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Supplementary Materials

Modulating up-conversion and non-radiative deactivation to achieve efficient red thermally activated delayed fluorescent emitters

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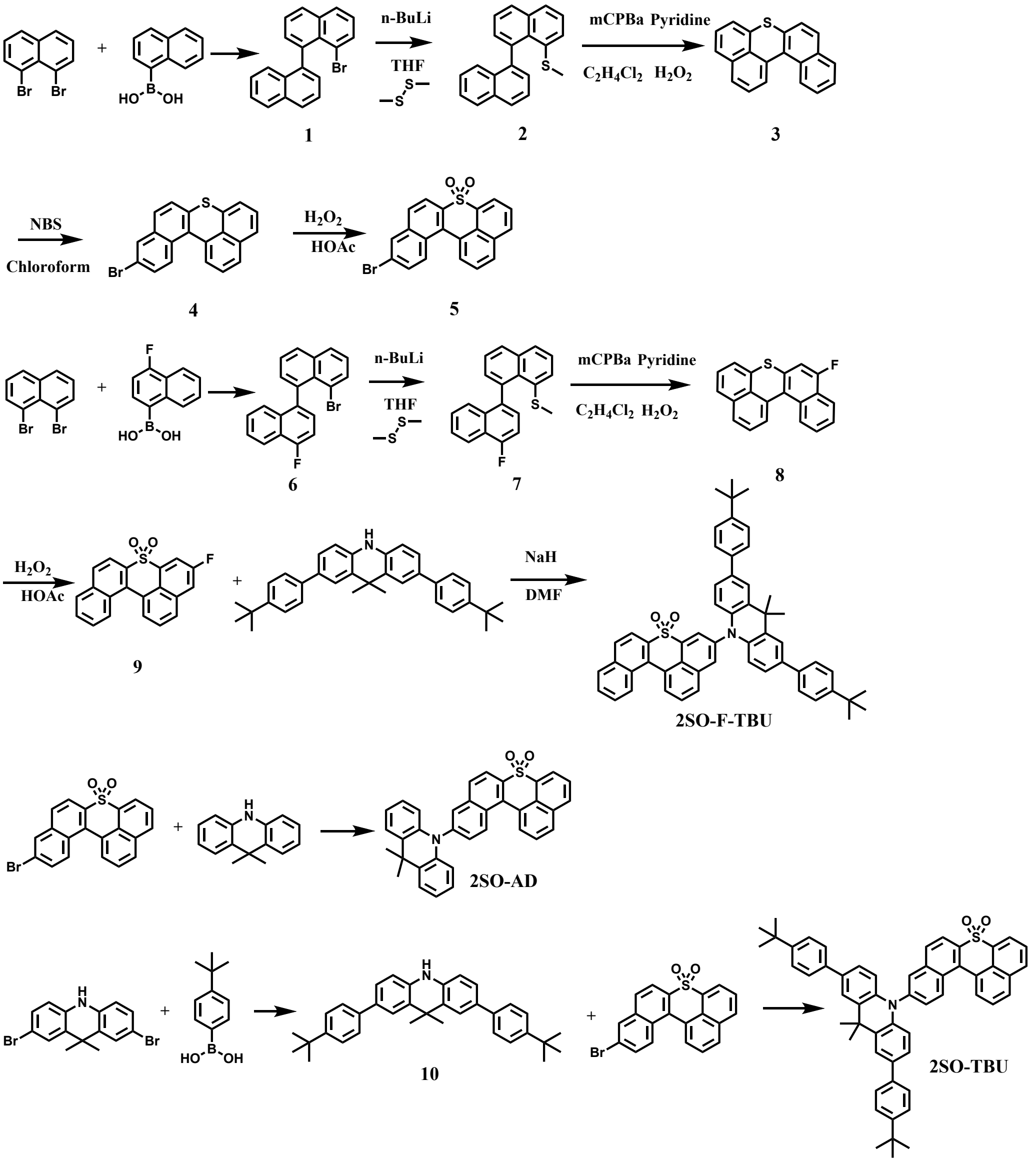
1. Materials and methods

1.1 General methods.

All solvents and materials were used as received from commercial suppliers without further purification. All reactions were monitored by thin layer chromatographic analysis on a pre-coated silica gel plate, which was visualized by a UV lamp at 254 or 365 nm. Flash column chromatography was performed on glass column of silica gel (200-300 mesh) and solvent ratios were expressed in volume to volume. ^{1}H and ^{13}C NMR spectra for structural characterization were recorded on NMR spectrometer (400 MHz for ^{1}H; 400 MHz for ^{13}C). All NMR measurements were conducted in $CDCl_3$ at room temperature. The NMR spectra were recorded on VaRIAN-GEMINI-300 and Bruker Avance Π-400 spectrometer at room temperature and tetramethylsilane (TMS) as an internal reference. Chemical shifts were reported as parts per million in scale using the slvent residual peak as internal standard for ^{1}H and ^{13}C NMR. Coupling constants (J) were reported in Hertz (Hz). Mass spectra were recorded using a BIFLEXIII MALDI-TOF mass spectrometer in EI mode. UV-vis spectra and fluorescence spectra were obtained with Hitachi U-3900 and F-4600 spectrophotometers, respectively. The phosphorescence spectra were measured in 2-MeTHF glass matrix at 77 K using a Hitachi F-4600 fluorescence spectrometer. The absolute fluorescence quantum yields of the solid films and the solution are measured with an integrating sphere. Cyclic voltammetry was performed using a CHI600A analyzer with a scan rate of 100 mV S^{-1} at room temperature. The electrolytic cell was a conventional three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a SCE (Ag/Ag^+) reference electrode. The measurement of oxidation potentials was performed in CH_2Cl_2 with 0.1 M of tetra-n-butylammonium hexafluorophosphate (n-Bu4NPF6) as a supporting electrolyte, and the reduction part was performed in THF with 0.1 M of nBu4NPF6 as a supporting electrolyte. The DSC measurements were carried out using a TA Instruments DSC 2910 thermal analyzer at a heating rate of 10 °C min^{-1}. The TGA measurements were carried out using a TA In struments TGA Q50 thermal analyzer at a heat rate of 10 °C min^{-1}.

1.2 Synthesis.

All solvents and materials were used as received from commercial suppliers without further purification. Synthetic routes of these compounds are shown in scheme S1.



Scheme S1. Synthetic routes of 2SO-AD, 2SO-TBU and 2SO-F-TBU.

Synthesis of 8-bromo-1,1'-binaphthalene (1):

Naphthalen-1-ylboronic acid (285.88 mg, 1.0 mmol), 1,8-dibromonaphthalene (172.07 mg, 1.0 mmol), tetrakis(triphenylphosphine) palladium (0) (58 mg, 5 mol%), 2 M K_2CO_3 (8 ml, 10 min nitrogen bubbling) and toluene (20ml, 10 min nitrogen bubbling) were added and the resulting mixture was stirred under nitrogen atmosphere for 3 hours at 98 °C. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and organic phase was washed with brine. The combined organic fractions were dried with $MgSO_4$, filtered and the solvents were evaporated. The crude product was purified by column chromatography on silica gel using pure petroleum ether as the eluent. The product was isolated as a white solid. The yield of product was 78%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.87 (m, 4H), 7.72 (d, J = 7.2 Hz, 1H), 7.62 – 7.38 (m, 5H), 7.36 – 7.28 (m, 3H). EIMS m/z (%): calcd for $C_{20}H_{13}Br$, 332.02; found: 332.01965.

Synthesis of [1,1'-binaphthalen]-8-yl(methyl)sulfane (2):

Dried THF (50 ml) and 8-bromo-1,1'-binaphthalene (332.02 mg, 1 mmol) were mixed in a 250 ml three-necked flask equipped with a condenser and mechanical stirrer under nitrogen. n-BuLi (0.4 ml, 2.5 M in hexane) was added dropwise to the reaction mixture which was cooled to −78 °C over a period of 10min. The reaction mixture was stirred at −78 °C for 1 h. After lithiation, 1,2-dimethyldisulfane (0.1 ml, 1.2 mmol) was rapidly added to the reaction mixture which was cooled to −78 °C. The solution was stirred at room temperature for another 12 h. The reaction mixture was poured into a mixture of ice and water, acidified with 2 N HCl and extracted with dichloromethane successively. Then the organic phase was washed three times with water, and dried over $MgSO_4$. The product was isolated as a white solid. The yield of product was 68%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.87 (m, 4H), 7.72 (d, J = 7.2 Hz, 1H), 7.62 – 7.38 (m, 5H), 7.36 – 7.28 (m, 3H), 2.09 (s, 3H). EIMS m/z (%): calcd for $C_{21}H_{16}S$, 300.10; found: 300.09669.

Synthesis of dibenzo[a,kl]thioxanthene (3):

The arylated compound 2 (0.2 mmol, 1.0 eq) and mCPBA (contains ca. 30% H_2O) (0.22 mmol,1.1 eq) were dissolved in DCM (12 mL). The mixture was stirred at room temperature until the complete conversion of 2 on TLC (within 1 hour). $NaHCO_3$ was added and the organic layer was separated. The aqueous layer was extracted with DCM three times. Combined organic extract was dried over Na_2SO_4. After evaporation of the solvents, the mixture was purified by column chromatography (eluent: hexane/EtOAc = 1/1). The corresponding sulfoxide was placed in a Schlenk tube and DCE (3.0 mL) was added. With continuous N_2 streaming into the tube, TfOH (1.5 mL) was added dropwise. After stirring 24 hours at room temperature, H_2O (5.3 mL) and pyridine (0.7 mL) was charged and the resulting mixture was stirred for another hour at 120 °C. The mixture was poured into 2.5 mL of 4M aqueous HCl, and diluted with H_2O and DCM. The organic layer was separated and the aqueous layer was extracted with DCM three times. The combined organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The obtained crude material was purified through column chromatography (eluent: hexane/EtOAc = 80/1) to give the cyclized product. The yield of product was 58%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.58 (d, J = 6.5 Hz, 1H), 8.07 (d, J = 6.7 Hz, 1H), 7.81 (d, J = 3.3 Hz, 1H), 7.69 (t, J = 8.4 Hz, 2H), 7.59 – 7.38 (m, 4H), 7.30 (dd, J = 15.5, 8.4 Hz, 3H). EIMS m/z (%): calcd for $C_{20}H_{12}S$, 284.07; found: 284.06510.

Synthesis of 11-bromodibenzo[a,kl]thioxanthene (4):

Compound 3 (0.2 mmol, 1.0 eq) and NBS (0.22 mmol, 1.1 eq) were dissolved in chloroform (12 mL). After 2 hours in the dark, the reaction mixture was diluted with dichloromethane and the organic phase was washed with brine. The combined organic fractions were dried over $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by silica gel column chromatography using pure petroleum ether as eluent. The product was isolated as a yellow solid. The yield of product was 87%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.53 (d, J = 6.6 Hz, 1H), 8.14 (dd, J = 17.8, 7.9 Hz, 1H), 7.98 – 7.59 (m, 6H), 7.46 (d, J = 4.9 Hz, 2H), 7.31 (d, J = 8.5 Hz, 1H). EIMS m/z (%): calcd for $C_{20}H_{11}BrS$, 361.98; found: 361.97579.

Synthesis of 11-bromodibenzo[a,kl]thioxanthene 7,7-dioxide (5):

A mixture of 11-bromodibenzo[a,kl]thioxanthene (4) (361.98 mg, 1.0 mmol), glacial acetic acid (20ml) and 30% hydrogen peroxide (3 ml) was boiled for 1 hours at 120 °C, and then was cooled and poured into cold water. The precipitate was collected by filtration under a vacuum, washed with water, and dried in a vacuum oven. The product was collected as a yellow solid. The yield of product was 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.32 (m, 4H), 8.28 (d, J = 8.6 Hz, 1H), 8.10 (dd, J = 15.5, 6.7 Hz, 2H), 8.00 (d, J = 7.9 Hz, 1H), 7.94 – 7.81 (m, 1H), 7.72 – 7.58 (m, 2H). EIMS m/z (%): calcd for $C_{13}H_7BrO_3S$, 323.2; found: 323.9.

Synthesis of 8'-bromo-4-fluoro-1,1'-binaphthalene (6):

(4-fluoronaphthalen-1-yl)boronic acid (190.06 mg, 1.0 mmol), 1,8-dibromonaphthalene (285.88 mg, 1 mmol), tetrakis(triphenylphosphine)palladium(0) (58 mg, 5 mol%), 2 M K_2CO_3 (8 ml, 10 min nitrogen bubbling) and toluene (20ml, 10 min nitrogen bubbling) were added and the resulting mixture was stirred under nitrogen atmosphere for 3 hours at 98 °C. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and organic phase was washed with brine. The combined organic fractions were dried with $MgSO_4$, filtered and the solvents were evaporated. The crude product was purified by column chromatography on silica gel using pure dichloromethane as the eluent. The product was isolated as a white solid. The yield of product was 76%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.85 (ddd, J = 17.3, 8.2, 1.1 Hz, 2H), 7.61 (dd, J = 7.4, 1.2 Hz, 1H), 7.48 – 7.36 (m, 3H), 7.25 – 7.06 (m, 5H). EIMS m/z (%): calcd for $C_{20}H_{12}BrF$, 350.01; found: 350.00877.

Synthesis of 8'-bromo-4-fluoro-1,1'-binaphthalene (7):

Dried THF (50 ml) and 8'-bromo-4-fluoro-1,1'-binaphthalene (350.01 mg, 1 mmol) were mixed in a 250 ml three-necked flask equipped with a condenser and mechanical stirrer under nitrogen. n-BuLi (0.4 ml, 2.5 M in hexane) was added dropwise to the reaction mixture which was cooled to −78 °C over a period of 10min. The reaction mixture was stirred at −78 °C for 1 h. After lithiation, 1,2-dimethyldisulfane (0.1 ml, 1.2 mmol) was rapidly added to the reaction mixture which was cooled to −78 °C. The solution was stirred at room temperature for another 12 h. The reaction mixture was poured into a mixture of ice and water, acidified with 2 N HCl and extracted with dichloromethane successively. Then the organic phase was washed three times with water, and dried over $MgSO_4$. The product was isolated as a white solid. The yield of product was 66%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 1H), 7.86 (dd, J = 8.2, 1.3 Hz, 1H), 7.66 (dd, J = 8.1, 0.8 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.31 – 7.22 (m, 4H), 7.15 – 7.06 (m, 2H), 2.01 (s, 3H). EIMS m/z (%): calcd for $C_{21}H_{15}FS$, 318.09; found: 318.08628.

Synthesis of 9-fluorodibenzo[a,kl]thioxanthene (8):

The arylated compound 2 (0.2 mmol, 1.0 eq) and mCPBA (contains ca. 30% H_2O) (0.22 mmol,1.1 eq) were dissolved in DCM (12 mL). The mixture was stirred at room temperature until the complete conversion of 2 on TLC (within 1 hour). $NaHCO_3$ was added and the organic layer was separated. The aqueous layer was extracted with DCM three times. Combined organic extract was dried over Na_2SO_4. After evaporation of the solvents, the mixture was purified by column chromatography (eluent: hexane/EtOAc = 1/1). The corresponding sulfoxide was placed in a Schlenk tube and DCE (3.0 mL) was added. With continuous N_2 streaming into the tube, TfOH (1.5 mL) was added dropwise. After stirring 24 hours at room temperature, H_2O (5.3 mL) and pyridine (0.7 mL) was charged and the resulting mixture was stirred for another hour at 120 °C. The mixture was poured into 2.5 mL of 4M aqueous HCl, and diluted with H_2O and DCM. The organic layer was separated and the aqueous layer was extracted with DCM three times. The combined organic extracts was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The obtained crude material was purified through column chromatography (eluent: hexane/EtOAc = 80/1) to give the cyclized product. The yield of product was 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.6 Hz, 1H), 8.43 (d, J = 7.5 Hz, 2H), 8.30 (t, J = 8.8 Hz, 2H), 8.12 (d, J = 7.7 Hz, 1H), 7.97 (dd, J = 15.5, 8.2 Hz, 2H), 7.74 (dd, J = 15.7, 7.5 Hz, 3H). EIMS m/z (%): calcd for $C_{21}H_{15}FS$, 302.06; found: 302.05585.

Synthesis of 5-fluorodibenzo[a,kl]thioxanthene 7,7-dioxide (9):

A mixture of 9-fluorodibenzo[a,kl]thioxanthene (4) (302.06 mg, 1.0 mmol), glacial acetic acid (20ml) and 30% hydrogen peroxide (3 ml) was boiled for 1 hours at 120 °C, and then was cooled and poured into cold water. The precipitate was collected by filtration under a vacuum, washed with water, and dried in a vacuum oven. The product was collected as a yellow solid. The yield of product was 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.6 Hz, 1H), 8.43 (d, J = 7.5 Hz, 2H), 8.30 (t, J = 8.8 Hz, 2H), 8.12 (d, J = 7.7 Hz, 1H), 7.97 (dd, J = 15.5, 8.2 Hz, 2H), 7.74 (dd, J = 15.7, 7.5 Hz, 3H). EIMS m/z (%): calcd for $C_{13}H_7BrO_3S$, 323.2; found: 323.9.

Synthesis of 2,7-bis(4-(tert-butyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (10):

(4-(tert-butyl)phenyl)boronic acid (356.24 mg, 2.0 mmol), 2,7-dibromo-9,9-dimethyl-9,10-dihydroacridine (366.94 mg, 1 mmol), tetrakis(triphenylphosphine)palladium(0) (58 mg, 5 mol%), 2 M K_2CO_3 (8 ml, 10 min nitrogen bubbling) and toluene (20ml, 10 min nitrogen bubbling) were added and the resulting mixture was stirred under nitrogen atmosphere for 5 hours at 98 °C. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and organic phase was washed with brine. The combined organic fractions were dried with $MgSO_4$, filtered and the solvents were evaporated. The crude product was purified by column chromatography on silica gel using pure dichloromethane as the eluent. The product was isolated as a white solid. The yield of product was 83%. ^{1}H NMR (400 MHz, DMSO) δ 9.07 (s, 1H), 7.66 – 7.27 (m, 12H), 6.85 (d, J = 7.9 Hz, 2H), 1.61 (s, 6H), 1.30 (s, 18H). EIMS m/z (%): calcd for $C_{35}H_{39}N$, 473.31; found: 473.30717.

Synthesis of 11-(9,9-dimethylacridin-10(9H)-yl)dibenzo[a,kl]thioxanthene 7,7-dioxide (2SO-AD):

Palladium acetate (168.38 mg, 0.75 mmol) and tri-tert-butyltetrafluoroborate (217.59 mg, 0.75

mmol) were dissolved in m-xylene under argon atmosphere. After addition of 11-bromodibenzo[a,kl]thioxanthene 7,7-dioxide (393.97 mg, 1 mol), the reaction mixture was stirred for 10 minutes. To the mixture was added sodium tert-butoxide (288 mg, 3 mmol) and 9,9-dimethyl-9,10-dihydroacridine (250.94 mg, 1.2 mmol). The reaction mixture was reacted at 130°C for 5 hours and was considered complete by thin layer chromatography (TLC) analysis. After cooling to room temperature, the mixture was filtered through celite and washed with toluene and water. The organic layer was extracted with dichloromethane and dried over $MgSO_4$. The solvent was evaporated on a rotary evaporator and the dark brown mixture was subjected to column chromatography on silica gel using pure dichloromethane as eluent to give an orange solid. The yield of product was 73%. ^1H NMR (400 MHz, CD_2Cl_2) δ 8.71 (dd, J = 20.1, 7.0 Hz, 2H), 8.59 – 8.45 (m, 2H), 8.32 (d, J = 8.3 Hz, 1H), 8.21 (t, J = 7.1 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.93 (dd, J = 26.2, 6.9 Hz, 1H), 7.75 (td, J = 15.8, 8.0 Hz, 3H), 7.59 (d, J = 6.6 Hz, 2H), 7.01 – 6.85 (m, 4H), 6.15 (d, J = 8.0 Hz, 1H), 6.06 (d, J = 8.1 Hz, 1H), 1.89 (s, 3H), 1.81 (s, 3H).^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.88, 140.78, 140.65, 140.37, 136.89, 134.59, 133.71, 133.46, 133.07, 132.93, 132.25, 130.90, 130.71, 130.53, 130.37, 129.90, 129.60, 129.52, 128.67, 128.52, 128.30, 128.13, 127.58, 127.15, 126.45, 125.83, 125.74, 125.13, 121.60, 119.00, 118.94, 114.64, 36.35, 33.20, 32.59. EIMS m/z (%): calcd for $C_{35}H_{25}NO_2S$, 523.16; found: 523.16016.

Synthesis of 11-(2,7-bis(4-(tert-butyl)phenyl)-9,9-dimethylacridin-10(9H)-yl)dibenzo[a,kl]thioxanthene 7,7-dioxide (2SO-TBU):

Palladium acetate (168.38 mg, 0.75 mmol) and tri-tert-butyltetrafluoroborate (217.59 mg, 0.75 mmol) were dissolved in m-xylene under argon atmosphere. After addition of 11-bromodibenzo[a,kl]thioxanthene 7,7-dioxide (393.97 mg, 1 mol), the reaction mixture was stirred for 10 minutes. To the mixture was added sodium tert-butoxide (288 mg, 3 mmol) and 2,7-bis(4-(tert-butyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (567.97 mg, 1.2 mmol). The reaction mixture was reacted at 130°C for 5 hours and was considered complete by thin layer chromatography (TLC) analysis. After cooling to room temperature, the mixture was filtered through celite and washed with toluene and water. The organic layer was extracted with dichloromethane and dried over $MgSO_4$. The solvent was evaporated on a rotary evaporator and the dark brown mixture was subjected to column chromatography on silica gel using pure dichloromethane as eluent to give a red solid. The yield of product was 83%. ^1H NMR (400 MHz,

CD_2Cl_2) δ 8.75 (dd, J = 21.4, 7.5 Hz, 2H), 8.55 (dd, J = 18.2, 6.8 Hz, 2H), 8.33 (d, J = 7.9 Hz, 1H), 8.26 – 7.94 (m, 4H), 7.90 – 7.66 (m, 5H), 7.61 – 7.41 (m, 7H), 7.24 – 7.10 (m, 2H), 6.24 (d, J = 8.1 Hz, 1H), 6.15 (d, J = 9.0 Hz, 1H), 2.01 (s, 3H), 1.93 (s, 3H), 1.36 (s, 18H).^{13}C NMR (101 MHz, CD_2Cl_2) δ 150.21, 143.71, 140.20, 139.87, 139.75, 138.36, 138.34, 136.92, 134.90, 134.62, 134.37, 134.35, 134.11, 133.70, 133.61, 133.14, 132.87, 132.31, 132.24, 131.66, 130.95, 130.74, 130.64, 130.56, 130.48, 130.41, 130.38, 129.87, 129.62, 129.53, 128.68, 128.55, 128.27, 128.03, 127.73, 126.49, 126.41, 126.11, 125.84, 125.81, 125.67, 125.44, 125.31, 125.22, 119.02, 118.96, 115.15, 115.12, 36.81, 34.77, 33.66, 33.58, 33.12, 33.02, 31.50. EIMS m/z (%): calcd for $C_{55}H_{49}NO_2S$, 787.35; found: 787.35211.

Synthesis of 5-(2,7-bis(4-(tert-butyl)phenyl)-9,9-dimethylacridin-10(9H)-yl)dibenzo[a,kl]thioxanthene 7,7-dioxide (2SO-F-TBU):

Sodium hydride (28.78 mg, 1.2 mmol) and 2,7-bis(4-(tert-butyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (524.77 mg, 1.2 mmol) were dissolved in DMF under nitrogen atmosphere and stirred at room temperature for 1 hour. After adding 11-bromodibenzo[a,kl]thioxanthene 7,7-dioxide (334.05 mg, 1 mol), the reaction mixture was reacted at 130°for 5 hours, and the reaction was considered complete by thin layer chromatography (TLC) analysis. After cooling to room temperature, the organic layer was extracted with dichloromethane and dried over $MgSO_4$. The solvent was evaporated on a rotary evaporator and the dark brown mixture was subjected to column chromatography on silica gel using pure dichloromethane as eluent to give a red solid. The yield of product was 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, J = 18.7, 8.0 Hz, 2H), 8.53 (d, J = 7.0 Hz, 1H), 8.46 (s, 1H), 8.31 (d, J = 8.2 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.95 (t, J = 9.4 Hz, 2H), 7.86 (t, J = 7.7 Hz, 1H), 7.78 (s, 2H), 7.76 – 7.67 (m, 1H), 7.61 (dd, J = 16.0, 8.5 Hz, 1H), 7.47 (dd, J = 22.0, 8.0 Hz, 8H), 7.12 (d, J = 8.4 Hz, 2H), 6.19 (d, J = 8.4 Hz, 2H), 2.01 (s, 3H), 1.87 (s, 3H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 148.93, 148.82, 138.26, 138.01, 137.79, 137.19, 137.05, 134.70, 134.12, 133.79, 133.39, 133.09, 133.05, 132.43, 132.26, 132.07, 131.79, 131.53, 131.41, 129.95, 129.52, 129.10, 128.65, 128.55, 128.47, 128.42, 128.09, 127.82, 125.86, 125.50, 125.25, 124.83, 124.67, 124.54, 124.42, 124.02, 123.77, 123.65, 123.48, 123.35, 122.93, 122.85, 121.45, 121.34, 115.11, 113.89, 113.79, 112.59, 35.56, 33.49, 32.97, 32.65, 31.18, 30.49, 30.28. EIMS m/z (%): calcd for $C_{55}H_{49}NO_2S$, 787.35; found: 787.35211.

1.3 Theoretical calculations.

The geometry of ground states of all four compounds were optimized by DFT at the B3LYP /6-31G(d,p) level in toluene. All the excited-state properties of the molecules studied here were calculated by TDDFT at the M062X/6-31G(d,p) level in toluene. All the DFT and TDDFT calculation were performed by Gaussian16 program, version A03.

1.4 Transient photophysical measurement.

The transient photoluminescent decay characteristics were measured using an Edinburgh Instruments FLS1000 spectrometer. The temperature dependence experiment is conducted under low temperature refrigeration system from Advanced Research Systems Company. The transient decay curves were fitted with the multi-exponential equation:

$$I(t) = \sum_i A_i \, exp(-\ t/\ \tau_i)$$

where A_i is the pre-exponential factor, τ_i is the decay time, and $I(t)$ is the emission intensity. The Φ_{Prompt} and Φ_{TADF} were determined by using total PL quantum efficiency and the ratio between prompt and delayed components. The intensity ratio between prompt (r_1) and delayed (r_2) components were obtained by fitting. Then, Φ_{Prompt} and Φ_{TADF} were determined using intensity ratio (r_1, r_2) and total emission quantum yield, and the rate constants are calculated as follows[1].

$$\Phi_{Prompt} = \Phi_{Total} \cdot r_1$$

$$\Phi_{TADF} = \Phi_{Total} \cdot r_2$$

$$k_p = \frac{1}{\tau_s} \qquad (1)$$

$$k_d = \frac{1}{\tau_d} \qquad (2)$$

$$k_r^s = \frac{\Phi_{Prompt}}{\tau_s} \qquad (3)$$

$$\frac{k_r^s}{k_r^s + k_{nr}^s} = \Phi_{Total} \qquad (4)$$

$$k_r^s + k_{nr}^s + k_{ISC} = k_p \qquad (5)$$

$$\Phi_T = \frac{k_{ISC}}{k_p} \qquad (6)$$

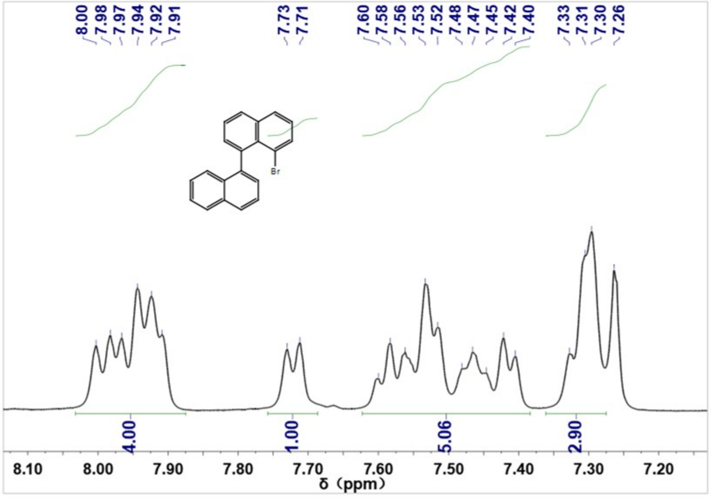
$$k_{RISC} = \frac{k_p \, . \, k_d \, . \, \Phi_{TADF}}{k_{ISC} \cdot \Phi_{Prompt}} \qquad (7)$$

Here, k_p and k_d the rate constants of prompt and delayed fluorescence, τ_s is the emission lifetime of the singlet excited state taken from lifetime measurements of the short range and τ_d is the emission lifetime of the delayed components. k_r^S and k_{nr}^S are the radiative and non-radiative rate constants from S_1 state, respectively, k_{ISC} is the intersystem crossing rate. The triplet formation efficiency (Φ_T) could be calculated by the intersystem crossing rate (k_{ISC}) and the emission lifetime of the prompted components (τ_s). The reverse intersystem crossing constant (k_{RISC}) was calculated by the rate constants of prompt fluorescence （k_p）, the rate constants of delayed fluorescence （k_d）, the quantum yield of the delayed components (Φ_{TADF}), the intersystem crossing rate (k_{ISC}) and the quantum yield of the prompt components (Φ_{Prompt}). The intersystem crossing constant (k_{ISC}), the radiative rate constants (k_r^S) and the non-radiative rate constant (k_{nr}^S) were calculated assuming that k_{ISC} was independent of temperature.

1.5 Device fabrication.

Before device fabrication, the ITO glass substrates were sequentially cleaned with detergents, de-ionized water, acetone, ethanol, dried at 75 °C, and treated with oxygen plasma for 10 min. After that, the clean substrates were transferred into a vacuum deposition system with a pressure below 5×10^{-4} Pa for organic and metal deposition. The devices were fabricated by evaporating organic materials onto the substrate at a rate of 1–2 Å s^{-1} while LiF at a rate of 0.05 Å s^{-1} and Al metal through a rate of 2 Å s^{-1}. Then capped with EL luminescence spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer and the current-voltage characteristics were measured with a computer-controlled Keithley 2400 Source Meter and CS-200 under ambient atmosphere.

2. Supplementary tables and figures.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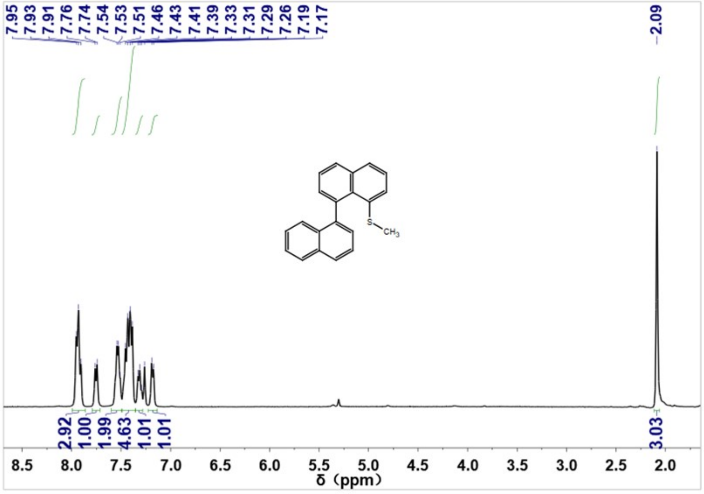
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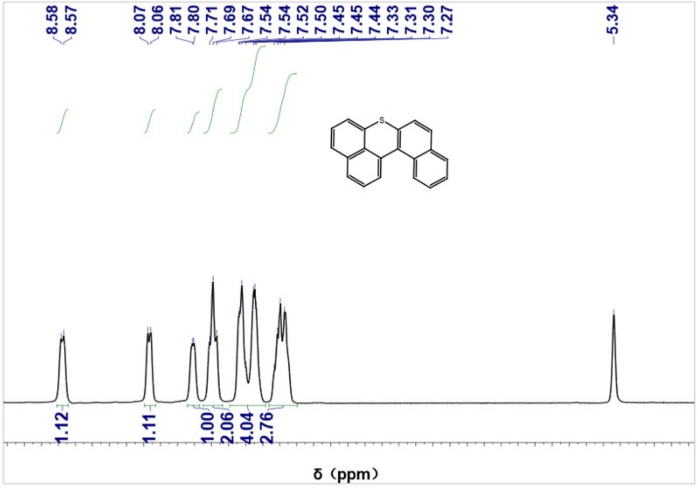
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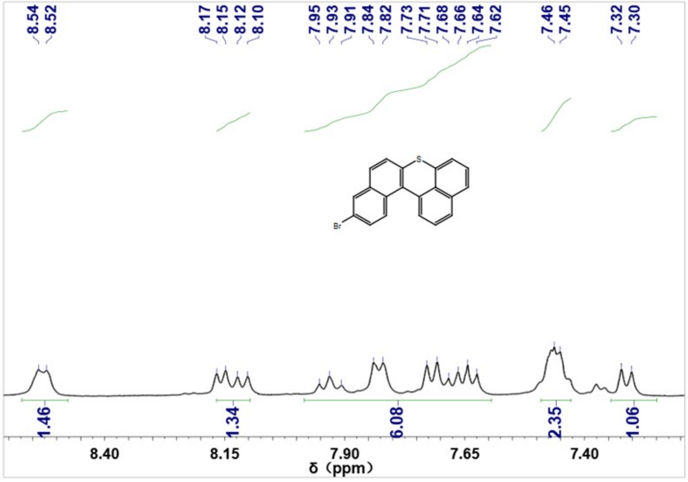
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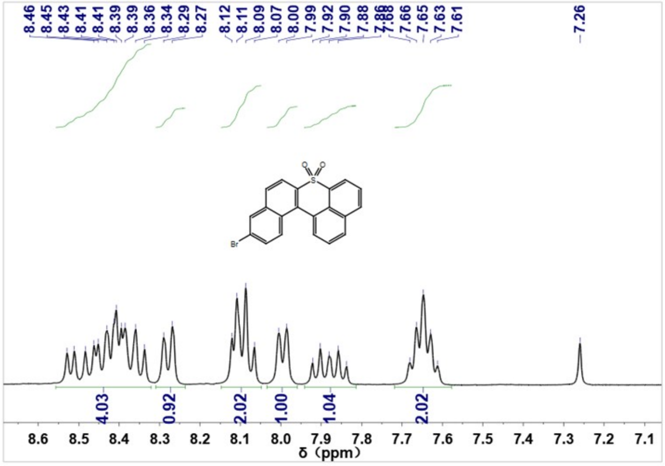
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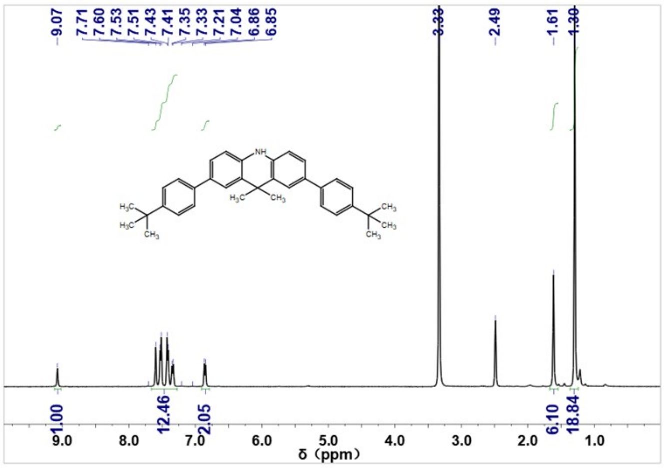
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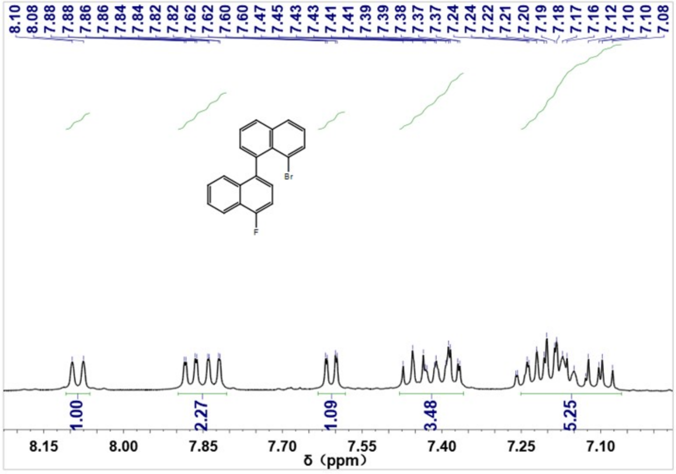
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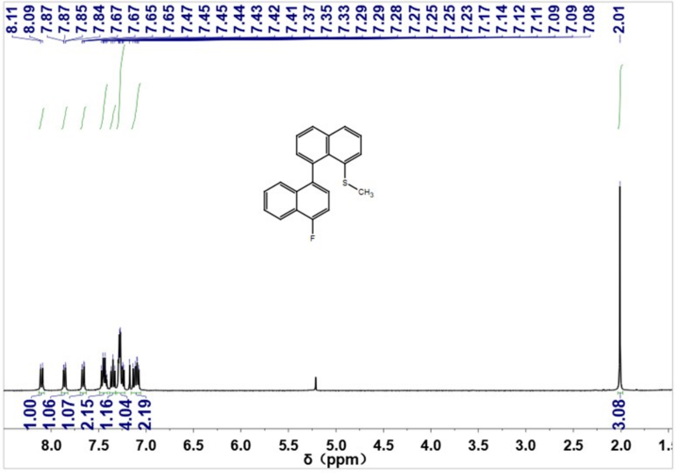
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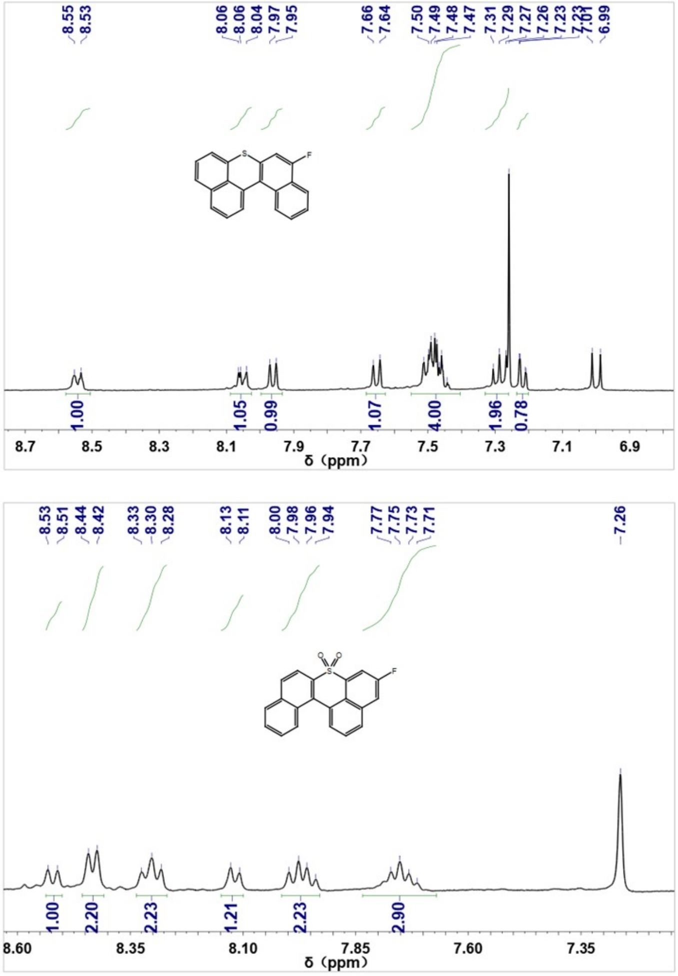
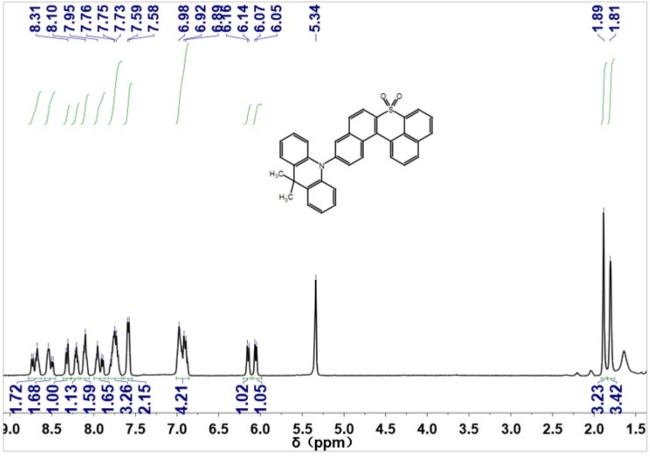


Fig S1. ^{1}H NMR spectrum of intermediate products.



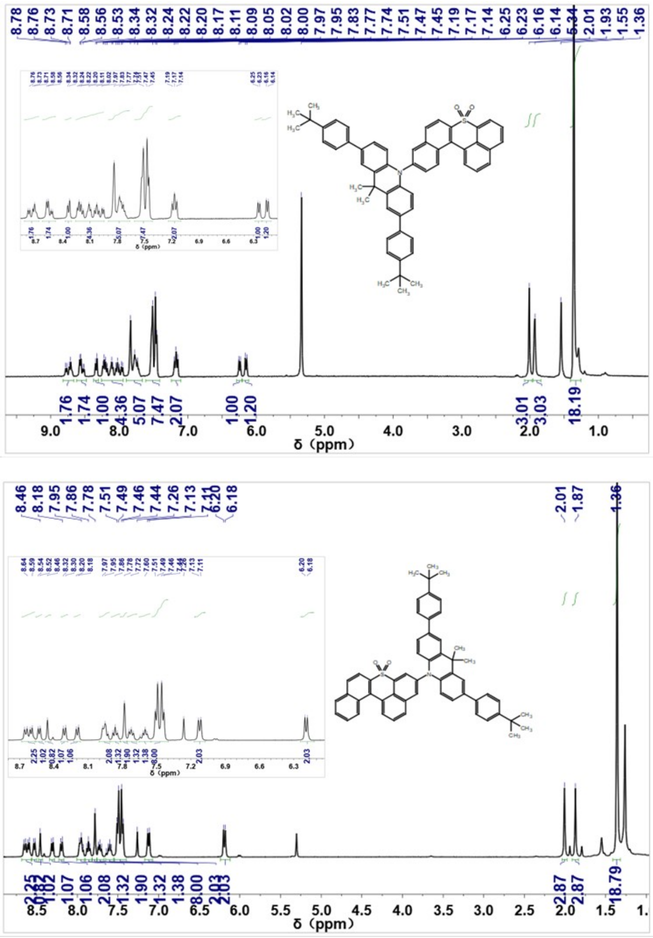
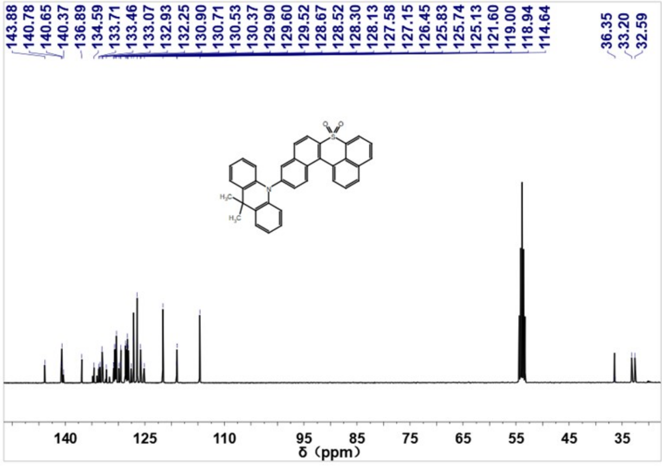


Fig S2. ^{1}H NMR spectrum of 2SO-AD,2SO-TBU and 2SO-F-TBU.



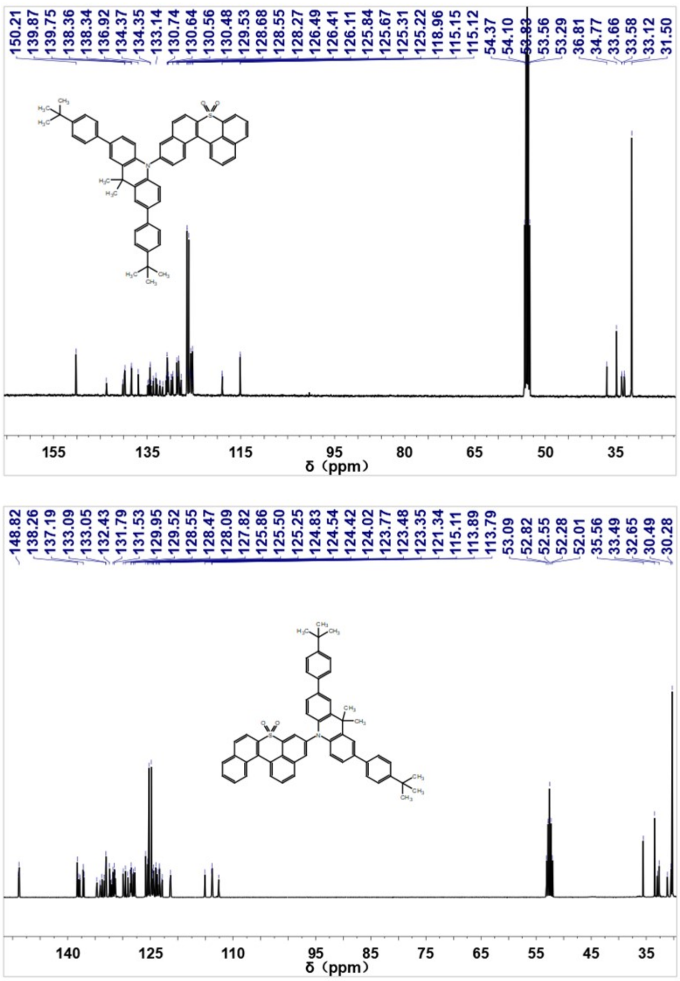
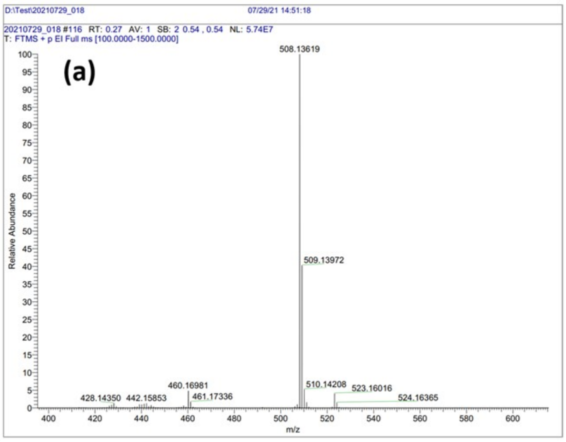


Fig S3. ^{13}C NMR spectrum of 2SO-AD,2SO-TBU and 2SO-F-TBU.



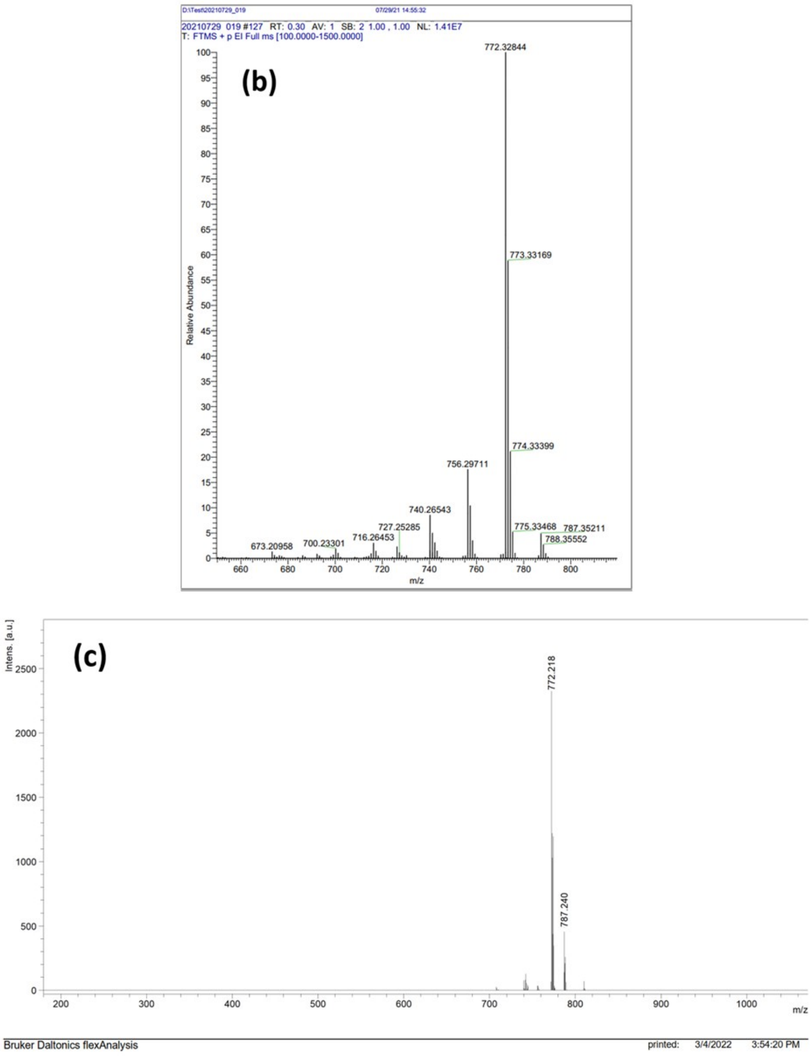


Fig S4. HRMS EI+ spectrum of (a)2SO-AD, (b)2SO-TBU and (c)2SO-F-TBU.

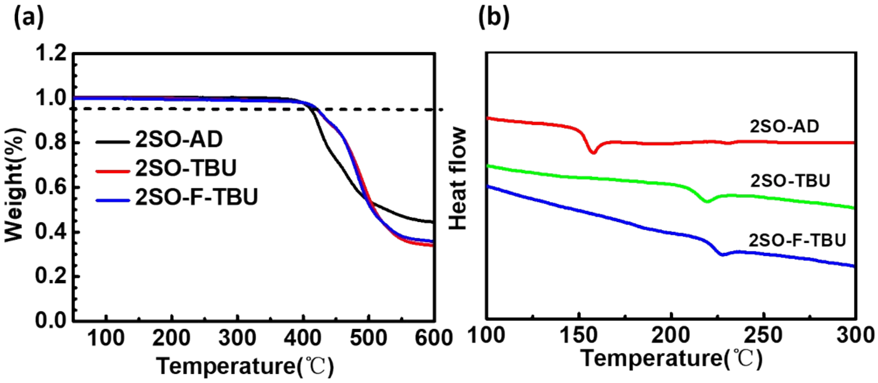


Fig S5. Thermodynamic properties of compounds. (a) TGA curves and (b) DSC curves of 2SO-AD, 2SO-TBU and 2SO-F-TBU.

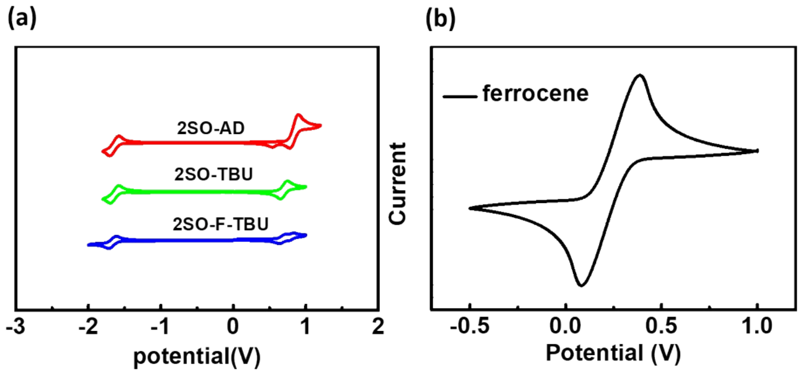


Fig S6. Cyclic voltammetry curves of (a) 2SO-AD, 2SO-TBU, 2SO-F-TBU and (b) reference: ferrocene.

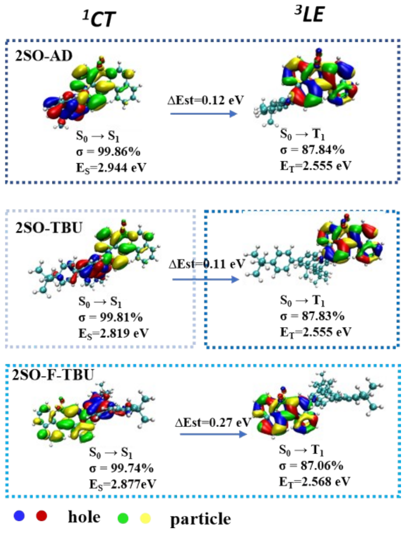


Fig S7. Natural transition orbitals (NTOs) character of the excited states for 2SO-AD, 2SO-TBU and 2SO-F-TBU. *f* and σ refer to oscillator strength and contribution weight, respectively.

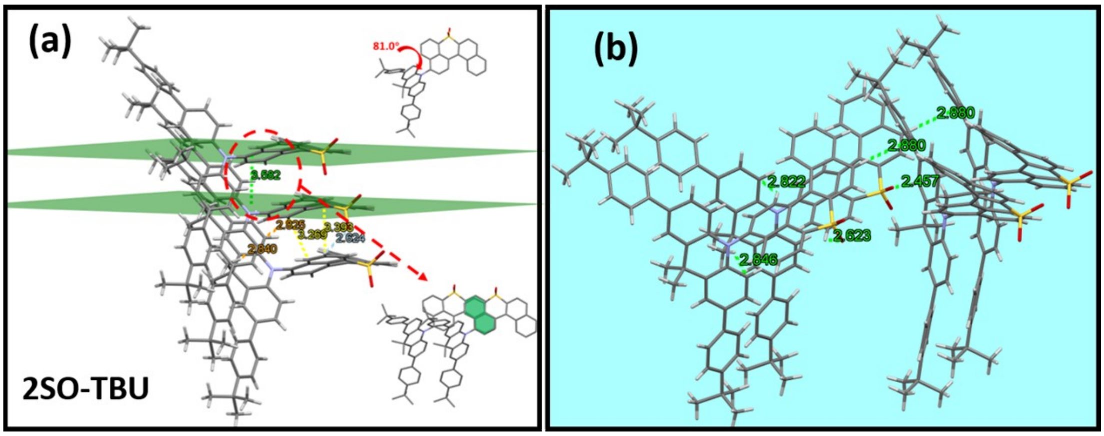


Fig S8. (a)Single crystal structure and (b)Molecular interactions of 2SO-TBU.

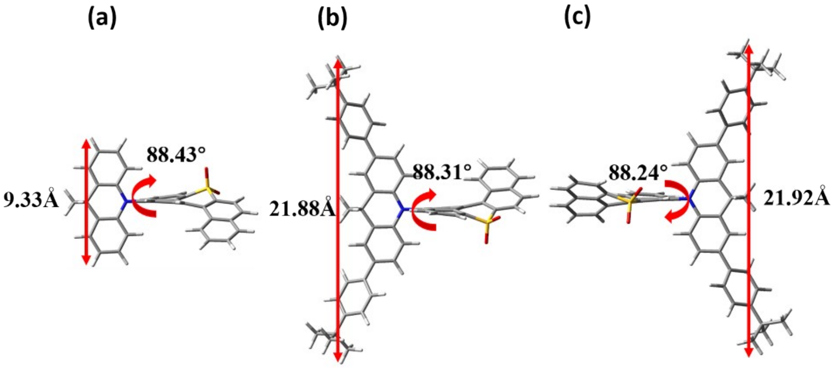


Fig S9. Molecular structures after optimization by DFT: (a) 2SO-AD, (b) 2SO-TBU and (c) 2SO-F-TBU.

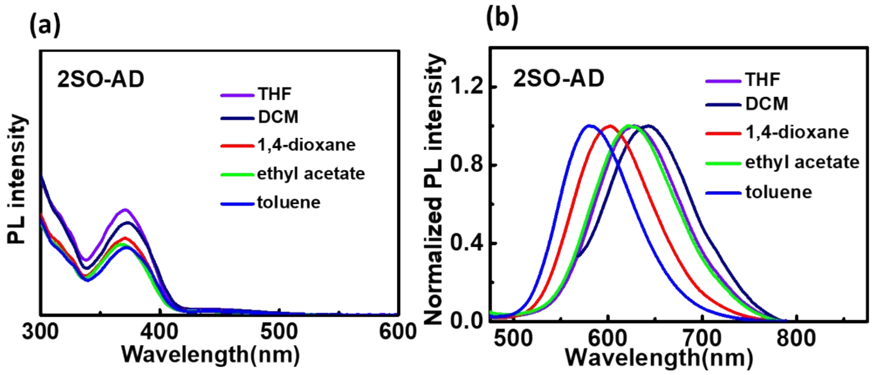


Fig S10. (a) Absorption spectra of 2SO-AD in different solvents. (b) Fluorescence spectra of 2SO-AD in different solvents. The concentration of 2SO-AD in all cases: 50μM.

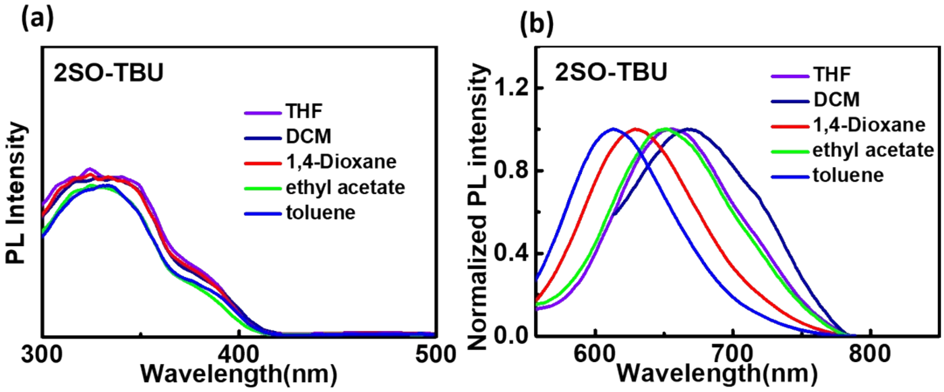


Fig S11. (a) Absorption spectra of 2SO-TBU in different solvents. (b) Fluorescence spectra of 2SO-TBU in different solvents. The concentration of 2SO-TBU in all cases: 50µM.

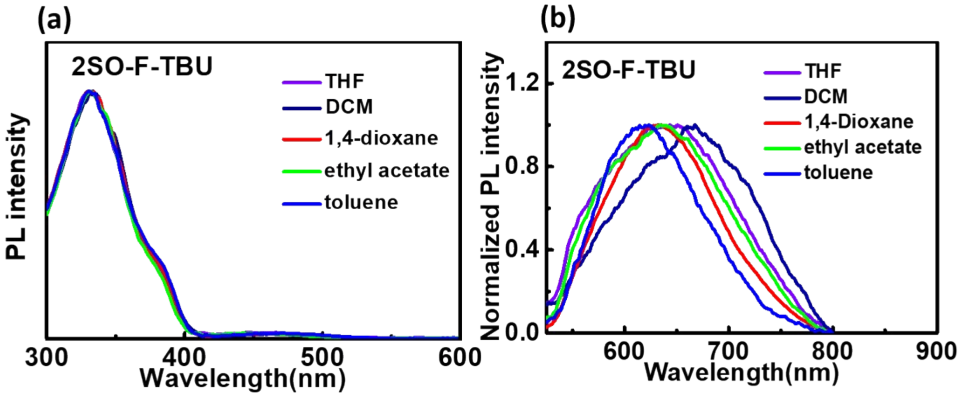


Fig S12. (a) Absorption spectra of 2SO-F-TBU in different solvents. (b) Fluorescence spectra of 2SO-F-TBU in different solvents. The concentration of 2SO-F-TBU in all cases: 50µM.

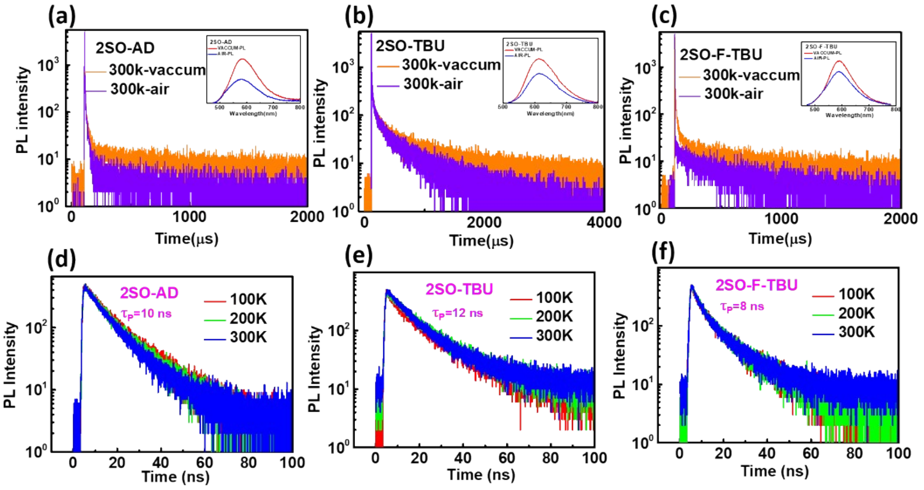


Fig S13. Transi3ent decay curves in vacuum/air at room temperature (The inset of graph is the corresponding PL graph) for (a) 2SO-AD, (b) 2SO-TBU and (c) 2SO-F-TBU; Temperature-dependence of the transient PL spectra of doped films for (d) 2SO-AD, (e) 2SO-TBU and (f) 2SO-F-TBU. (All films were doped in 35DCzPPY with the ratio of 10%. Excitation source: 475 nm EPL Laser)

Table S1

Photophysical, thermal and electrochemical properties for materials.

Compound	T_d[a]/T_g[b] (°C)	$\lambda_{abs}/\lambda_{PL}$ [nm] Sol[c]/Sol[d]/film[e]	Φ_{PL}[f] [%] film[e]	HOMO/LUMO[g] [eV]	E_g[h] [eV]	E_S/E_T[i] [eV]	ΔE_{ST}[j] [meV]
2SO-AD	411.7/ 157.3	452/ 580/581	0.250	−5.42/−3.13	2.29	2.30/2.03	270
2SO-TBU	420.0/ 219.1	465/614/615	0.583	−5.26/−3.10	2.16	2.17/2.03	140
2SO-F-TBU	421.6/ 227.7	463/618/591	0.530	−5.28/−3.11	2.17	2.25/2.05	200

[a] T_d: decomposition temperature.

[b] T_g: glass transition temperature.

[c] absorption measured in toluene.

[d] PL Measured in toluene.

[e] PL measured in 10 wt%-doped film in a 35DCzPPY host matrix.

[f] Absolute PL quantum yield evaluated using an integrating sphere under a nitrogen atmosphere.

[g] Calculated from the empirical formula HOMO = $-[E^{ox}-E(F_c/F_c^+) + 4.8]$ eV, LUMO = $-[E^{red}-E(F_c/F_c^+) + 4.8]$ eV, $E(F_c/F_c^+) = 0.13$ eV.

[h] Estimated from the difference between HOMO and LUMO measured by CV.

[i] Singlet (E_S) and triplet (E_T) excited energies estimated from the maximum peaks of fluorescence emission spectra and phosphorescence emission spectra at 77 K in 2-MeTHF, respectively.

[j] $\Delta E_{ST} = E_S - E_T$ estimated in 2-MeTHF.

Table S2

Summary of OLEDs Performance.

Dopant[a]	λ_{EL}(nm)[b]	V_{on}(V)[c]	EQE_{max} (%)[d]	PE (lm/W)[e]	CE (cd/A)[f]	Luminance[g](cd/m^2)
2SO-AD	599	3.5	3.20	6.01	6.89	1580
2SO-TBU	608	3.5	16.27	27.55	26.07	3844
2SO-F-TBU	612	3.0	14.47	20.44	26.31	1941

[a] The devices based on 2SO-AD, 2SO-TBU and 2SO-F-TBU in a structure of ITO/TAPC (35 nm)/mCP (10 nm)/3,5DCZPPY: TADF emitter (20 nm)/TmPYPB (45 nm)/LiF (1 nm)/Al

[b] Electroluminescence peak at 7V.

[c] Turn-on voltage at 1 cd m^{-2}.

[d] The maximum external quantum efficiency.

[e] The maximum power efficiency.

[f] The maximum current efficiency.

[g] The maximum luminance.

Table S3

Crystal data and structure refinement for 2SO-TBU

items	parameters
Empirical formula	$C_{55}H_{49}NO_2S$
Formula weight	788.01
Temperature/K	170.00(13)
Crystal system	monoclinic
Space group	P2/c
a/Å	29.9940(9)

b/Å	6.1565(2)
c/Å	25.4880(6)
α/°	90
β/°	106.326(3)
γ/°	90
Volume/Å^3	4516.8(2)
Z	4
ρ_{calc}g/cm^3	1.159
μ/mm^{-1}	0.950
F(000)	1672.0
Crystal size/mm^3	0.32 × 0.12 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.142 to 150.798
Index ranges	$-37 \le h \le 37$, $-7 \le k \le 6$, $-26 \le l \le 31$
Reflections collected	29090
Independent reflections	8891 [Rint = 0.0414, Rsigma = 0.0334]
Data/restraints/parameters	8891/108/571
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R1 = 0.1013, wR2 = 0.2732
Final R indexes [all data]	R1 = 0.1125, wR2 = 0.2812

References

[1] K.H. Kim, S.J. Yoo, J.J. Kim, Chem. Mater. 28 (2016) 1936-1941.