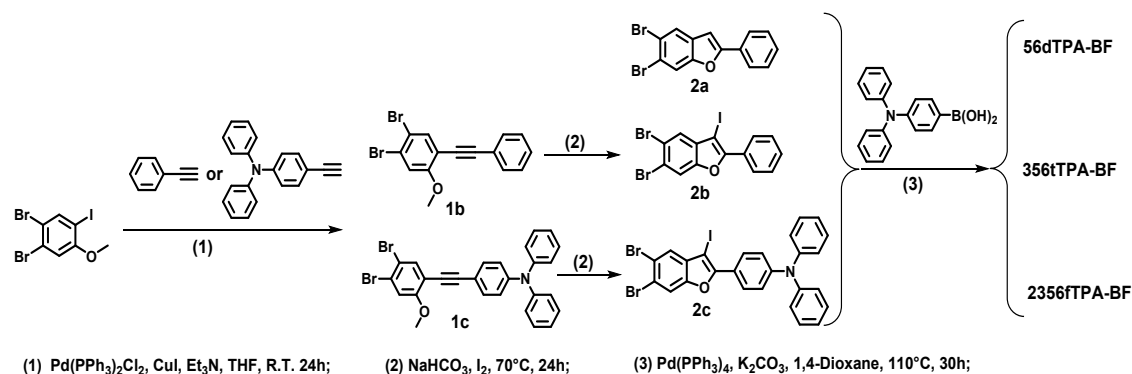


Tuning substituting numbers and position of triphenylamine on benzo[b]furan core to achieve high-efficient deep-blue and blue Emitters

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Section one: Synthesis and characterization



Scheme S1 The synthesis routes of three compounds.

General procedure for synthesizing of 56dTPA-BF, 356tTPA-BF and 2356fTPA-BF.

Synthesis of intermediates (1b and 1c)

1,2-dibromo-4-iodo-5-methoxybenzene (2.90 g, 7.50 mmol) was added to a three-neck flask, evacuated and backfilled with dry nitrogen for three times. Then $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.15 g, 0.21 mmol), CuI (0.08 g, 0.42 mmol) and phenylacetylene (0.84 g, 8.25 mmol) or 4-ethynyltriphenylamine (2.2 g, 8.25 mmol) were added. The reaction flask was then sealed and flushed with nitrogen. 40 mL dry tetrahydrofuran and 30 mL triethylamine was added to the reaction. Then the reaction mixture was stirred at room temperature for 24 h. Reaction process detected by TLC. After the reaction was complete, the organic phase was dried by rotary evaporation and dissolve the solid in dichloromethane. The residue was purified by silica gel column chromatography (CH_2Cl_2 /petroleum ether) to give the corresponding product.

1b: (2.00 g, Yield: 72.07%) ^1H NMR (400MHz, CDCl_3) δ (ppm): 7.69 (s, 1H), 7.57–7.49 (m, 2H), 7.37–7.30 (m, 3H), 7.13 (s, 1H), 3.89 (s, 3H).

1c: (1.35 g, Yield: 33.83%) ^1H NMR (400MHz, CDCl_3) δ (ppm): 7.66 (s, 1H), 7.39–7.34 (m, 2H), 7.31–7.26 (m, 3H), 7.11 (d, $J = 1.4$ Hz, 4H), 7.09 (s, 2H), 7.06 (dd, $J = 8.1, 6.7$ Hz, 2H), 7.01–6.95 (m, 2H), 3.87 (s, 3H); HRMS(ESI): calcd for $\text{C}_{27}\text{H}_{19}\text{Br}_2\text{NO}$ $[\text{M}+\text{H}]^+$ 531.99062, found 531.99115.

Synthesis of intermediate (2b and 2c)

The compound **1b** (2.00 g, 5.48 mmol)/**1c** (2.90 g, 5.48 mmol) and NaHCO_3 (1.38 g, 16.44 mmol) were added to a three-neck flask, evacuated and backfilled with dry nitrogen for three times. Then a solution of iodine (4.16 g, 16.44 mmol) in 1,2-dichloroethane was added to the flask. Then the reaction mixture was stirred at 70°C for 24 h. The reaction was quenched with 220 mL of saturated sodium thiosulfate

solution. And extracted with ethyl acetate several times, combining organic layers and then dried over anhydrous Na₂SO₄. After filtration and solvent evaporation under reduced pressure, the residue was purified by column chromatography on silica gel (dichloromethane/petroleum ether) to give the corresponding product.

2b: (1.12 g, Yield: 42.91%) ¹H NMR (400 MHz, CDCl₃) δ(ppm): 8.17–8.10 (m, 2H), 7.80 (d, J = 1.1 Hz, 1H), 7.70 (d, J = 0.9 Hz, 1H), 7.54–7.42 (m, 3H); HRMS(ESI): calcd for C₁₄H₇Br₂IO [M+H]⁺ 476.79811, found 476.79639.

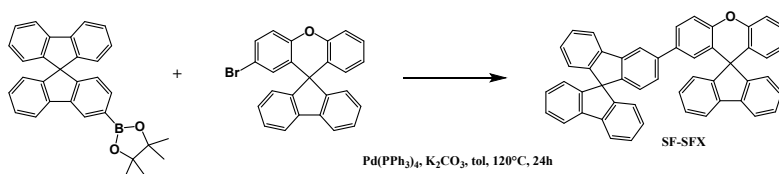
2c: (1.9g, Yield: 55.04%) ¹H NMR (400 MHz, CDCl₃) δ(ppm): 8.04–7.97 (m, 2H), 7.74 (d, J = 2.5 Hz, 1H), 7.64 (s, 1H), 7.30 (t, J = 7.7 Hz, 4H), 7.16 (d, J = 8.0 Hz, 4H), 7.10 (t, J = 7.3 Hz, 4H); HRMS(ESI): calcd for C₂₆H₁₆Br₂INO [M+H]⁺ 643.87161, found 643.87066.

Synthesis of 56dTPA-BF, 356fTPA-BF, 2356fTPA-BF and SF-SFX

56dTPA-BF: The compound **2a** (1.30, 3.70 mmol), (4-(diphenylamino)phenyl)boronic acid (2.70 g, 9.30 mmol), were added to a three-neck flask, evacuated and backfilled with dry nitrogen for three times. Tetrakis(triphenylphosphine)palladium (0.20 g, 0.18 mmol), dry 1,4-Dioxane (80 ml), a solution of K₂CO₃ (2.60 g, 18.00 mmol) in water (20 mL) were added to the flask. Then the reaction mixture was stirred at 110°C for 30 h. After the reaction cooled to room temperature, add 200 mL of deionized water to the mixture. Collecting solids through filtration and dissolve with dichloromethane, then dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography (CH₂Cl₂/petroleum ether) to give the corresponding product. (1.30g, Yield: 51.67%) ¹H NMR (400 MHz, DMSO-d₆) δ(ppm): 8.24–8.19 (m, 2H), 7.68–7.48 (m, 5H), 7.30–7.22 (m, 8H), 7.10–7.03 (m, 6H), 7.01 (tt, J = 6.4, 1.3 Hz, 1H), 6.93–6.86 (m, 4H); ¹³C NMR (101 MHz, Chloroform-d) δ(ppm): 147.84, 131.15, 129.33, 129.23, 126.80, 124.31, 123.20, 122.78; HRMS(ESI): calcd for C₅₀H₃₆N₂O [M+H]⁺ 681.30422, found 681.30411.

356fTPA-BF: (2.66 g, Yield: 78.00%) ¹H NMR (400 MHz, Chloroform-d) δ(ppm): 7.78–7.74 (m, 2H), 7.60 (d, J = 17.7 Hz, 2H), 7.43–7.36 (m, 4H), 7.36 (d, J = 1.6 Hz, 1H), 7.34 (d, J = 1.6 Hz, 1H), 7.33–7.28 (m, 6H), 7.27 (d, J = 2.3 Hz, 1H), 7.25 (d, J = 1.1 Hz, 2H), 7.23 (d, J = 1.5 Hz, 3H), 7.21 (dd, J = 3.2, 1.5 Hz, 3H), 7.19–7.14 (m, 5H), 7.13–7.06 (m, 11H), 7.04 (d, J = 4.5 Hz, 2H), 7.03–6.96 (m, 5H), 6.96 (d, J = 2.0 Hz, 1H); ¹³C NMR (400 MHz, Chloroform-d) δ(ppm): 147.66, 131.20, 130.54, 129.45, 129.33, 128.55, 127.08, 124.87, 124.40, 124.22, 123.44, 123.28, 122.74; HRMS(ESI): calcd for C₆₈H₄₉N₃O [M+H]⁺ 924.39484, found 924.39360.

2356fTPA-BF: (3.33 g, Yield: 82.57%) ^1H NMR (400 MHz, Chloroform-*d*) δ (ppm): 7.65–7.57 (m, 2H), 7.52 (s, 1H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.35–7.30 (m, 4H), 7.28 (s, 4H), 7.27–7.26 (m, 3H), 7.24 (d, $J = 1.3$ Hz, 3H), 7.23 (d, $J = 1.4$ Hz, 3H), 7.21 (d, $J = 1.8$ Hz, 2H), 7.18 (d, $J = 1.4$ Hz, 3H), 7.17–7.14 (m, 5H), 7.13 (d, $J = 2.0$ Hz, 3H), 7.12–7.05 (m, 12H), 7.05–7.02 (m, 4H), 7.02–7.00 (m, 2H), 7.00–6.96 (m, 4H), 6.95 (d, $J = 1.9$ Hz, 1H); ^{13}C NMR (400 MHz, Chloroform-*d*) δ (ppm): 147.87, 131.21, 129.44, 129.32, 124.91, 124.37, 124.20, 123.39, 123.32, 123.13, 122.71; HRMS(ESI): calcd for $\text{C}_{80}\text{H}_{58}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$ 1091.46834, found 1091.47054.



Scheme S2 The synthesis route of SF-SFX

SF-SFX: The compound 2-(9,9'-Spirobi[fluorene]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.28, 2.88 mmol), 2'-bromospiro[fluorene-9,9'-xanthene] (0.98 g, 2.4 mmol) and cesium carbonate (2.5g, 7.68mmol) were added to a three-neck flask, evacuated and backfilled with dry nitrogen for three times. Tetrakis(triphenylphosphine)palladium (0.14 g, 0.12 mmol) and dry toluene (100 ml) were added to the flask. Then the reaction mixture was stirred at 120°C for 24 h. After the reaction cooled to room temperature, add 200 mL of deionized water to the mixture. Collecting solids through filtration and dissolve with dichloromethane, then dried over anhydrous Na_2SO_4 . The residue was purified by silica gel column chromatography (CH_2Cl_2 /petroleum ether) to give the corresponding product. (0.74g, Yield: 49.74%) ^1H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.79-7.81 (d, $J = 8.0\text{Hz}$, 3H), 7.73-7.76 (d, $J = 9.0$ Hz, 1H), 7.67 (s, 1H), 7.48-7.50 (d, $J = 8.0\text{Hz}$, 1H), 7.31–7.38 (m, 5H), 7.20–7.26 (m, 8H), 7.04–7.08 (m, 3H), 6.90-6.91 (d, $J = 4.0$ Hz, 1H), 6.77-6.80 (t, 1H), 6.64-6.70 (m, 4H), 6.58-6.60 (d, $J = 8.0\text{Hz}$, 1H), 6.42-6.44 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) 154.95, 151.49, 151.17, 148.71, 147.57, 142.19, 141.78, 141.58, 140.29, 139.80, 136.54, 128.51, 128.22, 128.00, 127.89, 127.78, 127.22, 126.80, 126.62, 125.81, 125.41, 125.10, 124.12, 124.07, 123.48, 120.16, 120.04, 118.34, 117.24, 116.87, 65.67, 54.47, 53.53; HRMS(ESI): calcd for $\text{C}_{50}\text{H}_{30}\text{O}$ $[\text{M}+\text{H}]^+$ 647.23694, found 647.23494.

Section two: theory calculation

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⁻

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Section three: supplementary Figures

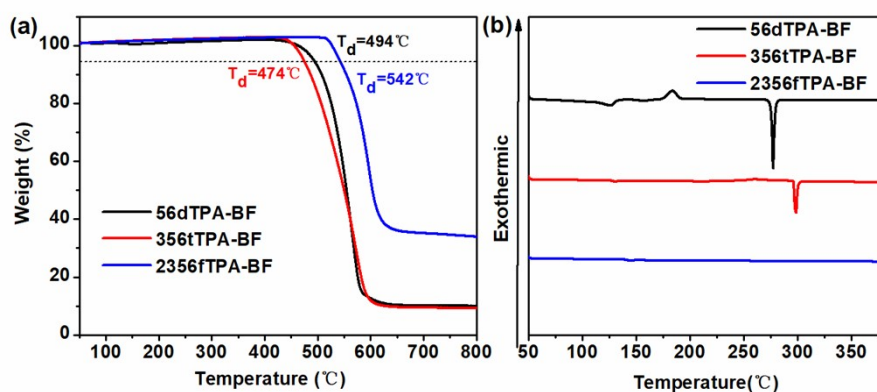


Figure S1. The thermogravimetric (a) and differential scanning calorimetry curves (b) of three compounds

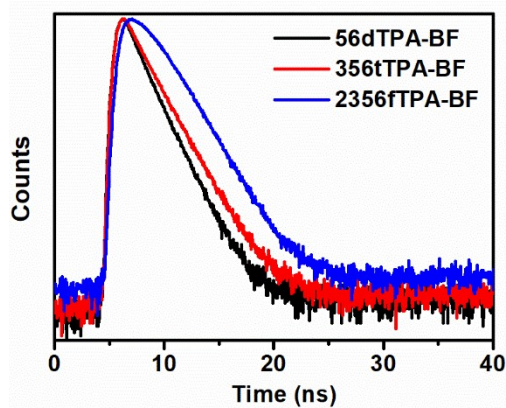


Figure S2. The transient PL spectra of three compounds in toluene.

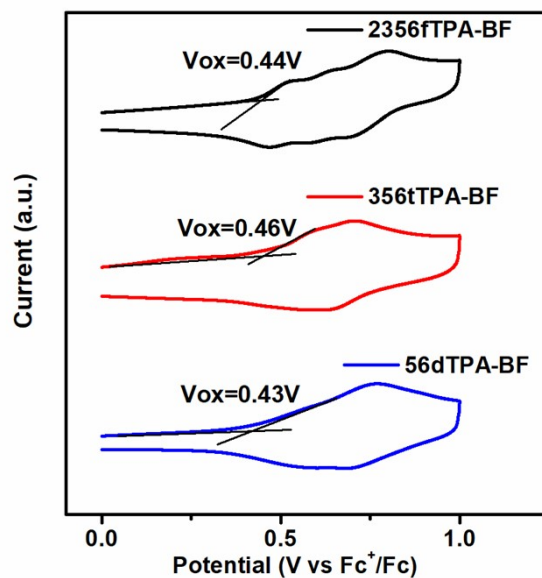


Figure S3. The cyclic voltammetry (CV) curves of three compounds in CH_2Cl_2 solution for forward scanning.

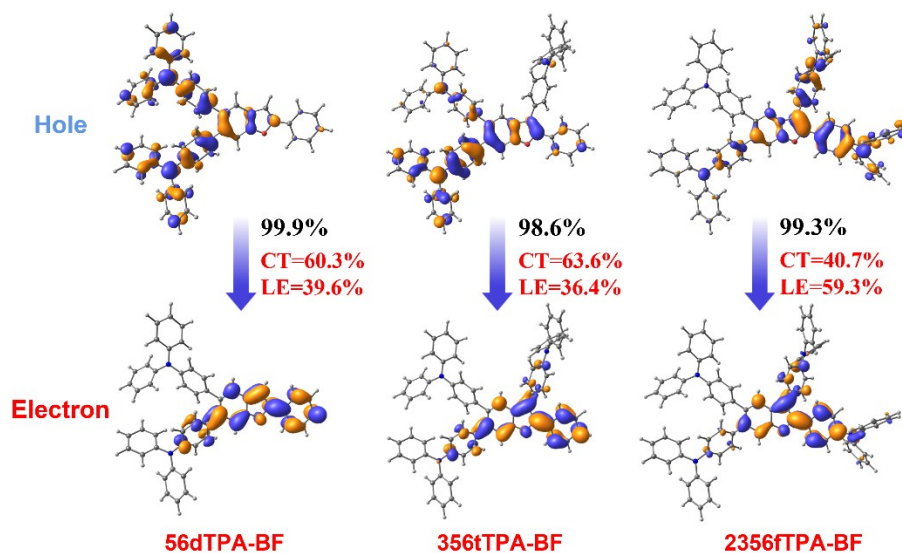


Figure S4. The calculated Natural transition orbitals (NTOs) of the $S_0 \rightarrow S_1$ transition.

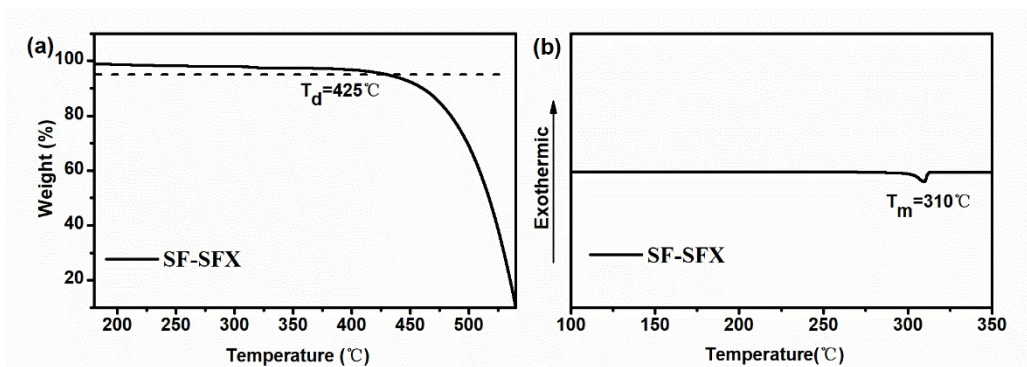


Figure S5. The thermogravimetric (a) and differential scanning calorimetry curves (b) of the SF-SFX

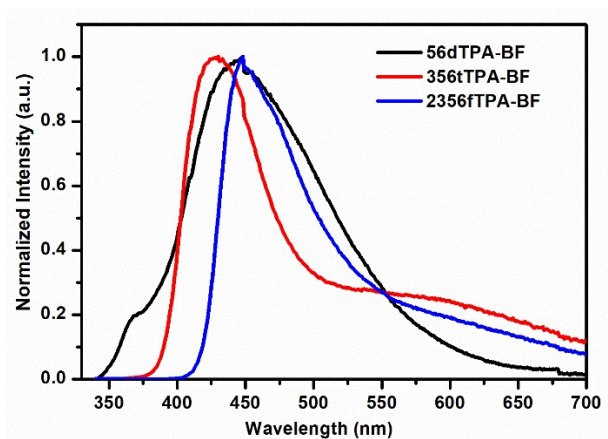


Figure S6. The PL spectra of three compounds in neat film.

Table S1. Absorption, Fluorescence, and Phosphorescence Spectra Obtained by the TDDFT Method for These Complexes, together with the Experimental Values.

	Electronic transition	λ (nm)	f	Excitation energies(eV)	Configuration
56dTPA-BF	$S_0 \rightarrow S_1$	350	0.9431	3.54	H \rightarrow L (90%)
	$S_0 \rightarrow S_2$	321	0.1679	3.87	H-1 \rightarrow L (53%)
	$S_0 \rightarrow S_3$	316	0.8660	3.92	H \rightarrow L+1 (42%)
	$S_1 \rightarrow S_0$	401/412 ^{exp}	0.9335	3.09	H \rightarrow L (97%)
	$S_2 \rightarrow S_0$	359	0.2673	3.46	H-1 \rightarrow L (86%)
	$S_3 \rightarrow S_0$	339	1.0175	3.66	H \rightarrow L+1 (74%)
	$T_1 \rightarrow S_0$	664	-	1.86	H \rightarrow L (70%)
	$T_2 \rightarrow S_0$	479	-	2.58	H-1 \rightarrow L+1(40%)
356tTPA-BF	$S_0 \rightarrow S_1$	352	0.5608	3.53	H \rightarrow L (70%)
	$S_0 \rightarrow S_2$	339	0.7202	3.65	H-2 \rightarrow L (57%)
	$S_0 \rightarrow S_3$	321	0.2714	3.86	H-3 \rightarrow L (61%)
	$S_1 \rightarrow S_0$	420/426 ^{exp}	1.0549	2.95	H \rightarrow L (90%)
	$S_2 \rightarrow S_0$	386	0.3563	3.21	H-1 \rightarrow L (71%)
	$S_3 \rightarrow S_0$	362	0.3490	3.42	H-2 \rightarrow L (62%)
	$T_1 \rightarrow S_0$	704	-	1.76	H \rightarrow L (82%)
	$T_2 \rightarrow S_0$	490	-	2.53	H-1 \rightarrow L (46%)
2356fTPA-BF	$S_0 \rightarrow S_1$	378	1.3676	3.2740	H \rightarrow L (80%)
	$S_0 \rightarrow S_2$	338	0.7673	3.6583	H-1 \rightarrow L (56%)
	$S_0 \rightarrow S_3$	326	0.2617	3.7938	H-3 \rightarrow L (61%)
	$S_1 \rightarrow S_0$	462/445 ^{exp}	1.2172	2.68	H \rightarrow L (91%)
	$S_2 \rightarrow S_0$	381	0.8263	3.24	H-1 \rightarrow L (66%)
	$S_3 \rightarrow S_0$	358	0.0894	3.45	H-2 \rightarrow L (56%)
	$T_1 \rightarrow S_0$	802	-	1.55	H \rightarrow L (80%)
	$T_2 \rightarrow S_0$	510	-	2.43	H-3 \rightarrow L (44%)

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