**Supplementary Materials to**

# Energy Transfer in Supramolecular Calix[4]arene – Perylene Bisimide Dye Light Harvesting Building Blocks: Resolving Loss Processes with Simultaneous Target Analysis

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## Chemical structures of the calix[4]arene – perylene bisimide supramolecular systems

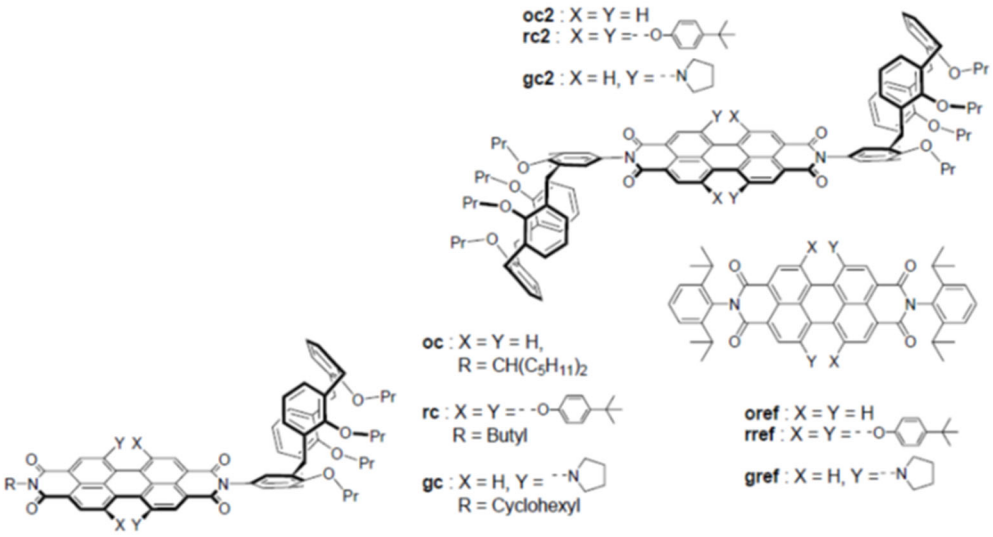


Figure S 1. Chemical structures of PBI–calix[4]arene conjugates and reference compounds studied. Figure adopted from [37]. **coc**=**oc2**, **crc**=**rc2**, **cgc**=**gc2**.

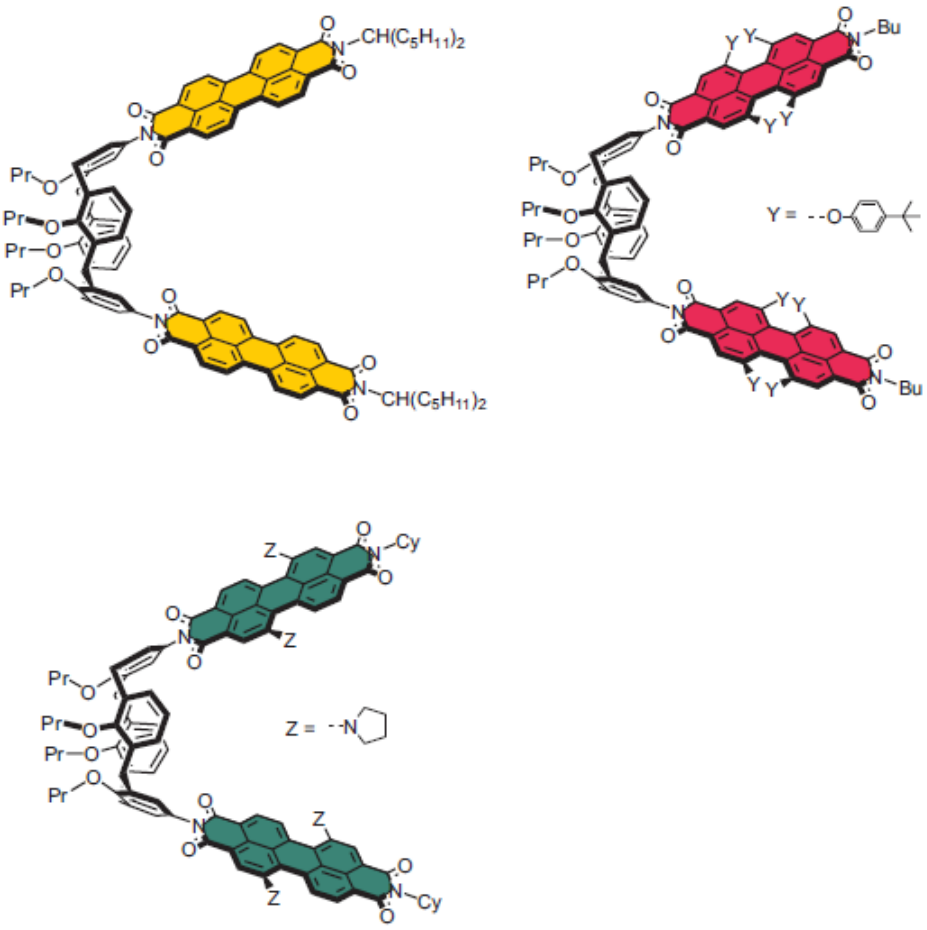


Figure S 2. Chemical structures of the bichromophoric supramolecular systems **oco**, **rcr** and **gcg**. Figure adopted from [37].

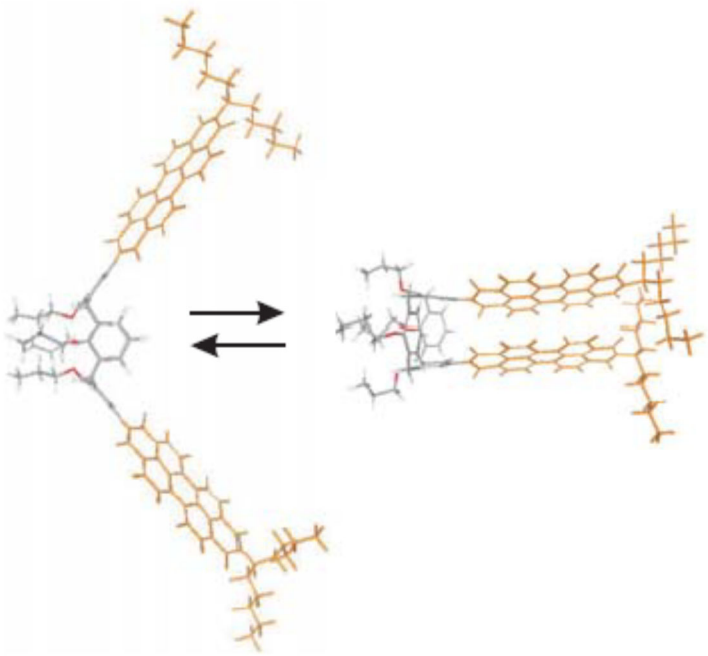

Figure S 3. Schematic representation of the equilibrium between non-stacked (left) and π-stacked (right) pinched cone conformation of the calix[4]arene unit upon substitution with two orange PBI units (for the chemical structure of **oco** see Figure S 2). Molecular structures obtained from force field calculations (Macromodel 8.0, potential MMFF). Color of the PBI chromophore is applied for clarity. Figure taken from [37].

## Spectral evolution in oref, rref, gref, rc, crc, gc and cgc

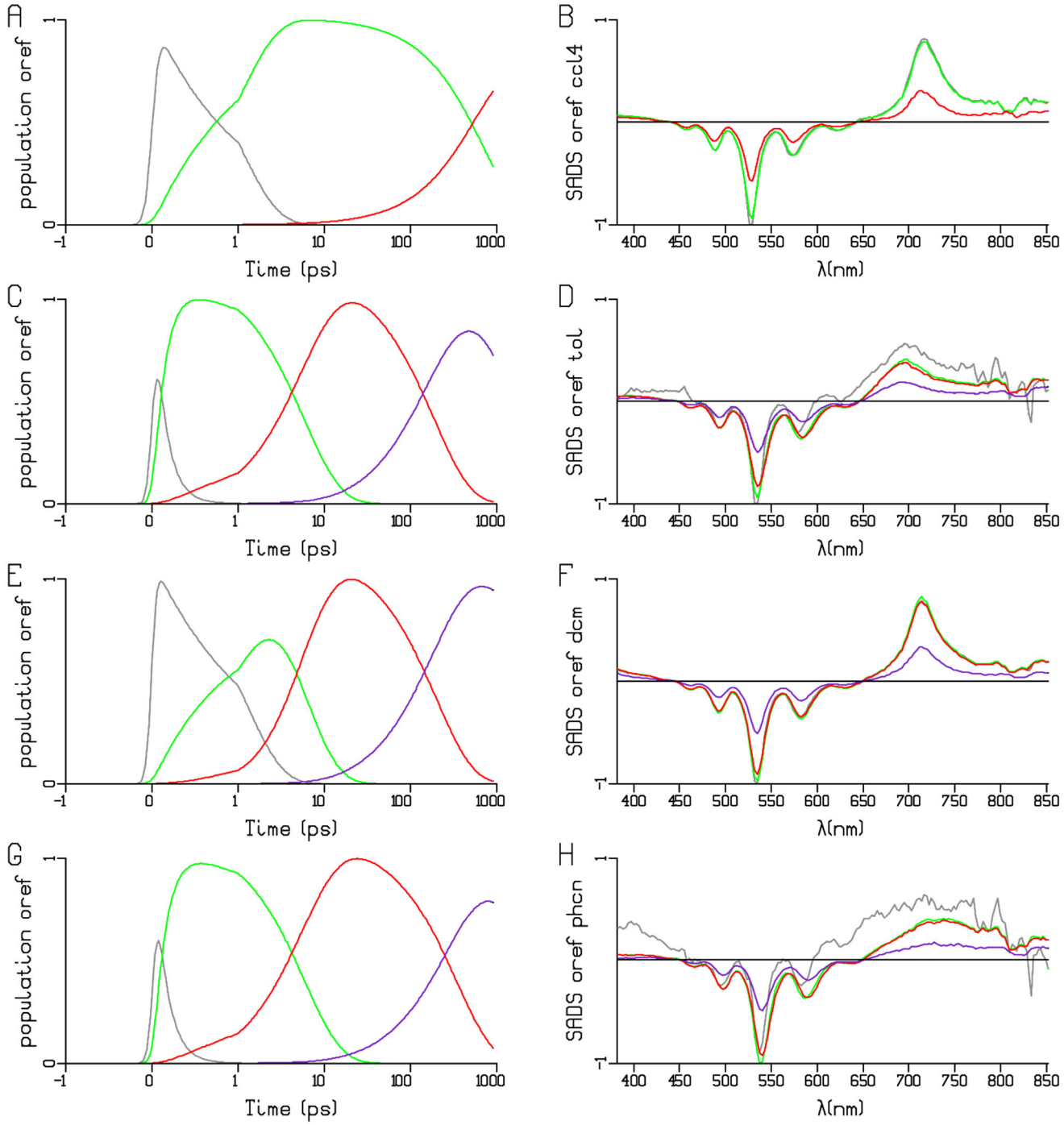


Figure S 4. Populations of a sequential kinetic scheme (A,C,E,G) and estimated SADS (B,D,F,H) of reference compound **oref** in CCl4, toluene, $CH_2Cl_2$ and benzonitrile. Key: grey, **oref*FC**: excited **oref** chromophore in the Franck-Condon state; green, red, purple: successively relaxed **oref*** states. Lifetimes are collated in Table S 1. The SADS in the Supplementary figures have all been scaled to the maximum absolute value.

| compound | solvent | τ1 | τ2 | τ3 | τ4 |
|---|---|---|---|---|---|
| oref | CCl4 | 1.08 | 713.7 | 5000 | |
| | toluene | 0.14 | 5.8 | 185 | 1759 |
| | CH2Cl2 | 1.21 | 5.1 | 197 | 5000 |
| | benzonitrile | 0.14 | 5.8 | 337 | 2574 |
| rref | methylcyclohexane | 0.49 | 10.4 | 241 | 5000 |
| | CCl4 | 0.75 | 14.3 | 344 | 5000 |
| | toluene | 0.40 | 8.3 | 222 | 4160 |
| | CH2Cl2 | 0.32 | 4.4 | 120 | 1147 |
| | benzonitrile | 0.53 | 14.0 | 255 | 4425 |
| gref | toluene | 0.25 | 3.2 | 290 | 4032 |
| | CH2Cl2 | 0.14 | 1.4 | 220 | 2120 |
| | benzonitrile | 0.31 | 8.1 | 339 | 3163 |

Table S 1. Lifetimes (in ps) of the reference compounds in the different solvents.

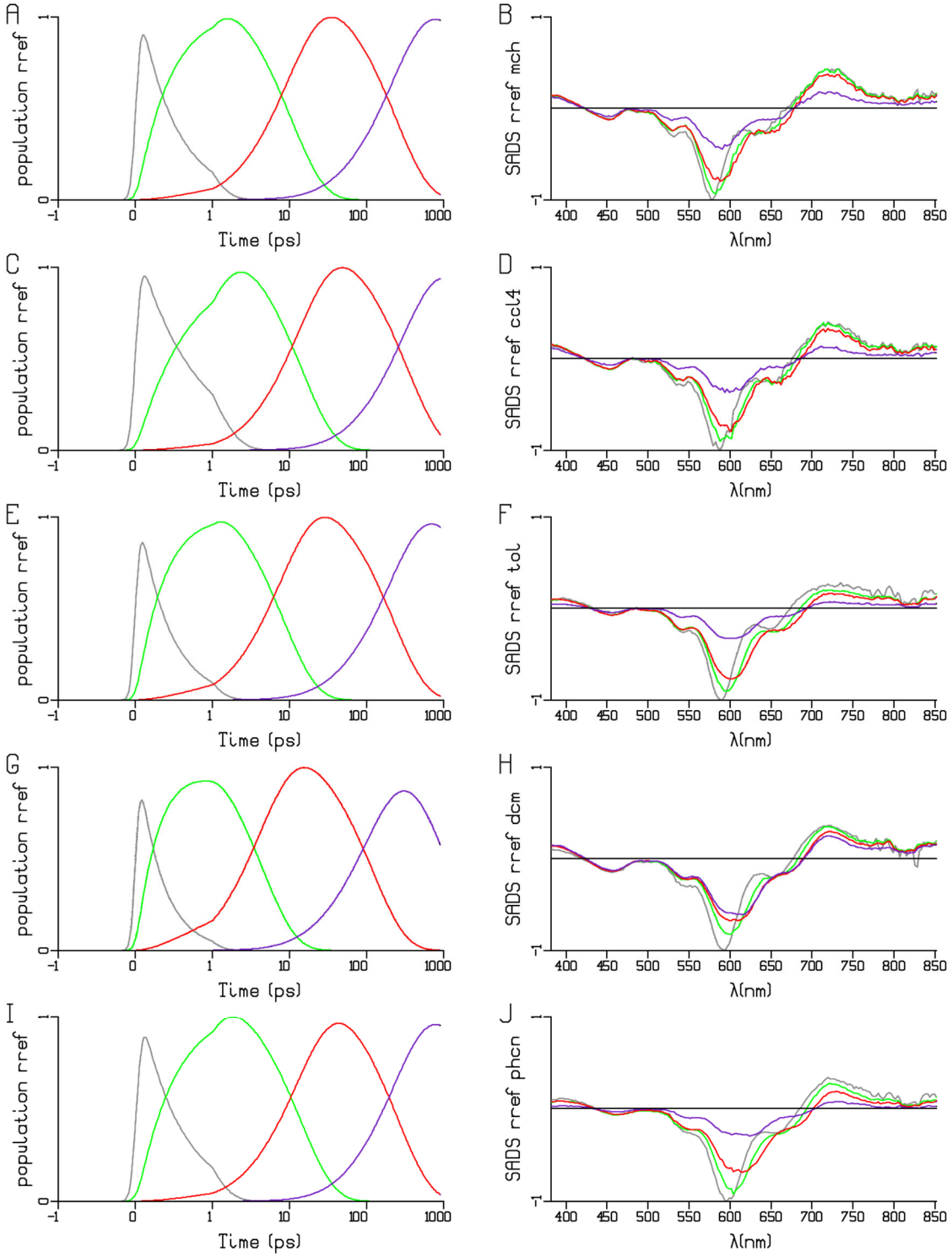


Figure S 5. Populations of a sequential kinetic scheme (A,C,E,G) and estimated SADS (B,D,F,H) of reference compound **rref** in methylcyclohexane, CCl4, toluene, $CH_2Cl_2$ and benzonitrile. Key: grey, **rref*FC**: excited **rref** chromophore in the Franck-Condon state; green, red, purple: successively relaxed **rref*** states. Lifetimes are collated in Table S 1.

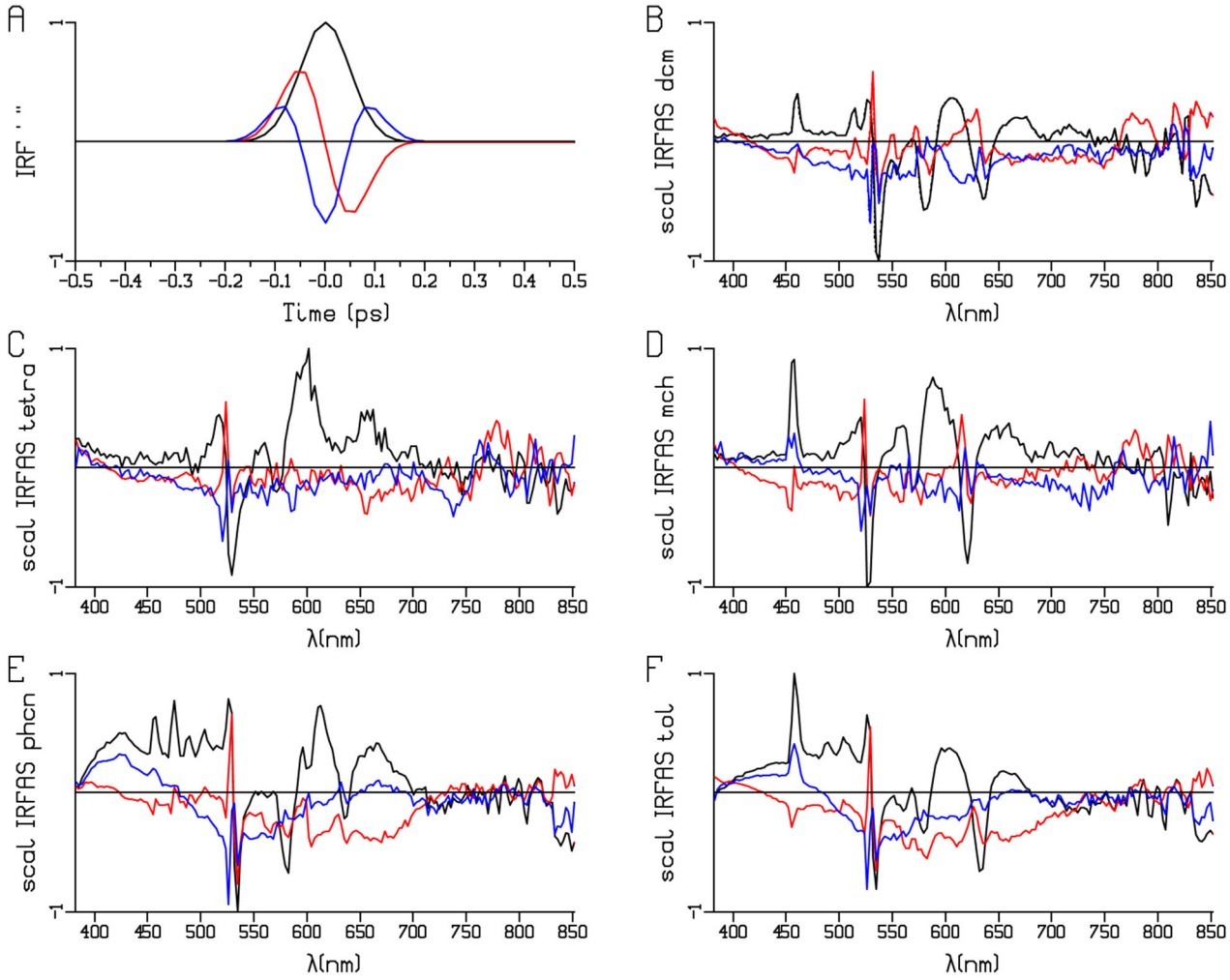


Figure S 6. Coherent artefact of the reference compound **rref** in $CH_2Cl_2$, CCl4, methylcyclohexane, benzonitrile and toluene. (A) 0th, 1st and 2nd derivative of the IRF (black, red and blue) which possessed a Full Width at Half Maximum of 119 fs. (B) scaled IRFAS in $CH_2Cl_2$. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. Thus, the black IRFAS has the largest contribution to the fit. It shows large amplitudes straddling 530 nm, the excitation wavelength. In addition, Raman scattering is visible as negative peaks at 580 and 636 nm, and positive peaks at 460 and 512 nm. (C-F) scaled IRFAS in CCl4, methylcyclohexane, benzonitrile and toluene.

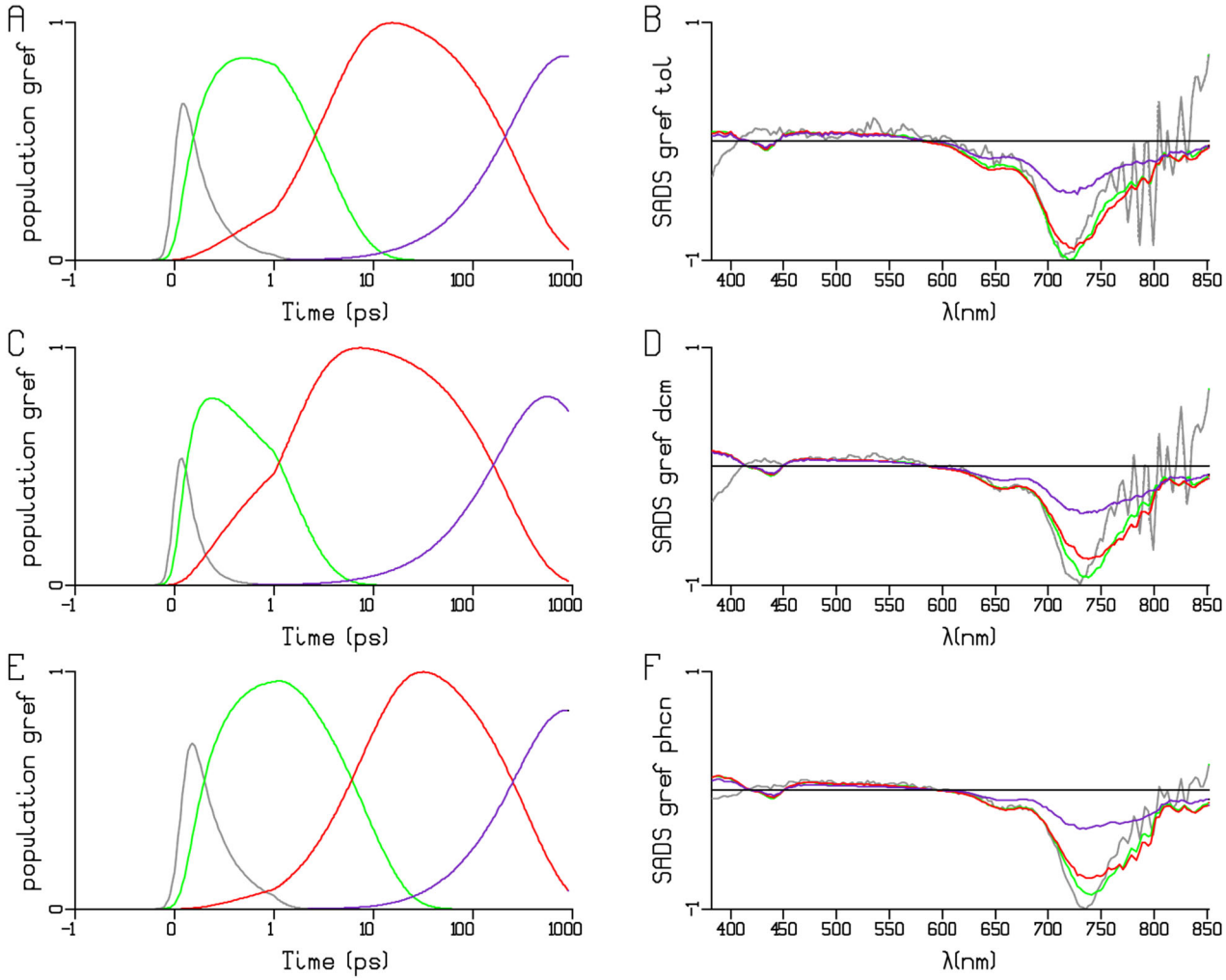


Figure S 7. Populations of a sequential kinetic scheme (A,C,E,G) and estimated SADS (B,D,F,H) of reference compound **gref** in toluene, $CH_2Cl_2$ and benzonitrile. Key: grey, **gref*FC**: excited **gref** chromophore in the Franck-Condon state; green, red, purple: successively relaxed **gref*** states. Lifetimes are collated in Table S 1.

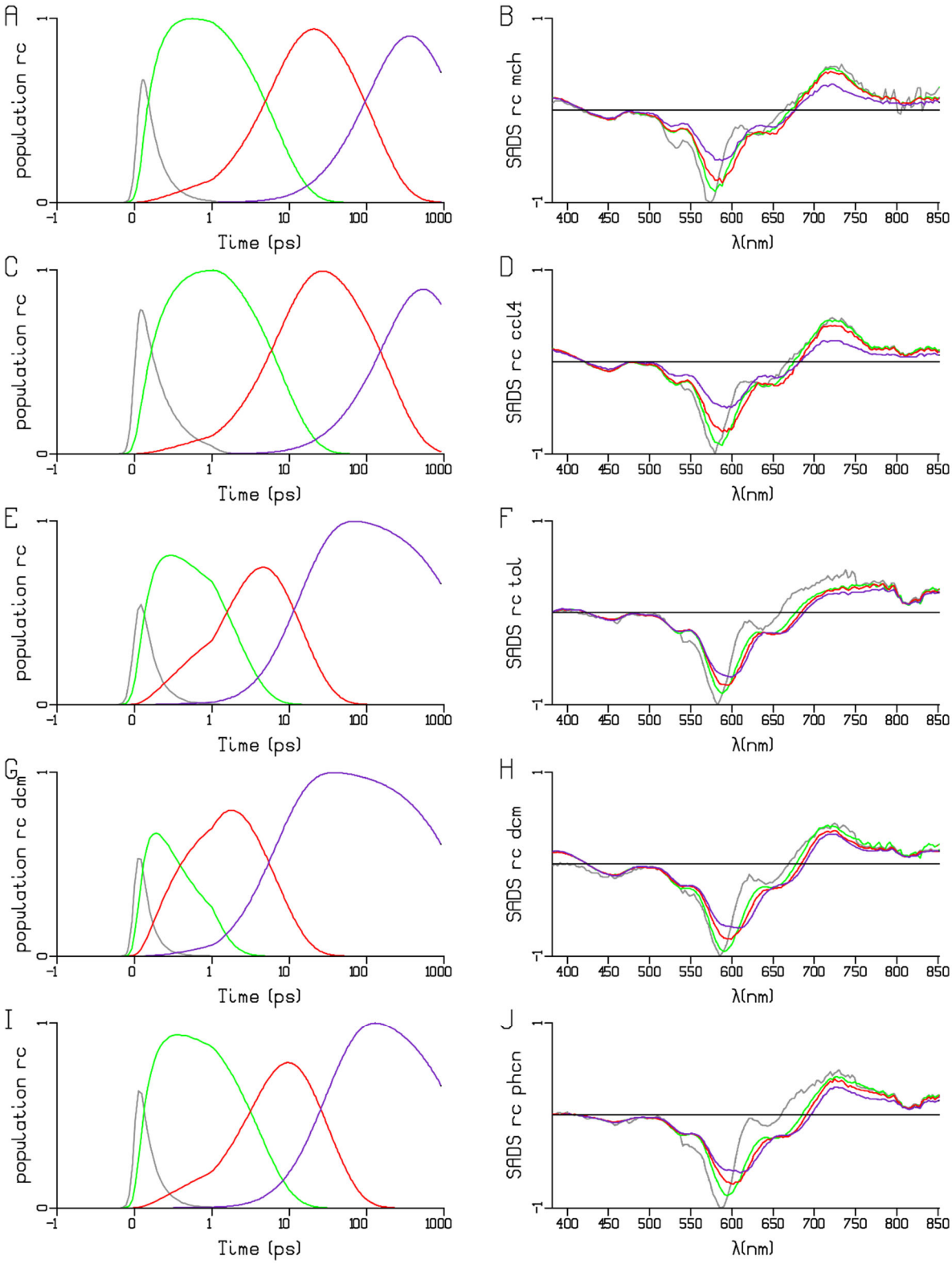


Figure S 8. Populations of a sequential kinetic scheme (A,C,E,G) and estimated SADS (B,D,F,H) of **rc** and **crc** in methylcyclohexane, CCl4, toluene, $CH_2Cl_2$ and benzonitrile. Key: grey, green, red, purple: successively relaxed $\mathbf{r_1}$*, $\mathbf{r_2}$*, $\mathbf{r_3}$*, $\mathbf{r_4}$*. Lifetimes are collated in Table S 2.

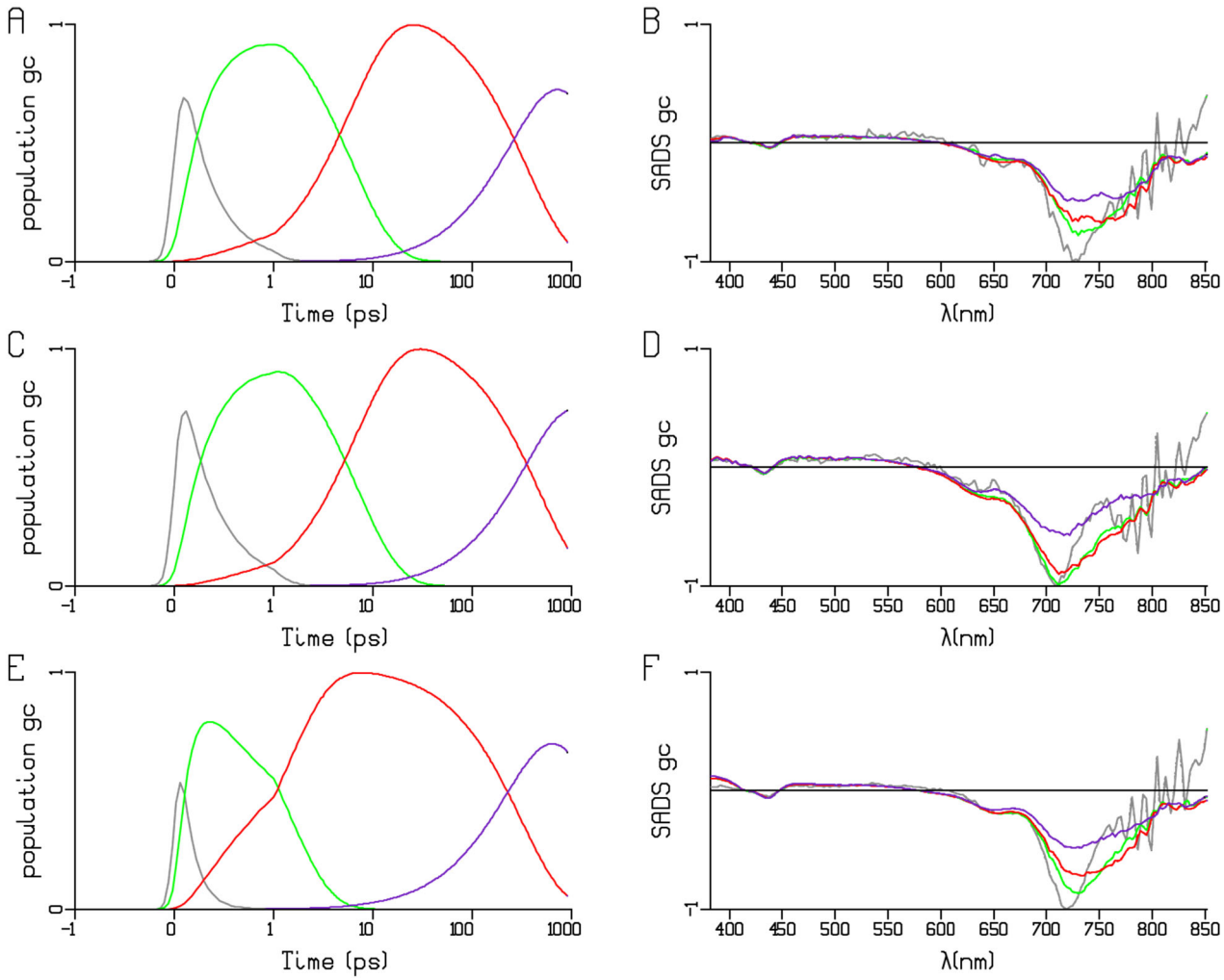


Figure S 9. Populations of a sequential kinetic scheme (A,C,E,G) and estimated SADS (B,D,F,H) of **gc** and **cgc** in toluene, $CH_2Cl_2$ and benzonitrile. Key: grey, **g*FC**: excited **g** chromophore in the Franck-Condon state; green, red, purple: successively relaxed **g*** states. Lifetimes are collated in Table S 2.

| compound | solvent | τ1 | τ2 | τ3 | τ4 |
|---|---|---|---|---|---|
| rc | methylcyclohexane | 0.19 | 6.6 | 124 | 1721 |
| | CCl4 | 0.30 | 7.9 | 198 | 2183 |
| | toluene | 0.17 | 1.9 | 13 | 1964 |
| | CH2Cl2 | 0.13 | 0.6 | 7 | 1749 |
| | benzonitrile | 0.17 | 4.1 | 30 | 1805 |
| gc | toluene | 0.36 | 6.9 | 473 | 2829 |
| | CH2Cl2 | 0.13 | 1.4 | 308 | 1669 |
| | benzonitrile | 0.31 | 6.1 | 349 | 1813 |

Table S 2. Lifetimes (in ps) of the **rc** and **gc** complexes in the different solvents.

## Spectral evolution in oc, coc and ocg

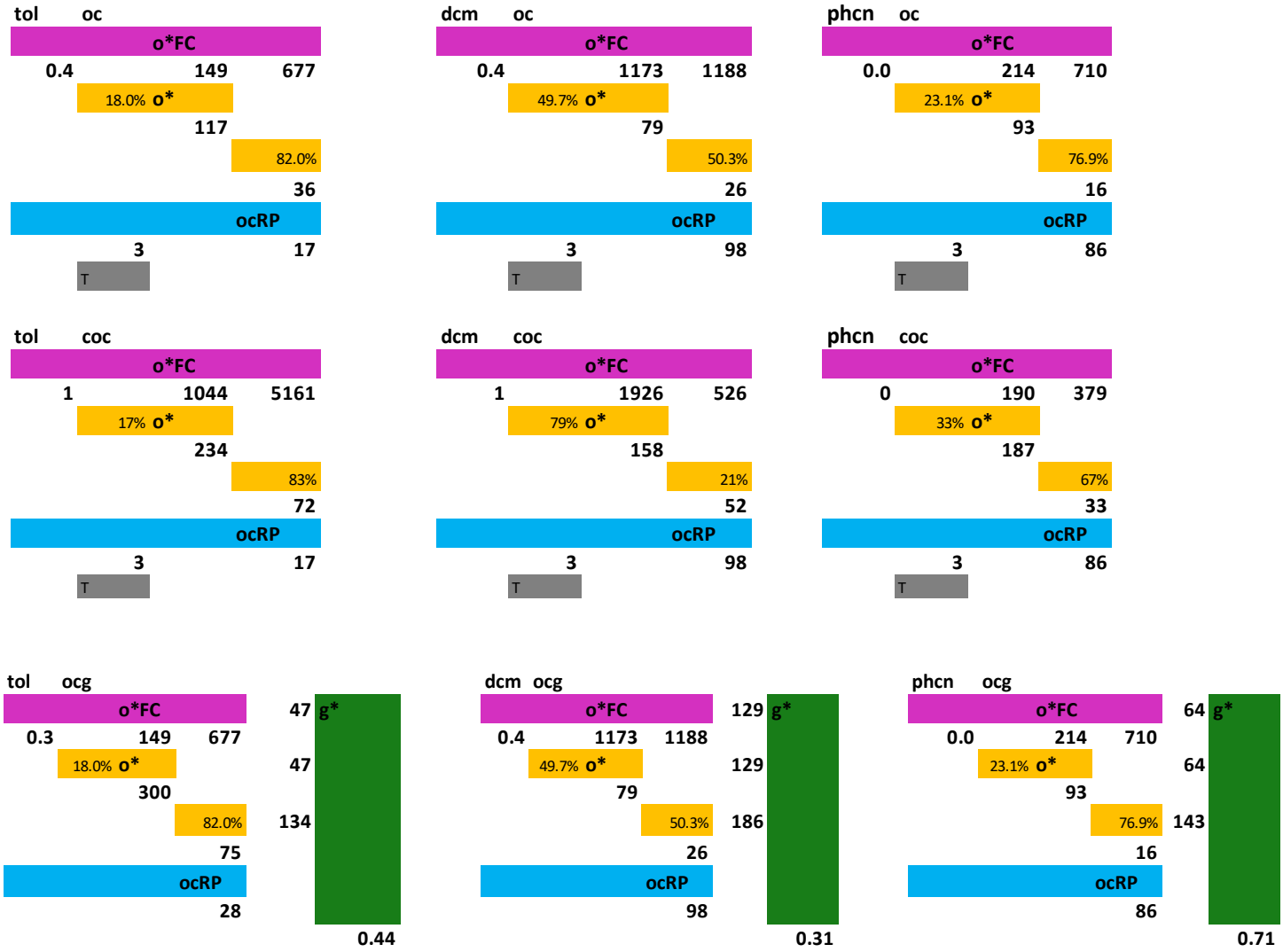


Figure S 10. Kinetic schemes used for the simultaneous target analysis of **oc**, **coc** and **ocg** in toluene, $CH_2Cl_2$ and benzonitrile. All rate constants in $ns^{-1}$. Key: magenta, **o*FC**: excited **o** chromophore in the Franck-Condon state; orange, two different conformations of **o*** with identical SADS; blue, **ocRP**: $\mathbf{c^{+\cdot}o^{-\cdot}}$ radical ion pair; dark green: **g***; dark grey, T: triplet. Note that the RP formation and decay rates of **ocg** in toluene differ from those with **oc**. Further explanation in the caption of Figure 5.

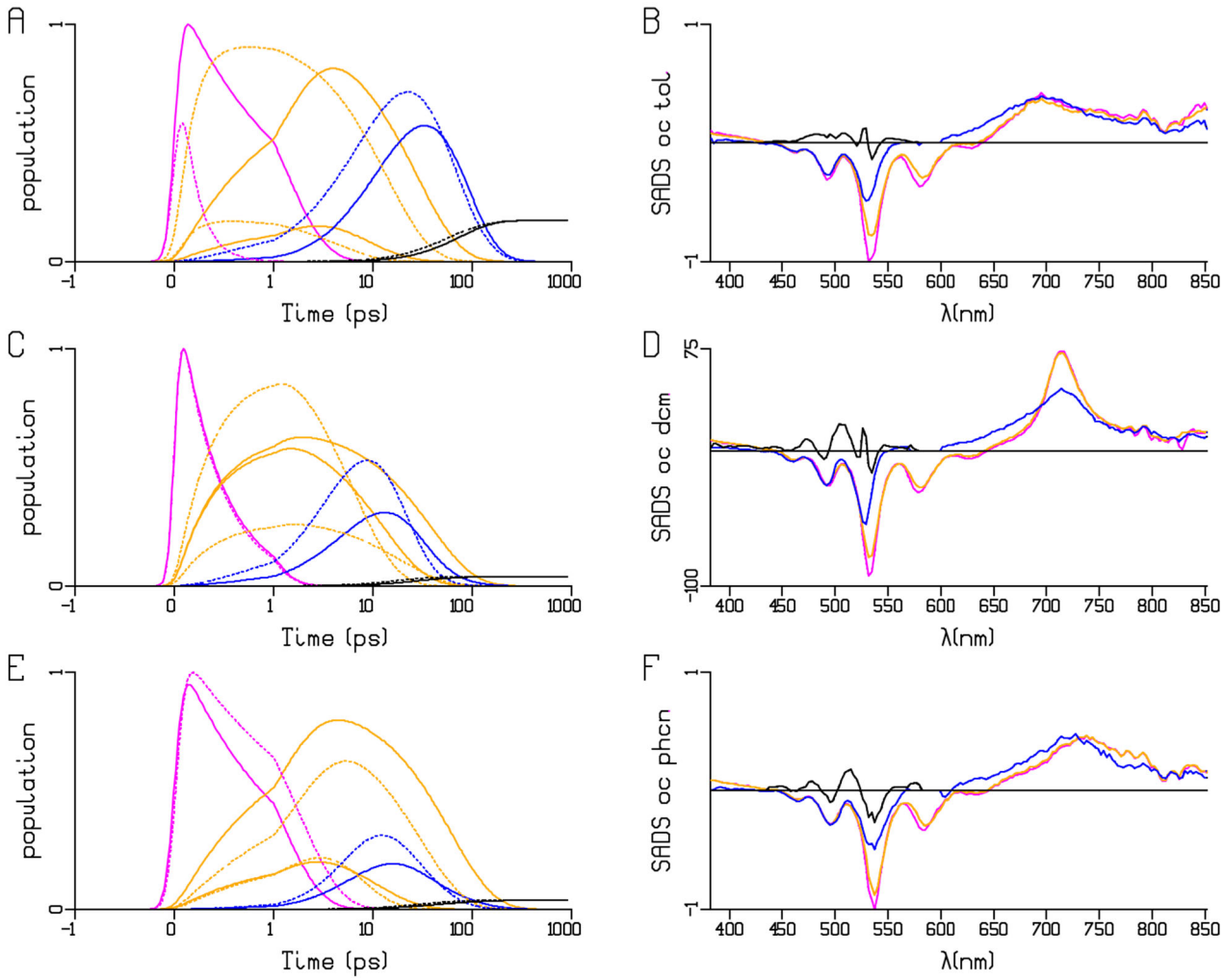


Figure S 11. Populations of the target kinetic schemes from Figure S 10 (A,C,E) and estimated SADS (B,D,F) of **oc** and **coc** in toluene, $CH_2Cl_2$ and benzonitrile, respectively. The **oc** and **coc** populations are depicted as solid and dotted lines, respectively. Key: magenta, **o*FC**: excited **o** chromophore in the Franck-Condon state; orange, **o*** relaxed; blue, **ocRP**: $\mathbf{c}^{+\cdot}\mathbf{o}^{-\cdot}$ radical ion pair; dark grey, T: triplet.

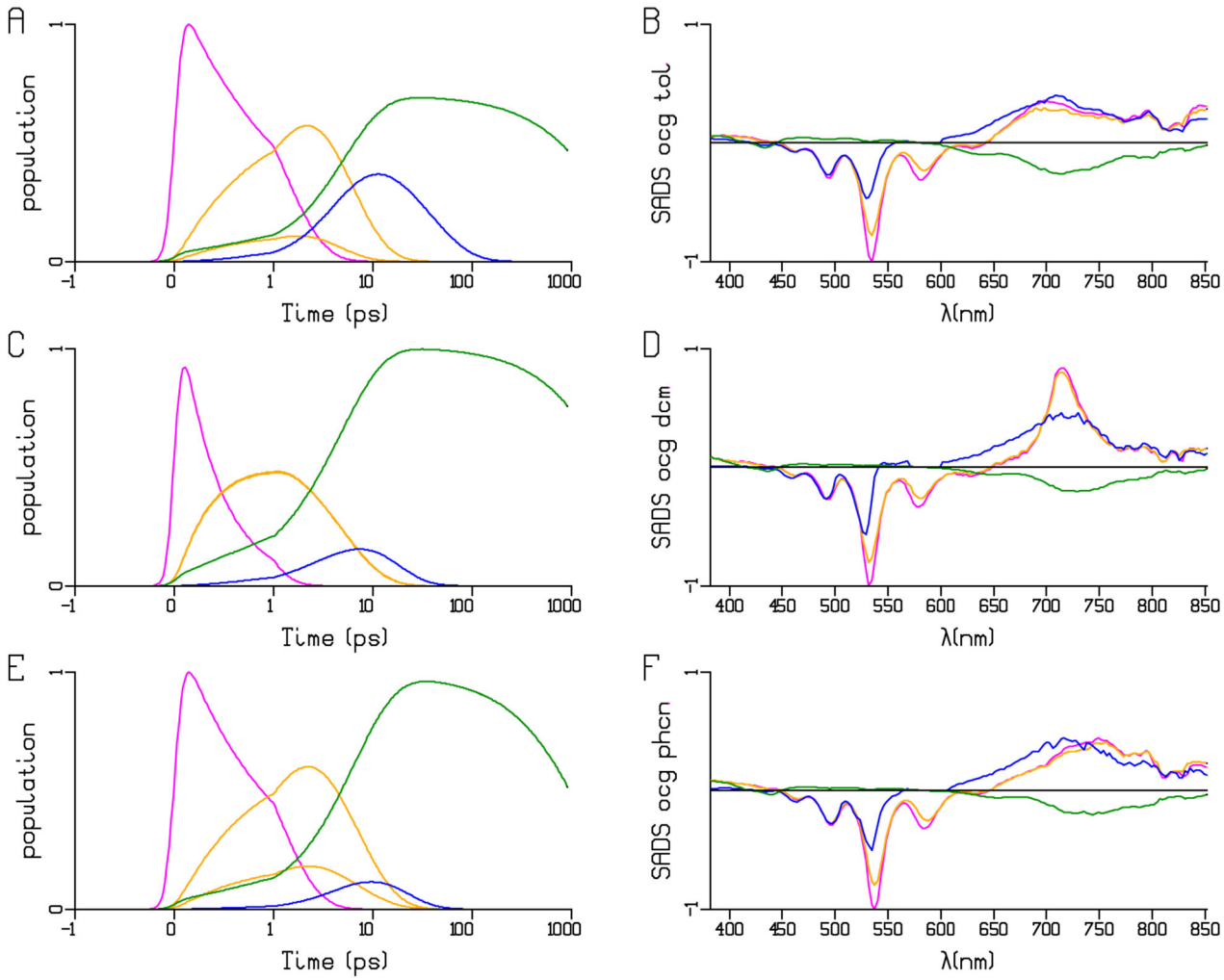


Figure S 12. Populations of the target kinetic schemes from Figure S 10 (A,C,E) and estimated SADS (B,D,F) of **ocg** in toluene, $CH_2Cl_2$ and benzonitrile, respectively. Key: magenta, **o*FC**: excited **o** chromophore in the Franck-Condon state; orange, **o*** relaxed; blue, **ocRP**: $\mathbf{c^{+\cdot}o^{-\cdot}}$ radical ion pair; dark green: **g***.

## Spectral evolution in oco, rcr and gcg

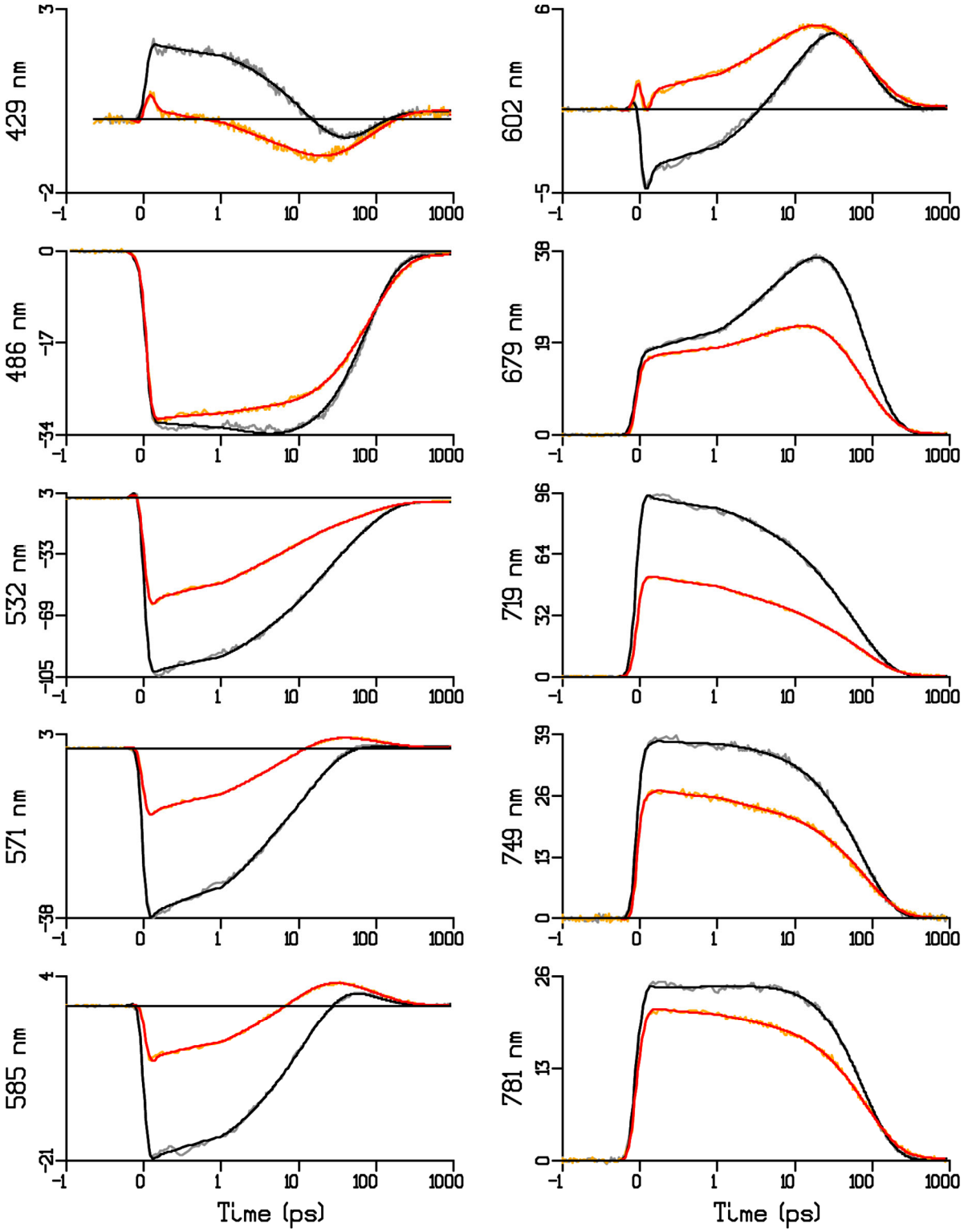


Figure S 13. Selected time traces in $CCl_4$ after excitation at 530 nm data (in mOD, grey, orange) and fit (black, red) of **oc** and **oco**, respectively. Wavelength is indicated in the ordinate label. Note that the time axis is linear until 1 ps (after the maximum of the IRF), and logarithmic thereafter.

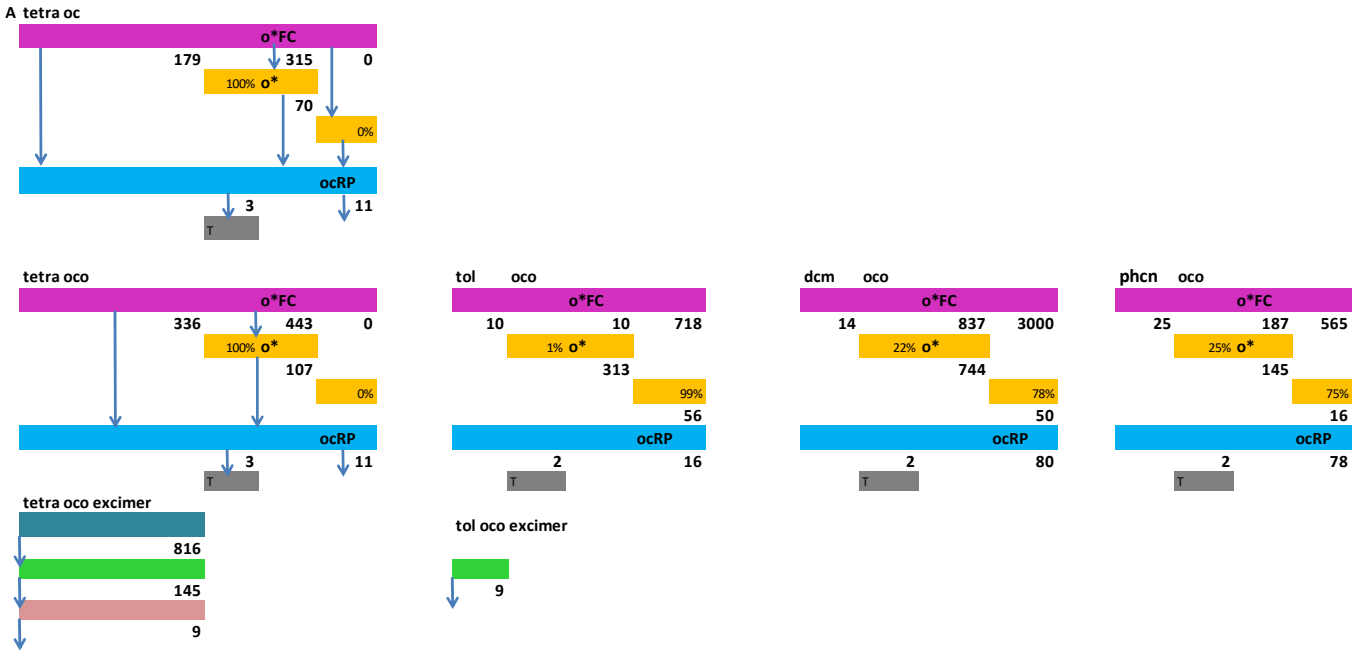


Figure S 14. Kinetic schemes used for the simultaneous target analysis of **oco** in $CCl_4$, toluene, $CH_2Cl_2$ and benzonitrile. All rate constants in $ns^{-1}$. Key nonstacked conformation: magenta, **o*FC**: excited **o** chromophore in the Franck-Condon state; orange, two different conformations of **o*** with identical SADS; blue, **ocRP**: $\mathbf{c^{+}\cdot o^{-}\cdot}$ radical ion pair; black, grey: triplet. Key π-stacked sandwich arrangement: turquoise, green, brown sequential evolution of the excimer state in $CCl_4$.

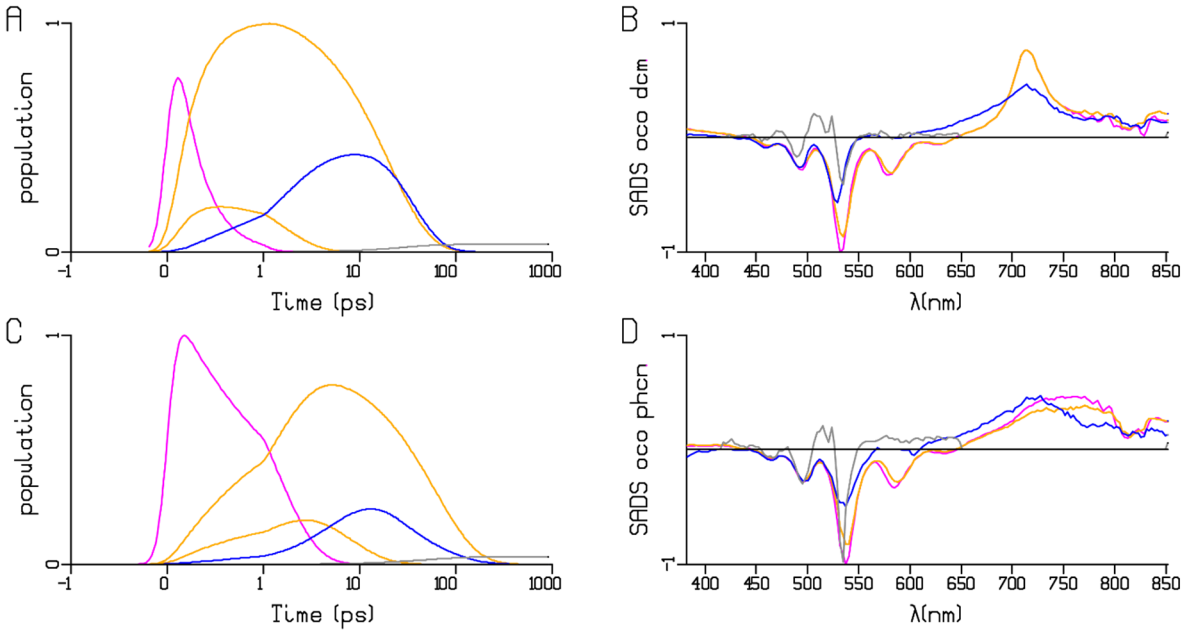


Figure S 15. Populations of the target kinetic schemes from (A,C) and estimated SADS (B,D) of **oco** in $CH_2Cl_2$ and benzonitrile, respectively. Key nonstacked conformation: magenta, **o*FC**: excited **o** chromophore in the Franck-Condon state; orange, **o*** relaxed; blue, **ocRP**: $\mathbf{c^{+}\cdot o^{-}\cdot}$ radical ion pair; grey: triplet.

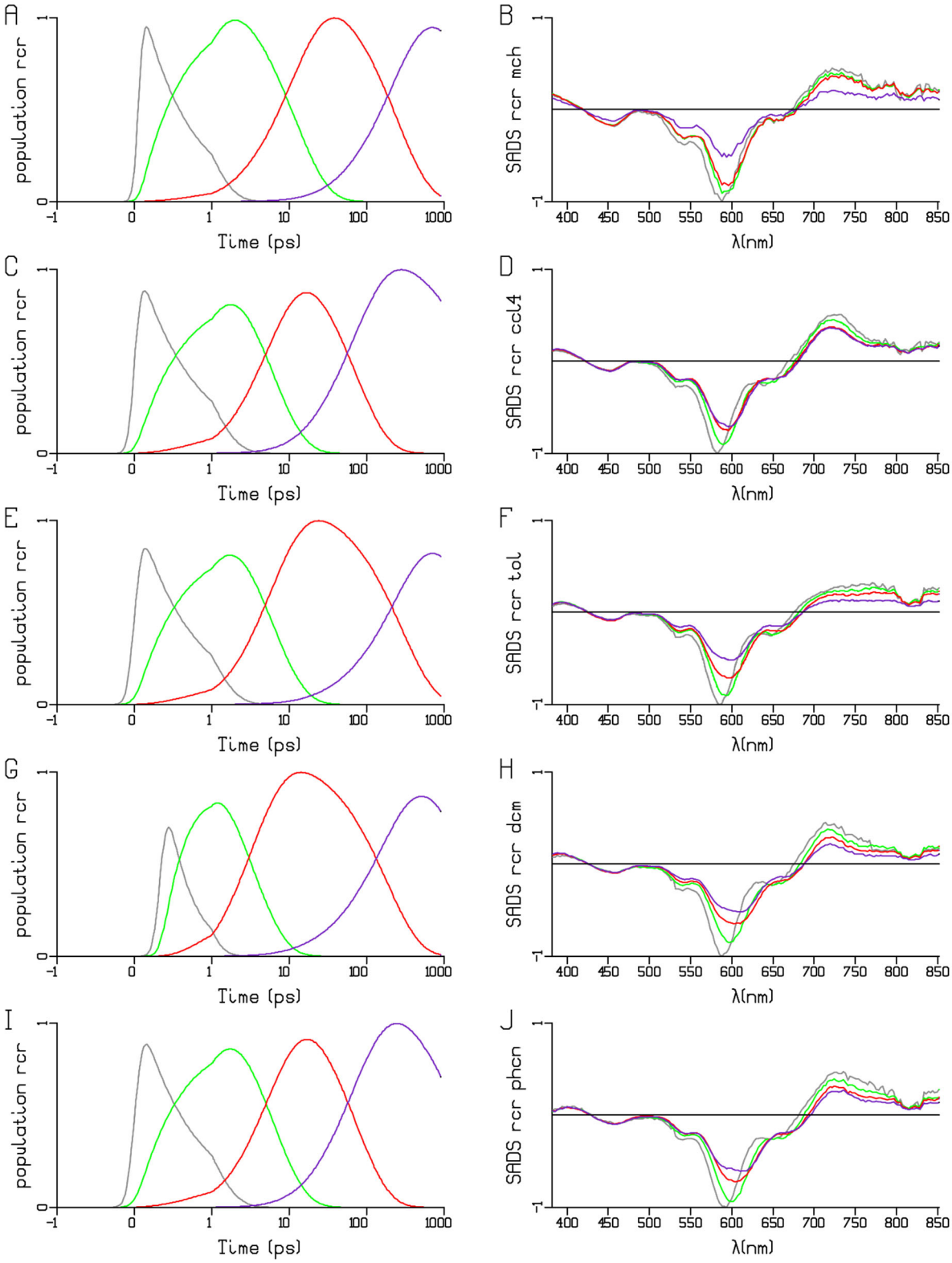


Figure S 16. Populations of a sequential kinetic scheme (A,C,E,G) and estimated SADS (B,D,F,H) of **rcr** in methylcyclohexane, CCl4, toluene, $CH_2Cl_2$ and benzonitrile. Key: grey, **r*FC**: excited **r** chromophore in the Franck-Condon state; green, red, purple: successively relaxed **r*** states. Lifetimes are collated in Table S 3.

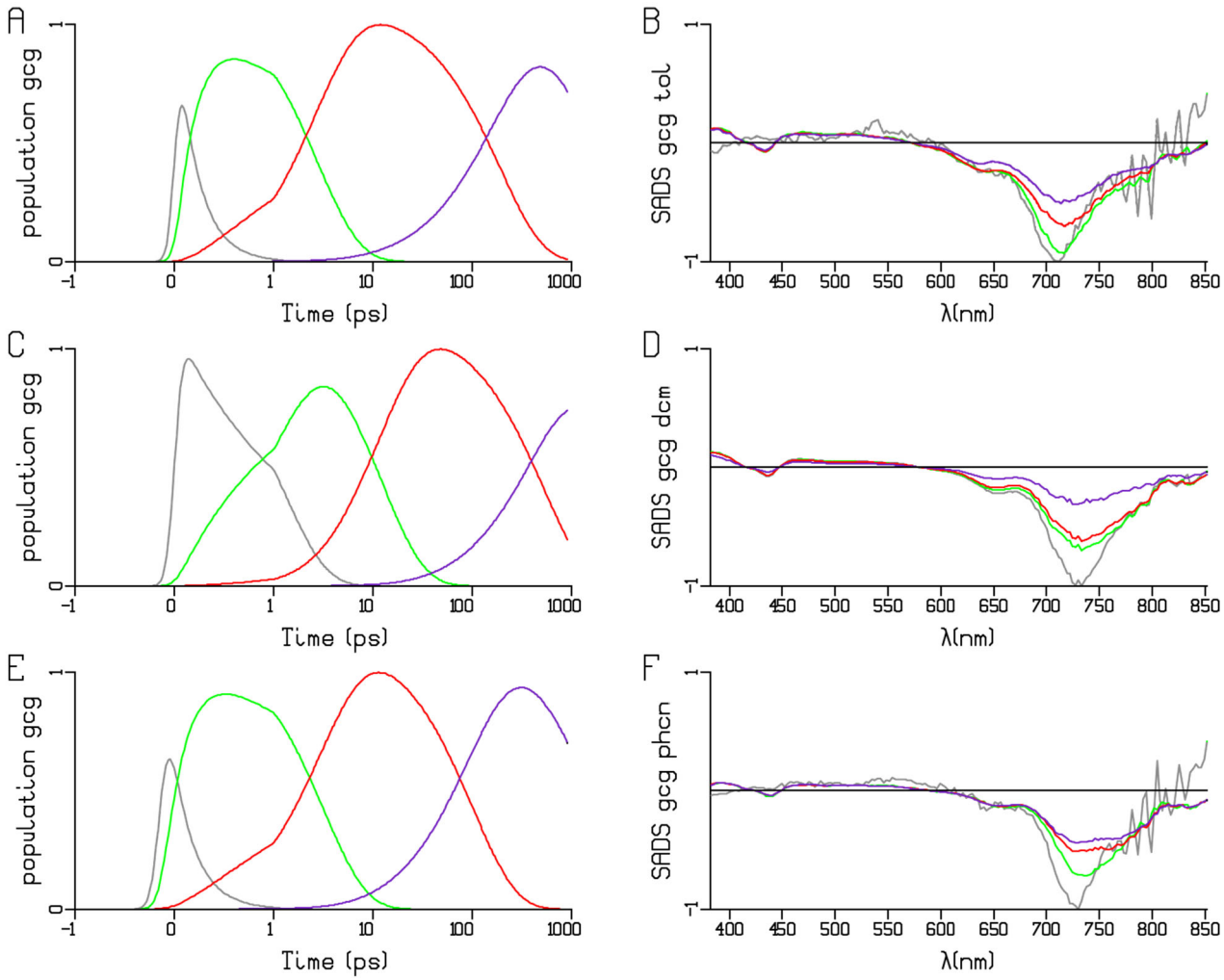


Figure S 17. Populations of a sequential kinetic scheme (A,C,E,G) and estimated SADS (B,D,F,H) of **gcg** in toluene, $CH_2Cl_2$ and benzonitrile. Key: grey, **g*FC**: excited **g** chromophore in the Franck-Condon state; green, red, purple: successively relaxed **g*** states. Lifetimes are collated in Table S 3.

| compound | solvent | τ1 | τ2 | τ3 | τ4 |
|---|---|---|---|---|---|
| rcr | methylcyclohexane | 0.62 | 11.7 | 245 | 3333 |
| | CCl4 | 0.73 | 5.8 | 71 | 3025 |
| | toluene | 0.71 | 5.9 | 285 | 2533 |
| | CH2Cl2 | 0.33 | 3.3 | 182 | 2373 |
| | benzonitrile | 0.70 | 6.0 | 71 | 1731 |
| gcg | toluene | 0.21 | 2.7 | 189 | 1857 |
| | CH2Cl2 | 1.24 | 12.0 | 520 | 2912 |
| | benzonitrile | 0.22 | 3.1 | 102 | 1731 |

Table S 3. Lifetimes (in ps) of the **rcr** and **gcg** complexes in the different solvents

## Spectral evolution in rc, rcg, rcgcr and gcrcg

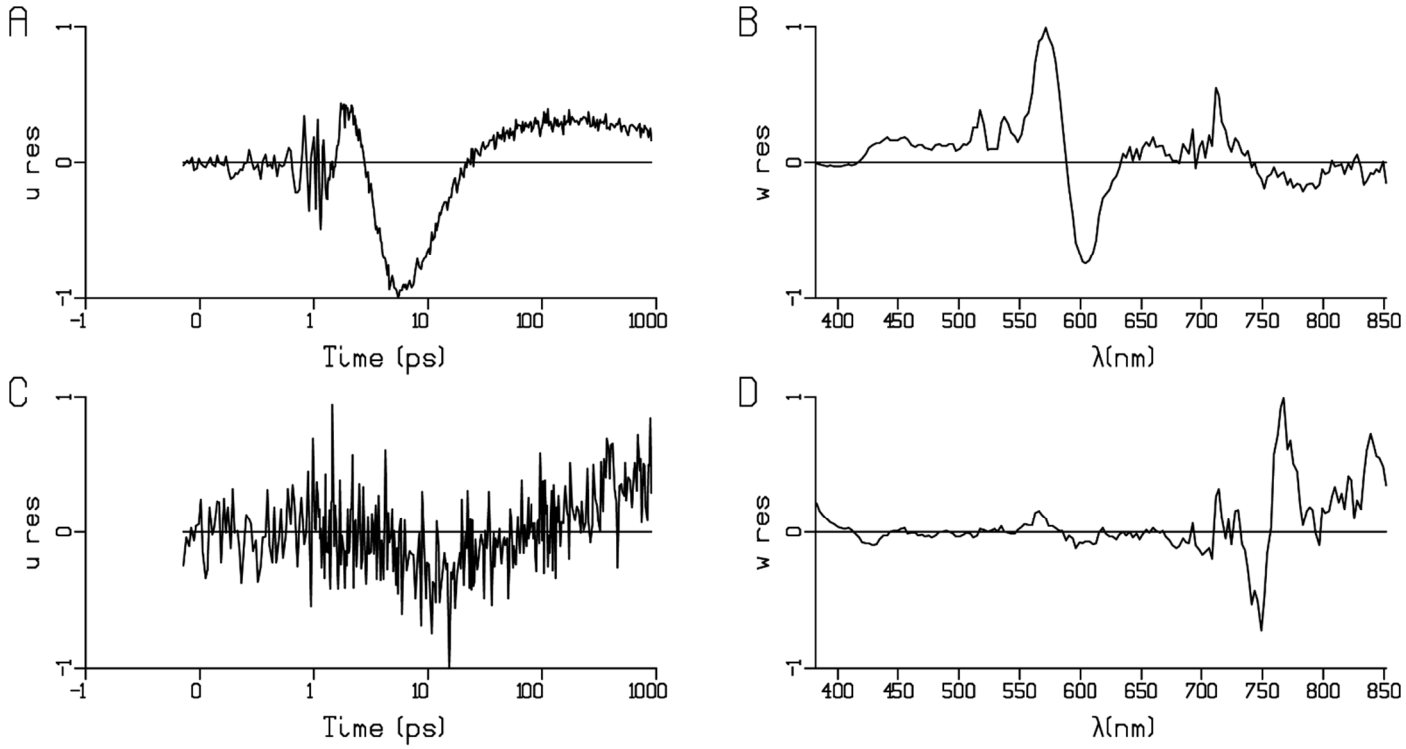


Figure S 18. First left and right singular vectors resulting from the singular value decomposition (SVD) of the residual matrix of **rcg** in $CH_2Cl_2$ resulting from a target analysis using a kinetic scheme without (A,B) or with (C,D) the **rcg** radical pair state. Note that panels (A,B) show large trends, whereas panels (C,D) show only small trends.

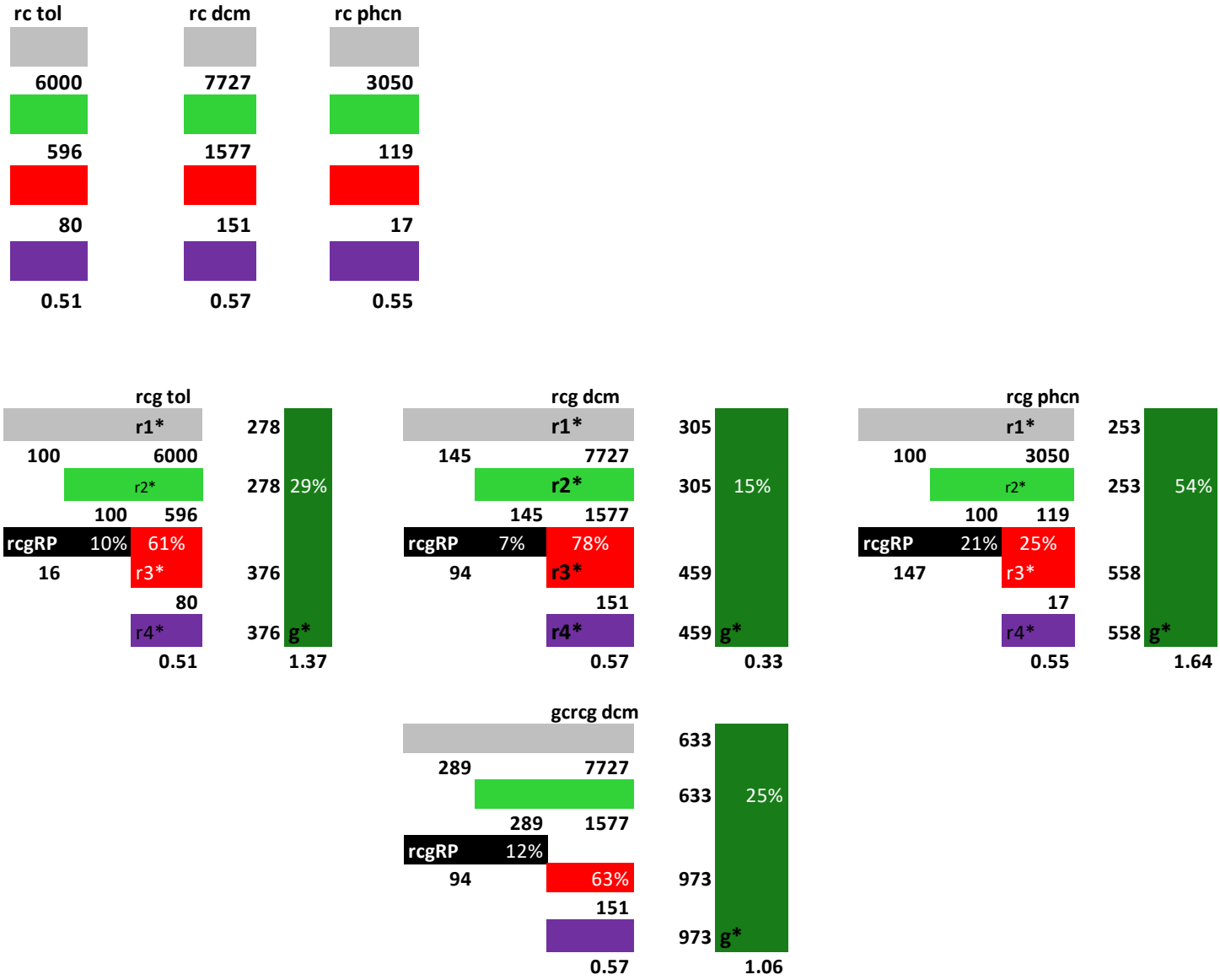


Figure S 19. Kinetic schemes used for the simultaneous target analysis of **rc**, **crc** and **rcg** in toluene, $CH_2Cl_2$ and benzonitrile, and for **gcrcg** in $CH_2Cl_2$. The kinetic scheme for **rcgcr** is identical to that of **rcg**, since there is only one **g** acceptor. All rate constants in $ns^{-1}$. Key: grey, green, red, purple: successively relaxed $\mathbf{r_1}$*, $\mathbf{r_2}$*, $\mathbf{r_3}$*, $\mathbf{r_4}$*; dark green: **g***; black, **rcgRP**: **rcg** radical pair. **rcgRP** is an important loss population formed from **rcg** (only from the $\mathbf{r_1}$* and $\mathbf{r_2}$* state). For further explanation cf. the arrows in Figure 9.

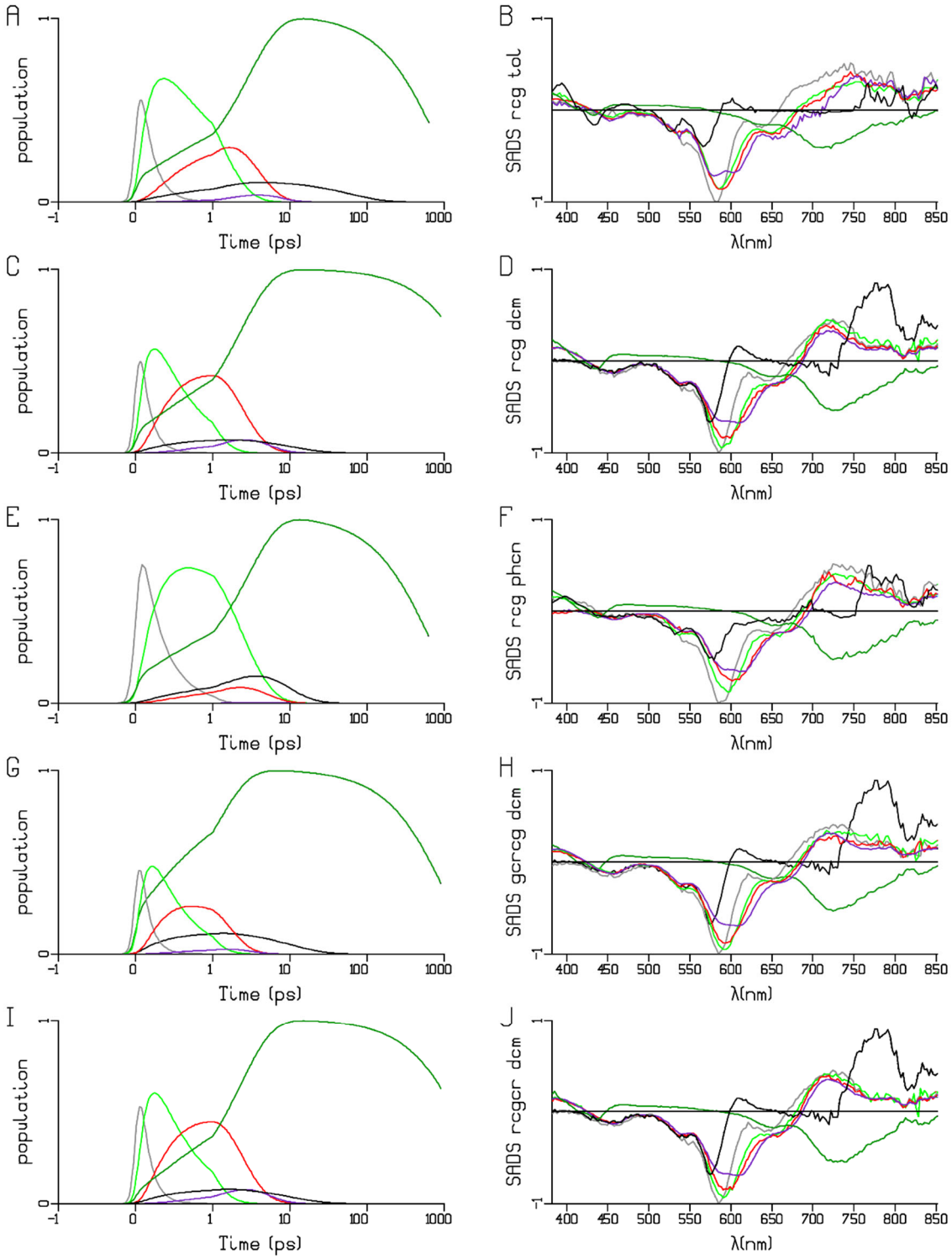


Figure S 20. Populations of the target kinetic schemes from Figure S 19 (A,C,E,G,I) and estimated SADS (B,D,F,H,J) of **rcg** in toluene, $CH_2Cl_2$ and benzonitrile, respectively, and **gcrcg** and **rcgcr** in $CH_2Cl_2$. Key: grey, green, red, purple: successively relaxed $\mathbf{r_1}$*, $\mathbf{r_2}$*, $\mathbf{r_3}$*, $\mathbf{r_4}$*; dark green: **g***; black, **rcgRP**: **rcg** radical pair. Note that the black SADS of rcg in toluene in (B) contains an additional bleach of **g** near 430 nm.

## Spectral evolution in ocr, rcocr and ocrco

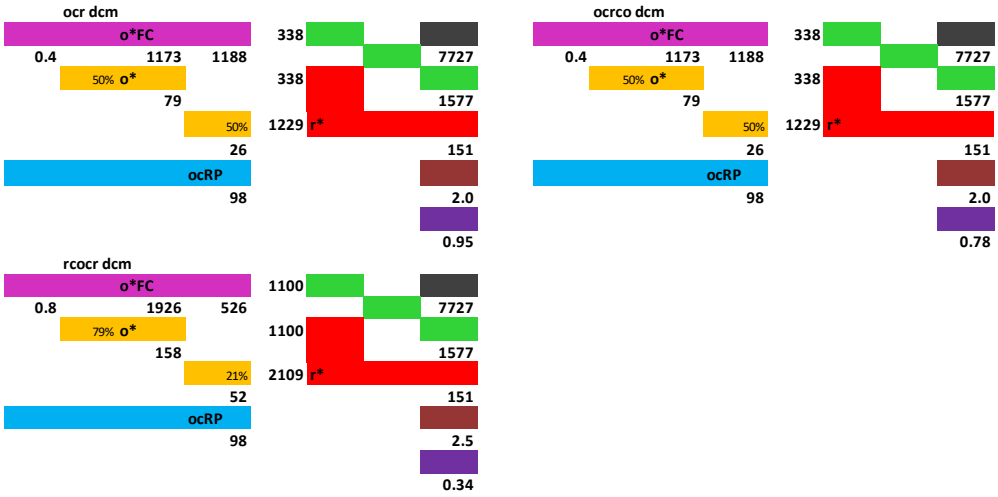


Figure S 21. Kinetic schemes used for the simultaneous target analysis of **ocr**, **rcocr** and **ocrco** in $CH_2Cl_2$. All rate constants in $ns^{-1}$. Key: magenta, **o*FC**: excited **o** chromophore in the Franck-Condon state; orange, two different conformations of **o*** with identical SADS; blue, **ocRP**: $\mathbf{c^{+\cdot}o^{-\cdot}}$ radical ion pair; grey, green, red, brown, purple: successively relaxed $\mathbf{r_1}$*, $\mathbf{r_2}$*, $\mathbf{r_3}$*, $\mathbf{r_4}$*, $\mathbf{r_5}$*.

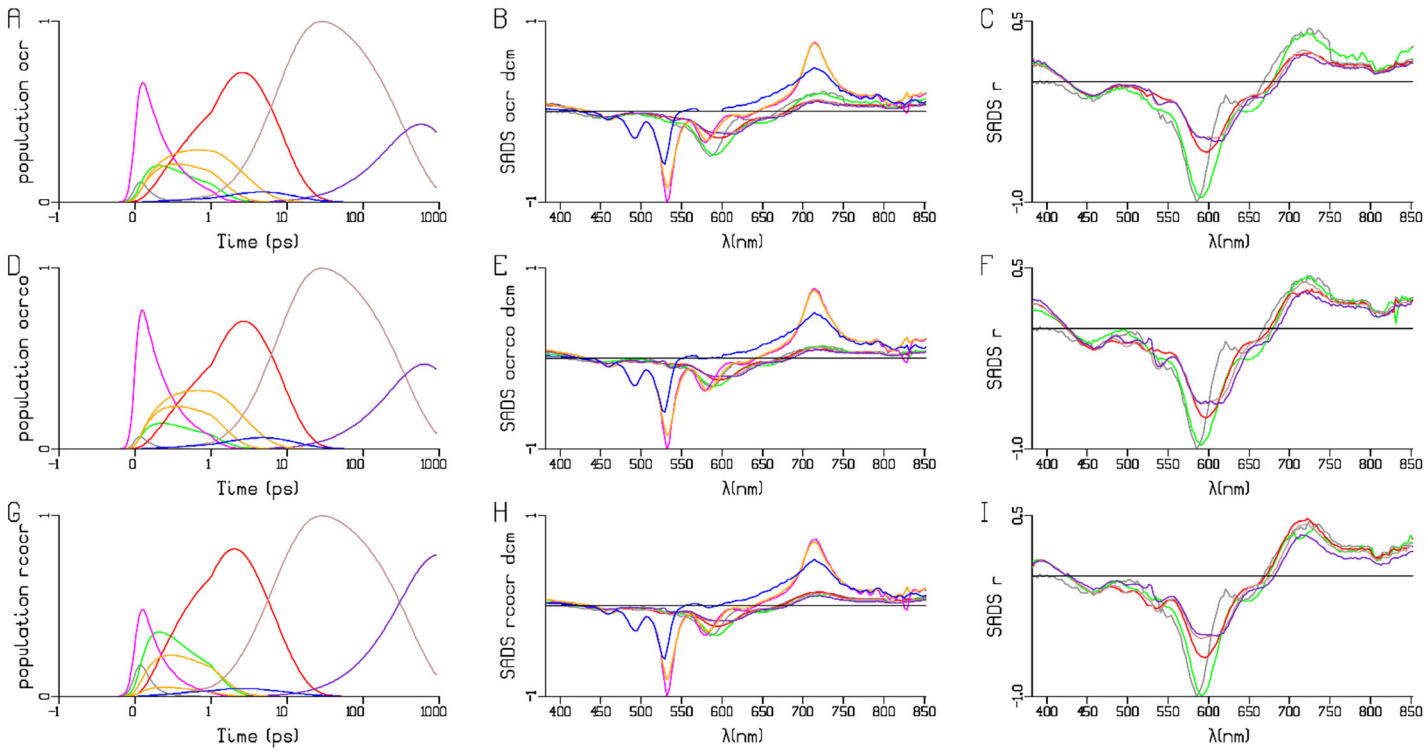


Figure S 22. Populations of the target kinetic schemes from Figure S 21 (A,D,G), estimated SADS (B,E,H) and SADS of the five **r*** states (C,F,I) of **ocr**, **rcocr** and **ocrco** in $CH_2Cl_2$. Key: magenta, **o*FC**: excited **o** chromophore in the Franck-Condon state; orange, two different conformations of **o*** with identical SADS; blue, **ocRP**: $\mathbf{c^{+\cdot}o^{-\cdot}}$ radical ion pair; grey, green, red, brown, purple: successively relaxed $\mathbf{r_1}$*, $\mathbf{r_2}$*, $\mathbf{r_3}$*, $\mathbf{r_4}$*, $\mathbf{r_5}$*.

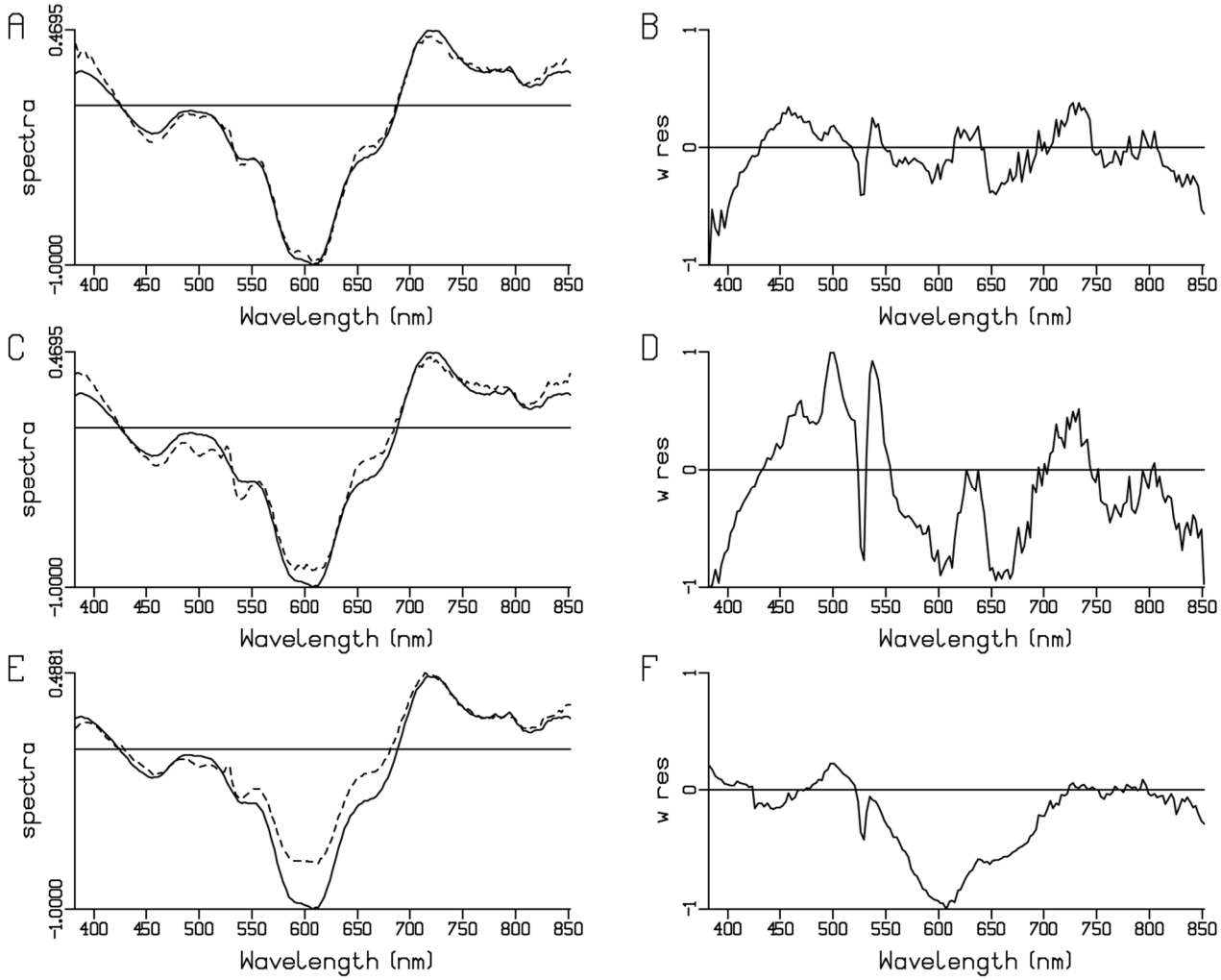


Figure S 23. Overlay of the final **r*** SADS from **rc** (solid lines in panels A,C,E) and from **ocr**, **ocrco** and **rcocr** in CH2Cl2 (dashed lines in panels A,C,E, respectively). The difference between the final **r*** SADS from **rc** and from **ocr**, **ocrco** and **rcocr** is depicted in panels B,D,F, respectively. Note the **o** bleach features near 490 and 530 nm.

## Spectral evolution in ocrcg and gcrcocrcg

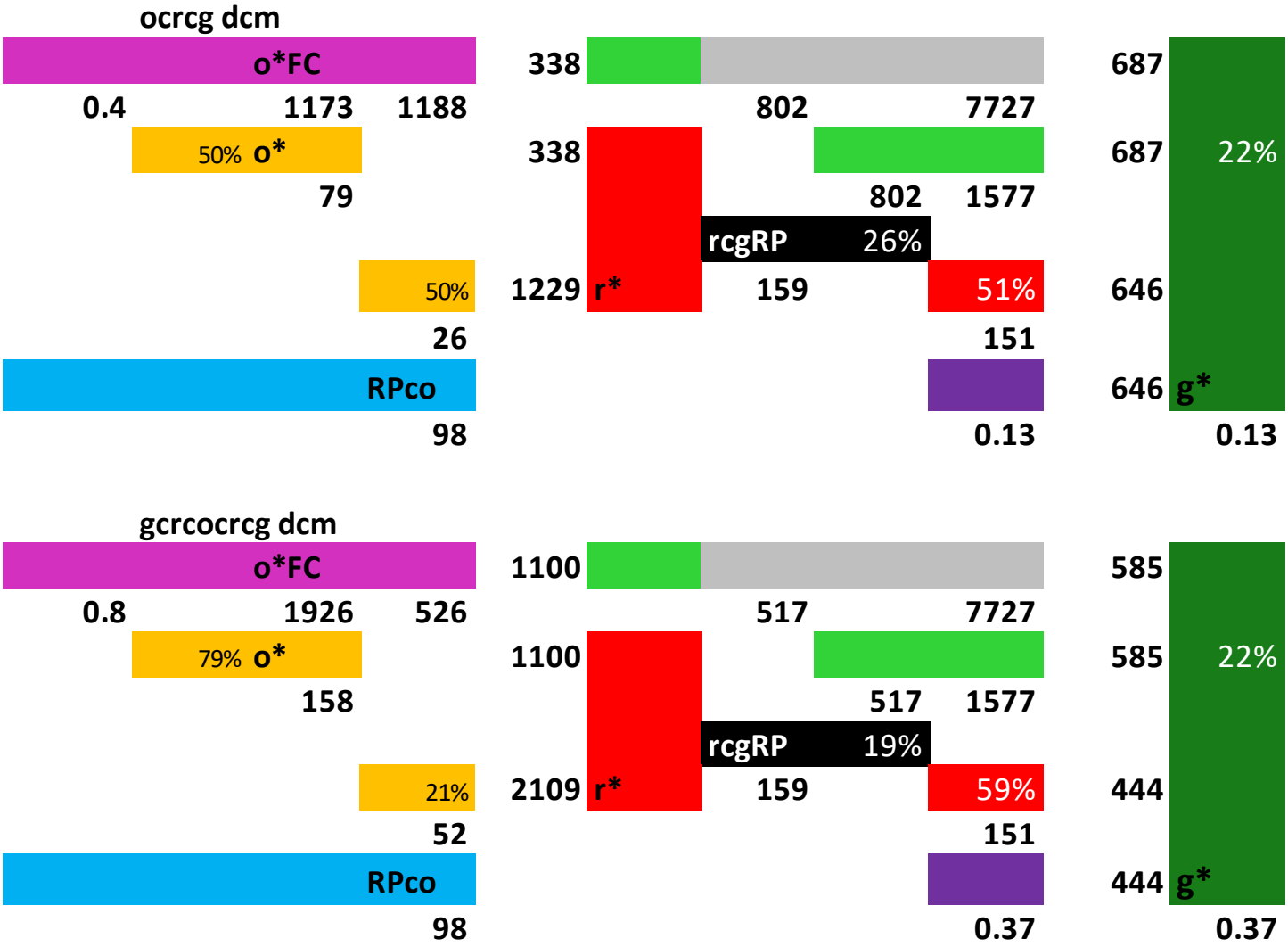


Figure S 24. Kinetic schemes used for the simultaneous target analysis of **ocrcg** and **gcrcocrcg** in $CH_2Cl_2$. All rate constants in $ns^{-1}$. Key: magenta, **o*FC**: excited **o** chromophore in the Franck-Condon state; orange, two different conformations of **o*** with identical SADS; blue, **ocRP**: $\mathbf{c^{+\cdot}o^{-\cdot}}$ radical ion pair; grey, green, red, purple: successively relaxed $\mathbf{r_1}$*, $\mathbf{r_2}$*, $\mathbf{r_3}$*, $\mathbf{r_4}$*; dark green: **g***; black, **rcgRP**: **rcg** radical pair.

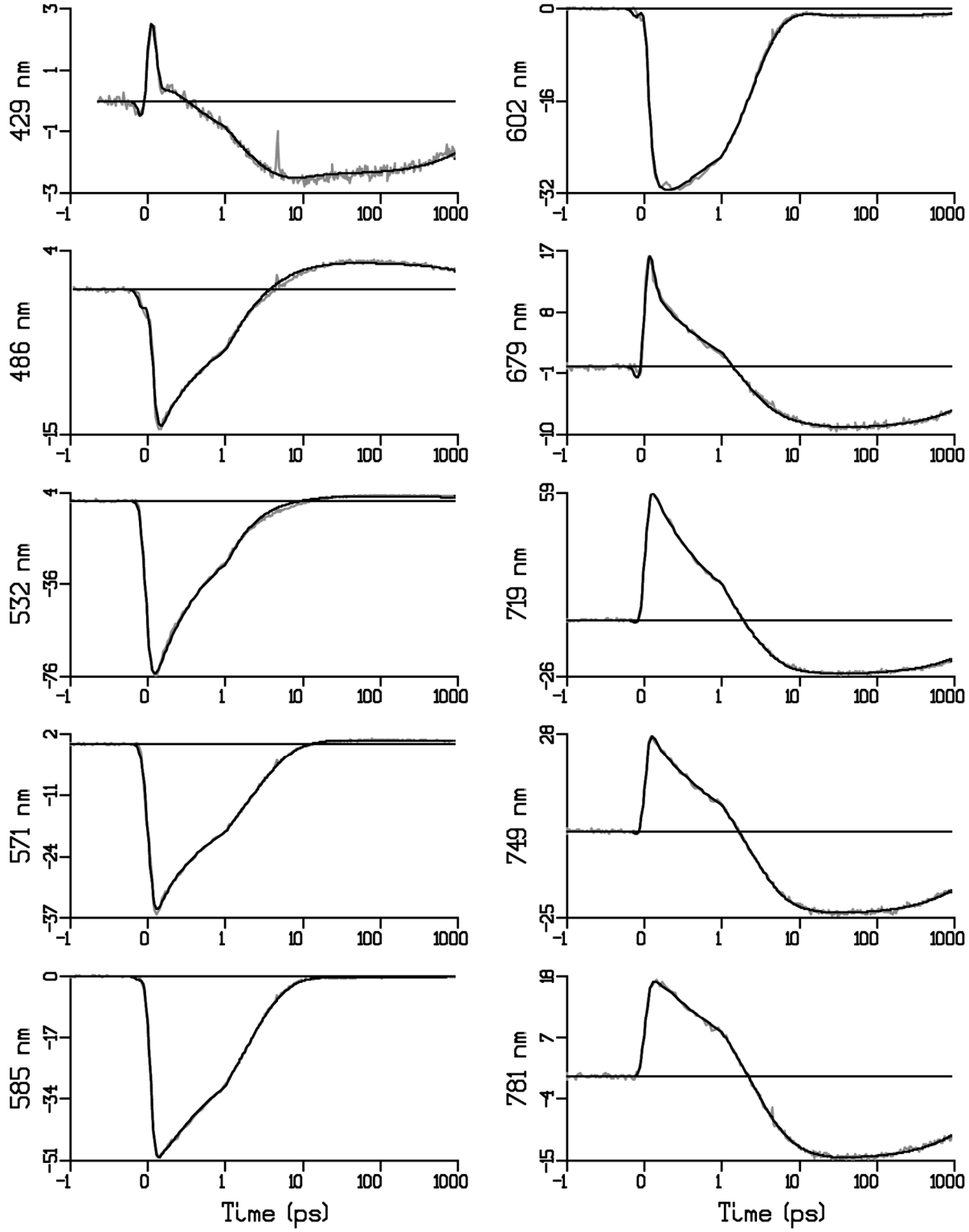


Figure S 25. Selected time traces of **gcrcocrcg** in $CH_2Cl_2$ after excitation at 530 nm data (in mOD, grey) and fit (black). Wavelength is indicated in the ordinate label. Note that the time axis is linear until 1 ps (after the maximum of the IRF), and logarithmic thereafter.

## References

[37] C. Hippius, Multichromophoric Arrays of Perylene Bisimide Dyes - Synthesis and Optical Properties; Multichromophore Perylenbisimidkaskaden - Synthese und optische Eigenschaften, in, Universität Würzburg, Fakultät für Chemie und Pharmazie, Würzburg, 2007, pp. 237.