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Electronic Supplementary Information

Strongly Oxidizing Perylene-3,4-dicarboximides for Use in Water Oxidation Photoelectrochemical Cells

Rebecca J. Lindquist,[a] Brian T. Phelan,[a] Anna Reynal,[b,c] Eric A. Margulies,[a] Leah E. Shoer,[a] James R. Durrant,[b] Michael R. Wasielewski*,[a]

[a]Department of Chemistry and Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, IL 60208-3113, USA

[b]Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, UK.

[c]Current address School of Chemistry, Newcastle University, Newcastle Upon Tyne NE1 7RU, UK.

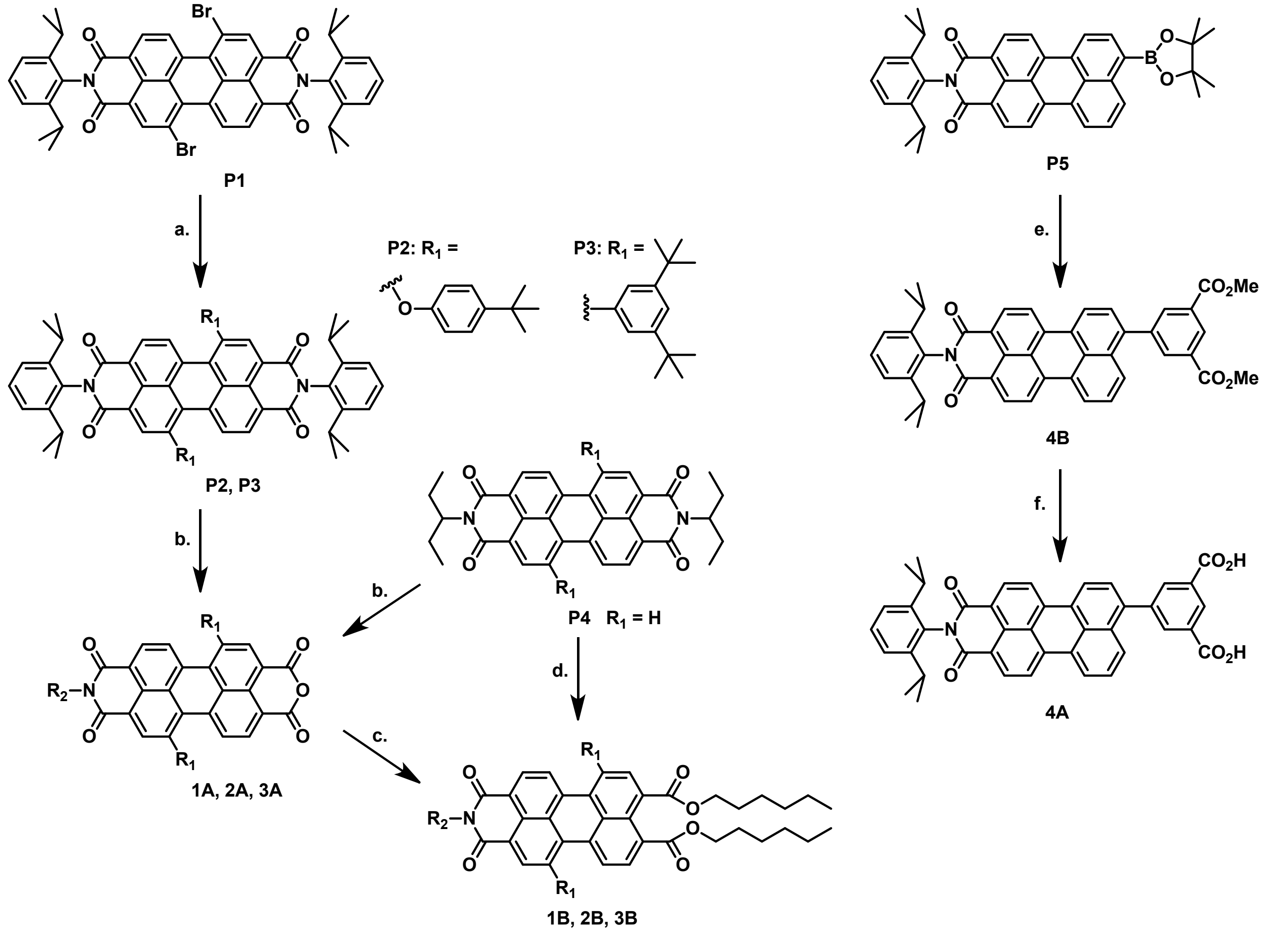
*Address correspondence to this author. E-mail: m-wasielewski@northwestern.edu

Contents:

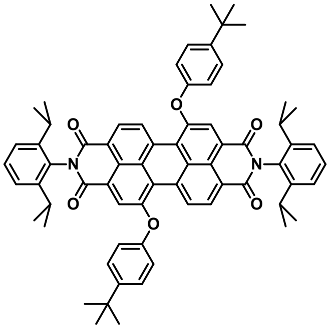
I. Synthesis

^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature at 500 MHz and 126 MHz, respectively, using a Bruker Avance III spectrometer. Mass spectrometry was performed using a Bruker Autoflex III MALDI-TOF instrument. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Reagents **P1**,[1] **P3**,[1] **P4**,[2] **P5**,[3] **P6**,[4] 2-phenylpyridin-4-ylamine (**NH_2-ppy**),[5] and $[Cp^*IrCl_2]_2$[6] were synthesized according to reported methods.

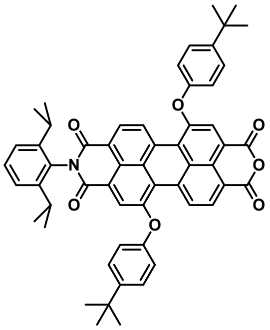
Scheme S1. Synthesis of 1A-4A and 1B-4B [a]



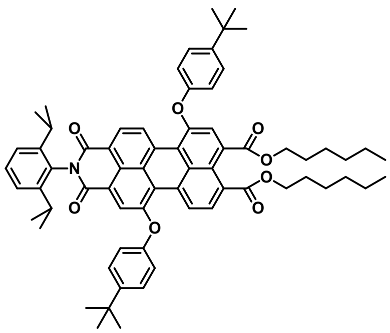
[a]Reaction conditions: (a, **P2**) (1) 4-*tert*-butylphenol, Cs_2CO_3, DMF, 160 °C, 75 min, (2) HOAc, RT, 1.5 h, 80%; (a, **P3**) previously reported.[1] (b) (1) KOH, ($KF\cdot 2H_2O$), *t*-BuOH, 70-105 °C, 35-120 min; (2) HOAc, 2 N HCl, RT, overnight, 7-68%. (c, **1B**, **2B**) 1-bromohexane, K_2CO_3, 1-hexanol, 90 °C, 19-29 h, 44-51%. (d) (1) KOH, *t*-BuOH, 100 °C, 20 min; (2) HOAc, 2 N HCl, RT, overnight; (3) 1-bromohexane, K_2CO_3, 1-hexanol, 90 °C, 13 h, 17%. (e) 5-bromoisophthalate, K_2CO_3, $Pd(PPh_3)_4$, toluene/H_2O/EtOH,80 °C, 13 h, 97%. (f) (1) KOH, THF, H_2O, 80 °C, 12 h; (2) 2 N HCl, 97%.



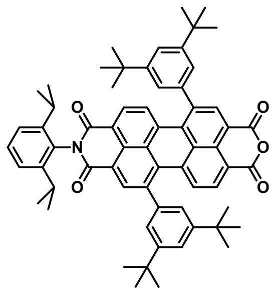
Compound P2.[7] Compound **P1** (804 mg, 0.926 mmol), 4-*tert*-butylphenol (461 mg, 3.07 mmol), and Cs_2CO_3 (560 mg, 1.72 mmol), were combined in DMF (32 mL) and heated to 160 °C under N_2. After 75 min, the mixture was cooled, and 5 mL acetic acid was added and stirred for 1.5 h. Brine was added until a precipitate was formed, and the crude product was collected by filtration. Column chromatography on a silica column with 4:1 CH_2Cl_2/hexanes as the eluent yielded the product as a mixture of isomers with the 1,6:1,7 isomers in a 1:5.4 ratio (749 mg, 80%). For the 1,7 isomer (not isolated): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (d, J = 8.3 Hz, 2H), 8.69 (d, J = 8.3 Hz, 2H), 8.45 (s, 2H), 7.50 – 7.43 (m, 6H), 7.32 (d, J = 7.8 Hz, 4H), 7.11 (d, J = 8.8 Hz, 4H), 2.72 (hept, J = 6.7 Hz, 4H), 1.35 (s, 18H), 1.17 – 1.12 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.51, 162.99, 155.31, 152.64, 148.02, 145.59, 133.81, 130.81, 130.44, 129.73, 129.65, 129.02, 127.46, 125.88, 124.78, 124.57, 124.07, 123.99, 122.28, 118.70, 34.55, 31.48, 29.18, 24.06, 24.02. HRMS (MALDI) m/z calcd for $C_{68}H_{67}N_2O_6$ $[M + H]^+$ 1007.500; found 1007.507.



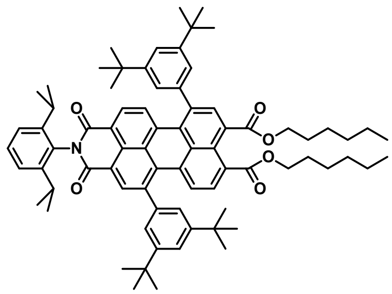
Compound 1A. KOH (35 mg, 0.62 mmol) was added to a solution of **P2** (57 mg, 0.056 mmol) in 5 mL *t*-BuOH and heated over 50 min. to 70 °C under N_2. The reaction mixture was then cooled, and 7 mL acetic acid and 3.5 mL 2 N HCl were added and stirred overnight. The crude product was collected by filtration then purified on a silica column with 1% acetic acid/15% hexanes/ 84% CH_2Cl_2 as eluent followed by HPLC to separate the 1,6 and 1,7 isomers with 40% hexanes/60% CH_2Cl_2 as eluent to yield the pure product (15 mg, 31%). ^1H NMR (500 MHz, $CDCl_3$) δ 9.74 – 9.62 (m, 2H), 8.70 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.43 (s, 1H), 8.37 (s, 1H), 7.52 – 7.43 (m, 5H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.16 – 7.08 (m, 4H), 2.70 (hept, *J* = 6.7 Hz, 2H), 1.38 (s, 9H), 1.36 (s, 9H), 1.81 – 1.11 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.47, 162.97, 159.97, 159.96, 156.27, 155.63, 152.50, 152.30, 148.77, 148.65, 145.67, 135.25, 133.25, 132.45, 130.78, 130.42, 129.96, 129.82, 129.79, 129.74, 129.07, 127.80, 127.71, 127.41, 125.83, 125.70, 125.56, 124.65, 124.20, 123.48, 122.90, 119.51, 119.29, 119.21, 117.95, 34.74, 34.72, 31.58, 29.30, 24.17, 24.11. MS (MALDI) m/z calcd for $C_{56}H_{50}NO_7$ $[M + H]^+$ 848.36; found 848.28.



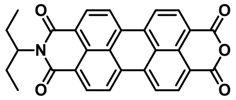
Compound 1B. To a solution of **1A** (11 mg, 0.013 mmol) and 1-bromohexane (0.03 mL, 0.2 mmol) in 2 mL 1-hexanol was added K_2CO_3 (13 mg, 0.094 mmol). The reaction flask was heated to 90 °C under N_2. After 29 h, the mixture was cooled to RT and chloroform was added. This mixture was extracted 4 × H_2O, and solvent was removed under vacuum. Column chromatography on a silica column with 20% hexanes/80% CH_2Cl_2 as the eluent yielded the pure product (5.7 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 – 9.37 (m, 2H), 8.62 (d, *J* = 8.3 Hz, 1H), 8.39 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.79 (s, 1H), 7.48 – 7.38 (m, 5H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.09 – 7.04 (m, 4H), 4.30 (t, *J* = 6.9 Hz, 2H), 4.24 (t, *J* = 6.9 Hz, 2H), 2.71 (hept, *J* = 6.8 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.73 – 1.65 (m, 2H), 1.49 – 1.39 (m, 4H), 1.37 – 1.25 (m, 8H), 1.35 (s, 9H), 1.33 (s, 9H), 1.16 – 1.11 (m, 12H), 0.95 – 0.81 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.53, 167.79, 163.83, 163.29, 153.91, 153.23, 153.02, 147.69, 147.55, 145.74, 134.45, 132.80, 132.25, 131.04, 130.96, 130.89, 130.78, 129.63, 129.55, 129.33, 128.94, 128.54, 127.98, 127.39, 127.32, 125.98, 125.87, 125.38, 124.99, 124.12, 122.93, 121.63, 121.27, 118.66, 118.49, 66.00, 65.91, 34.60, 31.65, 31.59, 31.53, 29.24, 28.70, 28.44, 25.82, 25.64, 24.16, 24.11, 22.70, 22.64, 14.19, 14.16. HRMS (MALDI) m/z calcd for $C_{68}H_{76}NO_8$ $[M + H]^+$ 1034.557; found 1034.555.



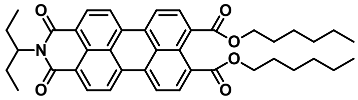
Compound 2A. Compound **P3** (20 mg, 0.019 mmol), KOH (34 mg, 0.61 mmol), and KF·2H_2O (51 mg, 0.54 mmol) in 2 mL *t*-BuOH were heated to 105°C under N_2. After 2 h, the mixture was cooled to RT and 3 mL acetic acid and 1.5 mL 2 N HCl were added. The reaction mixture was stirred overnight, and the crude product was collected by filtration. Column chromatography on a silica column with 1% ethyl acetate/ 29% hexanes/ 70% CH_2Cl_2 as the eluent yielded the product as a mixture of isomers (12 mg, 68%). For the 1,7 isomer: ^1H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.71 (s, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 1.4 Hz, 2H), 7.37 (d, *J* = 1.4 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.71 (hept, *J* = 7.0 Hz, 2H), 1.33 (s, 36H), 1.18 (d, *J* = 6.8 Hz, 6H), 1.12 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.52, 163.48, 160.41, 160.12, 153.49, 145.72, 143.45, 142.80, 141.02, 140.76, 137.38, 137.09, 135.78, 134.97, 134.55, 132.42, 131.22, 130.89, 130.67, 130.31, 130.09, 129.81, 129.76, 129.70, 128.31, 124.21, 123.41, 123.34, 122.97, 122.78, 122.33, 118.24, 117.57, 35.29, 35.27, 31.60, 31.52, 29.39, 24.06, 24.04. HRMS (MALDI) m/z calcd for $C_{64}H_{66}NO_5$ $[M + H]^+$ 928.494; found 928.496.



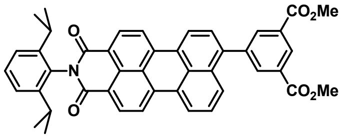
Compound 2B. To a solution of **2A** (15 mg, 0.016 mmol) in 2 mL 1-hexanol was added 1-bromohexane (0.03 mL, 0.2 mmol) and K_2CO_3 (17 mg, 0.12 mmol). The reaction flask was heated to 90 °C under N_2. After 19 h, the mixture was cooled to RT and dried under vacuum. Column chromatography on a silica column with 30% hexanes/70% CH_2Cl_2 as the eluent yielded the product as a mixture of isomers (9.4 mg, 51%). For the 1,7 isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.15 (s, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.37 (d, J = 1.4 Hz, 2H), 7.34 (d, J = 1.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 4.32 (t, J = 6.8 Hz, 2H), 4.28 (t, J = 6.9 Hz, 2H), 2.72 (hept, J = 6.6 Hz, 2H), 1.82 – 1.68 (m, 4H), 1.48 – 1.36 (m, 4H), 1.36 – 1.26 (m, 8H), 1.30 (s, 36H), 1.18 (d, J = 6.8 Hz, 6H), 1.11 (d, J = 6.8 Hz, 6H), 0.95 – 0.78 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.54, 168.41, 163.93, 163.89, 152.84, 145.78, 141.57, 141.52, 141.44, 141.22, 136.45, 135.60, 134.33, 134.20, 132.56, 131.88, 131.05, 131.02, 130.88, 130.35, 130.30, 130.16, 129.95, 129.67, 129.60, 129.56, 128.67, 128.09, 127.28, 124.12, 123.86, 123.76, 122.05, 121.97, 121.47, 120.57, 65.95, 65.76, 35.16, 31.65, 31.60, 31.56, 31.51, 31.47, 29.30, 28.66, 28.64, 25.85, 25.74, 24.05, 22.70, 22.69, 14.18. MS (MALDI) m/z calcd for $C_{76}H_{92}NO_6$ $[M + H]^+$ 1114.69; found 1114.73.



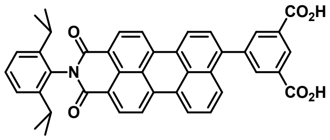
Compound 3A. Compound **P4** (200 mg, 0.376 mmol) and KOH (63 mg, 1.1 mmol) were dissolved in 30 mL *t*-BuOH and heated to 100 °C for 35 min. 20 mL acetic acid and 10 mL 2N HCl were added to the cooled reaction mixture, and it was stirred at room temperature overnight. The precipitated crude product was then collected by filtration, rinsed with H_2O, and dried on the filter paper with vacuum. The dried precipitate was then rinsed thoroughly with CH_2Cl_2. After solvent removal, the filtrate was subjected to column chromatography on a silica column with 2% acetone/98% CH_2Cl_2 → 5% acetone/10% acetic acid/85% CH_2Cl_2. The fractions were extracted 4×H_2O before solvent removal under vacuum. The isolated material was further purified by dissolution in CH_2Cl_2 and addition of hexanes until precipitate began to form. Isolation of the precipitate by filtration yielded pure product (13 mg, 7%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 – 8.63 (m, 8H), 5.12 – 5.01 (m, 1H), 2.33 – 2.20 (m, 2H), 2.01 – 1.88 (m, 2H), 0.93 (t, J = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.18, 136.60, 133.86, 133.78, 124.11, 123.37, 119.18, 57.98, 25.13, 11.49. MS (MALDI) m/z calcd for $C_{29}H_{19}NO_5$ $[M]^+$ 461.13; found 461.07.



Compound 3B. Compound **P4** (99 mg, 0.19 mmol) and KOH (162 mg, 2.88 mmol) were added to 15 mL *t*-BuOH at 110 °C and stirred for 20 minutes under nitrogen. The reaction mixture was cooled, 20 mL acetic acid and 10 mL 2 N HCl were added, and it was stirred overnight. The precipitate was collected by filtration with water and once dry rinsed with 50 mL CH_2Cl_2. The filtrate was collected and the volume reduced to 5 mL. 30 mL hexanes was added, and the precipitate was collected by filtration. It was dissolved again in CH_2Cl_2 and the process was repeated three more times. This resulting mixture enriched in **3A** (62 mg) was then dissolved in 10 mL pyridine. K_2CO_3 (186 mg, 1.35 mmol), 1-bromohexane (0.24 mL, 1.71 mmol), and 1-hexanol (10 mL) were added and the reaction mixture was purged with nitrogen. It was heated to 90 °C for 13 hours then cooled, filtered, and the precipitate rinsed thoroughly with CH_2Cl_2. The filtrate was extracted 4×H_2O and the solvent removed under vacuum. Column chromatography on a silica column with 5% ethyl acetate/50% hexanes/45% CH_2Cl_2 as the eluent yielded the pure product (21 mg, 17%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.0 Hz, 2H), 8.26 (t, *J* = 8.2 Hz, 4H), 8.00 (d, *J* = 7.9 Hz, 2H), 5.12 – 5.02 (m, 1H), 4.35 (t, *J* = 6.9 Hz, 4H), 2.34 – 2.21 (m, 2H), 2.03 – 1.89 (m, 2H), 1.87 – 1.77 (m, 4H), 1.53 – 1.42 (m, 4H), 1.41 – 1.29 (m, 8H), 0.98 – 0.87 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.39, 135.20, 132.15, 131.90, 130.35, 129.41, 129.27, 129.13, 125.90, 122.52, 121.85, 66.00, 57.63, 31.67, 28.70, 25.83, 25.17, 22.71, 14.17, 11.54. MS (MALDI) m/z calcd for $C_{41}H_{46}NO_6$ $[M]^+$ 647.32; found 647.26.

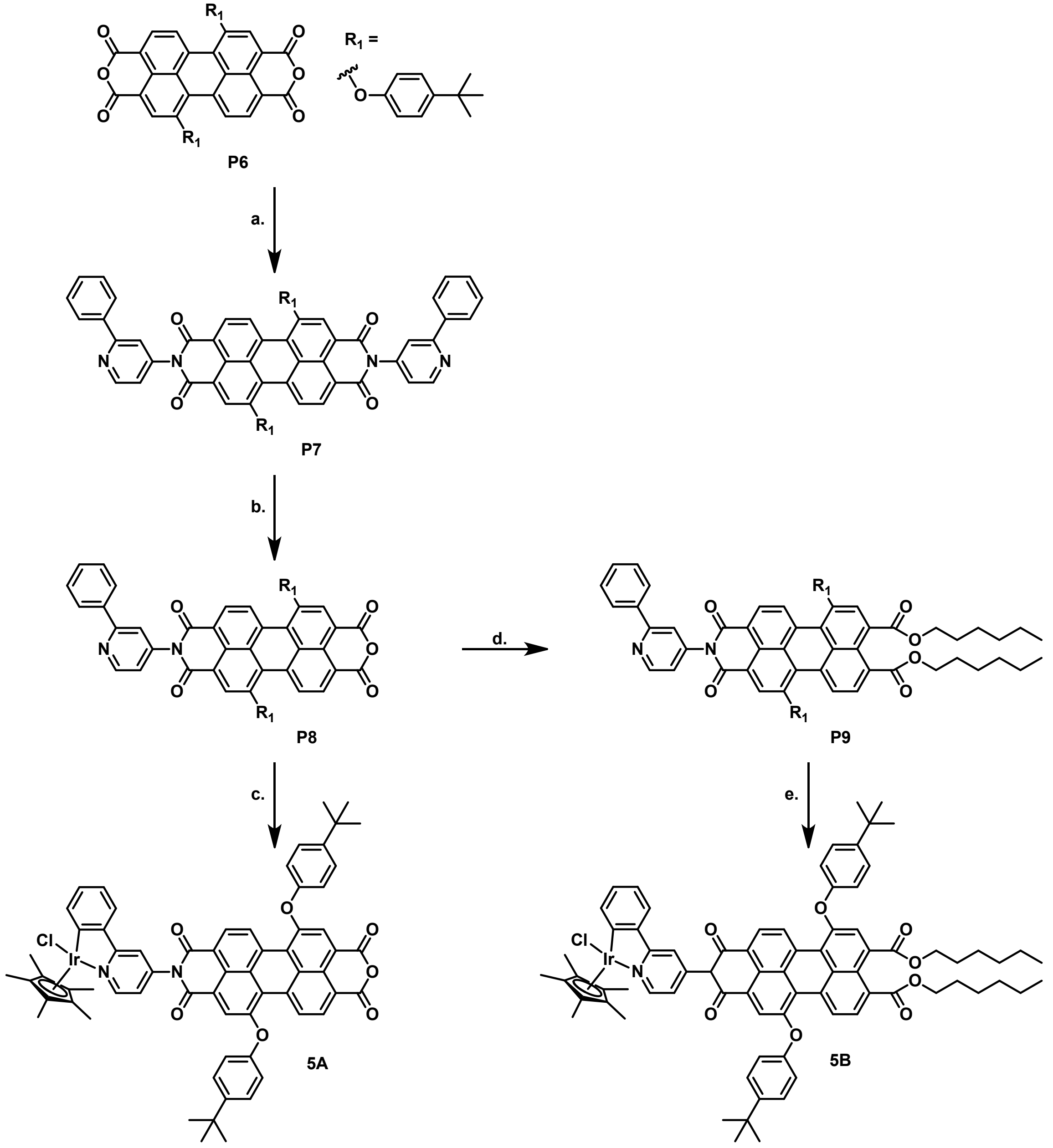


Compound 4B. K_2CO_3 (881 mg, 6.37 mmol) in 3 mL H_2O was added to a mixture of **P7** (166 mg, 0.273 mmol) and dimethyl 5-bromoisophthalate (50 mg, 0.18 mmol) in 7.7 mL toluene and 0.6 mL ethanol. The mixture was purged with nitrogen and $Pd(PPh_3)_4$ (15 mg, 0.013 mg) was added. The mixture was stirred at 80 °C under nitrogen for 13 hours and then cooled to room temperature. Chloroform was added to the cooled reaction mixture, it was extracted 3 × H_2O, and solvent was removed under vacuum. Column chromatography on a silica column with 1% acetone/30% hexanes/69% CH_2Cl_2 as the eluent yielded the pure product (119 mg, 97%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.82 (t, *J* = 1.6 Hz, 1H), 8.73 – 8.66 (m, 2H), 8.58 – 8.48 (m, 4H), 8.43 (d, *J* = 1.6 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.49 (dd, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 4.00 (s, 6H), 2.78 (hept, *J* = 6.8 Hz, 2H), 1.19 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.18, 164.10, 145.82, 140.96, 140.79, 137.63, 137.34, 135.26, 132.54, 132.27, 132.25, 131.28, 131.11, 130.66, 130.28, 129.75, 129.61, 129.55, 128.64, 128.52, 127.73, 127.09, 124.23, 124.18, 123.53, 121.35, 121.30, 120.73, 120.58, 52.78, 29.28, 24.16. HRMS (MALDI) m/z calcd for $C_{44}H_{36}NO_6$ $[M + H]^+$ 674.254; found 674.256.

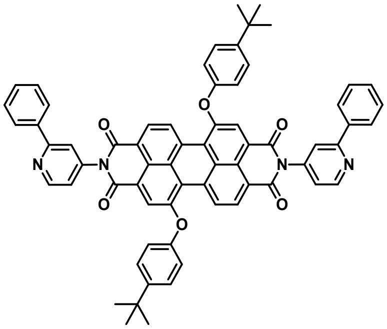


Compound 4A. To **4B** (41 mg, 0.061 mmol) in THF was added KOH (38 mg, 0.67 mmol) in 0.5 mL H_2O. After stirring at 80 °C for 12 h under nitrogen, the reaction mixture was cooled and the 10 mL 2 N HCl was added. The crude product was collected by filtration and rinsed with H_2O. The product was purified on a silica column with 50% acetone/50% CH_2Cl_2 → 5% acetic acid/50% acetone/45% CH_2Cl_2 as the eluent. Fractions were extracted 4 × H_2O before solvent removal under vacuum to yield the product (33 mg, 97%). ^{1}H NMR (500 MHz, THF-d8) δ 8.85 – 8.71 (m, 5H), 8.65 – 8.61 (m, 2H), 8.42 (d, *J* = 1.6 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 2.79 (hept, *J* = 6.8 Hz, 2H), 1.14 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (126 MHz, THF-d8) δ 166.87, 164.35, 146.86, 142.28, 141.54, 138.43, 138.19, 135.73, 133.53, 132.96, 132.73, 132.53, 131.49, 131.09, 130.70, 130.37, 129.66, 129.55, 129.40, 129.38, 128.54, 127.97, 125.35, 124.83, 124.35, 122.48, 121.85, 121.76, 30.01, 25.86. HRMS (MALDI) m/z calcd for $C_{42}H_{32}NO_6$ $[M + H]^+$ 646.223; found 646.226.

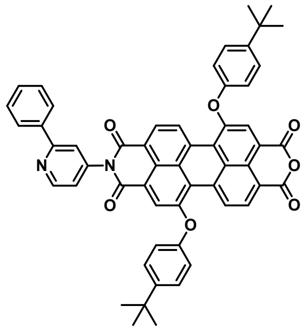
Scheme S2. Synthesis of 5A and 5B[a]



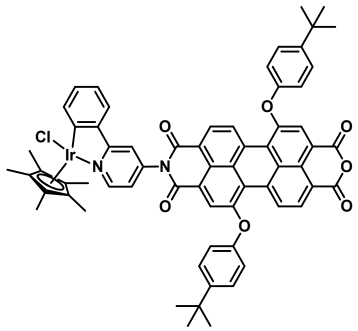
[a]Reaction conditions: (a) 2-phenylpyridin-4-ylamine, $Zn(OAc)_2$, pyridine, 100 °C, 48 h, 73%. (b) (1) KOH, *t*-BuOH, 70-80 °C, 70 min; (2) HOAc, 2 N HCl, RT, overnight, 17%. (c) $[Cp^*IrCl_2]_2$, $NaOAc\cdot 3H_2O$, CH_2Cl_2, RT, 36 h, 58%. (d) 1-bromohexane, K_2CO_3, 1-hexanol, 90 °C, 50 h, 23%. (e) $[Cp^*IrCl_2]_2$, $NaOAc\cdot 3H_2O$, CH_2Cl_2, RT, 24 h, 90%.



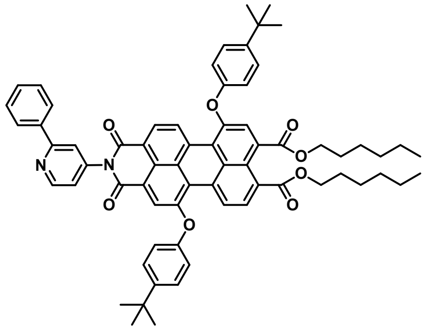
Compound P7. Compound **P6** (50 mg, 0.073 mmol) was dissolved in 10 mL pyridine and heated to 100 °C. **NH$_2$-ppy** (95 mg, 0.56 mmol) and Zn(OAc)$_2$ (64 mg, 0.35 mmol) were added and the reaction mixture was stirred for 48 hours. After solvent removal under vacuum, column chromatography on a silica column with 50% ethyl acetate/50% CH$_2$Cl$_2$ as the eluent yielded the pure product (53 mg, 73%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.56 (d, *J* = 8.4 Hz, 2H), 8.80 (dd, *J* = 5.1, 0.7 Hz, 2H), 8.57 (d, *J* = 8.4 Hz, 2H), 8.31 (s, 2H), 7.96 – 7.87 (m, 4H), 7.78 – 7.76 (m, 2H), 7.52 – 7.45 (m, 4H), 7.41 – 7.37 (m, 6H), 7.21 (dd, *J* = 5.2, 1.9 Hz, 2H), 7.15 – 7.07 (m, 4H), 1.35 (s, 18H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.78, 162.45, 159.46, 155.95, 152.31, 150.97, 148.88, 143.60, 138.60, 133.89, 130.56, 129.43, 129.30, 129.11, 128.81, 127.80, 127.14, 125.08, 124.06, 123.96, 123.47, 122.03, 121.89, 120.97, 119.38, 34.73, 31.56. HRMS (MALDI) m/z calcd for $C_{66}H_{49}N_4O_6$ [M + H]$^+$ 993.365; found 993.373.



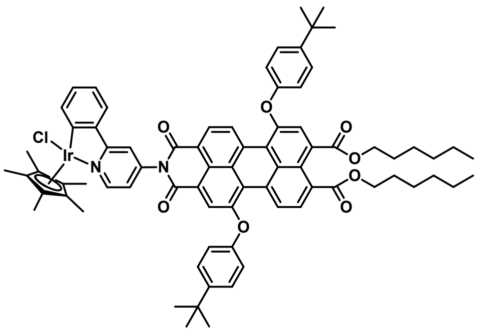
Compound P8. Compound **P7** (303 mg, 0.305 mmol) and KOH (31 mg, 0.56 mmol) were dissolved in 45 mL *t*-BuOH at 70 °C. The mixture was then heated to 80 °C over 70 min and then cooled slightly before adding 30 mL acetic acid and 15 mL 2 N HCl. The mixture was stirred at room temperature overnight. Water was added until all the colored material was precipitated, and the precipitate was collected by filtration. Column chromatography on a silica column with 1% acetic acid/5% ethyl acetate/95% CH_2Cl_2 as the eluent yielded the product, and access starting material was recovered by eluting with 50% ethyl acetate/CH_2Cl_2. The fractions were extracted 3 × H_2O before solvent removal under vacuum to yield the pure product (43 mg, 17%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.74 – 9.64 (m, 2H), 8.85 (dd, *J* = 5.1, 0.7 Hz, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 8.3 Hz, 1H), 8.35 (s, 1H), 8.30 (s, 1H), 8.07 – 7.99 (m, 2H), 7.75 (dd, *J* = 1.9, 0.7 Hz, 1H), 7.59 – 7.39 (m, 7H), 7.25 (dd, *J* = 5.2, 1.9 Hz, 1H), 7.21 – 7.12 (m, 4H), 1.38 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 163.22, 162.85, 160.37, 160.26, 159.46, 156.68, 156.26, 153.07, 152.96, 151.38, 149.32, 149.23, 144.45, 139.12, 135.42, 134.09, 132.51, 130.89, 130.31, 130.15, 130.03, 129.91, 129.68, 129.30, 128.18, 128.09, 127.66, 127.48, 125.89, 125.79, 125.63, 124.62, 124.54, 124.26, 123.01, 122.73, 121.11, 120.15, 119.73, 118.57, 35.06, 35.03, 31.73, 31.72. HRMS (MALDI) m/z calcd for $C_{55}H_{41}N_2O_7$ $[M + H]^+$ 841.291; found 841.291.



Compound 5A. Compound **P8** (10 mg, 0.012 mmol) was dissolved in 4 mL CH_2Cl_2 and purged with nitrogen. $[Cp^*IrCl_2]_2$ (10 mg, 0.012 mmol) and $NaOAc{\cdot}3H_2O$ (5 mg, 0.03 mmol) were added, and the reaction mixture was stirred at room temperature in the dark under nitrogen for 36 hours. The crude product was purified on a silica column with CH_2Cl_2 → 20% CH_2Cl_2/80% acetone as the eluent, and the solvent was removed under vacuum. Hexanes were added to a nearly saturated solution of the isolated material in CH_2Cl_2 until a precipitate formed, which was collected by filtration to yield the pure product (8 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 – 9.63 (m, 2H), 8.83 (d, *J* = 6.1 Hz, 1H), 8.66 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.40 (s, 1H), 8.32 (s, 1H), 7.83 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.82 (d, *J* = 2.1 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.21 (ddd, *J* = 7.4, 1.3 Hz, 1H), 7.15 – 7.08 (m, 5H), 7.04 – 6.96 (m, 1H), 1.70 (s, 15H), 1.39 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.18, 164.23, 162.57, 162.28, 159.80, 156.35, 156.01, 152.27, 152.24, 152.07, 149.06, 148.97, 143.74, 143.70, 136.00, 134.90, 133.71, 132.26, 131.52, 130.89, 129.79, 129.65, 129.33, 127.90, 127.83, 127.83, 127.12, 125.43, 125.25, 124.93, 124.42, 124.27, 123.88, 123.70, 122.60, 122.30, 119.66, 119.44, 119.41, 118.08, 88.93, 34.78, 34.75, 31.57, 9.09. HRMS (MALDI) m/z calcd for $C_{65}H_{55}ClIrN_2O_7$ $[M - Cl]^+$ 1167.36; found 1167.33.



Compound P9. Compound **P8** (37 mg, 0.044 mmol), 1-bromohexane (0.40 mL, 2.8 mmol), and K_2CO_3 (206 mg, 1.49 mmol) were dissolved in 8 mL 1-hexanol and heated to 90 °C for 50 hours. To the cooled reaction mixture was added $CHCl_3$ and 2 mL HOAc to re-dissolve the material. The mixture was filtered, the filtrate was extracted 4 × H_2O, and the solvent was removed under vacuum. Preparative TLC on silica with 1% ethyl acetate/99% CH_2Cl_2 yielded the pure product (10 mg, 23%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 – 9.37 (m, 2H), 8.87 (d, *J* = 5.2 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.35 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.79 (s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.48 – 7.39 (m, 7H), 7.25 (dd, *J* = 5.4, 2.0 Hz, 1H), 7.10 – 7.07 (m, 2H), 7.06 – 7.02 (m, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 4.24 (t, *J* = 6.9 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.73 – 1.64 (m, 2H), 1.64 – 1.53 (m, 2H), 1.50 – 1.40 (m, 2H), 1.36 (s, 9H), 1.35 – 1.20 (m, 8H), 1.33 (s, 9H), 0.94 – 0.79 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.43, 167.70, 163.23, 162.88, 159.42, 154.37, 154.18, 153.13, 152.79, 150.98, 147.94, 144.08, 138.84, 134.99, 133.10, 132.15, 131.22, 130.95, 130.72, 129.43, 129.42, 129.23, 128.88, 128.84, 127.91, 127.47, 127.38, 127.25, 125.96, 125.51, 125.01, 124.87, 123.83, 122.30, 122.17, 121.12, 120.68, 118.93, 118.88, 66.02, 65.94, 34.64, 34.62, 31.64, 31.59, 31.57, 31.52, 28.70, 28.43, 25.82, 25.64, 22.70, 22.63, 14.19, 14.15. MS (MALDI) m/z calcd for $C_{67}H_{66}N_2O_8$ $[M]^-$ 1026.48; found 1026.15.



Compound 5B. Compound **P9** (9 mg, 0.009 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.009 mmol), and $NaOAc\cdot 3H_2O$ (4 mg, 0.03 mmol) were dissolved in 2 mL CH_2Cl_2 and purged with nitrogen. The reaction mixture was stirred at room temperature in the dark for 24 hours. Column chromatography on a silica column with 5% ethyl acetate/95% $CH_2Cl_2 \rightarrow$ 10% acetone/90% CH_2Cl_2 as the eluent yielded the pure product (11 mg, 90%). ^1H NMR (500 MHz, $CDCl_3$) δ 9.43 – 9.36 (m, 2H), 8.81 (d, *J* = 6.1 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.37 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 2.2 Hz, 1H), 7.79 (s, 1H), 7.62 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.24 – 7.18 (m, 1H), 7.12 – 7.07 (m, 3H), 7.07 – 7.02 (m, 2H), 7.02 – 6.97 (m, 1H), 4.31 (t, *J* = 6.9 Hz, 2H), 4.24 (t, *J* = 6.9 Hz, 2H), 1.83 – 1.73 (m, 2H), 1.72 – 1.62 (m, 2H), 1.70 (s, 15H), 1.49 – 1.41 (m, 2H), 1.36 (s, 9H), 1.35 – 1.21 (m, 10H), 1.34 (s, 9H), 0.94 – 0.82 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.09, 168.41, 167.68, 164.12, 163.01, 162.67, 154.43, 154.16, 153.22, 152.81, 151.96, 147.98, 147.94, 144.20, 143.84, 135.97, 135.08, 133.18, 132.19, 131.41, 131.31, 131.04, 130.71, 129.47, 129.24, 128.89, 127.94, 127.50, 127.40, 126.14, 125.56, 125.26, 124.90, 124.43, 123.82, 122.78, 122.28, 122.12, 121.11, 120.61, 119.56, 118.96, 118.81, 88.88, 66.01, 65.93, 34.65, 34.63, 31.65, 31.59, 31.53, 28.72, 28.45, 25.82, 25.64, 22.69, 22.63, 14.17, 14.14, 9.08. MS (MALDI) m/z calcd for $C_{77}H_{80}ClIrN_2O_8$ $[M - Cl]^+$ 1353.55; found 1353.93.

II. Experimental details

Film Preparation.

Fluorine-doped tin oxide (FTO) coated glass plates (Hartford Glass, TEC 15) were sonicated in an Alconox solution for 15 min., rinsed with water, sonicated in ethanol for 15 min., sonicated in methanol for 15 min., then dried under a nitrogen stream. TiO_2 films were prepared by the doctor blade method using a commercially available TiO_2 paste (avg. 20 nm, Dyesol, DSL-90-T) and two parallel strips of adhesive tape as a mask. SnO_2 films were prepared according to a method reported by Bergeron *et al.*[8] Poly(ethylene glycol) (0.6 g, M_n ~2,000) and 0.5 mL of a pH 11 $NaHCO_{3(aq)}/NaOH_{(aq)}$ solution were combined with 10 mL of a 15% aqueous colloidal SnO_2 solution (Alfa Aesar) and stirred for two hours. This paste was spin coated onto FTO films masked with tape at 2,000 rpm for 10 s. To prepare Al_2O_3 nanoparticle pastes, 1.0 g acetic acid and 800 mg Al_2O_3 nanopowder (13 nm, Sigma Aldrich) were combined and sonicated for 5 minutes followed by the addition of 4.0 g H_2O and sonication for another 5 minutes. Poly(ethylene glycol) (M_n ~20,000, 0.9 g; and M_n ~100,000, 0.4 g) was added, and the mixture was stirred vigorously overnight. Films were prepared by the doctor blade method on glass with an adhesive tape mask. All films were dried in an oven for 1 h then heated to 450 °C over 2 hours, held at 450 °C for 30 minutes, and cooled to 110 °C over 2 hours.

Steady-State Optical Spectroscopy.

Steady-state absorption spectra were collected at room temperature using a Shimadzu 1800 spectrometer. Solution samples were measured in a 2 mm path length cuvette in dichloromethane (optical density 0.3−0.7 at the maximum, which precludes aggregation). Fluorescence measurements were made on a PTI Quanta-Master 1 single-photon-counting fluorimeter in a right-angle configuration with a 10 mm quartz cuvette in dichloromethane with $\lambda_{ex} = 450$ nm.

Electrochemistry.

Electrochemical measurements for **1B-4B** were performed using a CH Instruments Model 660A electrochemical workstation. All measurements were performed under argon using a 1.0 mm diameter platinum disk working electrode, a platinum wire counter electrode, a silver wire pseudoreference electrode, and 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocenium redox couple (0.40 V vs SCE)[9] was used as an internal standard. $TBAPF_6$ was recrystallized twice from ethanol prior to use.

nsTA and μsTA.

Nanosecond transient absorption (nsTA) experiments were performed by exciting samples translated in one dimension with 7 ns, 1.5 mJ, 490 nm pulses as previously described.[10] Kinetic traces were collected from 390 to 800 nm at 5 nm intervals, omitting 520−540 nm. Spectra were constructed by merging the kinetic traces (binned to 3 ns steps, 100 laser shots per kinetic trace).

Transient absorption decays in the microsecond-second timescale were measured using a Nd:YAG laser (Big Sky Laser Technologies Ultra CFR Nd:YAG laser system, 6 ns pulse width). The third harmonic of the pulsed laser (532 nm), at a frequency of 0.8 Hz, was used as the excitation source. The laser intensity was adjusted to 20 $\mu J\ cm^{-2}$ using neutral density filters. A liquid light guide with a diameter of 0.5 cm was used to transmit the laser pulse to the sample. A 100 W Bentham IL1 tungsten lamp was used as the probe light source, and the probing wavelength was selected using a monochromator (OBB-2001, Photon Technology International) placed prior to the sample. Several high pass and neutral density filters (Comar Instruments) were used to decrease the light intensity arriving to the detector. Transient absorption data were collected with a Si photodiode (Hamamatsu S3071). The information was passed through an amplifier box (Costronics) and recorded using a Tektronics TDS 2012c oscilloscope (microsecond to millisecond timescale) and a National Instruments (NI USB-6211) DAQ card (millisecond to second timescale). The decays observed are the average of ~500 laser pulses. The data were processed using home-built software based on LabVIEW.[11]

III. Steady-State Optical Characterization

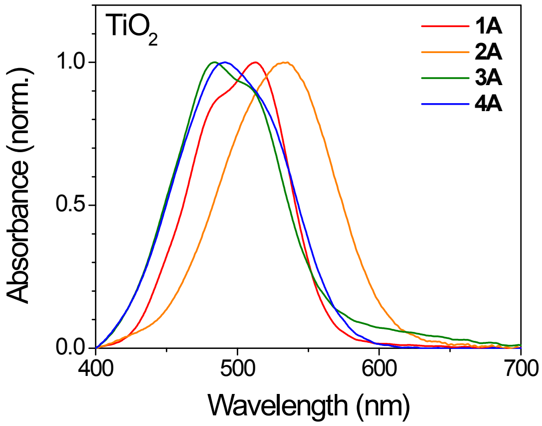


Figure S1. Normalized absorption spectra of **1A** (red), **2A**, (orange), **3A** (green), and **4A** (blue) on TiO_2 under nitrogen after subtraction of the TiO_2 background.

Table S1. UV-Vis absorption maxima for 1A-4A on Al_2O_3 and TiO_2

	Abs_{max} Al_2O_3	Abs_{max} TiO_2
1A	507 nm	513 nm
2A	522 nm	535 nm
3A	481 nm	484 nm
4A	490 nm	491 nm

IV. fsTA data of 1A-4A on Al_2O_3

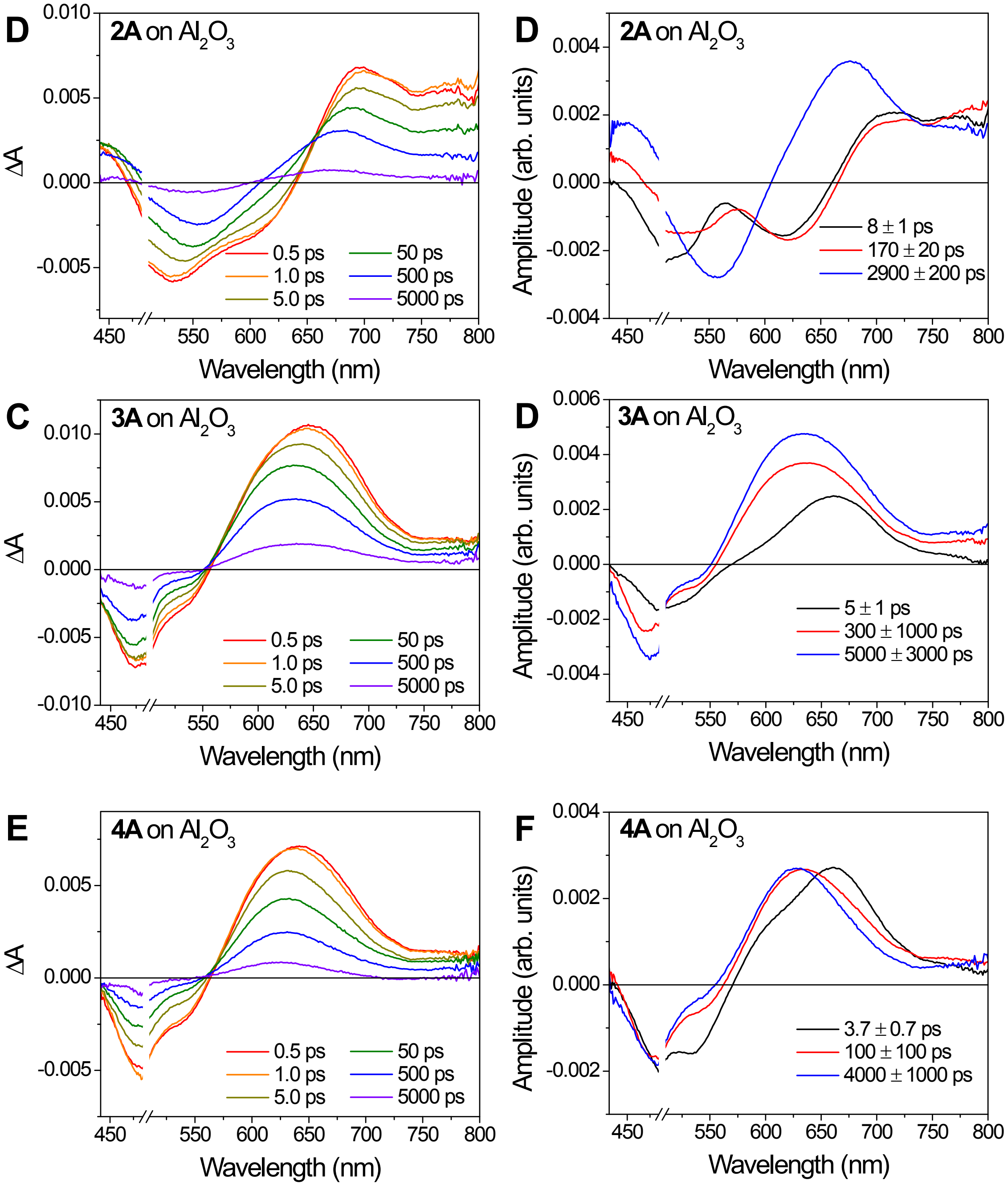


Figure S2. (A, C, E) fsTA spectra and (B, D, F) decay-associated spectra obtained by SVD and global analysis of the fsTA spectra of **2A-4A** on Al_2O_3.

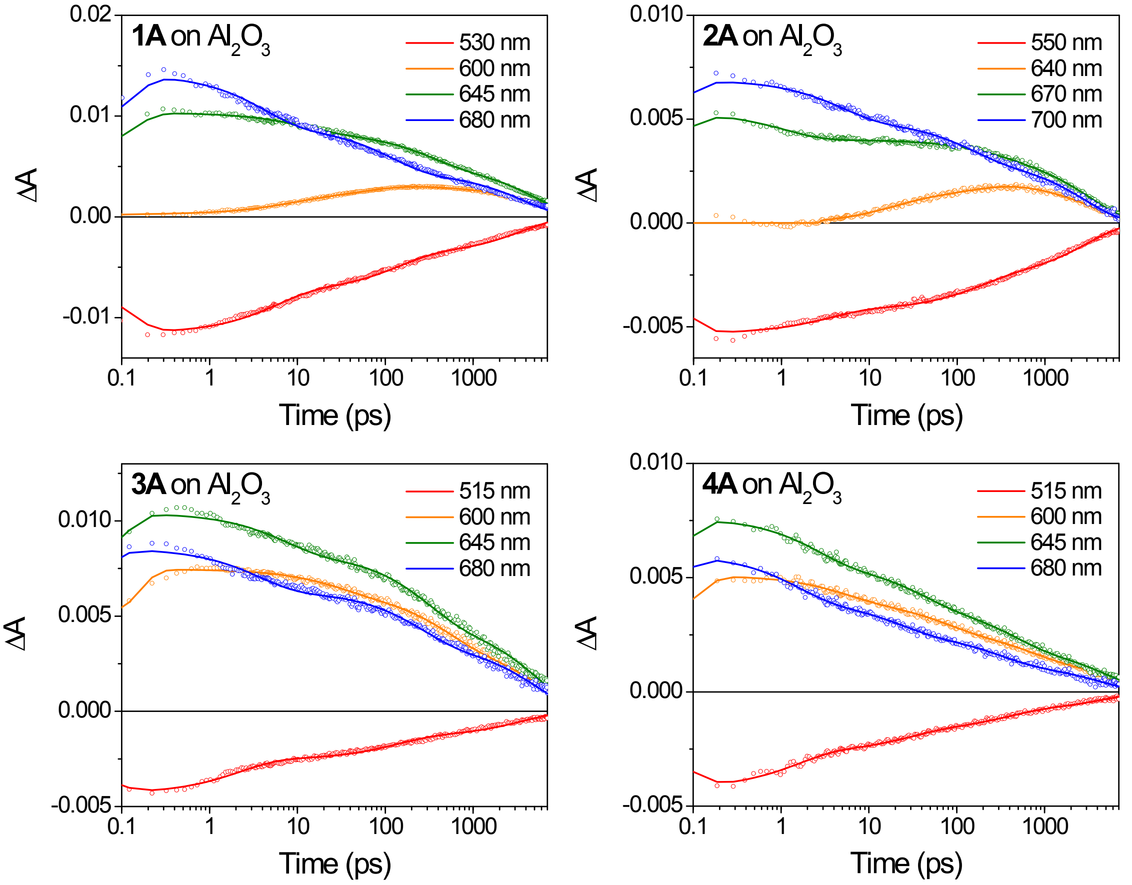


Figure S3. fsTA single wavelength traces (circles) and fits (lines) of **1A**-**4A** on Al_2O_3. See the main text for descriptions of fitting procedures.

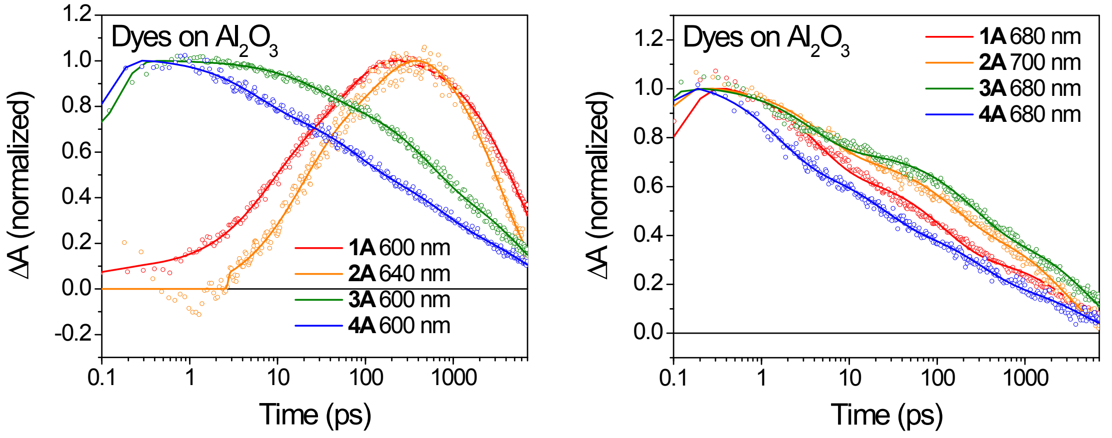


Figure S4. fsTA single wavelength traces (circles) and fits (lines) of **1A** (red), **2A** (orange), **3A** (green), and **4A** (blue) on Al_2O_3.

V. fsTA data of 1A-4A on TiO_2

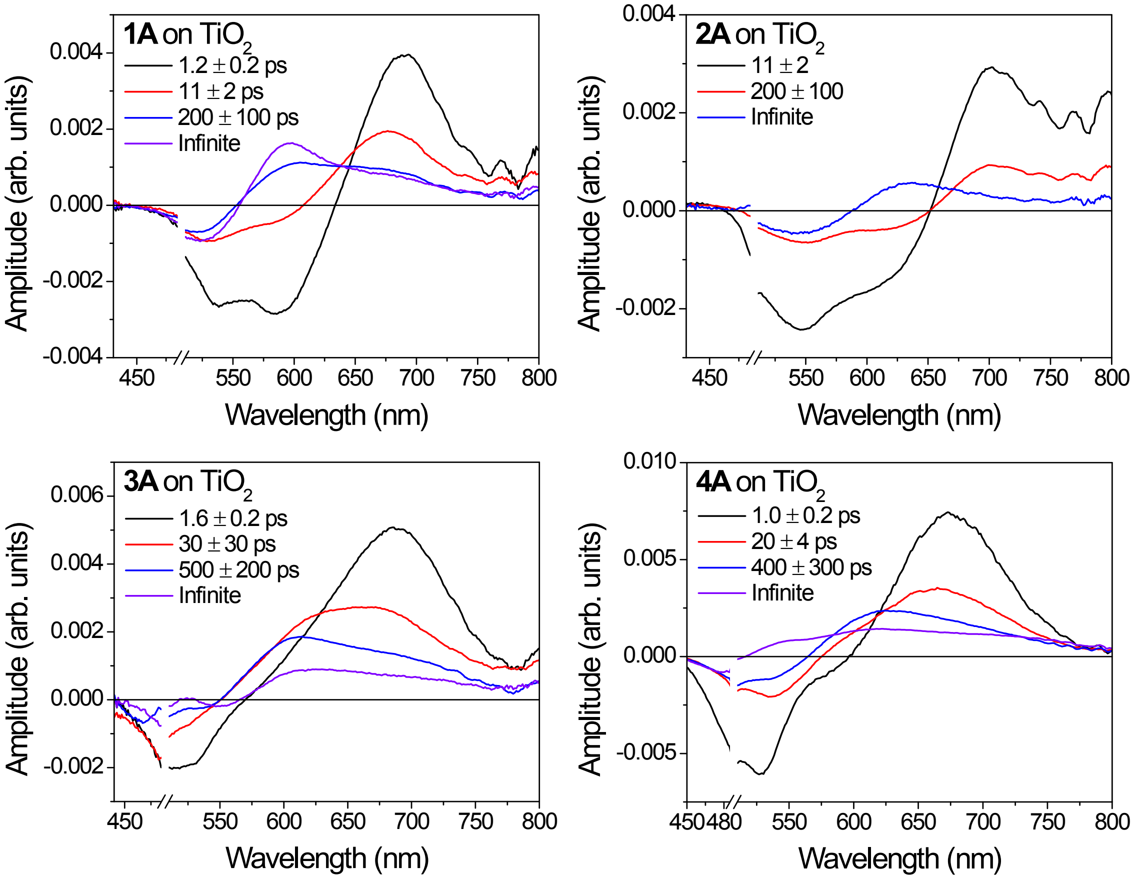


Figure S5. Decay-associated spectra obtained by SVD and global analysis of the fsTA spectra of **1A**-**4A** on TiO_2 (Figure 7).

Table S2. fsTA fits of 1A-4A on TiO_2

Sample	Decay-associated global fits τ (ps)	Single wavelength fits (% amplitude)[a] τ (ps)				% Al_2O_3[b]
1A		**530 nm**	**600 nm**	**645 nm**	**680 nm**	
Al_2O_3	6.0 ± 0.5	6.1 ± 0.2 (35%)	6.8 ± 0.8 (-42%)	13.1 ± 0.7 (18%)	4.5 ± 0.2 (36%)	100%
	160 ± 20	141 ± 6 (32%)	56 ± 5 (-50%)	310 ± 10 (32%)	119 ± 5 (33%)	
	4500 ± 300	3720 ± 90 (33%)	6000 ± 100 (100%)	5.2 ± 0.1 ns (50%)	3.7 ± 0.2 ns (31%)	
TiO_2		Al_2O_3 (11%)	Al_2O_3 (18%)	Al_2O_3 (16%)	Al_2O_3 (11%)	14%
	1.2 ± 0.2	1.2 ± 0.1 (46%)	1.1 ± 0.1 (-64%)	1.6 ± 0.3 (25%)	1.0 ± 0.1 (45%)	
	11 ± 2	11 ± 2 (16%)	150 ± 10 (38%)	11 ± 2 (21%)	8.3 ± 0.7 (24%)	
	200 ± 100	160 ± 30 (10%)	Inf. (44%)	110 ± 10 (19%)	110 ± 10 (10%)	
	Inf.	Inf. (18%)		Inf. (19%)	Inf. (9%)	
2A		**550 nm**	**640 nm**	**670 nm**	**700 nm**	
Al_2O_3	8 ± 1	3.5 ± 0.2 (21%)	17 ± 2 (-46%)	1.09 ± 0.07 (25%)	4.7 ± 0.2 (29%)	100%
	170 ± 20	168 ± 8 (29%)	150 ± 10 (-48%)	280 ± 20 (14%)	136 ± 8 (28%)	
	2900 ± 200	3020 ± 60 (50%)	3600 ± 80 (100%)	3320 ± 50 (61%)	2860 ± 70 (44%)	
TiO_2		Al_2O_3 (7%)	Al_2O_3 (16%)	Al_2O_3 (11%)	Al_2O_3 (10%)	11%
	11 ± 2	1.0 ± 0.3 (20%)	6.4 ± 0.5 (-85%)	0.8 ± 0.2 (24%)	0.9 ± 0.2 (22%)	
	200 ± 100	12.9 ± 0.8 (53%)	81 ± 9 (-56%)	12 ± 1 (43%)	13.1 ± 0.9 (50%)	
	Infinite	280 ± 60 (11%)	Inf. (84%)	180 ± 50 (10%)	210 ± 40 (13%)	
		Inf. (9%)		Inf. (12%)	Inf. (4%)	
3A		**515 nm**	**600 nm**	**645 nm**	**680 nm**	
Al_2O_3	5 ± 1	2.21 ± 0.09 (41%)	28 ± 2 (16%)	6.9 ± 0.4 (21%)	3.6 ± 0.2 (26%)	100%
	300 ± 1000	131 ± 7 (28%)	460 ± 30 (37%)	290 ± 10 (35%)	240 ± 10 (32%)	
	5000 ± 3000	3800 ± 100 (31%)	6100 ± 200 (47%)	5500 ± 100 (45%)	5300 ± 200 (41%)	
TiO_2		Al_2O_3 (21%)	Al_2O_3 (12%)	Al_2O_3 (7%)	Al_2O_3 (7%)	7%
	1.6 ± 0.2	1.8 ± 0.2 (45%)	1.9 ± 0.2 (23%)	1.7 ± 0.1 (37%)	1.5 ± 0.1 (45%)	
	30 ± 30	21 ± 3 (25%)	44 ± 3 (33%)	33 ± 2 (32%)	26 ± 2 (28%)	
	500 ± 200	250 ± 60 (10%)	500 ± 70 (21%)	460 ± 50 (15%)	370 ± 40 (13%)	
	Inf.		Inf. (11%)	Inf. (9%)	Inf. (7%)	
4A		**515 nm**	**600 nm**	**645 nm**	**680 nm**	
Al_2O_3	3.7 ± 0.7	2.3 ± 0.1 (41%)	9.0 ± 0.5 (27%)	4.5 ± 0.2 (32%)	2.8 ± 0.1 (40%)	100%
	100 ± 100	90 ± 4 (31%)	200 ± 10 (35%)	141 ± 6 (34%)	88 ± 5 (32%)	
	4000 ± 1000	3400 ± 100 (28%)	4900 ± 200 (37%)	4000 ± 100 (34%)	3000 ± 100 (28%)	
TiO_2		Al_2O_3 (10%)	Al_2O_3 (36%)	Al_2O_3 (21%)	Al_2O_3 (19%)	20%
	1.0 ± 0.2	0.99 ± 0.05 (48%)	46 ± 3 (24%)	1.0 ± 0.1 (36%)	0.69 ± 0.04 (42%)	
	20 ± 4	16.6 ± 0.9 (24%)	500 ± 40 (18%)	19 ± 1 (22%)	12.0 ± 0.7 (21%)	
	400 ± 300	250 ± 10 (17%)	Inf. (22%)	260 ± 20 (12%)	190 ± 20 (10%)	
	Inf.			Inf. (9%)	Inf. (8%)	

[a] For "Al_2O_3 (%)", this is fixed as the triexponential decay for the Al_2O_3 sample at the corresponding wavelength.
[b] The average of the weights at the two reddest wavelengths.

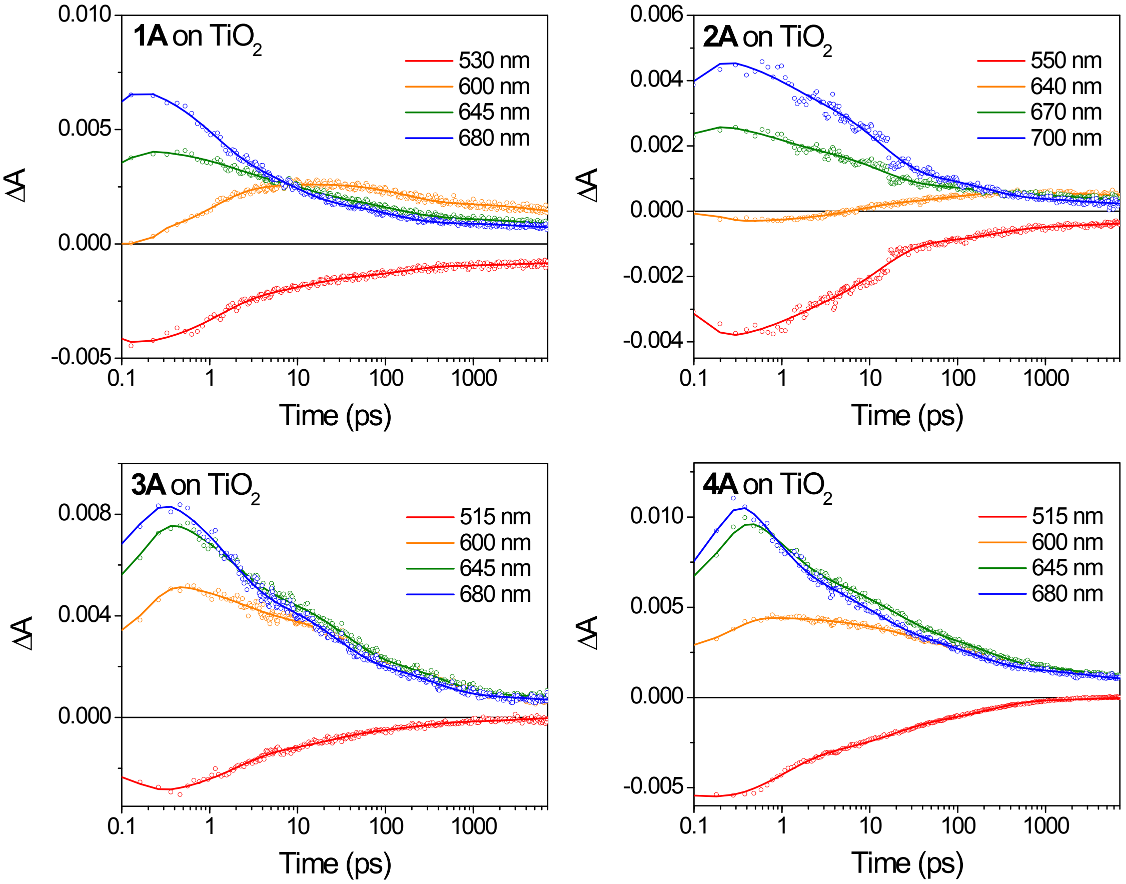


Figure S6. fsTA single wavelength traces (circles) and fits (lines) of **1A**-**4A** on TiO_2.

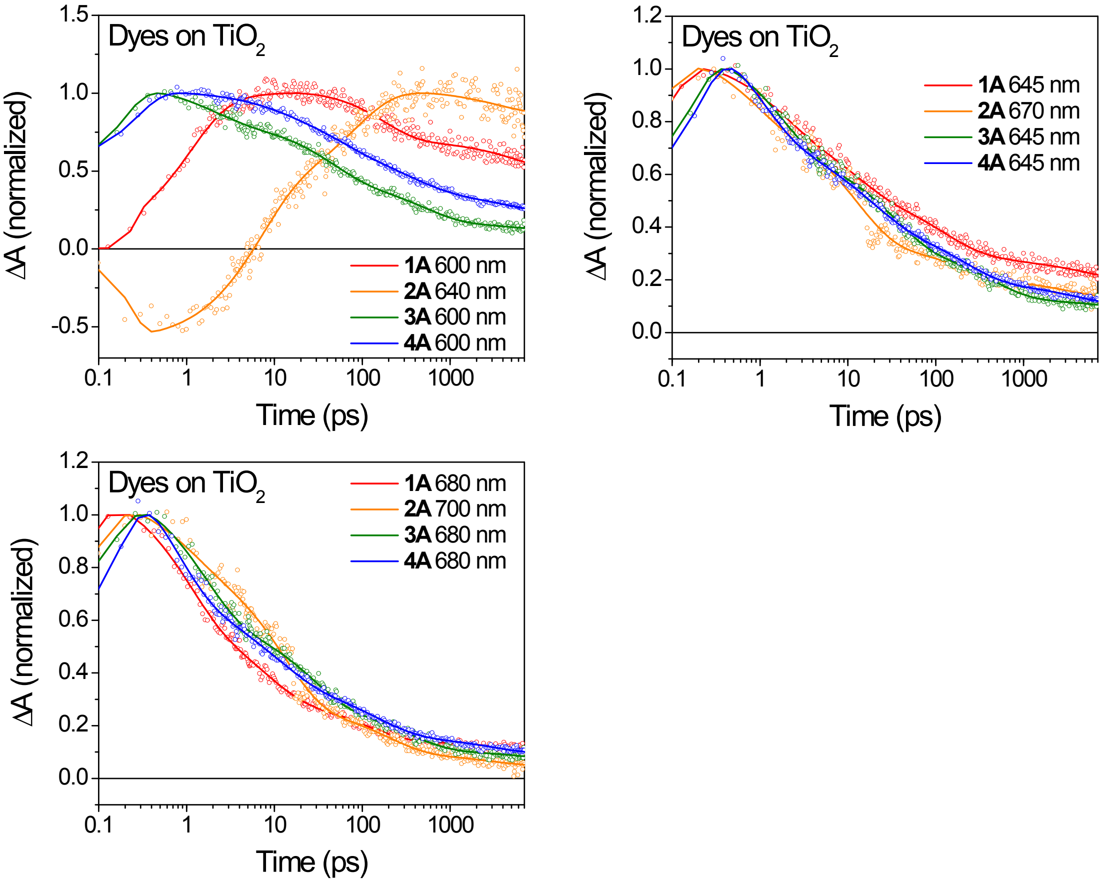


Figure S7. fsTA single wavelength traces (circles) and fits (lines) of **1A** (red), **2A** (orange), **3A** (green), and **4A** (blue) on TiO$_2$.

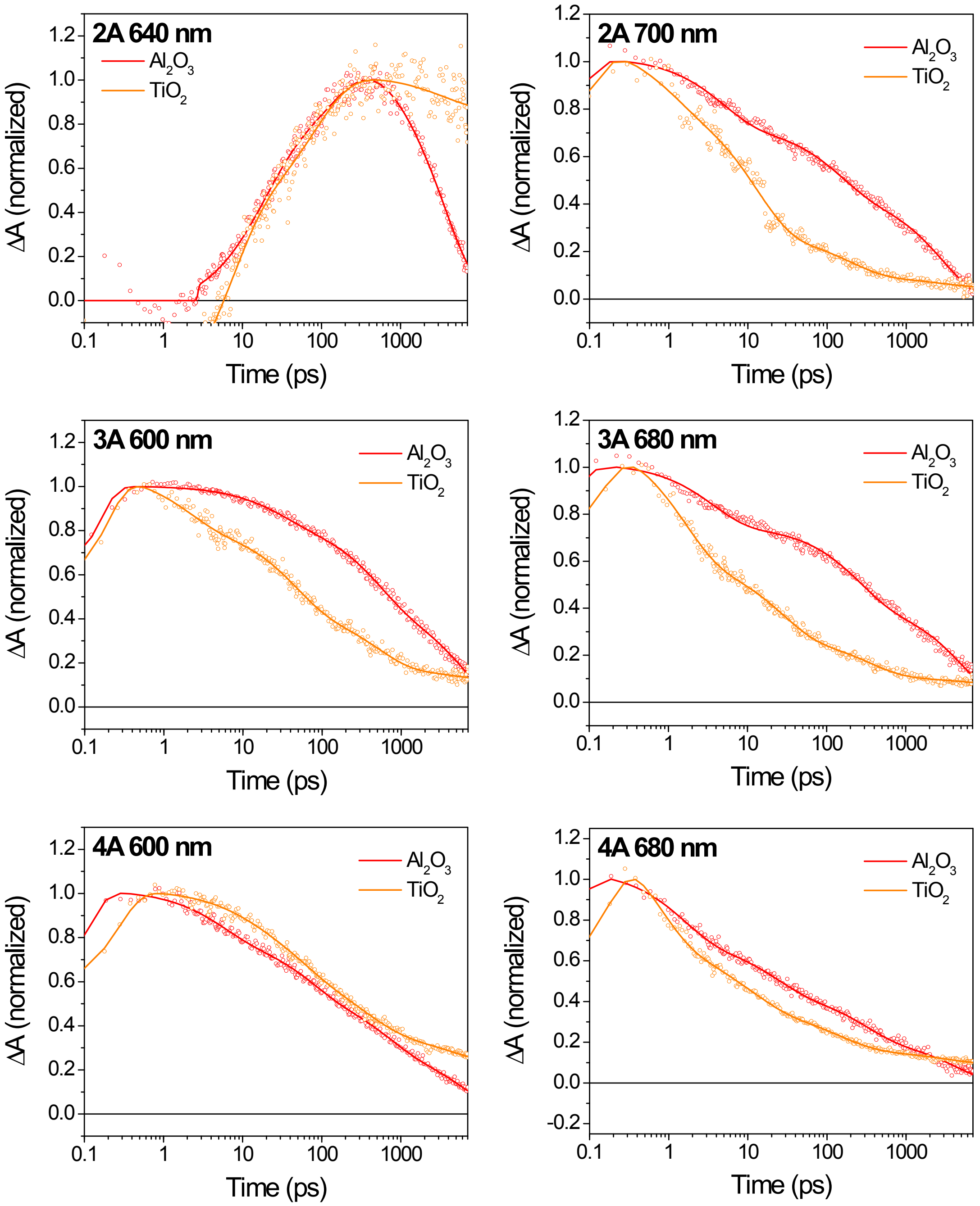


Figure S8. fsTA single wavelength traces (circles) and fits (lines) of **2A**-**4A** on Al_2O_3 (red) and TiO_2 (orange).

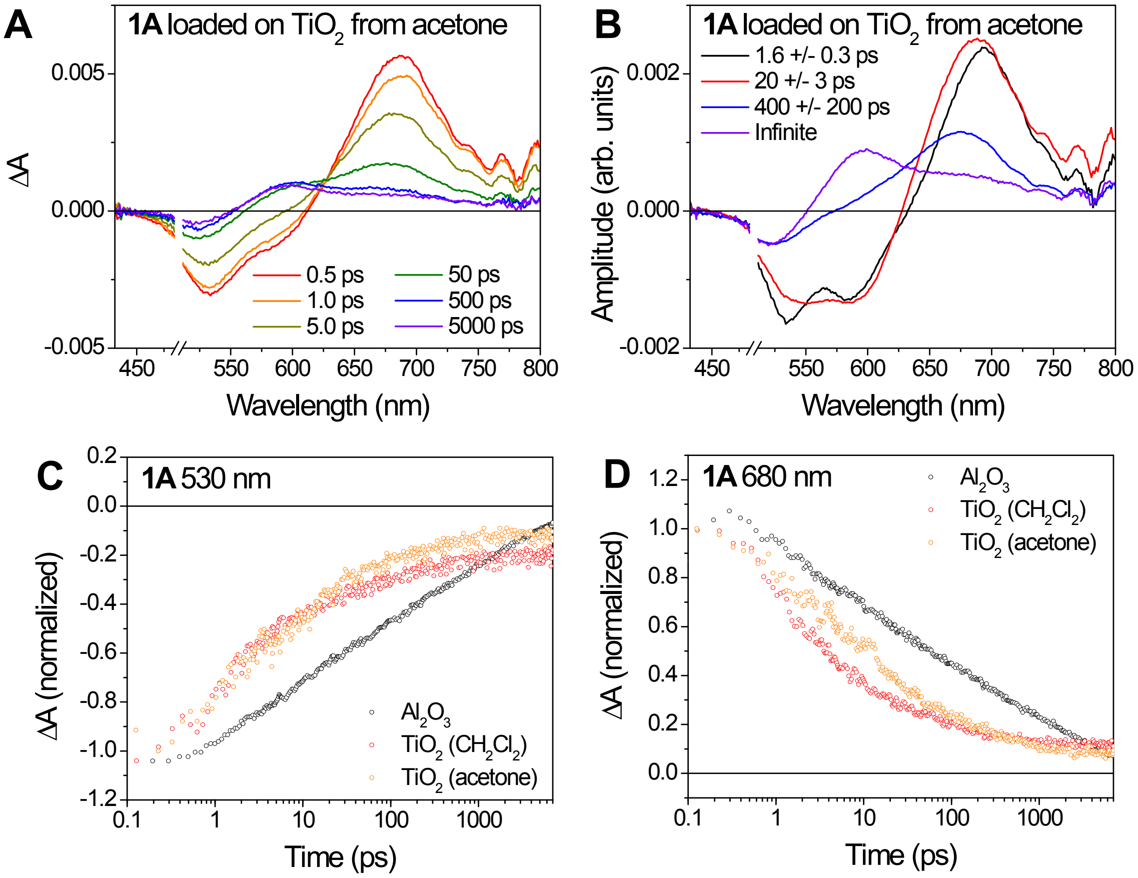


Figure S9. fsTA (A) spectra and (B) decay-associated spectra obtained by SVD and global analysis of the fsTA spectra of **1A** on TiO_2 loaded from acetone. (C) and (D) Normalized single wavelength traces for **1A** on Al_2O_3 loaded from CH_2Cl_2 (black), TiO_2 loaded from CH_2Cl_2 (red), and TiO_2 loaded from acetone (orange) at 530 nm and 680 nm.

VI. fsTA data of 1A on TiO$_2$ with Li$^+$ and on SnO$_2$

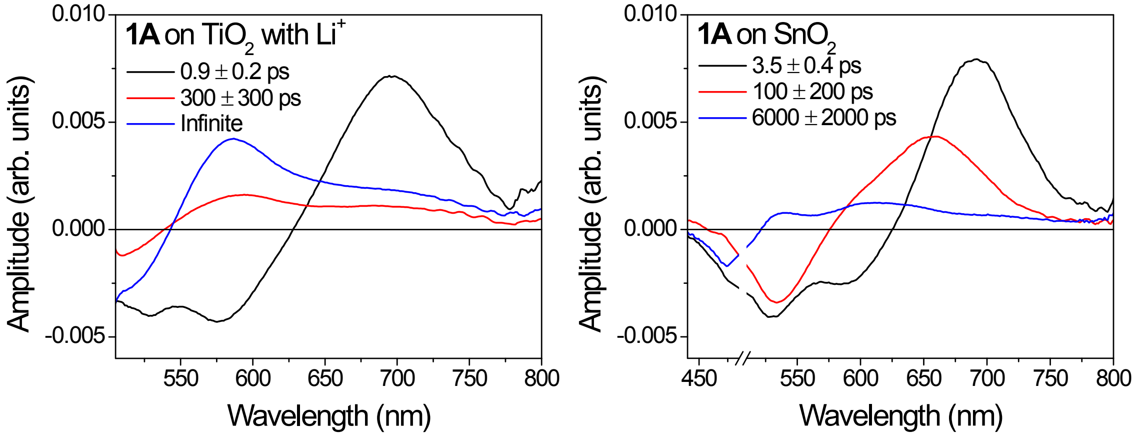


Figure S10. Decay-associated spectra obtained by SVD and global analysis of the fsTA spectra (Figure 8) of **1A** on TiO$_2$ with Li$^+$ and on SnO$_2$.

Table S3. fsTA fits of 1A on TiO$_2$ with Li$^+$ and on SnO$_2$

1A sample	Decay-associated global fits τ (ps)	Single wavelength fits (% amplitude)[a] τ (ps)				% Al$_2$O$_3$[b]
		530 nm	600 nm	645 nm	680 nm	
TiO$_2$ with Li$^+$		Al$_2$O$_3$ (12%)	Al$_2$O$_3$ (23%)	Al$_2$O$_3$ (26%)	Al$_2$O$_3$ (24%)	25%
	0.9 ± 0.2	0.70 ± 0.02 (61%)	0.44 ± 0.04 (-62%)	1.4 ± 0.1 (26%)	0.81 ± 0.03 (57%)	
	300 ± 300	15 ± 5 (2%)	63 ± 3 (32%)	44 ± 7 (8%)	Inf. (19%)	
	Inf.	Inf. (24%)	Inf. (46%)	Inf. (40%)		
SnO$_2$		Al$_2$O$_3$ (8%)	Al$_2$O$_3$ (22%)	Al$_2$O$_3$ (20%)	Al$_2$O$_3$ (19%)	19%
	3.5 ± 0.4	2.4 ± 0.1 (42%)	2.0 ± 0.1 (-58%)	2.7 ± 0.2 (26%)	1.8 ± 0.1 (44%)	
	100 ± 200	27 ± 2 (30%)	97 ± 9 (41%)	40 ± 4 (33%)	21 ± 1 (27%)	
	6000 ± 200	230 ± 20 (20%)	530 ± 70 (33%)	290 ± 30 (22%)	230 ± 20 (10%)	
		Inf. (-9%)	Inf. (5%)			

[a] For “Al$_2$O$_3$ (%)”, this is fixed as the triexponential decay for the Al$_2$O$_3$ sample at the corresponding wavelength.
[b] The average of the weights at the two reddest wavelengths.

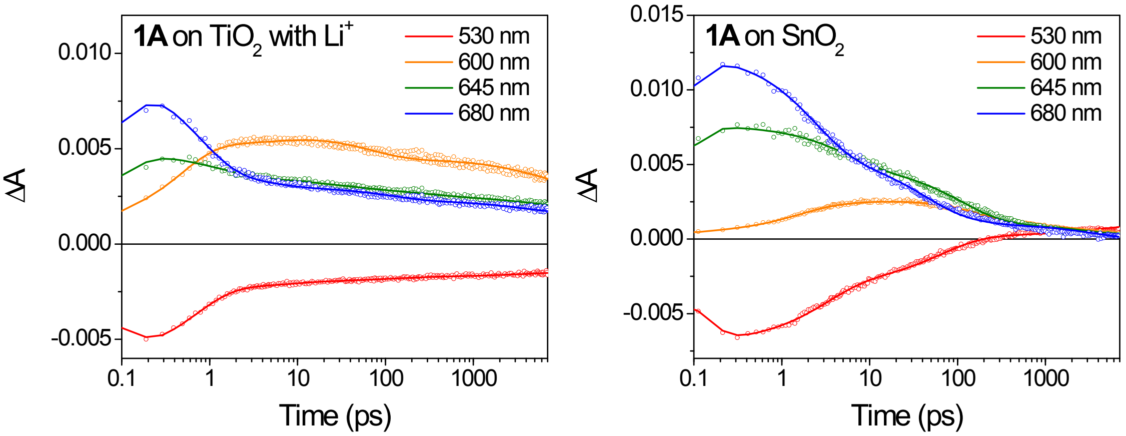


Figure S11. fsTA single wavelength traces (circles) and fits (lines) of **1A** on TiO$_2$ with Li$^+$ and on SnO$_2$.

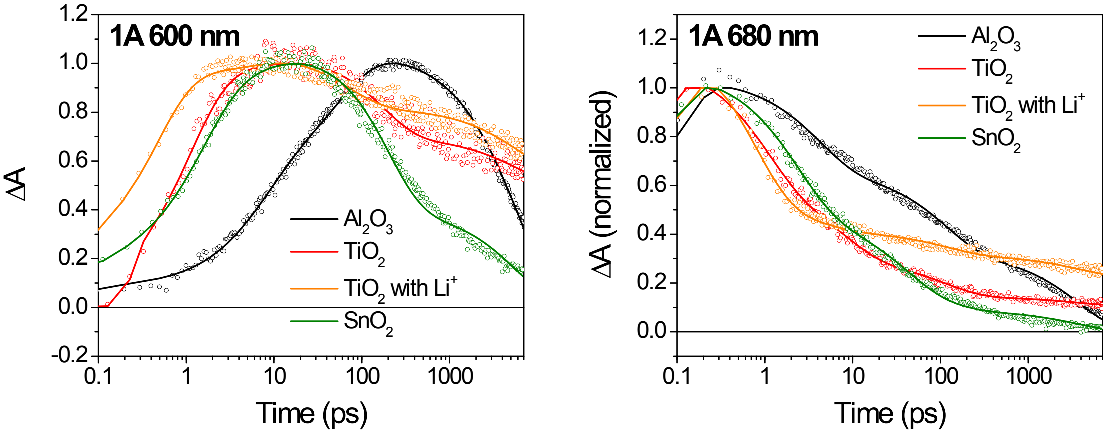


Figure S12. fsTA single wavelength traces (circles) and fits (solid lines) at 600 nm and 680 nm of **1A** on Al$_2$O$_3$ (black), TiO$_2$ (red), TiO$_2$ with Li$^+$ (orange), and SnO$_2$ (green).

VII. fsTA data after subtraction of non-injecting signal

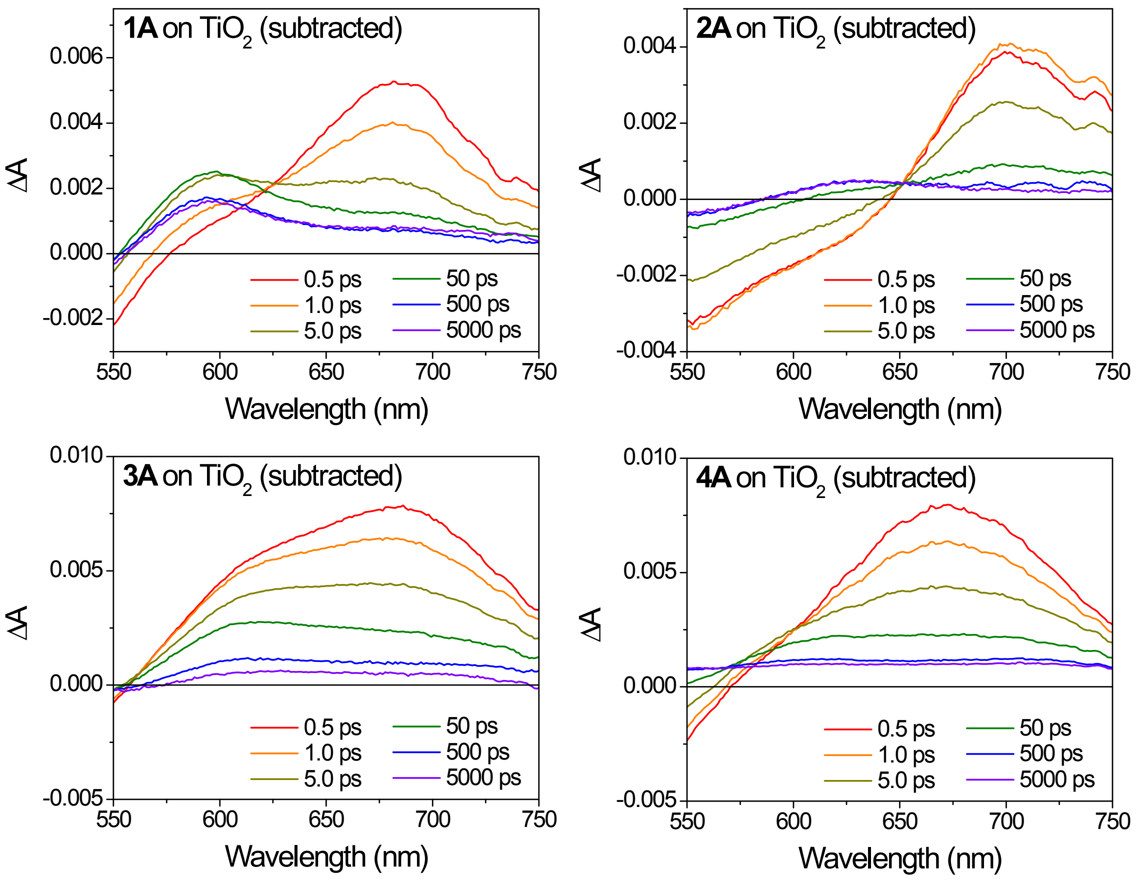


Figure S13. fsTA spectra of **1A**-**4A** on TiO_2 after subtraction of the non-injecting signal.

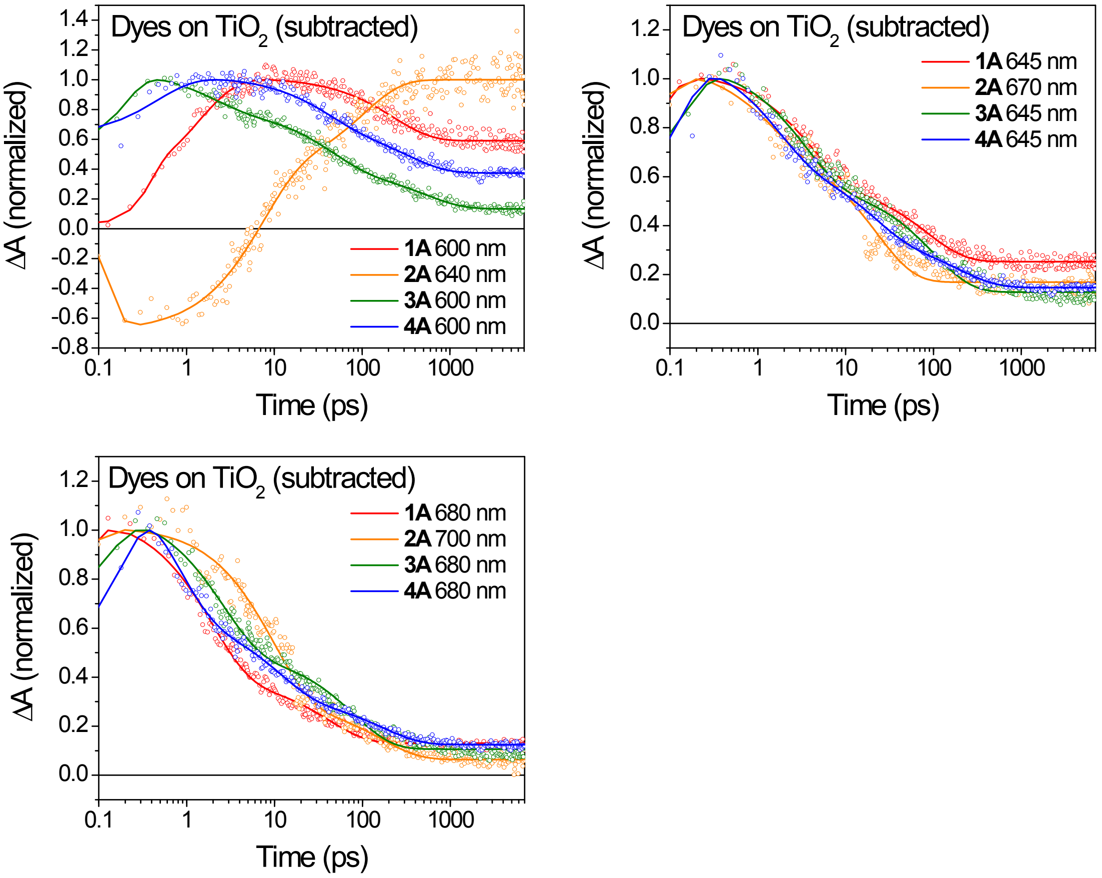


Figure S14. fsTA single wavelength traces (circles) and fits (lines) of **1A** (red), **2A** (orange), **3A** (green), and **4A** (blue) on TiO_2 after subtraction of the non-injecting signal.

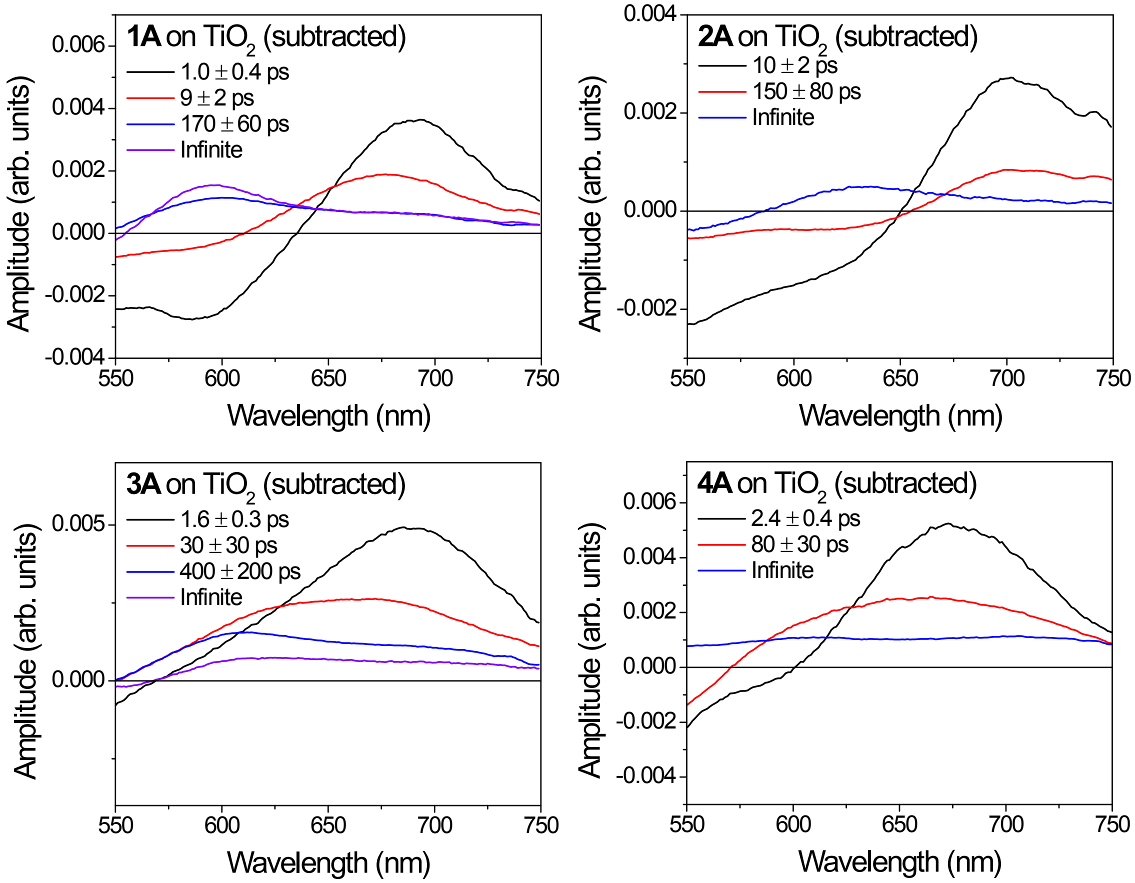


Figure S15. Decay-associated spectra obtained by SVD and global fitting of the fsTA spectra after subtraction of the non-injecting signal of **1A**-**4A** on TiO_2 (Figure S12).

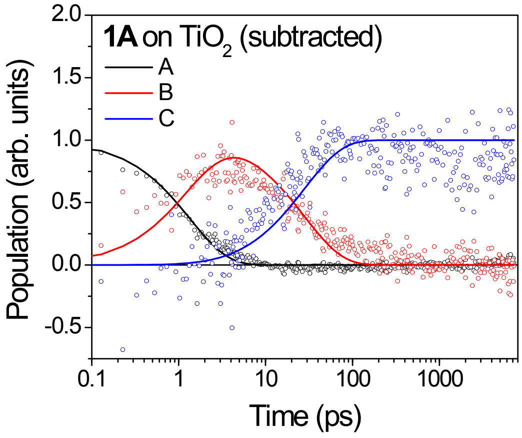


Figure S16. SVD/global fit of the fsTA spectra after subtraction of the non-injecting signal of **1A** on TiO_2 (Figure S12) to an A to B to C model (Figure 11).

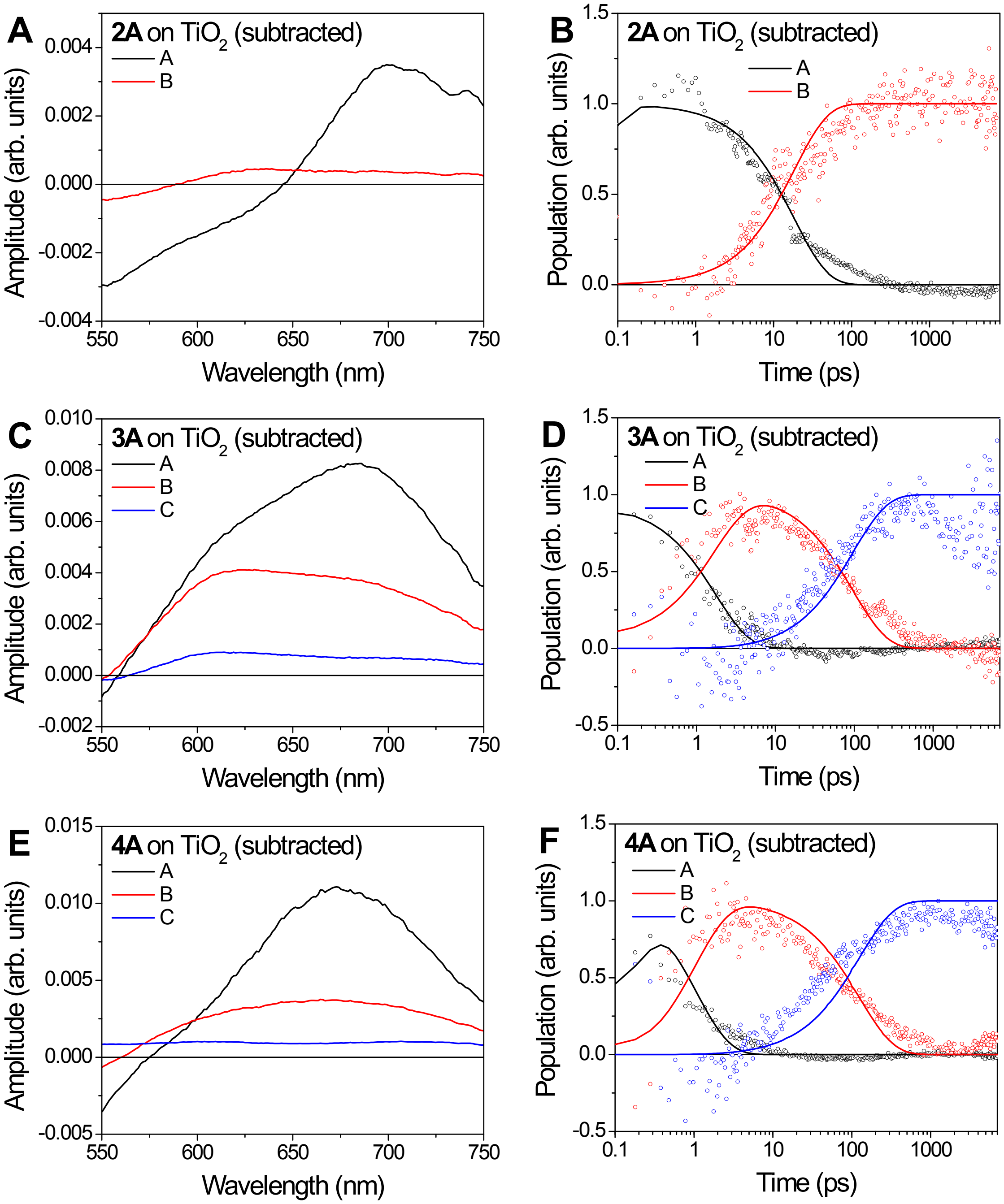


Figure S17. (A, C, E) Species-associated spectra obtained by (B, D, F) SVD/global fit of the fsTA spectra after subtraction of the non-injecting signal of **2A** on TiO$_2$ to an A to B model and of **3A** and **4A** on TiO$_2$ to A to B to C models (Figure S12).

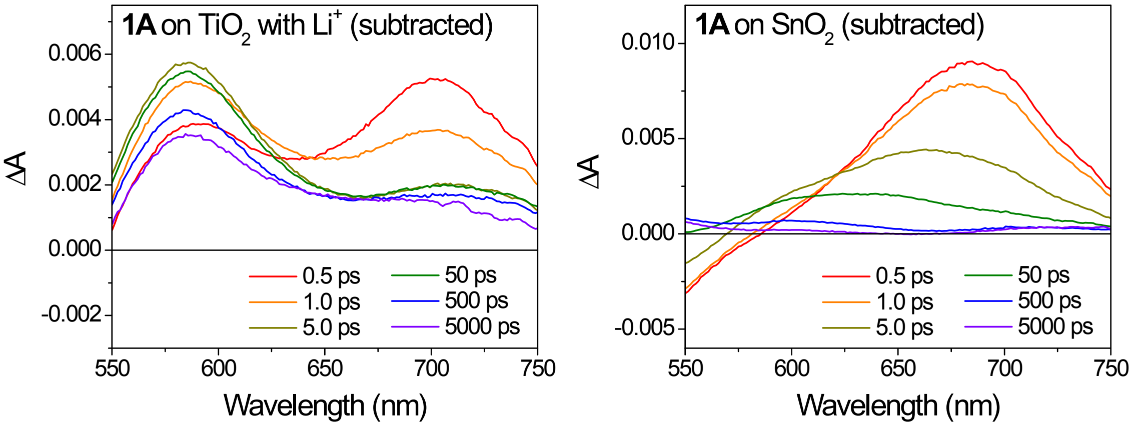


Figure S18. fsTA spectra of **1A** on TiO_2 with Li^+ and on SnO_2 after subtraction of the non-injecting signal.

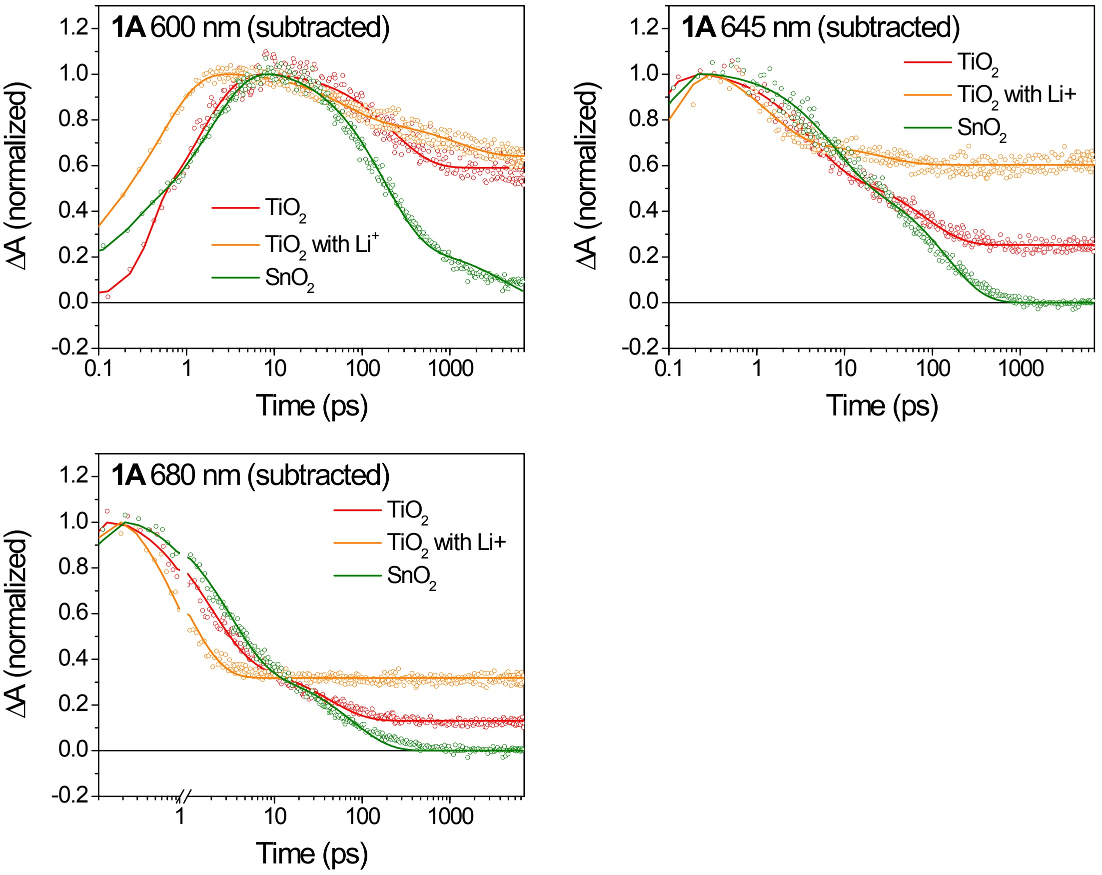


Figure S19. fsTA single wavelength traces (circles) and fits (lines) of **1A** on TiO_2 (red), TiO_2 with Li^+ (orange), and SnO_2 (green) after subtraction of the non-injecting signal.

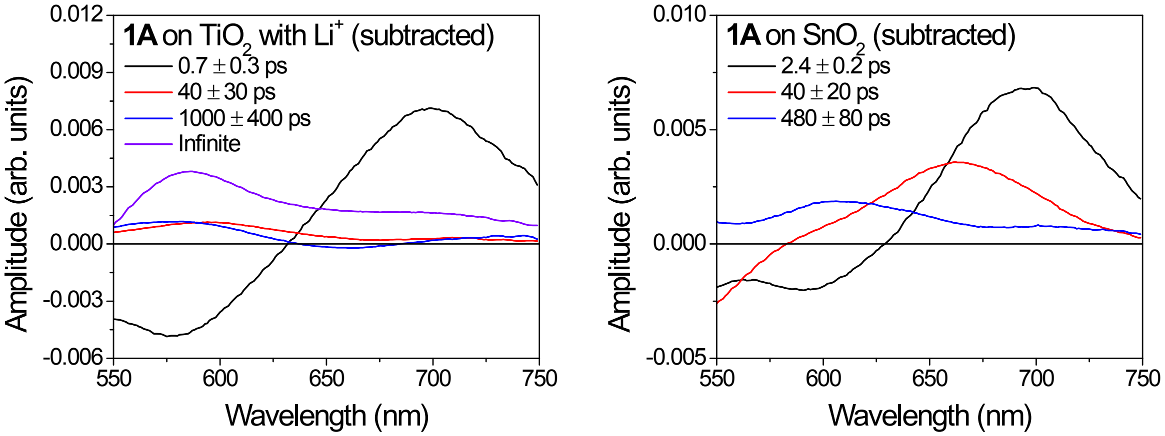


Figure S20. Decay-associated spectra obtained by SVD and global fitting of the fsTA spectra after subtraction of the non-injecting signal of **1A** on TiO_2 with Li^+ and on SnO_2 (Figure S17).

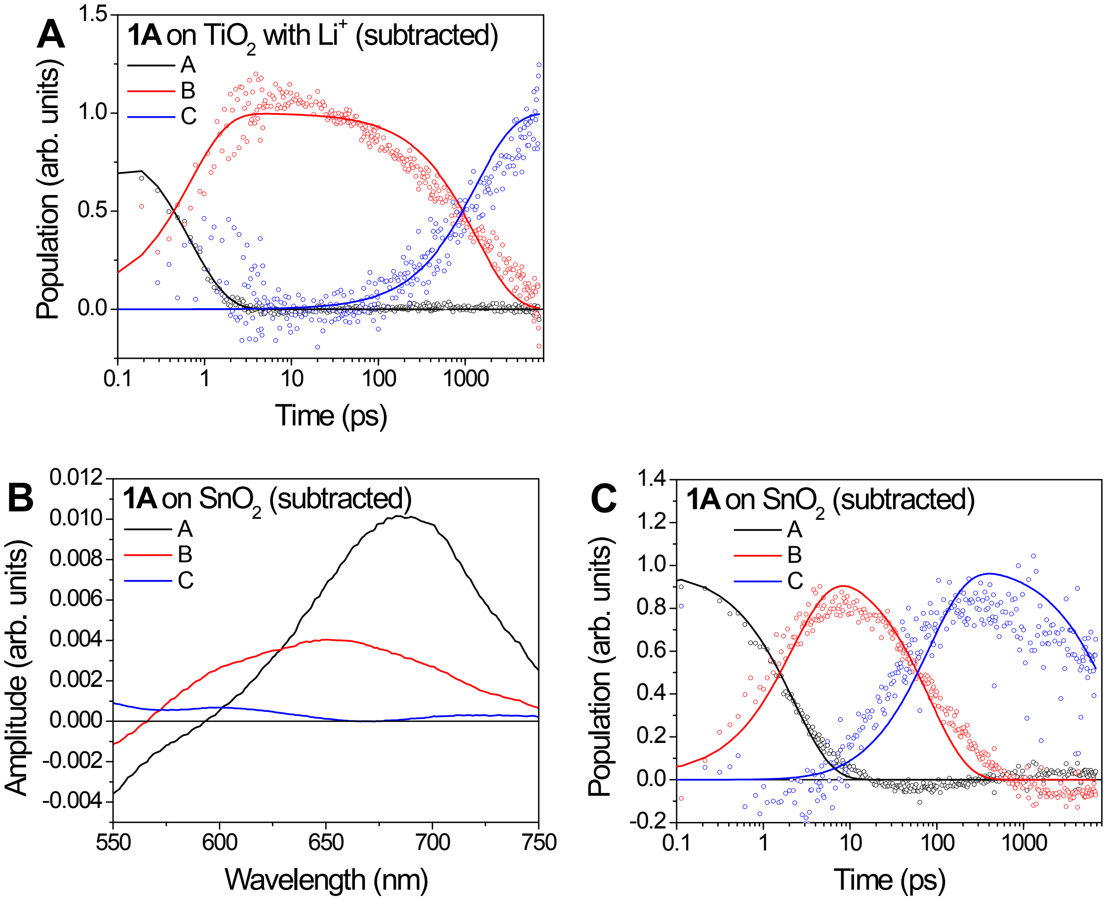


Figure S21. (A) SVD/global fit of the fsTA spectra after subtraction of the non-injecting signal of **1A** on TiO_2 with Li^+ (Figure S17) to an A to B to C model (Figure 11). (B) Species-associated spectra obtained by (C) SVD/global fit of the fsTA spectra after subtraction of the non-injecting signal of **1A** on SnO_2 (Figure S17) to an A to B to C to ground state model.

Table S4. fsTA fits after subtraction of non-injecting signal

Sample	Decay-associated global fits τ (ps)	Species-associated global fits to models τ (ps)	Single wavelength fits (% amplitude) τ (ps)		
1A on			**600 nm**	**645 nm**	**680 nm**
TiO$_2$	1.0 ± 0.2	[a]1.35 ± 0.06	1.4 ± 0.1 (-62%)	3.9 ± 0.2 (44%)	1.91 ± 0.07 (63%)
	9 ± 2	28 ± 1	230 ± 10 (42%)	84 ± 5 (31%)	41 ± 2 (24%)
	170 ± 60	Inf.	Inf. (58%)	Inf. (25%)	Inf. (12%)
	Inf.				
1A on			**600 nm**	**645 nm**	**680 nm**
TiO$_2$	0.7 ± 0.3	[a]0.68 ± 0.02	0.50 ± 0.04 (-68%)	1.3 ± 0.2 (35%)	0.95 ± 0.03 (73%)
with Li$^+$	40 ± 30	1380 ± 60	58 ± 5 (21%)	27 ± 6 (9%)	Inf. (27%)
	1000 ± 400	Inf.	1200 ± 200 (16%)	Inf. (56%)	
	Inf.		Inf. (63%)		
1A on			**600 nm**	**645 nm**	**680 nm**
SnO$_2$	2.4 ± 0.2	[b]2.27 ± 0.08	1.89 ± 0.08 (-69%)	7.1 ± 0.4 (46%)	3.07 ± 0.09 (66%)
	40 ± 20	84 ± 4	180 ± 5 (76%)	145 ± 5 (54%)	76 ± 3 (34%)
	490 ± 80	10,000 ± 1000	4300 ± 300 (24%)		
2A on			**640 nm**	**670 nm**	**700 nm**
TiO$_2$	10 ± 2	[c]18.5 ± 0.5	7.1 ± 0.6 (-104%)	1.4 ± 0.3 (32%)	9.6 ± 0.5 (71%)
	150 ± 80	Inf.	100 ± 10 (-63%)	22 ± 1 (52%)	160 ± 20 (22%)
	Inf.		Inf. (100%)	Inf. (16%)	Inf. (6%)
3A on			**600 nm**	**645 nm**	**680 nm**
TiO$_2$	1.6 ± 0.3	[a]1.76 ± 0.06	1.9 ± 0.2 (25%)	3.3 ± 0.2 (47%)	2.5 ± 0.1 (54%)
	30 ± 30	97 ± 5	43 ± 3 (37%)	100 ± 4 (41%)	79 ± 4 (36%)
	400 ± 200	Inf.	510 ± 40 (25%)	Inf. (12%)	Inf. (10%)
	Inf.		Inf. (13%)		
4A on			**600 nm**	**645 nm**	**680 nm**
TiO$_2$	2.4 ± 0.4	[a]1.05 ± 0.05	0.47 ± 0.03 (-98%)	1.6 ± 0.2 (39%)	0.75 ± 0.06 (49%)
	80 ± 30	126 ± 8	38 ± 4 (33%)	19 ± 3 (29%)	10.8 ± 0.8 (26%)
	Inf.	Inf.	330 ± 40 (31%)	190 ± 30 (19%)	170 ± 10 (15%)
			Inf. (36%)	Inf. (13%)	Inf. (10%)

[a] A to B to C

[b] A to B to C to ground state

[c] A to B

VIII. nsTA data of 1A-4A on Al_2O_3 and TiO_2

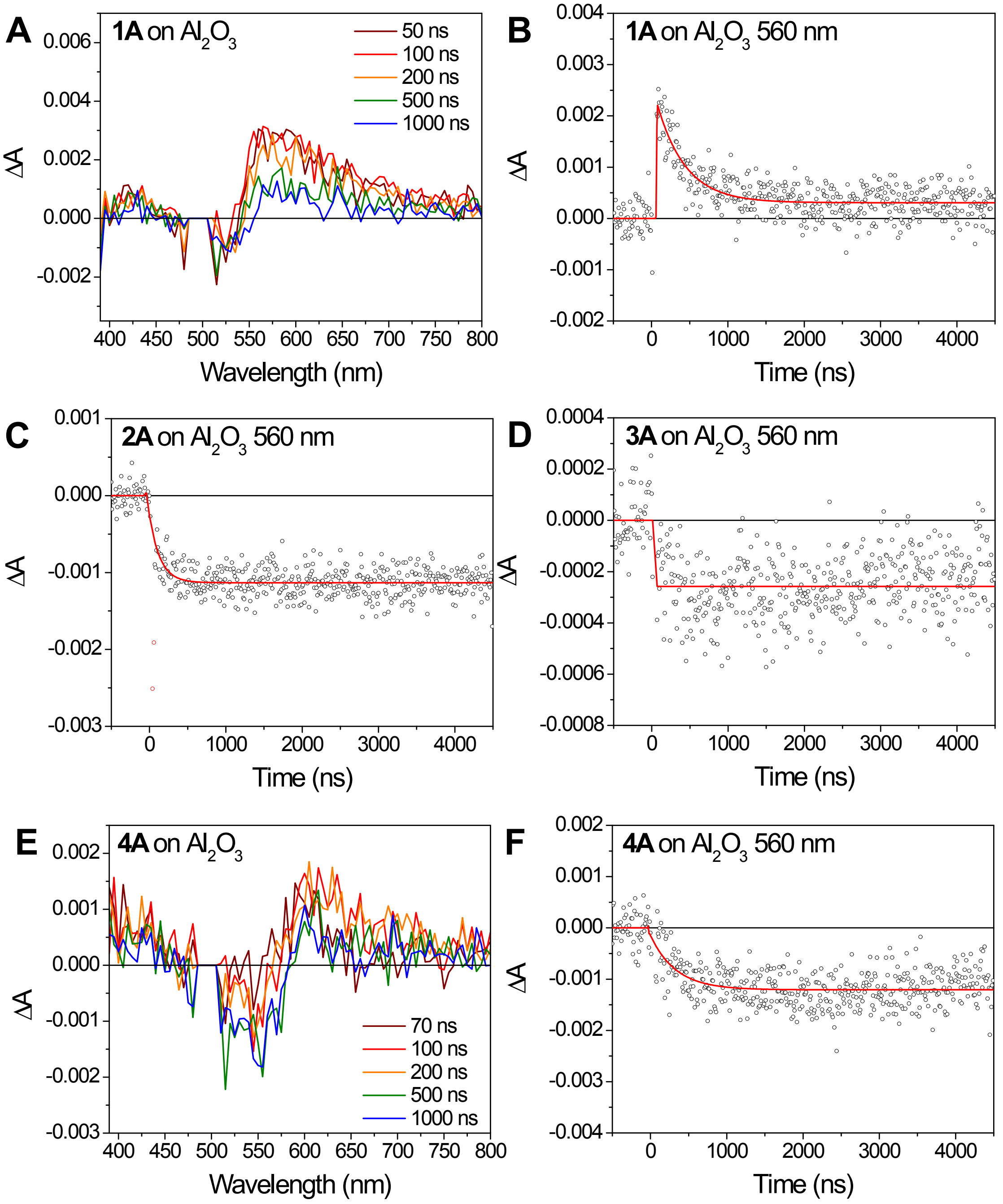


Figure S22. nsTA (A, E) spectra and (B-D, F) 560 nm traces (circles) and fits (lines) of **1A-4A** on Al_2O_3.

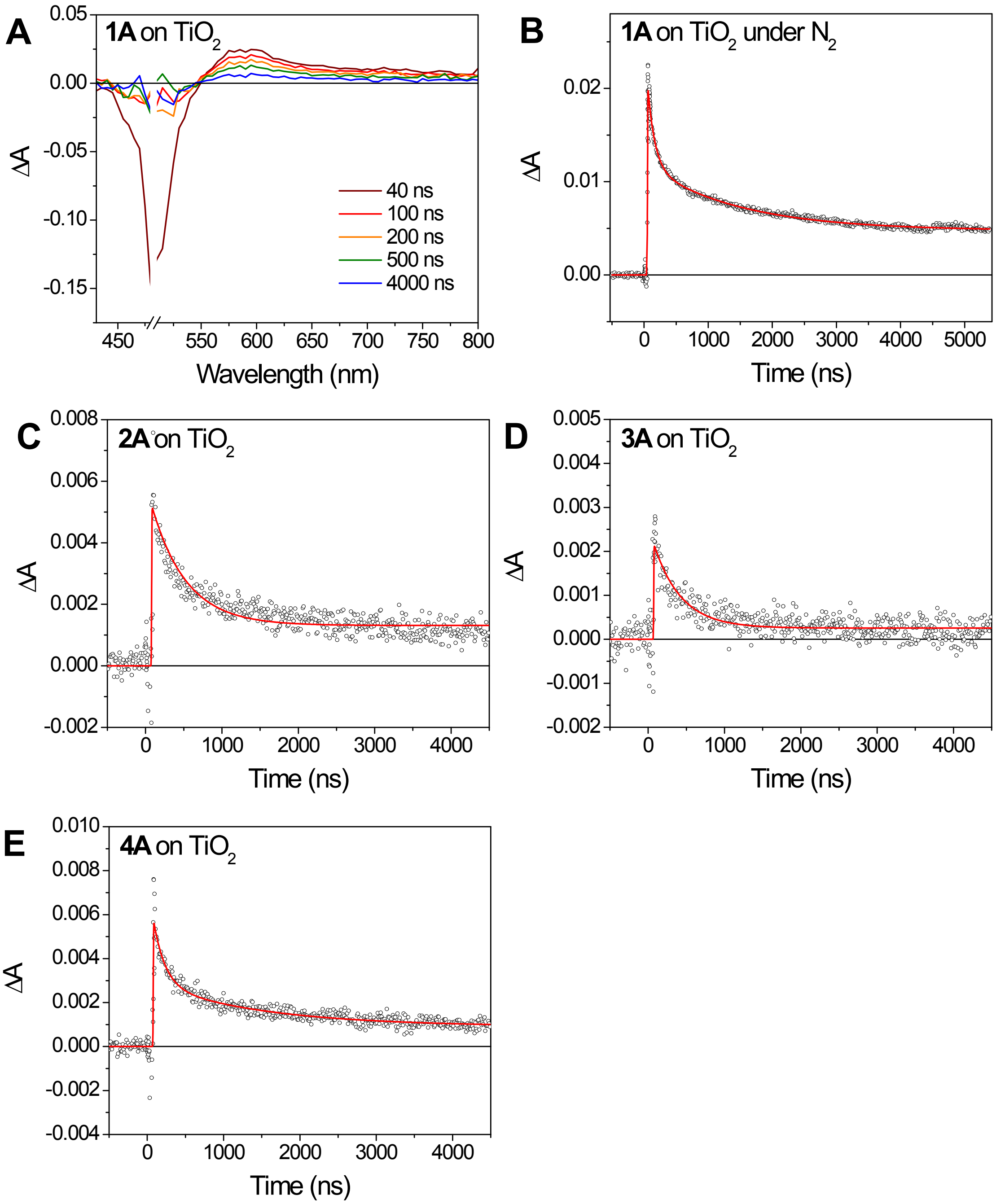


Figure S23. nsTA (A) spectra and (B-E) 610 nm traces (circles) and fits (lines) of **1A**-**4A** on TiO$_2$.

IX. TAS data of 2A-4A on TiO$_2$

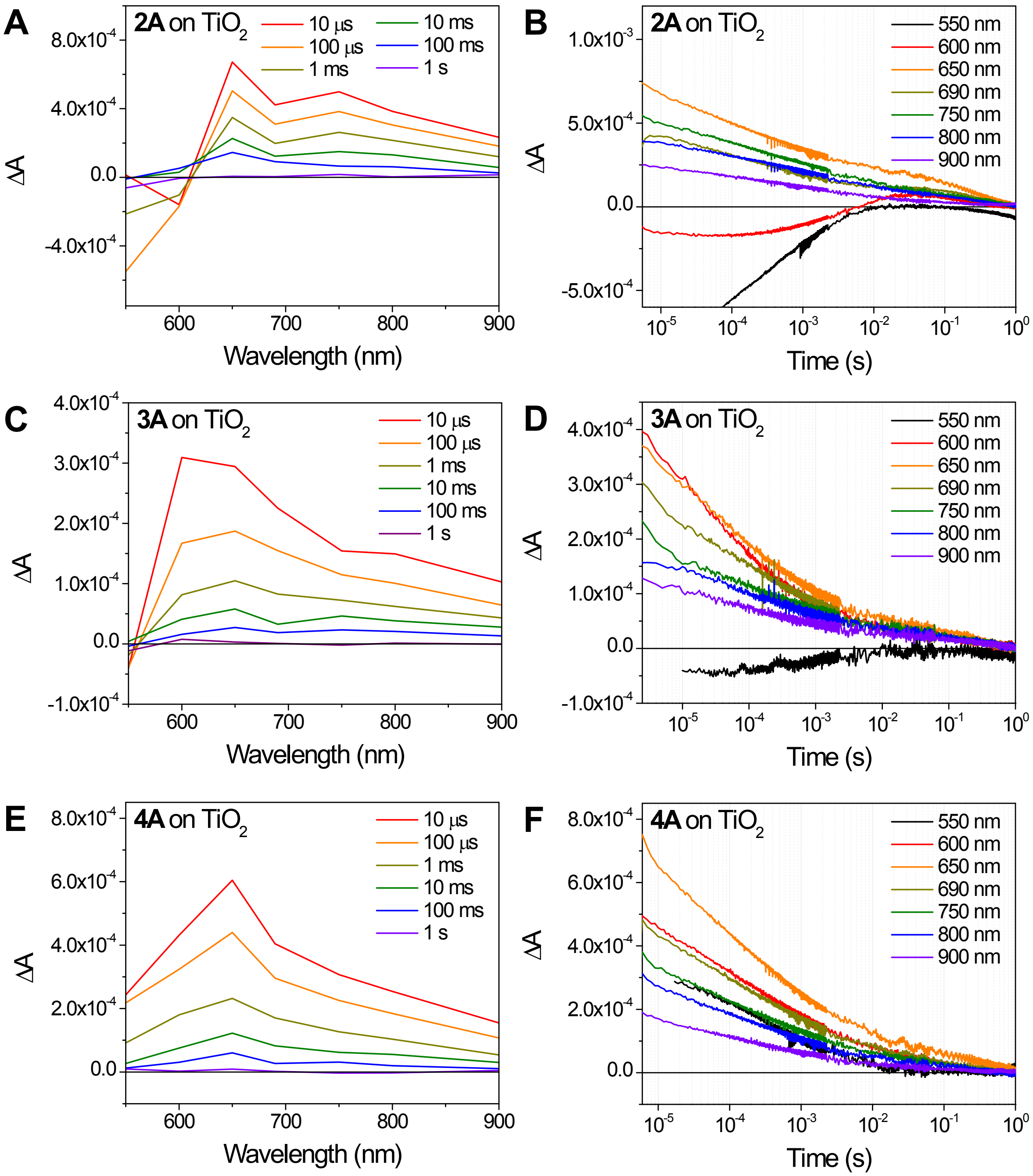


Figure S24. µsTA (A, C, E) spectra and (B, D, F) single wavelength traces of **2A-4A** on TiO$_2$.

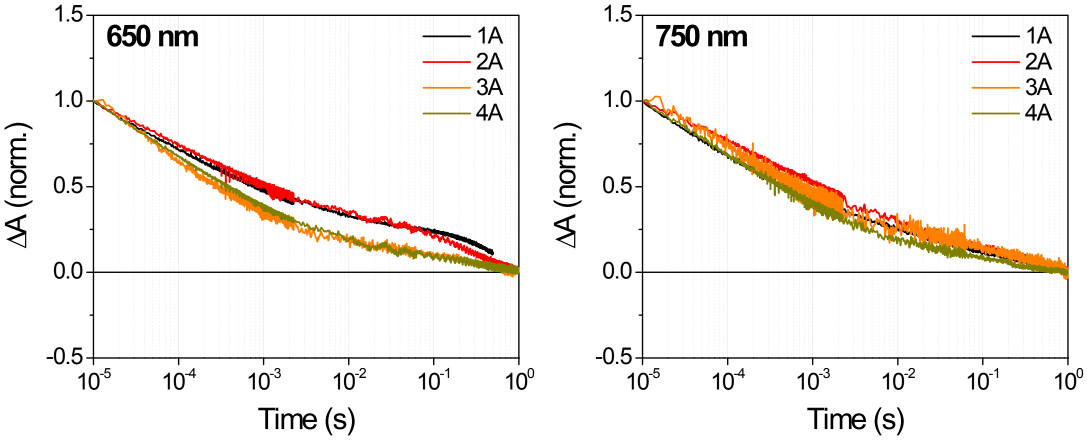


Figure S25. Normalized μsTA single wavelength traces of **1A** (black), **2A** (red), **3A** (orange), and **4A** (yellow) at 650 and 750 nm.

X. fsTA data of 5A and 5B

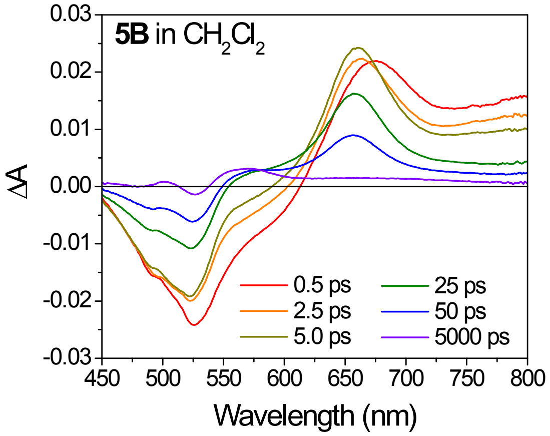


Figure S26. fsTA spectra of **5B** in CH_2Cl_2.

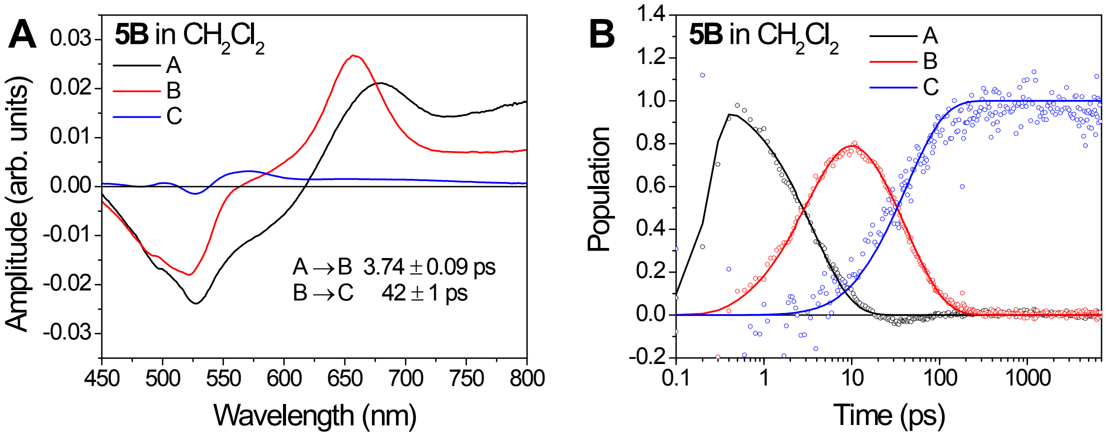


Figure S27. (A) Species-associated spectra obtained by (B) SVD/global fit of the fsTA spectra of **5B** in CH_2Cl_2 (Figure S24) to an A to B to C model.

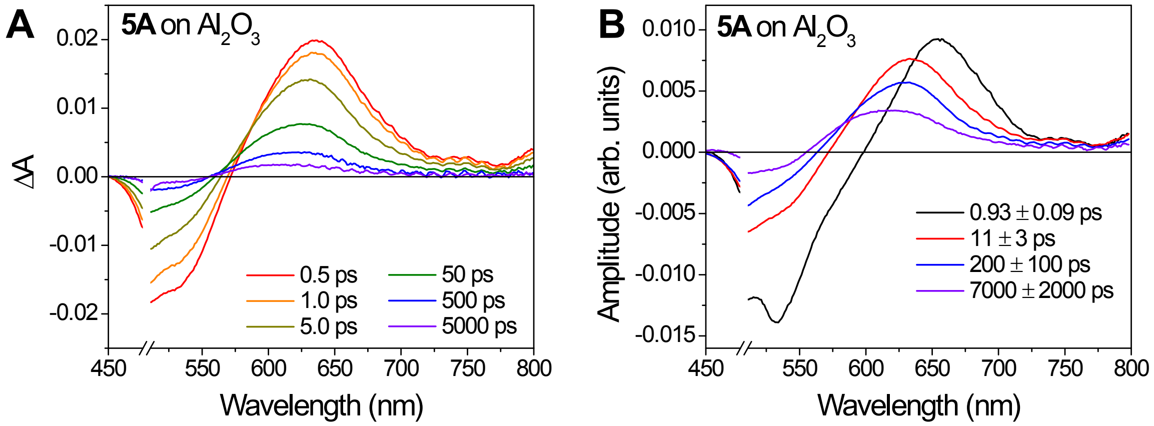


Figure S28. fsTA (A) spectra and (B) decay-associated spectra obtained by SVD and global analysis of the fsTA spectra of **5A** on Al_2O_3.

Differences in the spectral shape for this fsTA data set compared to all the others can be attributed to the addition of a reference channel in the fsTA apparatus.

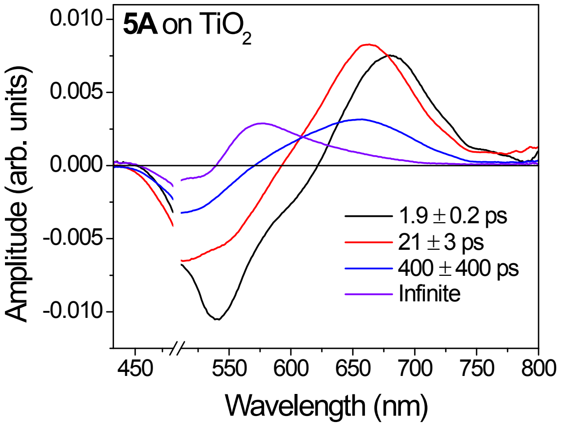


Figure S29. Decay-associated spectra obtained by SVD and global analysis of the fsTA spectra of **5A** on TiO_2.

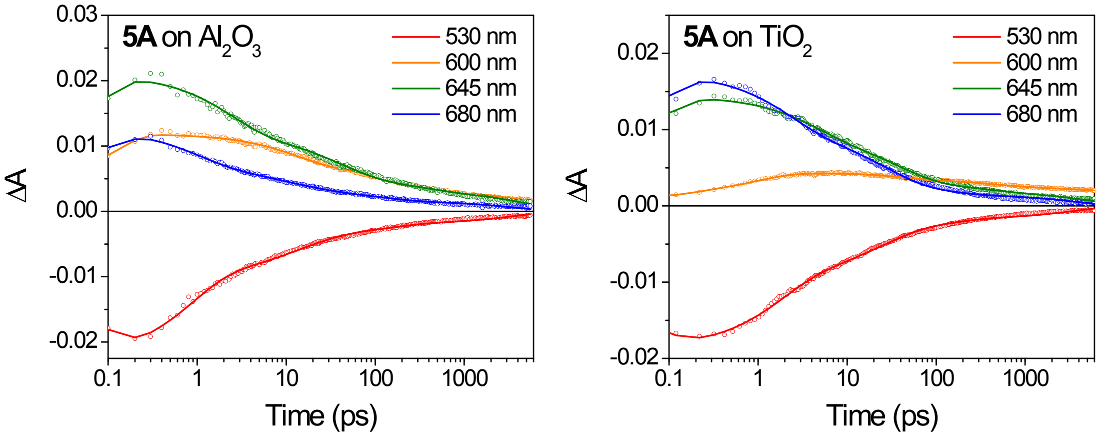


Figure S30. fsTA single wavelength traces (circles) and fits (lines) of **5A** on Al$_2$O$_3$ and TiO$_2$.

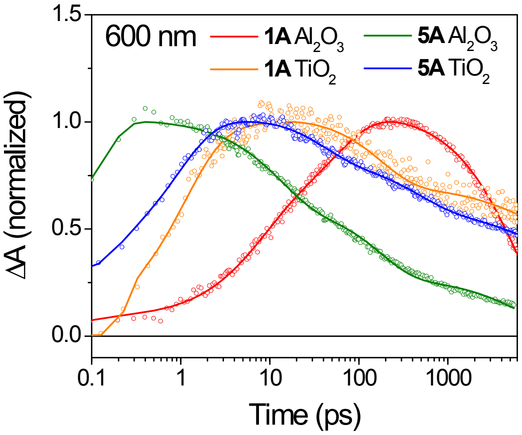


Figure S31. fsTA single wavelength traces (circles) and fits (lines) of **1A** on Al$_2$O$_3$ (red) and TiO$_2$ (orange) and **5A** on Al$_2$O$_3$ (green) and TiO$_2$ (blue) at 600 nm.

Table S5. fsTA fits of 5A on Al_2O_3 and TiO_2

5A sample	Decay-associated global fits τ (ps)	Single wavelength fits (% of amplitude)[a] τ (ps)				% Al_2O_3[b]
		530 nm	600 nm	645 nm	680 nm	
Al_2O_3	0.93 ± 0.09 11 ± 3 200 ± 100 7000 ± 2000	**1A**/Al_2O_3 (26%) 0.84 ± 0.03 (55%) 18.6 ± 0.7 (19%)	**1A**/Al_2O_3 (19%) 11.3 ± 0.3 (42%) 142 ± 5 (36%) Inf. (3%)	**1A**/Al_2O_3 (30%) 2.30 ± 0.09 (42%) 44 ± 2 (28%)	**1A**/Al_2O_3 (40%) 0.92 ± 0.04 (42%) 16.8 ± 0.8 (18%)	35%
TiO_2	1.9 ± 0.2 21 ± 3 400 ± 400 Inf.	**1A**/Al_2O_3 (28%) 1.66 ± 0.05 (44%) 26.9 ± 0.7 (28%)	**1A**/Al_2O_3 (16%) 0.90 ± 0.04 (-55%) 39 ± 2 (28%) 430 ± 40 (21%) Inf. (35%)	**1A**/Al_2O_3 (27%) 4.0 ± 0.2 (34%) 40 ± 1 (39%)	**1A**/Al_2O_3 (28%) 1.9 ± 0.1 (36%) 27.0 ± 0.8 (36%)	27%

[a] For "Al_2O_3 (%)", this is fixed as the triexponential decay for the Al_2O_3 sample at the corresponding wavelength.
[b] The average of the weights at the two reddest wavelengths.

REFERENCES

1. C. Ramanan, A. L. Smeigh, J. E. Anthony, T. J. Marks and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2012, **134**, 386-397.
2. Y. Yang, Y. Wang, Y. Xie, T. Xiong, Z. Yuan, Y. Zhang, S. Qian and Y. Xiao, *Chem. Commun.*, 2011, **47**, 10749-10751.
3. T. Weil, M. A. Abdalla, C. Jatzke, J. Hengstler and K. Müllen, *Biomacromolecules*, 2004, **6**, 68-79.
4. L. I. Hernández, R. Godin, J. J. Bergkamp, M. J. Llansola Portolés, B. D. Sherman, J. Tomlin, G. Kodis, D. D. Méndez-Hernández, S. Bertolotti, C. A. Chesta, E. Mariño-Ochoa, A. L. Moore, T. A. Moore, G. Cosa and R. E. Palacios, *J. Phys. Chem. B*, 2013, **117**, 4568-4581.
5. M. T. Vagnini, A. L. Smeigh, J. D. Blakemore, S. W. Eaton, N. D. Schley, F. D'Souza, R. H. Crabtree, G. W. Brudvig, D. T. Co and M. R. Wasielewski, *Proc. Natl. Acad. Sci.*, 2012, **109**, 15651-15656.
6. N. A. Owston, A. J. Parker and J. M. J. Williams, *Org. Lett.*, 2006, **9**, 73-75.
7. J. Choi, C. Sakong, J.-H. Choi, C. Yoon and J. P. Kim, *Dyes and Pigments*, 2011, **90**, 82-88.
8. B. V. Bergeron, A. Marton, G. Oskam and G. J. Meyer, *J. Phys. Chem. B*, 2004, **109**, 937-943.
9. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.
10. R. J. Lindquist, K. M. Lefler, K. E. Brown, S. M. Dyar, E. A. Margulies, R. M. Young and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2014, **136**, 14912-14923.
11. L. Duan, L. Tong, Y. Xu and L. Sun, *Energy Environ. Sci.*, 2011, **4**, 3296-3313.