# The effect of molecular configuration and donor on the photophysical property of 2-phenylfuro[2,3-*b*]quinoxaline based emitters

MingXin Wu, ChuanMing Wu, BoHua Zhang, MeiTing Luo, Lei Gou* and Dongdong Wang*

Section one: Synthesis of materials

All reagents were used without further purification. The ^{1}HNMR and ^{13}CNMR spectra were recorded on Bruker Avance 400MHz and 600MHz spectrometers, respectively, and the HRMS experiments were carried out on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany).
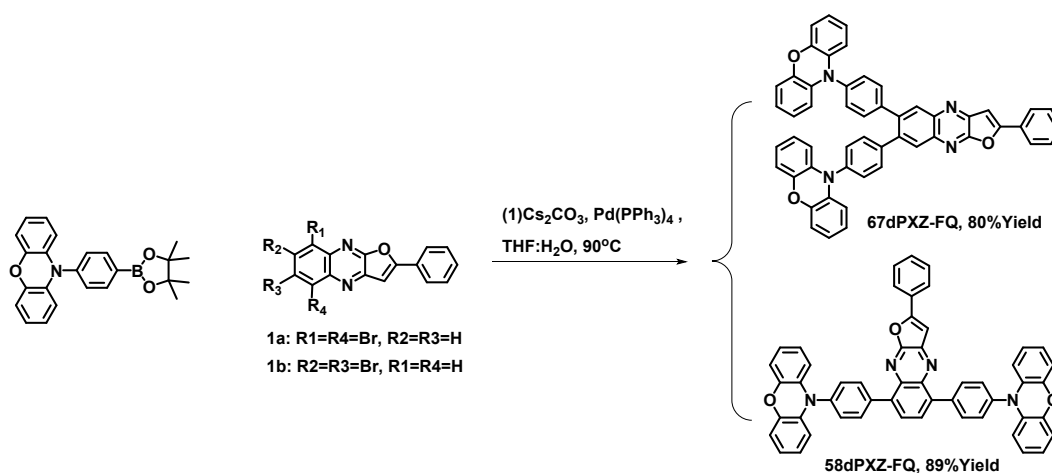
The synthetic routes for two compounds.

Synthesis of the 67dPXZ-FQ and 58dPXZ-FQ

5,8-dibromo-2-phenylfuro[2,3-*b*]quinoxaline (0.81 g, 2.0 mmol)/ 6,7-dibromo-2-phenylfuro[2,3-*b*]quinoxaline (0.81 g, 2.0 mmol), 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10*H*-phenoxazine (1.85 g, 4.8 mmol), Cs_2CO_3 (4.17 g, 12.8 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) were added to 100 ml anhydrous toluene. Then the reaction mixture was stirred at 110 °C under a nitrogen atmosphere until TLC revealed complete conversion of the starting material. The mixture was cooled, diluted with H_2O and filtered. The residue was purified by silica gel column chromatography (CH_2Cl_2 : petroleum ether=2:1) to give expected product.

67dPXZ-FQ: (1.22 g, 80%, Orange solid).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.31 (s,

1H), 8.13-8.06 (m, 3H), 7.66-7.44 (m, 7H), 7.40 (s, 2H), 7.30 (s, 2H), 6.58 (d, J=7.8Hz, 12H), 5.90 (s, 4H). ^{13}C NMR (150MHz, Chloroform-d) δ 164.9, 155.2, 144.8, 141.4, 141.1(1C), 140.5, 138.4, 132.8, 131.8, 130.7, 129.7, 129.4, 128.3(1C), 126.4, 123.5, 121.5, 115.4, 113.1, 100.7. HRMS(ESI) calcd for $C_{52}H_{32}N_4O_3$[M+H]$^+$ 761.2547, found 761.2536.

58dPXZ-FQ: (1.35g, 89%, Green solid).^{1}H NMR (400 MHz, Chloroform-d) δ 8.09-8.03 (m, 6H), 7.96 (s, 2H), 7.55-7.50 (m, 7H), 7.39 (s, 1H), 6.75-6.63 (m, 12H), 6.18 (s, 4H); ^{13}CNMR (150 MHz, Chloroform-d) δ 164.6, 153.9, 144.1, 140.4, 139.2, 138.8, 136.9, 133.6, 133.4, 131.4, 129.5, 129.3, 129.0, 128.5, 126.3, 113.7, 101.3. HRMS(ESI) calcd for $C_{52}H_{32}N_4O_3$[M+H]$^+$ 761.2547, found 761.2512.

Section two: Supplemental Tables and Figures

Table S1 Photophysical properties of **67dTPA-FQ**.

| Compound	λ_{abs} [nm][a]	λ_{em}[nm]		PLQY[%]		t_p [ns][c]	S_1[eV]	T_1[eV]	ΔE_{S1T1} [eV]	HOMO [eV][f]	LUMO [eV][g]
		sol[a] / film[b]		sol[a] /film[b]			mea[d]/cal[e]	mea[d]/cal[e]	mea[d]/cal[e]		
67dTPA-FQ	310,366,431	519/552		91/29.2		4.55	2.59/2.427	2.19/2.199	0.40/0.228	−5.90	−3.33

[a] Measured in toluene solution (10^{-5} M); [b] Measured in vacuum-deposited neat film; [c] Lifetime in toluene solution (10^{-5} M)excited using nanosecond laser with excited wavelength of 400 nm; [d] Obtained from onset value of high energy edge of fluorescence and phosphorescence spectra of these emitters in toluene solution; [e] Calculated S_1, T_1, T_2 and T_3 energies in CH_2Cl_2 solution using DFT and TD-DFT theory; [f] Calculated from the formula LUMO $=-[E_{Re}- E_{(Fc/Fc+)} +4.8]$ eV; [g] Calculated from the formula HUMO = [LUMO− Eg] eV.

Table S2 EL performances of devices based on **67dPXZ-FQ**, **58dPXZ-FQ** as dopant and mCBP as host.

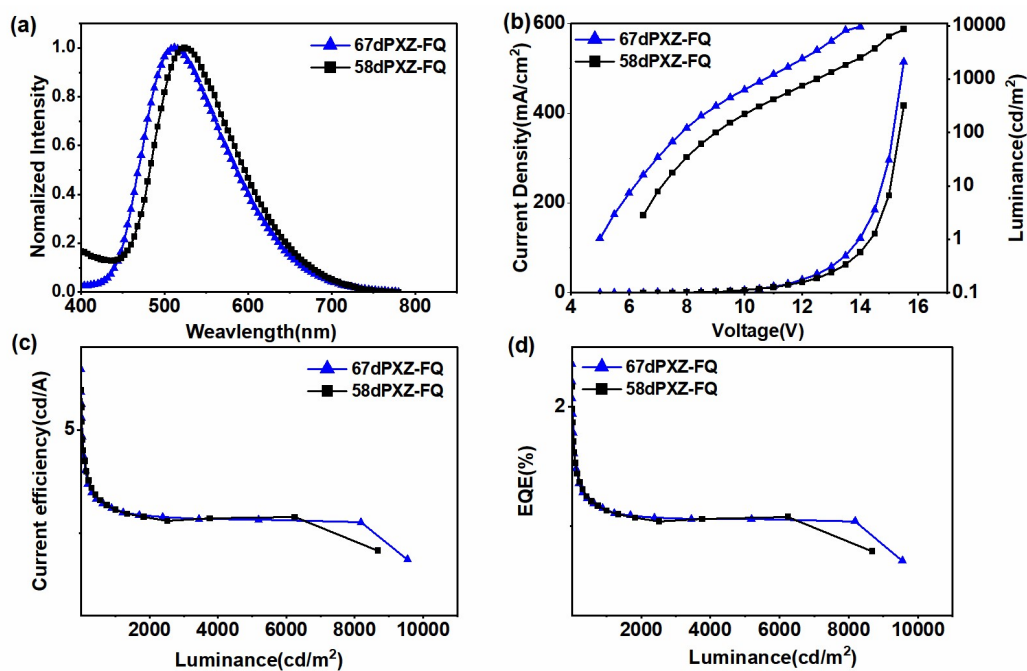| EML	λ_{EL}[nm][a]	V_{on}[V][b]	L_{max}[cd· m^{-2}]	EQE[%][c]	PE[lm· W^{-1}][c]	CE[cd· A^{-1}][c]
67dPXZ-FQ	504	5	9553	2.2	4.1	6.5
58dPXZ-FQ	556	6.5	8681	2.1	2.9	6.0
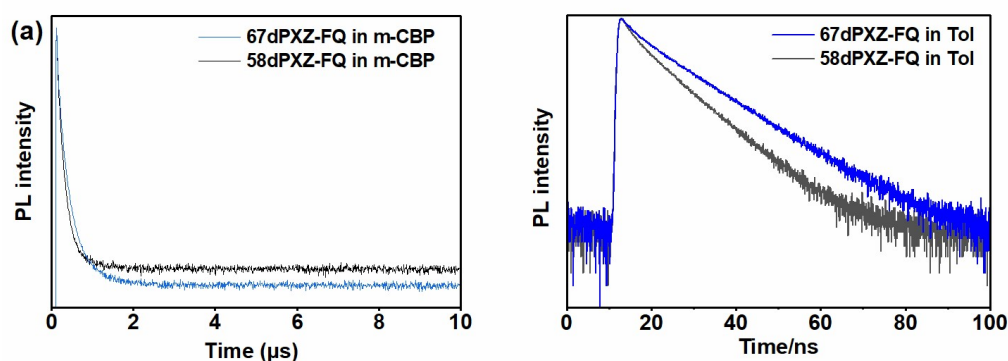
Figure S1 The transient PL decay curves of two compounds in toluene.

	HOMO	LUMO
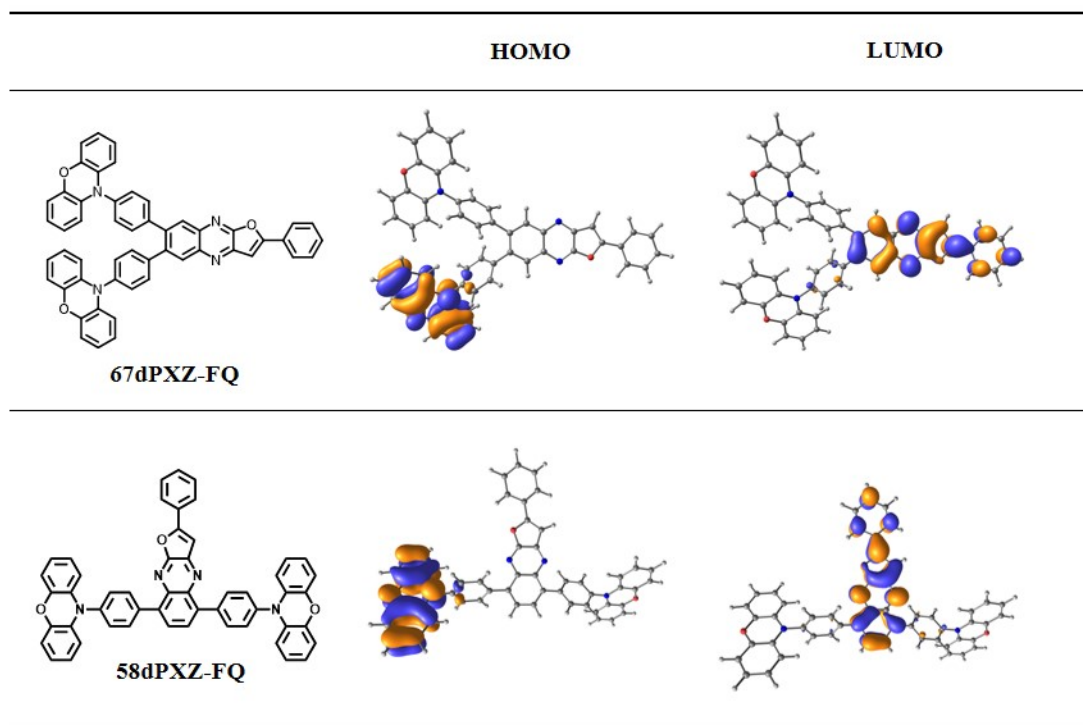
67dPXZ-FQ

58dPXZ-FQ

Figure S2 The electron distribution of HOMO and LUMO orbitals for compounds **67dPXZ-FQ** and **58dPXZ-FQ**.


Figure S3 (a) EL spectra of the devices; (b) the current density–voltage-luminance (J-V-L) curves; (c) the current efficiency and (d) the EQE versus luminance relationships of the device based on mCBP host.

Section three: Computational details

All calculations were performed using the Gaussian 09 program package. The ground state geometries were optimized via DFT calculations at the PBE0-1/3 and 6-31G* level in vacuum.

Frequency analysis was used to confirm that the structures are at the global minimum point of the potential surfaces. Based on the optimized ground state, the lowest excited singlet state (S_1) and related triplet states (T_1 and T_2) configurations are optimized using the TD-DFT method at the PBE0-1/3 and 6-31G* level. Furthermore, the implicit polarizable continuum model (PCM) is used to consider the solvent effects of toluene. Spin–orbit coupling matrix elements (SOCMEs) are gained using the TD-PBE0/TZVP method with the zero-order regular approximation (ZORA) as implemented in the ORCA4.2.1 program.[1-3]
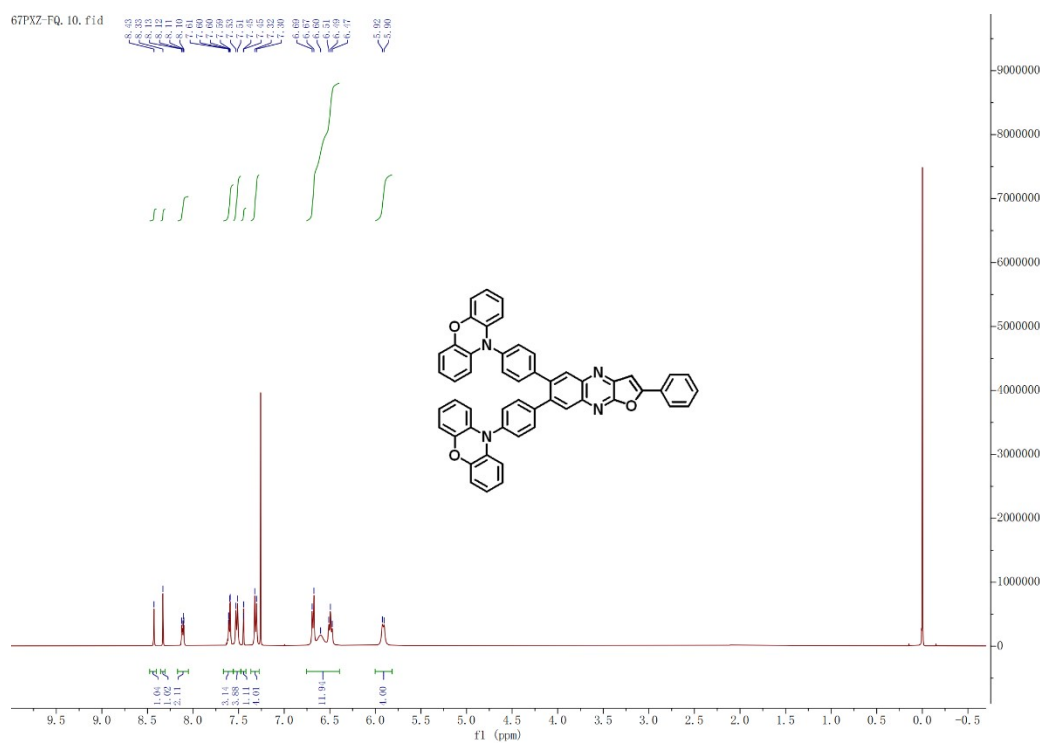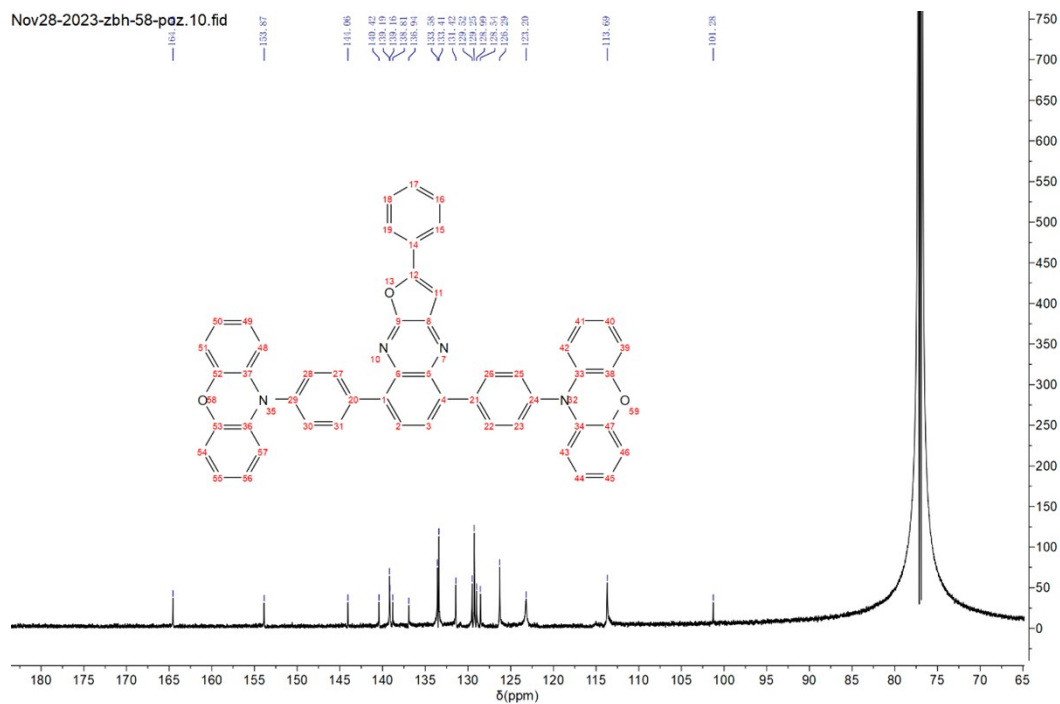
REFERENCE

1   W. Liu, G. Hong, D. Dai, L. Li and M. Dolg, The Beijing four-component density functional program package (BDF) and its application to EuO, EuS, YbO and YbS, *Theor. Chem. Acc.*, 1997 , **96** , 75-83.

2   W. Liu, F. Wang and L. Li, The Beijing density functional (BDF) Program package: methodologies and applications, *J. Theor. Comput. Chem.*, 2003 , **2** , 257-272.

3   Z. Li, Y. Xiao and W. Liu, On the spin separation of algebraic two-component relativistic hamiltonians, *J. Chem. Phys.*, 2012 , **137** , 154114.