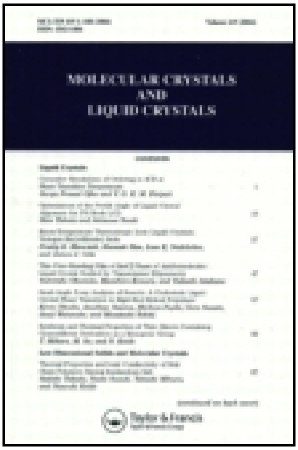

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Chirality Probed by Sum-Frequency Vibrational Spectroscopy for Helically Structured Conjugated Liquid Crystalline Polymers

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Sum-frequency vibrational spectroscopy (SFVS) has been used to probe the chirality of a polymer thin film. The polymer used has a $\pi-$electron conjugated structure in the main chain, and a chiral center in the side chains that is close to the main chain, giving rise to the helically twisted main chain. The vibrational modes probed are stretches associated with the main chain. As expected for chiral responses, we find that the chiral SFVS spectra are identical for the two enantiomers, and the signal vanishes for the racemic polymer. We also confirm experimentally that the chiral nonlinear susceptibilities for SFVS for the two enantiomers have opposite signs.

Keywords: chirality; nonlinear optics; optical activity; polymer; sum-frequency; vibrational spectroscopy

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Chirality is of great importance from the viewpoint of chemistry and biology, and probing chirality is one of interesting issues to understand the optical activity in the nonlocality of the light-matter interaction [1]. Conventional probing techniques for chirality, such as circular dichroism and optical rotation, are electric-dipole forbidden [2]. Therefore, they have limited sensitivity and hence difficulty to detect chirality from a monolayer or thin film that is often important in a chemical or biological system. Recently, second-harmonic generation (SHG) and sum-frequency generation (SFG) have been developed as effective probes for molecular chirality [3–5]. Being second-order nonlinear processes, they are allowed under electric-dipole approximation in media without inversion symmetry [6]. They also have the sensitivity to probe a monolayer. In contrast to conventional chiral probes, SHG and SFG have the advantage that both chiral and achiral nonlinear polarizability elementsare electric-dipole allowed [7]. Optical activity in sum-frequency vibrational spectroscopy (SFVS) [8] was observed for the first time in chiral liquid by the Shen's group and the electric-dipole allowed chiral elements proved to be 2–3 order magnitude smaller than typical allowed achiral elements [5]. One would then expect that the same technique can be extended to other materials such as polymers and biomaterials. To see a chiral response of chiral polymers which show a chiral nematic (colesteric) liquid crystal (LC) phase, we have conducted SFVS on thin films of unique polymers that have both helically structured and $\pi-$electron conjugated systems. We report here the first application of the technique to probe vibrational chirality in chiral LC polymer films.

The chemical structure of the chiral polymer used in this study, poly(bithienylene-phenylene) (PBTP*) derivatives [9], are shown in Figure 1. The main chain consists of two thienylene rings and one phenylene ring as a polymer unit, resulting in a $\pi-$electron conjugated structure in the main chain. In the side chain, an (R)− or (S)−chiral alkyl group is introduced and a chiral center located closely to the main chain induces the helically twisted structure of the main chain [10]. The polymer shows a colesteric LC phase with oily streaks and fingerprint textures observed under a microscope [9]. Interaction between the chiral side chains and the main chain presumably causes the main chain to twist helically. Depending on the (R)− or (S)−enantiomer, the Cotton effect was observable as shown in Figure 1. For the preparation of samples, a solution of the polymer was prepared by dissolving the material in chloroform and then dropped on a substrate to be spin-coated at 3000 rpm for 60 seconds. The film with a layer thickness was about 10–20 nm.

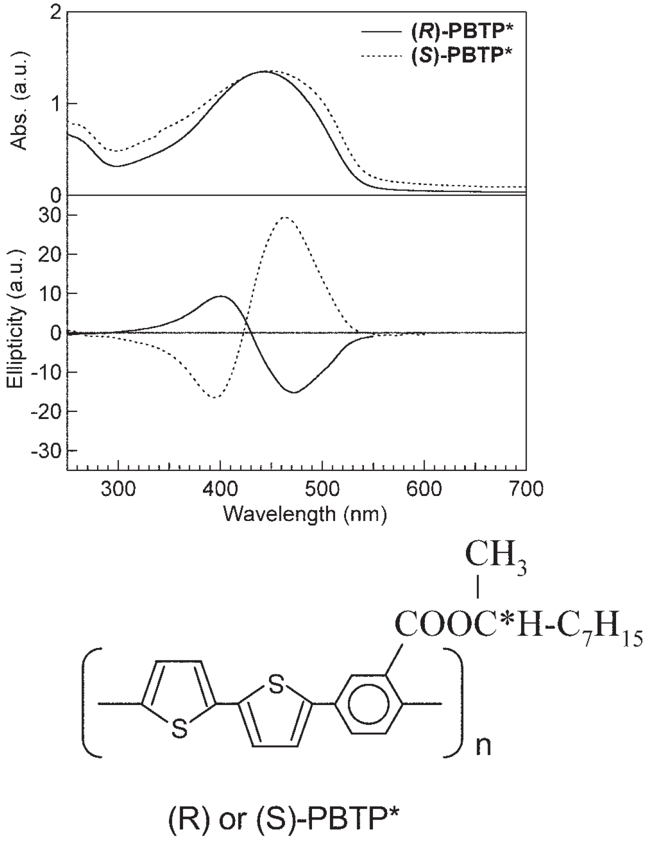

FIGURE 1 Absorption and CD spectra of (R)– and (S)–PBTP* with the chemical structure of the chiral polymer.

In a typical SFVS experiment, two input laser beams at frequencies ω_{vis} and ω_{ir} are overlapped in a medium to induce a nonlinear polarization. The effective nonlinear polarization induced is generally given by [11]

$$\vec{P}^{(2)}_{\text{eff}}(\omega) = \vec{P}^{(2)}(\omega) - i\vec{k}\cdot\overleftrightarrow{Q}^{(2)}(\omega) - \frac{1}{\omega}\vec{k}\times\overleftrightarrow{M}^{(2)}(\omega) + \cdots, \tag{1}$$

$$\overleftrightarrow{Q}^{(2)}(\omega) = \varepsilon_0\overleftrightarrow{\chi}^{qee} : \vec{E}_{\text{vis}}\vec{E}_{\text{ir}},$$

$$\overleftrightarrow{M}^{(2)}(\omega) = \omega\varepsilon_0\overleftrightarrow{\chi}^{mee} : \vec{E}_{\text{vis}}\vec{E}_{\text{ir}},$$

where $\omega = \omega_{\text{vis}} + \omega_{\text{ir}}$, and $\vec{P}^{(2)}(\omega)$, $\overleftrightarrow{Q}^{(2)}(\omega)$ and $\overleftrightarrow{M}^{(2)}(\omega)$ denote the electric-dipole polarization, electric-quadrupole polarization and magnetization, respectively. The electric-dipole term $\vec{P}^{(2)}(\omega)$ can be rewritten in the form

$$P^{(2)}(\omega) = \varepsilon_0\{\overset{\leftrightarrow}{\chi}^{eee} + i\overset{\leftrightarrow}{\chi}^{eqe} : \vec{k}_{\mathrm{vis}}\vec{E}_{\mathrm{vis}}\vec{E}_{\mathrm{ir}} + i\overset{\leftrightarrow}{\chi}^{eeq} : \vec{k}_{\mathrm{ir}}\vec{E}_{\mathrm{vis}}\vec{E}_{\mathrm{ir}} + i\overset{\leftrightarrow}{\chi}^{eme} : (\vec{k}_{\mathrm{vis}} \times \vec{E}_{\mathrm{vis}})\vec{E}_{\mathrm{ir}} + i\overset{\leftrightarrow}{\chi}^{eem} : \vec{E}_{\mathrm{vis}}(\vec{k}_{\mathrm{ir}} \times \vec{E}_{\mathrm{ir}})\}, \quad (2)$$

where $\overset{\leftrightarrow}{\chi}$'s are the second-order nonlinear susceptibilities, and "e", "q" and "m" of the superscript symbolize the electric-dipole, quadrupole and magnetic-dipole transitions, respectively. Since an achiral bulk has inversion symmetry, $\overset{\leftrightarrow}{\chi}_B^{eee} = 0$ holds good, and the only nonvanishing elements are electric-quadrupole and magnetic-dipole terms $\overset{\leftrightarrow}{\chi}_B^{QM}$ such as $\overset{\leftrightarrow}{\chi}_B^{eqe}$ and $\overset{\leftrightarrow}{\chi}_B^{eme}$ that are about 2 orders of magnitude smaller than the electric-dipole contribution $\overset{\leftrightarrow}{\chi}_S^{eee}$ that comes from the surface [12]. In a chiral bulk, however, there is no inversion symmetry, allowing us to have $\overset{\leftrightarrow}{\chi}_{B,ijk}^{eee} = \chi_{B,chiral} \cdot e_{ijk} \neq 0$ (e_{ijk} : Levi-Civita symbol), and symmetry arguments yield $\overset{\leftrightarrow}{\chi}_B^{QM} = 0$ because the different enantiomers should give the different sign of elements. Therefore one would expect to see optically active SF signal if the signal magnitude of χ_{chiral} is the same as that of a typical electric-dipole allowed element. However, Belkin *et al.* proved that χ_{chiral} appears to be 2–3 orders of magnitude smaller than typical allowed achiral elements [5]. The polarizability tensor of a medium is the orientational average of the corresponding molecular polarizability elements $\alpha^{(2)}_{\xi\eta\zeta}$, and χ_{chiral} is given by

$$\begin{aligned}\chi_{chiral} &= N \cdot \langle \alpha_{chiral} \rangle \\ &= N \cdot \frac{\alpha^{(2)}_{\xi\eta\zeta} - \alpha^{(2)}_{\xi\zeta\eta} + \alpha^{(2)}_{\zeta\xi\eta} - \alpha^{(2)}_{\zeta\eta\xi} + \alpha^{(2)}_{\eta\zeta\xi} - \alpha^{(2)}_{\eta\xi\zeta}}{6},\end{aligned} \quad (3)$$

where N is the number of molecules per unit volume. Knowing $\alpha^{(2)}_{q,\xi\eta\zeta} \sim \dfrac{\partial\alpha_{\xi\eta}}{\partial Q_q} \cdot \dfrac{\partial\mu_\zeta}{\partial Q_q}$ for the qth vibrational mode [13], where Q_q is the normal coordinate, $\dfrac{\partial\alpha_{\xi\eta}}{\partial Q_q}$ is the Raman polarizability element, and μ_ζ is the dipole moment, Eq. (3) indicates that the symmetric part of the Raman polarizability element are canceled out. The remaining terms are the antisymmentric Raman elements that are only $\sim 10^{-2}$ times as large as the symmetric components of the Raman polarizability element even beyond the Born–Oppenheimer approximation, as long as ω and ω_{vis} are far from resonance [5,14].

As for the polarizability tensor elements $\chi^{(2)}_{ijk}$ in an isotropic bulk [15], under the electric-dipole approximation, $\overset{\leftrightarrow}{\chi}_B$ vanishes for achiral bulk, but has the nonvanishing elements for chiral bulkin the form of $\chi^{(2)}_{B,xyz} = -\chi^{(2)}_{B,yxz} = \chi^{(2)}_{B,yzx} = -\chi^{(2)}_{B,xzy} = \chi^{(2)}_{B,zxy} = -\chi^{(2)}_{B,zyx}$. An achiral surface with taking the z axis along the surface normal yields the nonvanishing elements, $\chi^{(2)}_{S,xxz} = \chi^{(2)}_{S,yyz}$, $\chi^{(2)}_{S,xzx} = \chi^{(2)}_{S,yzy}$, $\chi^{(2)}_{S,zxx} = \chi^{(2)}_{S,zyy}$, and $\chi^{(2)}_{S,zzz}$. For a chiral surface, the nonvanishing elements are, in addition, $\chi^{(2)}_{S,xyz} = -\chi^{(2)}_{S,yxz}$, $\chi^{(2)}_{S,yzx} = -\chi^{(2)}_{S,xzy}$, and $\chi^{(2)}_{S,zxy} = -\chi^{(2)}_{S,zyx}$. Each chiral element should change sign for different enantiomers in a chiral medium and vanish for a racemic mixture [7]. The achiral elements $\chi_{achiral}$ are accessed by the *SSP*, *PPP* and *SPS* polarization combinations, while the chiral elements χ_{chiral} can separately be accessed by the *SPP*, *PSP* and *PPS* polarization combinations.

The SFVS experiment has been described elsewhere [16]. In this experiment, we used a EKSPLA Nd:YAG laser with 30 mJ pulse energy, and 25 ps pulsewidth, operating at a repetition rate of 20 Hz. The laser pumped an optical parametric/difference-frequency generation system to produce tunable infrared output in the 6.0–7.0 μm range with ∼30 μJ μJ pulse energy, 25 ps pulsewidth, and 6 cm^{-1} bandwidth. The tunable IR beam and a frequency-doubled output (532 nm) from the laser overlapped at the air/polymer interface with incidence angles of 45° and 57°, respectively. The reflected SF signal was detected by a gated photodectector system. To minimize possible laser damage of the sample, we limited the pulse energy of the 532-nm input to ∼50 μJ pulse energy, and the laser spot on the sample was moved frequently.

Shown in Figure 2 are the SFVS spectra in the phenylene C−C stretch region from 1500 to 1650 cm^{-1} for the two enantiomers, (R)− and (S)−PBTP* and the racemic PBTP obtained in reflection with six input/output polarization combinations: *SSP* (denoting *S*−polarized SF output, *S*−polarized visible input, and *P*−polarized infrared input, respectively), *PPP*, *SPS*, *SPP*, *PSP* and *PSP*. The spectra were normalized with respect to a reference crystalline quartz. The details of the vibrational mode have not been identified so far, but the observed modes were confirmed to come from the phenylene ring in the main chain by comparing an IR spectrum of PBTP* with that of poly(trithienylene) which has no phenylene ring in the structure. The *SSP*, *PPP* and *SPS* spectra come only from the achiral elements, whereas the *SPP*, *PSP* and *PPS* spectra originate only in the chiral elements. From the spectra, we can readily obtain some information for the chirality. The SFVS for the two enantiomers appear to be the same, however, no chiral signal that appears in *SPP*, and *PSP* and *PPS* polarization combinations can be detected for the racemic

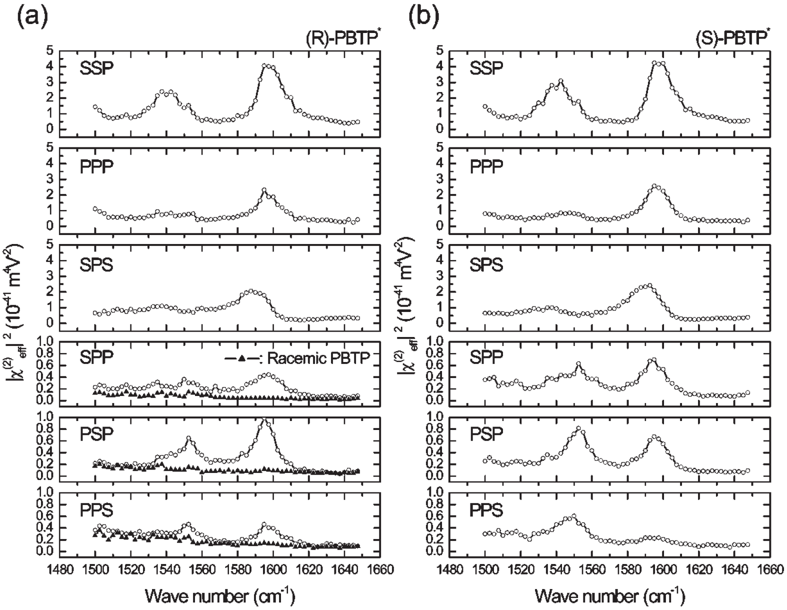

FIGURE 2 SFVS spectra of (a) (R)−PBTP* with the data for Racemic-PBTP (▲), and (b) (S)-PBTP* thin films in reflection with *SSP*, *PPP*, *SPS* (achiral spectra), *SPP*, *PSP*, and *PPS* (chiral spectra) polarization combinations. The spectra are normalized by the SF signal from a z-cut quartz.

polymer film. This clearly indicates that we have optically active signal and the associated vibrational spectrum for chiral polymer. Since the SFVS measurement was done by in reflection, the dominating achiral signal must be contributed by the surface as the previous study pointed out [12]. The shape of the *SPP*, *PSP* and *PPS* spectra appears more or less similar, indicating that the chiral signal must come from the bulk because the film is isotropic due to the spin-coating and the number of the independent chiral elements is only one. However, while this is roughly true with our experimental results shown in Figure 2, there are appreciable differences. The discrepancy is mainly due to experimental difficulty to attain pure *S* or *P* polarization and reproducible experimental geometry. Because $\left|\frac{(\chi_B^{(2)})_{(chiral)}}{\Delta k}\right|$ is significantly smaller than $\left|(\chi_S^{(2)})_{(achiral)}\right|$, impure polarization could result in mixing of an appreciable contribution of achiral response into the chiral response.

We experimentally confirmed that χ_{chiral} should change sign for the two enantiomers by measuring the spectra with *PMP* polarization

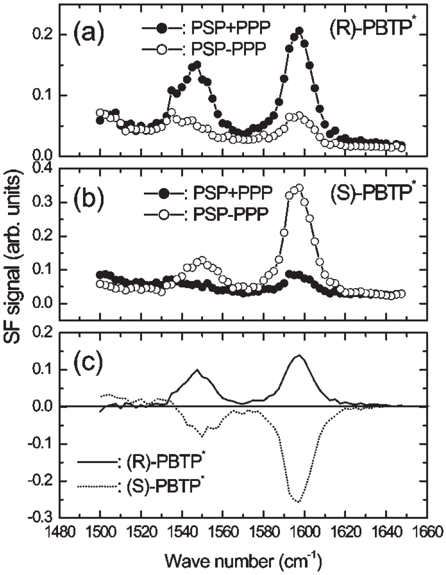

FIGURE 3 SFVS spectra of (a) (R)−PBTP*, and (b) (S)−PBTP* with the *PMP* polarization combinations. (c) Difference spectra of the *PMP* polarization combinations proportional to $\left|\left(\chi_{eff}^{(2)}\right)_+\right|^2 - \left|\left(\chi_{eff}^{(2)}\right)_-\right|^2$ for (R)− and (S)−PBTP*.

combination, where $M = 1/\sqrt{2}(S \pm P)$ refers to a linear of the visible beam at ±45° from its plane of incidence. So the effective $\overset{\leftrightarrow}{\chi}^{(2)}$ measured by the *PMP* polarization combinations can be given by $\left(\chi_{eff}^{(2)}\right)_\pm = \frac{1}{\sqrt{2}}\left(\chi_{eff}^{(2)}(PSP) \pm \chi_{eff}^{(2)}(PPP)\right)$, indicating that the SF signal $\left|\left(\chi_{eff}^{(2)}\right)_\pm\right|^2$ should give us interference between χ_{chiral} and $\chi_{achiral}$. Figure 3 shows the SFVS spectra of (R)- and (S)-PBTP* enantiomers with the *PMP* polarization combinations. The bottom figure is the difference spectra by $\left|\left(\chi_{eff}^{(2)}\right)_+\right|^2 - \left|\left(\chi_{eff}^{(2)}\right)_-\right|^2$ for each enantiomer. The difference spectrum proportional to $\left|\left(\chi_{eff}^{(2)}\right)_+\right|^2 - \left|\left(\chi_{eff}^{(2)}\right)_-\right|^2$ is written by

$$\left|\left(\chi_{eff}^{(2)}\right)_+\right|^2 - \left|\left(\chi_{eff}^{(2)}\right)_-\right|^2 = \chi_{eff}^{(2)}(PSP)\chi_{eff}^{(2)^*}(PPP) + \chi_{eff}^{(2)^*}(PSP)\chi_{eff}^{(2)}(PPP), \quad (4)$$

Since $\chi_{eff}^{(2)}(PSP)$ changes sign, the difference spectrum should also change sign as (R)$-$PBTP* is replaced by (S)$-$PBTP*. As expected, the inverted spectra were observed by (R)$-$ and (S)$-$PBTP* as seen in Figure 3(c), allowing us to conclude that optically activity in SFVS has been observed with PBTP* thin films.

As mentioned earlier, optical activity in SFVS was observed for the first time in chiral liquids such as limonene [5]. The transmission measurements were required to observe chirality, while no chiral signal could be distinguished in reflection. This is because the electric-dipole allowed χ_{chiral} elements are smaller than the typical allowed achiral elements $\chi_{achiral}$ and the longer coherence length in the transmission measurement can help gain the chiral signal. Interestingly, all our spectra for PBTP* were measured in reflection and the chiral signal was appreciable as seen in the spectra. Presumably this is related to the electronic pump by the visible beam. Recent studies indicate that the chiral response can be enhanced in SFG near electronic resonances and delocalized electrons associated with the chiral molecular structure can be effective to let the chiral SFG above the detection limit [15,17–19]. Actually, any chiral signal was hardly discernible in the region of the C$-$H stretch directly associated with the side chain, while the lower frequency region associated with the main chain along which $\pi-$electrons were delocalized gave us the chiral response. As another evidence, a 1.06 μm beam used as visible input for SFVS did generate no chiral response, although a 532 nm visible beam allowed us to have the appreciable chiral responses. These facts are consisting with the recent studies that chiral responses are enhancednear electronic resonances and doubly resonance SFG would be more effective to measure chirality [15,17–19].

In conclusion, we have shown the first application of the SFVS technique to probe vibrational chirality in chiral polymer films and proved the versatile capability of SFVS as a vibrational spectroscopic tool for probing chirality. As is the case for chiral responses, the chiral SFVS spectra are identical for the two enantiomers, and the signal vanishes for the racemic polymer. We also confirm experimentally that the chiral nonlinear susceptibilities for SFVS for the two enantiomers have opposite signs. The chiral SFVS spectra of the polymer are relatively strong due to near-resonance enhancement since the visible input is close to the first electronic transition band of the conjugated main chain.

REFERENCES

[1] See, for example, L. D. Barron, (1982). *Molecular Light Scattering and Optical Activity*, Cambridge University Press: Cambridge, UK.

[2] Condon, E. U. (1937). *Rev. Mod. Phys.*, 432.

[3] Petralli-Mallow, T., Wong, T. M., Byers, J. D., Yee, H. I., & Hicks, J. M. (1993). *J. Phys. Chem.*, 1383; Byers, J. D., Yee, H. I., Petralli-Mallow, T., & Hicks, J. M. (1994). *Phys. Rev. B*, 14643; Byers, J. D., Yee, H. I., & Hicks, J. M. (1994). *J. Chem. Phys.*, 6233; Hicks, J. M., Petralli-Mallow, T., & Byers, J. D. (1994). *Faraday Discuss.*, 341; Byers, J. D. & Hicks, J. M. (1994). *Chem. Phys. Lett.*, 216.

[4] Maki, J. J., Kauranen, M., & Persoons, A. (1995). *Phys. Rev. B*, 1425; Kauranen, M., Verbiest, T., & Persoons, A. (1998). *J. Mod. Opt.*, 403.

[5] Belkin, M. A., Kulakov, T. A., Ernst, K.-H., Yan, L., & Shen, Y. R. (2000). *Phys. Rev. Lett.*, 4474.

[6] Shen, Y. R. (1984). *The Principle of Nonlinear Optics*, Willy: New York.

[7] Giordmaine, J. A. (1965). *Phys. Rev.*, A1599.

[8] Zhu, X. D., Suhr, H., & Shen, Y. R. (1987). *Phys. Rev. B*, 3047; Shen, Y. R. (1994). In: *Proceedings of the International School of Physics "Enrico Fermi"*, *Course CXX*, *Frontier in Laser Spectroscopy*, Hansch, T. W. & Inguscio M. (Eds.), Amsterdam: North Holland, 139; Shen, Y. R. (1994). *Surf. Sci. /300*, 551.

[9] Akagi, K., Piao, G., Kaneko, S., Sakamaki, K., Shirakawa, H., & Kyotani, M. (1998). *Science*, 1683; Osaka, I., Nakamura, A., Inoue, Y., & Akagi, K. (2002). *Trans. Mater. Res. Soc. Jpn.*, 567; Yorozuya, S., Osaka, I., Nakamura, A., Inoue, Y., & Akagi, K. (2003). *Synth. Met.*, *-136*, 93.

[10] Langerveld-Voss, B. M. W., Janssen, R. A. J., Christiaans, M. P. T., Meskers, S. C. J., Dekkers, H. P. J. M., & Meijer, E. W. (1996). *J. Am. Chem. Soc.*, 4908; Langerveld-Voss, B. M. W., Janssen, R. A. J., & Meijer, E. W. (2000). *J. Mol. Str.*, 285; Other references are therein.

[11] Guyot-Sionnest, P. & Shen, Y. R. (1988). *Phys. Rev. B*, 7985.

[12] Wei, X., Hong, S.-C., Lvovsky, A. I., Held, H., & Shen, Y. R. (2000). *J. Phys. Chem. B*, 3349.

[13] Superfine, R., Huang, J. Y., & Shen, Y. R. (1990). *Chem. Phys. Lett.*, 303.

[14] Liu, F. (1991). *J. Phys. Chem.*, 7180.

[15] Han, S. H., Ji, N., Belkin, M. A., & Shen, Y. R. (2002). *Phys. Rev. B*, 165415.

[16] Zhuang, X., Miranda, P. B., Kim, D., & Shen, Y. R. (1999). *Phys. Rev. B*, 12632.

[17] Belkin, M. A., Han, S. H., Wei, X., & Shen, Y. R. (2001). *Phys. Rev. Lett.*, 113001.

[18] Belkin, M. A., Flytzains, C., & Shen, Y. R. (2002). *Chem. Phys. Lett.*, 479.

[19] Belkin, M. A. & Shen, Y. R. (2003). *Phys. Rev. Lett.*, 213907.