Supporting Information

Ru(II) Sensitizers with Tridentate Heterocyclic Cyclometalate for Dye-Sensitized Solar Cells

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Device fabrication

Fluorine-doped tin oxide (FTO) coated glasses (3.2 mm thickness, 9 Ω per square sheet resistance, Pilkington) were washed with detergent, water, acetone and ethanol, sequentially. After UV-ozone treatment (PSD series UV-ozone cleaning, Novascan Technologies, Inc.) for 15 min, the FTO glasses were immersed into an aqueous $TiCl_4$ solution (40 mM) at 75 °C for 30 min and rinsed with water, followed by ethanol. The mesoporous TiO_2 layer (particle size 20 nm) were screen-printed on FTO glasses as an electron-collecting substrate with techniques reported in literature.[1] Next, a 7 μm light-scattering layer of anatase particles (400 nm, PST-400, JGC Catalysts and Chemicals, Japan) was applied on top of the previous mesoporous TiO_2 layer. The TiO_2 photoanodes (active area of 4×4 mm^2 per pattern) were heated up to 500 °C for 30 min, cooled down to room temperature, treated with a 80 mM aqueous solution of $TiCl_4$, at 75 °C for 30 min and sintered at 500 °C for 30 min. Upon cooled down to 80 °C, the TiO_2 anodes were immersed into dye solutions (0.3 mM) in absolute ethanol with 20% (*v/v*) dimethyl sulfoxide (DMSO) and 1 mM CDCA for 18 h. The Pt-coated counter electrodes were prepared by dropping 10 μL of H_2PtCl_6 solution (5 mM) in isopropyl alcohol on pre-drilled FTO glass plates (15×15 mm^2) and heated up to 400 °C for 15 min. A hot-melt Surlyn film (25 μm) pre-cut as a homocentric square was sandwiched between TiO_2 electrode and Pt-coated FTO glass, and heated up to 130 °C for completing the device assembly. The electrolyte consists of 0.05 M lithium iodide (LiI), 0.03 M iodine (I_2), 0.1 M guanidinium thiocyanate (GuNCS), 0.5 M *tert*-butylpyridine, and 1.0 M (or 2.0 M) 1,3-dimethylimidazolium iodide (DMII) in a mixed acetonitrile and valeronitrile (*v/v*, 85/15). The ionic liquid, DMII, was dried under 0.1 torr at elevated temperature overnight. The electrolyte was injected into the cell through the pre-drilled hole, and the hole was sealed by a Surlyn film and a cover glass.

Loading of Sensitizers

Loading was measured by immersing TiO_2 anode into a solution of 0.1 M TBAOH in MeOH and water (*v/v* 1:1), followed by measuring the concentration of desorbed dyes according to its absorbance.

Photovoltaic Characterization

Photovoltaic performances were measured with a 4-wired setup by a digital source meter (Keithley 2400). An external potential bias was applied to the cell under a solar simulator (Model 91159, Class A, Newport Oriel) equipped with a 150 W xenon lamp and a power supply (Model 69907, Newport). The light output was adjusted to 100 mW/cm^2 within an effective illumination area of 2×2 $inch^2$ using a certified Si reference cell (SRC-1000-TC-QZ, VLSI standard S/N: 10510-0031). The spectrum mismatch between the simulated light and AM 1.5G solar spectrum in the region of 350 – 750 nm was reduced to ≤ 4% using a correction filter (Newport Oriel). Photovoltaic performance was measured using a metal mask with a square aperture of 6×6 mm^2, for which each edge was offset by 1 mm from the edges of photoelectrode (active area 4×4 mm^2). The incident photon-to-current conversion efficiency (IPCE) spectra were calculated using the equation $1240 \cdot J_{SC}(\lambda)/(\lambda \cdot P_{in}(\lambda))$, where J_{SC} is the short-circuit current density under 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, plotted as a function of incident wavelength with an increment of 10 nm. It should be noted that 20 values of J_{SC} (within interval of 50 ms) were collected after illuminating the device for 3 seconds, and were averaged for IPCE calculation. A 300 W Xe lamp (Model 6258, Newport Oriel) combined with an Oriel cornerstone 260 1/4 m monochromator (Model 74100) provided an unchopped monochromatic beam onto a photovoltaic cell. The beam intensity was calibrated with a power meter (Model 1936-C, Newport) equipped with a Newport 818-UV photodetector. The J_{SC} was also calculated by integration of IPCE data with solar power density between 350 and 900 nm (AM 1.5G, ASTM G137-03) for making a comparison with the measured J_{SC}.

Device Performance

Table S1. The performances for DSCs measured under AM 1.5 G solar illumination.

Dye	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%]	Dye loading [mol cm^{-2}]	Remarks
TF-22	0.70	16.26	0.686	7.97	–	[a]
	0.70	17.43	0.664	8.26	–	[b]
	0.71	18.09	0.682	8.76	1.69×10^{-7}	[c]
	0.73	16.65	0.677	8.24	–	[d]
TF-23	0.71	18.03	0.668	8.56	1.76×10^{-7}	[c]
TF-24	0.75	17.62	0.684	9.04	1.26×10^{-7}	[c]
	0.77	15.05	0.673	7.80	–	[d]
TF-21	0.63	11.93	0.633	4.76	1.52×10^{-7}	[c]
N749	0.72	17.33	0.701	8.75	1.17×10^{-7}	[c]

[a] Device with a 12+7 μm of TiO2 layer and the electrolyte that consists of 1.0 M DMII, 0.1 M GuSCN, 0.05 M LiI, 0.03 M I_2 and 0.5 M TBP in a 85:15 (v/v) mixture of acetonitrile and valeronitrile. [b] Device with a 12+7 μm of TiO_2 layer and an electrolyte with conc. of DMII increased to 2.0 M. [c] Electrolyte is the same as in [b] but with 15+7 μm of TiO_2 layer. [d] All conditions are identical to that of [c], but employed a dye solution with 3 equiv. of [TBA][DOC] to induce in-situ H^+/TBA^+ metathesis on the sensitizer.

Electrochemical Impedance Measurement

DSCs were tested with the electrochemical impedance spectroscopy, PARSTAT 2273 electrochemical workstation (AMETEK Princeton Applied Research, U.S.A.). These results were obtained under dark at a forward bias of 0.7 V and 1 sun illumination, respectively and by applying an external potential modulation of 10 mV with a frequency range of $0.05 - 10^6$ Hz.

Stability Test

The photoanodes of the device employed in this study composed of a 15 μm transparent TiO_2 thin film and a 7 μm thick layer of 400 nm TiO_2 particles. A 405 nm cut-off long pass filter film was attached on the cell surface during illumination. The cell was irradiated under a Suntest CPS plus lamp (ATLAS GmbH, $100 mW/cm^2$) during visible-light soaking at 60 °C. The electrolyte consists of 2.0 M DMII, 0.05 M LiI, 0.03 M iodine, 0.1 M GuNCS, and 0.5 M N-butyl-1H-benzimidazole (NBB) in 3-methoxypropionitrile.

Experimental Section

General procedures: All reactions were performed under argon atmosphere and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV254). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ^{1}H NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

Synthesis of **L1-1**

A solution of 1-bromo-3-(trifluoromethyl)benzene (5.0 g, 22 mmol) in dry THF (100 mL) was cooled to –78 °C under argon and treated with a 2.5 M solution of *n*-butyl lithium (9.8 mL, 24 mmol). The mixture was stirred at –78 °C for 30 min. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.0 mL, 24 mmol) was added. After adding, the mixture was stirred at room temperature overnight and the solvent was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried over $MgSO_4$. After then, the solvent was evaporated and the sample was used without further purification.

Spectral data of **L1-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 8.04 (s, 1H), 7.95 (d, J_{HH} = 7.6 Hz, 1H), 7.68 (d, J_{HH} = 7.6 Hz, 1H), 7.46 (t, J_{HH} = 7.6 Hz, 1H), 1.34 (s, 12H).

Synthesis of **L1-2**

Compound **L1-1** (0.68 g, 2.5 mmol), 2-bromo-6-acetylpyridine (0.50 g, 2.5 mmol), $Pd(PPh_3)_4$ (144 mg, 0.130 mmol) and potassium carbonate (0.69 g, 5.0 mmol) were suspended in THF (25 mL) and H_2O (5 mL). The mixture was refluxed for 16 h. After cooling to room temperature, the solvent was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 8) to give white solid (**L1-2**, 446 mg, 67%).

Spectral data of **L1-2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 8.34 (s, 1H), 8.27 (d, J_{HH} = 8.0 Hz, 1H), 8.02 (dd, J_{HH} = 6.8, 2.0 Hz, 1H), 7.98 ~ 7.90 (m, 2H), 7.70 (d, J_{HH} = 8.0 Hz, 1H), 7.63 (t, J_{HH} = 8.0 Hz, 1H), 2.82 (s, 3H).

Synthesis of **L1**

A solution of NaOEt (116 mg, 1.70 mmol) in dry THF (20 mL) was cooled to 0 °C under argon and added **L1-2** (300 mg, 1.1 mmol) in dry THF (20 mL). The mixture was stirred at 0 °C for 20 min. Ethyl trifluoroacetate (0.20 mL, 1.7 mmol) was added, and then heated to 80 °C for 4 h. After cooling, the mixture was justified to pH = 4 by 2N $HCl_{(aq)}$ and the solvent was removed *in vacuo*. The crude product was extracted with ethyl acetate and dried over $MgSO_4$. After then, the solvent was evaporated and without further purification.

Above crude product and hydrazine (0.33 mL, 6.4 mmol) in EtOH (30 mL) was heated to 80 °C for 8 h under argon. After cooling, the solvent was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried over $MgSO_4$. Then purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 3) to give white solid (**L1**, 120 mg, 30%).

Spectral data of **L1**: MS (EI^+): m/z 357 $(M)^+$. ^1H NMR (400 MHz, $CDCl_3$, 298K): δ 8.25 (s, 1H), 8.20 (d, J_{HH} = 7.6 Hz, 1H), 7.90 (d, J_{HH} = 7.6 Hz, 1H), 7.75 (d, J_{HH} = 7.6 Hz, 1H), 7.71 (d, J_{HH} = 8.0 Hz, 1H), 7.67 ~ 7.58 (m, 2H), 6.99 (s, 1H).

Synthesis of **L2-1**

Compound 6-bromo-2-pyridinecarbonitrile (424 mg, 2.30 mmol), (4-(trifluoromethyl)phenyl)boronic acid (440 mg, 2.30 mmol), $Pd(PPh_3)_4$ (134 mg, 0.120 mmol) and potassium carbonate (0.96 g, 7.0 mmol) were suspended in THF (30 mL) and H_2O (7 mL). The mixture was refluxed for 6 h. After cooling to room temperature, the solvent was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 4) to give white solid (**L2-1**, 460 mg, 80%).

Spectral data of **L2-1**: ^1H NMR (400 MHz, $CDCl_3$, 298K): δ 8.14 (d, J_{HH} = 8.0 Hz, 2H), 8.02 ~ 7.90 (m, 2H), 7.75 (d, J_{HH} = 8.0 Hz, 2H), 7.68 (d, J_{HH} = 7.2 Hz, 1H).

Synthesis of **L2**

A solution of NaOMe (9.8 mg, 0.18 mmol), **L2-1** (450 mg, 1.8 mmol) in MeOH (15 mL) was stirred under argon for 12 h at room temperature. The mixture was added NH_4Cl (107 mg, 2.00 mmol) and refluxed under argon for 4 h. After cooling, the solvent was removed *in vacuo*. Then the crude product was without further purification.

Another solution of ethyl trifluoroacetate (0.26 mL, 1.5 mmol) and hydrazine monohydrate (0.10 mL, 1.9 mmol) in dry THF (25 mL) was heated to 80 °C under argon for 1 h. After cooling, above crude product and NaOH (76 mg, 1.9 mmol) were added and the mixture refluxed under argon for 8 hr. The solvent was removed under reduced pressure and the crude product was washed by $NaHCO_{3(aq)}$, extracted with CH_2Cl_2 and dried over $MgSO_4$, then purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 2) to give white solid (**L2**, 190 mg, 40%).

Spectral data of **L2**: MS (EI^+): m/z 358 $(M)^+$. ^1H NMR (400 MHz, $CDCl_3$, 298K): δ 12.0 (br, 1H), 8.23 (d, J_{HH} = 8.0 Hz, 1H), 8.12 (d, J_{HH} = 8.0 Hz, 2H), 8.01 (t, J_{HH} = 8.0 Hz, 1H), 7.90 (d, J_{HH} = 8.0 Hz, 1H), 7.77 (d, J_{HH} = 8.0 Hz, 2H).

Synthesis of **L3-1**

Compound 6-bromo-2-pyridinecarbonitrile (0.50 g, 2.7 mmol), **L1-1** (0.89 g, 3.3 mmol), $Pd(PPh_3)_4$ (158 mg, 0.140 mmol) and potassium carbonate (0.94 g, 6.8 mmol) were suspended in THF (30 mL) and H_2O (7 mL). The mixture was refluxed for 4 h. After cooling to room temperature, the solvent was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 4) to give white solid (**L3-1**, 608 mg, 90%).

Spectral data of **L3-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 8.27 (s, 1H), 8.22 (d, J_{HH} = 8.0 Hz, 1H), 8.02 ~ 7.90 (m, 2H), 7.76 ~ 7.59 (m, 3H).

Synthesis of **L3**

A solution of NaOMe (13 mg, 0.24 mmol), **L3-1** (0.60 g, 2.4 mmol) in MeOH (15 mL) was stirred under argon for 12 h at room temperature. The mixture was added NH_4Cl (142 mg, 2.70 mmol) and refluxed under argon for 4 h. After cooling, the solvent was removed *in vacuo*. Then the crude product was without further purification.

Another solution of ethyl trifluoroacetate (0.29 mL, 1.7 mmol) and hydrazine monohydrate (0.12 mL, 2.3 mmol) in dry THF (30 mL) was heated to 80 °C under argon for 1 h. After cooling, above crude product and NaOH (94 mg, 2.3 mmol) were added and the mixture refluxed under argon for 8 hr. The solvent was removed under reduced pressure and the crude product was washed by $NaHCO_{3(aq)}$, extracted with CH_2Cl_2 and dried over $MgSO_4$, then purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 2) to give white solid (**L3**, 220 mg, 26%).

Spectral data of **L3**: MS (EI$^+$): m/z 358 (M)$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 8.26 (s, 1H), 8.22 (d, J_{HH} = 7.6 Hz, 1H), 8.18 (d, J_{HH} = 7.6 Hz, 1H), 8.01 (t, J_{HH} = 7.6 Hz, 1H), 7.89 (d, J_{HH} = 7.6 Hz, 1H), 7.73 (d, J_{HH} = 7.6 Hz, 1H), 7.63 (t, J_{HH} = 7.6

Hz, 1H).

Synthesis of **L4-1**

A solution of 4-bromo-1-fluoro-2-(trifluoromethyl)benzene (2.0 g, 8.2 mmol) in dry THF (50 mL) was cooled to –78 °C under argon and treated with a 2.5 M solution of *n*-butyl lithium (3.6 mL, 9.1 mmol). The mixture was stirred at –78 °C for 30 min. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.0 mL, 24 mmol) was added. After adding, the mixture was stirred at room temperature overnight and the solvent was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried over $MgSO_4$. After then, the solvent was evaporated and the sample was used without further purification.

Spectral data of **L4-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 8.03 (d, J_{HF} = 7.6 Hz, 1H), 7.98 ~ 7.90 (m, 1H), 7.16 (t, J_{HH} = 9.2 Hz, 1H), 1.35 (s, 12H).

Synthesis of **L4-2**

Compound 6-bromo-2-pyridinecarbonitrile (1.1 g, 6.0 mmol), **L4-1** (2.0 g, 6.9 mmol), $Pd(PPh_3)_4$ (346 mg, 0.300 mmol) and potassium carbonate (2.1 g, 15 mmol) were suspended in THF (30 mL) and H_2O (7 mL). The mixture was refluxed for 5 h. After cooling to room temperature, the solvent was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 4) to give white solid (**L4-2**, 983 mg, 61%).

Spectral data of **L4-2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 8.30 ~ 8.21 (m, 2H), 7.96 ~ 7.91 (m, 2H), 7.70 ~ 7.63 (m, 1H), 7.33 (t, J_{HF} = 9.2 Hz, 1H).

Synthesis of **L4**

A solution of NaOMe (14 mg, 0.26 mmol), **L4-2** (0.70 g, 2.6 mmol) in MeOH (20 mL) was stirred under argon for 12 h at room temperature. The mixture was added NH_4Cl (155 mg, 2.90 mmol) and refluxed under argon for 4 h. After cooling, the solvent was removed *in vacuo*. Then the crude product was without further purification.

Another solution of ethyl trifluoroacetate (0.32 mL, 1.9 mmol) and hydrazine monohydrate (0.13 mL, 2.5 mmol) in dry THF (30 mL) was heated to 80 °C under argon for 1 h. After cooling, above crude product and NaOH (106 mg, 2.60 mmol) were added and the mixture refluxed under argon for 8 hr. The solvent was removed under reduced pressure and the crude product was washed by $NaHCO_{3(aq)}$, extracted with CH_2Cl_2 and dried over $MgSO_4$, then purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 3) to give white solid (**L4**, 583 mg, 59%).

Spectral data of **L4**: MS (EI^+): m/z 376 $(M)^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 12.1 (br, 1H), 8.26 (d, J_{HF} = 6.8 Hz, 1H), 8.24 ~ 8.16 (m, 2H), 8.00 (t, J_{HH} = 8.0 Hz, 1H), 7.85 (d, J_{HH} = 8.0 Hz, 1H), 7.35 (t, J_{HF} = 9.2 Hz, 1H).

Synthesis of **TF-21**

A mixture of **L1** (54.4 mg, 0.15 mmol), Ru(tectpy)Cl_3 (100 mg, 0.15 mmol) and KOAc (74.7 mg, 0.760 mmol) in 30 mL of xylenes was heated at 140 °C under stirring for 20 h. After the removal of solvent, the crude product of **TF-21-Et** was purified by silica gel column chromatography (ethyl acetate/CH_2Cl_2 = 1:6). After then, the resulting solid was dissolved in a mixture of acetone (20 mL) and 1.0M NaOH solution (1.0 mL). The mixture was heated to 60 °C under argon for 2 h. The solvent was removed, and the residue was dissolved in H_2O solution (5 mL). This solution was titrated with 2N $HCl_{(aq)}$ to pH = 3 to afford a brown precipitate. This brown product was washed with CH_2Cl_2 and acetone, giving the final product (**TF-21**, 63.0 mg, 71 %).

Spectral data of **TF-21-Et**: ^1H NMR (400 MHz, d_6-acetone, 298K): δ 9.40 (s, 2H), 9.00 (s, 2H), 8.26 (t, J_{HH} = 5.6 Hz, 1H), 8.21 ~ 8. 13 (m, 2H), 8.00 (s, 1H), 7.83 (d, J_{HH} = 5.6 Hz, 2H), 7.61 (d, J_{HH} = 5.6 Hz, 2H), 7.30 (s, 1H), 6.58 (dd, J_{HH} = 7.6, 1.2 Hz, 1H), 5.44 (d, J_{HH} = 7.6 Hz, 1H), 4.35 ~ 3.80 (m, 6H), 1.40 ~ 0.80 (m, 9H).

Spectral data of **TF-21**: MS (FAB, ^{102}Ru): m/z 822 $(M)^+$. ^1H NMR (400 MHz, d_6-DMSO, 298K): δ 9.28 (s, 2H), 9.14 (s, 2H), 8.36 (d, J_{HH} = 7.2 Hz, 1H), 8.22 ~ 8.05 (m, 3H), 7.66 (d, J_{HH} = 6.0 Hz, 2H), 7.61 (d, J_{HH} = 6.0 Hz, 2H), 7.28 (s, 1H), 6.61 (d, J_{HH} = 7.6 Hz, 1H), 5.52 (d, J_{HH} = 7.6 Hz, 1H). ^{19}F-{^1H} NMR (470 MHz, d_6-DMSO, 298K): δ –58.33 (s, 3F), –60.13 (s, 3F). Anal. Calcd. for $C_{34}H_{18}F_6N_6O_6Ru\cdot H_2O$: C, 48.64; N, 10.01; H, 2.40. Found: C, 48.73; N, 9.59; H, 2.78.

Synthesis of **TF-22**

Following the similar procedures as described for **TF-21**, **TF-22** is isolated as a brown solid in 66% yield.

Spectral data of **TF-22-Et**: ^{1}H NMR (400 MHz, d$_6$-acetone, 298K): δ 9.37 (s, 2H), 9.10 (s, 2H), 8.36 (dd, J_{HH} = 6.4, 2.4 Hz, 1H), 8.30 ~ 8.22 (m, 2H), 8.02 (d, J_{HH} = 8.4 Hz, 1H), 7.83 (d, J_{HH} = 5.6 Hz, 2H), 7.67 (dd, J_{HH} = 5.6, 1.2 Hz, 2H), 6.95 (d, J_{HH} = 7.6 Hz, 1H), 5.72 (s, 1H), 4.45 ~ 4.21 (m, 6H), 1.40 ~ 1.20 (m, 9H).

Spectral data of **TF-22**: MS (FAB, ^{102}Ru): m/z 823 (M)$^+$. ^{1}H NMR (400 MHz, d$_6$-DMSO, 298K): δ 9.40 (s, 2H), 9.16 (s, 2H), 8.42 (t, J_{HH} = 4.8 Hz, 1H), 8.22 (d, J_{HH} = 4.8 Hz, 2H), 8.06 (d, J_{HH} = 8.4 Hz, 1H), 7.65 (d, J_{HH} = 5.6 Hz, 2H), 7.61 (d, J_{HH} = 5.6 Hz, 2H), 6.96 (d, J_{HH} = 5.6 Hz, 1H), 5.60 (s, 1H). ^{19}F-{^{1}H} NMR (470 MHz, d$_6$-DMSO, 298K): δ –61.22 (s, 3F), –62.12 (s, 3F). Anal. Calcd. for $C_{33}H_{17}F_6N_7O_6Ru$: C, 47.78; N, 11.47; H, 2.48. Found: C, 48.06; N, 11.29; H, 2.56.

Synthesis of **TF-23**

Following the similar procedures as described for **TF-21**, **TF-23** is isolated as a brown solid in 60% yield.

Spectral data of **TF-23-Et**: ^{1}H NMR (400 MHz, d$_6$-acetone, 298K): δ 9.32 (s, 2H), 9.00 (s, 2H), 8.43 (dd, J_{HH} = 7.6, 1.6 Hz, 1H), 8.32 ~ 8.22 (m, 2H), 8.06 (s, 1H), 7.82 (d, J_{HH} = 5.6 Hz, 2H), 7.62 (d, J_{HH} = 4.4 Hz, 2H), 6.62 (d, J_{HH} = 8.0 Hz, 1H), 5.56 (d, J_{HH} = 8.0 Hz, 1H), 4.38 ~ 4.00 (m, 6H), 1.32 ~ 1.02 (m, 9H).

Spectral data of **TF-23**: MS (FAB, ^{102}Ru): m/z 823 $(M)^+$. ^{1}H NMR (400 MHz, d$_6$-DMSO, 298K): δ 9.38 (s, 2H), 9.14 (s, 2H), 8.51 (t, J_{HH} = 4.8 Hz, 1H), 8.25 ~ 8.10 (m, 3H), 7.64 (d, J_{HH} = 6.0 Hz, 2H), 7.61 (d, J_{HH} = 6.0 Hz, 2H), 6.68 (d, J_{HH} = 7.6 Hz, 1H), 5.59 (d, J_{HH} = 7.6 Hz, 1H). ^{19}F-{^{1}H} NMR (470 MHz, d$_6$-DMSO, 298K): δ –60.21 (s, 3F), –62.11 (s, 3F). Anal. Calcd. for $C_{33}H_{17}F_5N_7O_6Ru{\cdot}MeOH$: C, 47.78; N, 11.47; H, 2.48. Found: C, 48.14; N, 11.25; H, 2.48.

Synthesis of **TF-24**

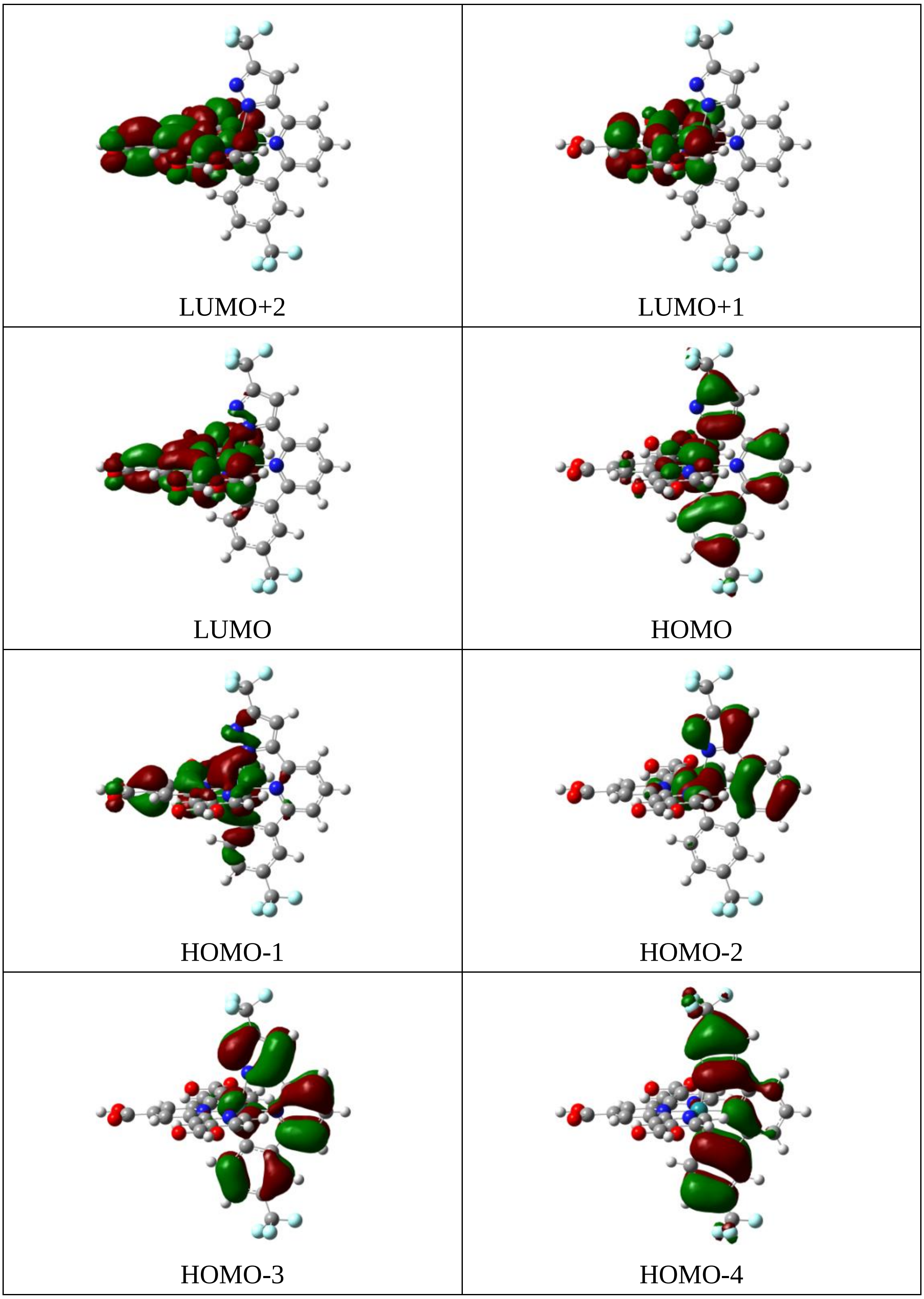
Following the similar procedures as described for **TF-21**, **TF-24** is isolated as a brown solid in 56% yield.

Spectral data of **TF-24-Et**: ^{1}H NMR (400 MHz, d$_6$-acetone, 298K): δ 9.34 (s, 2H), 9.07 (s, 2H), 8.42 ~ 8.36 (m, 1H), 8.25 (d, J_{HH} = 5.2 Hz, 2H), 8.10 (d, J_{HF} = 6.8 Hz, 1H), 7.81 (d, J_{HH} = 5.8 Hz, 2H), 7.67 (d, J_{HH} = 5.6 Hz, 2H), 5.37 (d, J_{HF} = 11.2 Hz, 1H), 4.40 ~ 4.20 (m, 6H), 1.35 ~ 1.25 (m, 9H).

Spectral data of **TF-24**: MS (FAB, ^{102}Ru): m/z 842 $(M+1)^+$. ^{1}H NMR (400 MHz, d$_6$-DMSO, 298K): δ 9.37 (s, 2H), 9.13 (s, 2H), 8.49 (t, J_{HH} = 4.6 Hz, 1H), 8.22 ~ 8.15 (m, 3H), 7.66 (d, J_{HH} = 5.6 Hz, 2H), 7.58 (d, J_{HH} = 6.0 Hz, 2H), 5.36 (d, J_{HF} = 10.8 Hz, 1H). ^{19}F-{^{1}H} NMR (470 MHz, d$_6$-DMSO, 298K): δ –59.07 (s, 3F), –62.12 (s, 3F), –117.76 (s, 1F). Anal. Calcd. for $C_{33}H_{16}F_7N_7O_6Ru{\cdot}H_2O$: C, 46.16; N, 11.42; H, 2.11. Found: C, 46.08; N, 11.15; H, 2.33.

TD-DFT Calculation

All calculations were performed by Gaussian 09 program.[3] Their ground state structures were first optimized with density functional theory (DFT) at B3LYP/LANL2DZ (Ru) and 6-31G* (H, C, N, O, S) level. The optimized structures were then used to calculate 30 lowest singlet energy optical excitations using the time-dependent density functional theory (TD-DFT) method. Their lowest ground triplet state energies, and the relaxed lowest singlet and triplet excited energies were also calculated. To mimic the realistic environmental perturbation, a polarizable continuum model (PCM) was applied using dimethylformamide (DMF) as solvent.



LUMO+2

LUMO+1

LUMO

HOMO

HOMO-1

HOMO-2

HOMO-3

HOMO-4

Figure S1. Frontier orbitals pertinent to the singlet optical transitions with oscillator strength > 0.01 for TF-21 dye. The isovalue for the contours are set to be 0.02.

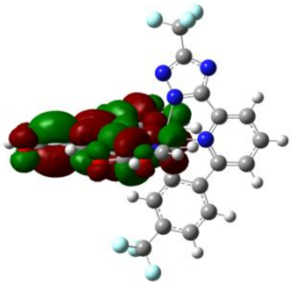
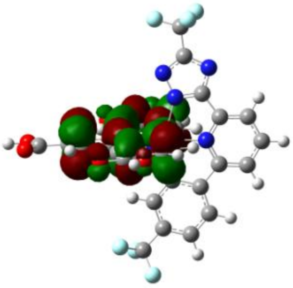
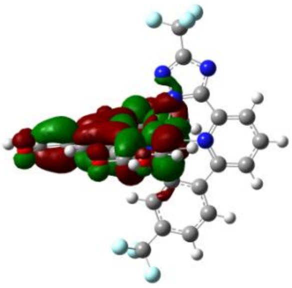
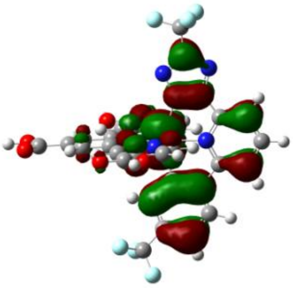
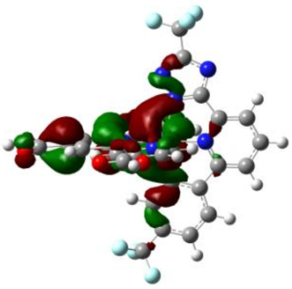
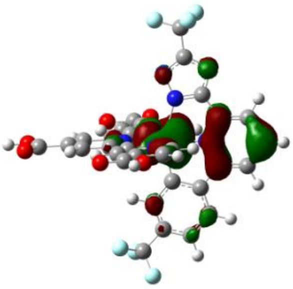
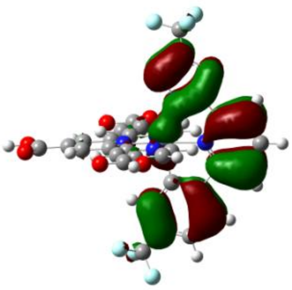
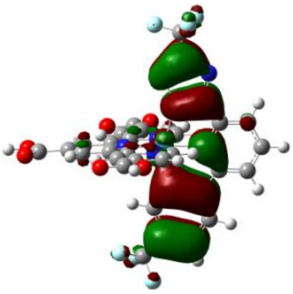
 LUMO+2	 LUMO+1
 LUMO	 HOMO
 HOMO-1	 HOMO-2
 HOMO-3	 HOMO-4

Figure S2. Frontier orbitals pertinent to the singlet optical transitions with oscillator strength > 0.01 for TF-22 dye. The isovalue for the contours are set to be 0.02.

Table S2. The calculated wavelength, oscillator strength (*f*), orbital transition probabilities and MLCT characteristics of the singlet optical transitions (listed with oscillator strength > 0.01) for TF-21 dye in DMF.

State	λ_{cal} (nm)	*f*	Assignments	MLCT
1	706.1	0.0255	HOMO → LUMO(92%)	30.89%
3	590.9	0.0128	HOMO → LUMO+1(52%) HOMO-1 → LUMO(46%)	41.05%
4	535.1	0.1019	HOMO-1 → LUMO+1(93%)	46.44%
5	497.9	0.0638	HOMO-1 → LUMO(38%) HOMO → LUMO+1(34%) HOMO → LUMO+3(11%) HOMO-1 → LUMO+2(10%) HOMO-2 → LUMO+1(5%)	43.61%
7	465.5	0.1734	HOMO → LUMO+2(86%) HOMO-3 → LUMO(6%)	40.29%
8	445.5	0.0339	HOMO-3 → LUMO(87%) HOMO → LUMO+2(7%)	2.71%
9	437	0.0914	HOMO-1 → LUMO+2(65%) HOMO → LUMO+3(30%)	48.61%
10	427.7	0.0197	HOMO-1 → LUMO+3(97%)	51.69%
11	421.3	0.1377	HOMO → LUMO+3(50%) HOMO-1 → LUMO+2(15%) HOMO-3 → LUMO+1(12%) HOMO → LUMO+1(7%) HOMO-1 → LUMO(7%)	38.52%
14	393.6	0.0898	HOMO-3 → LUMO+1(80%)	7.65%
19	355.5	0.0141	HOMO-3 → LUMO+2(97%)	12.27%
22	348.2	0.0801	HOMO-2 → LUMO+4(42%) HOMO → LUMO+5(29%) HOMO-7 → LUMO(9%)	39.99%
24	342.1	0.0404	HOMO-1 → LUMO+6(56%) HOMO-3 → LUMO+3(18%) HOMO-7 → LUMO(16%) HOMO-4 → LUMO+1(5%)	31.96%

26	338.3	0.012	HOMO-3 → LUMO+3(71%) HOMO-1 → LUMO+6(25%)	22.65%
30	335.7	0.0233	HOMO-2 → LUMO+5(38%) HOMO-3 → LUMO+4(23%) HOMO-7 → LUMO(15%) HOMO-5 → LUMO+1(6%)	27.16%

Table S3. The calculated wavelength, oscillator strength (*f*), orbital transition probabilities and MLCT characteristics of the singlet optical transitions (listed with oscillator strength > 0.01) for TF-22 dye in DMF.

State	λ_{cal} (nm)	*f*	Assignments	MLCT
1	700.2	0.028	HOMO → LUMO(94%)	35.12%
3	582.5	0.0128	HOMO → LUMO+1(51%) HOMO-1 → LUMO(47%)	44.49%
4	523.6	0.0928	HOMO-1 → LUMO+1(94%)	50.08%
5	490.8	0.0774	HOMO → LUMO+1(38%) HOMO-1 → LUMO(38%) HOMO → LUMO+3(12%) HOMO-1 → LUMO+2(9%)	45.55%
7	457.6	0.2006	HOMO → LUMO+2(92%)	46.29%
8	430.6	0.0697	HOMO-1 → LUMO+2(44%) HOMO → LUMO+4(28%) HOMO → LUMO+3(23%)	49.84%
10	419.5	0.0126	HOMO-1 → LUMO+3(97%)	54.65%
11	412.1	0.204	HOMO → LUMO+3(47%) HOMO-1 → LUMO+2(25%) HOMO-1 → LUMO(9%) HOMO → LUMO+1(8%)	45.40%
17	363.1	0.071	HOMO-3 → LUMO+1(77%) HOMO-2 → LUMO+4(16%)	14.51%
20	351	0.0133	HOMO-2 → LUMO+4(48%) HOMO-3 → LUMO+1(15%)	50.39%

			HOMO-2 → LUMO+5(14%) HOMO → LUMO+5(10%)	
23	334.3	0.0767	HOMO-2 → LUMO+5(52%) HOMO-1 → LUMO+6(28%)	54.36%
24	334.1	0.0149	HOMO-1 → LUMO+6(62%) HOMO-2 → LUMO+5(13%) HOMO-7 → LUMO(8%) HOMO-4 → LUMO+1(6%)	45.06%
30	322.3	0.0614	HOMO-2 → LUMO+9(65%) HOMO-2 → LUMO+13(13%) HOMO-2 → LUMO+11(7%)	14.78%

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