

Supporting Information for

Connectivity pattern modifies excited state relaxation dynamics of fluorophore-photoswitch molecular dyads

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Procedural Methods

All procedures linked to photochemistry were performed using spectrophotometric grade solvents. UV/vis absorption spectroscopy was performed on a Varian Cary 60 UV/vis spectrophotometer equipped with a Peltier thermostated cell holder at 25 ± 0.05 °C if not indicated otherwise. Analytical irradiation was performed employing an Oriel illumination setup consisting of a 500 W mercury arc lamp (model 68810) in an universal arc lamp housing (model 66055) equipped with an $\frac{1}{4}$ mm grating monochromator (model 77200), a timed shutter and water filter either at 313 nm for ring-closure or at 546 nm for ring-opening reactions or on a 1000 W xenon arc lamp (model 66924) using a timed shutter, water filter, and various cut-off filters. The lamp output beam was wired into the spectrophotometer orthogonal to the beamline of the respective spectrophotometer employing fiber-optics to enable simultaneous irradiation and probing. PSS compositions were determined either by NMR characterization or by ultraperformance liquid chromatography (UPLC) analyses using integration of the UV signal at the wavelengths of the isosbestic points. Irradiation of compounds for NMR analysis was performed in a Rayonet RPR 100 photochemical reactor equipped with 313 nm lamps. Fluorescence spectroscopy was performed on a Cary Eclipse Fluorescence spectrometer, and a Jasco FP-8500 spectrofluorometer. A slit width of 1 nm for excitation and 2.5 nm for emission was used. PMT voltage was set to 600 V. Emission spectra were baseline corrected and the absorption of the excitation light, the reabsorption and the wavelength-dependent instrument sensitivity were taken into account.

Relative quantum efficiencies of fluorescence were obtained by comparing the areas under the corrected emission spectrum of the test sample in various solvents with that of oxazine 170 (0.58 in MeOH)¹, respectively. Dilute solutions (OD < 0.1) were used to minimize reabsorption effects. Fluorescence quantum yields were determined using the following equation²:

$$\phi_X = \phi_S \frac{I_X \cdot A_S}{I_S \cdot A_X} \cdot \left(\frac{\eta_X}{\eta_S}\right)^2 \quad (1)$$

Where ϕ_S stands for the reported quantum yield of the standard, I stands for the integrated emission spectra, A stands for the absorbance at the excitation wavelength and η stands for the refractive index of the solvent being used. X subscript stands for the test sample, and S subscript stands for the standard.

Förster radii R_0 were calculated using the equation described in reference 3.

$$\frac{R_0}{nm} = 0.02108 \cdot \sqrt[6]{\frac{\kappa^2 \cdot \Phi_{Fl}}{n^4} \cdot \frac{\int_0^\infty F_D(\lambda) \cdot \varepsilon_A(\lambda) \cdot \lambda^4 d\lambda}{mol^{-1} dm^3 cm^{-1} nm^4}} \quad (2)$$

Herein n is the solvent refractive index, $n = 1.424$ (DCM), Φ_{Fl} is the fluorescence quantum yield of the donor, $F_D(\lambda)$ is the area normalized emission spectrum of the donor, $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor, λ is the wavelength and κ represents the orientation between the transition dipole moments of donor and acceptor and was calculated quantum chemically.

To prepare the samples for these measurements visible light at 565 nm was supplied by a LED (Thorlabs M565L3). The UV light for the closing reaction was supplied by a lamp (Hamamatsu L9588-01) in combination with an UG1 filter (Schott) and solution filter composed of a 0.7 mM solution of potassium chromate (1 cm cuvette).

Isomerization quantum yields were determined using the initial slope method.⁴⁻⁶ Due to the intrinsic error in the mathematical approximation (linear fitting of the initial slope) employed and the varying time intervals for photoisomerization reactions, the quantum yields obtained by this method exhibit an estimated relative uncertainty of 10 % of the obtained value.

Light intensities required for the evaluation of the isomerization quantum yields at 310 nm, were determined by potassium ferrioxalate actinometry.⁷ The "micro-version"⁸ consisting of

irradiation of 3 mL of a fresh potassium ferrioxalate solution (0.006 M in 0.05 M H₂SO₄) in a cuvette for 2 – 4 min, subsequent addition of 0.5 mL of phenanthroline buffer (0.1 wt% in 0.5 M H₂SO₄/1.6 M NaOAc), and absorbance readout at 510 nm was applied. I_0 is obtained from:

$$I_0 = \frac{\Delta A_{510 \text{ nm}}}{\Delta t \cdot 1000 \cdot \phi_\lambda \cdot \varepsilon_{510 \text{ nm}}} \cdot \frac{3.5 \text{ ml}}{3 \text{ ml}} \quad (3)$$

with $\Delta A_{510 \text{ nm}}$ the difference in absorbance between sample and reference, $\varepsilon_{510 \text{ nm}} = 11\,100 \text{ M}^{-1} \text{ cm}^{-1}$, and ϕ_λ depending on the literature value for the wavelength to be determined. For the described Hg(Xe) lamp setup light intensities of $I_0 = 4.0 \cdot 10^{-10} - 1.1 \cdot 10^{-9} \text{ E s}^{-1} \text{ cm}^{-3}$ have been obtained.

Light intensities at 546 nm were determined using the commercial furyl fulgide Aberchrome 670⁹ as reference. Therefore, 3 mL of a hexane solution of Aberchrome 670 ($1.0 \cdot 10^{-4} \text{ M}$) were irradiated for 4 min at 365 nm (1000 W Xe, interference filter) before irradiation with $\lambda = 546 \text{ nm}$ was performed in 6 steps each consisting of 5% conversion (15 s irradiation time). I_0 is obtained from the depletion of absorbance at 519 nm:

$$I_0 = - \frac{\Delta A_{519 \text{ nm}}}{\Delta t \cdot 1000 \cdot \phi_\lambda \cdot \varepsilon_{519 \text{ nm}} \cdot (1 - 10^{-A'})} \quad (4)$$

with A' the initial absorbance at the irradiation wavelength, ϕ_λ depending on the literature value for the wavelength to be determined, and $\varepsilon_{519 \text{ nm}} = 7760 \text{ M}^{-1} \text{ cm}^{-1}$. The typical standard deviation of the six measurements is 2%.

Transient Spectroscopy

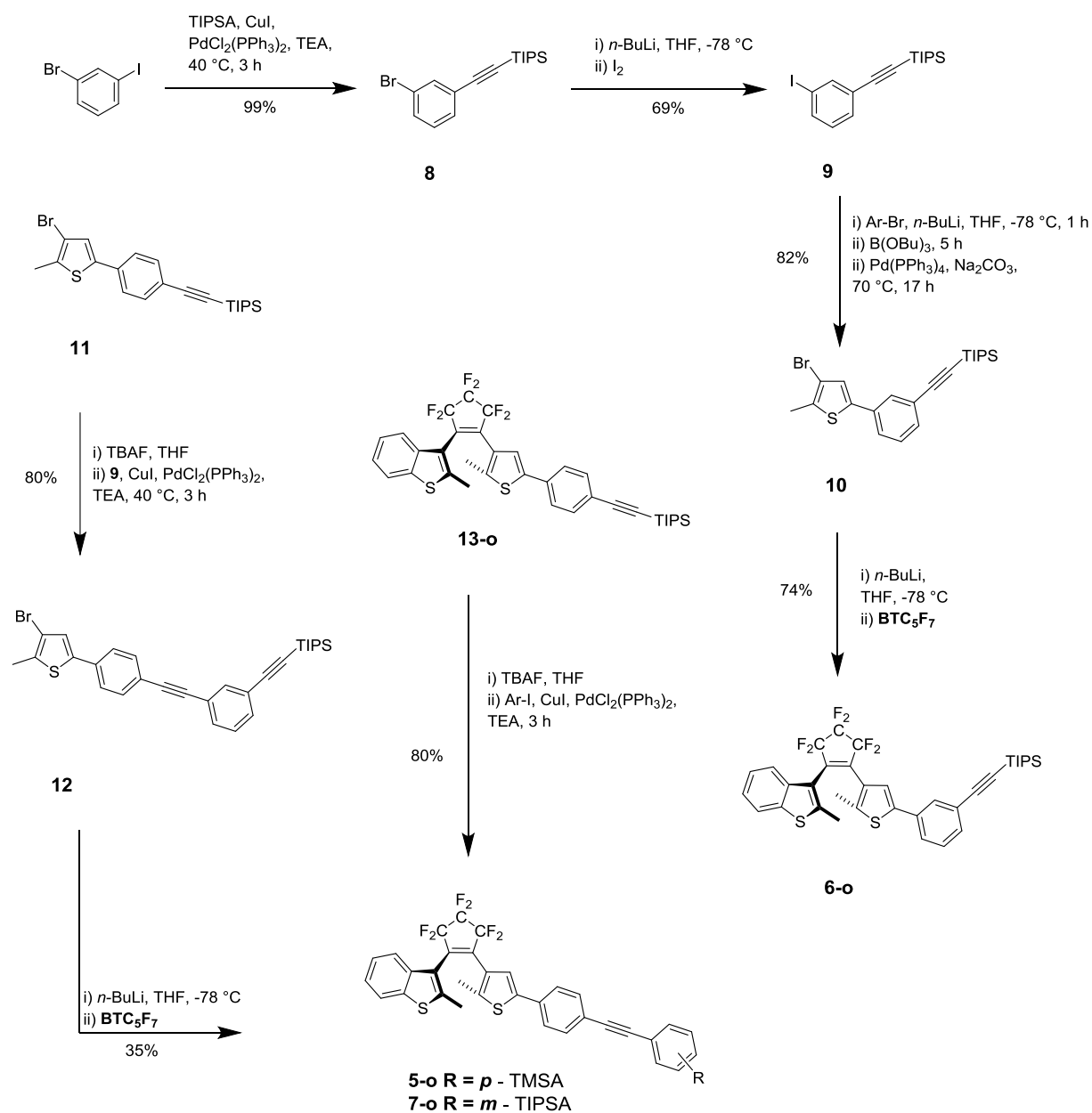
The time resolved transient absorption (TA) measurements were performed using a self-built pump-probe setup. A detailed description of this setup is given elsewhere.¹⁰ Ultra-short laser pulses (150 fs) were provided by a laser-amplifier system (Clark, MXR-CPA iSeries or CPA2100) operating at a repetition rate of 1 kHz at a central wavelength of 775 nm. For the probe pulses, a single filament white light was generated by focusing the laser fundamental in a CaF₂ crystal of 5 mm thickness or a Sapphire crystal of 2 mm thickness, respectively. The pump pulses at 600 nm, 630 nm and 685 nm were produced using a non-collinearly phase matched optical parametric amplifier.¹¹ The pump pulse energy was roughly adjusted to ~80 nJ. The experiments were performed under magic angle (54.7° pump-probe polarization angle difference) and back illumination (permanent illumination with light of either 550 nm or 313 nm) conditions. The samples were measured in a 1 mm cuvette (fused silica) with optical densities of ~0.3.

General Synthetic and Analytical Methods

NMR spectra were recorded on a 500 MHz (125 MHz for ¹³C, 470 MHz for ¹⁹F) Bruker AVANCE II 500 spectrometer or a 300 MHz (75 MHz for ¹³C, 282 MHz for ¹⁹F) Bruker AVANCE II 300 spectrometer at 25 °C using residual protonated solvent signals as internal standards¹² (¹H: $\delta(\text{CDCl}_3) = 7.26$ ppm, $\delta(\text{CD}_2\text{Cl}_2) = 5.32$ ppm; ¹³C: $\delta(\text{CDCl}_3) = 77.16$ ppm, $\delta(\text{CD}_2\text{Cl}_2) = 53.84$ ppm) or CFCl₃ as external standard for ¹⁹F-spectra ($\delta(\text{CFCl}_3) = 0$ ppm). Ultrahigh-performance liquid chromatography / mass spectrometry (UPLC/MS) was performed on a Waters Acquity UPLC equipped with a Waters LCT Premier XE Mass detector for high-resolution MS (HR-MS, ESI⁺-ionization) and with Waters Alliance systems (consisting of a Waters Separations Module 2695, a Waters Diode Array Detector 996 and a Waters Mass Detector ZQ 2000). TLC was performed on Merck Silica Gel 60 F254 TLC plates

with a fluorescent indicator employing 254 nm UV-lamp for visualization. Solvents and commercial starting materials were used as supplied. The solvents were dried before use, if necessary, employing an Innovative Technologies solvent purification system (multi-unit micro series). Silica gel for chromatography (0.035-0.070 mm, 60 Å) was used for column chromatography. The petroleum ether (PE) used had a boiling range of 40-60 °C. The synthesis of 3-(2-fluoro-3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)-2-methylbenzo[b]thiophene **BTC₅F₇** was described elsewhere.¹³

Synthesis and Compound Characterization Data

Scheme S1. Synthesis of precursor DAEs required for obtaining molecular dyads **2-o**, **3-o** and**4-o**.

Diarylethene-BODIPY Dyad (2-o)

To a solution of **5-o** (0.15 g, 0.15 mmol, 1 equiv.) in dry THF (30 mL), TBAF (0.18 mL, 0.18 mmol, 1.2 equiv.) was added. The resulting solution was stirred for 15 min at room temperature. TLC analysis showed completion of the reaction. The mixture was then diluted with Et₂O and washed with sat. NH₄Cl solution and H₂O. The organic layer was then dried over MgSO₄ and concentrated under reduced pressure. The residue was then dissolved in dry THF (30 mL) and cooled to -78 °C. Subsequently, *n*-BuLi (0.08 mL, 0.18 mmol, 1.2 equiv.) was added and the solution was left stirring at that temperature for 1 h. Then SnCl(Bu)₃ (0.05 mL, 0.18 mmol, 1.2 equiv.) was added and left stirring 2 h slowly reaching room temperature. Afterwards the mixture was then diluted with Et₂O and washed with brine and H₂O. The organic layer was then dried over MgSO₄ and concentrated under reduced pressure. The residue was then dissolved in dry toluene (5 mL) and the resulting solution was deoxygenated by letting bubble Ar for 15 min. To the deoxygenated solution, **bdp** (0.05 g, 0.15 mmol, 1.0 equiv.), Pd₂(dba)₃ (0.01 g, 0.012 mmol, 0.08 equiv.) and P^tBu₃ (0.03 mL, 0.024 mmol, 0.16 equiv.) were added. Finally the solution was heated for 4 h at 105 °C. TLC analysis showed completion of the reaction. It was then proceeded to dilute the solution with Et₂O, and washed once with brine (100 mL). The organic layer was dried over MgSO₄ and concentrated under reduced pressure. It was then purified by column chromatography over silica gel (PE : CH₂Cl₂, 4:1). Removal of solvent from the main fraction yielded **2-o** as a dark blue solid. 0.03 g (22 %). **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.88 (d, ³J_{H,H} = 8.1 Hz, 1 H, CH_{ar}), 7.83 (d, ³J_{H,H} = 8.2 Hz, 1 H, CH_{ar}), 7.79 – 7.74 (m, 1 H, CH_{ar}), 7.72 – 7.66 (m, 2 H, CH_{ar}), 7.62 – 7.29 (m, 12 H, CH_{ar}), 7.26 (s, 1 H, CH_{ar}), 2.56 (s, 3 H, CH₃), 2.41 (q, ³J_{H,H} = 7.6 Hz, 2 H, CH₂), 2.33 (s, 3 H, CH₃), 2.23 (s, 3 H, CH₃), 1.96 (s, 3 H, CH₃), 1.09 (t, ³J_{H,H} = 7.6 Hz, 3 H, CH_{ar}). **¹⁹F-NMR (282 MHz, CD₂Cl₂):** δ (ppm) = -109.30 (s, 2 F, CF₂), -110.27 (q, *J* = 263.4 Hz, 2 F, CF₂), -132.29 (q, *J* = 245.6 Hz, 2 F, CF₂), -144.16 (dd, ¹J_{B,F} = 61.2 Hz,

$^2J_{F,F} = 29.8$ Hz, 2 F, BF_2). ^{13}C -NMR (75 MHz, CD_2Cl_2): δ (ppm) = 157.75, 143.40, 143.11, 141.42, 138.72, 138.50, 138.46, 134.71, 133.92, 133.68, 133.41, 132.58, 132.38, 132.08, 129.43, 128.78, 126.15, 125.73, 125.67, 125.34, 124.94, 124.59, 123.53, 122.52, 122.49, 120.49, 119.45, 116.31, 110.41, 110.38, 104.48, 92.16, 90.64, 84.04, 17.61, 15.14, 15.04, 14.62, 13.11, 9.68. HRMS (ESI⁺): $m/z = 914.232$ (calcd. 914.222 for $[C_{52}H_{35}BF_8N_2S_2]^+$).

Diarylethene-BODIPY Dyad (3-o)

To a solution of **6-o** (0.24 g, 0.36 mmol, 1.2 equiv.) in dry THF (30 mL), TBAF (0.42 mL, 0.42 mmol, 1.4 equiv.) was added. The resulting solution was stirred for 15 min at room temperature. TLC analysis showed completion of the reaction. The mixture was then diluted with Et_2O and washed with sat. NH_4Cl solution and H_2O . The organic layer was then dried over $MgSO_4$ and concentrated under reduced pressure. The residue was then dissolved in dry THF (30 mL) and cooled to -78 °C. Subsequently, *n*-BuLi (0.17 mL, 0.36 mmol, 1.2 equiv.) was added and the solution was left stirring at that temperature for 1 h. Then $SnCl(Bu)_3$ (0.10 mL, 0.36 mmol, 1.2 equiv.) was added and left stirring 2 h slowly reaching room temperature. Afterwards the mixture was then diluted with Et_2O and washed with brine and H_2O . The organic layer was then dried over $MgSO_4$ and concentrated under reduced pressure. The residue was then dissolved in dry toluene (5 mL) and the resulting solution was deoxygenated by letting bubble Ar for 15 min. To the deoxygenated solution, **bdp** (0.10 g, 0.3 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (0.02 g, 0.024 mmol, 0.08 equiv.) and P^tBu_3 (0.05 mL, 0.048 mmol, 0.16 equiv.) were added. Finally the solution was heated for 4 h at 105 °C. TLC analysis showed completion of the reaction. It was then proceeded to dilute the solution with Et_2O , and washed once with brine (100 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. It was then purified by column chromatography over

silica gel (PE : CH₂Cl₂, 4:1). Removal of solvent from the main fraction yielded **3-o** as a dark blue solid. 0.05 g (20 %). **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.89 (dt, ³J_{H,H} = 8.2 Hz, ⁴J_{H,H} = 0.9 Hz, 1 H, CH_{ar}), 7.83 (dt, ³J_{H,H} = 8.2 Hz, ⁴J_{H,H} = 0.9 Hz, 1 H, CH_{ar}), 7.79 – 7.75 (m, 2 H, CH_{ar}), 7.64 – 7.55 (m, 2 H, CH_{ar}), 7.51 – 7.28 (m, 8 H, CH_{ar}), 2.56 (s, 3 H, CH₃), 2.40 (q, ³J_{H,H} = 6.9 Hz, 2 H, CH₂), 2.35 (s, 3 H, CH₃), 2.22 (s, 3 H, CH₃), 1.98 (s, 3 H, CH₃), 1.08 (t, ³J_{H,H} = 6.9 Hz, 3 H, CH_{ar}). **¹⁹F-NMR (282 MHz, CD₂Cl₂):** δ (ppm) = -109.29 (s, 2 F, CF₂), -110.24 (q, J = 338.2 Hz, 2 F, CF₂), -132.48 (q, J = 245.6 Hz, 2 F, CF₂), -144.14 (dd, ¹J_{B,F} = 61.7 Hz, ²J_{F,F} = 30.6 Hz, 2 F, BF₂). **¹³C-NMR (75 MHz, CD₂Cl₂):** δ (ppm) = 157.70, 143.43, 143.03, 141.00, 138.74, 138.48, 134.66, 134.13, 133.91, 133.42, 131.72, 129.67, 129.42, 128.95, 128.65, 127.03, 126.10, 125.58, 125.35, 124.95, 123.69, 123.32, 122.53, 122.38, 120.41, 119.46, 116.42, 110.41, 110.38, 104.02, 82.54, 17.60, 15.18, 15.02, 14.62, 13.09, 9.67. **HRMS (ESI⁺):** m/z = 814.196 (calcd. 814.190 for [C₄₄H₃₁BF₈N₂S₂]⁺).

Diarylethene-BODIPY Dyad (4-o)

To a solution of **7-o** (0.18 g, 0.23 mmol, 1.15 equiv.) in dry THF (30 mL), TBAF (0.24 mL, 0.24 mmol, 1.2 equiv.) was added. The resulting solution was stirred for 15 min at room temperature. TLC analysis showed completion of the reaction. The mixture was then diluted with Et₂O and washed with sat. NH₄Cl solution and H₂O. The organic layer was then dried over MgSO₄ and concentrated under reduced pressure. The residue was then dissolved in dry THF (30 mL) and cooled to -78 °C. Subsequently, *n*-BuLi (0.11 mL, 0.24 mmol, 1.2 equiv.) was added and the solution was left stirring at that temperature for 1 h. Then SnCl(Bu)₃ (0.07 mL, 0.24 mmol, 1.2 equiv.) was added and left stirring 2 h slowly reaching room temperature. Afterwards the mixture was then diluted with Et₂O and washed with brine and H₂O. The organic layer was then dried over MgSO₄ and concentrated under reduced pressure.

The residue was then dissolved in dry toluene (5 mL) and the resulting solution was deoxygenated by letting bubble Ar for 15 min. To the deoxygenated solution, **bdp** (0.07 g, 0.20 mmol, 1.0 equiv.), Pd₂(dba)₃ (0.015 g, 0.016 mmol, 0.08 equiv.) and P^tBu₃ (0.03 mL, 0.032 mmol, 0.16 equiv.) were added. Finally the solution was heated for 4 h at 105 °C. TLC analysis showed completion of the reaction. It was then proceeded to dilute the solution with Et₂O, and washed once with brine (100 mL). The organic layer was dried over MgSO₄ and concentrated under reduced pressure. It was then purified by column chromatography over silica gel (PE : CH₂Cl₂, 4:1). Removal of solvent from the main fraction yielded **4-o** as a dark blue solid. 0.04 g (22 %). **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.93 -7.88 (m, 1 H, CH_{ar}), 7.87 – 7.82 (m, 2 H, CH_{ar}), 7.80 – 7.75 (m, 1 H, CH_{ar}), 7.71 – 7.65 (m, 1 H, CH_{ar}), 7.61 – 7.28 (m, 12 H, CH_{ar}), 7.26 (s, 1 H, CH_{ar}), 2.57 (s, 3 H, CH₃), 2.43 (q, ³J_{H,H} = 7.6 Hz, 2 H, CH₂), 2.34 (s, 3 H, CH₃), 2.25 (s, 3 H, CH₃), 1.96 (s, 3 H, CH₃), 1.09 (t, ³J_{H,H} = 7.6 Hz, 3 H, CH₃). **¹⁹F-NMR (282 MHz, CD₂Cl₂):** δ (ppm) = -109.35 (s, 2 F, CF₂), -110.32 (q, J = 270.6 Hz, 2 F, CF₂), -132.39 (q, J = 241.1 Hz, 2 F, CF₂), -144.21 (dd, ¹J_{B,F} = 61.2 Hz, ²J_{F,F} = 29.8 Hz, 2 F, BF₂). **HRMS (ESI⁺):** m/z = 914.232 (calcd. 914.222 for [C₅₂H₃₅BF₈N₂S₂]⁺).

((3-Bromophenyl)ethynyl)triisopropylsilane (8)

To a solution of 1-bromo-3-iodobenzene (4.53 g, 35.5 mmol) in degassed Et₃N (50 mL) CuI (0.17 g, 0.88 mmol, 0.025 equiv.), PdCl₂(PPh₃)₂ (1.25 g, 1.78 mmol, 0.05 equiv.) and TIPSA (8.76 mL, 39.05 mmol, 1.1 equiv.) were added. Subsequently the mixture was heated at 40 °C for 17 h. The reaction was monitored by TLC, and upon completion the brown mixture was then dissolved in PE and passed through a celite plug. The solvent was then evaporated. Final residue was purified through a silica gel column using PE as eluent. Removal of solvent from the main fraction yielded a colorless oil. Yield 11.84 g, 99 %. **¹H-NMR (300 MHz, CD₂Cl₂):**

δ (ppm) = 7.61 (dd, $^3J_{\text{H,H}} = 2.6$ Hz, $^4J_{\text{H,H}} = 0.9$ Hz, 1 H, CH_{ar}), 7.50 – 7.35 (m, 2 H, CH_{ar}), 7.19 (t, $^3J_{\text{H,H}} = 7.9$ Hz, 1 H, CH_{ar}), 1.12 (s, 21 H). **^{13}C NMR (75 MHz, CD_2Cl_2)** $\delta = 134.97, 131.87, 130.90, 130.17, 125.84, 122.28, 105.57, 92.82, 18.76, 11.64$. **HRMS (ESI⁺):** $m/z = 337.947$ (calcd. 338.089 for $[\text{C}_{17}\text{H}_{25}\text{BrSi}]^+$).

((3-Iodophenyl)ethynyl)triisopropylsilane (9)

To a solution of **8** (2.43 g, 35.5 mmol) in 100 mL anhydrous THF under Ar at -78 °C *n*-BuLi (8.64 mmol, 1.2 equiv.) was added and left stirring at that temperature for 1 h. Then I_2 (2.19 g, 8.64 mmol, 1.2 equiv.) was added and left stirring for 17 h slowly reaching room temperature. TLC analysis showed completion of the reaction. The mixture was then diluted with Et_2O and washed with a sat. solution of $\text{Na}_2\text{S}_2\text{O}_3$, brine and H_2O . The organic layer was dried over MgSO_4 and evaporated. Final residue was purified through a silica gel column using PE as eluent. Removal of solvent from the main fraction yielded a colorless oil. Yield 1.9 g, 69 %. **^1H -NMR (300 MHz, CD_2Cl_2):** δ (ppm) = 7.82 (t, $^3J_{\text{H,H}} = 1.6$ Hz, 1 H, CH_{ar}), 7.66 (ddd, $^3J_{\text{H,H}} = 8.0$ Hz, $^4J_{\text{H,H}} = 1.7$ Hz, $^4J_{\text{H,H}} = 1.1$ Hz, 1 H, CH_{ar}), 7.44 (ddd, $^3J_{\text{H,H}} = 8.0$ Hz, $^4J_{\text{H,H}} = 1.7$ Hz, $^4J_{\text{H,H}} = 1.1$ Hz, 1 H, CH_{ar}), 7.05 (t, $^3J_{\text{H,H}} = 7.9$ Hz, 1 H, CH_{ar}), 1.11 (s, 21 H). **^{13}C -NMR (75 MHz, CD_2Cl_2)** $\delta = 140.84, 137.79, 131.45, 130.19, 125.88, 105.45, 18.77, 11.64$. **HRMS (ESI⁺):** $m/z = 384.045$ (calcd. 384.077 for $[\text{C}_{17}\text{H}_{25}\text{ISi}]^+$).

((3-(4-Bromo-5-methylthiophen-2-yl)phenyl)ethynyl)triisopropylsilane (10)

To a solution of 3,5-dibromo-2-methylthiophene (3.0 g, 11.7 mmol, 1.0 equiv.) in 100 mL anhydrous THF under Ar at -78 °C *n*-BuLi (5.85 mL, 12.87 mmol, 1.1 equiv.) was added and left stirring at that temperature for 1 h. Then $\text{B}(\text{O}i\text{Bu})_3$ (3.47 mL, 12.87 mmol, 1.1 equiv.) was added and left stirring overnight slowly reaching room temperature. Afterwards a 2 M Na_2CO_3

(19.31 mL, 38.61 mmol, 3.3 equiv.) solution was added and the resulting solution was deoxygenated by letting bubble Ar for 15 min. To the deoxygenated solution, **9** (4.49 g, 11.7 mmol, 1.0 equiv.) and the Pd(PPh₃)₄ (1.08 g, 0.94 mmol, 0.08 equiv.) catalyst were added. Finally the solution was refluxed for 17 h at 80 °C. TLC analysis showed completion of the reaction. It was then proceeded to dilute the solution with Et₂O, and wash once with brine (100 mL). The organic layer was dried over MgSO₄ and concentrated under reduced pressure. It was then purified by column chromatography over silica gel (PE) yielding 4.20 g (83 %) of **10** as a colorless oil. **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.62 (t, ⁴J_{H,H} = 1.74 Hz, 1 H, CH_{ar}), 7.51 – 7.45 (m, 1 H, CH_{ar}), 7.42 – 7.28 (m, 2 H, CH_{ar}), 7.17 (s, 1 H, CH_{ar}), 2.42 (s, 3 H, CH₃), 1.15 (s, 21 H). **¹³C-NMR (75 MHz, CD₂Cl₂):** δ (ppm) = 143.31, 134.84, 133.95, 131.57, 129.34, 128.83, 126.39, 125.71, 125.59, 124.63, 110.23, 91.77, 18.83, 15.05, 11.71. **HRMS (ESI⁺):** *m/z* = 432.159 (calcd. 434.090 for [C₂₂H₂₉BrSSi]⁺).

*((3-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenyl)ethynyl)triisopropylsilane (6-o)*

To a solution of **10** (1.69 g, 3.9 mmol, 1.0 equiv.) in 100 mL anhydrous THF under Ar at -78 °C *n*-BuLi (1.83 mL, 4.10 mmol, 1.05 equiv.) was added and left stirring at that temperature for 1 h. Then **BTC₅F₇** (1.53 g, 4.49 mmol, 1.15 equiv.) was added and left stirring for 2 h slowly reaching room temperature. TLC analysis showed completion of the reaction. The mixture was then diluted with Et₂O and washed with brine and H₂O. The organic layer was dried over MgSO₄ and evaporated. Final residue was purified through a silica gel column (PE : CH₂Cl₂, 8:1). Removal of solvent from the main fraction yielded 1.96 g (74 %) of **6-o** as a colorless oil. **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.82 – 7.73 (m, 1 H, CH_{ar}), 7.58 – 7.50 (m, 2 H, CH_{ar}), 7.43 – 7.26 (m, 5 H, CH_{ar}), 7.21 (s, 1 H, CH_{ar}), 2.33 (s, 3 H, CH₃), 1.99 (s, 3 H, CH₃),

1.15 (s, 21 H). **¹⁹F-NMR (282 MHz, CD₂Cl₂):** δ (ppm) = -109.34 (m, 2 F, CF₂), -110.32 (q, J = 280.21 Hz, 2 F, CF₂), -132.47 (q, J = 262.71 Hz, 2 F, CF₂). **¹³C-NMR (75 MHz, CD₂Cl₂):** δ (ppm) = 143.36, 142.80, 141.23, 138.73, 138.51, 133.75, 133.10, 131.72, 129.32, 129.00, 125.92, 125.51, 125.32, 124.94, 124.61, 123.44, 122.51, 122.35, 120.42, 110.41, 106.66, 91.85, 18.83, 15.14, 15.00, 11.71. **HRMS (ESI⁺):** m/z = 674.159 (calcd. 674.190 for [C₃₆H₃₆F₆S₂Si]⁺).

*((3-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenyl)ethynyl)triisopropylsilane (6-c)*

6-o was dissolved in an NMR tube in CD₂Cl₂ and irradiated with a 313 nm UV-lamp for 20 min. **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.83 – 7.78 (m, 1 H, CH_{ar}), 7.69 (s, 1 H, CH_{ar}), 7.64 – 7.50 (m, 1 H, CH_{ar}), 7.48 – 7.11 (m, 5 H, CH_{ar}), 6.78 (m, 1 H, CH_{ar}), 2.10 (s, 6 H, CH₃), 1.26 – 1.08 (m, 21 H). **¹⁹F-NMR (282 MHz, CD₂Cl₂):** δ (ppm) = -103.71 (d, J = 256.7 Hz, 1 F, CF₂), -103.85 (d, J = 256.7 Hz, 1 F, CF₂), -120.40 (d, J = 264.2 Hz, 1 F, CF₂), -122.64 (d, J = 261.1 Hz, 1 F, CF₂), -128.14 (d, J = 252.7 Hz, 1 F, CF₂), -138.16 (d, J = 252.0 Hz, 1 F, CF₂).

((3-((4-(4-Bromo-5-methylthiophen-2-yl)phenyl)ethynyl)phenyl)ethynyl)triisopropylsilane (12)

To a solution of **11** (1.30 g, 3.0 mmol, 1.0 equiv.) in dry THF (30 mL), TBAF (4.2 mL, 4.2 mmol, 1.4 equiv.) was added. The resulting solution was stirred for 15 min at room temperature. TLC analysis showed completion of the reaction. The mixture was then diluted with Et₂O and washed with sat. NH₄Cl solution and H₂O. The organic layer was then dried over MgSO₄ and concentrated under reduced pressure. The residue was then dissolved in Et₃N (50 mL) and degassed. Afterwards CuI (0.01 g, 0.08 mmol, 0.025 equiv.), PdCl₂(PPh₃)₂

(0.11 g, 0.15 mmol, 0.05 eq.) and **9** (1.21 g, 3.15 mmol, 1.05 equiv.) were added. Subsequently, the mixture was heated at 40 °C for 3 h. The reaction was monitored by TLC, and upon completion the brown mixture was then dissolved in PE and passed through a celite plug. The solvent was then evaporated. Final residue was purified through a silica gel column (PE : CH₂Cl₂, 8:1). Removal of solvent from the main fraction yielded 1.30 g (80 %) of **12** as a white solid. **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.65 (td, ⁴J_{H,H} = 1.6 Hz, ⁵J_{H,H} = 0.6 Hz, 1 H, CH_{ar}), 7.53 (s, 4 H, CH_{ar}), 7.50 (dt, ³J_{H,H} = 7.7 Hz, ⁴J_{H,H} = 1.2 Hz, 1 H, CH_{ar}), 7.46 (dt, ³J_{H,H} = 7.8 Hz, ⁴J_{H,H} = 1.2 Hz, 1 H, CH_{ar}), 7.32 (td, ³J_{H,H} = 7.7 Hz, ⁴J_{H,H} = 0.6 Hz, 1 H, CH_{ar}), 7.19 (s, 1 H, CH_{ar}), 2.43 (s, 3 H, CH₃), 1.14 (s, 21 H). **¹³C-NMR (75 MHz, CD₂Cl₂):** δ (ppm) = 140.63, 135.25, 135.15, 133.79, 132.56, 132.10, 131.72, 128.91, 126.50, 125.43, 124.28, 123.74, 122.53, 110.44, 106.38, 91.96, 89.93, 18.81, 15.10, 11.69. **HRMS (ESI⁺):** *m/z* = 534.159 (calcd. 534.120 for [C₃₀H₃₃BrSSi]⁺).

((4-((4-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methylbenzo[b]thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenyl)ethynyl)phenyl)ethynyl)trimethylsilane (5-o)

To a solution of **13-o** (0.47 g, 0.7 mmol, 1.0 equiv.) in dry THF (30 mL), TBAF (0.84 mL, 0.84 mmol, 1.2 equiv.) was added. The resulting solution was stirred for 15 min at room temperature. TLC analysis showed completion of the reaction. The mixture was then diluted with Et₂O and washed with sat. NH₄Cl solution and H₂O. The organic layer was then dried over MgSO₄ and concentrated under reduced pressure. The residue was then dissolved in Et₃N (50 mL) and degassed. Afterwards CuI (0.04 g, 0.02 mmol, 0.03 equiv.), PdCl₂(PPh₃)₂ (0.06 g, 0.05 mmol, 0.05 equiv.) and ((4-iodophenyl)ethynyl)trimethylsilane (0.23 g, 0.77 mmol, 1.1 equiv.) were added. The reaction was monitored by TLC, and upon completion the brown mixture was then dissolved in PE and passed through a celite plug. The solvent was then

evaporated. Final residue was purified through a silica gel column. (PE : CH₂Cl₂, 8:1). Removal of solvent from the main fraction yielded 0.38 g (80 %) of **5-o** as a yellow solid. **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.81 – 7.74 (m, 1 H, CH_{ar}), 7.56 (d, ³J_{H,H} = 8.4, 1 H, CH_{ar}), 7.53 – 7.41 (m, 8 H, CH_{ar}), 7.40 – 7.29 (m, 2 H, CH_{ar}), 7.25 (s, 1 H, CH_{ar}), 2.34 (s, 3 H, CH₃), 1.97 (s, 3 H, CH₃), 0.25 (s, 9 H, CH₃). **¹⁹F-NMR (282 MHz, CD₂Cl₂):** δ (ppm) = -109.33 (m, 2 F, CF₂), -110.37 (q, J = 262.94 Hz, 2 F, CF₂), -132.39 (q, J = 247.32 Hz, 2 F, CF₂). **¹³C-NMR (75 MHz, CD₂Cl₂):** δ (ppm) = 143.08, 141.42, 138.73, 133.60, 132.51, 132.24, 131.80, 125.72, 125.34, 124.94, 123.54, 123.50, 122.64, 122.52, 122.38, 122.36, 122.31, 110.41, 104.71, 96.84, 91.25, 90.44, 15.04, -0.08. **HRMS (ESI⁺):** m/z = 690.132 (calcd. 690.128 for [C₃₈H₂₈F₆S₂Si]⁺).

*((4-((4-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methylbenzo[b]thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenyl)ethynyl)phenyl)ethynyl)trimethylsilane (**5-c**)*

5-o was dissolved in an NMR tube in CD₂Cl₂ and irradiated with a 313 nm UV-lamp for 20 min. **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.83 – 7.76 (m, 1 H, CH_{ar}), 7.65 – 7.56 (m, 4 H, CH_{ar}), 7.55 – 7.40 (m, 4 H, CH_{ar}), 7.33 – 7.26 (m, 2 H, CH_{ar}), 7.20 – 7.11 (m, 1 H, CH_{ar}), 6.84 – 6.78 (m, 1 H, CH_{ar}), 2.08 (s, 6 H, CH₃), 0.25 (s, 9 H, CH₃). **¹⁹F-NMR (282 MHz, CD₂Cl₂):** δ (ppm) = -103.72 (d, J = 256.5 Hz, 1 F, CF₂), -103.98 (d, J = 127.0 Hz, 1 F, CF₂), -120.31 (d, J = 260.4 Hz, 1 F, CF₂), -122.56 (d, J = 254.7 Hz, 1 F, CF₂), -128.14 (d, J = 236.4 Hz, 1 F, CF₂), -138.13 (d, J = 259.0 Hz, 1 F, CF₂).

((3-((4-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methylbenzo[b]thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenyl)ethynyl)phenyl)ethynyl)triisopropylsilane (7-o)

To a solution of **12** (0.77 g, 1.45 mmol, 1.0 equiv.) in 100 mL anhydrous THF under Ar at -78 °C *n*-BuLi (0.70 mL, 1.52 mmol, 1.05 equiv.) was added and left stirring at that temperature for 1 h. Then **BTC₅F₇** (0.57 g, 1.67 mmol, 1.15 equiv.) was added and left stirring for 2 h slowly reaching room temperature. TLC analysis showed completion of the reaction. The mixture was then diluted with Et₂O and washed with brine and H₂O. The organic layer was dried over MgSO₄ and evaporated. Final residue was purified through a silica gel column (PE : CH₂Cl₂, 8:1). Removal of solvent from the main fraction yielded 0.39 g (35 %) of **7-o** as a yellow oil. **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.80 – 7.75 (m, 1 H, *CH_{ar}*), 7.66 – 7.62 (m, 1 H, *CH_{ar}*), 7.56 (d, ³*J*_{H,H} = 7.7 Hz, 1 H, *CH_{ar}*), 7.53 – 7.42 (m, 7 H, *CH_{ar}*), 7.40 – 7.29 (m, 4 H, *CH_{ar}*), 7.25 (s, 1 H, *CH_{ar}*), 2.34 (s, 3 H, *CH₃*), 1.97 (s, 3 H, *CH₃*), 1.14 (s, 21 H). **¹⁹F-NMR (282 MHz, CD₂Cl₂):** δ (ppm) = -109.33 (m, 2 F, *CF₂*), -110.31 (q, *J* = 263.00 Hz, 2 F, *CF₂*), -132.41 (q, *J* = 241.30 Hz, 2 F, *CF₂*). **¹³C-NMR (75 MHz, CD₂Cl₂):** δ (ppm) = 143.10, 141.02, 138.31, 138.18, 134.83, 133.16, 132.11, 131.71, 131.29, 128.50, 128.02, 127.04, 125.31, 124.93, 124.52, 123.87, 123.28, 123.08, 122.22, 122.11, 121.95, 105.94, 89.53, 89.44, 18.39, 14.73, 14.63, 11.27. **HRMS (ESI⁺):** *m/z* = 774.219 (calcd. 774.221 for [C₄₄H₄₀F₆S₂Si]⁺).

((3-((4-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methylbenzo[b]thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenyl)ethynyl)phenyl)ethynyl)triisopropylsilane (7-c)

7-o was dissolved in an NMR tube in CD₂Cl₂ and irradiated with a 313 nm UV-lamp for 20 min. **¹H-NMR (300 MHz, CD₂Cl₂):** δ (ppm) = 7.80 (d, ³*J*_{H,H} = 8.1 Hz, 1 H, *CH_{ar}*), 7.69 – 7.55 (m, 5 H, *CH_{ar}*), 7.55 – 7.41 (m, 2 H, *CH_{ar}*), 7.39 – 7.25 (m, 3H, *CH_{ar}*), 7.20 – 7.10 (m, 1 H, *CH_{ar}*), 6.81 (s, 1 H, *CH_{ar}*), 2.09 (s, 6 H, *CH_{ar}*), 1.14 (s, 21 H). **¹⁹F-NMR (282 MHz,**

CD₂Cl₂: δ (ppm) = -103.72 (d, $J = 256.5$ Hz, 1 F, CF_2), -103.98 (d, $J = 127.0$ Hz, 1 F, CF_2), -120.31 (d, $J = 260.4$ Hz, 1 F, CF_2), -122.56 (d, $J = 254.7$ Hz, 1 F, CF_2), -128.14 (d, $J = 236.4$ Hz, 1 F, CF_2), -138.13 (d, $J = 259.0$ Hz, 1 F, CF_2).

Encapsulation Experiments

Preparation and loading of compounds in SDS micelles aqueous solutions.¹⁴ SDS (1.0 g) was added into water (100 mL) and subsequently ultrasonicated until a clear homogenous solution was established indicating the formation of micelles. A portion of 10 μ L of a CH₂Cl₂ solution of compounds **4-o**, **7-o** or **Ph-bdp** ($c \approx 10^{-4}$ M) was added into the SDS micelle solution (10 mL) under stirring, followed by 3 cycles of 5 min ultrasonication and evaporation of the organic solvent to form a clear homogenous solution.

Preparation and loading of compounds in GUVs and multilamellar vesicles of DOPC

Giant unilamellar vesicles (GUVs) were prepared according to the electroformation method described in the literature,¹⁴ with minor modifications. Briefly, DOPC (10 μ L of 13 mM stock solution in CHCl₃) were spread onto the charged surface of two ITO-coated thin glasses, previously mixed with the appropriate amount of dyad **4-o** (0.5 mol%, 10 μ L of 0.65 mM in CHCl₃) and fastDIO (0.5 mol%, 10 μ L of 0.65 mM in CHCl₃). The deposition of the mixture was carried on onto pre-heated plates, at 50 °C. The glasses were inserted in a home-built chamber of 2 mm thickness, filled with deionized water and connected with a function generator. The liposomes were formed overnight, using a sinusoidal signal of 1.2 V and a frequency of 10 Hz.

Multilamellar vesicles were obtained from 15.6 μL of a 10 mM DOPC stock solution in CHCl_3 . The lipids were mixed with compound **4-o** (1 mol%, 10 μL of 1 mM in CHCl_3), dried under nitrogen and then hydrated again with PBS. This solution was then diluted to the appropriated concentration for fluorescence spectroscopy.

Additional Spectra

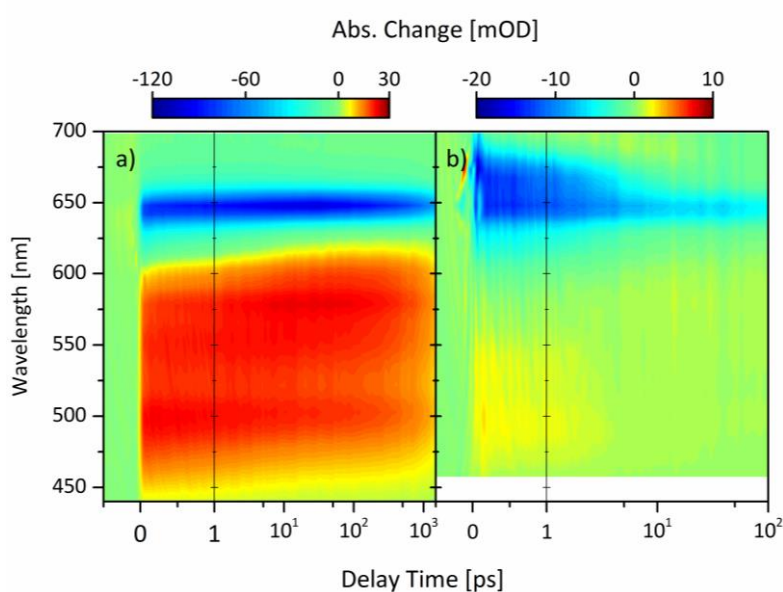


Figure S1: Transient absorption data of a) **1-o** ($\lambda_{\text{exc}} = 600$ nm) and b) **1-PSS** ($\lambda_{\text{exc}} = 685$ nm) obtained in CH_2Cl_2 ($c \approx 10^{-5}$ M) at 25 °C.

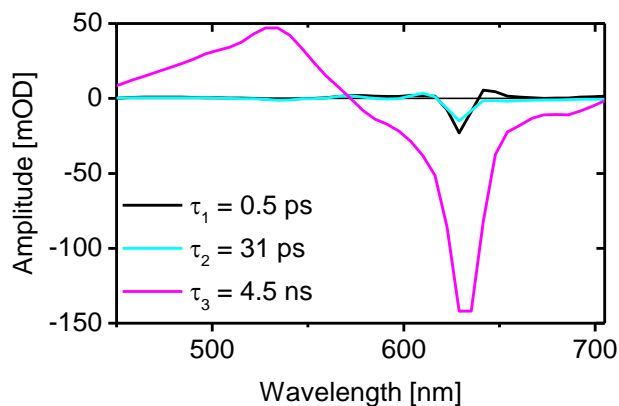


Figure S2: Decay associated spectra resulting from a global lifetime analysis of the TA data from dyad **4-o** ($\lambda_{\text{exc}} = 630$ nm).

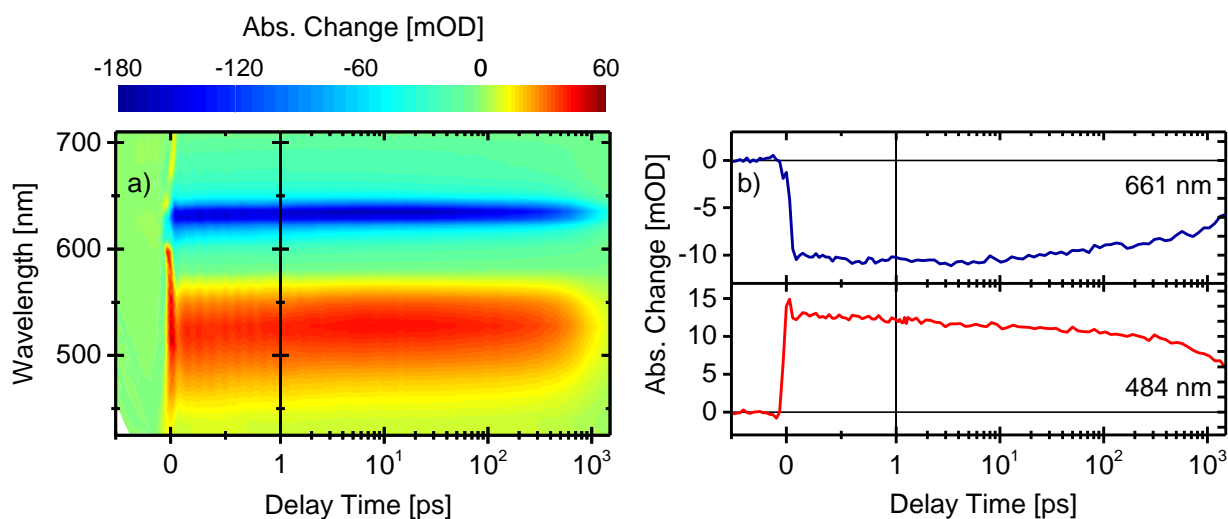


Figure S3: TA data of model BODIPY **Ph-bdp**. a) 2D data set and b) single transient traces at $\lambda_{\text{pr}} = 661$ nm and $\lambda_{\text{pr}} = 484$ nm, respectively.

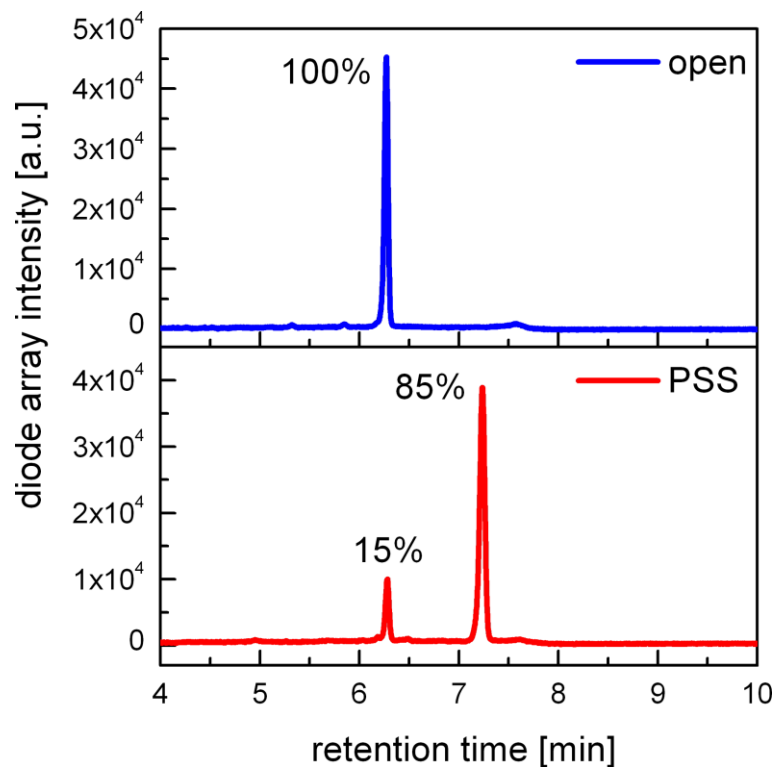


Figure S4: UPLC traces (diode-array detector at 568 nm) of the molecular dyad **4-o** before irradiation (top) and after irradiation with 313 nm light (bottom).

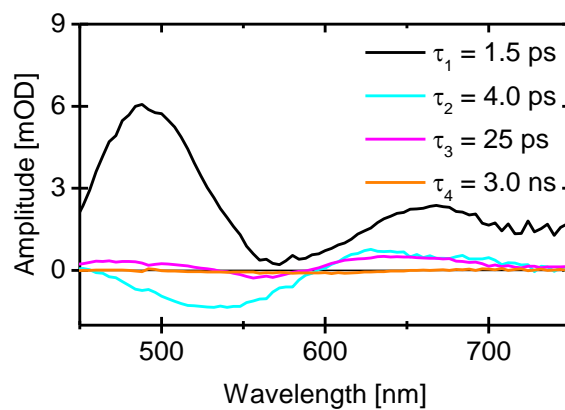


Figure S5: Decay associated spectra resulting from a global lifetime analysis of the TA data from model DAE **7-PSS** ($\lambda_{\text{exc}} = 495$ nm).

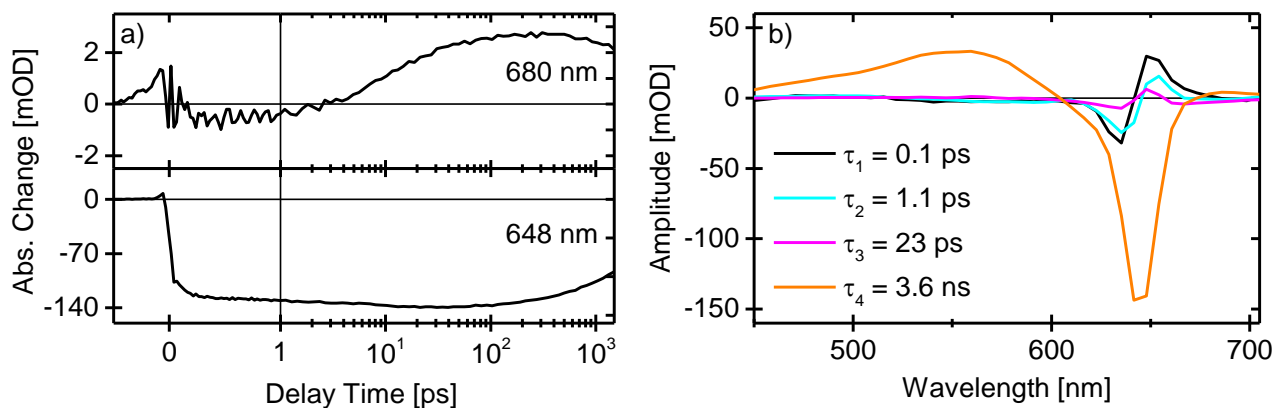


Figure S6: Transient absorption data of dyad **2-o** ($\lambda_{\text{exc}} = 630$ nm). a) Single transient traces at $\lambda_{\text{pr}} = 680$ nm and $\lambda_{\text{pr}} = 684$ nm, respectively. b) Decay associated spectra resulting from a global lifetime analysis.

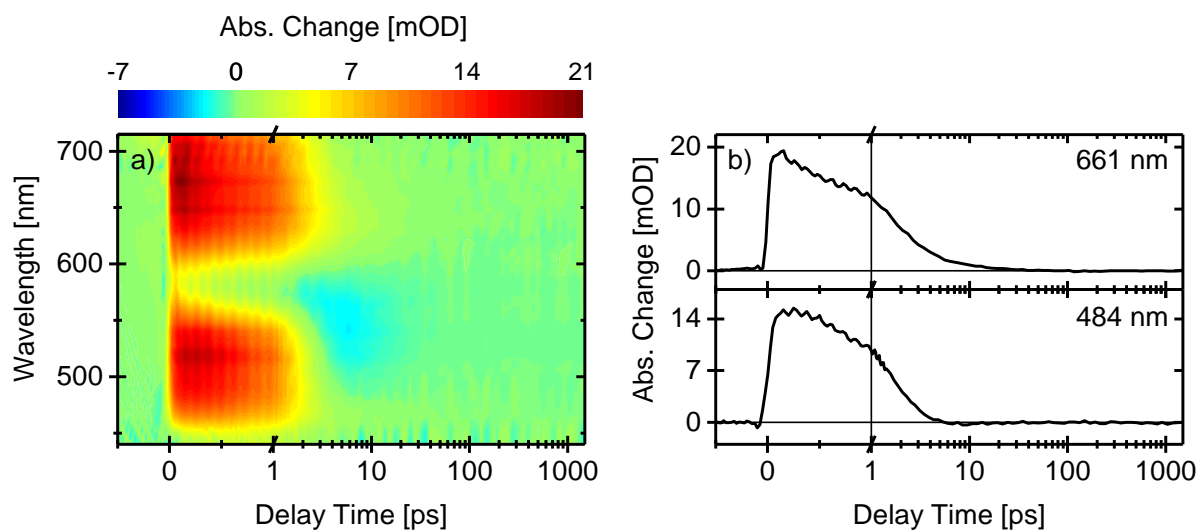


Figure S7: TA data of model DAE **5**. a) 2D data set and b) single transient traces at $\lambda_{\text{pr}} = 661$ nm and $\lambda_{\text{pr}} = 484$ nm, respectively.

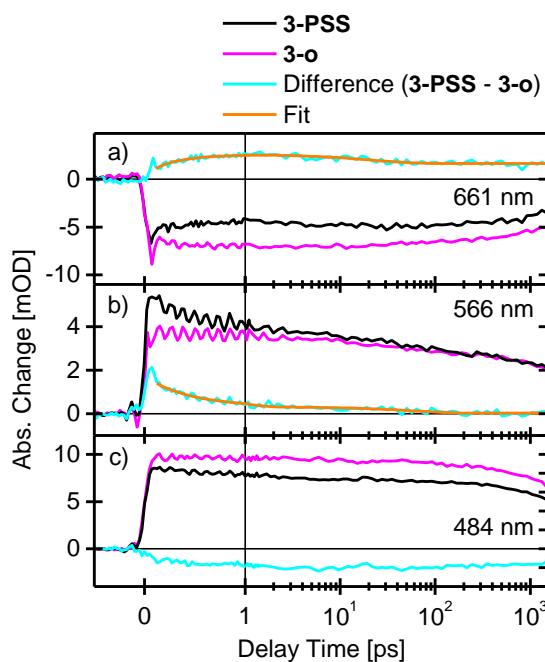


Figure S8: Single transient traces of the **3-PSS**, **3-o**, the difference of both and the model DAE **6**: a) at $\lambda_{pr} = 661$ nm, b) at $\lambda_{pr} = 566$ nm and c) at $\lambda_{pr} = 484$ nm. The TA data of **3-o** was weighted with a factor of 0.63.

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