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Supramolecular Nonlinearity of Chromophore-Functionalized Poly-L-Tyrosine

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Nonlinear optical chromophores can be organized as orientationally correlated side groups of polypeptides with a rigid backbone. In such an organization, each chromophore contributes coherently to the second-order nonlinear response of the polymer structure. The synthesis of poly-L-tyrosine, functionalized with the NLO-phores 4-nitroaniline, 2,4-dinitroaniline, 2-cyano-4-nitroaniline and 4-nitro-4'-nitroazobenzene, which is organized in α -helix conformation are presented. Solvatochromic measurements show that the hyperpolarizability of the supramolecular structure is a module factor of 18.7 higher than that of the model chromophore and that conformational organization leads to a strong enhancement of the molecular hyperpolarizability β .

Keywords: Nonlinear optics, chromophore-functionalized poly-L-tyrosine, solvatochromism

Second-order nonlinear-optical (NLO) materials are important for high-performance electro-optic modulators, frequency doublers, and holographic memories [1]. It has been proposed that supramolecular structures, *e.g.*, polypeptides, can lead to improved NLO properties, but the secondary structure of the polypeptide has not been clarified [2]. Peptide polymers have many advantages over conventional synthetic polymers

since they are able to assemble hierarchically into stable ordered conformations [3]. The achievement of such macroscopic ordering is a formidable task, because the permanent dipole moments of noncentrosymmetric molecules tend to pair in opposite directions to give rise to a centrosymmetric macroscopic structure. Construction of the 3D structure of polypeptides by combination of α -helices and β -strands may achieve the arrangement of functional chromophoric side chains to afford artificial proteins such as polypeptide electronic devices [4].

Our assumption was to combine the nonlinearity of relative simple chromophores with the possibility for covalent bonding with the side chains of the tyrosyl chromophoric system for creating a novel NLO-phoric system with own sterical conformation.

In this study we demonstrate that the attachment of NLO chromophores to a polytyrosine backbone yields structures in which the chromophores are oriented noncentrosymmetrically. This is due to the supramolecular organised structure of the polypeptide. The high dipole moment of the supramolecular structure together

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with the noncentrosymmetric alignment of chromophores yields a structure that has improved NLO properties.

The peptide poly-L-tyrosine was designed to have α -helix conformation. Poly-L-tyrosine was prepared according to Katchalski and Sela [5] with some modifications. The reaction conditions were chosen to have low molecular weight polytyrosine, concerning its sterical organization. GPC-measurements showed weight average molecular weight $M_w \approx 2200$. Poly-L-tyrosine was functionalized with the NLO-phores 4-nitroaniline, 2,4-dinitroaniline, 2-cyano-4-nitroaniline and 4-nitro-4'-nitroazobenzene by standard azo-coupling reaction. The model chromophores were synthesized by standard methods [6]. The chemical structures of the model chromophores (C1–C4) and the functionalized polypeptides (P1–P4) are shown in Figure 1.

The chromophore functionalization percentages were 56–79 mol% estimated by UV-VIS quantitative spectroscopy. The relative high functionalization percentage was chosen to achieve maximal concentration of chromophore, which is one of the main advantages of covalently bonding of the chromophore to the polymer [7].

The hyperpolarizability β was determined using the solvatochromic method [8, 9]. Dipole moments μ were determined from capacitance measurements [10, 11]. The concentration of the polymer solution was in the range $3.10^{-4} \div 3.10^{-5}$ M. The experimental results are given in Table I.

The dipole moment of a rigid supramolecular unit containing NLO chromophores can be written as a vector sum of the dipole moments of the individual chromophores (μ_{chrom}). The permanent dipole moment of such a structure can be very large, either because of the coherent addition of the dipole moments of the chromophores or because of the dipole moment associated with the supramolecular structure itself [12]. In the limit case where the supramolecular dipole moment is solely due to the chromophores, we have

$$\mu = n\mu_{\text{chrom}} \langle \cos \theta \rangle \quad (1)$$

where n is the number of chromophores in the superstructure and θ is the angle between μ_{chrom} and the net dipole moment μ of the superstructure [2]. Using Eq. (1), we obtain an order parameter $\langle \cos \theta \rangle$ of $0.42 \div 0.49$. If we assume that all chromophores make an approximately equal angle θ with respect to the net dipole moment of the supramolecular structure, we obtain an angle θ of $60 \div 65^\circ$. The observation, that in all functionalized polymers (P1–P4) the angle is approximately the same, show that the alignment of the chromophores is due to the polypeptide backbone.

All results were compared to the classical NLO-prototype 4-nitroaniline (p-NA), measured by the same conditions.

The model chromophores (C1–C4) exhibit negative solvatochromism and respectively

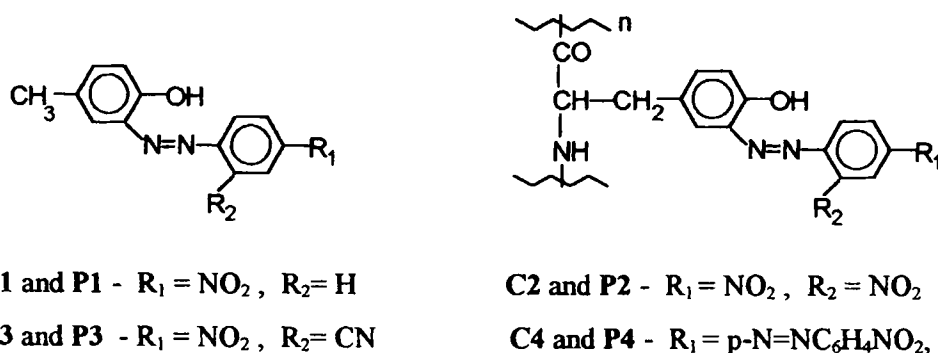


FIGURE 1 Chemical structures of the model chromophores C1–C4 and the functionalized poly-L-tyrosine P1–P4.

TABLE I Spectroscopic and NLO properties of the model chromophores (C1–C4), poly-L-tyrosine (P) and the functionalized polymers (P1–P4)

Compound	Funct. rate %	λ_{\max} (DMSO) nm	f^*	$\Delta\nu^{**}$ cm^{-1}	μ^{***} $\times 10^{30}$ C.m	$\beta_{(-2\omega; \omega\omega)}$ $\times 10^{30}$ esu	$\mu\beta_{(-2\omega; \omega\omega)}$ $\times 10^{48}$ $\text{esu}^2.\text{cm}$
p-NA	–	390	0.31	2600	17.3	0.9	4.7
C1	–	420	0.40	335	21.8	–1.6	–10.6
C2	–	429	0.33	1800	32.8	–9.4	–92.3
C3	–	441	0.44	1030	40.2	–5.6	–68.2
C4	–	387	0.57	1700	31.2	–42.0	–392.3
P	–	280	0.06	630	93.9	–1.9	–54.6
P1	79	420	4.14	1895	101.4	28.4	864.9
P2	57	420	2.00	–	116.4	–	–
P3	56	420	3.28	–	122.6	–	–
P4	60	384	4.17	3780	122.4	123.2	4521.6

* oscillator strength in DMSO.

** solvatochromic shift in toluene-dimethylsulfoxide (DMSO).

*** $3.334 \times 10^{-30} \text{C.m} = 10^{-18} \text{esu}$.

negative sign of β . Chromophores with negative β -values are uncommon [13]. We assume that the possible explication of this phenomena is the azoquinonehydrazone tautomerism [6]. In the ground state, one ring of the π -system is aromatic, and the other ring is quinonal. In the charge-separated state, the aromatic-quinonal nature of each ring is reversed, preversing the π -electron degeneracy. Molecules like these generally have negative β , since the excited-state dipole moment is usually less than the ground-state dipole moment. Similar reasoning has been used to design low band gap polymers [14].

In compounds C1 and C4 predominate the hydrazo form, whereas in C2 and C3 the azo form, probably due to the intramolecular hydrogen bond between the o,o' -substituents. The interatomic distance in C-2 is 0.154 nm and 0.185 nm in C-3 and allows for the occurrence of H-bonding (AM1) [15]. The model chromophores have reduced ground-state aromaticity and the molecules gain aromatic stabilization on charge separated resonance form [16]. Poly-L-tyrosine allone showed also negative solvatochromism. Surprisingly the functionalized polypeptides P1 and P4 showed positive solvatochromism, respectively positive β -values. That means that the NLO-properties of the supramolecular structure are not additive and the

interaction between the chromophore and the polymer backbone results in a novel NLO-phoric system. The hyperpolarizabilities of the polymer compounds P1 and P4 were much larger than those of the respective model chromophores and that of p-NA (Tab. I). This finding indicates that the chromophores are organized in a non-centrosymmetric arrangement in the polymer chain and each chromophore contributes coherently to the hyperpolarizability of the polymer. Hence, the backbone of the polypeptide contributes a significant fraction to the total dipole moment and improves the nonlinear response of the supramolecular structure. The functionalized polypeptides P2 and P3 showed not solvatochromic shift. Recently a class of NLO-chromophores which have not solvatochromic shift, but show hyperpolarizability by electric field induced second harmonic generation (EFISHG) has been described [17]. For this reason EFISHG measurements will be carried on in order to study this anomalous behavior.

The exact conformation of the polymers was studied by FT-IR spectroscopy, using Fourier self-deconvolution and second derivative spectroscopy [18]. The poly-L-tyrosine in this study was organized in α -helix structure. One helix turn seems to consist of three to four monomeric units. The centrosymmetry of the structure is

broken in the direction of the axis of the helical backbone, because all chromophores form fast the equal angle with respect to this axis. The polymers P2 and P3 preserved the helical conformation (amide I–1662 cm⁻¹), while in P1 and P4 was observed some distortion of the helical conformation and appearance maxima for β -sheet (amide I–1635 cm⁻¹). P2 and P3 have a more rigid conformation possibly due to the intramolecular H-bond and the hydrophobe stacking interactions.

Preliminary studies of the polymers indicated good thermal, photochemical and environmental stability.

Our results provide a conclusive demonstration of the principle of the enhancement of nonlinear optical response through the supra-molecular engineering of biopolymers. They show that the covalent attachment of different chromophores to the same polymer backbone results in functionalized polymers with different conformation and properties.

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