Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Dynamics of ion-regulated photoinduced electron transfer in BODIPY-BAPTA conjugates

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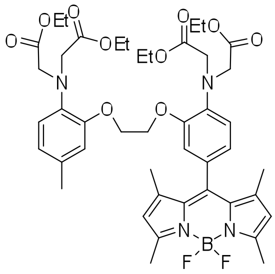
Experimental Section

General Synthetic Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 200 MHz, on Bruker Avance 300 and 200 spectrometers. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS). Mass spectroscopy was performed at the CESAMO. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled under nitrogen over sodium benzophenone ketyl. Triethylamine and CH_2Cl_2 were distilled over CaH_2 under nitrogen. All other reagents were purchased from commercial suppliers and used without further purification. Flash column chromatography was carried out using silica gel (230-400 mesh). Thin layer chromatography (TLC) was carried out on plates coated with silica gel 40 F254 purchased from Aldrich. All reactions were conducted under a dry oxygen-free atmosphere using oven-dried glassware unless otherwise stated. **3**, **5** and **7** were prepared using literature procedures. Mass spectra were performed by the CESAMO (Bordeaux, France) on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source and spectra were recorded in the positive mode. The electrospray needle was maintained at 5000 V and operated at room temperature. Samples were introduced by injection through a 20 μL sample loop into a 4500 μL/min flow of methanol from the LC pump.

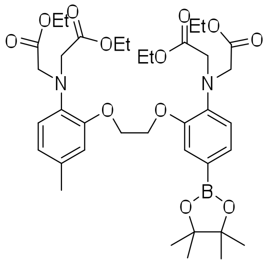


1a

Compound 1a. In a two neck round bottom flask under N_2, BAPTA carboxaldehyde **4** (0.4 g, 0.63 mmol, 1 eq) was dissolved in freshly distilled dichloromethane (80 mL). 2,4-dimethylpyrrole (0.2 mL, 1.9 mmol, 3 eq) and a drop of TFA were added and the mixture was stirred at room temperature overnight. *p*-Chloranil (160 mg, 0.63 mmol, 1 eq) in solution in 20 ml CH_2Cl_2 was added dropwise and the mixture was stirred for 30 min at room temperature. Then triethylamine (4.0 mL) and borontrifluoride etherate (4.0 mL) were added and the mixture was stirred for two additional hours. Water was added and the product extracted with CH_2Cl_2, the organic phase was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by chromatography (silica gel: Petroleum Ether / EtOAc, 8:2, v/v) followed by a recrystallization in ethanol to give **1** as an orange solid (140 mg, 0.16 mmol, 26 %).

MS: (ESI) *m/z* 871 $[M+Na]^+$; High Resolution LSI Calculated $[M+Na]^+$: ($C_{44}H_{55}BF_2N_4O_{10}Na^+$): 871.3871; Found: 871.3871.

^1H NMR (300 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.5 Hz, 1H), 7.79 – 7.74 (m, 3H), 6.67 (d, *J* = 7.2 Hz, 2H), 5.97 (s, 2H), 4.25 (m, 4H), 4.21 (s, 4H), 4.10 (q, *J* = 7.1 Hz, 4H), 4.09 (s, 4H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.54 (s, 6H), 2.24 (s, 3H), 1.48 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 6H), 1.16 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.33, 171.23, 155.28, 150.79, 150.28, 143.10, 140.12, 137.10, 132.24, 128.04, 122.26, 121.13, 121.02, 119.76, 119.08, 115.40, 113.22, 67.55, 67.23, 60.84, 60.52, 53.67, 20.86, 14.53, 14.13, 14.09.

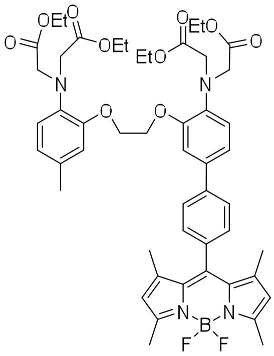


6

Compound 6. In a sealed tube, Bromo BAPTA (**5**) (100 mg, 0.15 mmol, 1 eq), bis(pinacolato) diboron (41 mg, 0.16 mmol, 1.1 eq), potassium acetate (43 mg, 0.44 mmol, 3 eq) and dry DMF (2 ml) were degassed under argon during 20 min. $PdCl_2(dppf)$ (5 mg, 7 μmol, 5%) was added and the mixture was heated under microwave irradiation at 120°C for 15 min. The crude reaction mixture was passed through a silica plug eluting with Et_2O and the solvent was removed under reduced pressure. The product was further purified by recrystallisation in ethanol to yield **6** as a white solid (70 mg, 65%).

MS: (ESI) *m/z* 751 $[M+Na]^+$; High Resolution ESI-MS Calculated $[M+Na]^+$: ($C_{37}H_{53}BN_2O_{12}Na$) 751.3583; Found: 751.3578.

^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.9 Hz, *J* = 1.2 Hz, 1H), 7.24 (d, *J* = 1.2 Hz, 1H), 6.77 - 6.64 (m, 4H), 4.29 - 4.27 (m, 4H), 4.17 (s, 4H), 4.15 (s, 4H), 4.05 (q, *J* = 7.1 Hz, 4H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.31 (s, 12H), 1.13 (t, *J* = 7.1 Hz, 12H); ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.58, 171.36, 150.27, 149.24, 142.04, 136.87, 131.94, 128.71, 121.71, 119.26, 118.65, 117.54, 114.33, 83.50, 67.05, 66.97, 60.76, 60.60, 53.60, 53.53, 24.82, 20.90, 14.05, 14.02.



2a

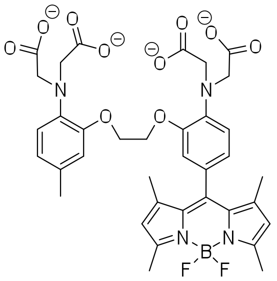
Compound 2a. In a Schlenk tube, BAPTA boronic ester (**6**) (50 mg, 0.07 mmol, 1.1 eq), iodobodipy (**7**) (28 mg, 0.06 mmol, 1 eq) and $Pd(PPh_3)_4$ (7 mg, 6 μmol, 10%), were dissolved in freshly distilled THF (5 ml). An aqueous solution of Na_2CO_3 (0.1 ml, 2M), previously degassed by 20 min argon bubbling, was added and the mixture was heated at 65°C overnight. The crude reaction mixture was evaporated under reduced pressure and the product was purified by column chromatography (SiO_2: Petroleum ether/AcOEt 70:30) followed by a recrystallisation in EtOH to yield **2** as an orange-red crystalline powder (38 mg, 45%).

MS: (MALDI-TOF) *m/z* 925 $[M+H]^+$; High Resolution ESI-MS Calculated $[M]^+$: ($C_{50}H_{59}BF_2N_4O_{10}Na$) 947.4184; Found: 947.4183.

^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.19 (m, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.70 - 6.67 (m, 2H), 5.99 (s, 2H), 4.40 (m, 2H), 4.32 (m, 2H), 4.21 (s, 4H), 4.13 (s, 4H), 4.10 (q, *J* = 7.1 Hz, 4H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 6H), 2.26 (s, 3H), 1.45 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 6H), 1.16 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.59, 171.50, 171.37, 171.33, 155.41, 150.53, 150.28, 149.25, 143.13, 142.05, 141.65, 141.19, 139.39, 136.95, 136.88, 133.74, 133.34, 132.13, 131.96, 131.48, 128.72, 128.68, 128.41, 127.01, 126.67, 121.95, 121.72, 121.17, 121.13, 120.15, 119.46, 119.27, 119.18, 118.66, 117.55, 114.72, 114.35, 112.42, 83.51, 67.53, 67.08, 66.98, 60.80, 60.60, 53.62, 24.83, 20.92, 14.60, 14.09.

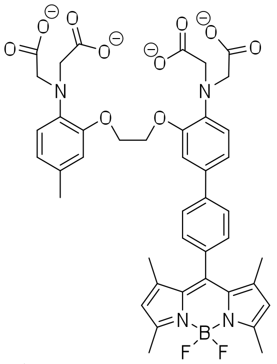
General hydrolysis procedure

BAPTA-BODIPY (**1a**) (5 mg, 6 µmol, 1eq) was dissolved in a mixture of THF (1 ml) and MeOH (1 ml), then LiOH (5 mg, 120 µmol, 20 eq) in 0.1 ml of water was added and the mixture was stirred at rt overnight. The solvent was evaporated under reduced pressure without heating and the crude product was dispersed in ethyl acetate and centrifuged. The solvent was pipetted off, the solid dissolved in water and acidified with 1M HCl. The precipitate was dissolved in an appropiate amount of KOH-solution to form the potassium salt and freeze dried to yield 5.2 mg BAPTA-BODIPY potassium salt.



1

Compound 1. ^{1}H NMR (200 MHz, MeOH-d_4) δ 7.25 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 6.87 – 6.83 (m, 2H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 2H), 4.52 (m, 2H), 4.43 (m, 2H), 3.73 (s, 4H), 3.54 (s, 4H), 2.45 (s, 6H), 2.26 (s, 3H), 1.50 (s, 6H).



2

Compound 2. ^{1}H NMR (200 MHz, MeOH-d_4) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.34 (s, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 6.86 (s, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 6.08 (s, 2H), 4.53 (m, 2H), 4.44 (m, 2H), 3.62 (s, 4H), 3.53 (s, 4H), 2.50 (s, 6H), 2.31 (s, 3H), 1.50 (s, 6H).

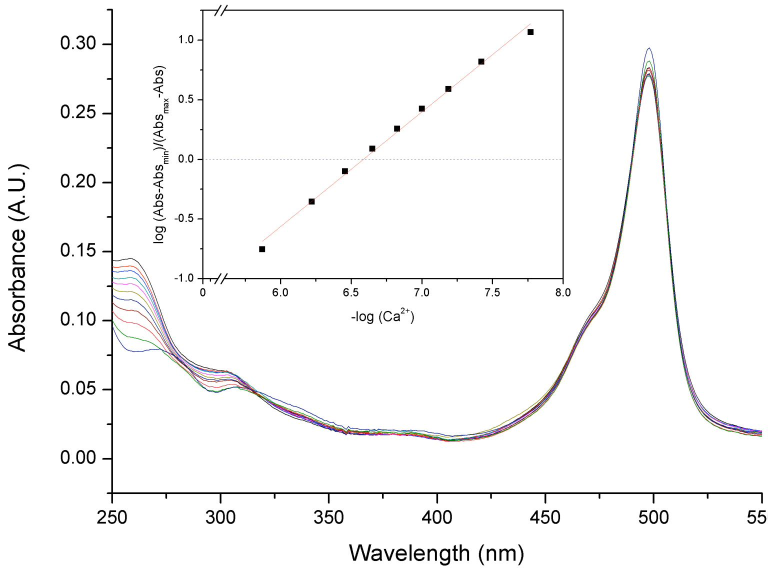


Figure S1 Electronic absorption spectra of **1** as a function of Ca^{2+} concentration. Inset: Hill plot for ion binding, monitored at λ_{ex} = 260 nm.

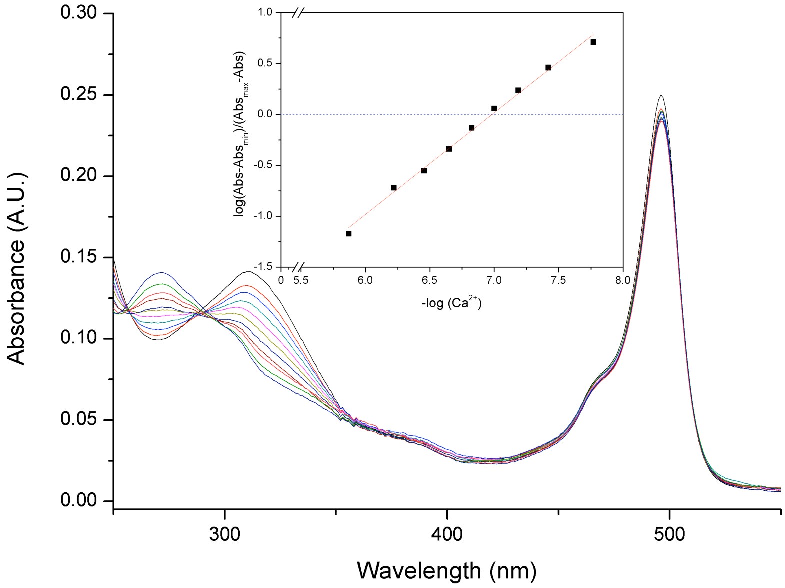


Figure S2 Electronic absorption spectra of **2** as a function of Ca^{2+} concentration (λ_{ex} = 316 nm). Inset: Hill plot for ion binding, monitored at λ_{ex} = 316 nm.

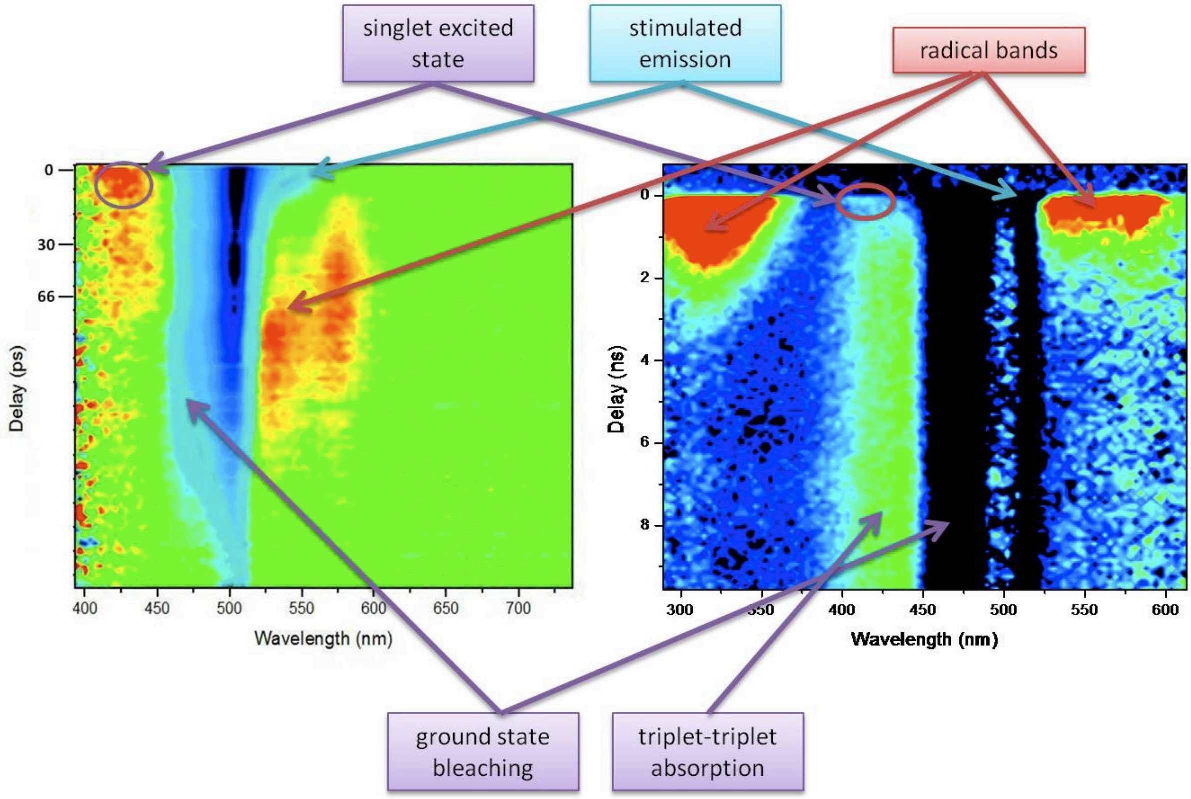


Figure S3 Transient absorption maps of **1a** in THF at 0-1 ns (left) and at 0-10 ns (right) (λ_{exc}=500 nm).

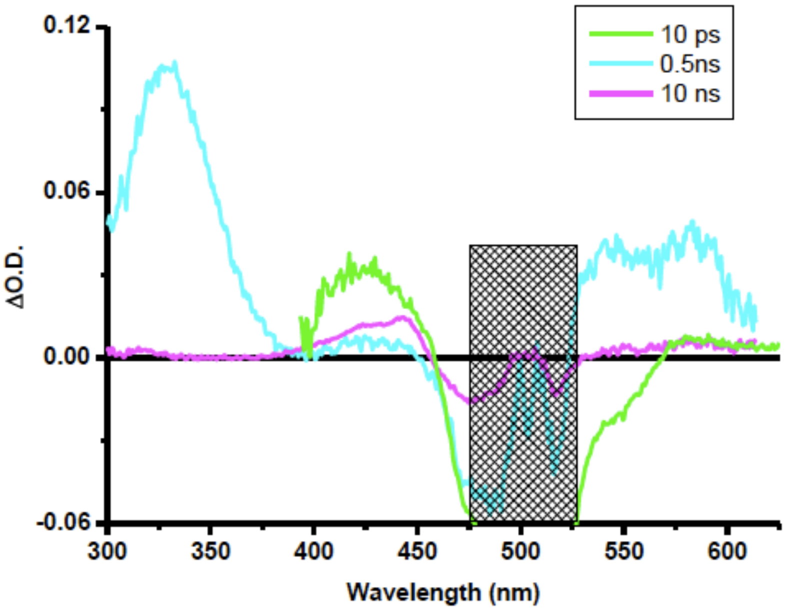


Figure S4 Transient absorption spectra of **1a** in THF at different time delays (λ_{exc} =500nm), corresponding predominantly to singlet excited state (10 ps), charge separated state (0.5 ns), triplet state (10ns).

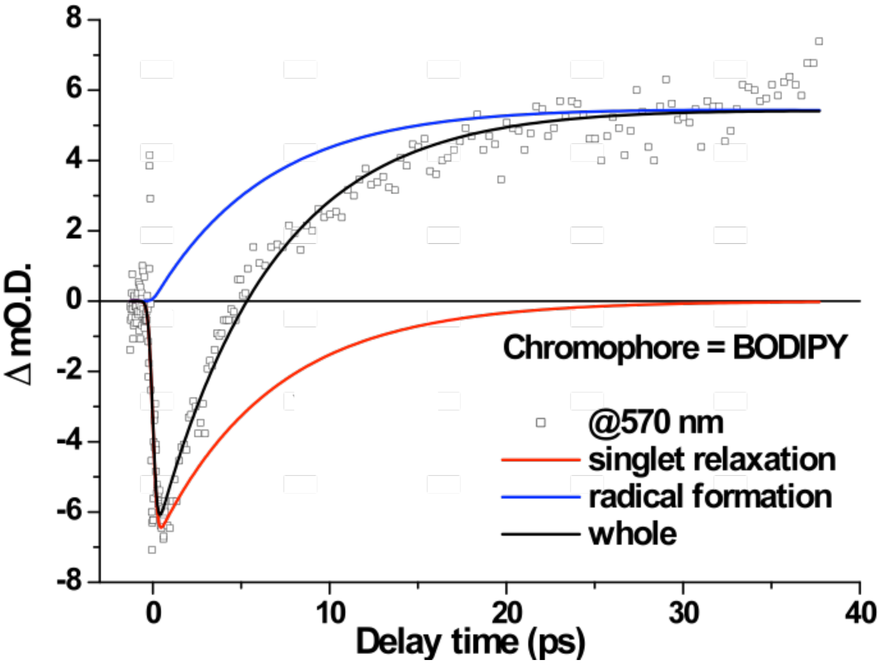


Figure S5 Kinetics of changes in transient absorption spectrum at 570 nm for **1a** in THF showing concerted singlet depopulation and radical rising.

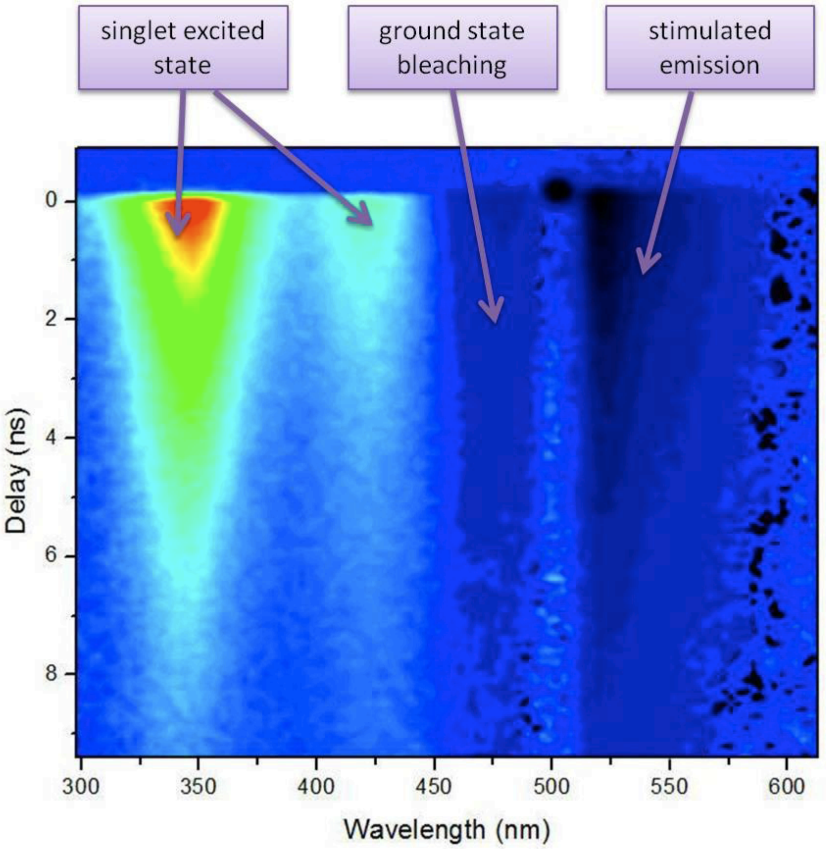


Figure S6 Transient absorption map of **1a** in THF in the presence of $HClO_4$ (λ_{exc} =500nm), where a common decay rate parameter is observed.

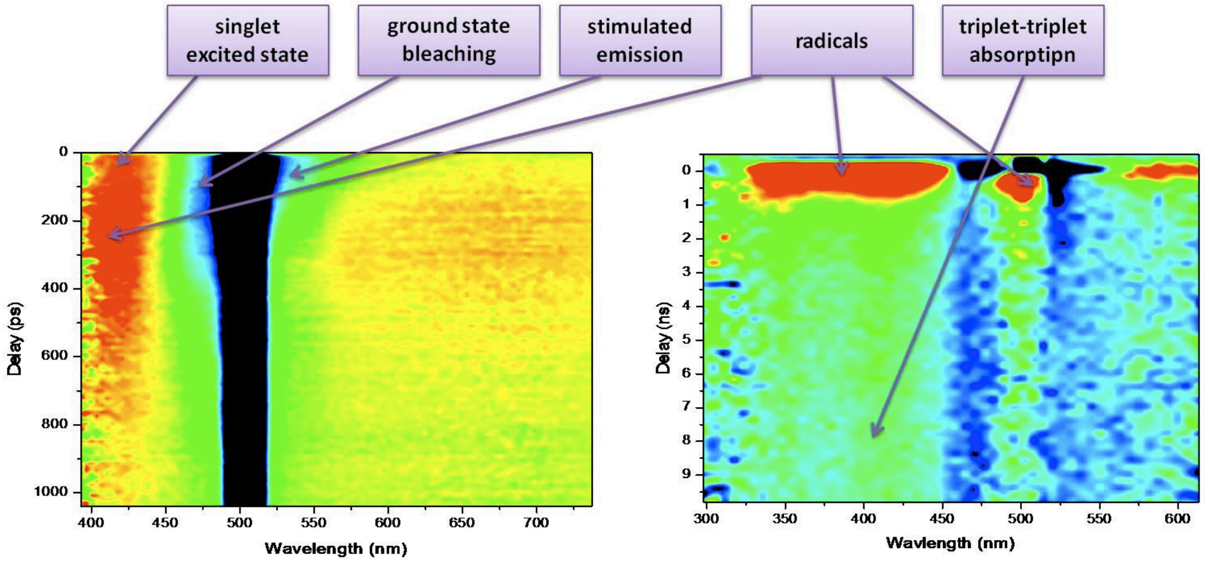


Figure S7 Transient absorption map for **2a** in THF at 0-1ns (left) and at 0-10ns (right) (λ_{exc} =500nm).

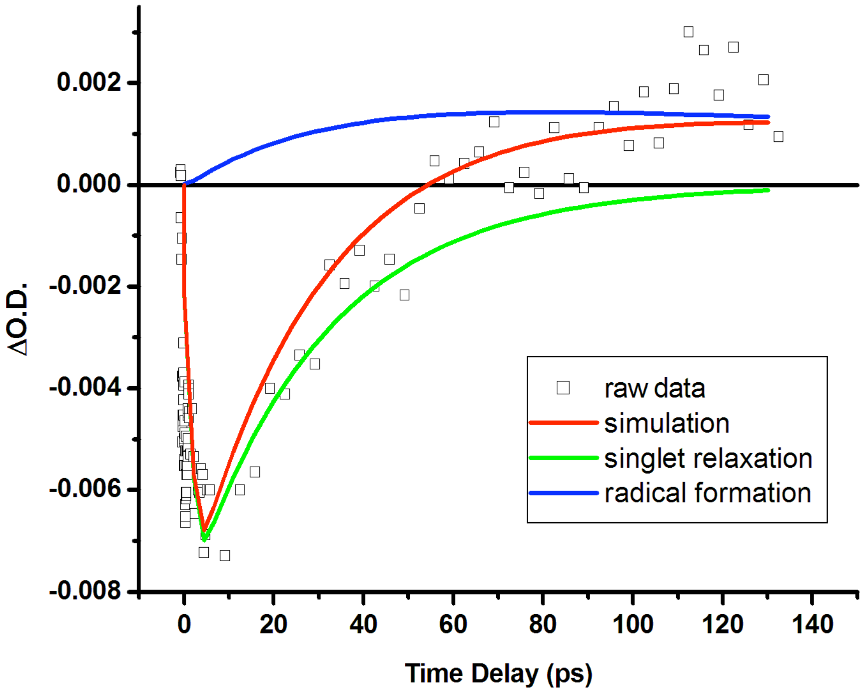


Figure S8 Kinetics of changes in transient absorption spectrum at 545 nm for **2a** in THF showing concerted singlet depopulation and radical rising.

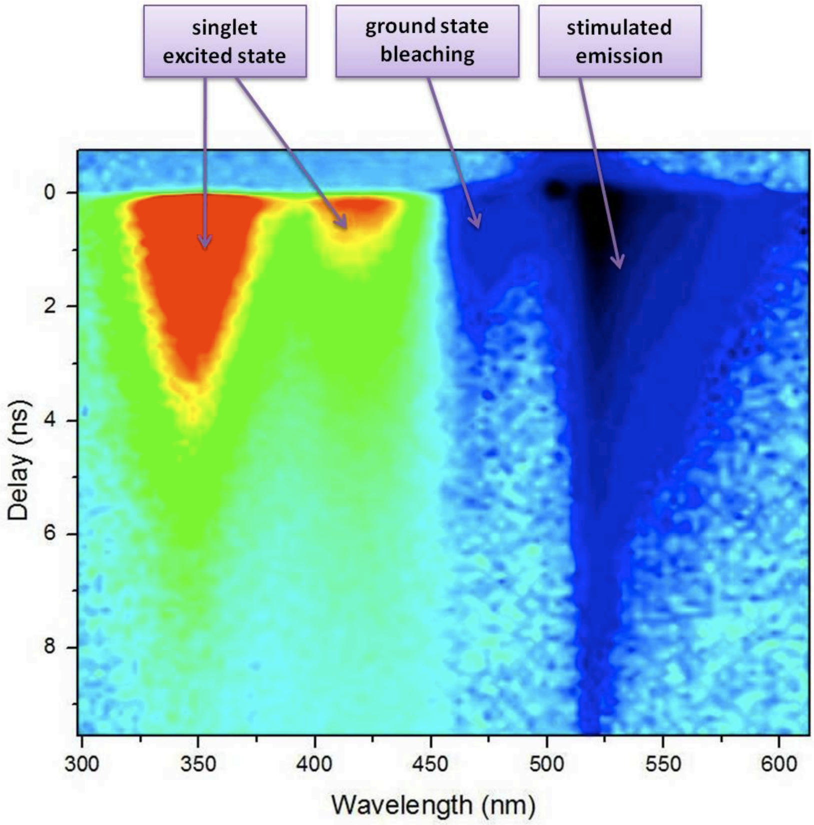


Figure S9 Transient absorption map for **2a**.H^+ in THF (λ_{exc} =500nm).

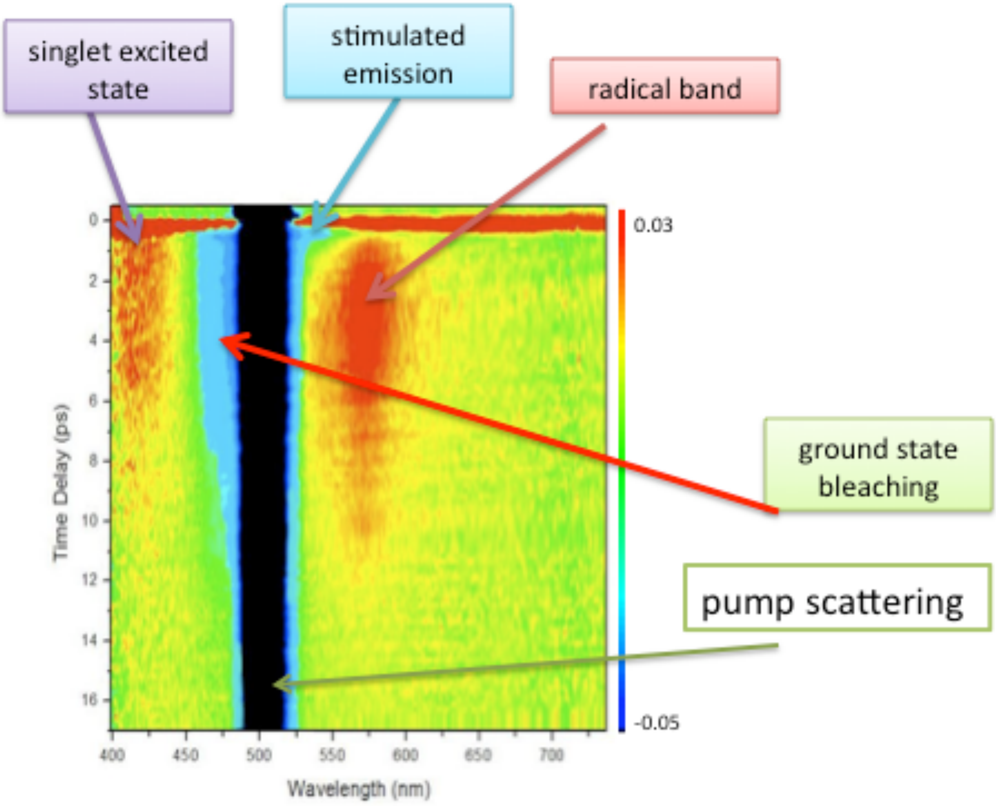


Figure S10 Transient absorption map for molecule **1** in buffered water (λ_{exc} =500nm).

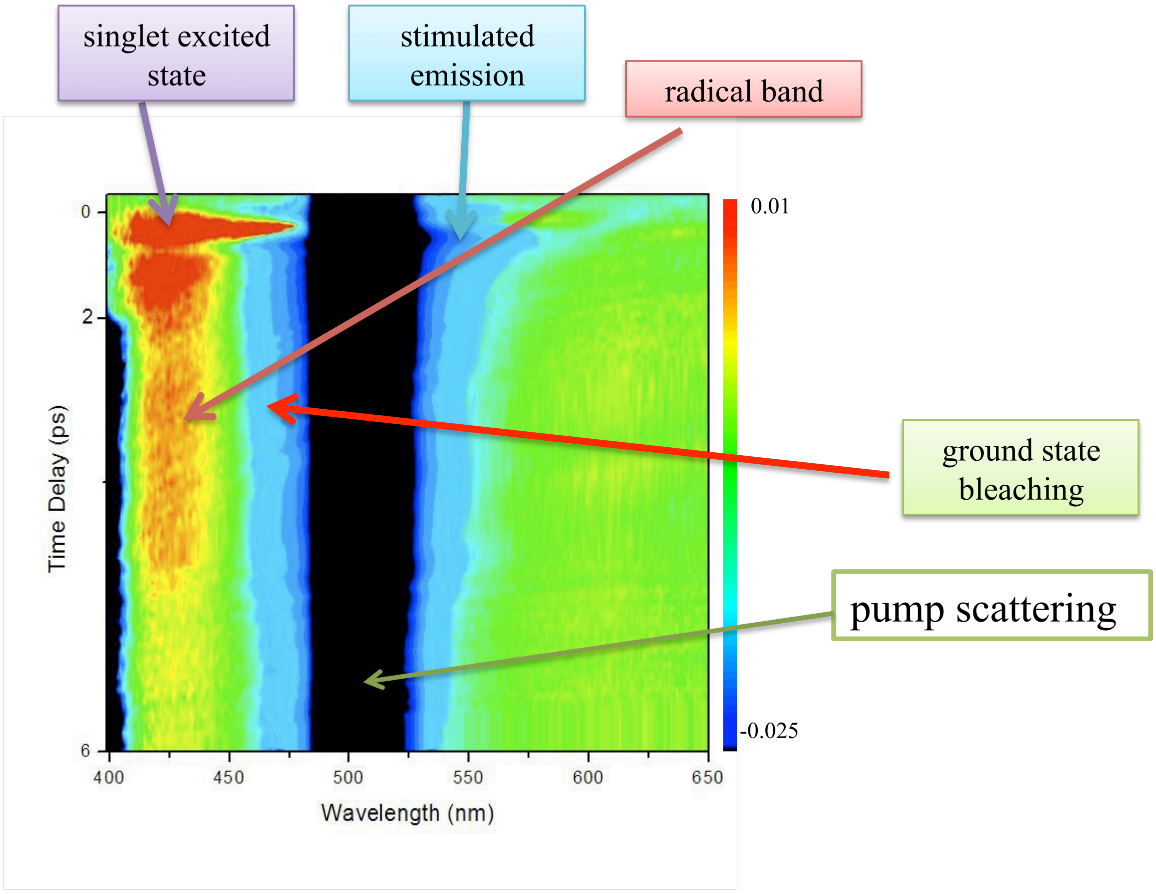


Figure S11 Transient absorption map for molecule **2** in buffered water (λ_{exc} =500nm).

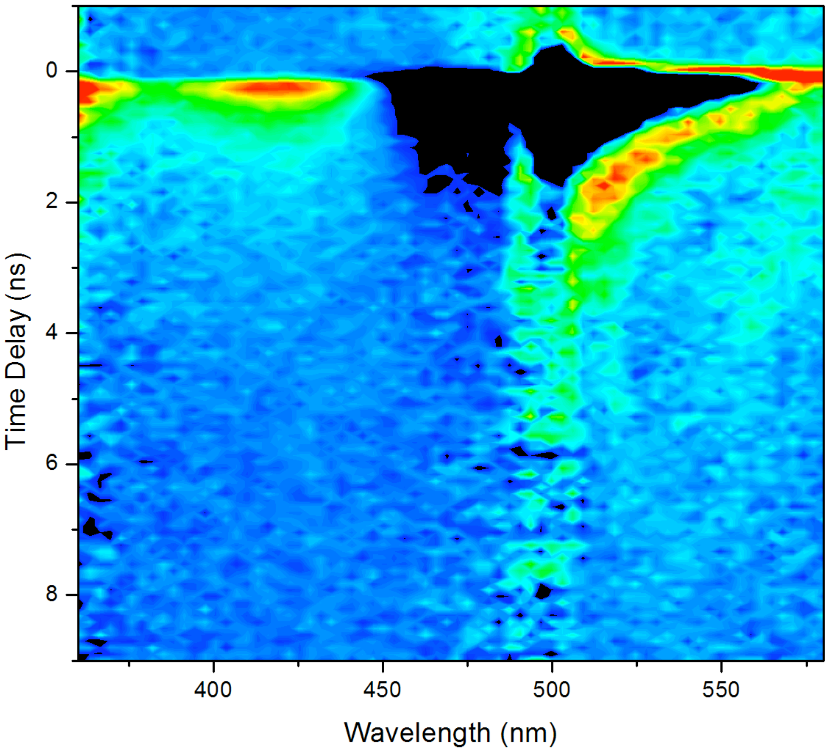


Figure S12 Transient absorption map of molecule **1** in buffered water in presence of Ca^{2+} (λ_{exc} =500nm).

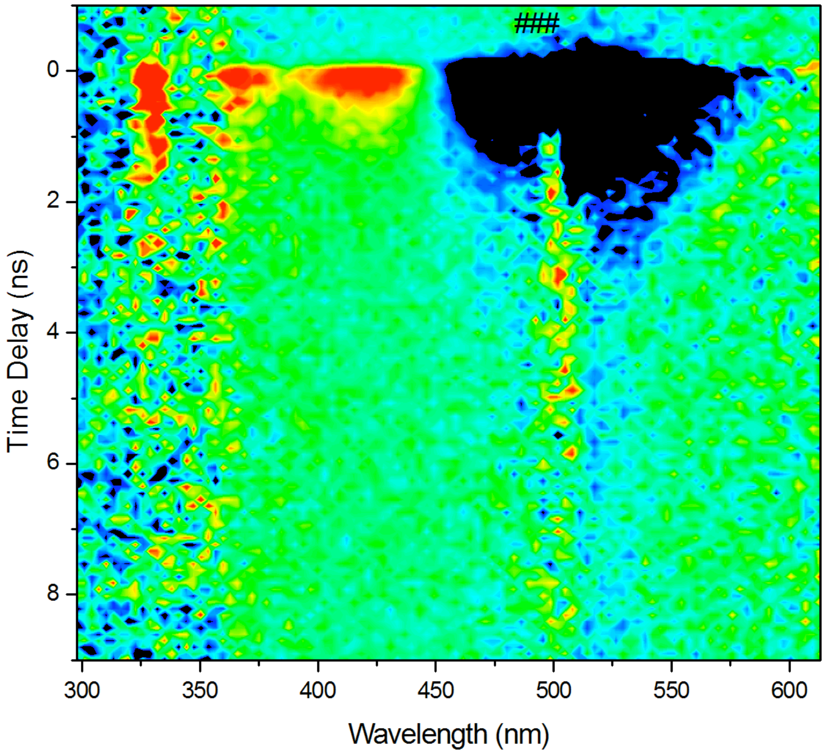


Figure S13 Transient absorption map of molecule **2** in buffered water in presence of Ca^{2+} (λ_{exc} =500nm).