Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information: Modulating electron injection from an organic dye to a titania nanoparticle with a photochromic energy transfer acceptor

George Vamvounis,[a] Christopher R. Glasson,[a] Evan J. Bieske[b] and Viktoras Dryza[b*]

[a]College of Science, Technology and Engineering, James Cook University, Queensland 4811, Australia.

[b]School of Chemistry, The University of Melbourne, Victoria, Australia 3010.

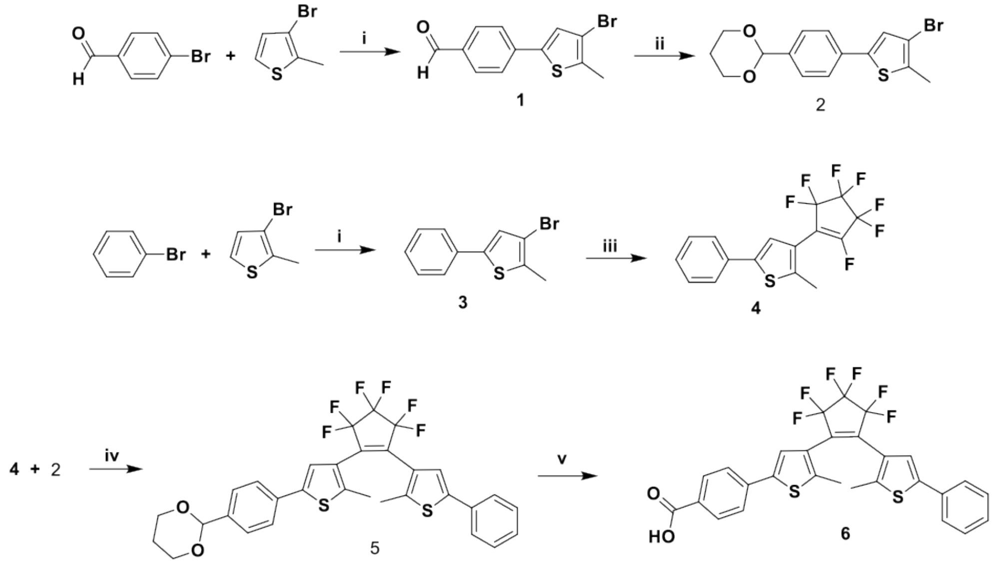
E-mail: vdryza@unimelb.edu.au

S1. Synthesis of DTE.

S1.1: Materials. 4-bromobenzaldehyde (Sigma Aldrich), 3-bromo-2-methylthiophene (Combi Blocks), palladium acetate (Sigma Aldrich), potassium carbonate (Univar), pivalic acid (Sigma Aldrich), dimethylacetamide (Sigma Aldrich), propandiol (Sigma Aldrich), p-toluenesulfonic acid (Sigma Aldrich), toluene (Univar), n-butyllithium (Sigma Aldrich), tetrahydrofuran (Unichrome), octafluorocyclopentene (Synquest Labs) were used as received.

S1.2: Characterisation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AscendTM 400 MHz spectrometer or a Varian 300 MHz. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak (chloroform, ^{1}H = 7.26 ppm and ^{13}C = 77 ppm). Coupling constants (J) are quoted in Hertz (Hz) and quoted to the nearest 0.5 Hz. Peak multiplicities are described in the following manner: singlet (s), doublet (d), multiplet (m). Infrared spectra of the neat materials were recorded using a

Nicolet 6700 FT-IR spectrometer equipped with an attenuated total reflection (ATR) crystal. Electrospray ionisation (ESI) mass spectra were recorded in negative ion mode using an Agilent 6520 Q-TOF, with acetonitrile used as the solvent.



Scheme: Synthetic route to carboxylate functionalised dithienylethene (**6**). Reagents and conditions: (i) $Pd(OAc)_2$, K_2CO_3, pivalic acid, dimethylacetamide, 100 °C, Ar, 18 h. (ii) 1,3-propandiol, p-toluenesulfonic acid, toluene, reflux, overnight. (iii) n-butyllithium (1.45 M), tetrahydrofuran, -78 °C; then octafluorocyclopentene, -78 °C to room temperature overnight. (iv) **4**, n-butyllithium (1.45 M), tetrahydrofuran, -78 °C; then **2**, -78 °C to room temperature overnight. (v) acetone, Jones reagent, 5 h.

S1.3: Synthetic methodology. 4-(4-Bromo-5-methyl-thiophen-2-yl)-benzaldehyde (**1**):[1] A stirred solution of 2-methyl-3-bromothiophene (3.54 g, 20 mmol), 2-bromobenzaldehyde (3.70 g, 20 mmol), pivalic acid (0.80 g, 8 mmol) and potassium carbonate (6.60 g, 48 mmol) in dimethylacetamide (40 cm^3) was purged with argon for 20 min. To this solution palladium acetate (0.122 g, 4 mol) was added prior to purging for a further 5 min. The reaction mixture was heated at 100 °C for 18 h then allowed to cool to room temperature. Water (200 cm^3) was added to the reaction mixture prior to extracting with diethyl ether (2 x 150 cm^3). The combined ether extract was washed with brine (2 x 100 cm^3) and dried over Na_2SO_4 prior to the removal of the solvent. The product was purified by column chromatography over silica gel with a 1:1 mixture of petroleum ether / dichloromethane as eluent to afforded the product as a white solid (3.18 g, 57 %). ν_{max} (neat)/cm^{-1} 2915, 2838, 2744, 1686, 1600, 1434, 1386, 1287, 1155, 1020, 980, 872, 785, 681; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.45 (s, ^{3}H), 7.27 (s, ^{1}H), 7.66 (d, J = 8.0 Hz, ^{2}H), 7.88 (d, J = 8.0 Hz, ^{2}H), 10.00 (s, ^{1}H).

3-Bromo-5-(4-(2,6-dioxolanyl)phenyl)-2-methylthiophene (2): A stirred solution of **1** (3.18 g, 11.3 mmol), 1,3-propandiol (1.72 g, 23.0 mmol) and p-TsOH (0.10 g, 5 mol%) in toluene (40 cm^3) was heated at reflux overnight using a Dean Stark apparatus. The toluene was then removed under reduced pressure and the resulting residue taken up in diethyl ether (150 cm^3). The ether solution was washed with water (100 cm^3) and brine (100 cm^3) prior to drying over Na$_2$SO$_4$ and removal of the solvent under vacuum. The product was purified with column chromatography on silica gel by elution with petroleum ether / DCM (4:1) to afford **2** as a white solid (3.3 g, 87 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.45 (s, ^{1}H), 2.17-2.30 (m, ^{1}H), 2.41 (s, ^{3}H), 3.96-4.03 (m, ^{2}H), 4.25-4.30 (m, ^{2}H), 5.50 (s, ^{1}H), 7.11 (s, ^{1}H), 7.46-7.52 (m, ^{4}H).

3-Bromo-2-methyl-5-phenylthiophene (**3**):[2] A stirred solution of 2-methyl-3-bromothiophene (3.54 g, 20 mmol), bromobenzene (3.14 g, 20 mmol), pivalic acid (0.80 g, 8 mmol) and potassium carbonate (6.60 g, 48 mmol) in dimethylacetamide (40 cm^3) was purged with argon for 20 min. To this solution palladium acetate (0.122 g, 4 mol) was added prior to purging for a further 5 min. The reaction mixture was heated at 100 °C for 18 h then allowed to cool to room temperature. Water (200 cm^3) was added to the reaction mixture prior to extracting with diethyl ether (2 x 150 cm^3). The combined ether extract was washed with brine (2 x 100 cm^3) and dried over Na$_2$SO$_4$ prior to the removal of the solvent. The product was purified by column chromatography over silica gel using petroleum ether as the eluent to afford **3** as a white solid (2.9 g, 58 %). ν_{max} (neat)/cm^{-1} 2915, 2838, 2744, 1686, 1599, 14910, 1434, 1386, 1320, 1287, 1251, 1183, 1156, 1020, 980, 872, 785, 685; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.42 (s, ^{3}H), 7.11 (s, ^{1}H), 7.28-7.30 (m, ^{1}H), 7.34-7.39 (m, ^{2}H), 7.49-7.52 (m, ^{2}H).

1-(2-methyl-5-phenylthiophen-3-yl)perfluorocyclopentene (**4**):[3] n-butyllithium (9.00 cm^3, 1.45 M) was added dropwise to a stirred solution of **3** (3.00 g, 12 mmol) in dry THF (100 cm^3) at -78 °C. The reaction was allowed to stir for 30 minutes prior to rapid addition of octafluorocyclopentene (4.8 cm^3, 32 mmol). This reaction mixture was allowed to stir for 2 h at -78 °C prior to slowly warming to room temperature overnight. The THF was removed under vacuum and the resulting residue taken up in diethyl ether (200 cm^3). This ether solution was consecutively washed with water (100 cm^3) and brine (2 x 100 cm^3) prior to drying over Na_2SO_4 and the removal of the solvent under vacuum. The product was purified by column chromatography on silica gel eluting with petroleum ether to afford **4** as a viscous oil (2.45 g, 56 %). ν_{max} (neat)/cm^{-1} 2915, 2838, 2744, 1686, 1600, 1599, 1580, 1490, 1434, 1386, 1288, 1156, 1020, 980, 872, 785, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (d, J = 3.0 Hz, ^{3}H), 7.24 (s, ^{1}H) 7.29-7.34 (m, ^{1}H), 7.37-7.41 (m, ^{2}H), 7.53-7.56 (m, ^{2}H).

1-(2-methyl-5-phenylthiophen-3-yl)-2-(5-(4-(2,6-dioxolanyl)phenyl)-2-methylthiophen-3-yl)perfluorocyclopentene (5): n-Butyllithium (1.51 cm^3, 1.45 M) was added dropwise to a stirred solution of **4** (0.75 g, 2.20 mmol) in dry THF (20 cm^3) at -78°C. The reaction was allowed to stir for 30 minutes prior to the dropwise addition of **2** (0.75 g, 2.42 mmol) in THF (5 cm^3). This reaction mixture was allowed to stir for 2 h at -78°C prior to slowly warming to room temperature overnight. The THF was removed under vacuum and the resulting residue taken up in diethyl ether (150 cm^3). This ether solution was consecutively washed with water (100 cm^3) and brine (100 cm^3) prior to drying over Na_2SO_4 and the removal of the solvent under vacuum. The product was purified by column chromatography on silica gel eluting with petroleum ether / DCM (1:1) to afford **5** as a pale blue solid (830 mg, 67 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.46 (m, ^{1}H), 1.96 (s, 6H), 2.16-2.32 (m, ^{1}H), 3.96-4.05 (m, ^{2}H), 4.25-4.31 (m, ^{2}H), 5.51 (s, ^{1}H), 7.27 (s, ^{2}H) 7.29-7.32 (m, ^{1}H), 7.35-7.41 (m, ^{2}H), 7.47-7.55 (m, ^{6}H).

1-(2-methyl-5-phenylthiophen-3-yl)-2-(5-(4-carboxylylphenyl)-2-methylthiophen-3-yl) perfluorocyclopentene (**6**): To a solution of **5** (0.41 g, 0.75 mmol) in acetone (20 cm^3), Jones reagent* (5.5 cm^3, 2.2 mmol) was added dropwise at room temperature. The reaction was quenched by the addition of propan-2-ol (2 cm^3). The acetone was then removed under vacuum and the aqueous residue taken up in diethyl ether (150 cm^3). The organic solution was then washed with water (2 x 100 cm^3) prior to drying over Na_2SO_4 and the removal of the solvent under vacuum. The product was purified by column chromatography on silica gel eluting with ethyl acetate / petroleum ether (1:4) to afford **6** as a pale blue solid (175 mg, 41 %). ν_{max} (neat)/cm^{-1} 2915, 2838, 2744, 1686, 1599, 1490, 1434, 1386, 1287, 1251, 1184, 1156, 980, 872, 785, 700; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, ^3H), 1.98 (s, ^3H), 7.05 (s, ^1H), 7.27-7.31 (m, ^2H), 7.35-7.39 (m, ^2H), 7.44-7.48 (m, ^2H), 7.52-7.58 (m, ^3H), 7.93-7.95 (m, ^1H); 13C NMR (100 MHz) δ 171,143, 143, 141, 141, 138, 133, 130, 129, 129, 128, 128, 126, 126, 126, 125, 124, 122, 32, 30, 15, 15; m/z (ESI: negative ion mode) 563.05 (100%), 564.06 (23%), 565.05 (9%), 566.06 (2%); $C_{28}H_{17}F_6O_2S_2$ requires 563.06 (100%), 564.06 (32%), 565.05 (9%), 565.06 (4%), 566.06 (3%); Found: C, 59.29; H, 3.29; $C_{28}H_{18}F_6O_2S_2$ requires C, 59.57; H, 3.21.

* Jones Reagent Preparation: A 3:1 ratio with respect to [H^+] and [$Cr_2O_7{}^{2-}$] was prepared in the following manner. To a solution of potassium dichromate (2.94 g, 10 mmol) in distilled water (20 cm^3) concentrated sulfuric acid (2.94 g; 1.6 cm^3; 30 mmol) was carefully added while keeping the temperature at room temperature or below. This solution was transferred quantitatively to a volumetric flask (25 cm^3) and made up to 25 cm^3 with distilled water.

S2. Experimental spectroscopic procedure.

The D35 organic dye sensitiser and chenodeoxycholic acid coadsorbent (CDCA) were sourced from Dyenamo and Sigma-Aldrich, respectively. The photochromic DTE dye was synthesised as described above. The structures of these molecules are shown in Figure 1. Dye solutions containing 0.2 mM D35, 0.2 mM DTE, and 4 mM CDCA were prepared in acetonitrile:tert-butanol (1:1 v/v). Sensitising solutions with a D35:DTE:CDCA ratio of 1:1:50 were made using 0.20 mL of the D35 solution, 0.20 mL of the DTE solution, and 0.50

mL of the CDCA solution. The dye-sensitised nanoparticle (NP) samples were prepared by adding 10 mg of zirconia (NanoAmor, ZrO_2, 3% Y_2O_3 stabilised, spherical, 20-30 nm) or 10 mg titania (Sigma Aldrich, TiO_2 , anatase, spherical, < 25 nm) NPs to the sensitising solution and then sonicating for 30 min. The solutions were then centrifuged, with the excess solution removed, followed by the addition of 1mL acetonitrile:tert-butanol solution and 10 minutes sonication. This cycle was repeated again to remove any dye not bound to the NP surface. Samples with only the D35 or DTE dye attached were prepared as above using sensitising solutions containing only a single dye with the coadsorbent. The absorption spectra of the sensitising solution were recorded before and after reaction with the NPs, and show that ∼95% of both the D35 and DTE dyes were adsorbed. We calculated each dye to have a surface coverage of ∼0.05 molecules/nm^2.

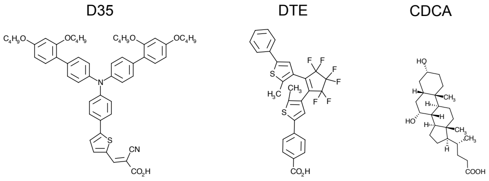


Figure 1: Structures of the D35 organic dye sensitiser, photochromic DTE dye, and inert CDCA coadsorbent.

Absorption spectra of the samples were obtained by placing several drops of the prepared NP solution on a sample holder, followed by air drying and examination with diffuse reflectance absorption spectroscopy (Thermo Scientific Evolution 220 Spectrophotometer). The bare zirconia NPs were used as a baseline reference for the spectra. Fluorescence measurements of the samples were obtained by placing a few drops of the prepared NP solution on a glass slide, followed by air drying. The slide was then inserted into a vacuum chamber containing 50 Torr of nitrogen buffer gas, which collisionally cooled the laser-heated molecules.

For dispersed emission experiments, the samples were excited with a laser beam ($\tau \sim 5$ ns, $f = 10$ Hz, ∼5 mW/cm^2, 20 sec) from a tunable optical parametric oscillator (Opotek Vibrant), with the emission collected by a F/1 lens and sent to a spectrometer (Jobin Yvon, Triax 552) interfaced with a cooled, 2-dimensional, charge-coupled device detector (Jobin Yvon, Symphony). For the time-correlated single photon counting (TCSPC) experiments, the samples were excited with a laser beam ($\tau \sim 12\,\text{ps}$, $f = 82\,\text{MHz}$, $\sim 5\,\text{mW/cm}^2$) from a 532 nm, picosecond, diode-pumped Nd:YAG laser (Time Bandwidth Products, Cheetah-X), with the emission collected by a F/1 lens and passed through a 580-630 nm band pass filter and sent to a cooled photomultiplier tube (Becker and Hickl, PMC-100) connected to a TCSPC card (Becker and Hickl, SPC-630). To record the instrument response function (IRF), the elastically scattered light was monitored.

The time-resolved fluorescence decay curves were fitted using a stretched exponential decay function convoluted with the IRF (FAST software, Edinburgh Photonics):

$$I(t) = I_0 e^{-(\frac{t}{\tau_c})^\beta}, \tag{1}$$

where I_0 is the initial intensity, τ_c is the characteristic lifetime, and β is the dispersion parameter. Fitted parameters were used to determine the average lifetime, τ:

$$\tau = \frac{\tau_c}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

$$\Gamma\left(\frac{1}{\beta}\right) = \int_0^\infty x^{\frac{1}{\beta}-1} e^{-x}\, \mathrm{d}x$$

The stretched exponential function is used because the fluorescence decays of dye sensitizers on metal oxide surfaces are nonexponential due to the disordered nature of the dye/surface interface (e.g., surface inhomogeneities, different dye binding modes), with the β parameter accounting for this distribution.[4] Furthermore, the stretched exponential function can fit non-exponential decays with a limited number of variable parameters, leading to a reliable and systematic approach for analysing the data. The derived τ values are proportional to the integrated areas under the fluorescence decay curves (once deconvoluted for the IRF).

An estimate of the Förster Resonance Energy Transfer (FRET) quantum yield (Φ_{FRET}) for the D35+DTE-Zr sample can be made using the τ values for the D35 donor dye in the absence (τ_{D35}) and presence ($\tau_{D35+cDTE}$) of the UV-activated c-DTE acceptor dye:

$$\Phi_{FRET} = \frac{k_{FRET}}{k_R + k_{IC} + k_{FRET}} \approx 1 - \frac{\tau_{D35+cDTE}}{\tau_{D35}} \tag{2}$$

Similarly, an estimate of the electron injection quantum yield (Φ_{inj}) can be made using τ values for the D35 dye on the insulating zirconia NPs (τ_{ZrO_2}) and on the injecting titania NPs (τ_{TiO_2}):

$$\Phi_{inj} = \frac{k_{inj}}{k_R + k_{IC} + k_{inj}} \approx 1 - \frac{\tau_{TiO_2}}{\tau_{ZrO_2}} \tag{3}$$

This approach assumes that radiative and internal conversion rates for D35 on zirconia NPs are the same on titania NPs.

UV irradiated samples were exposed to collimated, continuous-wave 365 nm light ($\sim$20 mW/cm^2) from a light-emitting diode (M365L2-C1, Thorlabs) for a total time of either 5 sec or 40 sec. Photos of the D35+DTE-Ti sample, before and after UV irradiation for 40 sec are shown in Figure 2. For the fluorescence experiments, a dichroic mirror (DMLP425, Thorlabs) was employed so that the area of the sample probed by both the UV and visible light remained constant throughout the experiment.

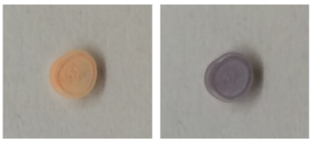


Figure 2: Photos of the D35+DTE-Ti sample before (left) and after (right) UV irradiation.

For the c-DTE →o-DTE kinetic recovery experiments, the emission of the sample was collected (λ_{ex} = 440 nm, $\sim$5 mW/cm^2, 20 sec), followed by UV irradiation (λ_{ex} = 365 nm, $\sim$20 mW/cm^2, 40 sec), followed by repeated emission collection (λ_{ex} = 440 nm, $\sim$5 mW/cm^2, 20 sec) and visible irradiation (λ_{ex} = 440 nm or 560 nm, $\sim$15 mW/cm^2, 600 sec). The kinetic data were fitted using a modified single exponential function:

$$I(t) = 1 - (I_b + [I_a e^{-(k_{c\to o} t)}]) \tag{4}$$

where the parameters are shown in Figure 3.

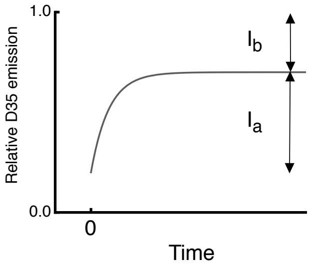


Figure 3: Parameters used for fitting the recovery kinetics of the D35 emission band's integrated area under visible irradiation following UV irradiation for 40 sec.

For the reversible o-DTE ↔ c-DTE switching experiments, the following cycle was applied: emission collected ($\lambda_{ex} = 440$ nm, $\sim$5 mW/cm^2, 20 sec), UV irradiation ($\lambda_{ex} = 365$ nm, $\sim$20 mW/cm^2, 40 sec), emission collected ($\lambda_{ex} = 440$ nm, $\sim$5 mW/cm^2, 20 sec), visible irradiation ($\lambda_{ex} = 560$ nm, $\sim$15 mW/cm^2, 2.5 hrs).

S3. Absorption spectra.

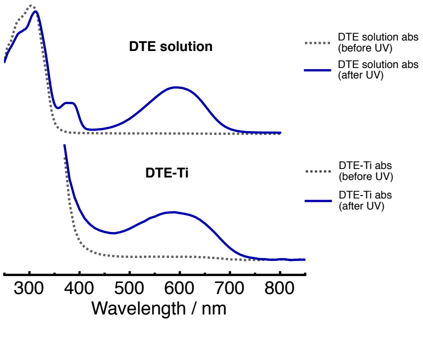


Figure 4: Absorption spectra of DTE in acetonitrile:tert-butanol solution (top panel) and the DTE-Ti sample (bottom panel), before and after UV irradiation.

S4. Time-resolved fluorescence decay curves.

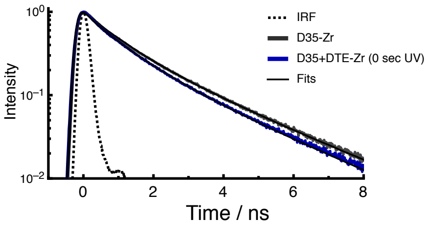


Figure 5: Fluorescence decay curves of D35 for the D35-Zr and D35+DTE-Zr (before UV irradiation) samples, with $\tau_{D35} = 1.13$ ns and 1.08 ns, respectively. The slightly shorter τ_{D35} value for D35+DTE-Zr is believed to be due to FRET involving a small population of c-DTE that is initially present before UV irradiation.

S5. Molecular orbital energy levels.

The alignment of the HOMO and LUMO for the D35 dye and ring-open and ring-closed isomers of the DTE dye with the titania conduction band are shown in Figure 6. The data were calculated using the oxidation potentials reported for the dyes and the $S_1 \leftarrow S_0$ origin transition energies,[5–8] which are estimated from the intersection of the normalised absorption and emission bands. Because no emission data is available for o-DTE, we use the onset of the $S_1 \leftarrow S_0$ absorption band.

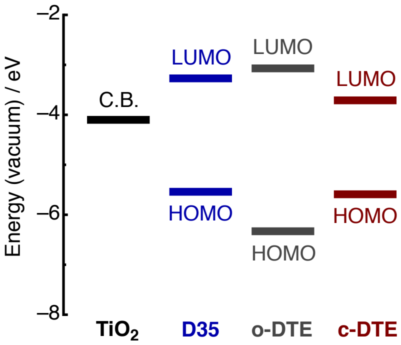


Figure 6: Energies for the conduction band edge of titania and the HOMO and LUMO of the D35 dye and the o-DTE and c-DTE isomers.

S6. Photoisomerisation efficiency.

Based on the solution-phase extinction coefficients reported for the $S_1 \leftarrow S_0$ absorption bands of the o-DTE (35600 $M^{-1}cm^{-1}$) and c-DTE (15600 $M^{-1}cm^{-1}$) isomers (without the carboxylic acid group),[9] if the isomeric population is initially entirely o-DTE and UV irradiation results in complete conversion to c-DTE, the absorption bands should have an intensity ratio of 1:0.44.

From the DTE-Zr absorption spectra recorded before UV irradiation and at the photostationary state, the o-DTE:c-DTE absorption bands' intensity ratio is 1:0.55. Although the presence of the carboxylic acid group and the binding interaction with the surface will slightly alter the extinction coefficients in our experiment, the spectra indicate essentially all the o-DTE is converted to c-DTE at the photostationary state. This is not surprising, with a conversion efficiency of 97% observed in solution, which is primarily driven by the much larger photoisomerisation quantum yield for ring closing (0.59) compared to ring opening (0.01).[9]

S7. Switching fatigue.

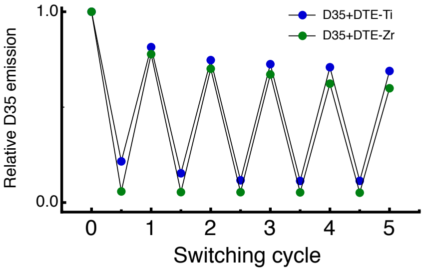


Figure 7: Relative intensity of the D35 emission ($\lambda_{ex} = 440\,\text{nm}$) for the D35+DTE-Zr and D35+DTE-Ti samples when switching between o-DTE and c-DTE dominant populations using UV and visible light irradiation cycles.

S8. Estimation of the Förster distance.

The Förster distance is the separation between a donor-acceptor pair where $\Phi_{FRET} = 0.50$.

A theoretical calculation of R_0 can be made using the parameters that dictate the FRET efficiency for a donor-acceptor pair: the donor's fluorescence quantum yield (Φ_R), the degree of overlap between the donor's emission and acceptor's absorption spectra, i.e., overlap integral (J), the relative alignment of the donor and acceptor's transition dipole moments, i.e., orientation factor (κ^2), and refractive index of the host medium (n):[10]

$$R_0 = 0.0211 \times (n^{-4} \Phi_R J \kappa^2)^{1/6} \tag{5}$$

The overlap integral (J) is calculated by:

$$J = \int_0^\infty F_D(\lambda)\,\varepsilon_A(\lambda)\,\lambda^4 \mathrm{d}\lambda$$

where λ is the wavelength of light, $F_D(\lambda)$ is the intensity of the fluorescence spectrum of the donor at that wavelength (when the integral of the donor's fluorescence band is normalised), and $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor at that wavelength.

We have previously estimated the Φ_R of the FRET donor D35 to be 0.41 when attached to a zirconia surface.[11] For the calculation of J, the molar extinction coefficient used for the c-DTE FRET acceptor is $15600\,\mathrm{M^{-1}cm^{-1}}$, which is the value reported for the DTE dye without the carboxylic acid group.[9] For κ we use 0.476, recommended for randomly distributed, but static donor-acceptors,[10] with n being 1.68.[11] The D35+c-DTE pair is calculated to have $R_0 = 3.9\,\mathrm{nm}$.

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