

SUPPORTING INFORMATION

How the Second-Order Nonlinear Optical Response of the Collagen Triple Helix Appears: A Theoretical Investigation

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The simplest way to estimate the impact of frequency dispersion in pseudo-dipolar chromophores is to consider the two-state approximation (TSA), which assumes that only one excited state contributes to the second-order NLO response. Considering a homogeneous damping γ and neglecting the non-resonant terms, the frequency-dispersion factor of the diagonal component of the first hyperpolarizability tensor, $F(\omega, \omega_{ge}, \gamma)$, reads:

$$F(\omega, \omega_{ge}, \gamma) = \frac{\beta_{ZZZ}(-2\omega, \omega, \omega)}{\beta_{ZZZ}(0, 0, 0)} = \frac{\omega_{ge}^2 (\omega_{ge} - i\gamma)^2}{\left([\omega_{ge} - i\gamma]^2 - 4\omega^2\right) \left([\omega_{ge} - i\gamma]^2 - \omega^2\right)}$$

where g and e are the two electronic, ground and excited, states contributing to the first hyperpolarizability, and $\hbar\omega_{ge}$ is the corresponding excitation energy. The two-state approximation can be improved by incorporating an inhomogeneous broadening based on the absorption spectrum, which implicitly contains information on the distribution of the transition frequencies as well as by taking into account the vibronic structure of the excited states. According to Campo *et al.*³⁵ for an incoherent process like HRS, the dispersion factor reads:

$$\left| \frac{\beta^{HRS}(-2\omega; \omega, \omega)}{\beta^{HRS}(0; 0, 0)} \right| = \left\{ \int N(\omega'_{ge}) \left| F(\omega, \omega'_{ge}, \gamma) \right|^2 d\omega'_{ge} \right\}^{1/2}$$

where $N(\omega'_{ge})$, the distribution of the transition frequencies is a single-mode vibronic model:

$$N(\omega'_{ge}) = \sum_n^{vib. levels} \left[\frac{S^n e^{-S}}{n!} \right] e^{-[(\omega'_{ge} - \omega_n)/\gamma_{vib}]^2}$$

where $\omega_n = \omega_{ge} + n \omega_{vib}$ corresponds to the transition from the ground state to the n^{th} vibrational level of the excited state. The Huang-Rhys factors (S) were chosen to reproduce the shape of the absorption band. Values of ω_{vib} and γ_{vib} were also chosen such to reproduce the absorption spectra as accurately as possible.

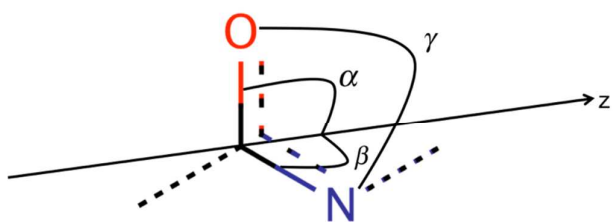


Figure S1: Representation of representative angles of each amide groups with respect to the z-axis.

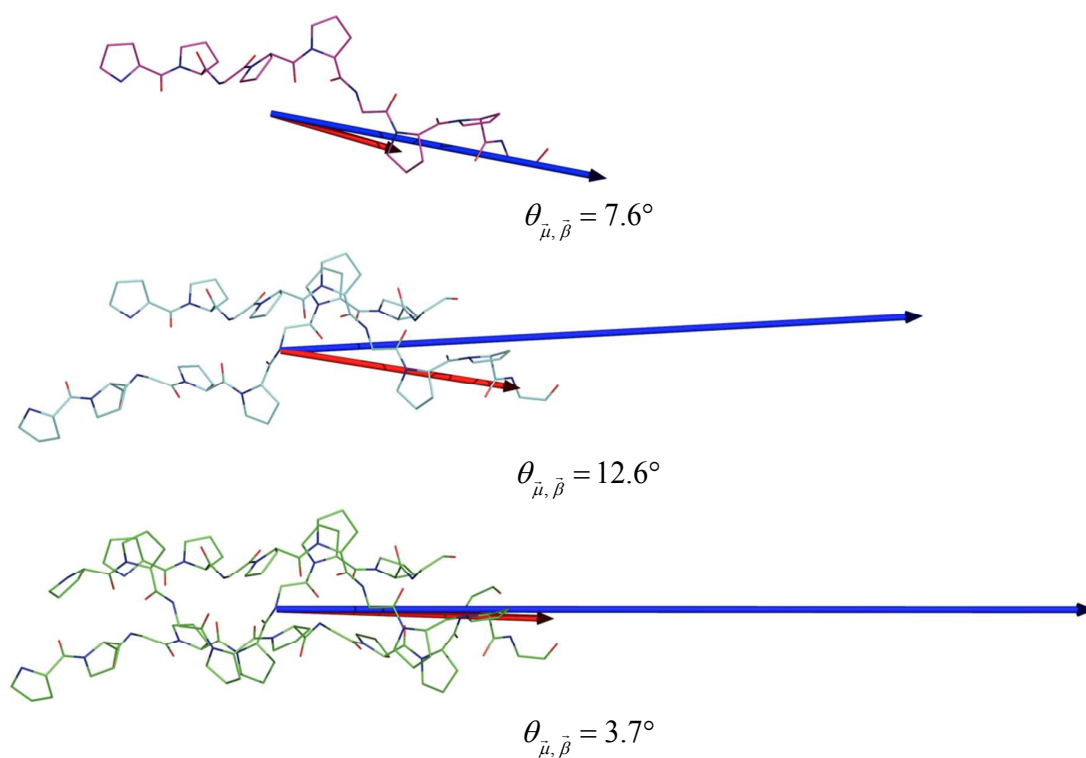


Figure S2: β (blue) and μ (red) vectors for one, two, and three helices of PPG3. These vectors have been determined at the CPHF level of calculation. The lengths of the μ and β vectors are proportional to their norms and are consistent for the three systems.

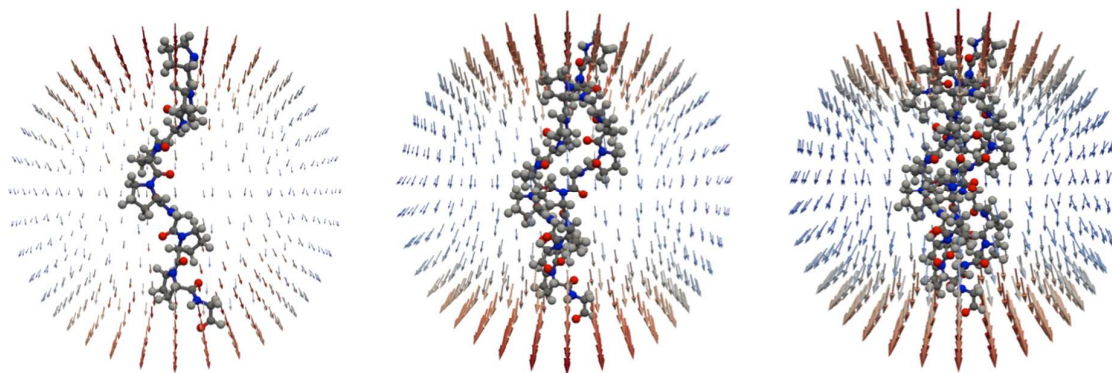


Figure S3: Unit sphere representations of the first hyperpolarizability tensor of PPG1 (left), PPG2 (middle), and PPG3 (right) obtained at the CPHF/6-31+G(d) level in vacuo.

Table S1: β_{HRS} of Pro-Pro-Gly calculated at the TDHF/CPHF level of theory with different basis sets (in a.u.).

<i>in vacuo</i>	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ
$\beta_{\text{HRS},\infty}$	54	58	56
$\beta_{\text{HRS},1900\text{nm}}$	55	59	58
$\beta_{\text{HRS},1064\text{nm}}$	58	62	61

Table S2: Representative angles (in °) that each amide group of PPG3 forms with the z-axis. The description of the angles can be found in figure S1.

	α	β	γ	$\alpha + \beta$
1st chain				
Pro1-Pro2	109	19	123	128
Pro2-Gly3	102	56	124	158
Gly3-Pro4	63	62	120	125
Pro4-Pro5	94	34	121	128
Pro5-Gly6	103	60	124	163
Gly6-Pro7	56	69	121	125
Pro7-Pro8	95	29	121	124
Pro8-Gly9	106	59	125	165
2nd chain				
Pro1-Pro2	84	39	122	123
Pro2-Gly3	112	49	124	161
Gly3-Pro4	67	61	121	128
Pro4-Pro5	93	35	121	128
Pro5-Gly6	103	53	124	156
Gly6-Pro7	65	64	121	129
Pro7-Pro8	89	39	121	128
Pro8-Gly9	82	73	125	155
3rd chain				
Pro1-Pro2	85	38	122	123
Pro2-Gly3	112	49	124	161
Gly3-Pro4	65	69	121	134
Pro4-Pro5	87	38	121	125
Pro5-Gly6	114	47	124	161
Gly6-Pro7	64	63	121	127
Pro7-Pro8	95	30	120	125
Pro8-Gly9	118	44	124	162

Table S3: Representative angles (in °) that each amide group of GGG3 forms with the z-axis. The description of the angles can be found in figure S1.

GGG3	α	β	γ	$\alpha + \beta$
1st chain				
Gly1-Gly2	65	63	126	128
Gly2-Gly3	113	14	125	127
Gly3-Gly4	92	32	124	124
Gly4-Gly5	97	47	123	144
Gly5-Gly6	106	47	124	153
Gly6-Gly7	81	47	122	128
Gly7-Gly8	91	51	123	142
Gly8-Gly9	67	76	124	143
2nd chain				
Gly1-Gly2	41	90	126	131
Gly2-Gly3	121	12	124	133
Gly3-Gly4	104	29	124	133
Gly4-Gly5	92	33	123	125
Gly5-Gly6	103	51	124	154
Gly6-Gly7	78	57	122	135
Gly7-Gly8	81	42	122	123
Gly8-Gly9	132	39	125	171
3rd chain				
Gly1-Gly2	42	83	126	125
Gly2-Gly3	131	-12	123	143
Gly3-Gly4	70	57	124	127
Gly4-Gly5	97	32	123	129
Gly5-Gly6	104	49	125	153
Gly6-Gly7	70	53	123	123
Gly7-Gly8	64	94	124	158
Gly8-Gly9	102	61	124	163

Table S4: frequency-dispersion of the HRS first hyperpolarizabilities (and depolarization ratios) of [(Pro-Pro-Gly)₁₀]₃ calculated at different levels of theory (in a.u.).

	ONIOM		ONIOM	
	HF/6-31+G(d):HF/6-31G(d)		LC-BLYP/6-31+G(d):HF/6-31G(d)	
	<i>in vacuo</i>	<i>in water</i> (IEFPCM)	<i>in vacuo</i>	<i>in water</i> (IEFPCM)
$\beta_{\text{HRS},\infty}$	2703 (8.84)	4232 (8.12)	2785 (8.85)	4480 (8.08)
$\beta_{\text{HRS},1900\text{nm}}$	2816 (8.86)	3483 (9.85)	2937 (8.88)	3521 (9.90)
$\beta_{\text{HRS},1064\text{nm}}$	3091 (8.91)	3763 (9.11)	3321 (8.92)	4140 (9.10)
$\beta_{\text{HRS},790\text{nm}}$	3472 (8.99)	4230 (9.24)	3881 (8.95)	4558 (9.28)
$\beta_{\text{HRS},694\text{nm}}$	3765 (9.04)	4861 (9.17)	4333 (8.96)	5643 (9.17)