Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A Chemometric Approach for Determining the Reaction Quantum Yields in Consecutive Photochemical Processes

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Figure S1: Evolution of Ω_A during the iterative minimization procedure with unknown spectra for the colored species in a A → B process using $\phi_{\text{initial}} = 0.1$ mol einstein^{-1} (left). Spectral changes along the iteration steps for the reactant (middle) and product (right). Initial guess colored in red, spectrum after last iteration in blue. λ_{irr} = 450 nm, see Figure 2 for the spectral density of the irradiation source.

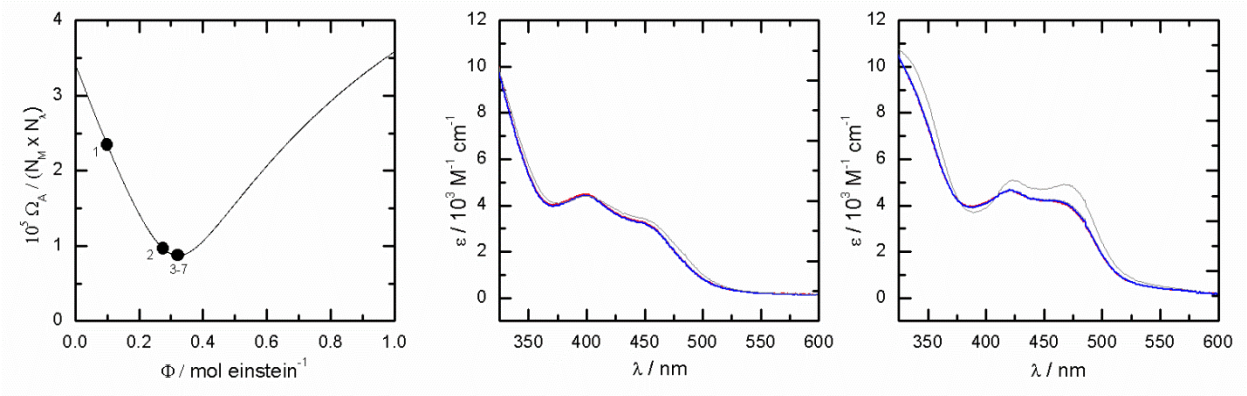

Figure S2: Evolution of Ω_A during the iterative minimization procedure with unknown spectra for the colored species in a A → B process using $\phi_{\text{initial}} = 0.8$ mol einstein^{-1} (left). Spectral changes along the iteration steps for the reactant (middle) and product (right). Initial guess colored in red, spectrum after last iteration in blue. λ_{irr} = 450 nm, see Figure 2 for the spectral density of the irradiation source.

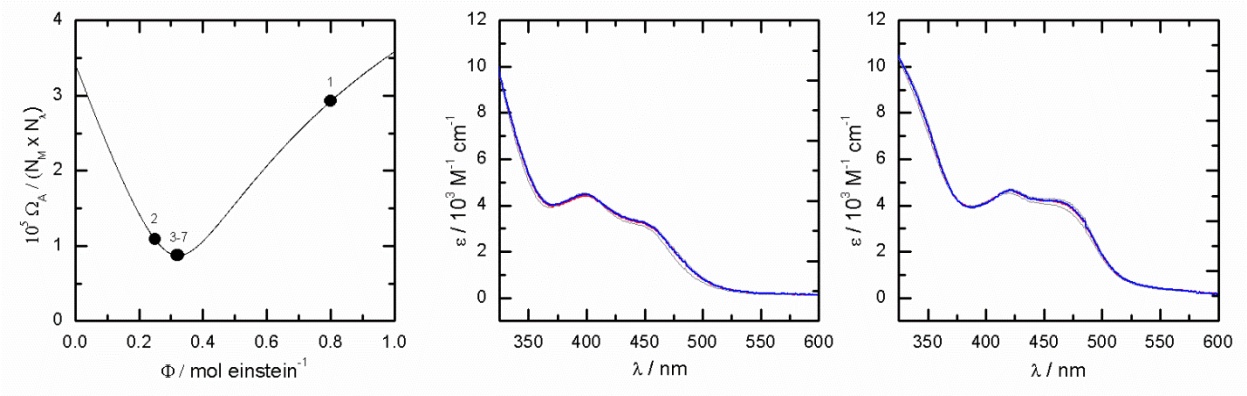

Figure S3: Evolution of Ω_A during the iterative minimization procedure with unknown spectra for the colored species in a A → B → C process. Initial values for $\phi_1 = 0.2$ mol einstein^{-1} and ϕ_2 = 0.02 mol einstein^{-1} (upper left). The contour plot corresponds to $\Delta\Omega_A/(N_M \times N_\lambda)$ = 1×10^{-5}. Spectral changes along the iteration steps for the reactant (upper right), intermediate (lower left) and product species (lower right). Initial guess colored in red, spectrum after last iteration in blue. λ_{irr} = 450 nm, see Figure 5 for the spectral density of the irradiation source.

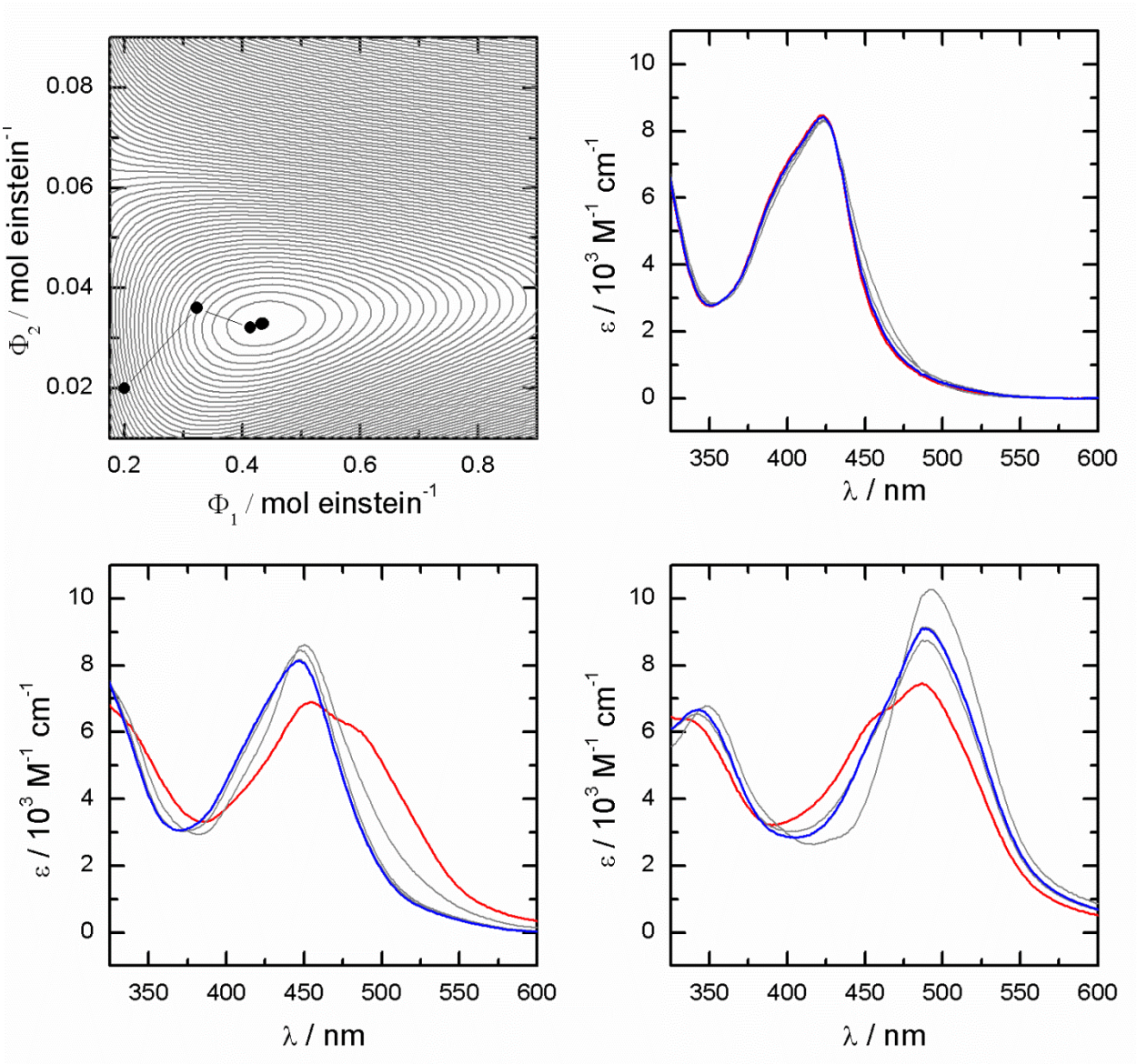

Figure S4: Evolution of Ω_A during the iterative minimization procedure with unknown spectra for the colored species in a A → B → C process. Initial values for $\phi_1 = 0.8$ mol einstein^{-1} and ϕ_2 = 0.08 mol einstein^{-1} (upper left). The contour plot corresponds to $\Delta\Omega_A/(N_M \times N_\lambda)$ = 1×10^{-5}. Spectral changes along the iteration steps for the reactant (upper right), intermediate (lower left) and product species (lower right). Initial guess colored in red, spectrum after last iteration in blue. λ_{irr} = 450 nm, see Figure 5 for the spectral density of the irradiation source.

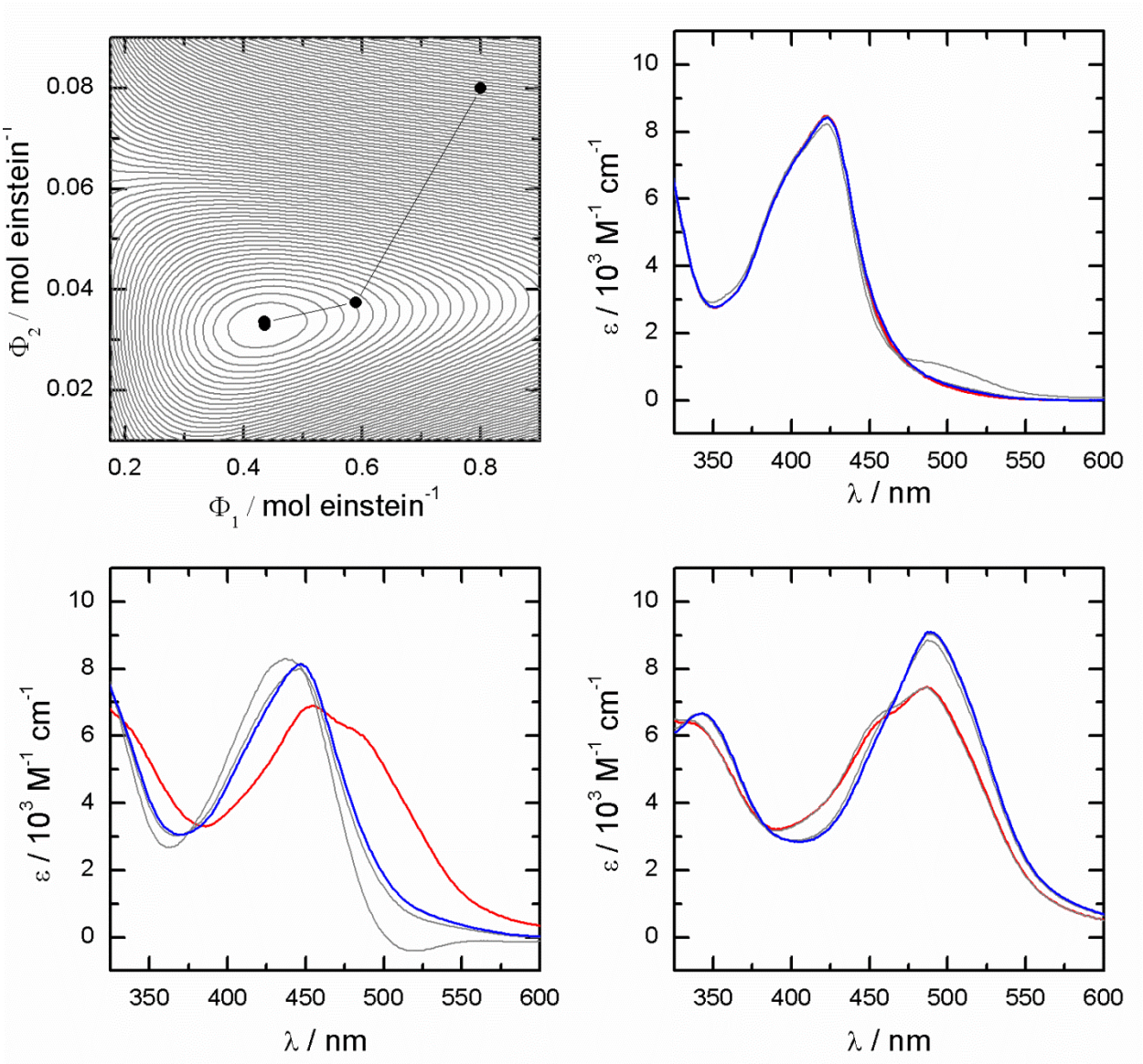

Table S1: List of symbols with units and dimensions involved in the procedure. Gray cells indicate dimensionless quantities.

Symbol	Description	Units	Type
N_M	Number of absorbance measurements for each λ		Scalar
N_λ	Number of wavelengths (channels) measured		Scalar
N_S	Number of species involved		Scalar
$\mathbf{A}_{exp}$	Measured absorbances		N_M x N_λ array
$\mathbf{E}_{exp}$	Independently measured spectra of pure species	M^{-1} cm^{-1}	N_S x N_λ array
$\mathbf{C}_{exp}$	$=A_{exp}\times E_{exp}^{t}\times\left(E_{exp}\times E_{exp}^{t}\right)^{-1}$	M	N_M x N_S array
C	Concentration profiles obtained from chemical model	M	N_M x N_S array
E	$=\left(C^{t}\times C\right)^{-1}\times C^{t}\times A_{exp}$	M^{-1} cm^{-1}	N_S x N_λ array
A	$=C\times E_{exp}$ or $=C\times E$, depending on the case (I, II or III)		N_M x N_λ array
Ω_C	Sum of quadratic residuals between C and C_{exp}	M	Scalar
Ω_A	Sum of quadratic residuals between A and A_{exp}		Scalar
$I_0(\lambda)$	Spectral density of the irradiation source	einstein s^{-1} dm^{-4}	Scalar
ϕ	Quantum yield of the process	mol $einstein^{-1}$	Scalar

Extras: Fitting routines and original dataset files.

Requieres Octave ver. 4.2.1 and the Optim-1.5.2 Octave-Forge package (both available free of charge form www.gnu.org/software/octave/).

The compressed file contains two folders with functional routines to be employed in the analysis of absorption profiles recorded from $A \rightarrow B$ and $A \rightarrow B \rightarrow C$ experiments. In both cases dataset files to test the procedures are provided. The data correspond to the actual experiments analyzed and discussed in the main text.