

Supporting Information

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Ruthenium(II) Sensitizers with Heteroleptic Tridentate Chelates for Dye-Sensitized Solar Cells**

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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. ^1H and ^{13}C 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 TF-2:

A mixture of 4-(5-hexylthiophen-2-yl)-2,6-bis(3-trifluoromethyl-1H-pyrazol-5-yl)pyridine (234 mg, 0.45 mmol), Ru(tectpy)Cl₃ (300 mg, 0.45 mmol) and 4-ethylmorpholine (0.15 mL, 1.17 mmol) in 30 mL of ethanol was heated at 80 °C under stirring for 3 h. After the removal of solvent, the residue was extracted with CH₂Cl₂ (3 × 25 mL), washed with water and concentrated to dryness. The crude product was further purified by silica gel column chromatography (hexane/ethyl acetate = 1:1). After then, the resulting solid was dissolved in a mixture of acetone (50 mL) and 1.5M NaOH solution (6.2 mL). The mixture was heated to 60 °C under N₂ for 3 h. The solvent was removed, and the residue was dissolved in H₂O solution (10 mL). This solution was titrated with 2 N HCl to pH 3 to afford a black precipitate. This black product was washed with CH₂Cl₂ and acetone, giving TF-2 (264 mg, 67 %).

Spectral data of TF-2: MS (FAB, ^{102}Ru): m/z 978 (M+1)⁺. ^1H NMR (400MHz, d₆-DMSO, 298K): δ 9.36 (s, 2H), 9.14 (s, 2H), 8.34 (s, 2H), 7.96 (d, $J_{\text{HH}} = 4$ Hz, 1H), 7.71 ~ 7.67 (m, 4H), 7.33 (s, 2H), 7.10 (d, $J_{\text{HH}} = 4$ Hz, 1H), 2.95 (t, $J_{\text{HH}} = 8$ Hz, 2H), 1.74 (quin, $J_{\text{HH}} = 8$ Hz, 2H), 1.41 ~ 1.31 (m, 6H), 0.98 (t, $J_{\text{HH}} = 8$ Hz, 3H). ^{19}F NMR (376 MHz, d₆-DMSO, 298K): δ -58.52 (s, 6F). Anal. Calcd. for C₄₁H₃₂F₆N₈O₇RuS·H₂O: C, 49.45; N, 11.25; H, 3.24. Found: C, 49.39; N, 11.14; H, 3.59.

DFT Calculation

The calculation was performed by the Gaussian 09 program^[1] using the time-dependent (TD)^[2] density functional theory with the hybrid functional of B3LYP.^[3] The molecular structure of **TF-2** was first calculated using the B3LYP/Lanl2dz theory in the gas phase. The TD-DFT PCM^[4] single-point calculation with the solvent DMF was then performed using a larger basis set. The basis set consists of the 6-31+G(d) set for H,C,N,O,S atoms and the Lanl2dz basis set for the Ru atom augmented with a set of diffuse s, p, d functions and a set of f polarization functions with orbital exponents of 0.0139, 0.0083, 0.05, and 1.235, respectively.

Device fabrication

The cells consisted of a mesoscopic TiO₂ film composed of a 15 μm thick transparent layer of 20 nm sized TiO₂ anatase nanoparticles and a second 5 μm thick scattering layer of 400 nm sized TiO₂; both were deposited by screen printing to form a square with dimension of 0.38 × 0.38 cm². The TiO₂ electrodes were gradually heated under an air flow at 325°C for 5 min, followed by 375°C for 5min, 450°C for 15min, and 500°C for 15 min. The TiO₂ electrodes were treated with a 40 mM aqueous solution of TiCl₄ and then sintered at 70°C for 30 min and at 500°C for another 30 min. After cooling to 80 °C, the TiO₂ electrode was immersed into the dye solution (0.3 mM) containing 20% DMSO in ethanol with 1 mM chenodeoxycholic acid as a coadsorbent for 18 h. The Pt counter electrodes were next prepared by spin-coating employing an H₂PtCl₆ solution (2 mg of Pt in 1 mL isopropyl alcohol) on FTO plates, followed by sintering at 400 °C for 15 min. The dye adsorbed TiO₂ electrodes and the Pt counter were assembled into a sandwich-type cell using a hot-melt ionomer film (Surlyn 1702, 25 μm) as a spacer between the electrodes and by heating at 120 °C. The electrolyte consists of acetonitrile solution containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1M of iodine, 0.5M *tert*-butylpyridine, and 0.1 M of lithium iodide, which was then injected into the cell through a drilled hole in the back of the counter electrode. Finally, the hole was sealed using a hot-melt ionomer film and a cover glass.

Photovoltaic Characterization

A 150 W xenon light source (Oriel, U.S.A.) was used to give an irradiance of 100 mW cm^{-2} (the equivalent of one sun at air mass (AM 1.5) at the surface of solar cells). Various incident light intensities were regulated with wavelength neutral wire mesh attenuators. The current-voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, U.S.A.). A similar data acquisition system was used to control the incident photon-to-collected electron conversion efficiency measurement. Under full computer control, light from a 300 W xenon lamp (Oriel, U.S.A.) was focused through a monochromator onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined by $\text{IPCE}(\lambda) = 12400(J_{sc}/\lambda\phi)$, where λ is the wavelength, J_{sc} is short-circuit photocurrent density (mA cm^{-2}), and ϕ is the incident radiative flux (mW cm^{-2}). Photovoltaic performance was measured by using a black tape as mask with an aperture area of 0.144 cm^2 .

Electrical Impedance Measurements

Electrical impedance experiments were carried out with a PARSTAT 2273 (AMETEK Princeton Applied Research, U.S.A.) electrochemical workstation, with a frequency range of $0.05 - 10^6 \text{ Hz}$ and a potential modulation of 5 mV .

Stability Test

The photoanodes of the device employed in this study composed of a $8 \mu\text{m}$ transparent TiO_2 thin film and $5 \mu\text{m}$ thick layer of 400 nm TiO_2 particles. A 405 nm cut-off long pass filter was placed 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 $60 \text{ }^\circ\text{C}$. Electrolyte consists of 1.0 M DMII, 0.15 M iodine, 0.1 M GNCS, and 0.5 M NBB (N-butyl-1H-benzimidazole) in 3-methoxypropionitrile, which is also known as Z946.

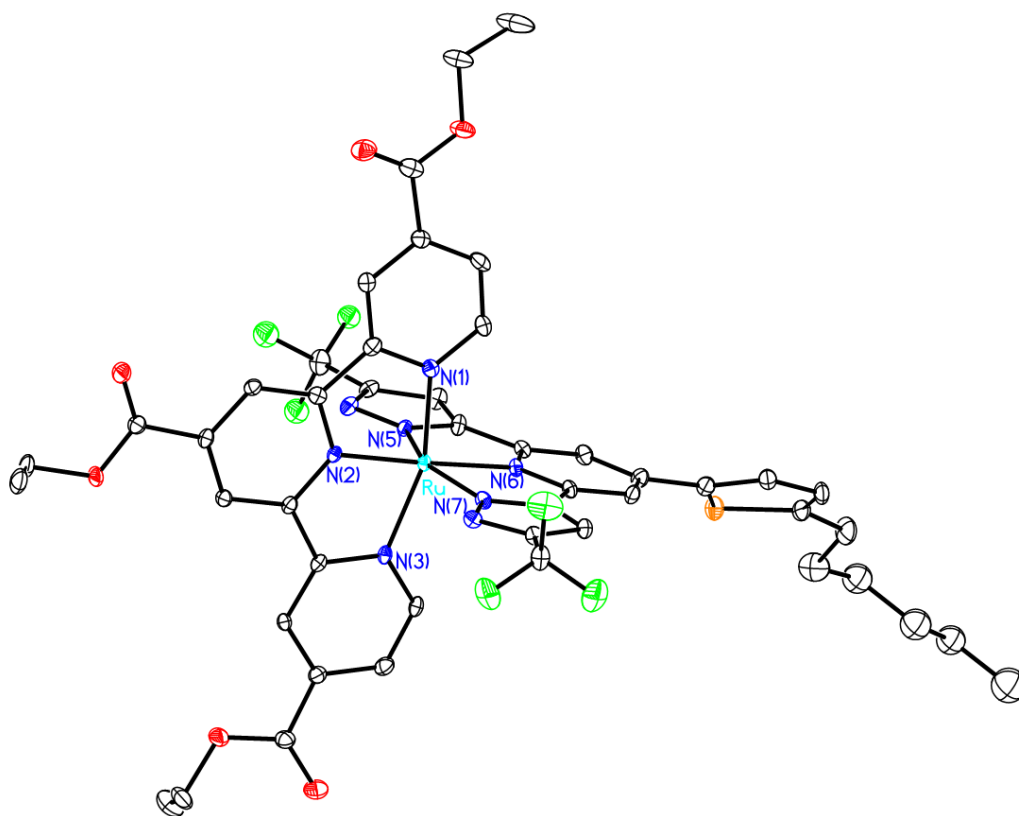
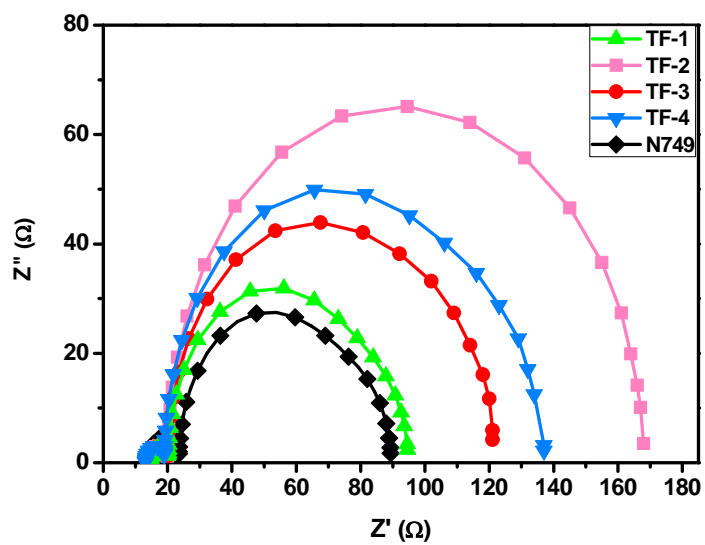


Figure S1. ORTEP diagram of complex **TF-2OEt**; selected bond lengths: Ru-N(2) = 1.947(4), Ru-N(6) = 2.030(4), Ru-N(1) = 2.037(4), Ru-N(5) = 2.041(4), Ru-N(3) = 2.044(4) and Ru-N(7) = 2.053(4) Å; selected bond angles: N(2)-Ru-N(6) = 176.12(17) and N(1)-Ru-N(3) = 159.37(16)°. Selected crystal data of **TF-2OEt**: C₅₅H₆₂F₆N₈O₈RuS; M = 1210.26; monoclinic; space group = P 2₁/c; a = 17.6842(11) Å, b = 14.2774(8) Å, c = 23.2852(15) Å, β = 107.752(2)°, V = 5599.2(6) Å³; Z = 4; ρ_{calcd} = 1.436 Mg m⁻³; μ = 0.398 mm⁻¹; F(000) = 2504; crystal size = 0.25 × 0.18 × 0.13 mm³; λ(Mo-K_α) = 0.71073 Å; T = 150(2) K; 33478 reflections collected, 9841 independent reflections (R_{int} = 0811), GOF = 1.153, final R₁[I > 2σ(I)] = 0.0731 and wR₂(all data) = 0.1682. Crystallographic data (excluding structure factors) was deposited in the Cambridge Crystallographic Data Centre with the deposition numbers CCDC 804179. It can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(A)



(B)

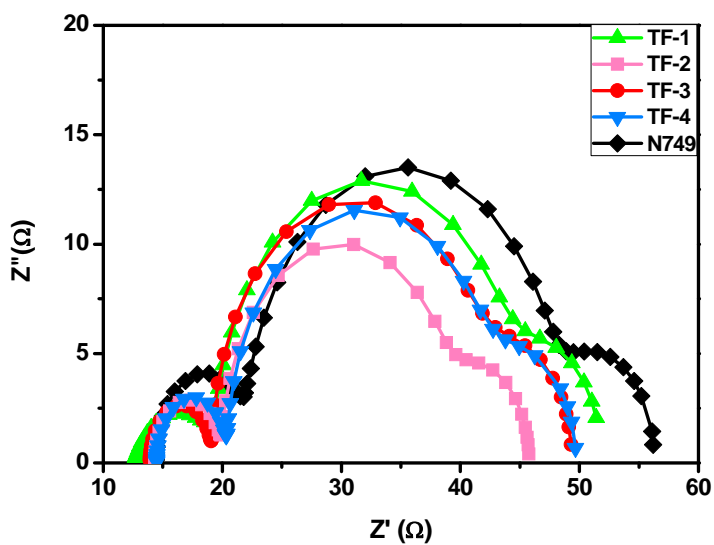


Figure S2. Electrochemical impedance spectra measured (A) at the dark and (B) under 1 sun illumination (100 mWcm^{-2}) for the cells employing different dyes. (i.e. **TF** dyes and **N749**).

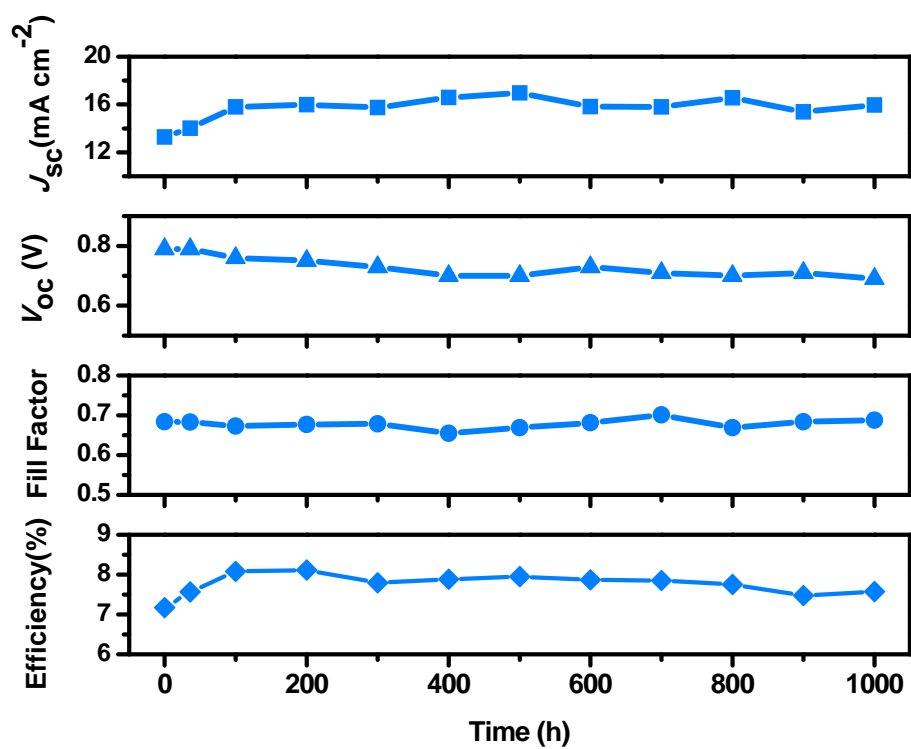


Figure S3. Evolution of solar cell parameters of TF-2 measured under the irradiance of AM 1.5 G sunlight-soaking at 60 °C. A 405 nm cut-off long pass filter was put on the cell surface during illumination. Electrolyte: 1.0 M DMII, 0.15 M iodine, 0.1 M GNCS, and 0.5 M NBB (N-butyl-1*H*-benzimidazole) in 3-methoxypropionitrile (Z946).

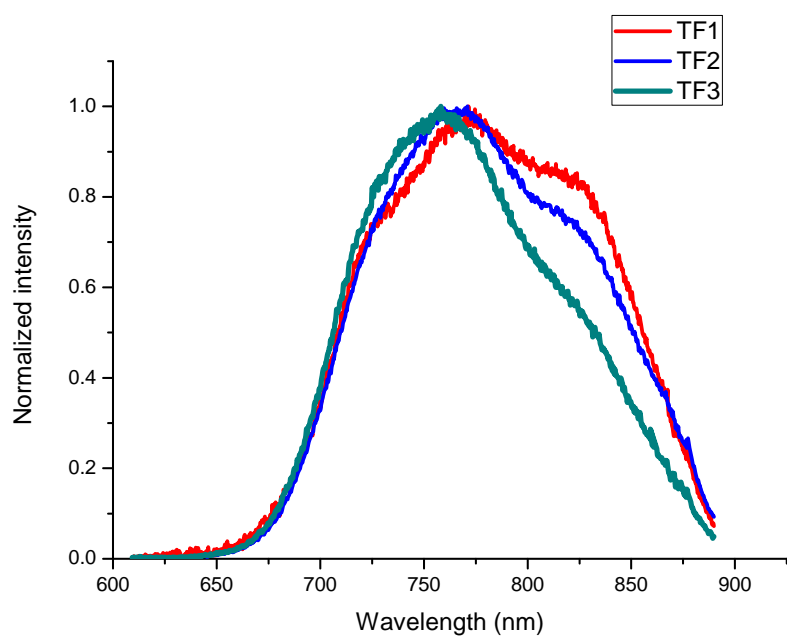


Figure S4. The emission spectra of various **TF** dyes recorded in DMF solution. To avoid complication, the emission of **TF4**, which is similar to that of **TF2**, is not shown here. The excitation wavelength: 514 nm. Note that the emission spectrum from 400-900 nm has been calibrated by the spectral response of the entire system.

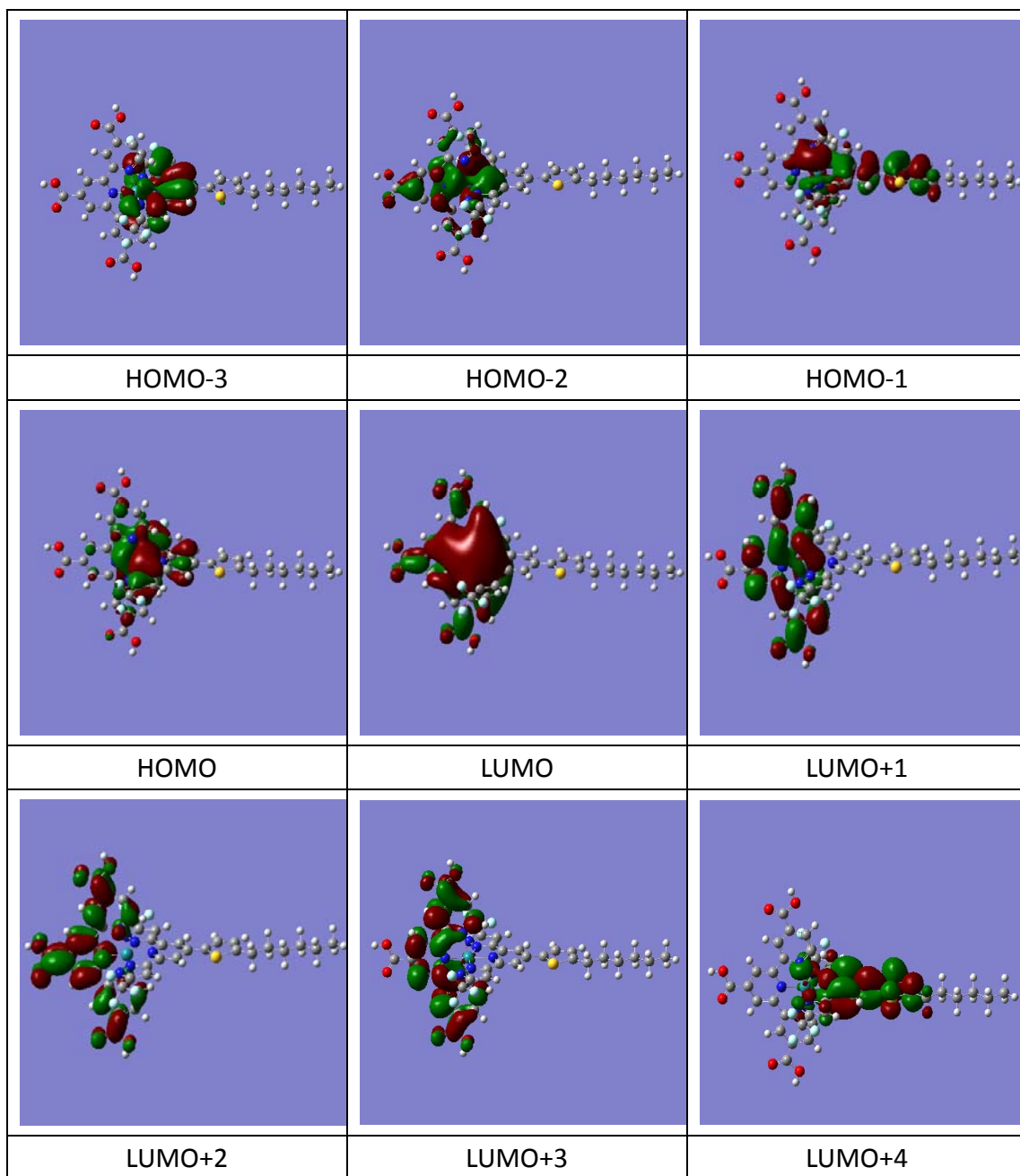


Figure S5. Calculated molecular orbitals relevant to the UV/Vis spectral assignments of TF-2.

Table S1. Peak assignment for the calculated absorption peaks of complex **TF-2**.

Calculated wavelength (nm)	Major Transitions and Contribution Coefficients	assignment
748	HOMO → LUMO (0.69)	MLCT and LLCT
493	HOMO-2 → LUMO (0.49) HOMO → LUMO+1 (-0.35) HOMO → LUMO+3 (-0.29)	MLCT and LLCT
476	HOMO-3 → LUMO (0.40) HOMO-2 → LUMO+1 (0.43) HOMO → LUMO+2 (0.39)	$\pi\pi^*$, MLCT and LLCT
412	HOMO-3 → LUMO+1 (-0.42) HOMO-2 → LUMO+2 (-0.40) HOMO-1 → LUMO+4 (0.38)	$\pi\pi^*$, MLCT and LLCT

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