Supporting information

Structural Tuning of Ancillary Chelate in Tri-carboxyterpyridine Ru(II) Sensitizers for Dye Sensitized Solar Cells

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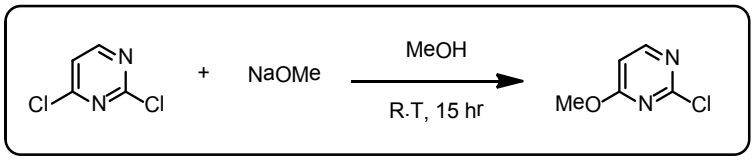
Experimental section

General Procedures. All reactions were performed under nitrogen. Solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification. All reactions were monitored by TLC with pre-coated silica gel plates (Merck, 0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV irradiation at 254 or 365 nm. Flash column chromatography was carried out using silica gel obtained from Merck (230 - 400 mesh). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker-400 or INOVA-500 instrument; chemical shifts are quoted with respect to the internal standard tetramethylsilane. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer. Photophysical data were obtained using an Edinburgh Fluorometer FLS928P.

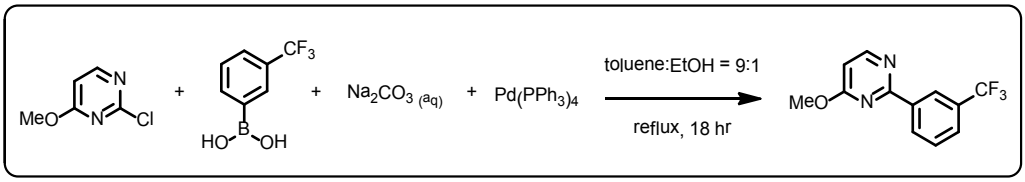


Synthesis of 2-chloro-4-methoxypyrimidine:

A solution of NaOMe (2.54 g, 47.0 mmol) in 100 mL MeOH was added to a solution of

2,4-dichloropyrimidine (7 g, 47.0 mmol) in 50 mL of MeOH at 0 °C. The mixture was stirred at room temperature overnight, and the excess solvent was removed under reduced pressure. The residue was dissolved in ether and the insoluble NaCl was filtered and washed with excess of ether. Finally, the filtrate was concentrated to give 2-chloro-4-methoxypyrimidine. Yield: 4 g, 59%.

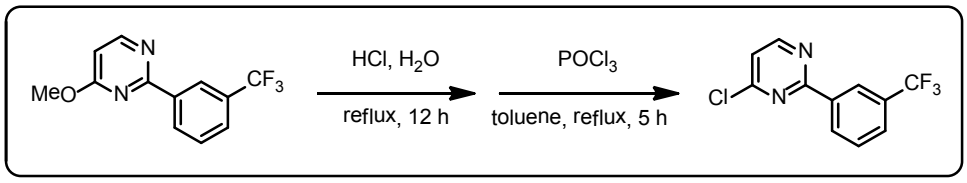
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.25 (d, J_{HH} = 5.6 Hz, 1H), 6.63 (d, J_{HH} = 5.6 Hz, 1H) 3.91 (s, 3H).



Synthesis of 4-methoxy-2-(3-(trifluoromethyl)phenyl)pyrimidine:

2-Chloro-4-methoxypyrimidine (4 g, 27.7 mmol), 3-(trifluoromethyl) phenylboronic acid (6.3 g, 33.2 mmol), $Pd(PPh_3)_4$ (1.6 g, 1.39 mmol) and sodium carbonate (14.6 g, 138 mmol) were suspended in a mixture of toluene (54 mL)/ethanol (6 mL)/water (60 mL). The mixture was refluxed for 18 h. After cooled to room temperature, the solvent was removed under reduced pressure, and the crude product was extracted with ethyl acetate and dried over Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel (ethyl acetate: hexane = 1: 5) to give white solid. Yield: 3.1 g, 45%.

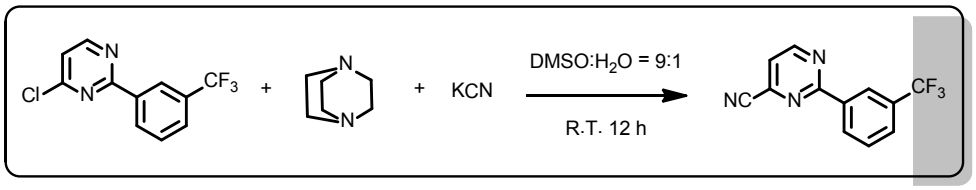
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.70 (s, 1H), 8.62 (d, J_{HH} = 7.6 Hz, 1H), 8.51 (d, J_{HH} = 4.8 Hz, 1 H), 7.71 (d, J_{HH} = 7.6 Hz, 1H), 7.58 (t, J_{HH} = 8 Hz, 1H), 6.66 (d, J_{HH} = 4.8 Hz, 1H), 4.09 (s, 3H).



Synthesis of 2-(3-(trifluoromethyl)phenyl) pyrimidine-4-chloride:

2-(4-Chlorophenyl)-4-methoxypyrimidine (2.35 g, 9.24 mmol) in water (20 mL) was treated with concentrated hydrochloric acid (8 mL, 92.4mmol) at room temperature. The suspension was heated to reflux during which the solution turned clear. After 12 h, the solution was cooled to room temperature and the resulting white suspension was washed with water and filtered to give 2-(3-(trifluoromethyl)phenyl)pyrimidine-4(3H)-one as a white solid. After suspended in toluene (15 mL), it was treated with phosphoryltrichloride (8.6 mL, 92.4 mmol) at room temperature. The suspension was heated to reflux at which point the solution became colorless. After 5 h, the reaction was cooled to room temperature and concentrated in *vacuo* to afford a white solid. The solution was diluted with CH_2Cl_2 and washed with saturated aqueous sodium bicarbonate. The organics were dried with Na_2SO_4, filtered, concentrated, and purified by flash column chromatography on silica gel (ethyl acetate: hexane = 1: 5) to provide the 2-(3-(trifluoromethyl)phenyl) pyrimidine-4-chloride. Yield: 2.2 g, 92%.

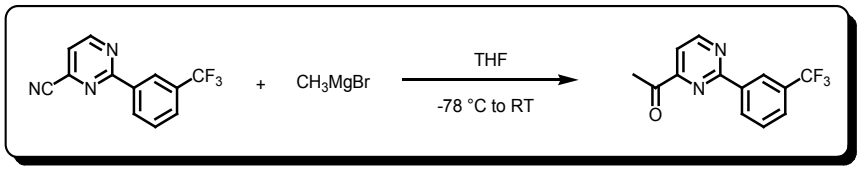
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.72 (s, 1H), 8.69 (d, J_{HH} = 5.2 Hz, 1H), 8.63 (d, J_{HH} = 7.6 Hz, 1 H), 7.75 (d, J_{HH} = 7.6 Hz, 1H), 7.61 (t, J_{HH} = 8 Hz, 1H), 7.28 (d, J_{HH} = 5.2 Hz, 1H).



Synthesis of 2-(3-(trifluoromethyl)phenyl)pyrimidine-4-carbonitrile:

2-(3-(Trifluoromethyl)phenyl)pyrimidine-4-chloride (1.1 g, 4.3 mmol), potassium cyanide (0.6 g, 8.6 mmol) and 1,4-diazabicyclo(2,2,2)octane (0.5 g, 4.3 mmol) were suspended in a mixture of DMSO (45 mL) and water (5 mL). The mixture was stirred at room temperature 12 h. The resultant mixture was poured into ice-H_2O mixture, extracted with ethyl acetate, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate: hexane = 1 : 5) to give white solid. Yield: 0.9 g, 81%. The waste of KCN solution were destroyed by addition of bleach.

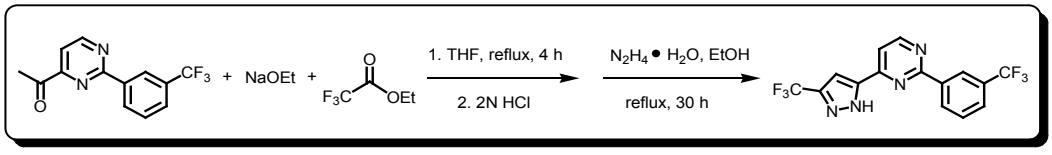
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.04 (d, J_{HH} = 4.8 Hz, 1H), 8.75 (s, 1H), 8.66 (d, J_{HH} = 8 Hz, 1H), 7.79 (d, J_{HH} = 7.6 Hz, 1H), 7.64 (t, J_{HH} = 8 Hz, 1H), 7.55 (d, J_{HH} = 4.8 Hz, 1H).



Synthesis of 1-(2-(3-(trifluoromethyl)phenyl)pyrimidin-4-yl)ethanone:

To a stirred solution of 2-(3-(trifluoromethyl)phenyl)pyrimidine-4-carbonitrile (0.86 g, 3.5 mmol) in 50 mL of dry THF was added 3M solution of methylmagnesium bromide in Et_2O (1.8 mL, 5.3 mmol) slowly at -78 °C. After then, the mixture was first stirred at this temperature for 1 h, and then allowed to warm up to room temperature. The reaction mixture was acidified with 2N HCl. THF was removed in *vacuo* and the product was extracted with ethyl acetate. The organic layers were combined and washed with aqueous $NaHCO_3$and saturated sodium chloride solution, dried over Na_2SO_4, and filtered. The residue was purified by column chromatography on silica gel (ethyl acetate: hexane = 1 : 3) to give white solid. Yield: 0.4 g, 42%.

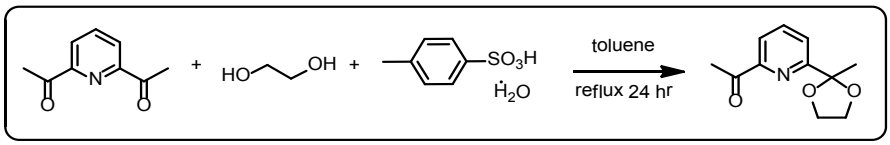
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.04 (d, J_{HH} = 4.8 Hz, 1H), 8.78 (s, 1H), 8.70 (d, J_{HH} = 7.6 Hz, 1 H), 7.79 (d, J_{HH} = 4.8 Hz, 1H), 7.76 (d, J_{HH} = 8.0 Hz, 1H), 7.63 (t, J_{HH} = 8 Hz, 1H), 2.82 (s, 3H).



Synthesis of L5:

A solution of NaOEt (150mg, 2.2 mmol) in dry THF (20 mL) was cooled to 0 °C under nitrogen and added 1-(2-(3-(trifluoromethyl)phenyl)pyrimidine-4-yl)ethanone (390 mg, 1.5mmol) in dry THF (20 mL). The mixture was stirred at 0 °C for 20 min. Ethyl trifluoroacetate (0.3 mL, 2.2 mmol) was added, and then heated to reflux for 4 h. After cooled, the mixture was acidified to pH = 4 with 2N $HCl_{(aq)}$ and the solvent was removed in *vacuo*. The crude product was extracted with ethyl acetate, dried over Na_2SO_4, and concentrated. Without further purification, hydrazine (1 mL, 14.5 mmol) in EtOH (30 mL) was added and heated to reflux for 30 h under nitrogen. After evaporating the volatiles, the crude product was extracted with ethyl acetate and dried over Na_2SO_4. It was then purified by column chromatography on silica gel (ethyl acetate: hexane = 1: 5) to give white solid. Yield: 220 mg, 42%.

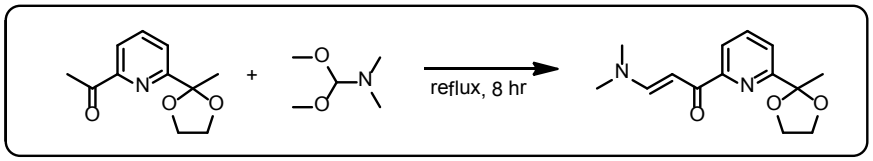
Spectral data: MS (EI): m/z 358 $(M)^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 11.58 (s, 1H), 8.93 (d, J_{HH} = 5.2 Hz, 1H), 8.76 (s, 1H), 8.68 (d, J_{HH} = 7.6 Hz, 1H), 7.78 (d, J_{HH} = 8 Hz, 1H), 7.65 (t, J_{HH} = 8.0 Hz, 1H), 7.49 (d, J_{HH} = 5.2 Hz, 1H), 7.14 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -62.40 (s, 3F), -62.66 (s, 3F).

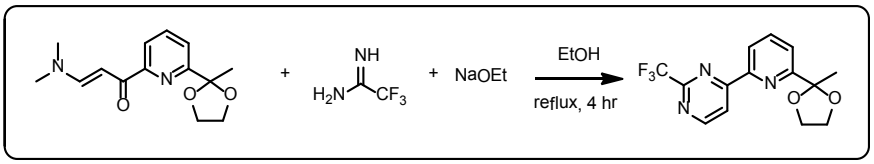


Synthesis of 1-[6-(2-methyl-[1,3]dioxolan-2-yl)-pyridin-2-yl]ethanone:

A toluene solution (100 mL) of 2,6-diacetylpyridine (2 g, 12.3 mmol), ethyleneglycol (0.8 g, 12.9 mmol), and *p*-toluenesulfonic acid (0.2 g, 1.1 mmol) was refluxed for 24 h. The solvent was evaporated under a reduced pressure and the resulting residue was purified by silica gel column chromatography. Yield: 1.1 g, 43%.

Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.94 (dd, J_{HH} = 8 Hz, 1H), 7.81 (t, J_{HH} = 8 Hz, 1H), 7.71 (dd, J_{HH} = 8 Hz, 1H), 4.14 ~ 4.10 (m, 2H), 3.97 ~ 3.94 (m, 2H), 2.73 (s, 3H), 1.79 (s, 3H).



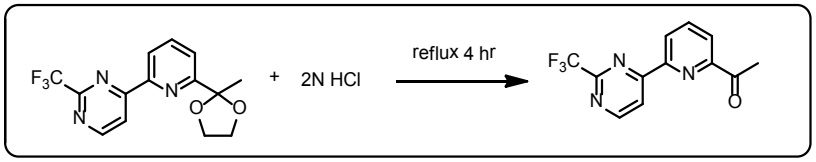


Synthesis of 4-(6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)-2-(trifluoromethyl)pyrimidine:

The mixture of 1-[6-(2-methyl-[1,3]dioxolan-2-yl)-pyridin-2-*yl*]ethanone (1.1 g, 5.3 mmol) and N,N-dimethylformamide dimethyl acetal (0.8 g, 6.7 mmol) was reflux for 8 h. Orange-brown solid precipitated after cooled to room temperature. Without further purification, trifluoroacetamidine (0.7 g, 6.4 mmol) and ethanol (10 mL) we re-added and stirred at room temperature for 20 min, followed by the

addition of sodium ethoxide (0.8 g, 11.7 mmol). The reaction mixture was then heated up to reflux for 4 h, and quenched by neutralizing with 2N HCl. The solvent was evaporated under reduced pressure and the resulting residue was purified by silica gel column chromatography. Yield: 0.8 g, 50%.

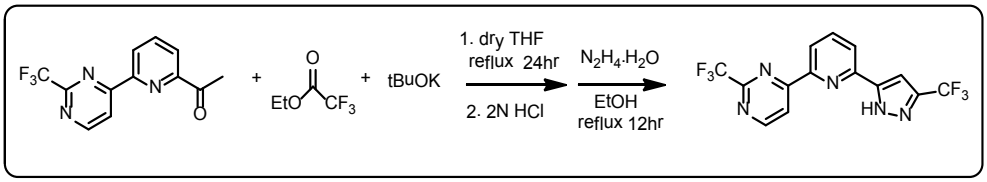
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.97 (d, J_{HH} = 5.2 Hz, 1H), 8.64 (d, J_{HH} = 5.2 Hz, 1H), 8.51 (dd, J_{HH} = 8 Hz, 1H), 7.90 (t, J_{HH} = 8 Hz, 1H), 7.72 (dd, J_{HH} = 8 Hz, 1H), 4.16 ~ 4.12 (m, 2H), 3.97 ~ 3.95 (m, 2H), 1.81 (s, 3H).



Synthesis of 1-(6-(2-(trifluoromethyl)pyrimidin-4-yl)pyridin-2-yl)ethanone:

The mixture of 4-(6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)-2-(trifluoromethyl)pyrimidine (0.8 g, 2.6 mmol) and 2N HCl (10 mL) was refluxed for 4 h. After cooled to room temperature, the mixture was extracted with CH_2Cl_2, washed with water and evaporated under a reduced pressure. The residue was purified by silica gel column chromatography. Yield: 0.65 g, 94%.

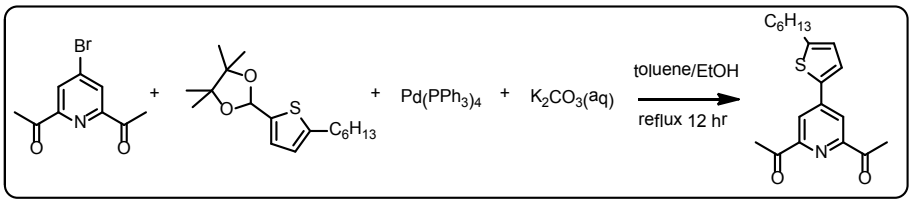
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.05 (d, J_{HH} = 5.2 Hz, 1H), 8.76 (d, J_{HH} = 8 Hz, 1H), 8.62 (d, J_{HH} = 5.2 Hz, 1H), 8.18 (d, J_{HH} = 8 Hz, 1H), 8.05 (t, J_{HH} = 8 Hz, 1H), 2.82 (s, 3H).



Synthesis of L6:

To a flask with 1-(6-(2-(trifluoromethyl)pyrimidin-4-yl)pyridin-2-yl)ethanone (0.28 g, 1.05 mmol) was added a mixture of *t*BuOK (0.14 g, 1.25 mmol) and THF (40 mL) at 0 °C, followed by the addition of ethyl trifluoroacetate (0.16 mL, 1.34 mmol). The mixture was heated for 24 h at 80 °C and then was quenched with 2 N HCl until pH 5–6. The resulting mixture was extracted with CH_2Cl_2 (3 × 80 mL). The combined extracts were washed with water, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give the corresponding β-diketone compound. Without further purification, hydrazine monohydrate (0.25 mL, 5.2 mmol) was added into a solution of the β-diketone reagent in EtOH (50 mL). After reflux for 12 h, the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (100 mL), and the solution was washed with water, dried over anhydrous Na_2SO_4, and concentrated. Finally, the product was purified by silica gel column chromatography using a 3:1 mixture of hexane and ethyl acetate, giving the tridentate ligand as a white solid. Yield: 0.26 g, 70%.

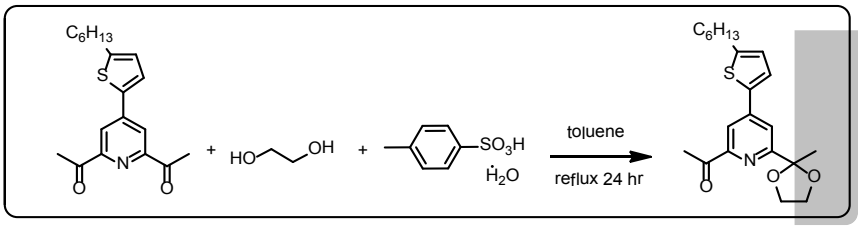
Spectral data: MS (EI): m/z 359 $(M)^+$.^{1}H NMR (400 MHz, d_6-acetone, 298 K): δ 13.81 (s, 1H), 9.22 (d, J_{HH} = 5.2 Hz, 1H), 9.11 (d, J_{HH} = 5.2 Hz, 1H), 8.60 (d, J_{HH} = 8 Hz, 1H), 8.26 ~ 8.17 (m, 2H), 7.46 (s, 1H).^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -62.61 (s, 3F), -70.52 (s, 3F).



Synthesis of 1,1'-(4-(5-hexylthiophen-2-yl)pyridine-2,6-diyl)diethanone:

2,6-Diacetyl-4-bromopyridine (2 g, 8.3 mmol), 2-(5-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.9 g, 9.9 mmol), $Pd(PPh_3)_4$ (0.5 g, 4.3 mmol), and K_2CO_3 (5.7 g, 41.2 mmol) were dissolved in a mixture of toluene (60 mL)/ethanol (30 mL)/water (20 mL). The mixture was refluxed for 12 h. After then, the solvent was removed under vacuum, and the residue was extracted with ethyl acetate (2 × 100 mL), dried over Na_2SO_4 and evaporated to dryness. The pure product was further purified by column chromatography. Yield: 2.0 g, 73%.

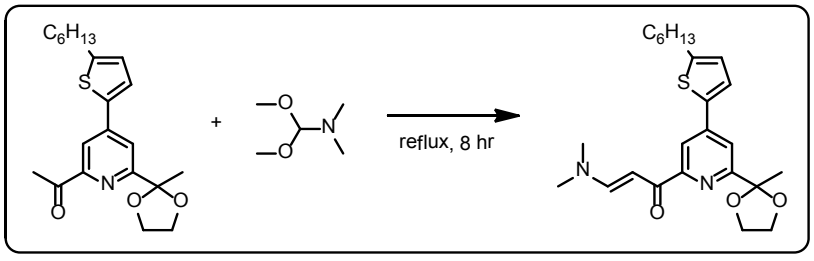
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.27 (s, 2H), 7.47 (d, J_{HH} = 4 Hz, 1H), 6.81 (d, J_{HH} = 4 Hz, 1H), 2.83 (t, J_{HH} = 8 Hz, 2H), 2.77 (s, 6H), 1.67 (quin, J_{HH} = 8 Hz, 2H), 1.38 ~ 1.22 (m, 6H), 0.87 (t, J_{HH} = 8 Hz, 3H).

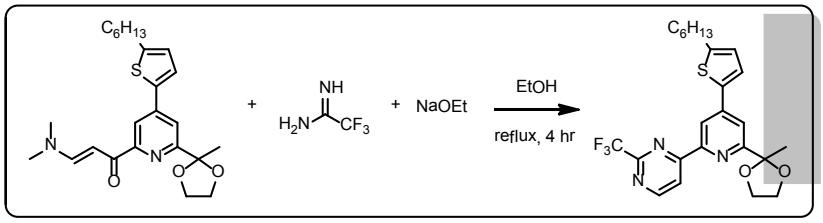


Synthesis of 1-(4-(5-hexylthiophen-2-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl) ethanone:

A toluene solution(60 mL) of 1,1'-(4-(5-hexylthiophen-2-yl)pyridine-2,6-diyl)diethanone (1 g, 3.0 mmol), ethyleneglycol (0.2 g, 3.3 mmol), and *p*-toluenesulfonic acid (0.06 g, 0.3 mmol) was refluxed for 24 h. The solvent was evaporated and the residue was purified by column chromatography to obtain 1-(4-(5-hexylthiophen-2-yl)-6- (2-methyl-1,3-dioxolan-2-yl)pyridine-2-yl)ethanone as a yellow oil. Yield: 0.5 g, 44%.

Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.04 (s, 1H), 7.78 (s, 1H), 7.39 (d, J_{HH} = 3.6 Hz, 1H), 6.76 (d, J_{HH} = 3.6 Hz, 1H), 4.11 ~ 4.09 (m, 2H), 3.97 ~ 3.94 (m, 2H), 2.79 (t, J_{HH} = 8 Hz, 2H), 2.71 (s, 3H), 1.77 (s, 3H), 1.66 (quin, J_{HH} = 8 Hz, 2H), 1.36 ~ 1.32 (m, 6H), 0.87 (t, J_{HH} = 8 Hz, 3H).

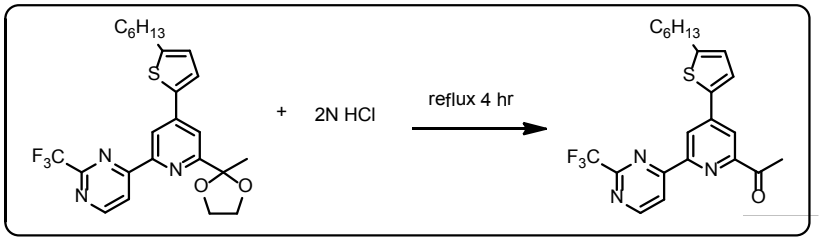




Synthesis of 4-(4-(5-hexylthiophen-2-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)- 2-(trifluoromethyl) pyrimidine:

The mixture of 1-(4-(5-hexylthiophen-2-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl) ethanone (0.5 g, 1.3 mmol) and N,N-dimethylformamide dimethyl acetal (0.2 g, 1.7 mmol) was reflux for 8 h. Orange-brown solid precipitated after cooled to room temperature. Without further purification, the crude product and trifluoroacetamidine (0.19 g, 1.7 mmol) were stirred in ethanol at room temperature for 20 min followed by the addition of sodium ethoxide (0.2 g, 2.9 mmol). The reaction mixture was then heated at reflux for 4 h, and neutralized by addition of 2N HCl. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography. Yield: 0.2 g, 31%.

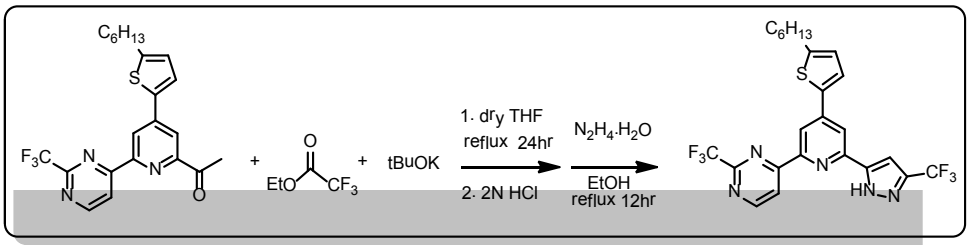
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.03 (d, J_{HH} = 5.2 Hz, 1H), 8.79 (s, 1H), 8.60 (d, J_{HH} = 5.2 Hz, 1H), 8.23 (s, 1H), 7.55 (d, J_{HH} = 3.6 Hz, 1H), 6.85 (d, J_{HH} = 3.6 Hz, 1H), 4.10 ~ 4.08 (m, 2H), 3.97 ~ 3.94 (m, 2H), 2.85 (t, J_{HH} = 8 Hz, 2H), 2.81 (s, 3H), 1.71 (quin, J_{HH} = 8 Hz, 2H), 1.40 ~ 1.31 (m, 6H), 0.88 (t, J_{HH} = 8 Hz, 3H).



Synthesis of 1-(4-(5-hexylthiophen-2-yl)-6-(2-(trifluoromethyl)pyrimidin-4-yl)pyridin-2-yl) ethanone:

The mixture of 4-(4-(5-hexylthiophen-2-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)-2-(trifluoromethyl)pyrimidine (0.2 g, 0.4 mmol) and 2N HCl (10 mL) was refluxed for 4 h. The solution was extracted with CH_2Cl_2, washed with water, and concentrated under reduced pressure. The resulting residue was purified by column chromatography. Yield: 0.13 g, 72%.

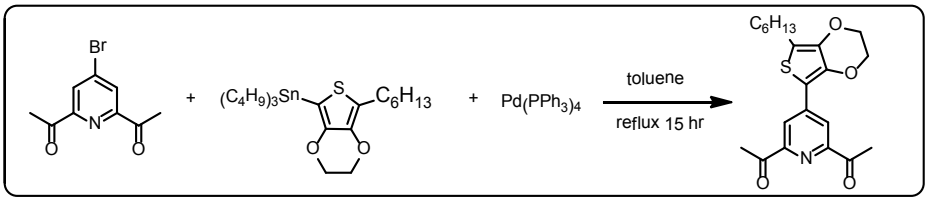
Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.04 (d, J_{HH} = 5.2 Hz, 1H), 8.81 (s, 1H), 8.62 (d, J_{HH}= 5.2 Hz, 1H), 8.25 (s, 1H), 7.55 (d, J_{HH} = 3.6 Hz, 1H), 6.85 (d, J_{HH} = 3.6 Hz, 1H), 2.85 (t, J_{HH} = 8 Hz, 2H), 2.81 (s, 3H), 1.71 (quin, J_{HH} = 8 Hz, 2H), 1.40 ~ 1.31 (m, 6H), 0.88 (t, J_{HH} = 8 Hz, 3H).



Synthesis of L6.1:

To a flask with 1-(4-(5-hexylthiophen-2-yl)-6-(2-(trifluoromethyl)pyrimidin-4-yl)pyridin-2-yl) ethanone (0.13 g, 0.3 mmol) was added tBuOK (0.05 g, 0.5 mmol), THF (40 mL) and ethyl trifluoroacetate (0.06 mL, 0.5 mmol)at 0 °C. The mixture was allowed to heat for 24 h at 80 °C and then quenched with 2 N HCl until pH 5−6. The resulting mixture was extracted with CH_2Cl_2 (3 × 80 mL). The combined extracts were washed with water, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give the corresponding β-diketone. Without further purification, hydrazine monohydrate (0.07 mL, 1.4 mmol) was added into a solution of the β-diketone in EtOH (50 mL). After refluxed for 12 h, the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (100 mL), and the solution was washed with water, dried over anhydrous Na_2SO_4, and concentrated. Finally, the product was purified by silica gel column chromatography using a 3:1 mixture of hexane and ethyl acetate, giving the tridentate ligand as a white solid. Yield: 0.1 g, 60%.

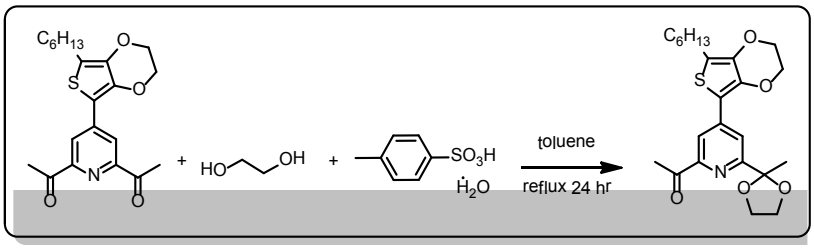
Spectral data: MS (EI): m/z 525 $(M)^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 11.53 (s, 1H), 9.06 (d, J_{HH} = 5.2 Hz, 1H), 8.67 (s, 1H), 8.57 (d, J_{HH} = 5.2 Hz, 1H), 7.81 (s, 1H), 7.55 (d, J_{HH} = 3.2 Hz, 1H), 7.09 (s, 1H), 6.88 (d, J_{HH} = 3.2 Hz, 1H), 2.87 (t, J_{HH} = 8 Hz, 2H), 1.72 (quin, J_{HH} = 8 Hz, 2H), 1.40 ~ 1.31 (m, 6H), 0.88 (t, J_{HH} = 8 Hz, 3H).^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -62.54 (s, 3F), -70.95 (s, 3F).



Synthesis of 2,6-diacetyl-4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4] dioxin-5-yl) pyridine:

2,6-Diacetyl-4-bromopyridine (1.8 g, 7.6 mmol), tributyl (7-hexyl-2,3-dihydrothieno [3,4-b][1,4]dioxin-5-yl)stannane (4.7 g, 9.1 mmol), and $Pd(PPh_3)_4$ (0.3 g, 0.26 mmol) were dissolved in toluene (50 mL), and the mixture was heated to reflux for 15 h. The solvent was evaporated *in vacuo* and the residue extracted with ethyl acetate (2 x 100 mL). The combined organic layer was washed with water, dried over $MgSO_4$ and concentrated to dryness. Further purification was conducted by silica gel column chromatography using a 3:1 mixture of hexane and EA. Yield: 1.45 g, 50%.

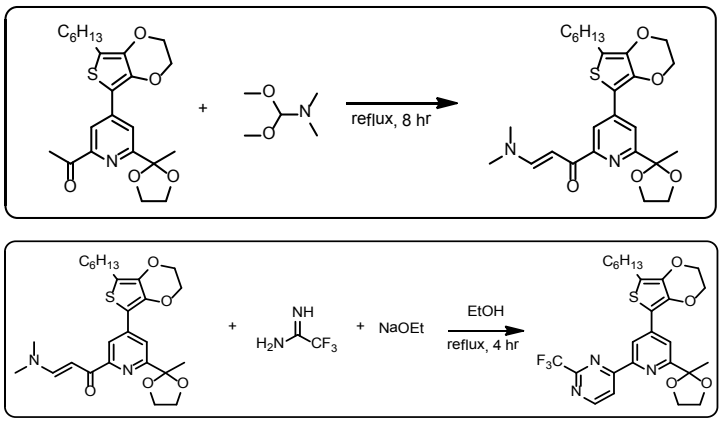
Spectral data: ^{1}H NMR (400 MHz, d_6-acetone, 298 K): δ 8.25 (s, 2H), 4.47 ~ 4.45 (m, 2H), 4.45 ~ 4.41 (m, 2H), 2.72 ~ 2.66 (m, 8H), 1.68 ~ 1.40 (m, 2H), 1.38 ~ 1.24 (m, 6H), 0.89 (t, J_{HH} = 8 Hz, 3H).



Synthesis of 1-(4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-6-(2-methyl-1,3-dioxolan-2-yl) pyridin-2-yl)ethanone:

A toluene solution (60 mL) of 2,6-diacetyl-4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4] dioxin-5-yl) pyridine (2 g, 5.2 mmol), ethyleneglycol (0.36 g, 5.7 mmol), and *p*-toluenesulfonic acid (0.1 g, 0.5 mmol) was refluxed for 24 h. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography to obtain 1-(4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4] dioxin-5-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)ethanone as a yellow oil. Yield: 1.0 g, 45%.

Spectral data: ^{1}H NMR (400 MHz, d_6-acetone, 298 K): δ 8.17(s, 1H), 7.87 (s, 1H), 4.34 ~ 4.32(m, 2H), 4.22 ~ 4.20 (m, 2H), 4.11 ~ 4.07 (m, 2H), 3.97~3.95 (m, 2H), 2.71 (s, 3H), 2.63 (t, J_{HH} = 8 Hz, 2H), 1.78 (s, 3H), 1.61 ~ 1.58 (m, 2H), 1.36 ~ 1.27 (m, 6H), 0.89 (t, J_{HH} = 8 Hz, 3H).

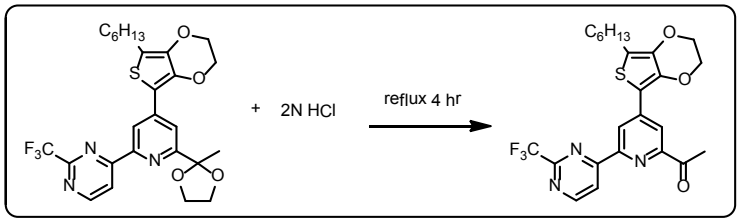


Synthesis of 4-(4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-6-(2-methyl-1,3-dioxolan-2-yl) pyridin-2-yl)-2-(trifluoromethyl)pyrimidine:

The mixture of 1-(4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4] dioxin-5-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)ethanone (0.4 g, 0.9 mmol) and N,N-dimethylformamide dimethyl acetal (0.13 g, 1.1 mmol) was reflux for 8 h. Orange-brown solid precipitated after cooled to room temperature. Without further purification, the crude product and trifluoroacetamidine (0.12 g, 1.1 mmol) were stirred in ethanol at room temperature for 20 min, followed by the addition of sodium ethoxide (0.13 g, 1.9 mmol). The reaction mixture was then heated up to reflux for 4 h, and quenched with addition of 2N HCl. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography. Yield: 0.42 g, 85%.

Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.01 (d, J_{HH} = 5.2 Hz, 1H), 8.91 (s, 1H), 8.60 (d, J_{HH} = 5.2 Hz, 1H), 8.38 (s, 1H), 4.34 ~ 4.31 (m, 2H), 4.20 ~ 4.18 (m, 2H), 4.10 ~ 4.05 (m, 2H), 3.95 ~ 3.92

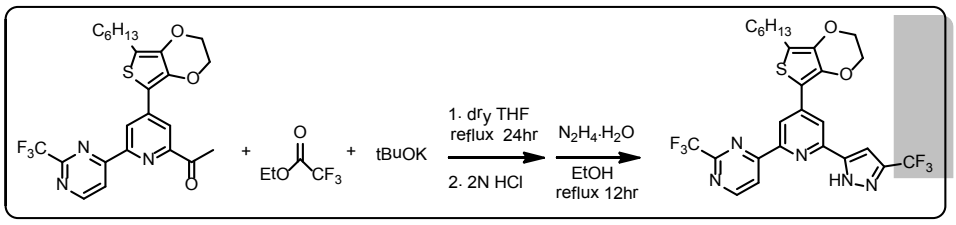
(m, 2H), 2.63 (t, J_{HH} = 8 Hz, 2H), 1.78 (s, 3H), 1.61 ~ 1.58 (m, 2H), 1.36 ~ 1.27 (m, 6H), 0.89 (t, J_{HH} = 8 Hz, 3H).



Synthesis of 1-(4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-6-(2-(trifluoromethyl) pyrimidin-4-yl)pyridin-2-yl)ethanone:

The mixture of 4-(4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)-2-(trifluoromethyl)pyrimidine (0.42 g, 0.8 mmol) and 2N HCl (10 mL) was refluxed for 4 h. The solution was mixed with CH_2Cl_2, washed with water and evaporated under reduced pressure. The resulting residue was purified by column chromatography. Yield: 0.35 g, 90%.

Spectral data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.02 (d, J_{HH} = 5.2 Hz, 1H), 8.93 (s, 1H), 8.60 (d, J_{HH} = 5.2 Hz, 1H), 8.37 (s, 1H), 4.41 ~ 4.39 (m, 2H), 4.28 ~ 4.26 (m, 2H), 2.81 (s, 3H), 2.67 (t, J_{HH} = 8 Hz, 2H), 1.64 (quin, J_{HH} = 8 Hz, 2H), 1.39 ~ 1.28 (m, 6H), 0.88 (t, J_{HH} = 8 Hz, 3H).



Synthesis of L6.2:

To a flask with 1-(4-(7-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-6-(2-(trifluoromethyl) pyrimidin-4-yl)pyridin-2-yl)ethanone (0.7 g, 1.4 mmol) was added a mixture of tBuOK (0.2 g, 1.8 mmol), ethyl trifluoroacetate (0.25 mL, 2.1 mmol)and THF (40 mL) at 0 °C. The mixture was allowed to heat for 24 h at 80 °C and then quenched with 2 N HCl until pH 5−6. The resulting mixture was extracted with CH_2Cl_2 (3 × 80 mL). The combined extracts were washed with water, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give the corresponding β-diketone. Without further purification, hydrazine monohydrate (0.35 mL, 7.1 mmol) was added into a solution of the β-diketone in EtOH (50 mL). The solution was refluxed for 12 h. The solvent was evaporated and residue was dissolved in CH_2Cl_2 (100 mL). The solution was washed with water, dried over anhydrous Na_2SO_4, and concentrated. Finally, the product was purified by silica gel column chromatography using a 3:1 mixture of hexane and ethyl acetate, giving the tridentate ligand as a white solid. Yield: 0.4 g, 48%.

Spectral data: MS (EI): m/z 583 $(M)^+$. ^{1}H NMR (400 MHz, d_6-acetone, 298 K): δ 14.12 (s, 1H), 9.54 (d, J_{HH} = 5.2 Hz, 1H), 9.42 (d, J_{HH} = 5.2 Hz, 1H), 9.10 (s, 1H), 8.58 (s, 1H), 7.75 (s, 1H), 4.89 ~ 4.81 (m, 2H), 4.76 ~ 4.68 (m, 2H), 3.07 (t, J_{HH} = 8 Hz, 2H), 2.44 (quin, J_{HH} = 8 Hz, 2H), 1.81 ~ 1.66 (m, 6H), 1.29 (t, J_{HH} =

8 Hz, 3H).^{19}F NMR (376 MHz, d_6-acetone, 298 K): δ -62.48 (s, 3F), -70.96 (s, 3F).

TD-DFT Calculation

All calculations were performed by Gaussian 09 program. Their ground state structures were first optimized with density functional theory (DFT) at B3LYP/LANL2DZ (Ru) and 6-31G* (H, C, N, O, S, F) level. The optimized structures were then used to calculate 60 lowest singlet energy optical excitations using the time-dependent density functional theory (TD-DFT) method. Their lowest ground triplet state energies were also calculated. A polarizable continuum model (PCM) in Gaussian 09 was applied using dimethylformamide (DMF) as the solvent.

For TD-DFT calculations, the calculated absorption bands (singlet state excitation) of **TF-25** (Figure 2a) and **TF-26** (Figure 2b) are identified as specific vertical lines. The frontier orbitals contributed to the major transition (occupied orbitals in pink and unoccupied orbitals in yellow) are also depicts in each Figure. Obviously, the lowest lying transitions (> 500 nm) for all titled complexes involve mainly the MLCT contribution.

Device fabrication

The FTO glass used as current collector (4.0 mm thickness, sheet resistance of 10 Ω/□, Nippon Sheet Glass) was first cleaned in a detergent solution using an ultrasonic bath for 30 min, and then rinsed with water and ethanol. After treatment in a UV-O_3 system for 15 min (PSD series UV-ozone cleaning, Novascan Technologies, Inc.), the FTO glass plates were immersed into a 40 mM aqueous $TiCl_4$ solution at 75 °C for 30 min and washed with water and ethanol. The photoanodes composed of nanocrystalline TiO_2 were prepared using literature procedures. The transparent TiO_2 electrodes (area, 5× 5 mm^2) of 15μm thickness were screen-printed on FTO glasses, followed by a 7μm scattering layer containing 400 nm TiO_2 particles (PST-400, JGC Catalysts and Chemicals, Japan). The TiO_2 electrodes were heated under oxygen flow at 325 °C for 5 min, followed by heating at 375 °C for 5min, 450 °C for 15 min, and 500 °C for 30 min. The TiO_2 electrodes were retreated with a 40 mM aqueous solution of $TiCl_4$ at 75 °C for 30 min. The electrodes were sintered again at 500 °C for 30 min and left to cool down to 80 °C before dipping them into dye solution for 18 h at room temperature. The dye solution (0.3 mM) was prepared in absolute ethanol and 20% DMSO (*v/v*) with addition of 2 equiv. of tetrabutylammonium deoxycholate [TBA][DOC] as an additive. Platinized counter electrodes were prepared by dripping down 10 μL H_2PtCl_6 solution (5 mM in isopropyl alcohol) on FTO plates, followed by pyrolysis at 400 °C for 10 min. The dye sensitized TiO_2 electrodes were assembled with counter electrodes by inserting a hot-melt Surlyn film (Meltonix 1170-25, 25 μm, Solaronix) as spacer. The electrolyte consists of 2.0 M 1,3-dimethylimidazolium iodide (DMII), 0.03 M of iodine, 0.5 M *tert*-butylpyridine (TBP), 0.1 M guanidinium thiocyanate (GuNCS) and 0.05 M of LiI in acetonitrile and valeronitrile (85 / 15, v / v), which was then injected into the cell. Finally, the hole was sealed using another Surlyn film and a cover glass. In order to reduce light piping from the cross sections of glass electrodes of dyed TiO_2 layer, all devices were covered with a large mask made of non-reflective black metal with a window area of 4×4 mm^2.

Photovoltaic Characterization

Photovoltaic measurements were tested under a class-AAA solar simulator (Model 11016A, Sun 3000, ABET Technologies) equipped with a 550 W xenon light source and water-cooling stage (25 °C). The output power density was calibrated to be 100 mW·cm^{-2} using a certificated KG-5 Si reference cell with a circular aperture of 8 mm diameter. The current-voltage characteristic of each cell was obtained with adopting 4-wire sense mode, delay time set as 100 ms and bias scan from short-circuit to open-circuit by using a Keithley digital source meter (Model 2400). The spectra of incident photon-to-current conversion efficiency (IPCE) were calculated with the equation of $1240 \cdot J_{SC}(\lambda)/(\lambda \cdot P_{in}(\lambda))$ where J_{SC} is the short-circuit current density under each monochromatic illumination in unit of A/cm^2, λ is the wavelength of incident monochromatic light in unit of nanometer, and P_{in} is the monochromatic light intensity in unit of W/cm^2 and were plotted as a function of incident wavelength with an increment of 10 nm. The current was pre-amplified by a current amplifier (SR570) and measured by Keithley 2400. It should be noted that 10 values of J_{SC}, which (interval 50 ms) were collected sequentially after a device was illuminated monochromatically 3 seconds later and were averaged for calculation of IPCE. A 300 W Xe lamp (Model 6258, Newport Oriel) combined with an Oriel cornerstone 260 1/4 m monochromator (Model 74100) provided a device under test with a monochromatic beam (dc mode). The beam power intensity was calibrated with a power meter (Model 1936-C, Newport) equipped with a Newport 818-UV photodetector.

Electrical Impedance Measurement

Electrical impedance experiments were carried out with a PARSTAT2273 electrochemical workstation (Princeton Applied Research, USA), with a frequency range of 0.1– 10^6 Hz and a potential modulation of 10 mV.

Table S1. The wavelengths, transition probabilities and charge transfer characters of the singlet optical transitions in selected states with oscillator strength > 0.01 for **TF-25** in DMF. The lowest triplet optical transition ($S_0 \rightarrow T_1$) is also listed.

State	λ_{cal} (nm)	*f*	Assignments	MLCT
T_1	924	0	HOMO-1→LUMO(94%) HOMO-1→LUMO+2(5%)	41.26%
S_1	677.5	0.0253	HOMO→LUMO(94%)	37.57%
S_2	587.1	0.0002	HOMO-2→LUMO(96%)	55.22%
S_3	577	0.0208	HOMO-1→LUMO(54%) HOMO→LUMO+1(44%)	44.16%
S_4	528.9	0.1098	HOMO-1→LUMO+1(94%)	48.02%
S_5	488.4	0.0549	HOMO→LUMO+1(35%) HOMO-1→LUMO(27%) HOMO-2→LUMO+1(20%) HOMO-1→LUMO+2(9%) HOMO→LUMO+3(7%)	50.67%
S_6	481.5	0.0139	HOMO-2→LUMO+1(78%) HOMO→LUMO+1(9%) HOMO-1→LUMO(5%)	59.27%
S_7	447.7	0.1982	HOMO→LUMO+2(93%)	49.25%
S_8	429.9	0.1442	HOMO-1→LUMO+2(73%) HOMO→LUMO+3(19%)	49.50%
S_9	423.3	0.0129	HOMO-1→LUMO+3(98%)	52.99%
S_{12}	407.6	0.1654	HOMO→LUMO+3(66%) HOMO-1→LUMO+2(9%) HOMO-1→LUMO(7%) HOMO→LUMO+1(7%)	46.23%
S_{18}	365.4	0.0201	HOMO-3→LUMO+1(93%) HOMO-2→LUMO+4(6%)	4.06%
S_{20}	357.4	0.0201	HOMO-2→LUMO+5(70%) HOMO-2→LUMO+4(25%)	65.95%
S_{21}	347	0.0564	HOMO-2→LUMO+4(43%) HOMO-2→LUMO+5(16%) HOMO-7→LUMO(16%)	40.06%
S_{23}	335.4	0.0527	HOMO-5→LUMO(66%) HOMO→LUMO+6(11%) HOMO→LUMO+9(6%)	-2.81%
S_{24}	334.8	0.0585	HOMO-1→LUMO+6(83%) HOMO-7→LUMO(7%)	45.24%
S_{25}	331.6	0.0198	HOMO-6→LUMO(93%)	-8.24%
S_{28}	327	0.032	HOMO→LUMO+9(70%) HOMO-5→LUMO(9%)	-6.79%
S_{29}	324.4	0.0174	HOMO-7→LUMO(65%) HOMO-2→LUMO+4(10%) HOMO-1→LUMO+6(5%)	7.52%
S_{31}	314.4	0.2595	HOMO-8→LUMO(80%)	-0.29%
S_{36}	302.5	0.1423	HOMO-3→LUMO+5(47%) HOMO-3→LUMO+4(43%)	1.34%

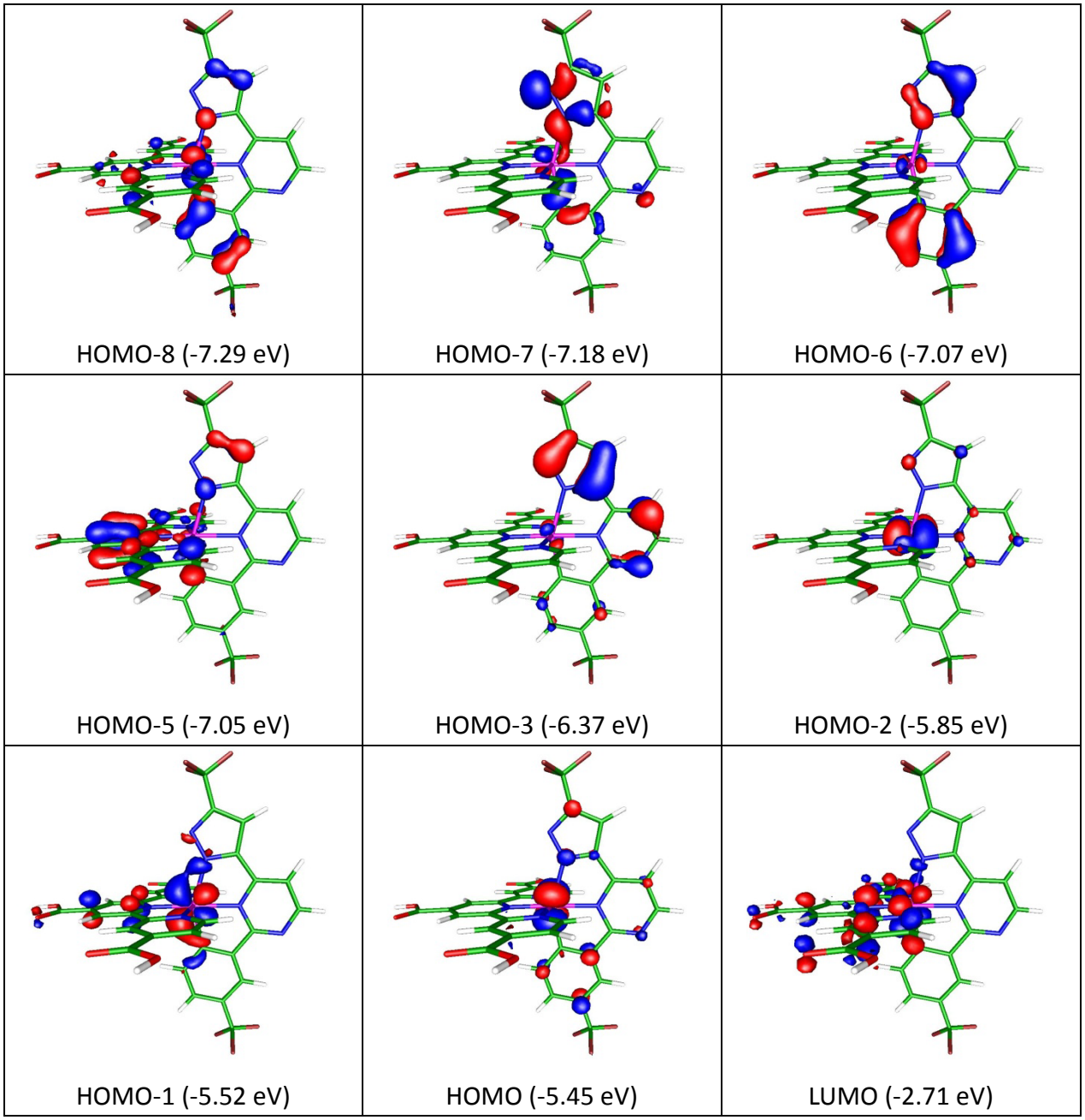


Figure S1-1. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-25**.

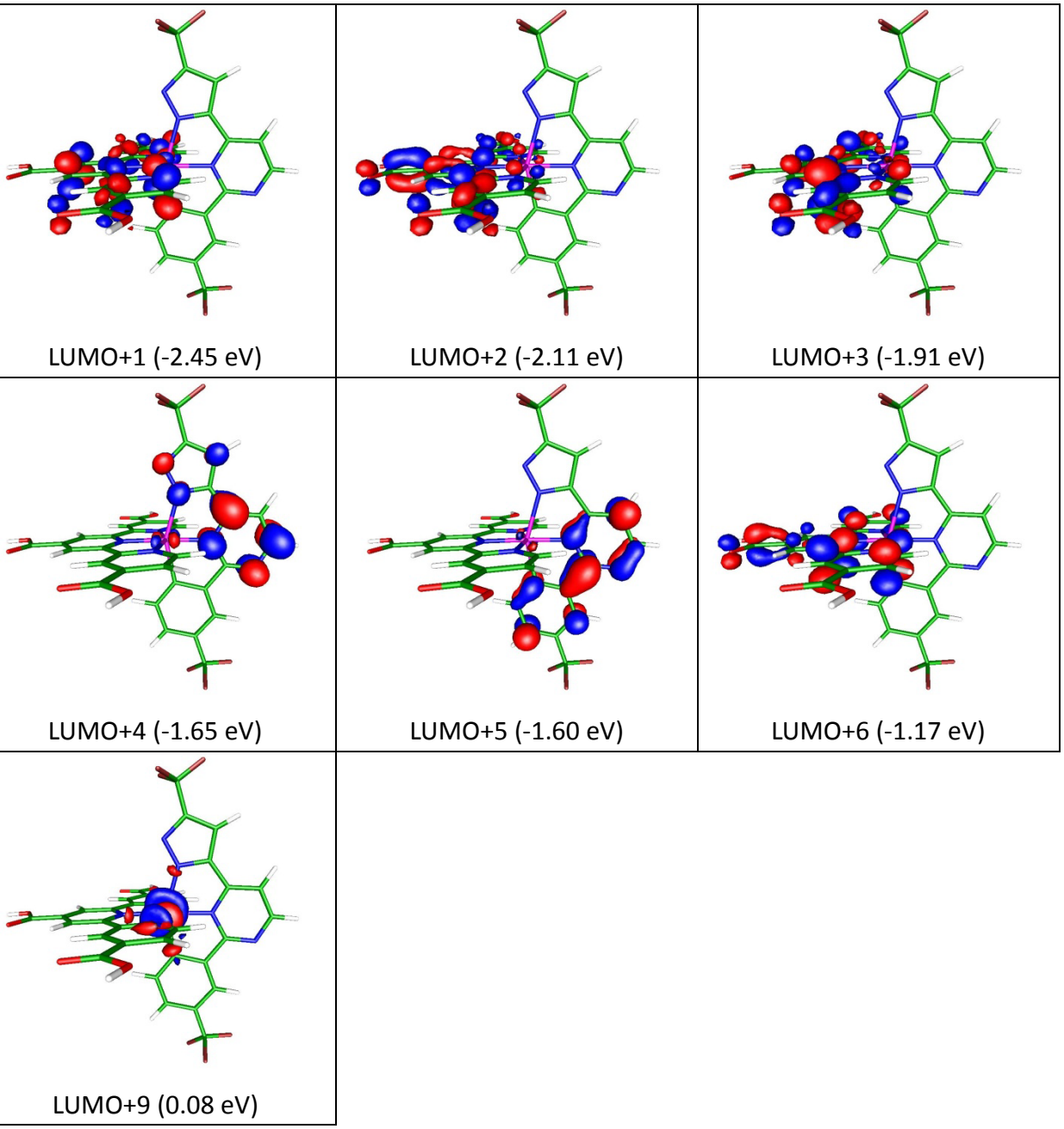


Figure S1-2. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-25**.

Table S2. The wavelengths, transition probabilities and charge transfer characters of the singlet optical transitions in selected states with oscillator strength > 0.02 for **TF-26** in DMF. The lowest triplet optical transition ($S_0 \rightarrow T_1$) is also listed.

State	λ_{cal} (nm)	*f*	Assignments	MLCT
T_1	880.3	0	HOMO-1→LUMO(94%) HOMO-1→LUMO+2(5%)	42.14%
S_1	668.2	0.0257	HOMO→LUMO(93%)	35.06%
S_2	584.1	0.0002	HOMO-2→LUMO(91%)	46.61%
S_3	569.1	0.021	HOMO-1→LUMO(54%) HOMO→LUMO+1(44%)	43.44%
S_4	520.6	0.1029	HOMO-1→LUMO+1(95%)	48.93%
S_5	484.8	0.0842	HOMO→LUMO+1(44%) HOMO-1→LUMO(32%) HOMO-1→LUMO+2(9%) HOMO→LUMO+3(8%)	43.01%
S_9	445	0.147	HOMO→LUMO+2(84%) HOMO-3→LUMO(6%)	42.41%
S_{10}	430.4	0.0346	HOMO-3→LUMO(85%) HOMO→LUMO+2(8%)	8.68%
S_{11}	424.6	0.1303	HOMO-1→LUMO+2(74%) HOMO→LUMO+4(17%)	48.80%
S_{13}	411	0.1165	HOMO→LUMO+4(51%) HOMO-2→LUMO+3(24%) HOMO→LUMO+3(6%) HOMO-1→LUMO+2(5%)	46.12%
S_{25}	331.5	0.0832	HOMO-1→LUMO+6(85%) HOMO-2→LUMO+5(5%)	49.75%
S_{26}	329.8	0.0985	HOMO-6→LUMO(47%) HOMO→LUMO+9(25%) HOMO-2→LUMO+9(9%) HOMO→LUMO+6(7%)	-5.88%
S_{27}	327.4	0.1167	HOMO→LUMO+9(49%) HOMO-6→LUMO(35%)	-10.70%
S_{29}	323	0.0578	HOMO-3→LUMO+4(54%) HOMO-2→LUMO+5(19%) HOMO-4→LUMO+1(13%) HOMO-5→LUMO(7%)	20.85%
S_{37}	305.9	0.1135	HOMO-8→LUMO(82%) HOMO-5→LUMO+1(8%)	-3.21%

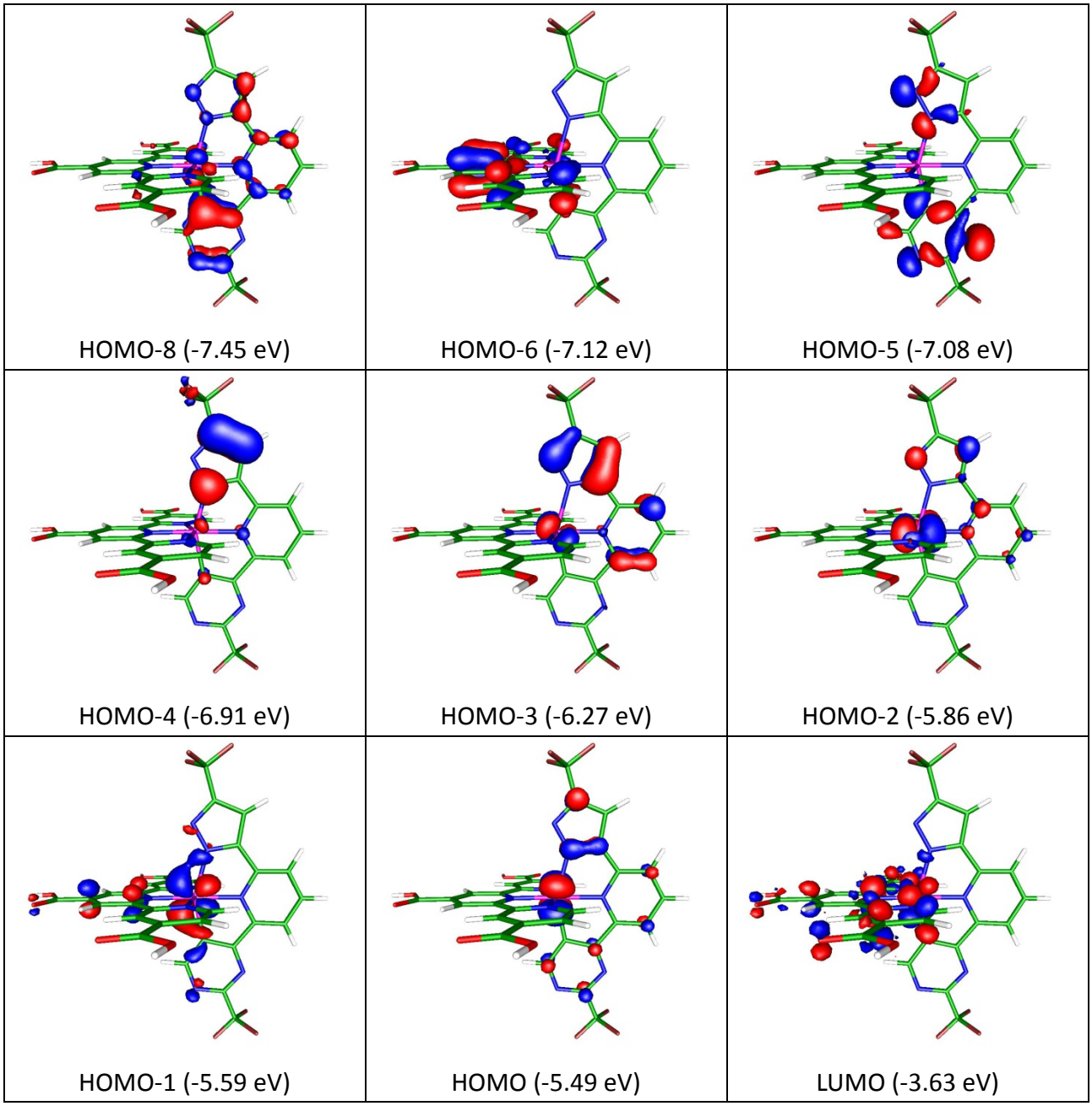


Figure S2-1. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-26**.

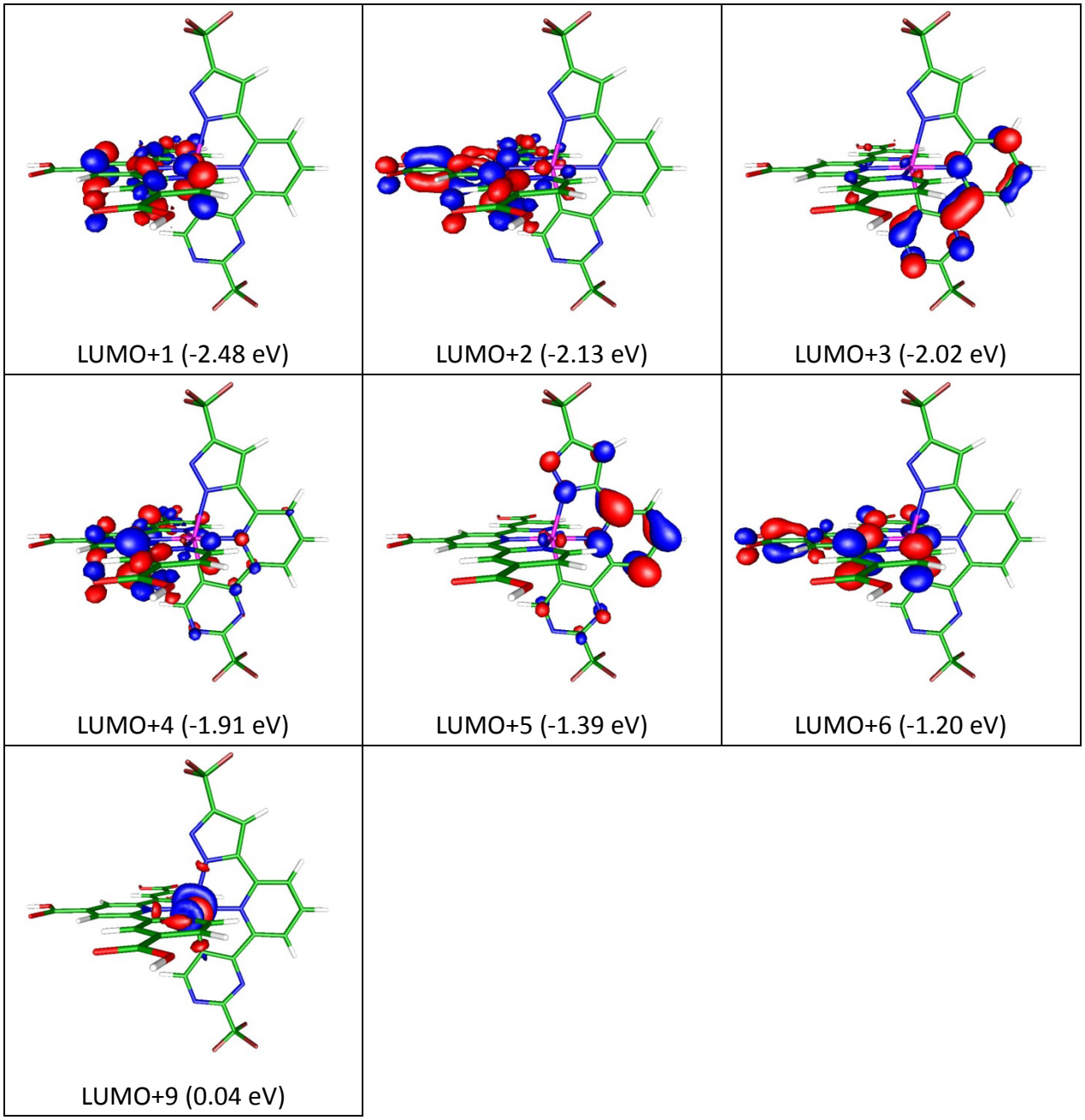


Figure S2-2. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-26**.

Table S3. The wavelengths, transition probabilities and charge transfer characters of the singlet optical transitions in selected states with oscillator strength > 0.03 for **TF-27** in DMF. The lowest triplet optical transition ($S_0 \rightarrow T_1$) is also listed.

State	λ_{cal} (nm)	*f*	Assignments	MLCT
T_1	884	0	HOMO-1→LUMO(94%) HOMO-1→LUMO+2(5%)	41.95%
S_1	666.5	0.0249	HOMO→LUMO(92%)	34.98%
S_2	606.7	0.0005	HOMO-2→LUMO(87%) HOMO-4→LUMO(7%)	32.23%
S_3	569.3	0.0337	HOMO-1→LUMO(55%) HOMO→LUMO+1(42%)	42.99%
S_4	521.9	0.1034	HOMO-1→LUMO+1(95%)	48.85%
S_6	487.5	0.1679	HOMO→LUMO+1(45%) HOMO-1→LUMO(29%) HOMO→LUMO+3(10%) HOMO-1→LUMO+2(7%)	42.21%
S_9	444.5	0.1551	HOMO→LUMO+2(85%) HOMO-3→LUMO(7%)	42.33%
S_{11}	428.6	0.4103	HOMO-1→LUMO+2(49%) HOMO-2→LUMO+3(44%)	47.03%
S_{15}	403.8	0.0476	HOMO→LUMO+4(43%) HOMO-2→LUMO+3(11%) HOMO-3→LUMO+1(9%) HOMO-1→LUMO+2(6%) HOMO→LUMO+1(6%) HOMO-1→LUMO(5%)	35.26%
S_{18}	385.4	0.161	HOMO-3→LUMO+1(49%) HOMO→LUMO+5(40%)	21.01%
S_{21}	361.1	0.1213	HOMO-2→LUMO+5(39%) HOMO-4→LUMO+1(31%) HOMO-3→LUMO+1(8%) HOMO-3→LUMO+3(8%)	26.15%
S_{22}	356.3	0.0492	HOMO-4→LUMO+1(54%) HOMO-2→LUMO+5(18%) HOMO-3→LUMO+3(12%)	21.04%
S_{23}	348.8	0.0626	HOMO-3→LUMO+3(66%) HOMO-2→LUMO+5(19%)	10.85%
S_{27}	333.5	0.1174	HOMO-7→LUMO(57%) HOMO-1→LUMO+6(22%) HOMO-9→LUMO(8%) HOMO-3→LUMO+4(5%)	5.69%
S_{29}	330.4	0.1427	HOMO-4→LUMO+3(82%) HOMO-3→LUMO+3(6%)	19.07%
S_{30}	330	0.0645	HOMO-8→LUMO(35%) HOMO→LUMO+10(29%) HOMO-2→LUMO+10(11%) HOMO→LUMO+6(7%)	-5.89%
S_{31}	327.5	0.1273	HOMO→LUMO+10(42%) HOMO-8→LUMO(39%)	-10.02%
S_{41}	310.4	0.2731	HOMO-3→LUMO+5(65%) HOMO-4→LUMO+4(16%)	6.94%
S_{44}	304.3	0.0979	HOMO-10→LUMO(82%) HOMO-6→LUMO(10%)	-4.68%

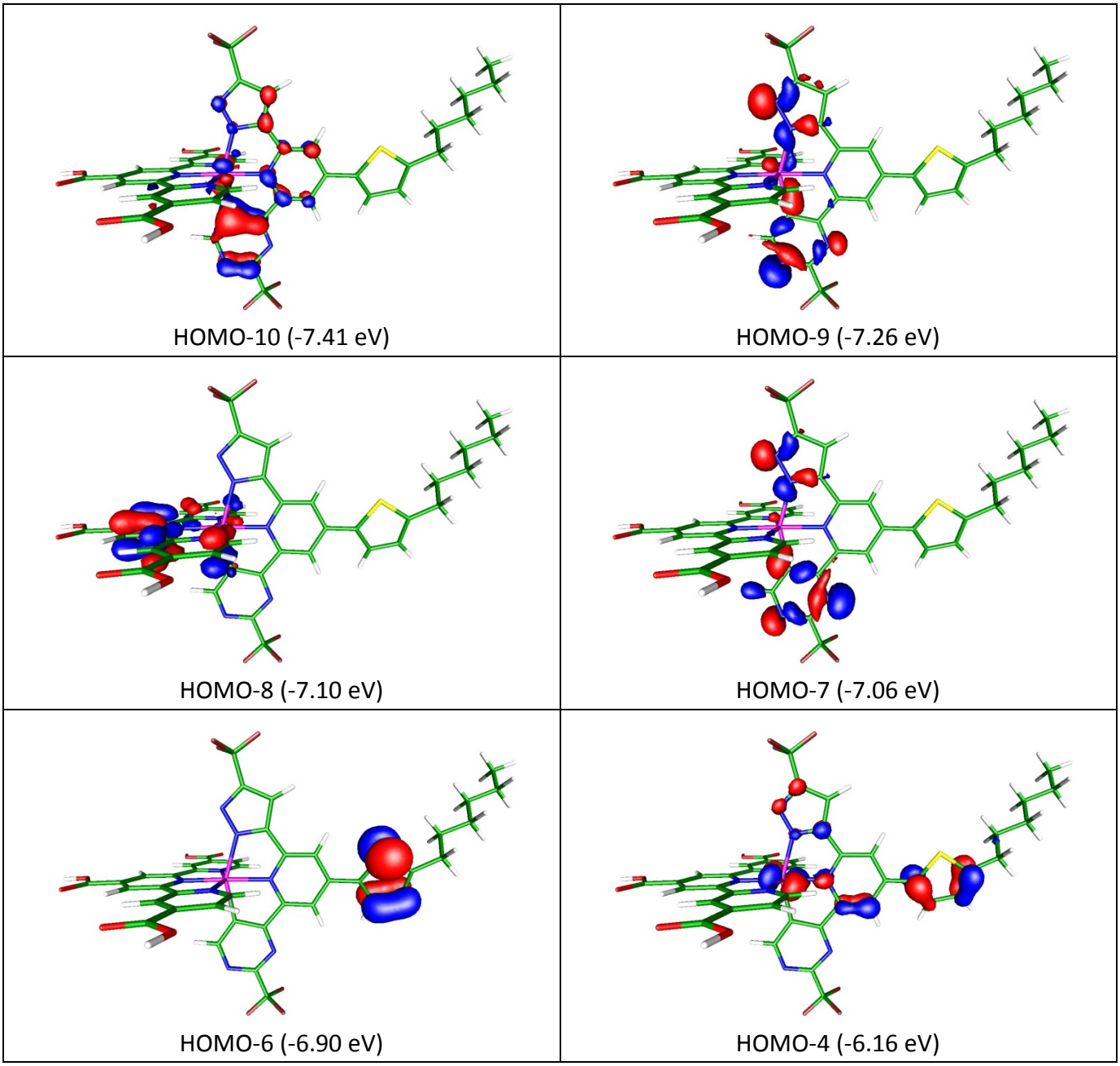


Figure S3-1. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-27**.

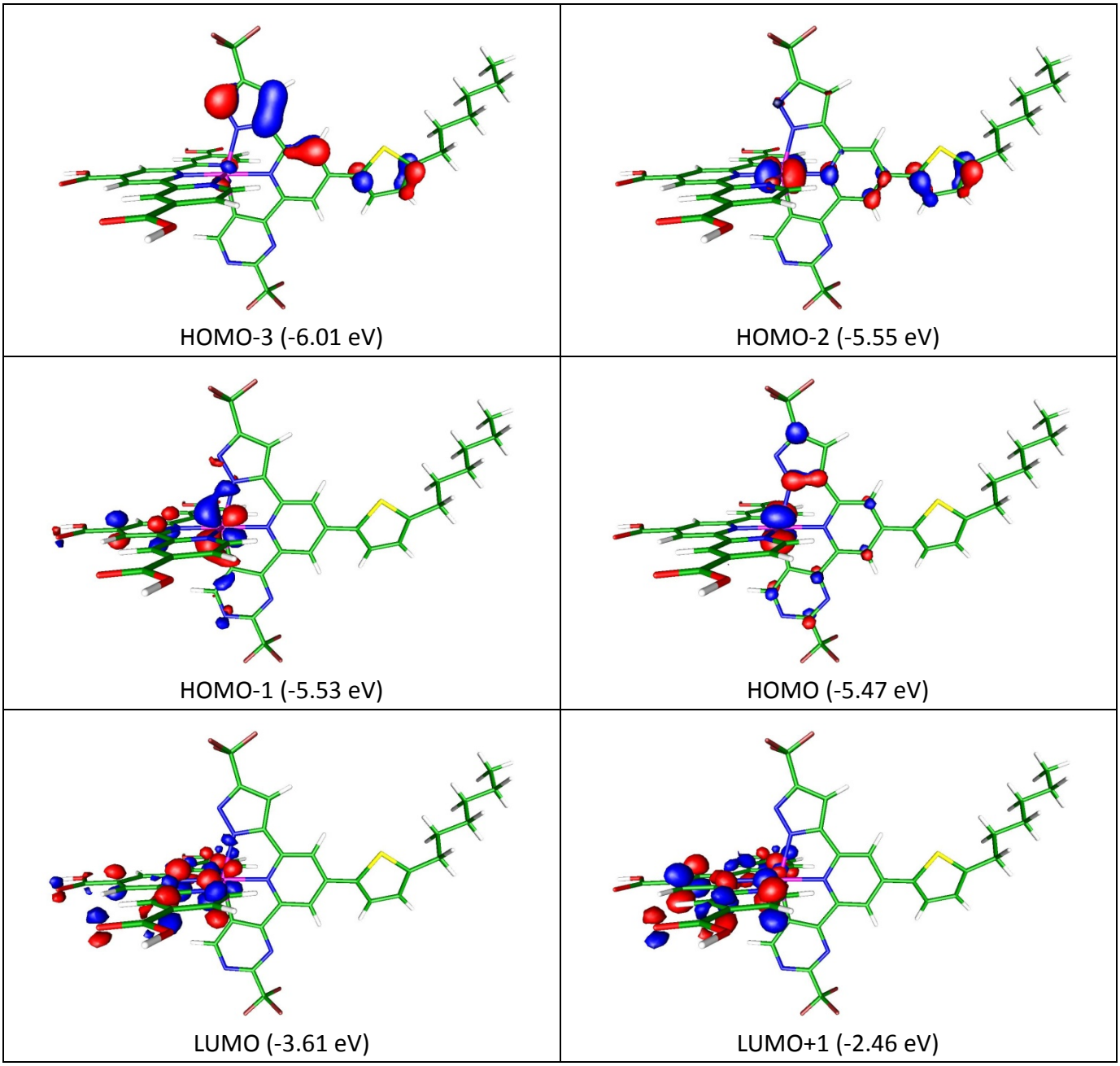


Figure S3-2. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-27**.

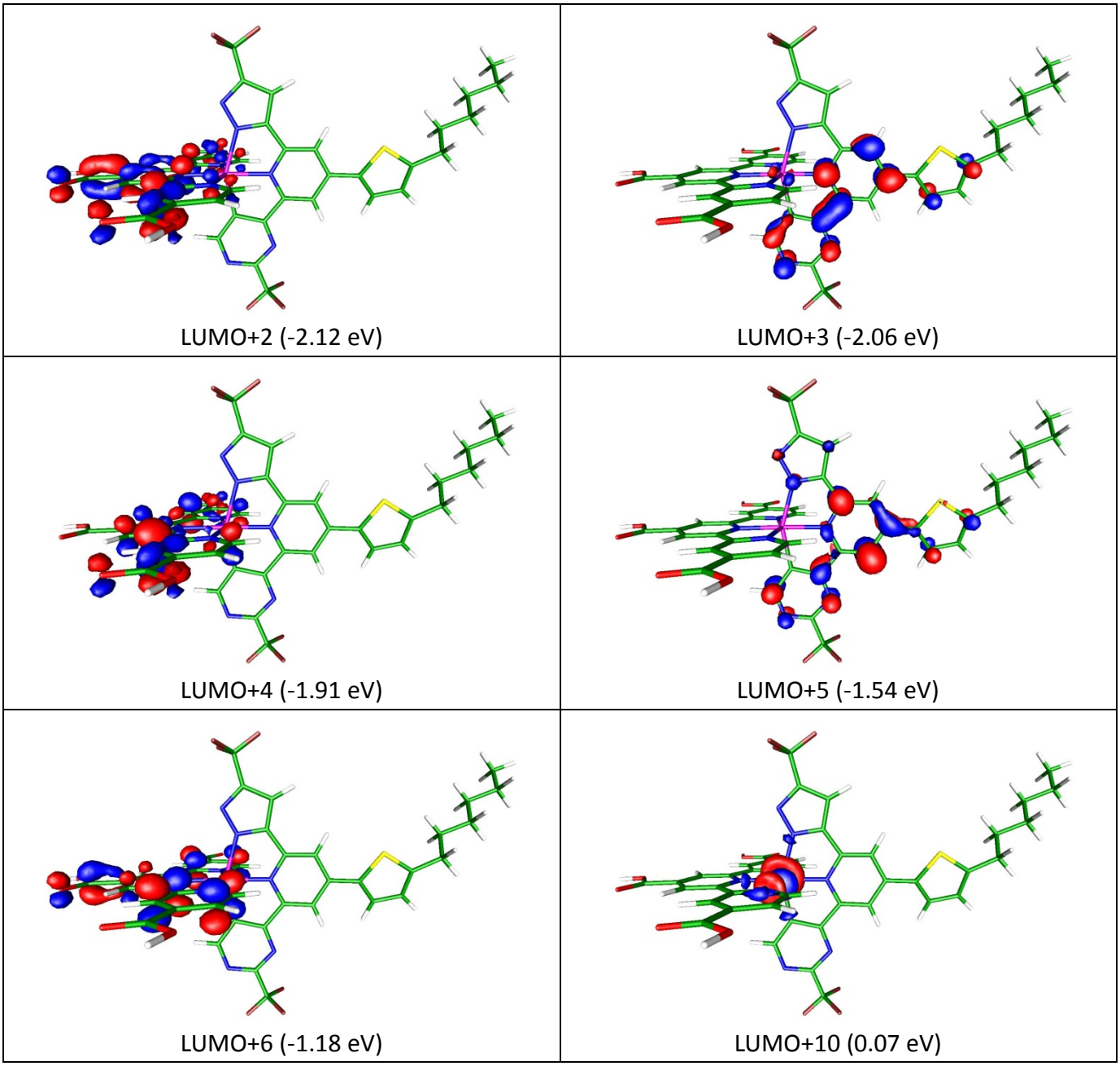


Figure S3-3. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-27**.

Table S4. The wavelengths, transition probabilities and charge transfer characters of the singlet optical transitions in selected states with oscillator strength > 0.02 for **TF-28** in DMF. The lowest triplet optical transition ($S_0 \rightarrow T_1$) is also listed.

State	λ_{cal} (nm)	*f*	Assignments	MLCT
T_1	896.4	0	HOMO-2→LUMO(93%) HOMO-2→LUMO+2(5%)	40.86%
S_1	671.7	0.024	HOMO→LUMO(92%)	34.44%
S_2	622.7	0.001	HOMO-1→LUMO(80%) HOMO-3→LUMO(8%) HOMO-5→LUMO(7%)	17.58%
S_3	572.6	0.0348	HOMO-2→LUMO(54%) HOMO→LUMO+1(43%)	42.48%
S_4	524.8	0.1041	HOMO-2→LUMO+1(94%)	47.80%
S_6	489.3	0.1852	HOMO→LUMO+1(45%) HOMO-2→LUMO(30%) HOMO-2→LUMO+2(8%) HOMO→LUMO+3(6%)	40.77%
S_9	449.8	0.0743	HOMO→LUMO+2(47%) HOMO-3→LUMO(33%) HOMO-4→LUMO(7%)	23.25%
S_{10}	442.5	0.1097	HOMO→LUMO+2(46%) HOMO-3→LUMO(39%) HOMO-4→LUMO(7%)	22.85%
S_{12}	433.8	0.4289	HOMO-1→LUMO+3(58%) HOMO-2→LUMO+2(30%)	34.29%
S_{19}	396.6	0.0517	HOMO-3→LUMO+1(52%) HOMO→LUMO+4(11%) HOMO-1→LUMO+1(6%) HOMO-4→LUMO+1(6%)	13.19%
S_{20}	377.6	0.1926	HOMO-5→LUMO+1(46%) HOMO→LUMO+5(36%)	29.96%
S_{24}	362.6	0.1041	HOMO-3→LUMO+3(46%) HOMO-1→LUMO+5(25%) HOMO-5→LUMO+1(6%)	15.61%
S_{26}	355.2	0.0721	HOMO-1→LUMO+5(41%) HOMO-3→LUMO+3(36%)	18.07%
S_{30}	339	0.1159	HOMO-5→LUMO+3(79%)	21.44%
S_{33}	333.9	0.071	HOMO-7→LUMO(43%) HOMO-2→LUMO+6(38%) HOMO-3→LUMO+4(7%) HOMO-9→LUMO(5%)	16.63%
S_{37}	327.7	0.0928	HOMO-7→LUMO(30%) HOMO→LUMO+7(28%) HOMO-1→LUMO+6(28%)	21.38%
S_{42}	316.2	0.117	HOMO-3→LUMO+5(53%) HOMO-9→LUMO(24%) HOMO-7→LUMO(7%) HOMO-4→LUMO+4(7%)	5.70%
S_{45}	313.6	0.1286	HOMO-9→LUMO(39%) HOMO-3→LUMO+5(27%) HOMO→LUMO+7(20%)	11.53%
S_{48}	306.4	0.1053	HOMO-10→LUMO(72%) HOMO-7→LUMO+1(11%) HOMO-7→LUMO+3(8%)	-3.12%
S_{50}	302.8	0.0771	HOMO-4→LUMO+5(80%) HOMO-3→LUMO+5(6%)	1.54%

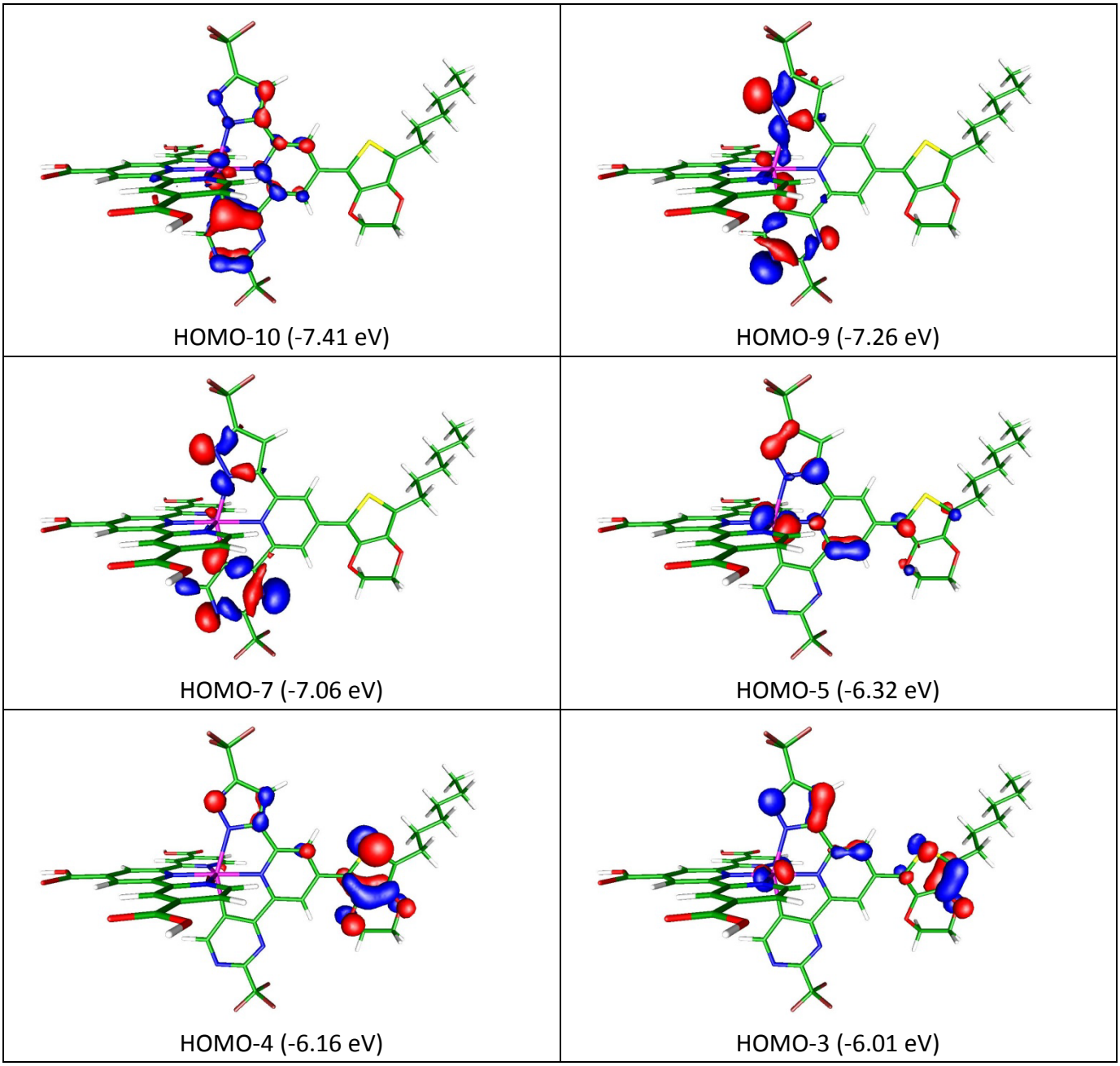


Figure S4-1. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-28**.

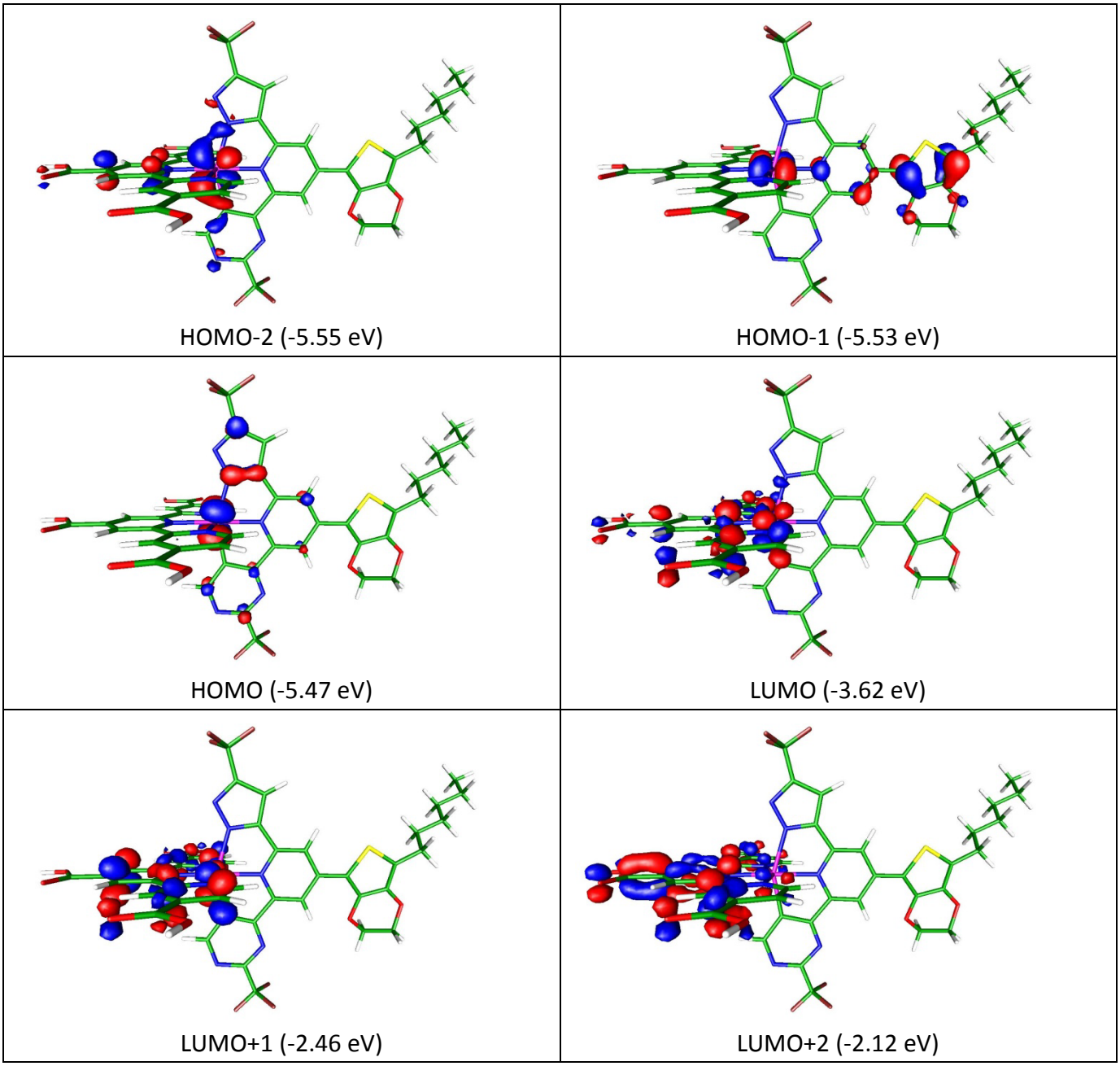


Figure S4-2. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-28**.

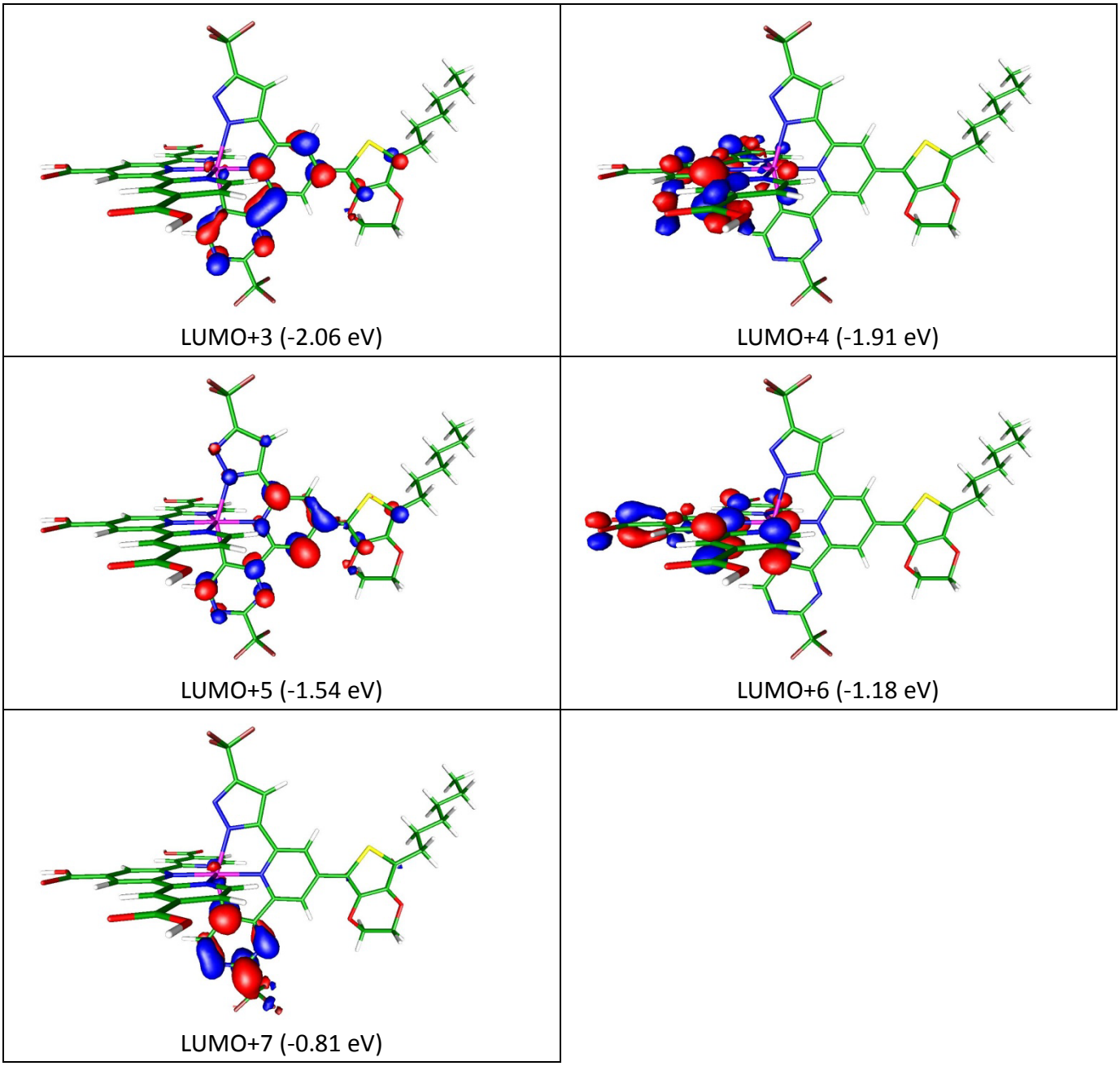


Figure S4-3. Frontier molecular orbitals pertinent to the singlet optical transitions in selected states for **TF-28**.