Supplementary information for:

Vibrational coherence and quantum yield of retinal-chromophore-inspired molecular switches

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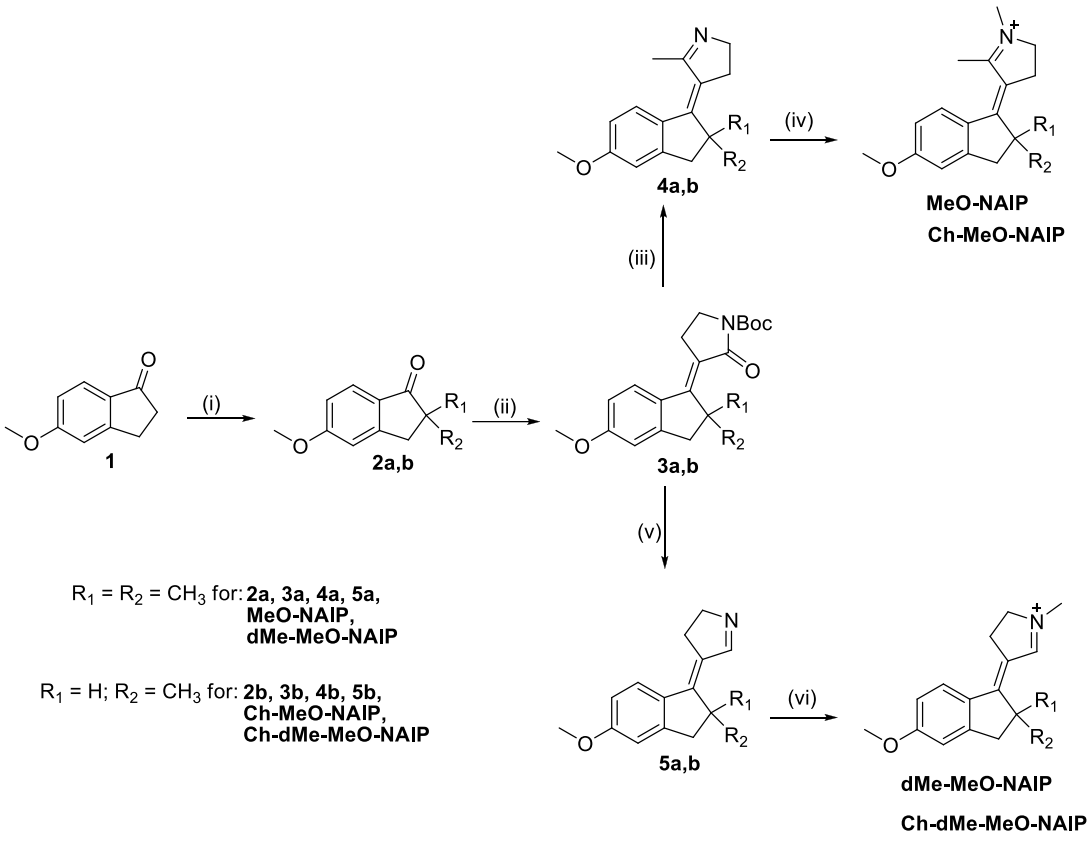
1) Synthesis.

Materials and Methods. All chemicals used were of reagent grade. Yields refer to purified products and are not optimized. Merck silica gel 60 (230−400 mesh) was used for column chromatography. Merck TLC plates and silica gel 60 F_{254} were used for TLC. ^{1}H NMR spectra were recorded at 400 MHz using a Bruker DRX-400 AVANCE spectrometer in the indicated solvents (TMS as internal standard). The values of the chemical shifts are expressed in ppm and the coupling constants (*J*) in Hz. An Agilent 1100 LC/MSD operating with an electrospray source was used in mass spectrometry experiments.

Compounds **MeO-NAIP**,[1] **dMe-MeO-NAIP**,[2] **Ch-MeO-NAIP**, and **Ch-dMe-MeO-NAIP** [3] were prepared as summarized in Scheme 1 modifying some synthetic procedure previously reported in literature. The new synthetic steps are described below and the characterization data result in agreement with the literature for each compounds. Compound **ZW-NAIP** was prepared as previously reported [4] and summarized in Scheme 2. The synthesis of compound **NAIP** is reported here for the first time. It was prepared as described in Scheme 3 and the details are given below.

Scheme 1. Synthesis of **MeO-NAIP**, **dMe-MeO-NAIP**, **Ch-MeO-NAIP** and **Ch-dMe-MeO-NAIP.**



Reagents: (i) CH_3I, t-BuOK, t-BuOH, Et_2O; (ii) N-Boc-pyrrolidinone, LiHDMS, $BF_3(Et)_2O$; (iii) CH_3MgBr, THF; TFA, DCM; (iv) CH_3OTf, benzene; (v) DIBAL-H, THF; TFA, DCM; (vi) CH_3OTf, benzene.

Compound **2a** was prepared as reported in reference [5]. Compounds **3a**, **5a**, and **dMe-MeO-NAIP** were prepared as reported in reference [2]. Compound **MeO-NAIP** was prepared as reported in reference [1]. Compounds **2b**, **3b**, **5b**, and **Ch-dMe-MeO-NAIP** were prepared as reported in reference [3]. Compounds **4a**, **4b**, and **Ch-MeO-NAIP** were prepared as reported below.

(Z)-4-(5-methoxy-2,2-dimethyl-2,3-dihydro-1H-inden-1-ylidene)-5-methyl-3,4-dihydro-2H-pyrrole (**4a**). [6]

Compound **4a** was prepared with a different approach with respect to the previously reported synthesis. To a solution of previously reported compound **3a** [2] (0.25 g, 0.70 mmol) in dry THF (10 mL) cooled at -20 °C under a nitrogen atmosphere, a solution of methylmagnesium bromide (1 M in diethylether 7.0 mL, 7.0 mmol) was added. The resulting mixture was stirred at the same temperature for 3 h. The excess of the Grignard reagent was destroyed by the dropwise addition of HCl until the gas evolution ceased. The mixture was dried over sodium sulfate and concentrated under reduced pressure. The oily residue was dissolved in dichloromethane (10 mL) and trifluoroacetic acid (1.0 mL) was added at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1 h, and the excess of acid was quenched by addition of solid sodium bicarbonate until the gas evolution ceased. The organic layer was washed with water, dried over sodium sulfate and concentrated under reduced pressure. The oily residue was purified by flash chromatography using ethyl acetate-methanol-triethylamine (9:0.8:0.2) as the eluent to obtain compound **4a** (0.086 g, 48%) as a yellow oil. ^{1}HNMR(400 MHz, $CDCl_3$): 1.25 (s, 6H), 2.52 (m, 3H), 2.77 (s, 2H), 2.89 (t, *J* = 7.0, 2H), 3.80 (s, 3H), 3.96 (t, *J* = 7.0, 2H), 6.74 (dd, *J* = 8.4, 2.0, 1H), 6.79 (d, *J* = 2.0, 1H), 7.24 (d, *J* = 8.4, 1H). ESI-MS *m/z*: [M + H^+] = 256.

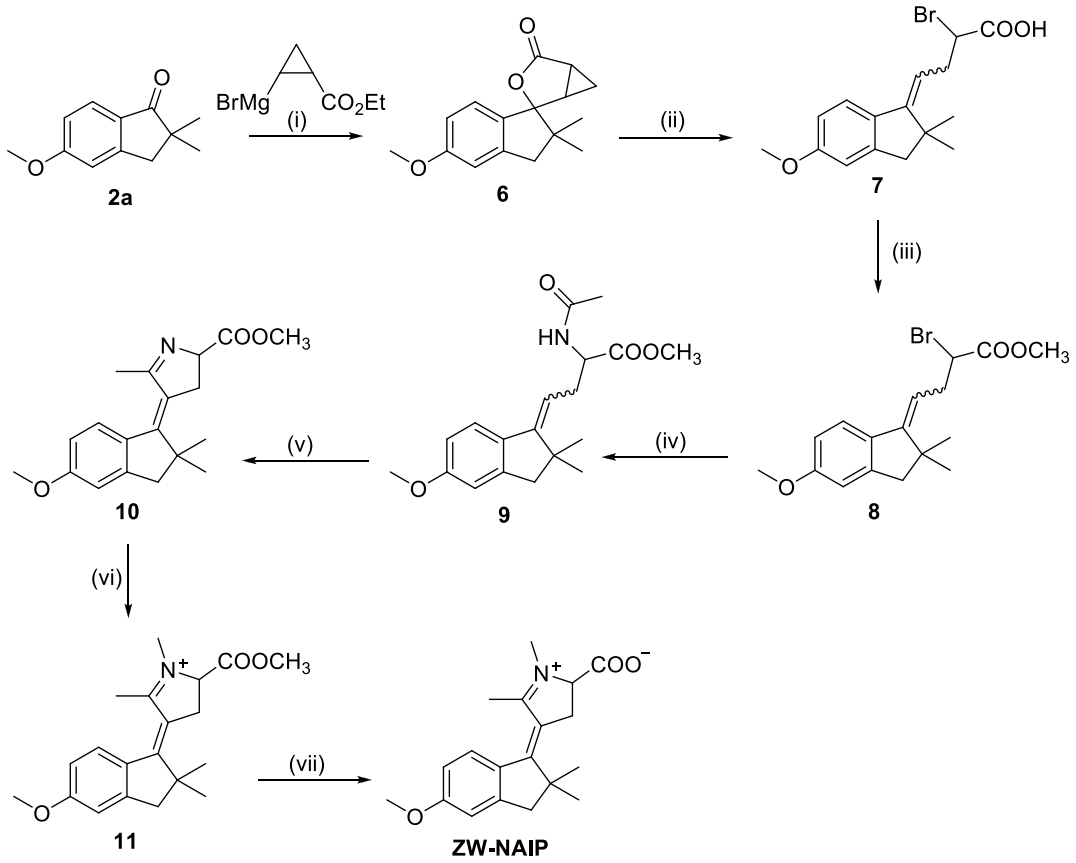
(E)-4-(5-methoxy-2-methyl-2,3-dihydro-1H-inden-1-ylidene)-5-methyl-3,4-dihydro-2H-pyrrole (**4b**). [6]

Compound **4b** was prepared with a different approach respect to the previously reported synthesis. To a solution of previously reported compound **3b** [3] (0.20 g, 0.58 mmol) in dry THF (10 mL) cooled at -20 °C under a nitrogen atmosphere, a solution of methylmagnesium bromide (1 M in diethylether 5.8 mL, 5.8 mmol) was added. The resulting mixture was stirred at the same temperature for 3 h. The excess of the Grignard reagent was destroyed by the dropwise addition of HCl until the gas evolution ceased. The mixture was dried over sodium sulfate and concentrated under reduced pressure. The oily residue was dissolved in dichloromethane (10 mL) and trifluoroacetic acid (1.0 mL) was added at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1 h, and the excess of acid was quenched by addition of solid sodium bicarbonate until the gas evolution ceased. The organic layer was washed with water, dried over sodium sulfate and concentrated under reduced pressure. The oily residue was purified by flash chromatography using ethyl ethyl acetate-methanol-triethylamine (9:0.8:0.2) as the eluent to obtain compound **4b** (0.060 g, 43%) as a brown waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.15 (d, *J* = 6.8, 3H), 2.42 (m, 3H), 2.56 (d, *J* = 16.0, 1H), 2.79 (ddd, *J* = 3.2, 8.0, 16.8, 1H), 2.99 (ddd, *J* = 3.2, 8.0, 16.8, 1H), 3.19 (dd, *J* = 7.2, 16.0, 1H), 3.61–3.70 (m, 1H), 3.82 (s, 3H), 3.84–3.89 (m, 1H), 3.95–4.47 (m, 1H), 6.80 (dd, *J* = 8.4, 2.6, 1H), 6.85 (d, *J* = 2.6, 1H), 7.45 (d, *J* = 8.4, 1H). ESI-MS *m/z*: $[M + H^+]$ = 242.

(E)-4-(5-methoxy-2-methyl-2,3-dihydro-1H-inden-1-ylidene)-1,5-dimethyl-3,4-dihydro-2H-pyrrolium (**Ch-MeO-NAIP**).

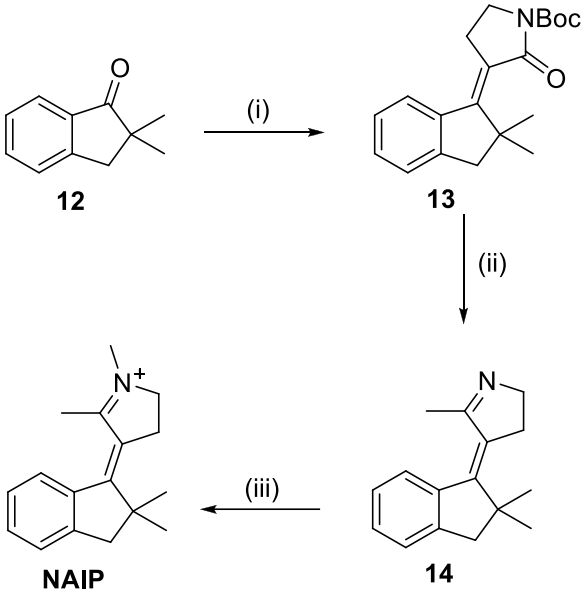
The methylation of compound **4b** to obtain compound **Ch-MeO-NAIP** was performed using the method previously reported for compound **Ch-dMe-MeO-NAIP**. [3] In particular, methyl trifluoromethanesulfonate (0.207 mmol, 24 µL) was added to a solution of compound **4b** (0.050 g, 0.207 mmol) in anhydrous benzene (5 mL). The reaction mixture was stirred for 1 h at room temperature under nitrogen atmosphere, then the solvent was removed under reduced pressure obtaining quantitatively the compound **Ch-MeO-NAIP** as orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.16 (d, *J* = 6.8, 3H), 2.44 (m, 3H), 2.58 (d, *J* = 16.0, 1H), 2.82 (ddd, *J* = 3.2, 8.0, 16.8, 1H), 3.01 (ddd, *J* = 3.2, 8.0, 16.8, 1H), 3.21 (dd, *J* = 7.2, 16.0, 1H), 3.58–3.71 (m, 1H), 3.69 (s, 3H), 3.91–4.01 (m, 1H), 4.05–4.50 (m, 1H), 6.83 (m, 2H), 7.46 (d, *J* = 8.4, 1H). ESI-MS *m/z*: $[M^+]$ = 256.

Scheme 2. Synthesis of compound **ZW-MeO-NAIP**. [4]



Reagents: (i) ethyl 2-iodocyclopropanecarboxylate, iPrMgCl; (ii) HBr/AcOH; (iii) $(CH_3)_3SiCHN_2$; (iv) (a) NaN_3-DMF, (b) Ph_3P-H_2O, (c) AcCl $(CH_3CH_3)_3N$; (v) PPSE; (vi) MeOTf ; (vii) LiOH.

Scheme 3. Synthesis of compound **NAIP**.



Reagents: (i) N-Boc-pyrrolidinone, LiHDMS, $BF_3(Et)_2O$; (ii) CH_3MgBr, THF; TFA, DCM; (iii) CH_3OTf, benzene.

tert-butyl 3-(2,2-dimethyl-2,3-dihydro-1H-inden-1-ylidene)-2-oxopyrrolidine-1-carboxylate (**13**E/Z)

A 1 M solution of lithium hexamethyldisilazide (LiHMDS) (0.82 mL, 0.82 mmol) in anhydrous THF was added at −78 °C under nitrogen atmosphere to N-Boc-2-pyrrolidinone (0.13 g, 0.70 mmol) dissolved in anhydrous THF (5 mL). After 1 h, a solution of the compound **12** [7] (0.12 g, 0.75 mmol) and $BF_3{\cdot}Et_2O$ (0.75 mmol, 94 µL) in anhydrous THF (5 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 3 h. Then, NH_4Cl (s.s.) was added, and the crude was extracted in Et_2O. The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and the residue filtered on silica gel using ethyl acetate/petroleum ether (3:7) as eluent. The filtrate was poured in $CHCl_3$ underwent spontaneous dehydration (checked by ESI-MS). The reaction mixture was concentrated under reduced pressure and purified by flash chromatography using ethyl acetate/petroleum ether (3:7) as eluent to afford compound **13** (0.15 g, 65%) as a brown solid (1:1 mixture of E/Z isomers). ^{1}H NMR (400 MHz, $CDCl_3$): 1.28 (s, 3H), 1.53 (m, 12H), 2.80 (s, 2H), 2.88 (t, *J* = 7.2, 2H), 2.93 (s, 2H), 2.99 (t, *J* = 7.2, 2H), 3.68-3.77 (m, 4H), 7.07-7.28 (m, 6H), 7.43 (d, *J* = 8.4, 1H), 8.54 (d, *J* = 8.4, 1H). ESI-MS *m/z*: [M + Na^+] = 350.

(Z)-4-(2,2-dimethyl-2,3-dihydro-1H-inden-1-ylidene)-5-methyl-3,4-dihydro-2H-pyrrole (**14**).

To a solution of compound **13** (0.15 g, 0.46 mmol) in dry THF (10 mL) cooled at -20 °C under a nitrogen atmosphere, a solution of methylmagnesium bromide (1 M in diethylether 4.6 mL, 4.6 mmol) was added. The resulting mixture was stirred at the same temperature for 3 h. The excess of the Grignard reagent was destroyed by the dropwise addition of HCl until the gas evolution ceased. The mixture was dried over sodium sulfate and concentrated under reduced pressure. The oily residue was dissolved in dichloromethane (10 mL) and trifluoroacetic acid (1.0 mL) was added at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1 h, and the excess of acid was quenched by addition of solid sodium bicarbonate until the gas evolution ceased. The organic layer

was washed with water, dried over sodium sulfate and concentrated under reduced pressure. The oily residue was purified by flash chromatography using ethyl acetate-methanol (9:1) as the eluent to obtain compound **14** (0.06 g, 58%) as a yellow oil. ^{1}HNMR (400 MHz, $CDCl_3$): 1.24 (s, 6H), 2.53 (s, 3H), 2.78 (s, 2H), 2.90 (t, *J* = 7.0, 2H), 3.95 (t, *J* = 7.0, 2H), 6.8-7.1 (m, 3H), 7.22 (d, *J* = 8.4, 1H). ESI-MS *m/z*: $[M + H^+]$ = 226.

(Z)-4-(2,2-dimethyl-2,3-dihydro-1H-inden-1-ylidene)-1,5-dimethyl-3,4-dihydro-2H-pyrrolium (**NAIP**).

Methyl trifluoromethanesulfonate (0.22 mmol, 26 µL) was added to a solution of compound **14** (0.050 g, 0.22 mmol) in anhydrous benzene (5 mL). The reaction mixture was stirred for 1 h at room temperature under nitrogen atmosphere, then the solvent was removed under reduced pressure obtaining quantitatively the compound **NAIP** as brown oil. ^{1}HNMR (400 MHz, $CDCl_3$): 1.28 (s, 6H), 2.59 (s, 3H), 2.88 (s, 2H), 3.15 (t, *J* = 7.0, 2H), 3.70 (s, 3H), 4.20 (t, *J* = 7.0, 2H), 6.8-7.1 (m, 3H), 7.42 (d, *J* = 8.4, 1H) ESI-MS *m/z*: $[M^+]$ = 240.

2) Transient absorption of isomer mixtures: recovering isomer-specific spectroscopic signatures

a. Isomer-specific excitation probability

Let's consider a solution of several molecules *i* (e.g. *E* and *Z* isomers) characterized by their extinction coefficients $\varepsilon_i(\lambda)$ and concentrations c_i. The absorbance of the solution is: $A(\lambda) = \sum_i \varepsilon_i(\lambda)\, c_i l$, with l the sample thickness. We excite the solution with a femtosecond pump pulse (frequency ν_p, wavelength λ_p, section S, energy per pulse $\mathcal{E}_p$) propagating along the *z* axis. Differentiating the Beer-Lambert law, the light energy $\delta\mathcal{E}_i$ absorbed by each solute *i* within a sample slice of elementary thickness dz is: $\delta\mathcal{E}_i = \ln(10)\, \mathcal{E}_p(z)\varepsilon_i(\lambda)c_i dz$, where $\mathcal{E}_p(z) = \mathcal{E}_p \times 10^{-\sum_i \varepsilon_i(\lambda)c_i z}$. Integrating along z from 0 to l, we get the light energy absorbed by solute *i*:

$$\Delta\mathcal{E}_i = \varepsilon_i(\lambda_p)c_i\mathcal{E}_p \int_0^l \exp\left(-ln(10)\sum\nolimits_i \varepsilon_i(\lambda_p)\, c_i z\right)\ln(10)\, dz = \frac{\varepsilon_i(\lambda_p)c_i}{\sum_i \varepsilon_i(\lambda_p)\, c_i}\, \mathcal{E}_p(1 - 10^{-A(\lambda_p)})$$

The number of molecules of solute *i* excited by the pump is equal to the number of photons $\Delta\mathcal{E}_i/(h\nu_p)$ absorbed over the entire column of solution (thickness l, section *S*). Hence we may define the initial pump-induced change in "column-averaged" concentration in solute *i*:

$$\Delta c_i = -\frac{\Delta\mathcal{E}_i}{h\nu_p N_A S l} = -\frac{\varepsilon_i(\lambda_p)c_i}{N_A}\frac{\mathcal{E}_p}{h\nu_p S}\frac{1 - 10^{-A(\lambda_p)}}{A(\lambda_p)} \qquad (1)$$

Here, $\Delta c_i < 0$ since the initial solute is "bleached" upon pump light absorption. We note here, that the quantity $-\Delta c_i/c_i$ as obtained from Formula (1) is the column-averaged **excitation probability** of the solute *i* as a function of the pump energy density $\mathcal{E}_p/S$. Typical experimental conditions are $\mathcal{E}_p = 30$ nJ, $S = \pi \times (50\ \mu m)^2 \approx 8\ 10^{-5}$ cm^2, λ_p = 400 nm = c/ν_p, $A(\lambda_p) = 0.5$, $\varepsilon_i(\lambda_p) = 20000$ M^{-1}cm^{-1} (see Figure 1.C). We then obtain: $-\Delta c_i/c_i \approx 3.5$ %.

b. Isomer-specific transient absorption (TA) signal

We assume that the TA signal $\Delta A(\lambda, t)$ can be written as the linear absorption of the non-stationary sample produced by the pump light absorption. For a mixture of two isomers *E* and *Z* with total concentration c_0, and a fraction x of *Z* isomer, we can write:

$$\Delta A(\lambda, t, x)/l = -\Delta c_E(x) \sum_{k=1}^{N_E} n_k^E(t)\varepsilon_k^E(\lambda, t) - \Delta c_Z(x) \sum_{k=1}^{N_Z} n_k^Z(t)\varepsilon_k^Z(\lambda, t)$$

where l is the sample thickness, $\Delta c_E(x)$ and $\Delta c_Z(x)$ are the initial pump-induced change in column-averaged concentration (Formula 1 above) in each isomer, $n_k^E(t)$ and $n_k^Z(t)$ are the normalized population kinetics of the transient species *k* which are successively formed during the photoreaction of isomer *E* and *Z*, respectively. We may thus define the isomer-specific TA signals as:

$$\Delta A_E(\lambda, t)/l = \Delta A(\lambda, t, x = 0)/l = -\Delta c_E(x = 0) \sum_{k=1}^{N_E} n_k^E(t)\varepsilon_k^E(\lambda, t) \quad (2)$$

$$\Delta A_Z(\lambda, t)/l = \Delta A(\lambda, t, x = 1)/l = -\Delta c_Z(x = 1) \sum_{k=1}^{N_E} n_k^E(t)\varepsilon_k^E(\lambda, t) \quad (3)$$

Hence we may write the TA signal of an isomer mixture x as a linear combination of the isomer-specific TA signals:

$$\Delta A(\lambda, t) = \frac{\Delta c_E(x)}{\Delta c_E(0)} \Delta A_E(\lambda, t) + \frac{\Delta c_Z(x)}{\Delta c_Z(1)} \Delta A_Z(\lambda, t)$$

with for $i = E, Z$

$$-\Delta c_i(x) = \frac{\varepsilon_i(\lambda_p) c_i(x)}{N_A} \frac{\mathcal{E}_p}{h\nu_p S} \frac{1 - 10^{-A_p(x)}}{A_p(x)}$$

and

$$c_Z(x) = x c_0, \qquad c_E(x) = (1 - x) c_0$$

$$A_p(x) = c_0 l \left(x\varepsilon_Z(\lambda_p) + (1 - x)\varepsilon_E(\lambda_p) \right)$$

We finally conclude:

$$\boxed{\frac{\Delta A(\lambda, t, x)}{g(x)} = (1 - x) \frac{\Delta A_E(\lambda, t)}{g(0)} + x \frac{\Delta A_Z(\lambda, t)}{g(1)}} \quad (4)$$

with

$$g(x) = \frac{1 - 10^{-A_p(x)}}{A_p(x)} \quad (5)$$

Now, if we perform two TA experiments on two samples characterized by the same total isomer concentration c_0, but two distinct isomer compositions x_1 and x_2, resulting in datasets $\Delta A(\lambda, t, x_1)$ and $\Delta A(\lambda, t, x_2)$, we can reconstruct the pure isomer TA data $\Delta A_E(\lambda, t)$ and $\Delta A_Z(\lambda, t)$ by computing:

$$\Delta A_{\mathrm{Z}}(\lambda, t) = \frac{g(1)}{x_1 - x_2} \left(\frac{1 - x_2}{g(x_1)} \Delta A(\lambda, t, x_1) - \frac{1 - x_1}{g(x_2)} \Delta A(\lambda, t, x_2) \right) \quad (6)$$

$$\Delta A_{\mathrm{E}}(\lambda, t) = \frac{g(0)}{x_2 - x_1} \left(\frac{x_2}{g(x_1)} \Delta A(\lambda, t, x_1) - \frac{x_1}{g(x_2)} \Delta A(\lambda, t, x_2) \right) \quad (7)$$

c. Determining relative photoisomerization quantum yields.

At long-enough time delays (typically >100ps), the photoisomerizations and subsequent vibrational relaxation and thermalization are completed, such that the $\Delta A(t)$ signals have become stationary. More specifically, if we define η_R the photoisomerization yield of a reactant *R* (which can be any isomer of any IP compound), the final TA signal will be the contribution of (i) the bleach of the initial reactant *R*, refilled with probability $(1-\eta_R)$ by the non-reactive, reconstitution of *R*, and (ii) the reactive formation with probability η_R of the product *P* (i.e. the other isomer). Using Formula 2 above, we can thus write the TA measured upon excitation of a pure solution of species *R* at "infinite" time delays:

$$\Delta A_R(\lambda, t=\infty)/l = -\Delta c_R \left(-\varepsilon_R(\lambda) + (1-\eta_R)\varepsilon_R(\lambda) + \eta_R \varepsilon_P(\lambda)\right)$$

$$\Delta A_R(\lambda, t=\infty)/l = -\Delta c_R\, \eta_R \big(\varepsilon_P(\lambda) - \varepsilon_R(\lambda)\big) = \Delta c_R\, \eta_R\, \Delta\varepsilon_{RP}(\lambda)$$

where we define $\Delta\varepsilon_{RP}(\lambda) = \varepsilon_R(\lambda) - \varepsilon_P(\lambda)$, the difference between the reactant (R) and photoproduct (P) extinction coefficients. Here Δc_R is given by formula (1), and is proportional to the pump light energy density $\mathcal{E}_p/S$, which is not accurately determined experimentally. Instead, if two TA experiments are performed in the same experimental conditions, we may compute the ratio of both final, stationary TA spectra:

$$\frac{\Delta A_1(\lambda, t=\infty)}{\Delta A_2(\lambda, t=\infty)} = \frac{\Delta c_1\, \eta_1\, \Delta\varepsilon_1(\lambda)}{\Delta c_2\, \eta_2\, \Delta\varepsilon_2(\lambda)} = \frac{\eta_1\, \Delta\varepsilon_1(\lambda)}{\eta_2\, \Delta\varepsilon_2(\lambda)} \times \frac{1-10^{-A_1}}{1-10^{-A_2}}$$

Since the absorbance of each sample (A_1, A_2, corresponding to pure isomers $x_{1,2} = 0$ or 1) and the differences between reactant and photoproduct extinction coefficients ($\Delta\varepsilon_1(\lambda)$, $\Delta\varepsilon_2(\lambda)$) are accurately measured, we can accurately infer the ratio η_1/η_2 of both photoreaction quantum yields:

$$\boxed{\frac{\eta_1}{\eta_2} = \frac{\Delta A_1(\lambda, t=\infty)}{\Delta A_2(\lambda, t=\infty)} \times \frac{\Delta\varepsilon_2(\lambda)\,(1-10^{-A_2})}{\Delta\varepsilon_1(\lambda)\,(1-10^{-A_1})}} \qquad (8)$$

3) Ch-MeO-NAIP: Raw TA datasets for the “dark state” (DS) and “photostationary state” (PSS) and reconstruction of the pure *E* and pure *Z* TA datasets.

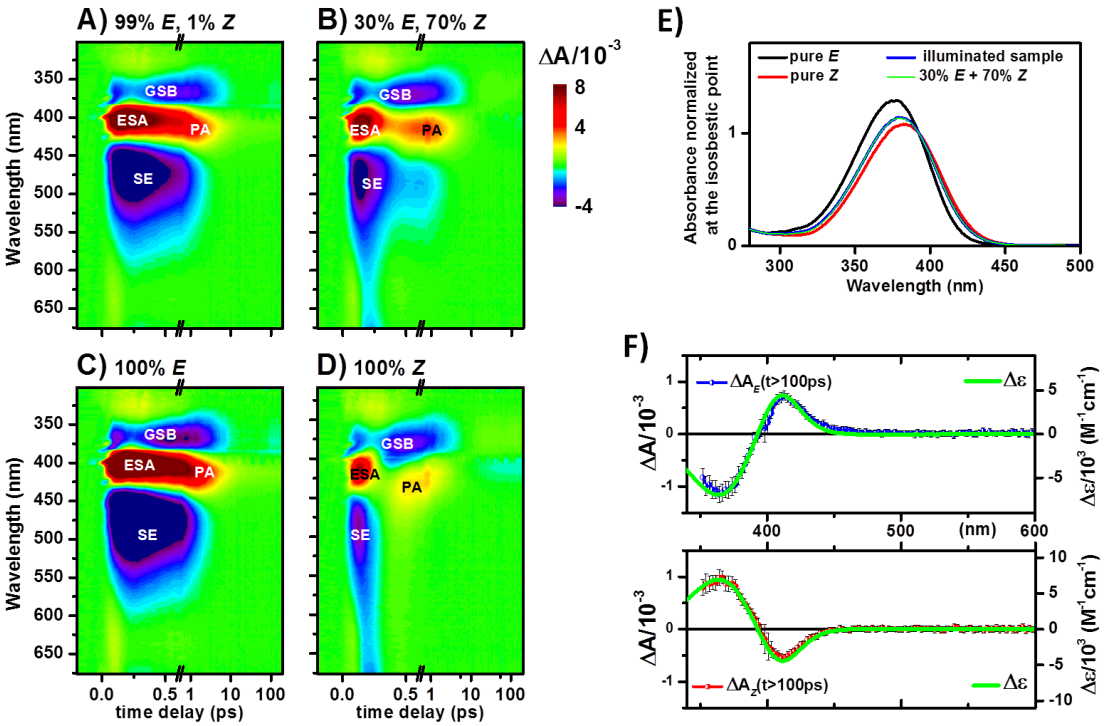


Figure S1: Illustration of the experimental approach for the determination of isomer-specific TA datasets and photoisomerization quantum yields, with the case of Ch-MeO-NAIP dissolved in MeOH. A, B) 2D map representations of the TA signals (ΔA, coded in false colors, as a function of pump-probe delay in ps, and probe wavelength in nm) obtained on DS and PSS samples, respectively. C, D) *E*- and *Z*- isomer-specific ΔA maps reconstructed from DS and PSS samples, based on Formula (6) and (7) above. E) The spectrum of the PSS sample (in blue) is equal to the 30 % : 70 % linear superposition (green) of the pure *E* (black) and pure *Z* (red) absorption spectra. F) The isomer-specific *ΔA* signals at long time delays are proportional to the difference between *E* and *Z* extinction coefficients (in green). They have opposite signs since they result from forward (*E* to *Z*, top) and backward (*Z* to *E*, bottom) isomerizations. Their relative amplitude $-\Delta A_E/\Delta A_Z$ is proportional to the ratio of both photoisomerization quantum yields (QYs), which allows us to evaluate precisely the relative QY of both isomers, according to Formula (8) above.

4) dMe-MeO-NAIP: Reconstructed pure *E* and pure *Z* TA data (same procedure as above)

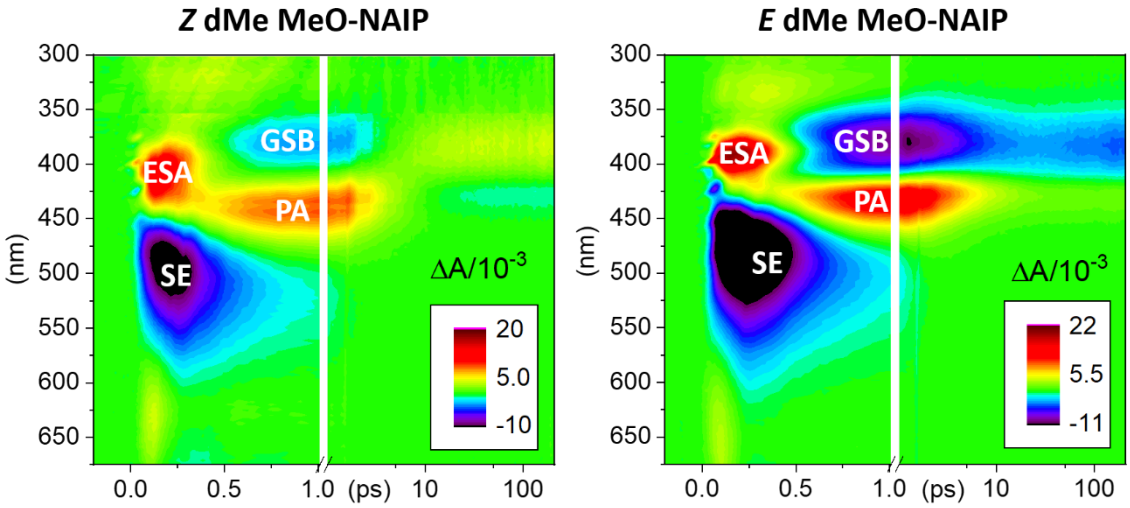


Figure S2: A) Pump-induced absorption change Δ*A* as function of probe wavelength (in nm) and time delay (ps) between pump and probe pulses of the pure *Z* (left) and *E* (right) isomers of dMe-MeO-NAIP in MeOH. These data are reconstructed by computing the appropriate linear combination of TA datasets of DS and PSS samples of dMe-MeO-NAIP, using Formula (6) and (7) above. Both isomers undergo a photoisomerization belonging to scenario II.

5) Comparison of the Excited state lifetimes of all compounds

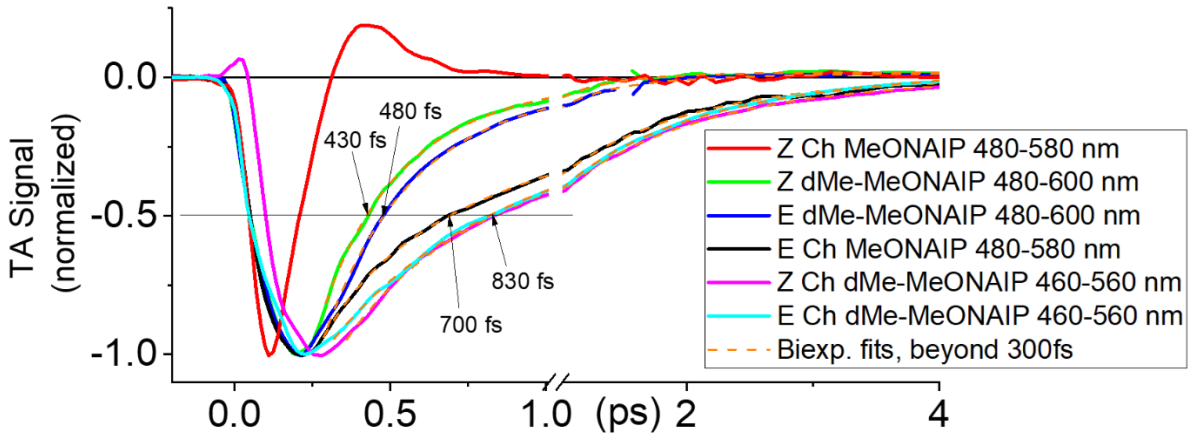


Figure S3: Comparison of the SE decay kinetics of all compounds obeying scenario II, together with the vibrationally coherent Z Ch MeO-NAIP (in red). They all display a similar SE signal rise over 250 to 300 fs time scale, followed by a biexponential decay (dashed orange lines). The half-lifes of the corresponding bright S_1 states are determined as shown with the arrows, and the values reported in Table 2. All decay kinetics are averaged over a spectral window specified in the caption. The original TA datasets for Z and E Ch-MeO-NAIP are displayed in Figure 5 of the paper, those for Z and E dMe-MeO-NAIP are displayed in Figure S2 above, those for E Ch dMe MeO NAIP are published in REF [3].

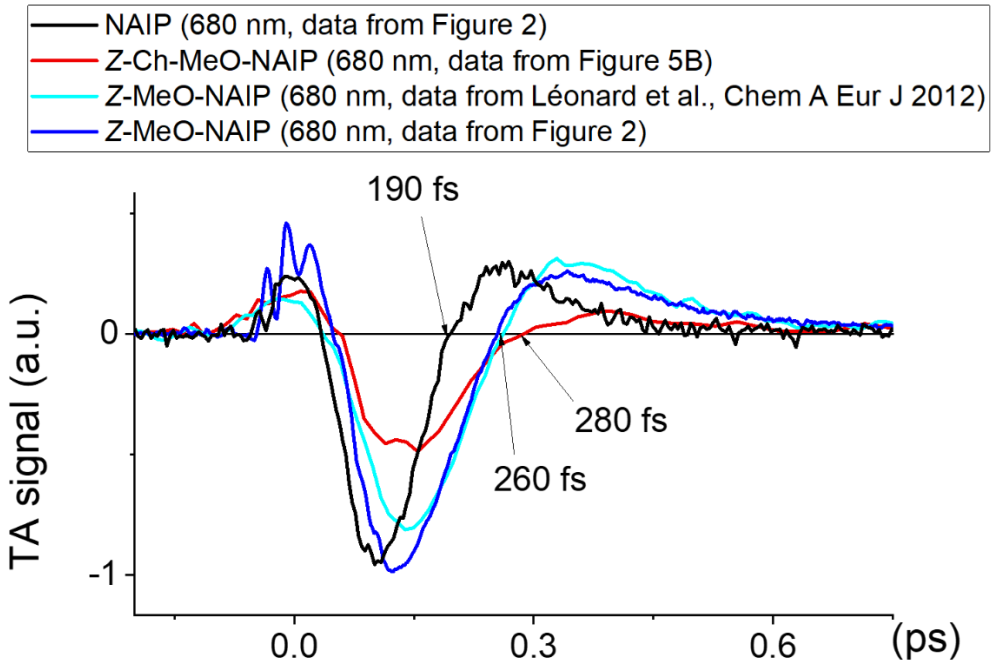


Figure S4: Comparison of the excited state life times for the compounds obeying scenario I. The TA kinetics are recorded with a 70-fs time resolution (red and cyan) or with a sub-30fs time resolution (black and deep blue), with two distinct pump pulses (see Section II of the paper).

6) Bibliography

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