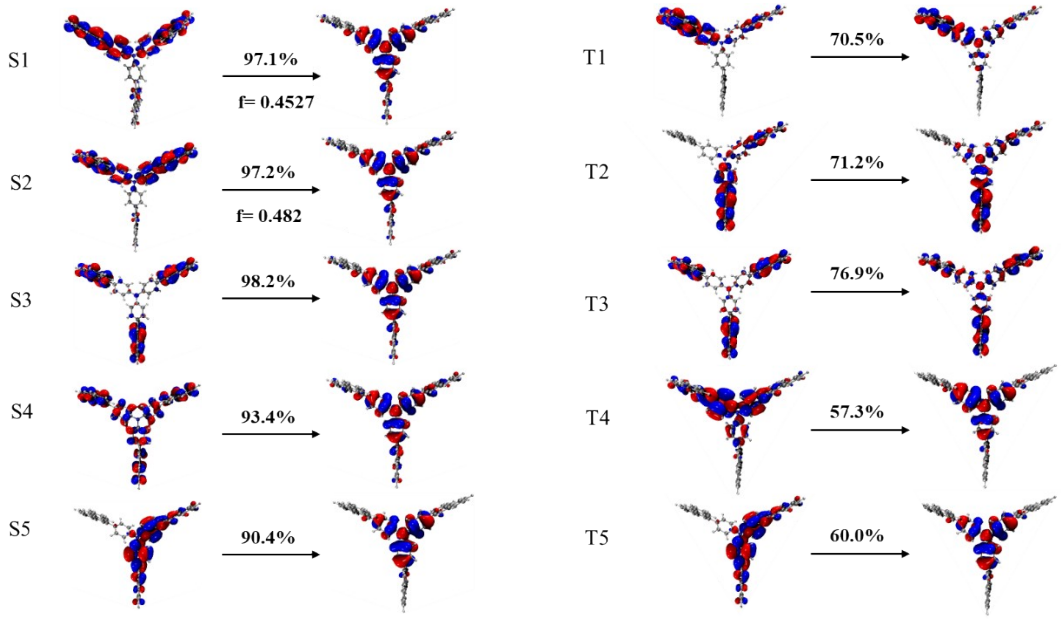


Figure S6 The Natural Transition Orbitals of TPA-1PN

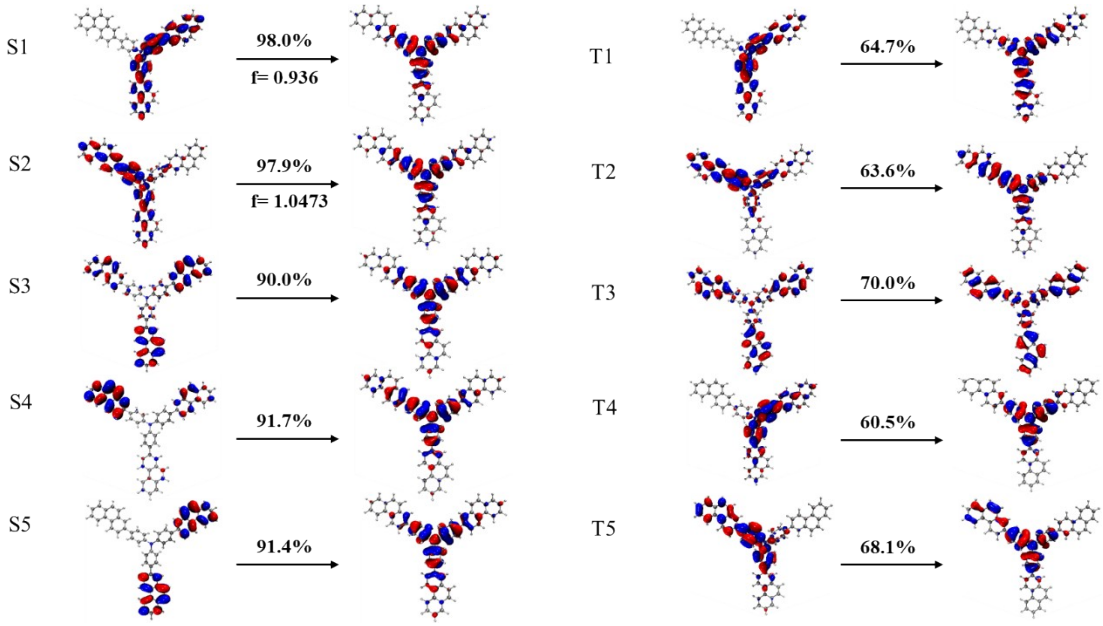


Figure S7 The Natural Transition Orbitals of TPA-4PN

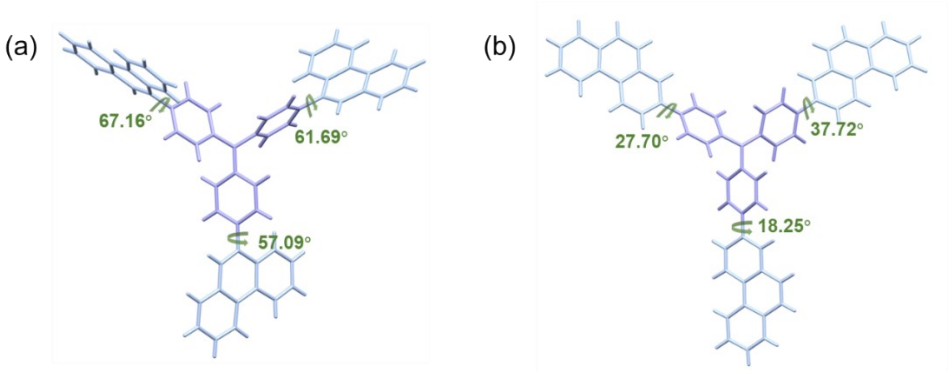


Figure S8 (a) TPA-1PN and (b) TPA-4PN single-crystal structure.

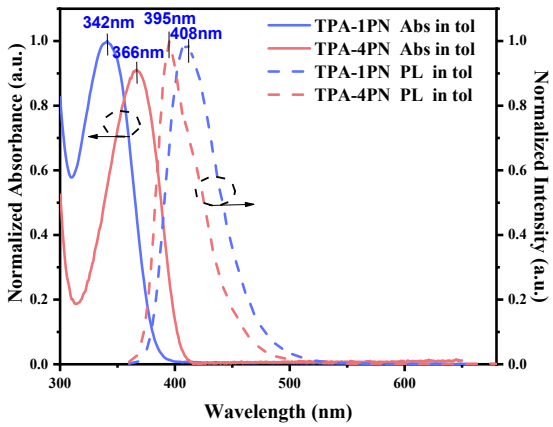


Figure S9 Absorption and PL spectra of the TPA-1PN and TPA-4PN in in toluene solution (10^{-5} M).

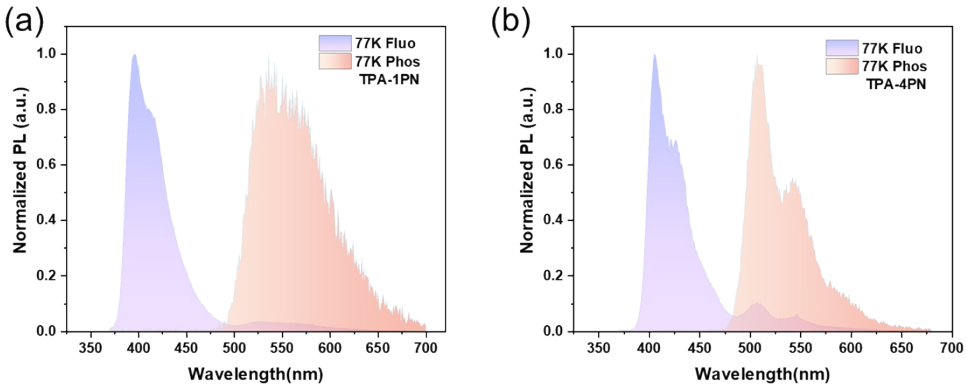


Figure S10 Fluorescence and phosphorescence spectra of (a) TPA-1PN and (b) TPA-4PN in toluene solution (10^{-5} M) under 77 K (λ_{ex} = 370 nm).

Table S1 Summary of photophysical characteristics of TPA-1PN and TPA-4PN.

Emitter	λ_{abs} [a/b] [nm]	λ_{em} [a/b] [nm]	Φ_{pl} [a/b] [%]	τ_1 [ns]	k_r [$10^7\ s^{-1}$]	k_{nr} [$10^7\ s^{-1}$]	ΔE_{st} [eV]	T_g [℃]	T_d [℃]	HOMO [eV]	LUMO [eV]
TPA-1PN	342/348	408/437	77/ 35.84	1.27	28.19	55.55	0.81	155	547	2.78	5.80
mTPA-4PN	366/375	395/446	91/ 46.20	1.10	42.00	48.90	0.62	156	586	3.04	5.88

[a]: Solution in Toluene. [b]: In neat film.

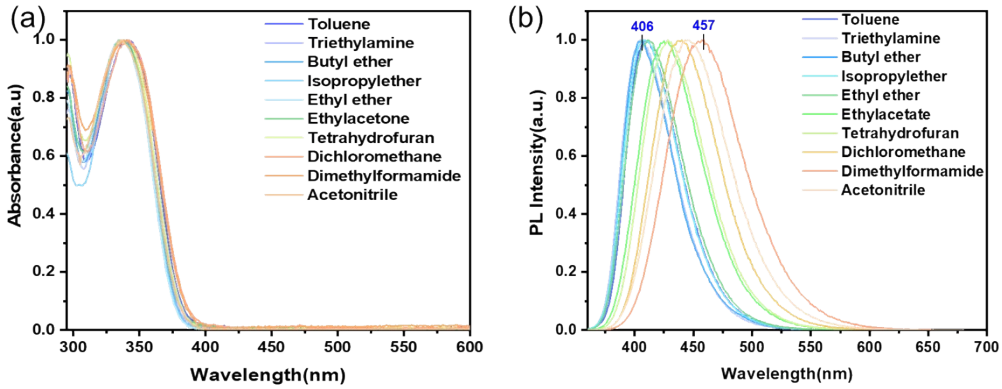


Figure S11 (a) UV-vis absorption spectra and (b) Photoluminescence spectra in different solvents for TPA-1PN.

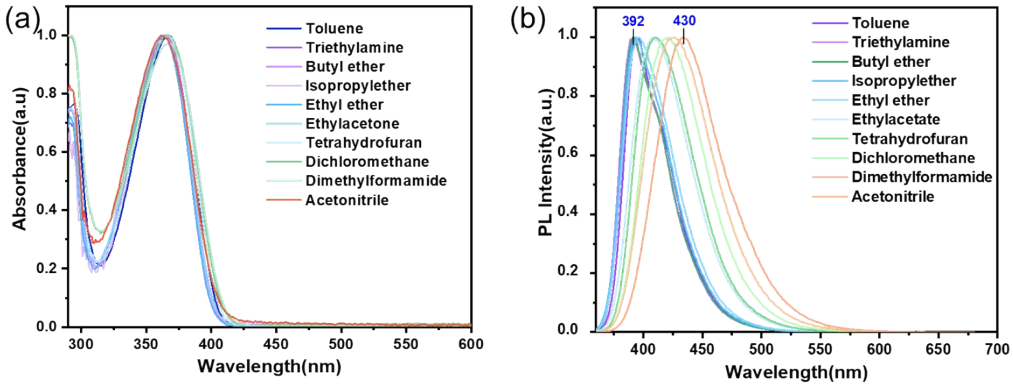


Figure S12 (a) UV-vis absorption spectra and (b) Photoluminescence spectra in different solvents for TPA-4PN.

Table S2 UV-vis absorption spectra and Photoluminescence spectra in different solvents for TPA-1PN and mTPA-4PN.

Solvent	ε	n	f(ε, n)	TPA-1PN			TPA-4PN		
				λ_a (nm)	λ_f (nm)	$v_a - v_f$ (nm)	λ_a (nm)	λ_f (nm)	$v_a - v_f$ (nm)
Toluene	2.38	1.494	0.014	342	408	4609	366	395	2006
Triethylamine	2.42	1.401	0.048	337	405	4982	362	392	2049
Butyl ether	3.08	1.399	0.096	338	407	5016	363	392	2038
Isopropyl ether	3.88	1.368	0.145	336	408	5252	363	393	2102
Ethyl ether	4.34	1.352	0.167	336	412	5490	362	396	2372
Ethyl acetate	6.02	1.373	0.2	336	428	6397	363	408	3038
Tetrahydrofuran	7.58	1.407	0.21	338	428	6221	366	410	2932
Dichloromethane	8.93	1.424	0.217	342	440	6512	367	421	3494
Dimethylformamide	37	1.427	0.276	340	455	7434	368	429	3863
Acetonitrile	37.5	1.344	0.305	338	457	7703	368	430	3918

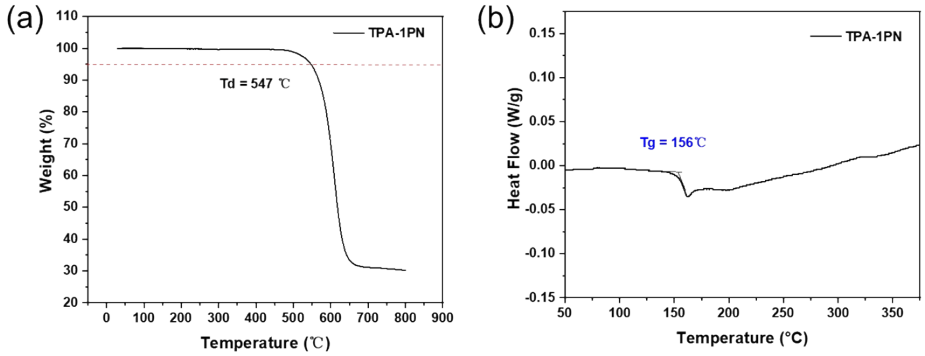


Figure S13 TGA and DSC curve of TPA-1PN.

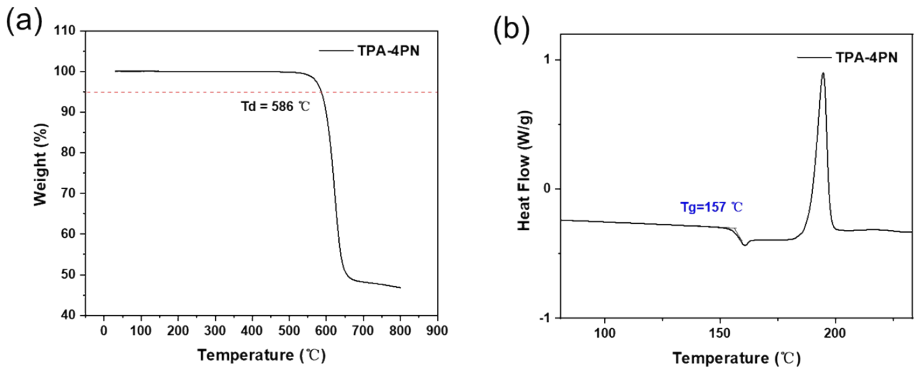


Figure S14 TGA and DSC curve of TPA-4PN.

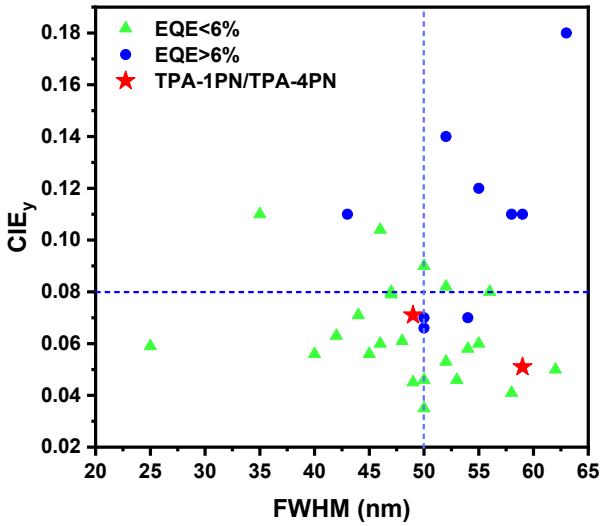


Figure S15 Summary of FWHM and EQE values of EL spectra versus emission wavelength for non-doped blue OLED.

Table S3 Summary of narrow-spectrum non-doped blue OLED Performance.

Emitter	V_{on} [V]	EQE_{max} [%]	CE_{max} [cd A^{-1}]	PEmax [lm W^{-1}]	Lmax [cd m^{-2}]	CIE(x,y)	Peak Wl [nm]	FWHM [nm]
TPA-1PN	4.4	6.60	2.97	1.98	1915	(0.158, 0.051)	425	59
TPA-4PN	4.0	7.76	5.87	4.19	5769	(0.157, 0.071)	440	49
PIAnTP	3.2	8.36	11.28	8.39	27745	(0.16, 0.14)	456	52
PIAnTPh	3.1	6.87	7.13	5.28	15,818	(0.15,0.12)	456	55
PyIAnTPh	3.2	7.04	10.66	8.51	40,209	(0.16,0.18)	460	63
PPO15NCzDPA	2.8	6.4	4.12	3.20	5146	(0.151, 0.066)	444	50
ATPNF-1	2.9	7.0	4.9	5.2		(0.15, 0.07)	446	54
ATPNF-2	3.3	4.3	2.1	2.1		(0.15, 0.06)	444	55

2 Cz-PI	3.1	4.54			3267	(0.15,0.05)		62
DTPA2F		1.5				(0.165, 0.056）	427	45
DPM	3.1	4.0	1.77	1.39		(0.157,0.053)	428	52
TDPM	3.1	2.9	0.99	0.95		(0.157,0.045)	424	49
SAFpCN	3.2	3.18			6420	(0.160, 0.046)	413	50
P-2CzDQ	5.5	14.6			6240	(0.14,0.11)	458	59
IDCz-BPSP	3.2	4.61	5.81	4.82	7105	(0.154,0.059)		25
4BCzPT	3.0	1.96	4.0		8669	(0.147,0.082)		52
IDC-Py	2.9	3.51				(0.15,0.08)	440	56
DCz2F	3.3	5.62			1047	(0.163,0.03)		50
BCN	3.0	5.6	4.4		2620	(0.15, 0.08)	451	47
SiPIM		2.4				(0.157,0.047)	420	58
PFCP-2	4.0	1.17	3.47	3.03	421	(0.17,0.11)		35
DPP-EPY	3.1	2.9				(0.161, 0.104)	456	46
BACN	3.2	5.83	4.19		3376	(0.149, 0.071)	455	44
pCzAnN	3.3	6..0			7750	(0.15, 0.07)		50
3CzAnN	3.3	5.3			8733	(0.15, 0.09)		50
TPA-PPI-OH		7.37	5.51		8669	(0.15, 0.11)	454	58
p-DSiTP	4.0	2.7			1358	(0.162, 0.061）	416	48
M2		3.02	1.53	0.86	4329	(0.166, 0.056)	428	40
DSiTPI	3.0	5.3	1.19	1.25	2233	（0.16, 0.06)	404	46
p-TP-EPY		1.88				（0.173, 0.063）	423	42
TBSA						(0.14, 0.08)	442	48
BDNA		3.94				(0.157, 0.058)	435	54
BDPA		3.23	4.19			(0.156, 0.046)	434	53
m-TP-EPY		4.61				(0.157, 0.079)	440	47
BPPyA		7.0				(0.14, 0.11)	455	43
TPA-PPI-OH		7.37	5.51		8669	(0.15, 0.11)	454	58
p-DSiTP	4.0	2.7			1358	(0.162, 0.061）	416	48
DSiTPI	3.0	5.3	1.19	1.25	2233	(0.16, 0.060)	404	46
p-TP-EPY		1.88				(0.173, 0.063)	423	42

Table S4 Summary of crystallographic and structural refinement data.

Identification code	TPA-1PN	TPA-4PN
Empirical formula	$C_{60}H_{39}N$	$C_{60}H_{39}N$
Formula weight	773.92	773.92
Temperature/K	223.00	223.00
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	7.9644(6)	10.1980(11)

b/Å	13.6790(11)	25.865(3)
c/Å	22.3497(17)	25.865(3)
α/°	79.967(5)	63.934(6)
β/°	86.095(5)	89.348(7)
γ/°	85.560(5)	81.575(7)
Volume/Å3	2386.8(3)	5791.0(11)
Z	2	4
ρ_{calc}g/cm^3	1.077	0.888
μ/mm^{-1}	0.469	0.386
F(000)	812.0	1624.0
Crystal size/mm3	0.13×0.12×0.11	0.13×0.12×0.1
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for	4.02 to 137.04	3.81 to 136.016
data collection/°	-9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26	-12 ≤ h ≤ 12, -26 ≤ k ≤ 29, -31 ≤ l ≤ 31
Reflections collected	27535	55659
Independent reflections	8562 [R_{int} = 0.0470, R_{sigma} = 0.0400]	20388 [R_{int}= 0.0982, R_{sigma}= 0.1323]
Data/restraints/parameters	8562/0/551	20388/3198/1677
Goodness-of-fit on F^2	1.043	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0465, wR_2 = 0.1425	R_1 = 0.0940, wR_2 = 0.2303
Final R indexes [all data]	R_1= 0.0618, wR_2= 0.1544	R_1= 0.1533, wR_2= 0.2722
Largest diff. peak/hole / e Å^{-3}	0.25/-0.19	0.26/-0.21

Reference

1 F. Liu, G. Cao, Z. Feng, Z. Cheng, Y. Yan, Y. Xu, Y. Jiang, Y. Chang, Y. Lv and P. Lu, ACS Appl. Mater. Interfaces, 2023, 15, 47307-47316.
2 F. Liu, Z. Cheng, L. Wan, L. Gao, Z. Yan, D. Hu, L. Ying, P. Lu and Y. Ma, Chem. Eng. J., 2021, 426, 131351.
3 S. Ye, Y. Wang, R. Guo, Q. Zhang, X. Lv, Y. Duan, P. Leng, S. Sun and L. Wang, Chem. Eng. J., 2020, 393, 124694.
4 Y. Jeong, K. M. Hwang, J. H. Lee, M. J. Kwon, T. Kim and W. P. Hong, J. Mater. Chem. C., 2023, 11, 10911-10922.
5 R.-T. Zhao, H.-S. Liao, D. Chen, B.-Y. Wang, H.-J. Chi, Y.-L. Lv, H.-M. Guan and X. Li, Dyes Pigments., 2024, 230,112345.
6 Y. Huo, J. Lv, M. Wang, Z. Duan, H. Qi, S. Wang, Y. Liu, L. Peng, S. Ying and S. Yan, J. Mater. Chem. C., 2023, 11, 6347-6353.
7 S. Xiao, S.-T. Zhang, Y. Gao, X. Yang, H. Liu, W. Li and B. Yang, Dyes Pigments., 2021, 193, 109482.
8 T. Sudyoadsuk, S. Petdee, C. Kaiyasuan, C. Chaiwai, P. Wongkaew, S. Namuangruk, P. Chasing and V. Promarak, J. Mater. Chem. C., 2021, 9, 6251-6256.
9 J. Wang, X. Zhai, C. Ji, M. Zhang, C. Yao, G. Xie, J. Zhang and X. Xi, Dyes Pigments., 2023, 219, 111586.
10 Y.-X. Zhang, Y. Yuan, Q. Wang, Y. Hu, A. Khan, Z.-Q. Jiang and L.-S. Liao, Dyes Pigments., 2018, 158, 396-401.
11 J. Li, L. Xu, X. Liu, X. Qiu, Y. Pan and D. Hu, Dyes Pigments., 2022, 204, 110456.
12 Z. Gao, G. Cheng, F. Shen, S. Zhang, Y. Zhang, P. Lu and Y. Ma, Laser Photonics Rev., 2014, 8(1), L6-L10.
13 L. Yan, Q. Lu, X. Liu, H. Zhao, Y. Wu, J. Li, Y. Miao and H. Wang, Tetrahedron, 2023, 140, 133475.
14 C.-H. Seok, Y.-I. Park, S.-K. Kim, J.-H. Lee and J. Park, J. Nanosci. Nanotechnol., 2011, 11, 4639-4643.
15 X. Qiu, L. Xu, S. Ying, X. Ye, P. Xu, B. Wang, D. Hu, D. Ma and Y. Ma, J. Mater. Chem. C., 2021, 9, 13697-13703.

16 Z. Wang, T. Yang, S. Dong, Z. Wen, H. Xu, Y. Miao, H. Wang and J. Yu, Dyes Pigments., 2022, 199,110047.
17 X. Qiu, Y. Xu, C. Wang, M. Hanif, J. Zhou, C. Zeng, Y. Li, Q. Jiang, R. Zhao, D. Hu and Y. Ma, J. Mater. Chem. C., 2019, 7, 5461-5467.
18 Z. Shen, X. Zhu, W. Tang, X. J. Feng, Z. Zhao and H. Lu, J. Mater. Chem. C., 2020, 8, 9401-9409.
19 Y. Zheng, X. Zhu, Z. Ni, X. Wang, Z. Zhong, X. J. Feng, Z. Zhao and H. Lu, Adv. Opt. Mater., 2021, 9(21), 2100965.