Electronic Supporting Information of The Absorption Spectrum of *cis*-Azobenzene

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1 The description of the minimization procedure of finding the concentrations of the *cis*- and *trans*-isomers from the absorption spectra of the mixure

The concentration of the *cis*- and *trans*-azobenzene was determined from spectral measurements of absorbance. Both concentrations were obtained from an analytic least-squares fit of the equation

$$A(\lambda) = [c_{cis} \times \varepsilon_{cis}(\lambda) + c_{trans} \times \varepsilon_{trans}(\lambda)] \times L,$$

where A is the measured absorbance, ε_{cis} and ε_{trans} are the molar absorption coefficients of *cis*- and *trans*-azobenzene, respectively, c_{cis} and c_{trans} are the molar concentrations of *cis*- and *trans*-azobenzene, respectively, and L is the length of the cuvette. The Matlab scripts (*find_concentrations.m, two_concentrations.m, all_twoconcentrations.m*) for the described calculations is freely available in the ESI together with an example (*measured_spectra*).

2 Molar absorption coefficients

The values of the molar absorption coefficients are given in separate files: *trans*-azobenzene ($trans\_epsilon$) and *cis*-azobenzene ($cis\_epsilon$).

3 Gaussian peaks fits

Gaussian peaks were fitted to the spectra of molar absorption coefficients in OriginLab. First, the maxima of the absorption bands were found by derivation analysis. These values were used as constraints for the first estimates of the positions of peak maxima and the Levenberg Marquardt minimization was performed. After the partial convergence the constraints were removed and another minimization was performed to reach the convergence criteria. Extra peak(s) was/were used to fit the absorption bands lying at lower wavelengths than shown. The Gaussian fits to the molar absorption coefficients of *trans*- and *cis*-azobenzene are presented in Figure S1 and Figure S2, the related parameters in Tables S1 and S2.

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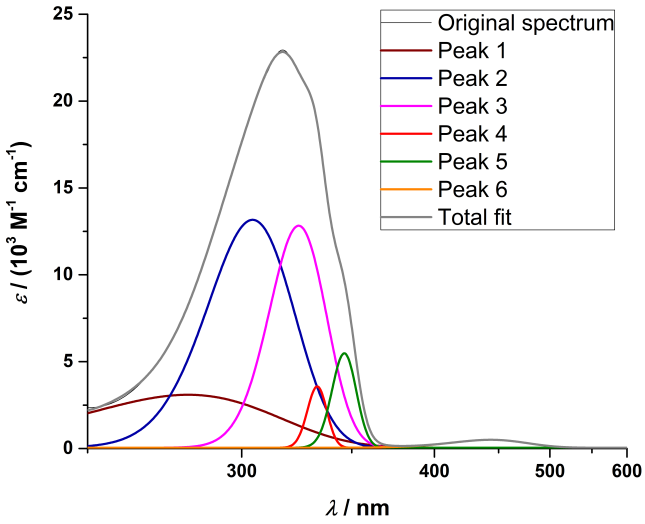

Fig. S1 The fit of Gaussian peaks to the spectrum of ε_{trans} of azobenzene in methanol.

Table S1 The parameters of fitted Gaussian peaks to the spectrum of the molar absorption coefficients of *trans*-azobenzene.

Peak number	λ_{max}/nm	σ	height
1	280.5	32.9	30500
2	304.3	17.4	13120
3	324.0	13.0	17780
4	332.6	4.65	3530
5	346.1	6.30	5440
6	443.3	32.5	460

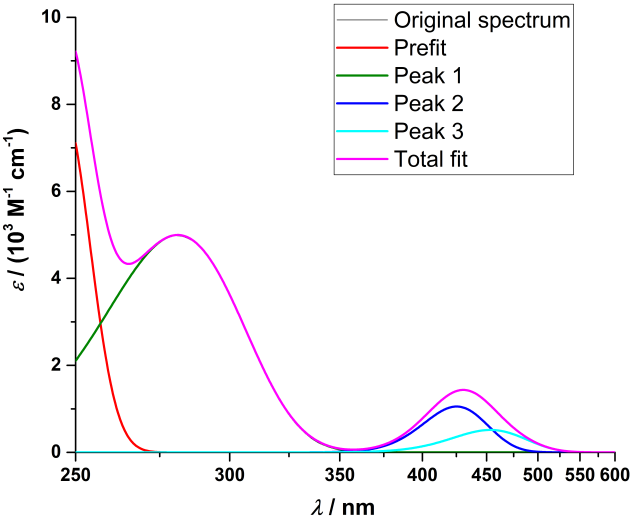

Fig. S2 The fit of Gaussian peaks to the spectrum of ε_{cis} of azobenzene in methanol.

Table S2 The parameters of fitted Gaussian peaks to the spectrum of molar absorption coefficients of *cis*-azobenzene.

Peak number	λ_{max}/nm	σ	height
1	281.1	23.6	5000
2	425.2	25.2	1050
3	453.4	33.0	510

4 Supplementary figures

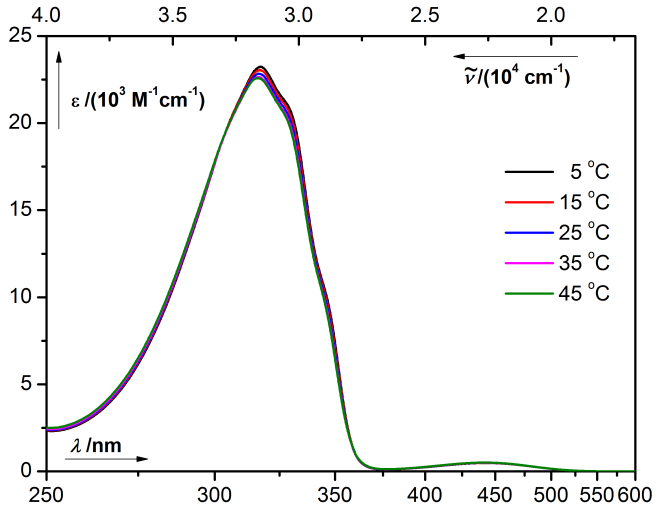

Fig. S3 The molar absorption coefficients (ε_{trans}) of *trans*-azobenzene in methanol at temperatures of 5, 15, 25, 35, and 45 °C.

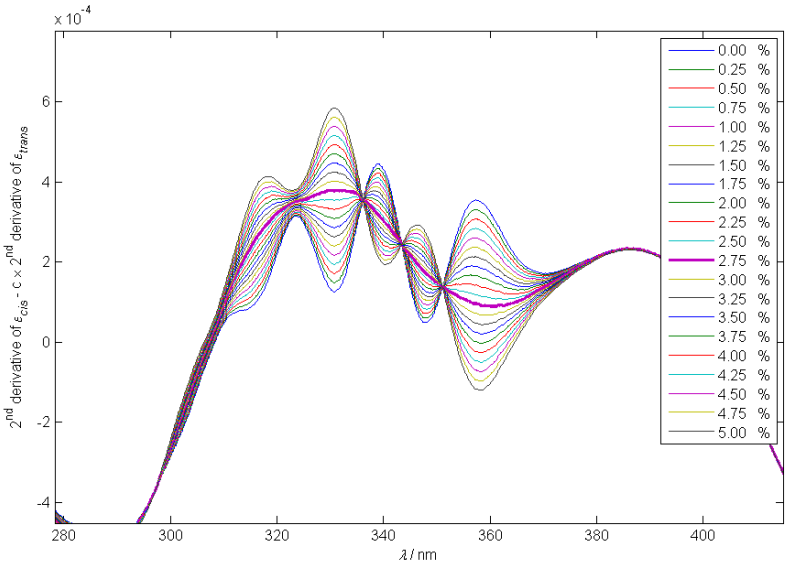

Fig. S4 An example of the TEM method. Subtraction of the indicated amount (in %) of the *trans* resulted in an estimate of 2.75 % *trans* contamination in the PSS.

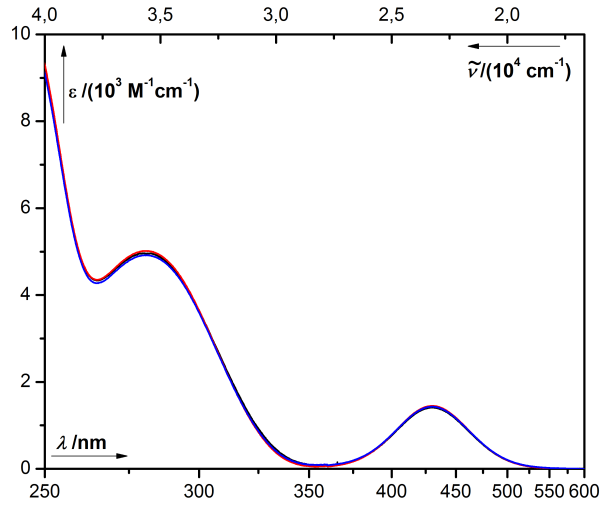

Fig. S5 Three independent determinations of the molar absorption coefficients ($\varepsilon_{cis}^{\mathrm{TEM}}$) of *cis*-azobenzene in methanol at 35 °C obtained by the TEM analysis.

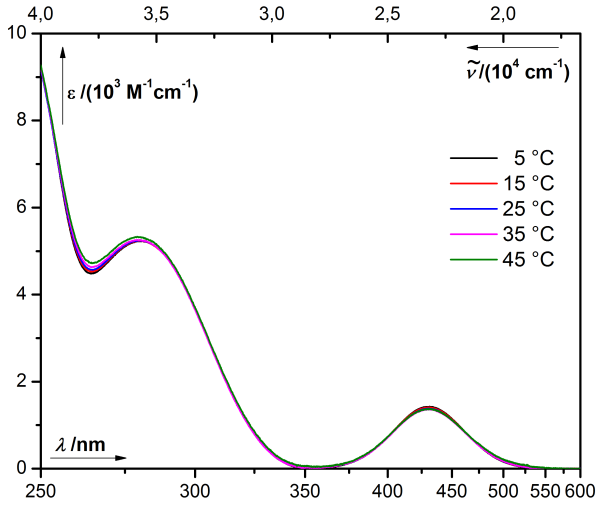

Fig. S6 The molar absorption coefficients ($\varepsilon_{cis}^{\mathrm{TEM}}$) of *cis*-azobenzene in methanol at temperatures of 5, 15, 25, 35, and 45 °C obtained by the TEM method.

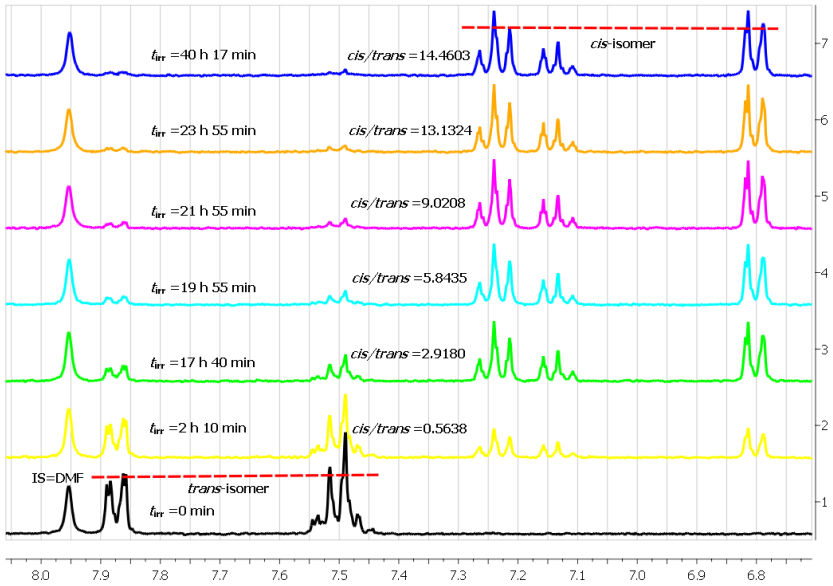

Fig. S7 Typical ^{1}H-NMR of the photoirradiated azobenzene mixture in CD_3OD with $c_0 = 6.84 \times 10^{-4}$ mol dm^{-3}. The internal standard (IS) sealed in a capillary tube was dimethylformamide in CD_3CN. The sample was irradiated by $\lambda_{\mathrm{irr}} = 348$ nm. The calculated ratios of cis/trans isomers are: 0.5638; 2.9180; 5.8435; 9.0208; 13.1324; 14.4603.

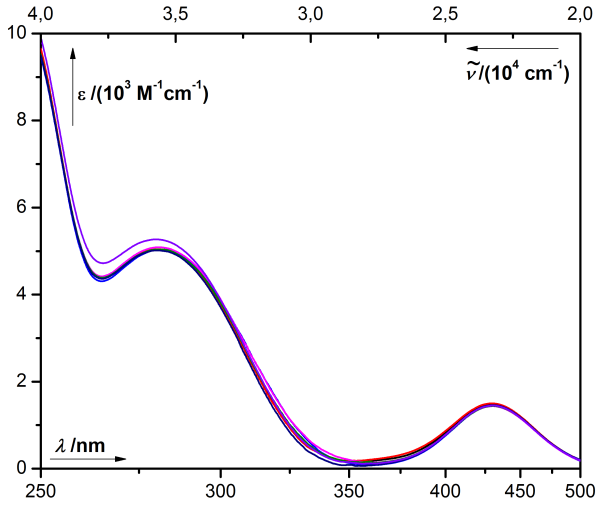

Fig. S8 Seven independent determinations of the molar absorption coefficients (ε_{cis}^{NMR}) of *cis*-azobenzene in methanol at 25 °C obtained from the ratio of isomers determined by NMR.

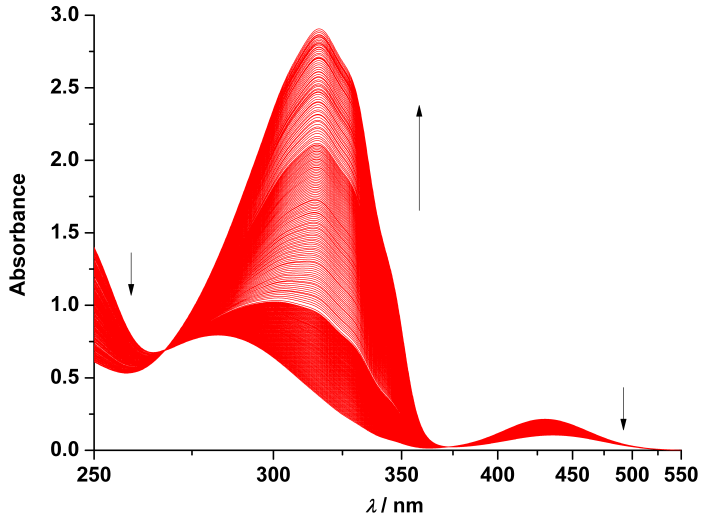

Fig. S9 The absorption spectra recorded during azobenzene thermal isomerization.

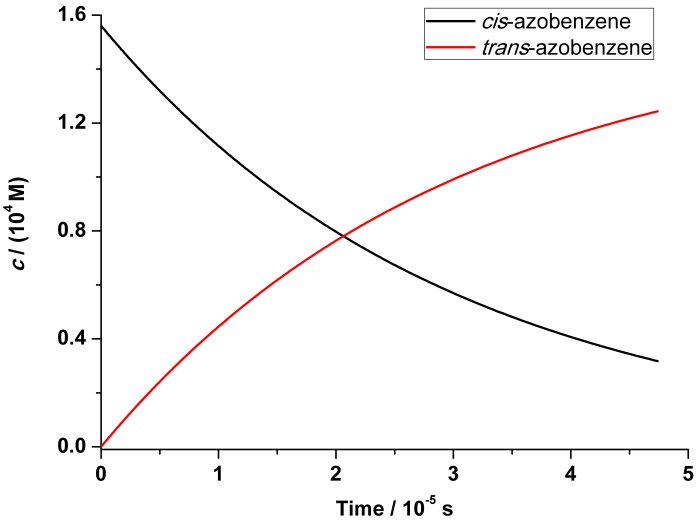

Fig. S10 The concentrations of *cis*- and *trans*-azobenzene during thermal isomerization.

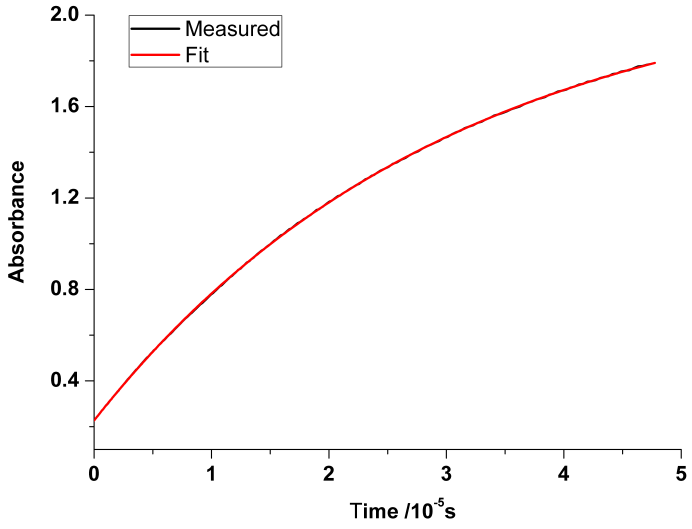

Fig. S11 The measured and fitted kinetic traces at 316 nm during azobenzene thermal isomerization.

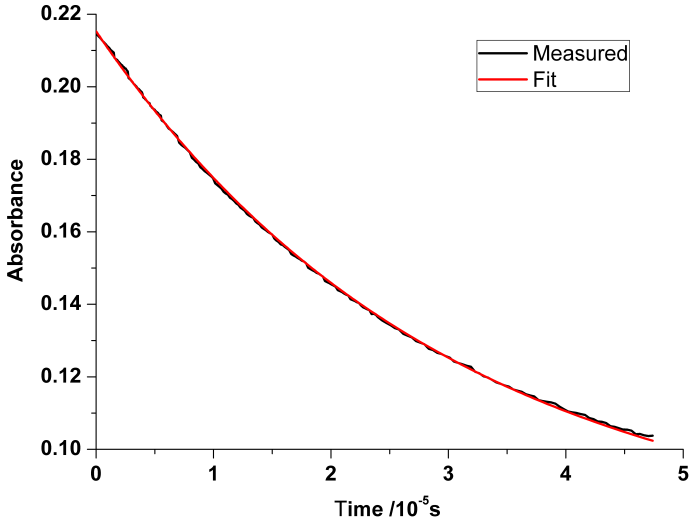

Fig. S12 The measured and fitted kinetic traces at 430 nm during azobenzene thermal isomerization.

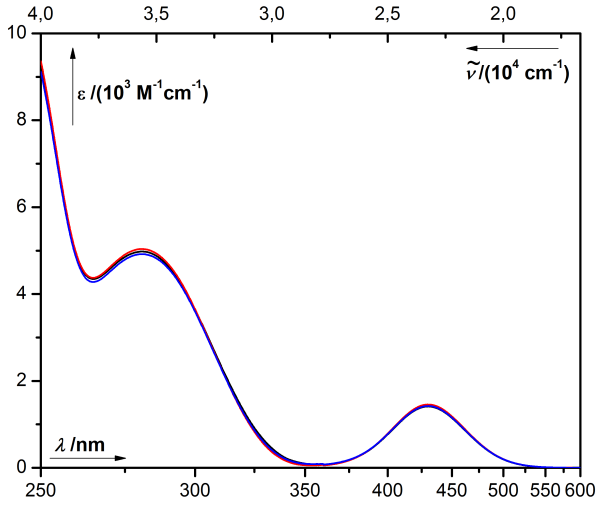

Fig. S13 Three independent determinations of the molar absorption coefficients (ε^{t}_{cis}) of *cis*-azobenzene in methanol at 35 °C obtained from the global analysis of the thermal reaction from the PSS towards *trans*-azobenzene.

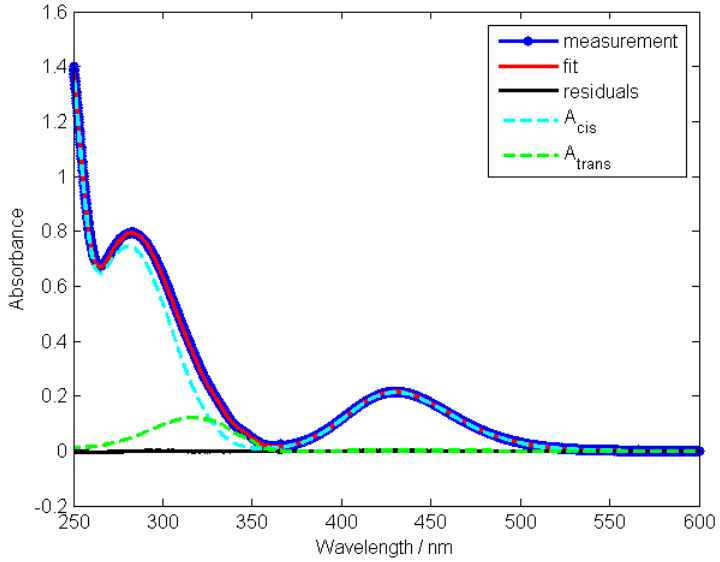

Fig. S14 Comparison of the measured absorbance spectra containing mainly *cis*-azobenzene with the fitted one. The blue and green curves show calculated absorbances of the *cis*- and *trans*-isomer, respectively.

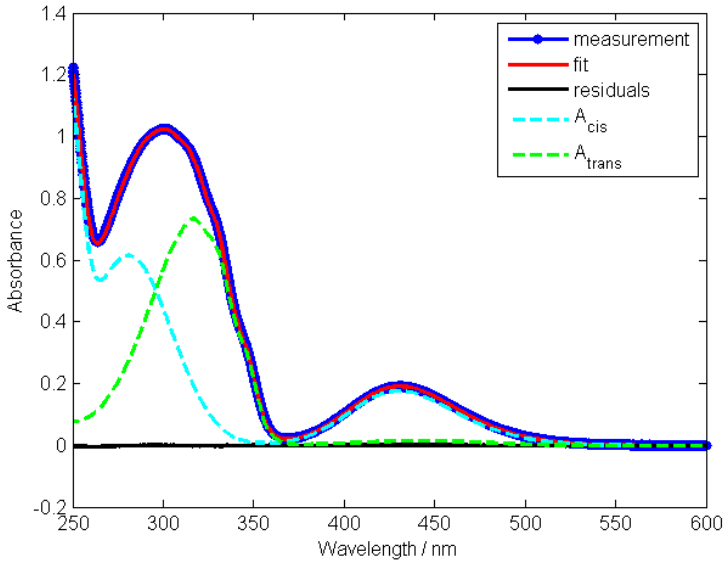

Fig. S15 Comparison of the measured absorbance spectra containing both *trans*- and *cis*-azobenzene with the fitted one. The blue and green curves show calculated absorbances of the *cis*- and *trans*-isomer, respectively.

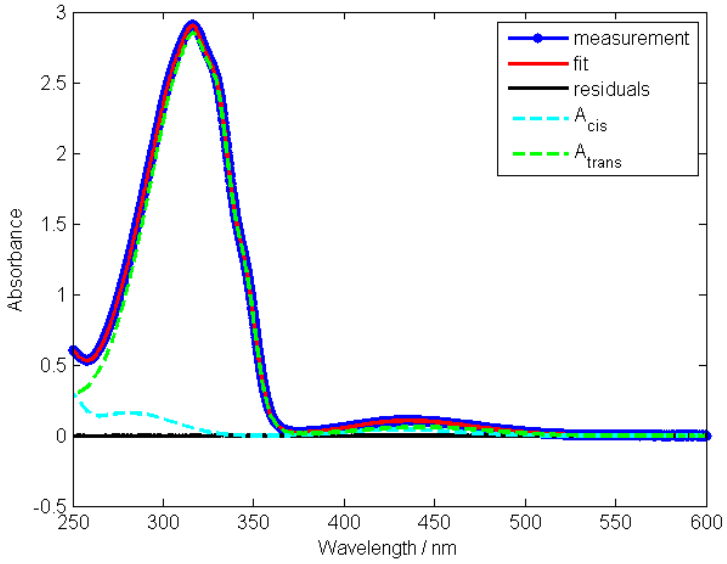

Fig. S16 Comparison of the measured absorbance spectra containing mainly *trans*-azobenzene with the fitted one. The blue and green curves show calculated absorbances of the *cis*- and *trans*-isomer, respectively.