# Supporting information to 'New light-harvesting roles of hot and forbidden carotenoid states in artificial photosynthetic constructs' by Miroslav Kloz, Smitha Pillai, Gerdenis Kodis, Devens Gust, Thomas A. Moore, Ana L. Moore, Rienk van Grondelle, John T.M. Kennis

## Synthesis of model carotenoids

The $^1$HNMR spectra were recorded on Varian spectrometers at 400 or 500 MHz, at 25°C. Samples were dissolved in deuteriochloroform with tetramethylsilane as an internal reference. Mass spectra were obtained on a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF) on positive ion mode employing a terthiophene matrix. Ultraviolet-visible ground state absorption spectra were measured on a Shimadzu UV2100 spectrometer. All chemicals were purchased from Aldrich and Alfa Aesar. Solvents were obtained from EM Science. Toluene was distilled from $CaH_2$, and dicloromethane was distilled from potassium carbonate. The reagent 8'-apo-*β*-carotene-8'-al (Hoffmann-La Roche) was purified by flash column chromatography, 100% dichloromethane, before use. The synthesis of 12'-apo-*β*-caroten-12'-al, 10'-apo-*β*-caroten-10'-al, 6'-apo-*β*-caroten-6'-al have been previously reported.[1,2]

**General procedure for the synthesis of iodocarotenoids:** The synthesis of 4-iodobenzyl(triphenyl)phosphonium bromide has been previously reported.[3] Carotenoid-aldehyde (0.5 mmol), 4-iodobenzyltriphenylphosphonium bromide (1 mmol), and sodium methoxide (1.25 mmol) were added to 30 mL of dimethylsulfoxide and stirred at 65°C for 24 h. The reaction was quenched by adding the dark orange solution to 250 mL water and extracting the compound with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude reaction mixture was then purified by column chromatography on silica using 20% dichloromethane in hexanes as the eluent. The product was recrystallized from dichloromethane/methanol.

**11'-Apo-11'-(4-iodophenyl)-*β*-carotene**

The general procedure using 12'-apo-*β*-caroten-12'-al gave 187 mg (68%): $^1$HNMR (400MHz, $CDCl_3$): *δ* 1.03 (6H, s, $CH_3$-16C and $CH_3$-17C), 1.45-1.49 (2H, m, $CH_2$-2C), 1.58-1.65 (2H, m, $CH_2$-3C), 1.72(3H, s, $CH_3$-19C), 1.96-2.05 (11H, m, $CH_3$-18C, $CH_3$-20C, $CH_3$-20'C, $CH_2$-4C), 6.04-6.86 (11H, m, vinyl H), 7.15 (2H, d, *J* = 8Hz, ArH), 7.6 (2H, d, *J* = 8Hz, ArH). MALDI-TOF-MS *m/z.* calcd. for $C_{32}H_{39}I$ 550.56, obsd.550.51; UV-vis (dichloromethane) 422, 440, 462 nm.

**9'-Apo-9'-(4-iodophenyl)-*β*-carotene**

The general procedure using 10'-apo-*β*-caroten-10'-al gave 198 mg (68%) of the desired compound: $^1$HNMR (400MHz, $CDCl_3$): *δ* 1.02 (6H, s, $CH_3$-16C and $CH_3$-17C), 1.43-1.48 (2H, m, $CH_2$-2C), 1.57-1.64 (2H, m, $CH_2$-3C), 1.7 (3H, s, $CH_3$ -19C), 1.9-2 (11H, m, $CH_3$ -18C, $CH_3$-20C, $CH_3$-20'C, $CH_2$-4C), 6.07-6.9 (13H, m, vinyl H, ArH), 7.11 (2H, d, *J* = 8.2Hz, ArH), 7.6 (2H, d, *J* = 8.2Hz, ArH). MALDI-TOF-MS *m/z.*: calcd. for $C_{34}H_{41}I$ 576.81, obsd. 576.85; UV-vis (dichloromethane) 434, 455, 483 nm.

**7'-Apo-7'-(4-iodophenyl)-*β*-carotene**

The general procedure using 8'-apo-*β*-caroten-8'-al gave 206 mg (66.8%) of the desired compound: $^1$HNMR (400MHz, $CDCl_3$): *δ* 1.03 (6H, s, $CH_3$-16C and $CH_3$-17C), 1.45-1.48 (2H, m, $CH_2$-2C), 1.58-1.63 (2H, m, $CH_2$-3C), 1.7(3H, s, $CH_3$-19C), 1.96-2.4 (14H, m, $CH_3$-18C, $CH_3$-20C, $CH_3$-20'C, $CH_2$-4C, and $CH_3$-19'C), 6.11-6.87(14H, m, vinyl H), 7.15 (2H, d, *J* = 8.4Hz, ArH), 7.62(2H, d, *J* = 8.4Hz, ArH). MALDI-TOF-MS *m/z.* calcd. for $C_{37}H_{45}I$ 616.20, obsd. 616.23; UV-vis (dichloromethane) 449, 475, and 507 nm.

**5'-Apo-5'-(4-iodophenyl)-*β*-carotene**

The general procedure using 6'-apo-*β*-caroten-6'-al gave 195 mg (60%) of the desired compound: $^1$HNMR (400MHz, $CDCl_3$): *δ* 1.03 (6H, s, $CH_3$-16C and $CH_3$-17C), 1.44-1.45 (2H, m, $CH_2$-2C), 1.58-1.66 (2H, m, $CH_2$-3C), 1.7(3H, s, $CH_3$-19C), 1.93-2 (14H, m, $CH_3$-18C, $CH_3$-20C, $CH_3$-20'C, $CH_2$-4C, and $CH_3$-19'C), 6.1-6.9 (16H, m, vinyl H), 7.13 (2H, d, *J* = 7.8Hz, ArH), 7.27 (2H, d, J=7.8Hz, ArH). MALDI-TOF-MS *m/z.* calcd. for $C_{39}H_{47}I$ 642.71, obsd. 642.72; UV-vis (dichloromethane) 453, 486, and 517 nm.

**General procedure for the amination reaction to prepare model aminocarotenoids:** Iodocarotene (0.1 mmol), 4-amino-1-methylbenzene (0.12 mmol), sodium *tert*-butoxide (0.14 mmol), tris(dibenzylideneacetone)dipalladium (0.003 mmol), and BINAP (0.008 mmol), were stirred in toluene (5 mL) at 80°C under argon atmosphere until the starting material was consumed (8 h).[4] The solution was then allowed to cool to room temperature and filtered through a short silica gel column to remove compounds having low solubility. The solvent was evaporated and the residue was chromatographed on silica gel using 30% dichloromethane in hexanes.

**11'-Apo-11'-(4-amino-N-[4-methylphenyl]phenyl)-*β*-carotene (Car-8)**

The general procedure using 11'-Apo-11'-(4-iodophenyl)-*β*-carotene gave 42 mg (66%) of the desired compound: $^1$HNMR (500MHz, $CDCl_3$): $\delta$ 1.02 (6H, s, $CH_3$-16C and $CH_3$-17C), 1.43-1.48 (2H, m, $CH_2$-2C), 1.58-1.65 (2H, m, $CH_2$-3C), 1.7 (3H, s, $CH_3$-19C), 1.93-2.05 (11H, m, $CH_3$ -18C, $CH_3$-20C, $CH_3$-20'C, $CH_2$-4C), 2.29 (3H, s, Ar-$CH_3$), 5.68 (1H, s, NH), 6.02-6.8 (11H, m, vinyl H), 6.9 (2H, d, $J$ = 8Hz, ArH), 7 (2H, d, $J$ = 8Hz, ArH), 7.08 (2H, d, $J$ = 8Hz, ArH), 7.3 (2H, d, $J$ = 8Hz, ArH). MALDI-TOF-MS *m/z* calcd. for $C_{39}H_{47}N$ 529.31, obsd. 529.30; UV-vis (dichloromethane) 356, 430,452, and 475 nm.

**9'-Apo-9'-(4-amino-N-[4-methylphenyl]phenyl)-*β*-carotene (Car-9)**

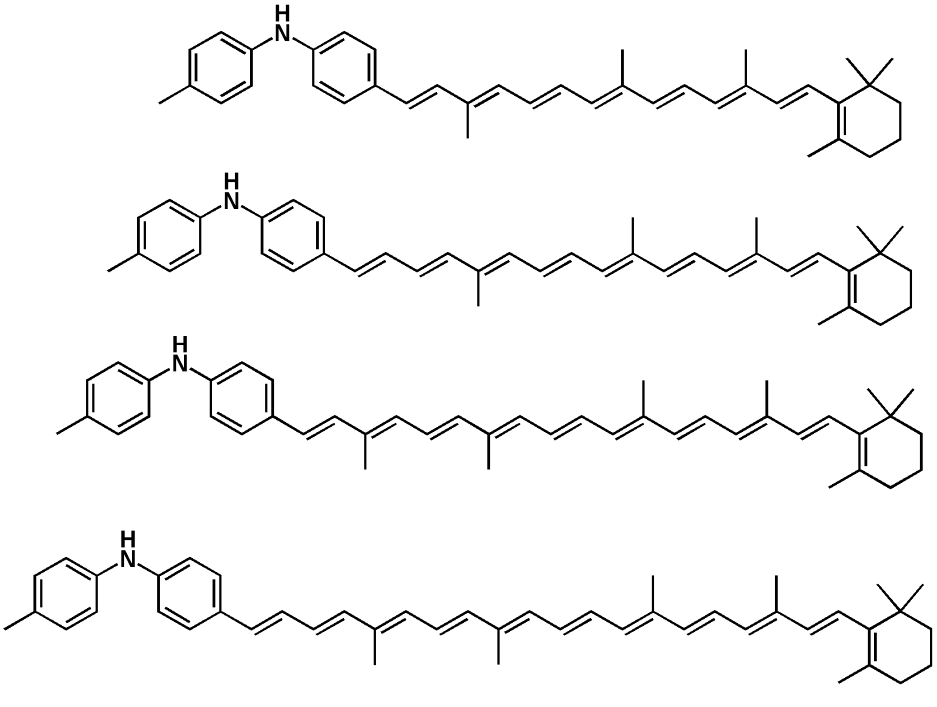
The general procedure using 9'-apo-9'-(4-iodophenyl)-*β*-carotene gave 35 mg (63%) of the desired compound: $^1$HNMR (400MHz, $CDCl_3$): $\delta$ 1.06 (6H, s, $CH_3$-16C and $CH_3$-17C), 1.48-1.52 (2H, m, $CH_2$-2C), 1.62-1.68 (2H, m, $CH_2$-3C), 1.75 (3H, s, $CH_3$-19C), 1.96-2 (11H, m, $CH_3$-18C, $CH_3$-20C, $CH_3$-20'C, $CH_2$-4C), 2.34 (3H, s, Ar-$CH_3$), 5.73 (1H, s, NH), 6.07-6.9 (13H, m, vinyl H, ArH), 6.97 (2H, d, $J$ = 8Hz, ArH), 7.04 (2H, d, $J$ = 8Hz, ArH), 7.12 (2H, d, $J$ = 8Hz, ArH), 7.32 (2H, d, $J$ = 8Hz, ArH). MALDI-TOF-MS *m/z.*: calcd. for $C_{41}H_{49}N$ 555.44, obsd. 555.46; UV-vis (dichloromethane) 371, 441, 466, 493 nm.

**7'-Apo-7'-(4-amino-N-[4-methylphenyl]phenyl)-*β*-carotene (Car-10)**

The general procedure using 7'-apo-7'-(4-iodophenyl)-*β*-carotene gave 46 mg (77%) of the desired compound: $^1$HNMR (500MHz, $CDCl_3$): $\delta$ 1.03 (6H, s, $CH_3$-16C and $CH_3$-17C), 1.45-1.49 (2H, m, $CH_2$-2C), 1.6-1.64 (2H, m, $CH_2$-3C), 1.72(3H, s, $CH_3$-19C), 1.97-2.03 (14H, m, $CH_3$-18C, $CH_3$-20C, $CH_3$-20'C, $CH_2$-4C, and $CH_3$-19'C), 2.31 (3H, s, Ar-$CH_3$), 6.09-6.77 (15H, m, vinyl H, NH), 6.96 (2H, d, *J* = 8.5Hz, ArH), 7.01 (2H, d, *J* = 8Hz, ArH), 7.1 (2H, d, *J* = 8Hz, ArH), 7.3 (2H, d, *J* = 8.5Hz, ArH). MALDI-TOF-MS *m/z*: calcd. for $C_{44}H_{53}N$ 595.21, obsd. 595.25; UV-vis (dichloromethane) 382, 455, 480, and 510 nm.

### 5'-Apo-5'-(4-amino-N-[4-methylphenyl]phenyl)-*β*-carotene (Car-11)

The general procedure using 5'-apo-5'-(4-iodophenyl)-*β*-carotene gave 38 mg (61%) of the desired compound. $^1$HNMR (400MHz, $CDCl_3$): $\delta$ 1.01 (6H, s, $CH_3$-16C and $CH_3$-17C), 1.45-1.46 (2H, m, $CH_2$-2C), 1.58-1.64 (2H, m, $CH_2$-3C), 1.7(3H, s, $CH_3$-19C), 1.96-2.1 (14H, m, $CH_3$-18C, $CH_3$-20C, $CH_3$-20'C, $CH_2$-4C, and $CH_3$-19'C), 2.2 (3H, s, Ar-$CH_3$), 6.06-6.9 (17H, m, vinyl H, NH), 6.95 (2H, d, *J* = 8Hz, ArH), 7.01 (2H, d, *J* = 8Hz, ArH), 7.08 (2H, d, *J* = 8Hz, ArH), 7.27 (2H, d, *J* = 8Hz, ArH). MALDI-TOF-MS *m/z*: calcd. for $C_{46}H_{55}N$ 621.94, obsd.621.93; UV-vis (dichloromethane) 395, 461, 491, and 521 nm.

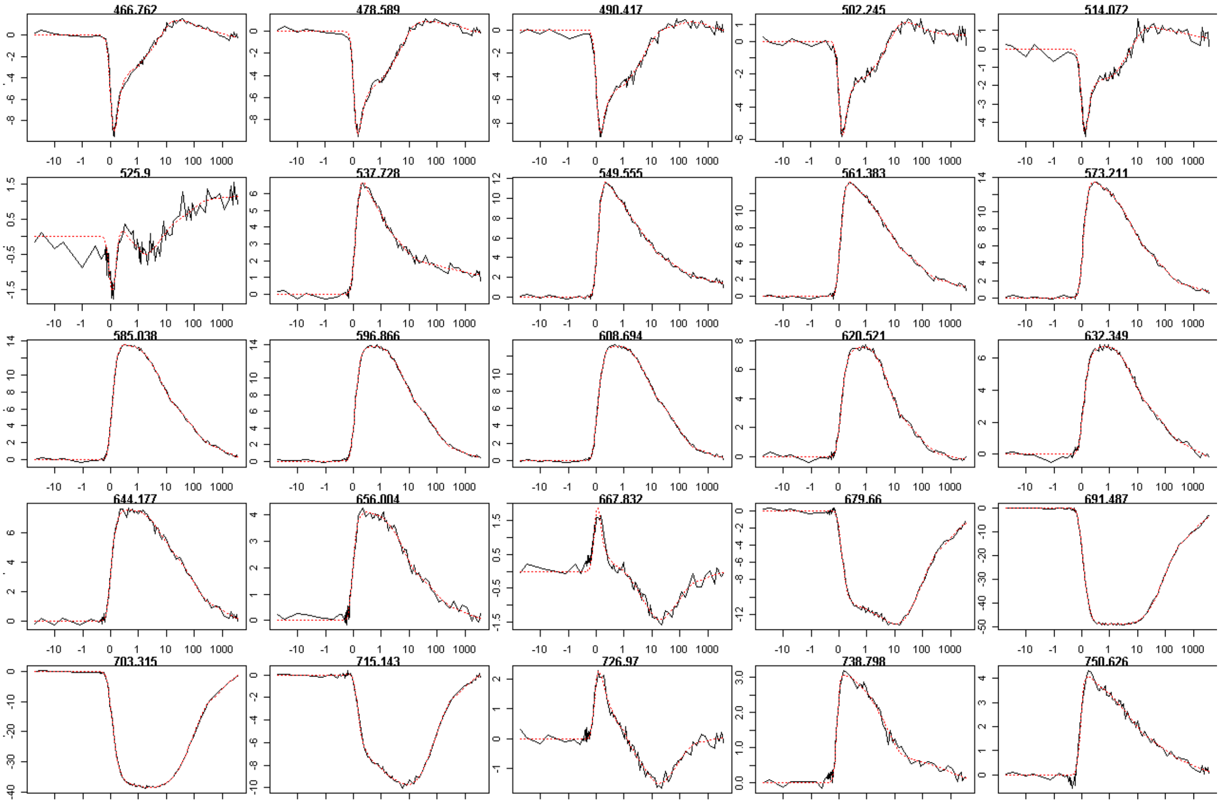


References:

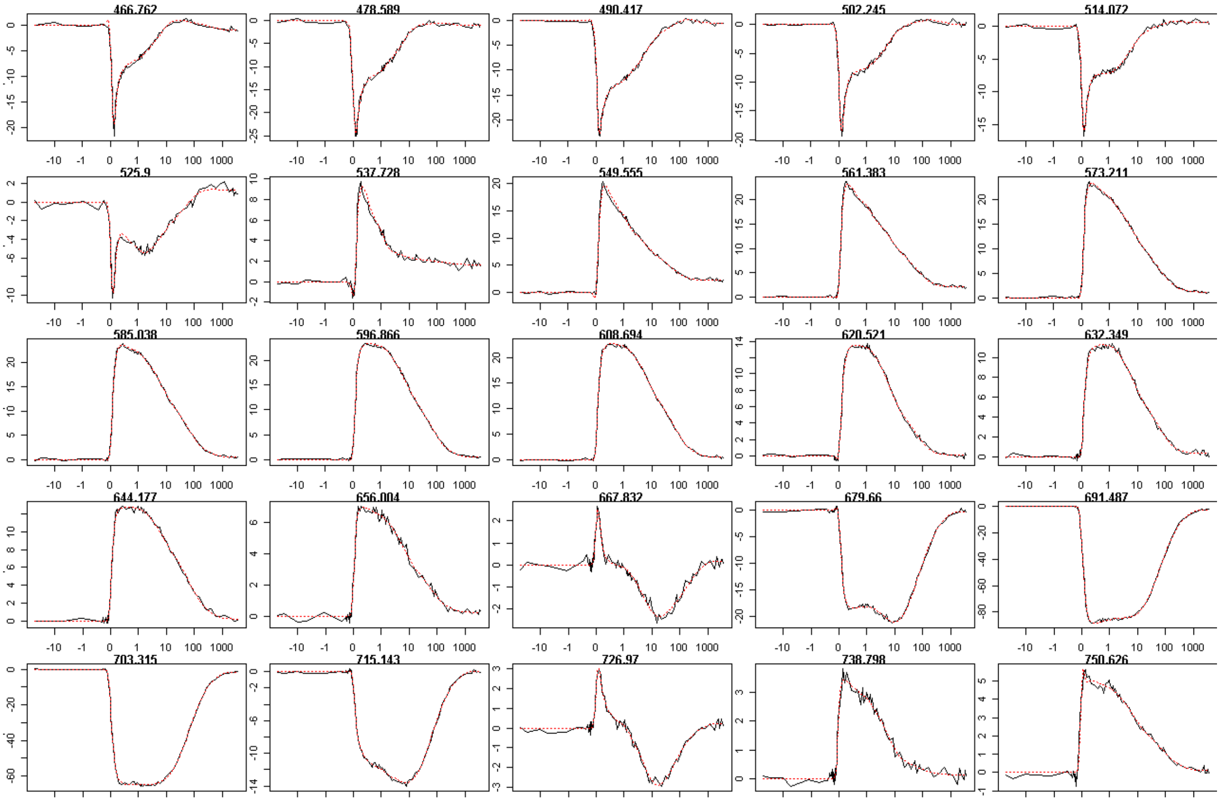
1. Reddy, P. V.; Rabago-Smith, M.; Borhan, B. *Journal of Labelled Compounds & Radiopharmaceuticals* **2002**, *45*, 79.

2. Cardoso, S. L.; Nicodem, D. E.; Moore, T. A.; Moore, A. L.; Gust, D. *Journal of the Brazilian Chemical Society* **1996**, *7*, 19.
3. Mylona, A., Nikokavouras, J., Takakis, I., *J. Org. Chem*. **1988**, *53*, 3838.
4. Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem*. **2000**, *65*, 1144– 1157.

## Raw transient absorption data and fit results



Dyad-10 415 nm excitation selected kinetic traces, raw data (full black line) and fit (red dashed line)



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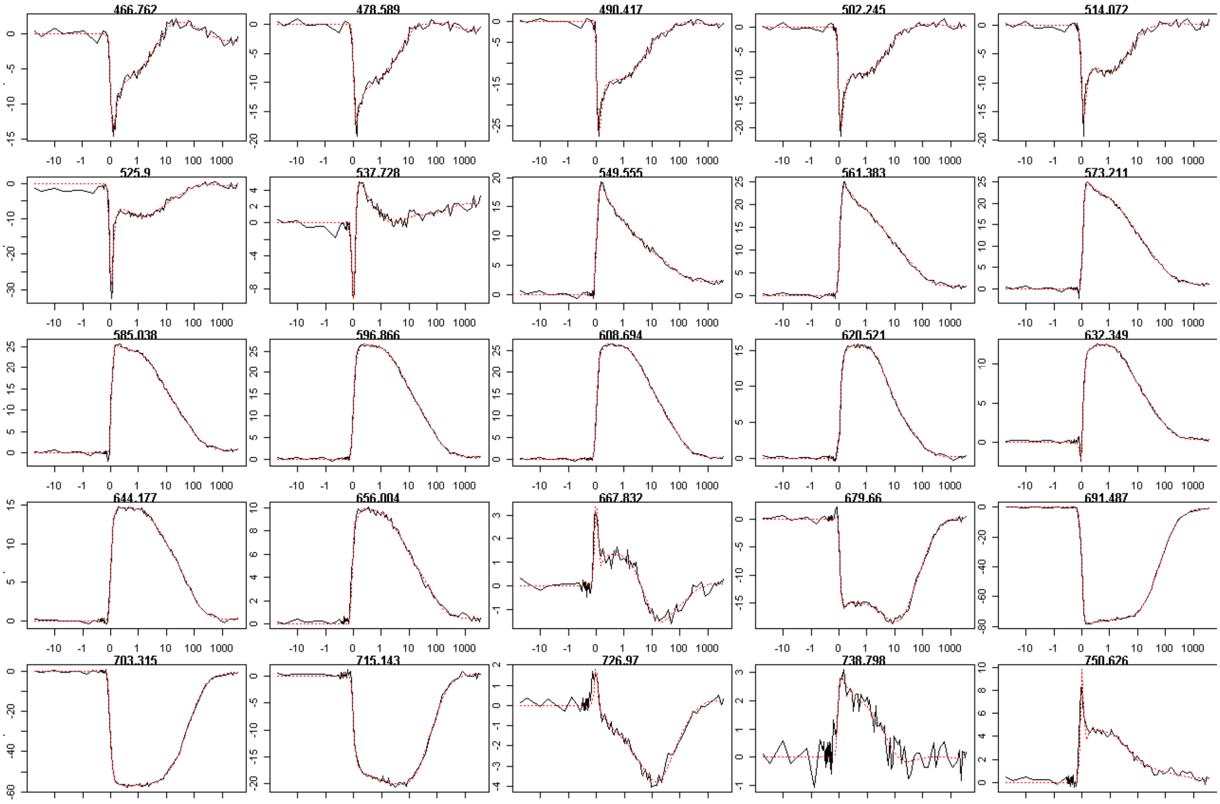

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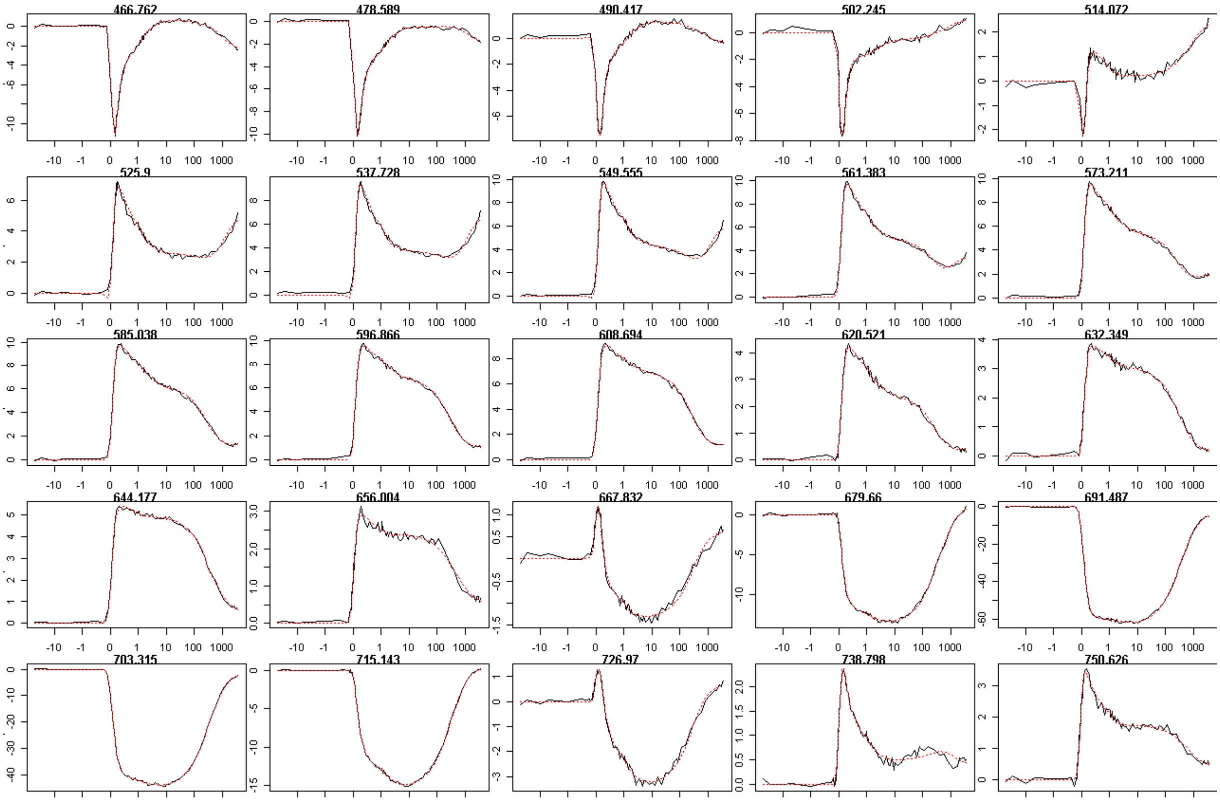
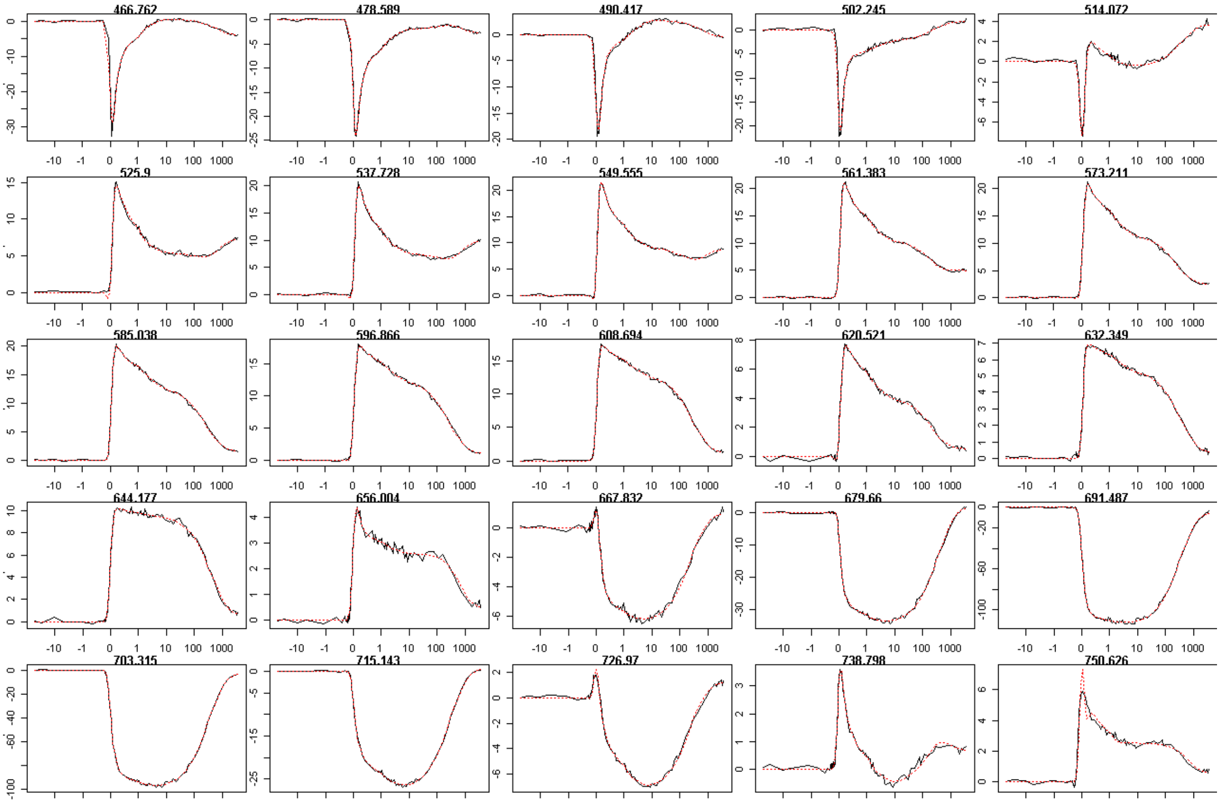
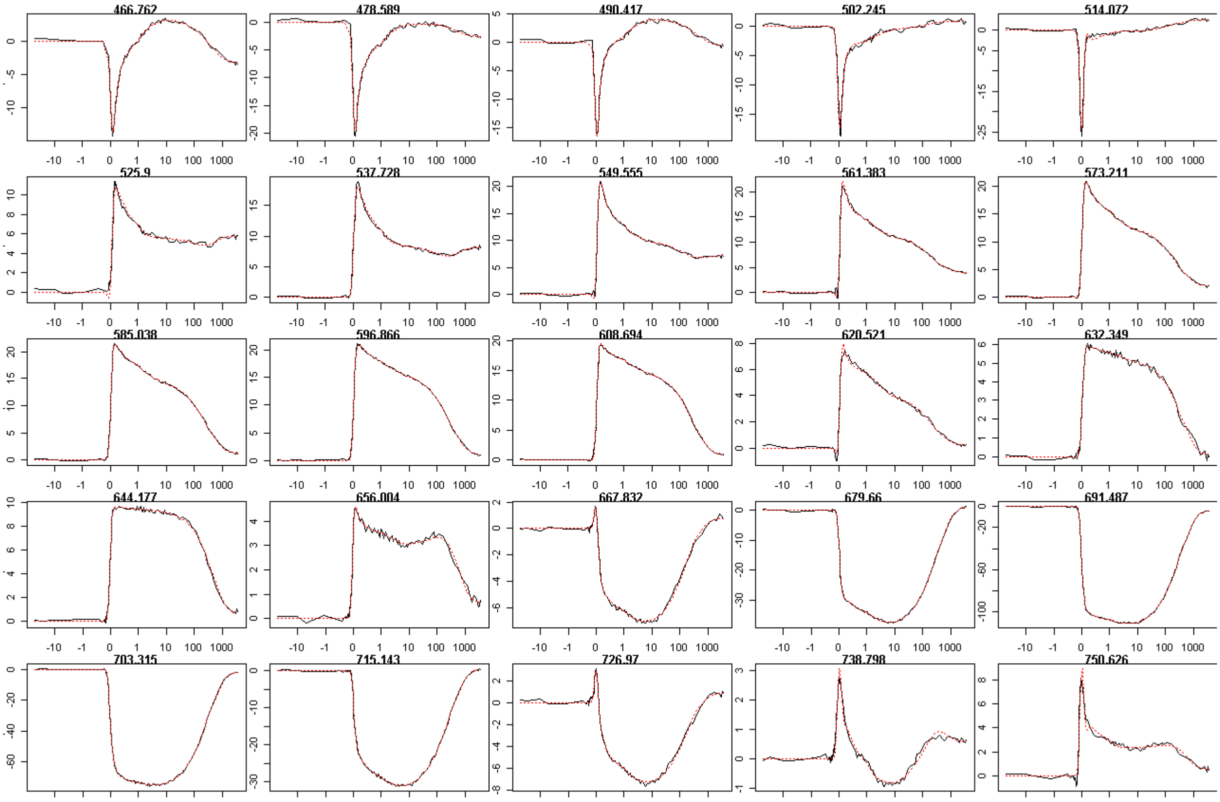


Dyad-9 435 nm excitation selected kinetic traces, raw data (full black line) and fit (red dashed line)



Dyad-9 469 nm excitation selected kinetic traces, raw data (full black line) and fit (red dashed line)



Dyad-9 515 nm excitation selected kinetic traces, raw data (full black line) and fit (red dashed line)