Electronic Supplementary Information for

Highly Efficient Cycloreversion of Photochromic Dithienylethene Compounds Using Visible Light-Driven Photoredox Catalysis

Sumin Lee,^a Youngmin You,^b* Kei Ohkubo,^c Shunichi Fukuzumi,^{a,c}* and Wonwoo Nam^a*

^aDepartment of Bioinspired Science, Ewha Womans University, Daehyun-dong, Seodaemun-gu, Seoul 120-750, Korea,

^bDepartment of Advanced Materials Engineering for Information and Electronics,

Kyung Hee University, Seocheon-dong, Yongin, Gyeonggi-do 446-701, Korea,

^cDepartment of Material and Life Science, Graduate School of Engineering,

Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan.

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Experimental Details

Materials.

The synthesis of cyclometalated Ir(III) complexes were performed according to the method reported previously.¹ The preparation of PDTE, PhDTE, MDTE, and CDTE was reported earlier.² Commercially available chemicals were used without further purification unless otherwise stated. All glassware and magnetic stirring bars were thoroughly dried in a convection oven. CH_2Cl_2 and THF were purified by filtering over anhydrous alumina columns prior to use. Reactions were monitored using thin layer chromatography (TLC). Commercial TLC plates (silica gel 60 F₂₅₄, Merck Co.) were developed and the spots were visualized under UV illumination at 254 or 365 nm. Silica gel column chromatography was performed using silica gel 60 (particle size 0.063-0.200 mm, Merck Co.). ¹H, ¹³C, and ¹⁹F NMR spectra referenced to deuterated solvents were collected with a Bruker Ultrashield 400 plus NMR spectrometer. Highresolution mass spectra were recorded using a JEOL JMS-600W mass spectrometer. Elemental analysis was performed using an EA1110 or EA1112 (CE Instrument, Italy) for C, H, N, and S. Fresh Cu(ClO₄)₂ stock solutions were prepared in CH₃CN (spectrophotometric grade, Aldrich) using Cu(ClO₄)₂·6H₂O before experiments. Closed and open forms of DTE were prepared by photoirradiation of 1.0 mM DTE solutions (CH₃CN, spectrophotometric grade) by using a handheld UV lamp (4W, VL-4.LC, VILBER LOURMAT) for 3 h and a Xenon light source (300 W, MAX-302, Asahi Spectra, Co.) equipped with a 500 nm cut-on filter (MJL Crystek Inc., 500FH90-50) for 1 h, respectively.



Scheme S1. Synthesis of ADTE.

3,5-Dibromo-2-methylthiophene (1). *N*-Bromosuccinimide (NBS) (72.5 g, 407 mmol) was slowly added to a stirred glacial acetic acid (200 mL) containing 2-methylthiophene (20.0 g, 204 mmol) at room temperature. After 1 h, the solution was neutralized with aqueous NaOH. The crude product was recovered by extraction with CH_2Cl_2 (100 mL, three times), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The desired product was isolated

by silica gel column chromatography with hexane to give transparent oil (46 g, 88%). ¹H NMR (400 MHz, CDCl₃) δ 2.33 (s, 3H), 7.26 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 15.0, 108.6, 108.9, 132.1, 136.2. HRMS (EI, positive) calcd for C₅H₄Br₂S, 253.8400; found, 253.8400.

2. Tetrakis(triphenylphosphine)palladium(0) (0.49)4g, 0.42 mmol) and (dimethylamino)phenylboronic acid (5.0 g, 30 mmol) was added to a stirred THF solution (120 mL) of 1 (6.5 g, 25 mmol). 2 N aqueous Na_2CO_3 (60 mL) was delivered to the reaction mixture, which was heated at 80 °C under an argon atmosphere. After 10 h, the solution was cooled down to room temperature and poured onto water. The organic layer was extracted with CH₂Cl₂ (100 mL, three times), dried over anhydrous MgSO₄, and concentrated. Silica gel column purification was performed with $CH_2Cl_2:CH_3OH$ (49:1, v/v), affording beige solid (6.5 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ 2.39 (s, 3H), 2.98 (s, 6H), 6.70 (d, J = 8.9 Hz, 2H), 6.93 (s, 1H), 7.38 (d, J= 8.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ : 14.7, 15.3, 40.4, 65.9, 76.7, 77.0, 77.33, 112.5, 123.2, 126.3.

ADTE. 2.5 M *n*-BuLi in hexane (11.8 mL, 30 mmol, Aldrich) was slowly added to a stirred anhydrous THF solution (150 mL) of **2** (7.6 g, 30 mmol) at -78 °C under an argon atmosphere. The solution was stirred at -78 °C for additional 0.5 h, and 2.0 mL of liquefied octafluorocyclopentene was injected to the solution using a gas-tight syringe. The reaction mixture was warmed to room temperature, and stirred overnight under an argon atmosphere. The solution was poured onto water, and the organic layer was recovered with CH₂Cl₂ (100 mL, three times), dried over anhydrous MgSO₄, and concentrated through vacuum. Silica gel column purification with CH₂Cl₂:CH₃OH (49:1, v/v) and subsequent reprecipitation in hexane afforded a greenish solid (0.36 g, 9.1%). ¹H NMR (400 MHz, CDCl₃) δ 1.92 (s, 6 H), 2.97 (s, 6 H), 2.98 (s, 6 H), 6.71 (d, *J* = 8.9 Hz, 4 H), 7.10 (s, 2 H), 7.41 (d, *J* = 8.8 Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ 14.5, 30.9, 40.8, 112.5, 120.0, 121.9, 125.7, 126.6, 139.2, 142.9, 150.2, 206.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -131.87 (q, *J* = 5.6 Hz, 4F), -109.94 (t, *J* = 5.6 Hz, 2F). LRMS (FAB, positive, *m*-NBA) calcd for C₃₁H₂₈F₆N₂S₂, 606; found 606. Anal. Calcd for C₃₁H₂₈F₆N₂S: C, 61.37; H, 4.65; N, 4.62; S, 10.57. Found: C, 61.38; H, 4.66; N, 4.64; S, 10.13.

Steady-state UV-vis absorption measurements. UV-vis absorption spectra were collected on a Varian Cary 50 spectrophotometer at 298 K. 10 μ M or 50 μ M CH₃CN solutions of DTEc and the Ir(III) complex were used for the measurements unless otherwise mentioned.

Stopped-flow UV–vis absorption measurements. Kinetic measurements were performed on a Unisoku RSP-601 stopped-flow spectrometer equipped with a MOS-type highly sensitive photodiode array using a 10 mm quartz cuvette at 263 K, 273 K, and 283 K. Acetonitrile solutions of 50 μ M DTEc and 200 μ M Cu(ClO₄)₂ were prepared before the measurements. The

electrochemical generation of the radical cation of DTEc compounds was initiated by a singlemixing technique, and the spectral changes in the region between 500–800 nm were acquired for the indicated periods at 100 ms interval. Spectra at wavelength > 800 nm could not be acquired due to the instrumental limit. The decay of the absorption band at 790 nm (PDTE), 791 nm (PhDTE), and 750 nm (MDTE, CDTE, and ADTE) after the induction periods were selected and fitted with a single exponential decay model.

Photoluminescence lifetime measurements. Ar-saturated 50 μ M solutions in CH₃CN were used for determination of the phosphorescence lifetimes of the Ir(III) complexes. Phosphorescence decay traces were acquired based on time-correlated single-photon-counting (TCSPC) techniques using a FluoTime 200 instrument (PicoQuant, Germany). A 377 nm diode laser (PicoQuant, Germany) was used as the excitation source. The phosphorescence signals were obtained using an automated motorized monochromator. Phosphorescence decay profiles were analyzed (OriginPro 8.0, OriginLab) using a single exponential decay model.

Determination of photoluminescence quantum yields (PLQYs). Phosphorescence spectra were obtained using a Quanta Master 40 scanning spectrofluorimeter at room temperature. 10 μ M solutions in CH₃CN were thoroughly degassed through the repeated vacuum–freeze–thaw cycles prior to performing the measurements. The solutions were excited at the following wavelengths: 393 nm (IrdCF3), 359 nm (Irdfppy), 362 nm (Irfppy), 412 nm (Irpbt), 377 nm (Irppy), 434 nm (Irbtp), and 377 nm (IrOMe) throughout the phosphorescence measurements. The phosphorescence quantum yields (Φ) were determined relatively according to following standard equation: $\Phi = \Phi_{ref} \times (I/I_{ref}) \times (A_{ref}/A) \times (n/n_{ref})^2$, where *A*, *I*, and *n* are the absorbance at the excitation wavelength, integrated photoluminescence intensity, and the refractive index of the solvent, respectively. Fluorescein in an aqueous 0.1 N NaOH solution was used as the external reference ($\Phi_{ref} = 0.79$). The refractive index of the 0.1 N NaOH solution was assumed to be identical to the value for pure water.

Nanosecond laser flash photolysis. An Ar-saturated CH_3CN sample solution in a 1 cm × 1 cm quartz cell was excited by a Nd:YAG laser (Continuum, SLII-10; 4–6 ns fwhm) at 426 nm with 5 mJ/pulse. Time courses of the transient absorption were measured by an InGaAs-PIN photodiode (Hamamatsu 2949) as a detector. The output from the photodiodes and a photomultiplier tube was recorded with a digitized oscilloscope (Tektronix, TDS3032; 300 MHz). All experiments were performed at 298 K.

Determination of quantum yields for cycloreversion (P(e)CQY_{C→O}). The quantum yields for cycloreversion were determined by the standard ferrioxalate actinometry. A 0.0060 M $K_3[Fe(C_2O_4)_3]$ solution served as the chemical actinometer. 500 µL of the $K_3[Fe(C_2O_4)_3]$ solution was transferred to a 1 cm \times 1 mm quartz cell, and the solution was photoirradiated with a monochromatized beam at 410 nm or 420 nm for 20 s. Then same amount of 1 % 1,10phenanthroline in sodium acetate buffer solution (4.09 g CH₃COONa dissolved in 18 mL of 0.5 M H₂SO₄ and 32 mL of distilled water) were added and stored under dark for 1h. The absorbance change at 510 nm was recorded. Inserting the value to eq 1 returned the light intensity value of 8.3 \times 10⁻¹⁰ einstein s⁻¹ and 6.7 \times 10⁻¹⁰ einstein s⁻¹ at 410 nm and 420 nm, respectively:

Light intensity (
$$I_0$$
, einstein s⁻¹) = ($\Delta Abs(510 \text{ nm}) \times V$)/($\Phi \times 11050 \text{ M}^{-1} \text{ cm}^{-1} \times \Delta t$) (1).

In eq 1, $\Delta Abs(510 \text{ nm})$, V, Φ , and Δt are the absorbance change at 510 nm, volume (L), the quantum yield (1.1) of the ferrioxalate actinometer at 410 nm or 420 nm,³ and photoirradiation time (s), respectively. A CH₃CN solution containing 1.0 mM closed form of DTE and 0.20 mM photoredox catalyst was photoirradiated under the identical condition for 37 s. Change in the absorbance at the peak wavelength of the closed form of DTE was recorded, which was inserted to eq 2:

Quantum yield
$$(\Phi) = (\Delta Abs(\text{peak}) \times V)/(I_0 \times (1 - 10^{-A\lambda}) \times \epsilon(\text{peak}) \times \Delta t)$$
 (2).

In eq2, ΔA is the decrease in the absorbance of the peak wavelength of the closed form of DTE during the photoirradiation period, Δt , V is the volume of the photoirradiated solution (L), ϵ (peak) is the molar absorption coefficient of the closed form of DTE (M⁻¹ cm⁻¹) at the peak wavelength, I_0 are the light intensity obtained by eq 1 (einstein s⁻¹), A_{λ} is the absorbance at the photoirradiation wavelength (mean value during the photoirradiation period), and Δt is the photoirradiation time (s).

Electrochemical Characterization. Cyclic voltammetry and differential pulse voltammetry experiments were carried out using a CHI630 B instrument (CH Instruments, Inc.) using a threeelectrode cell assembly. A Pt wire and a Pt microdisc were used as the counter and the working electrodes, respectively. A Ag/AgNO₃ couple was used as a pseudo reference electrode. Measurements were carried out in Ar-saturated CH₃CN (3 mL) using 0.10 M tetra-*n*-butylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte at scan rates of 100 mV/s (cyclic voltammetry) and 4.0 mV/s (differential pulse voltammetry). The concentration of the Ir(III) complex and DTE compounds was 1.0 mM. A ferrocenium/ferrocene reference was employed as the external reference.

DFT/TD-DFT calculations. Quantum chemical calculations based on density functional theory (DFT) were carried out using a Gaussian 09 program.⁴ Geometry optimization and single point calculations for DTEc and DTEc^{•+} compounds were performed using unrestricted Becke's three parameter uB3LYP exchange-correlation functional⁵⁻⁷ and the 6-311+G(d,p) basis set. Frequency calculations were subsequently performed to assess stability of the convergence. For TD-DFT calculations, the unrestricted uB3LYP functional and the identical basis sets used for the geometry optimization were applied to the optimized geometry. The polarizable continuum model (C-PCM) with a parameter set for acetonitrile was applied to account for solvation effects. Twenty lowest singlet states were calculated and analyzed. Simulation of the UV-vis absorption spectra were performed by employing a GaussSum program.⁸ An N,N-trans structure was employed as the starting geometry of IrOMe. Ground state geometry optimization and single point calculations were performed using Becke's three-parameter B3LYP exchange-correlation functional, the "double- ξ " quality LANL2DZ basis set for the Ir atom, and the 6–31+G(d,p) basis set for all other atoms. A pseudo potential (LANL2DZ) was applied to replace the inner core electrons of the Ir atom, leaving the outer core $[(5s)^2(5p)^6]$ electrons and the $(5d)^6$ valence electrons. The polarizable continuum model (C-PCM), parameterized for acetonitrile solvent, was applied during the geometry optimization step. Frequency calculations were subsequently performed to assess the stability of the convergence. For TD–DFT calculations, the unrestricted B3LYP functional and basis sets identical to those used for the geometry optimization were applied. C-PCM, parameterized for acetonitrile solvent, was applied to account for solvation effects. The twenty lowest triplet and singlet states were calculated and analyzed. AOMix program was employed to estimate the MLCT character.^{9,10}



Figure S1. Differential pulse voltammograms of the Ir(III) complexes. Conditions: scan rate, 0.4 mV/s; 1.0 mM Ir complex in an Ar-saturated CH_3CN containing 0.10 M Bu_4NPF_6 supporting electrolyte; a Pt wire counter electrode and a Pt microdisc working electrode; a Ag/AgNO₃ couple for the pseudo reference electrode.



Figure S2. Cyclic voltammograms (CV, blue) and differential pulse voltammograms (DPV, black) of ADTEo (a) and ADTEc (b). Conditions: scan rate, 100 mV/s and 0.4 mV/s for CV and DPV, respectively; 1.0 mM Ir complex in an Ar-saturated CH_3CN containing 0.10 M Bu_4NPF_6 supporting electrolyte; a Pt wire counter electrode and a Pt microdisc working electrode; a Ag/AgNO₃ couple for the pseudo reference electrode.



Figure S3. UV–vis absorption spectra of the Ir(III) complexes (100 μ M, CH₃CN).



Figure S4. UV–vis absorption spectra of the DTEc compounds (100 μ M, CH₃CN).



Figure S5. ¹H NMR spectra (400 MHz, CD_3CN) showing the photoelectrocatalytic cycloreversion of 2.0 mM PhDTEc by 420 nm photoirradiation of 0.20 mM IrOMe.



Figure S6. Photoelectrocatalytic cycloreversion quantum yields ($PeCQY_{C\rightarrow O}$) for 1.0 mM PhDTEc in the presence of various concentrations (0.010–3.0 equiv) of IrOMe (Ar-saturated CH₃CN solution). PeCQY_{C→O} determination was performed in triplicate.



Figure **S7**. Plots of the photoelectrocatalytic cycloreversion quantum yields (PeCQY_{C \rightarrow O}) as a function of the inverse of the phosphorescence lifetimes (1/ τ_{obs}) of the photoredox catalysts.



Figure S8. Determination of the rate constants for photoinduced electron transfer (k_{PeT}) from DTEc compounds to Irpbt (Ar-saturated CH₃CN): a, PDTEc; b, MDTEc; c, CDTEc; d, ADTEc: Left panels, phosphorescence decay traces of 50 µM Irpbt in the presence of various concentrations (0–100 µM) of DTEc compounds after 377 nm nanosecond pulsed photoexcitation (λ_{obs} = 525 nm); right panels, plot of the electron transfer rate as a function of the DTEc concentration. The electron transfer rate was calculated by the relationship, electron transfer rate = $1/\tau - 1/\tau_0$, where $1/\tau$ and $1/\tau_0$ are the phosphorescence lifetimes of Irpbt in the presence of the DTEc compounds, respectively.



Figure S9. Determination of the rate constants for photoinduced electron transfer (k_{PeT}) from PDTEc to various Ir(III) complexes (Ar-saturated CH₃CN): a, Irdfppy ($\lambda_{obs} = 510$ nm); b, IrdCF3 ($\lambda_{obs} = 499$ nm); c, Irfppy ($\lambda_{obs} = 545$ nm); d, Irpbt ($\lambda_{obs} = 525$ nm); e, Irppy ($\lambda_{obs} = 582$ nm); f, Irbtp ($\lambda_{obs} = 600$ nm): Left panels, phosphorescence decay traces of 50 µM Ir(III) complex in the presence of various concentrations (0–100 µM) of PDTEc after 377 nm nanosecond pulsed photoexcitation; right panels, plot of the electron transfer rate as a function of the PDTEc concentration. The electron transfer rate was calculated by the relationship, electron transfer rate = $1/\tau - 1/\tau_0$, where $1/\tau$ and $1/\tau_0$ are the phosphorescence lifetimes of Ir(III) complexes in the presence and absence of the PDTEc, respectively.



Figure S10. Laser flash photolysis of 500 μ M PDTEc of Ar-saturated CH₃CN solutions after 426 nm nanosecond pulsed photoexcitation of 100 μ M Ir(III) complexes: a, Irdfppy; b, Irfppy; c, Irppy; d, Irbtp. Transient absorption spectra (left) and decay traces at 810 nm (right).



Figure S11. Laser flash photolysis of 500 μ M PhDTEc of Ar-saturated CH₃CN solutions after 426 nm nanosecond pulsed photoexcitation of 100 μ M Ir(III) complexes: a, IrdCF3; b, Irpbt; c, Irbtp. Transient absorption spectra (left) and decay traces at 810 nm (right).



Figure **S12**. Laser flash photolysis of 500 μ M MDTEc of Ar-saturated CH₃CN solutions after 440 nm nanosecond pulsed photoexcitation of 100 μ M Ir(III) complexes: a, Irdfppy; b, IrdCF3; c, Irfppy; d, Irpbt; e, Irbtp; f, IrOMe. Transient absorption spectra (left) and decay traces at 810 nm (right).



Figure S13. Laser flash photolysis of 500 μ M CDTEc of Ar-saturated CH₃CN solutions after 440 nm nanosecond pulsed photoexcitation of 100 μ M Ir(III) complexes: a, Irdfppy; b, IrdCF3; c, Irfppy; d, Irpbt; e, Irppy; f, Irbtp. Transient absorption spectra (left) and decay traces at 810 nm (right).



Figure S14. Laser flash photolysis of 500 μ M ADTEc of Ar-saturated CH₃CN solutions after 426 nm nanosecond pulsed photoexcitation of 100 μ M Ir(III) complexes: a, Irdfppy; b, IrdCF3; c, Irfppy; d, Irppy; e, Irbtp; f, IrOMe. Transient absorption spectra (left) and decay traces at 1000 nm (right).



Figure S15. Plots of PeCQY_{C→O} values vs $-\Delta G_{BeT}$ for photoelectrocatalytic cycloreversion of DTEc compounds by the Ir(III) complexes (1, IrOMe; 2, Irppy; 3, Irfppy; 4, Irpbt; 5, Irdfppy; 6, Irbtp; 7, IrdCF3) vs $-\Delta G_{BeT}$.



Figure S16. Plots of log k_{BeT} vs $-\Delta G_{BeT}$ for photoelectrocatalytic cycloreversion of DTEc compounds by the Ir(III) complexes. Solid lines are fits to eq 1 shown in the main text.



Figure **S17**. Determination of the rate constants for ring opening reaction (k_0) of PhDTEc^{•+} at -10 °C (a) and 0 °C (b): left, stopped flow UV–vis absorption spectra (single mixing) of 50 μ M PhDTEc after mixing with 4 equiv Cu(ClO₄)₂; right, decay traces of the 781 nm absorption band of PhDTEc^{•+}.



Figure S18. Determination of the rate constants for ring opening reaction (k_0) of PDTEC^{•+} at -10 °C (a), 0 °C (b), and 10 °C (c): left, stopped flow UV–vis absorption spectra (single mixing) of 50 μ M PDTEc after mixing with 4 equiv Cu(ClO₄)₂; right, decay traces of the 791 nm absorption band of PDTEC^{•+}.



Figure **S19**. Determination of the rate constants for ring opening reaction (k_0) of MDTEc^{•+} at $-10 \, ^{\circ}C$ (a), $0 \, ^{\circ}C$ (b), and $10 \, ^{\circ}C$ (c): left, stopped flow UV–vis absorption spectra (single mixing) of 50 μ M MDTEc after mixing with 4 equiv Cu(ClO₄)₂; right, decay traces of the 750 nm absorption band of MDTEc^{•+}.



Figure S20. Determination of the rate constants for ring opening reaction (k_0) of CDTEc⁺⁺ at -10 °C (a), 0 °C (b), and 10 °C (c): left, stopped flow UV–vis absorption spectra (single mixing) of 50 μ M CDTEc after mixing with 4 equiv Cu(ClO₄)₂; right, decay traces of the 750 nm absorption band of CDTEc⁺⁺.



Figure S21. Determination of the rate constants for ring opening reaction (k_0) of ADTEc^{•+} at -10 °C (a), 0 °C (b), and 10 °C (c): left, stopped flow UV–vis absorption spectra (single mixing) of 50 μ M ADTEc after mixing with 4 equiv Cu(ClO₄)₂; right, decay traces of the 750 nm absorption band of ADTEc^{•+}.



Figure S22. Delayed photoluminescence emission of Irfppy by back electron transfer Arsaturated CH₃CN solutions at 298 K. (a) Prompt photoluminescence spectra of 100 μ M Irfppy in the absence (blue) and presence of 100 μ M PDTEc (red) or 100 μ M ADTEc (green) under the photoexcitation at 410 nm. Slit width = 0.75 mm × 0.75 mm. (b) Delayed photoluminescence spectra of 100 μ M Irfppy in the absence (blue) and presence of 100 μ M PDTEc (red) or ADTEc (red) or ADTEc (sky blue) ca 10 s after exposure to the 410 nm photoirradiation (integration rate = 0.02 s/nm; baseline-corrected). Slit width = 5 mm × 5 mm. Slit width at the excitation compartment was kept identical throughout the measurements.



Figure S24. ¹H NMR (CDCI₃, 400 MHz) spectrum of 2.



Figure S26. ¹³C NMR (CDCl₃, 100 MHz) spectrum of ADTE.



Figure S27. ¹⁹F NMR (CDCI₃, 376 MHz) spectrum of ADTE.

Table S1. The Rate Constants for Photoinduced Electron Transfer (k_{PeT} , M^{-1} s⁻¹) from DTEc Compounds to the Ir Complexes

-		PDTEc		DTEc	MDTEc	CDTEc	ADT	Ec
-	Irpbt	4.25 × 2	10 ⁹ 5.6	61 × 10 ⁹	6.27×10^9	8.12 × 10	⁹ 9.33	× 10 ⁹
-								
		Irdfppy	IrdCF3	Irfppy	Irpbt	Irppy	Irbtp	IrOMe
PD	TEc	8.92×10^9	6.72×10^9	5.89×10^9	4.25×10^9	5.18×10^9	2.97×10^9	N.D. ^a

^aNot determined due to low phosphorescence intensity.

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