Supporting information

Ru(II) sensitizers bearing dianionic biazolate ancillaries: ligand synergy for high performance dye sensitized solar cells

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Synthesis of bipyrazole dtpzH_2: To a 100 mL reaction flash was added anhydrous THF (50 mL), sodium ethoxide (870 mg, 12.8 mmol), ethyl trifluoroacetate (1.820 g, 12.8 mmol) and 2,3-butanedione (500 mg, 5.8 mmol) at 0 °C under N_2. This mixture was stirred at RT for 24 h. The solvent was completely removed under vacuum and the residue was taken into excess of ethyl acetate. The solution was then neutralized with dilute HCl to pH ~ 4, washed with water three times, dried over $MgSO_4$ and concentrated to dryness. The residue was refluxed with 98 % of hydrazine monohydrate (1.4 mL, 29.0 mmol) in ethanol for 24 h. Flash column chromatography (ethyl acetate : hexane = 1 : 1) over silica gel and vacuum sublimation gave colorless dtpzH_2 (429 mg, 1.6 mmol, 27 %).

Selected spectral data of dtpzH_2: MS (EI), observed (actual) [assignment]: *m*/*z* 270

(270) $[M]^+$. ^{1}H NMR (400 MHz, acetone-d_6, 298K): δ 13.53 (s, 2H), 7.16 (s, 2H); ^{19}F (470 MHz, $CDCl_3$, 294 K): δ -62.74 (s, CF_3). Anal. Calcd. for $C_8H_4F_6N_4$: C, 35.57; N, 20.74; H, 1.49. Found: C, 35.78; N, 20.61; H, 1.88.

Synthesis of bitriazole dttzH_2: An ethanol solution of oxalyl dihydrazide (1.0 g, 8.5 mmol) and trifluoroacetamidine (2.4 g, 21 mmol) was refluxed for 24 h, during which a large amount of off-white solid was gradually precipitated. The solid was filtered, rinsed with water and dried under vacuum. The solid was first heated at 280 °C for 2 h for inducing the dehydration and triazole cyclization. Finally, the obtained product was subjected to vacuum sublimation at 180 °C, affording the colorless dttzH_2 (973 mg, 3.6 mmol, 42%).

Selected spectral data of dttzH_2: MS (EI), observed (actual) [assignment]: *m*/*z* 272 (272) $[M]^+$. ^{19}F (470 MHz, DMSO-d_6, 294 K): δ -65.80 (s, CF_3). Anal. Calcd. for $C_6H_2F_6N_6$: C, 26.48; N, 30.88; H, 0.74. Found: C, 26.63; N, 31.13; H, 0.87.

Synthesis of TFRS-61: A 50 mL DMF solution of [Ru(*p*-cymene)Cl_2]$_2$ (100 mg, 0.16 mmol) and 4 equiv. of ecbpy (198 mg, 0.66 mmol) was stirred at 140 ºC for 4 h. After removal of DMF solvent, dtpzH2 (88 mg, 0.33 mmol), NaOAc (268 mg, 3.27 mmol) and toluene (50 mL) was added and the mixture was refluxed for 8 h. Next, toluene was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2, washed with water, drying under vacuum, and subjected to silica gel column chromatography, eluting with a mixture of ethyl acetate and CH_2Cl_2. Finally, hydrolysis of ecbpy chelates was conducted in a mixture of acetone (20 mL) / NaOH (aq) (0.5 N, 2 mL). **TFRS-61** sensitizer was precipitated by adjusting the pH value to 3. It was collected and washed with water, diethyl ether and dried in air; yield: 104 mg, 0.12 mmol, 37 %. Other bipyrazolate derivatives, i.e. **TFRS-62 and TFRS-63**, were synthesized using the same procedures described for **TFRS-61**.

Selected spectral data of **TFRS-61**: MS (FAB), observed (actual) [assignment]: m/z

858 (858) $[M]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, 294 K): δ 9.03 (s, 2H), 8.93 (s, 2H), 7.96 (d, $^3J_{HH}$ = 6, 2H), 7.91 (d, $^3J_{HH}$ = 6, 2H), 7.82 (d, $^3J_{HH}$ = 6, 2H), 7.67 (d, $^3J_{HH}$ = 6, 2H), 6.67 (s, 2H); ^{19}F (470 MHz, d_6-DMSO, 294 K): δ -57.59 (s, CF_3). Anal. Calcd. for $C_{32}H_{18}F_6N_8O_8Ru \cdot 2\ H_2O$: C, 43.01; N, 12.54; H, 2.48. Found: C, 43.34; N, 12.34; H, 2.74.

Synthesis of TFRS-62: The ethyl ester derivative of TFRS-62 was prepared by treatment of [Ru(*p*-cymene)Cl_2]$_2$ (103 mg, 0.17 mmol) with 2 equiv. of ecbpy (101 mg, 0.34 mmol) and then with 2 equiv. of htbpy (164 mg, 0.34 mmol) in DMF, followed by reaction with dtpzH2 (91 mg, 0.34 mmol) and NaOAc (276 mg, 3.37 mmol) in refluxed toluene. After chromatographic separation on a SiO_2 column with ethyl acetate and dichloromethane, it was then hydrolyzed in acetone (20 mL) / NaOH (aq) (0.5 N, 2 mL), the desired TFRS-62 was obtained after neutralization and rinsed with deionized water and CH_2Cl_2. (140 mg, 0.13 mmol, 39%).

Selected spectral data of TFRS-62: MS (FAB), observed (actual) [assignment]: *m*/*z* 1104 (1102) $[M+2]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, 294K): δ 8.77 (s, 1H), 8.64 (s, 1H), 8.73 (s, 1H), 8.68 (s, 1H), 7.87 (br.s, 1H), 7.77 (d, $^3J_{HH}$ = 6 Hz, 1H), 7.72 (d, $^3J_{HH}$ = 6Hz, 1H), 7.62 ~ 7.49 (m, 6H), 7.32 (br.s, 1H), 6.95 (m, 2H), 6.55 (s, 1H), 6.53 (s, 1H), 2.84 ~ 2.80 (m, 4H), 1.29 ~ 1.26 (m, 16H), 0.85 ~ 0.84 (m, 6H); ^{19}F NMR (470 MHz, DMSO-d_6, 298K): δ -57.32 (s, CF_3), -57.41 (s, CF_3). Anal. Calcd. for $C_{50}H_{46}F_6N_8O_4RuS_2 \cdot 3H_2O$: C, 51.94; N, 9.69; H, 4.53. Found: C, 51.91; N, 9.61; H, 4.48.

Synthesis of TFRS-63: The ethyl ester derivative of TFRS-63 was prepared by direct treatment of [Ru(*p*-cymene)Cl_2]$_2$ (100 mg, 0.16 mmol) with ecbpy (98 mg, 0.33 mmol), and then with hSbpy (182 mg, 0.33 mmol) in DMF, followed by reaction with dtpzH2 (88 mg, 0.33 mmol) and NaOAc (268 mg, 3.30 mmol) in refluxed toluene. After chromatographic separation on a SiO_2 column with a mixture of ethyl acetate /

CH_2Cl_2 (1 / 5 V:V) as eluent, it was then hydrolyzed in a mixture of acetone (10 mL) / NaOH (aq) (0.5 N, 2 mL). The desired complex TFRS-63 was obtained after neutralization and treatment with deionized water and CH_2Cl_2. (130 mg, 0.11 mmol, 34%).

Selected spectral data of TFRS-63: MS (FAB), observed (actual) [assignment]: *m*/*z* 1166 (1166) $[M]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, 294K): δ 8.90 (s, 1H), 8.85 (s, 1H), 8.73 (s, 2H), 8.68 (d, $^3J_{HH}$ = 5.2 Hz, 1H), 7.88 ~ 7.05 (m, 5H), 7.54 ~ 7.45 (m, 3H), 7.25 (br.s, 1H), 6.95 ~ 6.90 (m, 2H), 6.61 (s, 1H), 6.58 (s, 1H), 2.89 ~ 2.80 (m, 4H), 1.70 ~ 1.60 (m, 4H), 1.41 ~ 1.30 (m, 12H), 0.92-0.81 (m, 6H); ^{19}F NMR (470 MHz, DMSO-d_6, 298K): δ -57.42 (s, CF_3), -57.50 (s, CF_3). Anal. Calcd. for $C_{50}H_{46}F_6N_8O_4RuS_4 \cdot 5H_2O$: C, 47.80; N, 8.92; H, 4.49. Found: C, 48.12; N, 8.45; H, 4.48.

Synthesis of TFRS-64: Similar to the procedures described for **TFRS-61**, the reaction of $[Ru(p\text{-cymene})Cl_2]_2$ (100 mg, 0.16 mmol) with ecbpy (196 mg, 0.65 mmol), and treatment with dttzH2 (89 mg, 0.33 mmol) in presence of NaOAc (268 mg, 3.27 mmol) afforded, after NaOH hydrolysis and acidification, a brown solid TFRS-64 (0.13 mmol, 110 mg, 39%).

Selected spectral data of TFRS-64: MS (FAB), observed (actual) [assignment]: m/z 860 (860) $[M]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, 294 K): δ 9.12 (s, 2H), 9.09 (s, 2H), 8.03 ~ 8.01 (m, 4H), 7.90 (d, $^3J_{HH}$ = 5.6, 2H), 7.75 (d, $^3J_{HH}$ = 5.6, 2H); ^{19}F (470 MHz, DMSO-d_6, 294 K): δ -61.62 (s, CF_3). Anal. Calcd. for $C_{32}H_{18}F_6N_8O_8Ru \cdot 2H_2O$: C, 43.01; N, 12.54; H, 2.48. Found: C, 43.34; N, 12.34; H, 2.74.

Synthesis of TFRS-65: Similar to the procedures described for TFRS-62, the reaction of $[Ru(p\text{-cymene})Cl_2]_2$ (100 mg, 0.16 mmol) with ecbpy (98 mg, 0.33 mmol), and with htbpy (159 mg, 0.33 mmol), followed by reaction with dttzH2 (89 mg, 0.33 mmol) in presence of NaOAc (268 mg, 3.27 mmol) afforded, after NaOH hydrolysis

and subsequent acidification, a brown solid TFRS-65 (141 mg, 0.13 mmol, 40 %).

Selected spectral data of TFRS-65: MS (FAB), observed (actual) [assignment]: m/z 1105 (1104) $[M+1]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, 294 K): δ 9.07 (s, 1H), 9.06 (s, 1H), 8.92 (s, 1H), 8.91 (s, 1H), 8.18 (d, $^3J_{HH}$ = 6 Hz, 1H), 8.10 ~ 7.90 (m, 4H), 7.80 (d, $^3J_{HH}$ = 6 Hz, 1H), 7.76 (d, $^3J_{HH}$ = 6 Hz, 1H), 7.59 (d, $^3J_{HH}$ = 6 Hz, 1H), 7.52 (d, $^3J_{HH}$ = 6Hz, 1H), 7.43 (d, $^3J_{HH}$ = 4.4Hz, 1H), 7.05 (m, 2H), 2.85 (m, 4H), 1.64 (m, 4H), 1.28 ~ 1.26 (m, 12H), 0.86 ~ 0.84 (m, 6H); ^{19}F (470 MHz, DMSO-d_6, 294 K): δ -61.62 (s, CF_3), -61.59 (s, CF_3). Anal. Calcd. for $C_{48}H_{44}F_6N_{10}O_4RuS_2$: C, 52.21; N, 12.69; H, 4.02. Found: C, 51.90; N, 12.77; H, 3.96.

Synthesis of TFRS-66: Similar to the procedures described for TFRS-63, the reaction of [Ru(*p*-cymene)Cl_2]$_2$ (100 mg, 0.16 mmol) with ecbpy (98 mg, 0.33 mmol) and hSbpy (182 mg, 0.33 mmol) in DMF, followed by treatment with dttzH2 (88 mg, 0.33 mmol) in presence of NaOAc (278 mg, 3.40 mmol) in toluene afforded, after chromatographic separation, neutralization and acidification, a brown TFRS-66 (148 mg, 0.13 mmol, 41%).

Selected spectral data of TFRS-66: MS (FAB), observed (actual) [assignment]: m/z 1169 (1168) $[M+1]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, 294 K): δ 9.08 (s, 1H), 9.06 (s, 1H), 8.93 (s, 1H), 8.92 (s, 1H), 8.17 (d, $^3J_{HH}$ = 6 Hz, 1H), 8.01 ~ 7.96 (m, 4H), 7.80 (d, $^3J_{HH}$ = 6 Hz, 2H), 7.64 (d, $^3J_{HH}$ = 6 Hz, 1H), 7.55 (d, $^3J_{HH}$ = 6 Hz, 1H), 7.47 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.31 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.30 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 2.96 (m, 4H), 1.58 (m, 4H), 1.37 ~ 1.22 (m, 12H), 0.86 ~ 0.84 (m, 6H); ^{19}F (470 MHz, DMSO-d_6, 294 K): δ -61.53 (s, CF_3), -61.61 (s, CF_3). Anal. Calcd. for $C_{48}H_{44}F_6N_{10}O_4RuS_4$: C, 49.35; N, 11.99; H, 3.80. Found: C, 49.09; N, 12.27; H, 3.90.

For TD-DFT calculations, the absorption bands (singlet state excitation) of **TFRS-61** and **TFRS-64** (Figure 2a), **TFRS-62** and **TFR-65** (Figure 2b), **TFRS-63** and **TFRS-66** (Figure S1) 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 mainly involve MLCT.

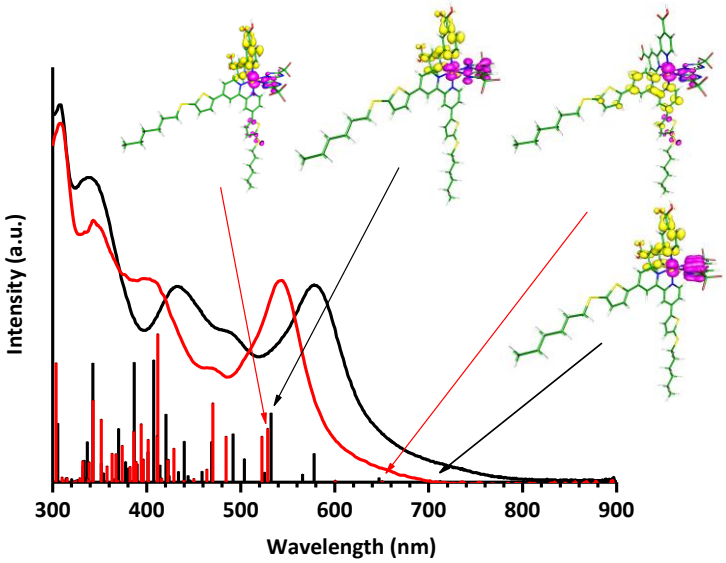

Figure S1. The experimental absorption spectra and the associated TD-DFT calculated absorption wavelengths of **TFRS-63** (black) and **TFRS-66** (red). The vertical lines represent the calculated energy and the relative intensity of the singlet state excitations. Also depicted are the frontier orbitals contributed to the major transition (occupied orbitals in pink and unoccupied orbitals in yellow).

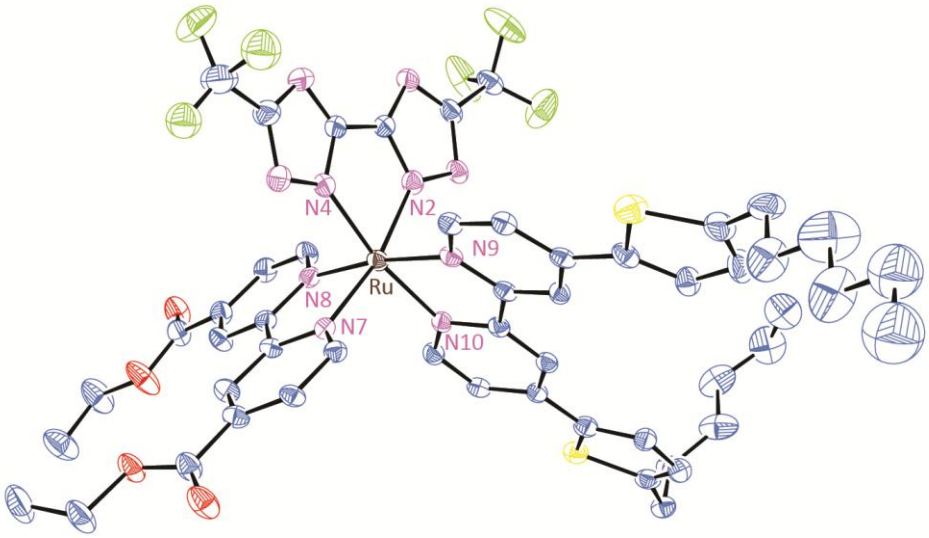

Figure S2. ORTEP diagram of complex **TFRS-65OEt.**

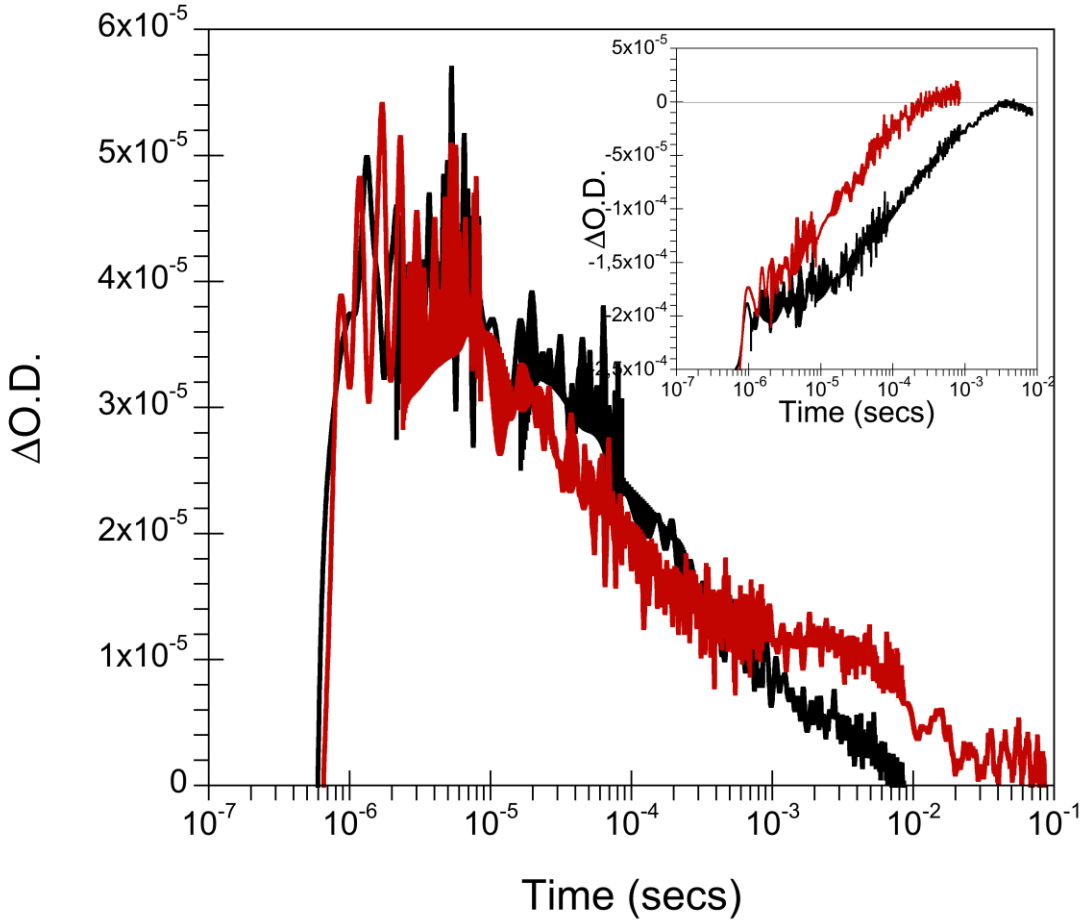

Figure S3. Transient absorption kinetics of a **TFRS-61** transparent TiO_2 DSC device in the presence (red) and absence (black) of iodide/tri-iodide red/ox couple. In the main panel kinetics were recorded at 800nm and in the insets at 550nm. In all cases kinetics were recorded following excitation at 500nm and under 1 sun illumination intensity.

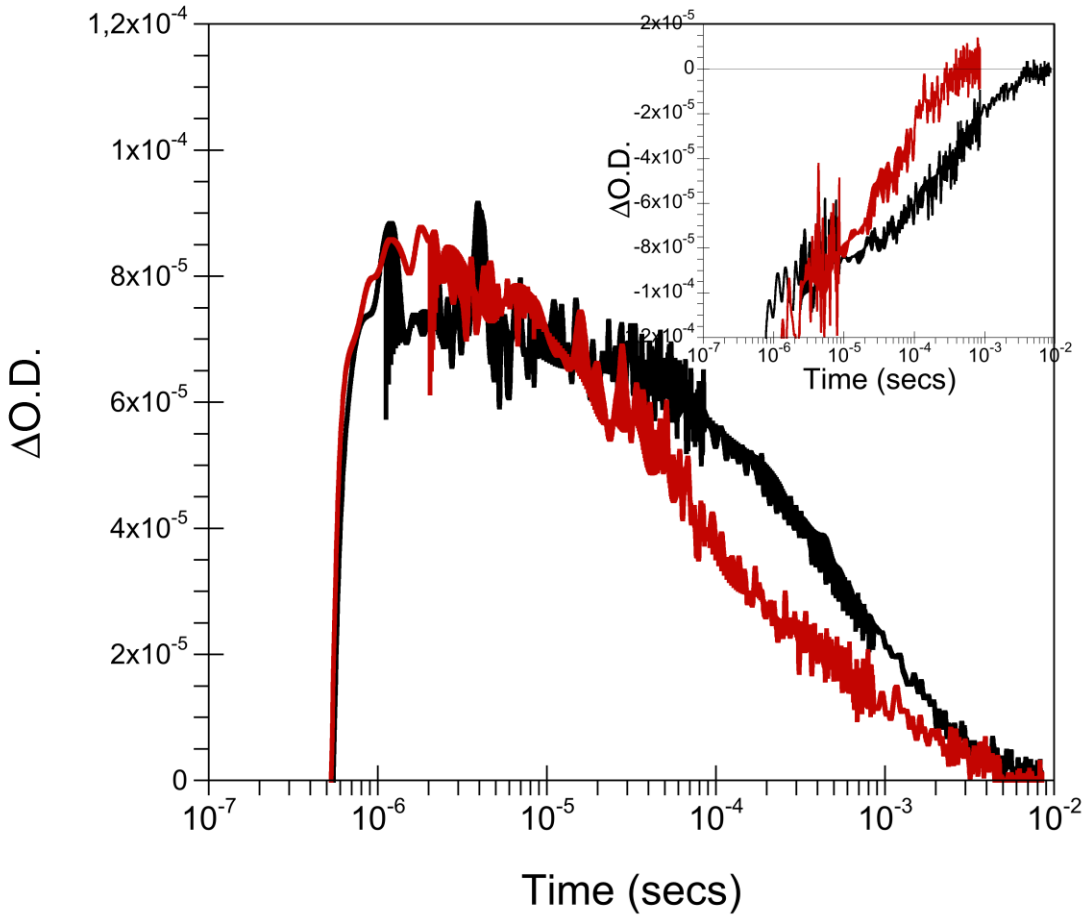

Figure S4. Transient absorption kinetics of a **TFRS-62** transparent TiO_2 DSC device in the presence (red) and absence (black) of iodide/tri-iodide red/ox couple. In the main panel kinetics were recorded at 800nm and in the insets at 550nm. In all cases kinetics were recorded following excitation at 500nm and under 1 sun illumination intensity.

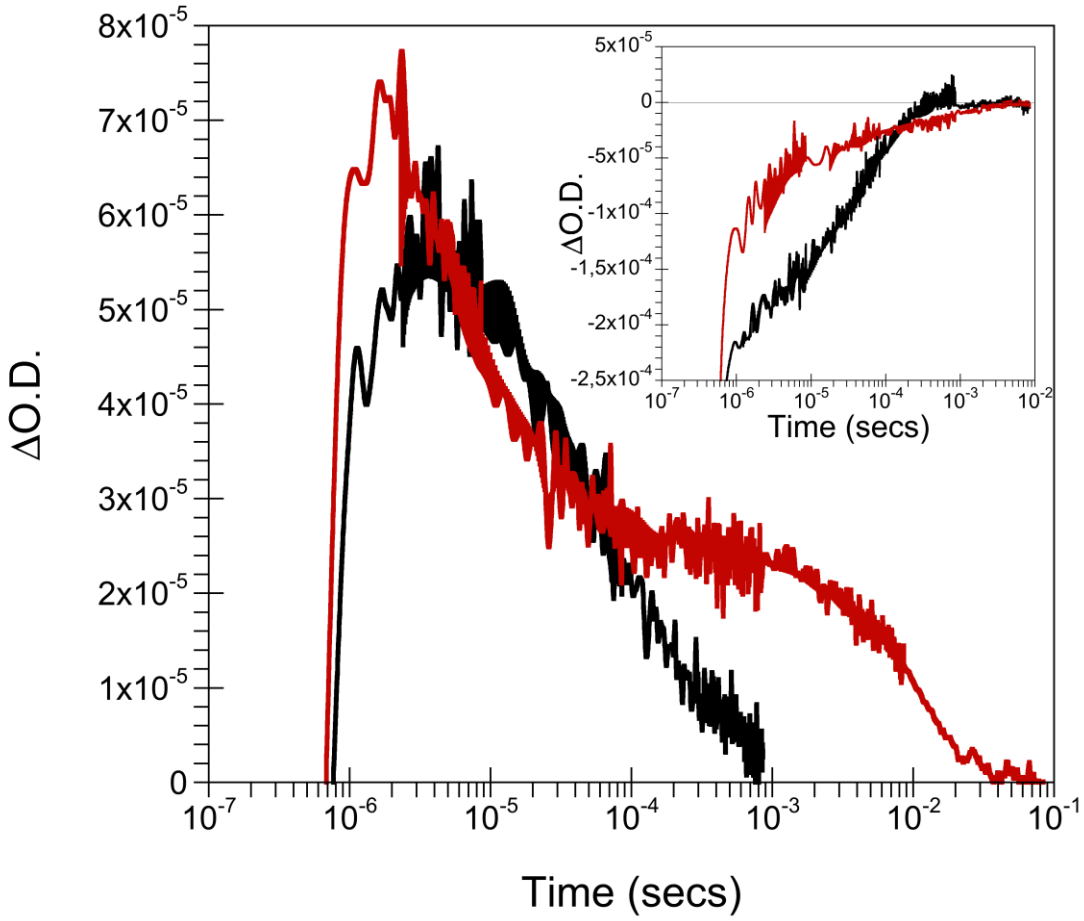

Figure S5. Transient absorption kinetics of a **TFRS-64** transparent TiO_2 DSC device in the presence (red) and absence (black) of iodide/tri-iodide red/ox couple. In the main panel kinetics were recorded at 800nm and in the insets at 550nm. In all cases kinetics were recorded following excitation at 500nm and under 1 sun illumination intensity.

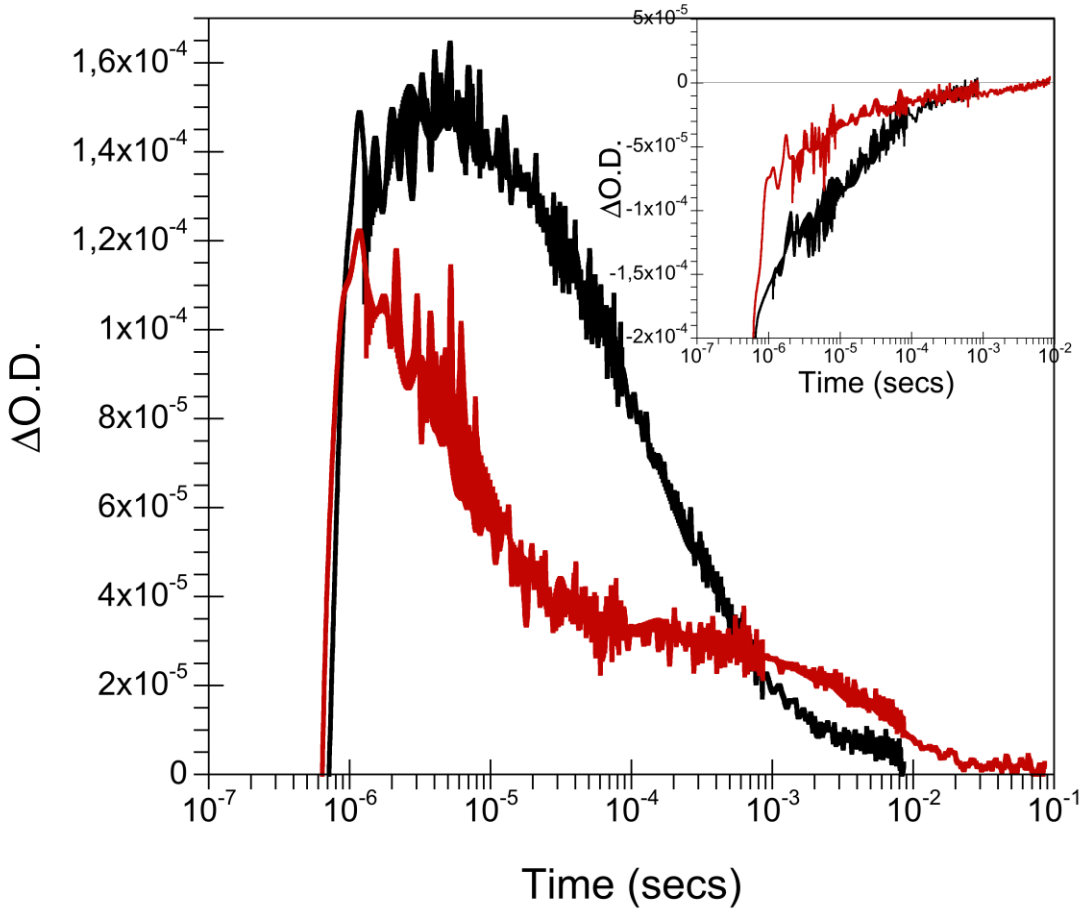

Figure S6. Transient absorption kinetics of a **TFRS-65** transparent TiO_2 DSC device in the presence (red) and absence (black) of iodide/tri-iodide red/ox couple. In the main panel kinetics were recorded at 800nm and in the insets at 550nm. In all cases kinetics were recorded following excitation at 500nm and under 1 sun illumination intensity.

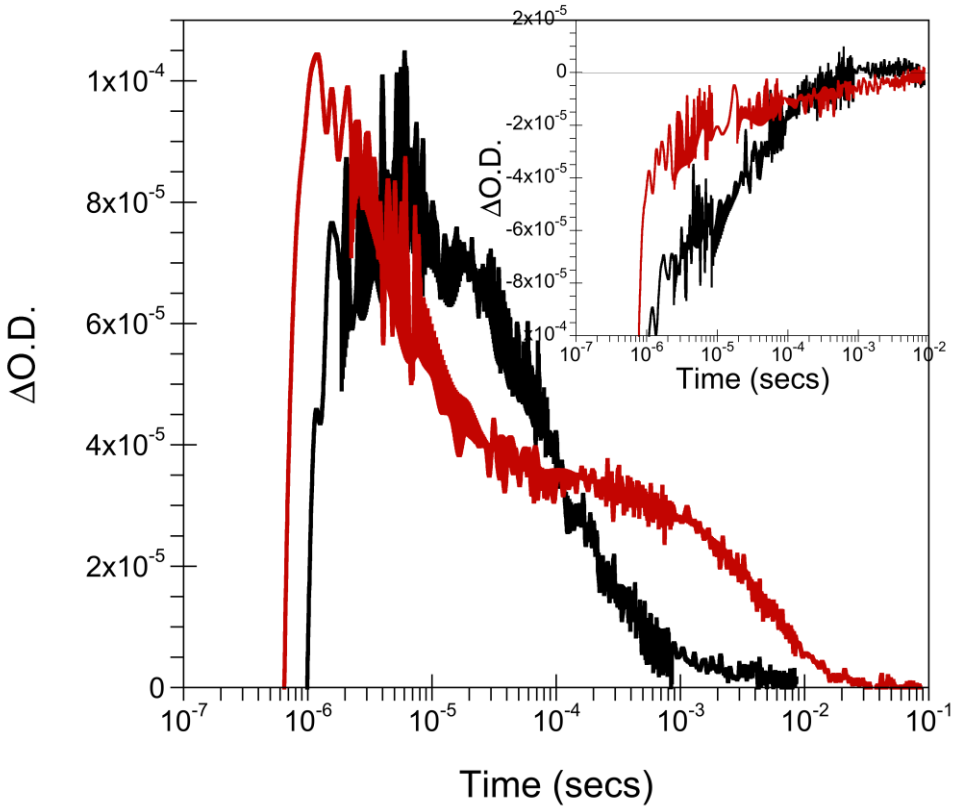

Figure S7. Transient absorption kinetics of a **TFRS-66** transparent TiO_2 DSC device in the presence (red) and absence (black) of iodide/tri-iodide red/ox couple. In the main panel kinetics were recorded at 800nm and in the insets at 550nm. In all cases kinetics were recorded following excitation at 500nm and under 1 sun illumination intensity.