

Supporting information for the manuscript: Nonlinear optical response of photochromic azobenzene-functionalized self-assembled monolayers[†]

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1 Quantum Chemical Methods

In general, to accurately calculate hyperpolarizabilities extended basis sets, correlated electronic structure methods and taking the deviation between static and dynamic hyperpolarizabilities into account are required. In this work, we account for these three components by following a computational procedure extensively used and tested by Champagne and coworkers^{Ref-S1,Ref-S2} to calculate dynamical hyperpolarizabilities for molecular switches. In an own previous paper, we have applied this computational protocol for non-linear response of fulgimides^{Ref-S3}.

In this procedure we first optimize molecular structures by hybrid (B3LYP^{Ref-S4}) density functional theory (DFT), using a 6-311++G** basis set which contains two sets of polarization and two sets of diffuse functions^{Ref-S5}. In a second step, we perform MP2 (Møller-Plesset perturbation theory to 2nd order) and CPHF (Coupled Perturbed Hartree Fock) calculations at the optimized geometries with this basis set, to obtain static hyperpolarizabilities $\beta_{\text{CPHF}}(0;0,0)$ and $\beta_{\text{MP2}}(0;0,0)$, respectively. In the MP2 case, the finite-field method was used in order to do so. Dynamic first hyperpolarizabilities $\beta_{\text{TDHF}}(-2\omega; \omega, \omega)$ were calculated for a frequency ω corresponding to the experimental excitation wavelength of 800 nm, by TDHF (Time-Dependent Hartree Fock)^{Ref-S6}. In a third step, the scaling relation

$$\beta_{\text{MP2}}(-2\omega; \omega, \omega) \approx \beta_{\text{MP2}}(0;0,0) \frac{\beta_{\text{TDHF}}(-2\omega; \omega, \omega)}{\beta_{\text{CPHF}}(0;0,0)} \quad (1)$$

was adopted, to arrive at dynamic hyperpolarizabilities at the correlated MP2 level, $\beta_{\text{MP2}}(-2\omega; \omega, \omega)$. This scaling procedure assumes that the frequency dispersions of β are the same for the correlated (MP2) and uncorrelated cases (HF). We used the Gaussian09 program package to perform all the calculations^{Ref-S7}.

β_{ijk}	<i>cis</i>	<i>trans</i>
xxx	14.3	11.0
yxx	-801	0.14
xyx	-194	4.85
yyx	90.2	-15.5
xyy	68.1	-230
yyy	191	-13.1
xzx	8247	-134
zxx	-4762	57.7
yxz	1655	12.0
xzy	-184	3.54
zyx	-416	-1.03
zyy	8.14	-4.06
zzy	-724	-12.4
zzx	1071	-1797
xzz	1921	-1840
zzy	459	56.6
yzz	-3289	14.5
zzz	-2833	7684
β_x	1452	-1887
β_y	-996	32.7
β_z	842	7607
β_0	1951	7838
a	0.68	5.70

Table 1 Tensor elements of β_{ijk} for the *cis*- and *trans*-form as well as vector elements β_i as defined in the main text. All results were calculated according to the outlined procedure. The value a for asymmetry of the “hyperpolarizability orthogonal” and “parallel to the surface” is shown as well. All values are given in atomic units. 1 a.u. = $8.641 \cdot 10^{-33}$ esu or $3.62 \cdot 10^{-42}$ m⁴V⁻¹.

2 Results

In table 1, we summarize certain quantities obtained with this method, as explained in the table caption.

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