LETTER TO THE EDITOR

Scanning second-harmonic microscopy of a thin film of σ–π copolymer with 2,2'-bipyridine in the backbone

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Abstract. Scanning second-harmonic microscopy was used to study the lateral distribution of the second-order optical nonlinearity of a σ–π copolymer [poly(disilanylene-2,2'-bipyridine-5,5'-diyl) ruthenium complex (PDSBpy–Ru)] thin film on a glass substrate. The orientation of the dipolar chromophores and establishment of the noncentrosymmetry required by the macroscopic second-order optical nonlinearity were resulted from natural coordination of the PDSBpy–Ru molecules to the surface Si–O–H groups on the glass substrate. A homogeneous lateral distribution of the coordination-induced poling was observed.

Significant progress has been made in polymer photonics and optoelectronics in the past years. Much effort has been devoted to characterizing known polymers, synthesizing novel polymeric materials, demonstrating fundamental photonic and optoelectronic functions, and inventing new polymer devices [1]. It is well-known that π-conjugation gives rise to large optical nonlinearities. 2,2'-bipyridine is a very interesting π-system, whose electron affinity may be tunable by regulating coordination to a Lewis acid or transition metal [2]. Recently, there has been increasing interest in the synthesis and analysis of novel polymers incorporating 2,2'-bipyridines [3]. An intriguing example is a copolymer consisting of a regular alternating arrangement of silicon σ and 2,2'-bipyridine π units in the backbone, such as poly(disilanylene-2,2'-bipyridine-5,5'-diyl) ruthenium complex (PDSBpy–Ru). On the one hand, a PDSBpy–Ru molecule incorporates tris(bipyridine) ruthenium complexes, which exhibit interesting electron-transfer properties through metal-to-ligand charge transfer (MLCT) processes [4]. Recent research has revealed that MLCT excitations are generally accompanied by large nonlinear-optical responses, owing to the large oscillator strengths and large difference between ground and first excited-state dipole moments [5]. On the other hand, a PDSBpy–Ru molecule has silicon σ units which are believed to offer efficient photoconductivity, due to the high hole mobility arising from σ-conjugated Si–Si bonds. The PDSBpy–Ru (σ–π copolymer) belongs to a novel type of photoconductive polymer [6]. Its efficient photoconductivities come from the efficient photogeneration of charge carriers by MLCT photoexcitations, and high charge carrier mobility originates from the σ-conjugated silicon units. The high charge carrier mobility may provide further photocharge separation inside the PDSBpy–Ru molecule after the MLCT photoexcitation, which may consequently induce inter-molecular interaction. Moreover, since 2,2'-bipyridine is able to coordinate an acidic H to form the s-cis conformation [7], while glass is considered to have acidic Si–O–H groups, PDSBpy–Ru molecules can be aligned to the

surface Si–O–H groups on a glass substrate. This may give rise to orientation of the dipolar chromophores of the PDSBpy–Ru thin film on a glass substrate, and therefore establishes the noncentrosymmetry required by the second-harmonic generation. For comparison, one may note that electric poling of nonlinear optical polymers under a strong static electric field near the glass transition temperature is a widely-used technique to achieve macroscopic second-order nonlinearity. However, the standard electric poling procedures do not trivially lead to homogeneous distributions of polar orientation, due to the poling field distortions, particularly in the areas around the edges of patterned poling electrodes. We will demonstrate in this letter that coordination-induced natural poling gives rise to homogeneously poled thin films of PDSBpy–Ru on glass substrates.

The chemical structure of the PDSBpy–Ru molecule is shown in figure 1. Chemical synthesis of this polymer was reported elsewhere [8]. Briefly speaking, in a PDSBpy–Ru molecule, Si–Si bonds connect 2,2'-bipyridines and planar structures of 2,2'-bipyridyl ruthenium complexes. The silicon σ units offer not only electron conjugation but also electronic connection of the π units. The ruthenium content was determined to be about 35 mol% per bipyridine in the polymer backbone by ^{1}H NMR spectroscopy. The PDSBpy–Ru thin film was prepared by spin-coating a chloroform solution of PDSBpy on a glass substrate, which was precleaned step-by-step with acetone and methanol, and followed by sufficient baking in a vacuum oven. After baking gradually in a vacuum oven to remove all traces of solvent, the thickness of the film was a few micrometers. Figure 2 shows the absorption and fluorescence spectra of a PDSBpy–Ru thin film on a glass substrate and chloroform solution of the PDSBpy–Ru. Absorption maximum of bipyridine $\pi-\pi^*$ transition appears around 318 nm for the PDSBpy–Ru in chloroform. Another absorption peak around 460 nm is assigned to the MLCT band. The PDSBpy–Ru complex emits red light when irradiated by a UV laser. As shown in figure 2, fluorescence of the PDSBpy–Ru in chloroform peak occurs at 630 nm. Fine structures of the fluorescence peaks were not revealed. Spectral broadening and redshifts occur for the fluorescence of a PDSBpy–Ru thin film.

We implemented scanning second-harmonic microscopy (SSHM) to study the lateral distribution of the macroscopic second-order nonlinearity. The basic concept of the SSHM is the lateral scanning of the polymer thin film by a spatially confined laser beam that generates a second-harmonic wave. The square root of the second-harmonic signal is a relative measure for the local second-order nonlinear susceptibility $\chi^{(2)}$. Such an idea was first introduced in 1978 and was applied to image inorganic single crystals like KD*P and LiNbO$_3$ [9]. Similar techniques, based on scanning electro-optical and pyroelectrical microscopy, were also developed [10, 11]. SSHM was recently used to map the lateral $\chi^{(2)}$ distribution of electrically poled nonlinear optical polymer thin films [12, 13]. Since SSHM was an optical measurement technique, the lateral resolution was limited by the diameter of the probing beam
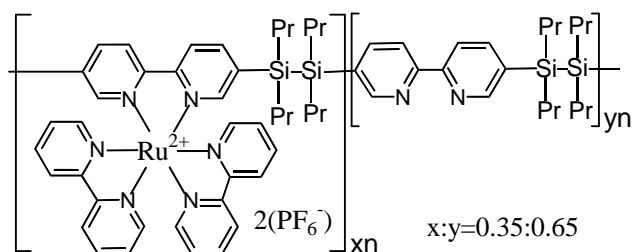

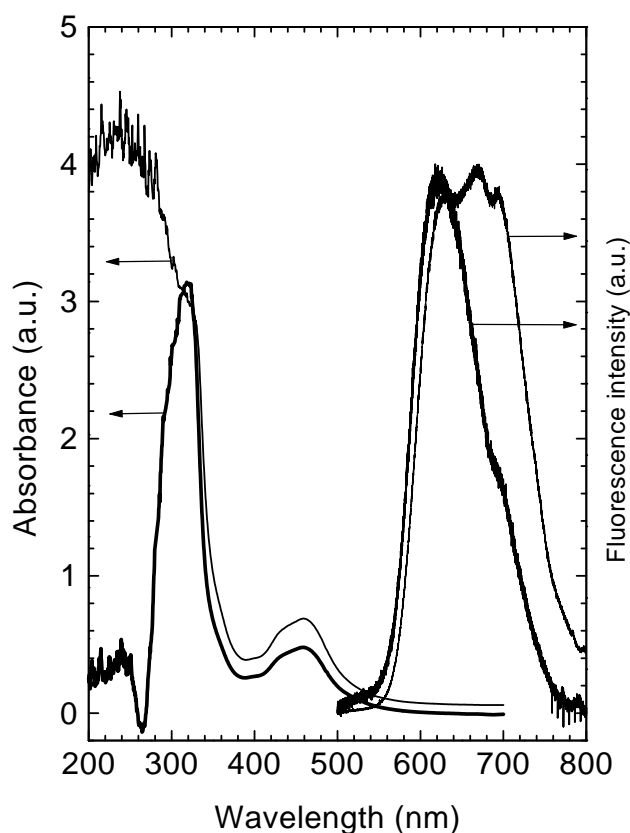**Figure 1.** The chemical structure of the PDSBpy–Ru molecule.

Figure 2. UV-vis absorption and fluorescence spectra of PDSBpy–Ru in chloroform (thick curves), and the PDSBpy–Ru thin film on the glass substrate (thin curves).

at the position of the sample. We have used a microscope objective to get a lateral resolution of a few micrometers, which was enough to map the molecular orientation inside the PDSBpy–Ru thin film. The experimental set-up is shown in figure 3. The fundamental beam for the SSHM experiment was provided by a CW mode-locked Ti:Sapphire laser with a line width of about 0.25 nm, a pulse width of 2 ps, and a repetition rate of 76 MHz. The maximum output power was about 400 mW at a wavelength near 800 nm. Tight focusing of the fundamental beam was attained by the use of a microscope objective lens (40×) with a numeric aperture (NA) of 0.65, and a focal length of about 2.5 mm, yielding a beam diameter of $2w_0 \approx 4$ μm at the focus point, where w_0 is the minimum $1/e^2$ beam radius. The second-harmonic generation was collected in a reflection configuration with the same microscope objective. Two-photon fluorescence was very weak with a peak near 600 nm, which could be easily separated from the second-harmonic signal. The collected signal was detected by an intensified CCD camera through a poly-grating monochromator with a spectral resolution of 0.1 nm. The intensity and polarization of the fundamental beam were controlled by neutral density filters and a half-wave plate, respectively. The PDSBpy–Ru thin film was placed in an x–y–z micro-translation stage. In our experimental geometry, the sample can only be scanned under the normal incidence.

The fundamental Ti:Sapphire laser beam may be approximately regarded as a TEM$_{00}$ Gaussian beam. As mentioned above, a tight focusing with the microscope objective yielded
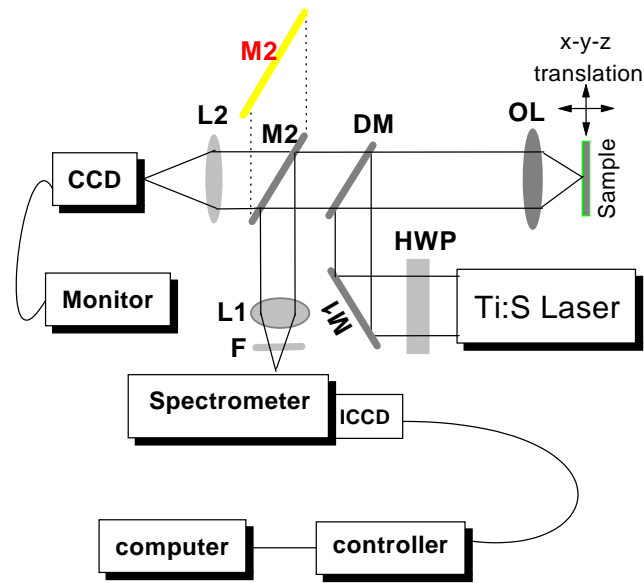
Figure 3. Experimental set-up of the size-selective second-harmonic generation. The sample was placed in an x–y–z three-dimensional micro-translation stage. HWP: half wave plate; M1, M2: mirrors; OL: objective lens; DM: dichroic mirror; L1,L2: lenses; F: filter. The mirror M2 was movable for the switch between the CCD imaging and spectrometer/ICCD detectors. The CCD imaging system was used to monitor the beam focusing condition and measure the tightly focused beam diameter.

a minimum beam radius of $w_0 \approx 2$ μm at the focus point. Nevertheless, the sample was intentionally positioned slightly out of the focus point with a distance of about 3 μm to get the optimum second-harmonic generation. This reduced the lateral resolution slightly. The beam radius on the sample was monitored by a CCD imaging system, which was measured to be less than 5 μm under our tight focusing condition. The second-harmonic generation can be observed mainly due to the large angle of aperture of the high NA microscope objective. It was assumed to take a Gaussian form [14]

$$E_2(r, z, t) = A_2(r, z, t) \exp[\mathrm{i}(\vec{k}_2 \cdot \vec{r} - 2\omega t)] + c.c.$$

$$A_2(r, z) = \frac{\mathcal{A}_2(z)}{1 + \mathrm{i}\zeta} \exp[-2r^2/w_0^2(1 + \mathrm{i}\zeta)]$$

$$\mathcal{A}_2 = \frac{\mathrm{i}4\pi\omega}{nc} \chi^{(2)} \mathcal{A}^2 J_2(\Delta k, z_0, z) \tag{1}$$

where $\Delta k = \vec{e}_z \cdot (2\vec{k} - \vec{k}_2)$ with $\vec{e}_z$ the unit vector along the z-axis, $\vec{k}$ and $\vec{k}_2$ are the wave vectors of the fundamental and second-harmonic beams, respectively, and

$$J_2(\Delta k, z_0, z) = \int_{z_0}^{z} \frac{\exp[\mathrm{i}\Delta k z']\mathrm{d}z'}{1 + 2\mathrm{i}z'/b} \tag{2}$$

where $\zeta = 2z/b$ is a dimensionless longitudinal coordinate defined in terms of the confocal parameter $b \equiv 2\pi w_0^2/\lambda = k w_0^2$, and z_0 and z represent the z-axis position values at the entrance to and exit from the polymer thin film, respectively. The parameter b is a measure of the longitudinal extent of the focal region of the Gaussian beam.

In our measurement, all the reflected second-harmonic generation was collected into the detector (ICCD after the monochromator). The reflection of the second-harmonics occurred
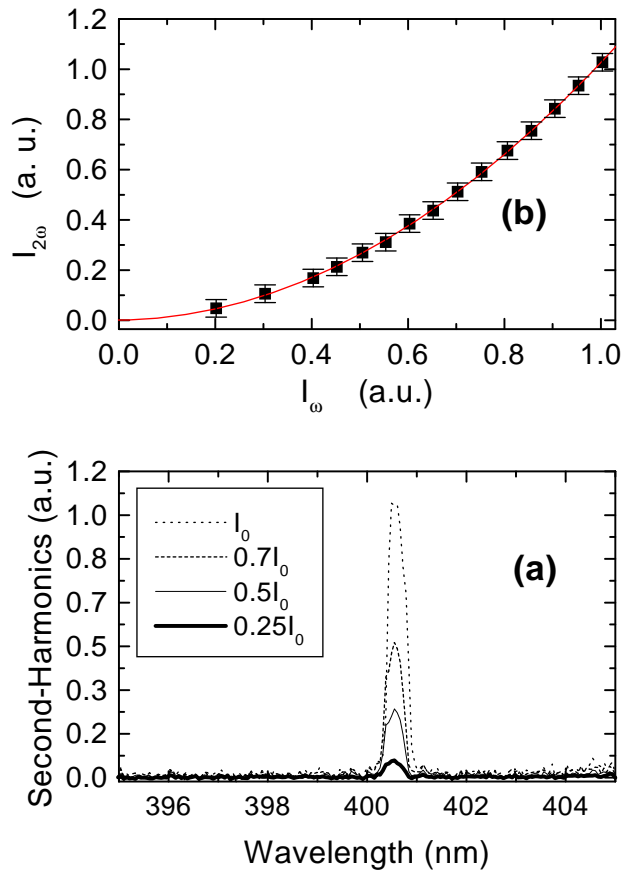
Figure 4. (a) The second-harmonic generation spectrum of the PDSBpy–Ru thin film at a fundamental wavelength of 801 nm. (b) The intensity dependence of the second-harmonic generation upon the fundamental intensity.

in the interface between the PDSBpy–Ru film and the glass substrate. The measured signal $\mathcal{P}_2 = \int I_2 2\pi r \, dr$ was proportional to the square of the second-harmonic susceptibility $\chi^{(2)}$, where $I_2 = (nc/2\pi)|A_2|^2$ was the intensity of the second-harmonic generation. The second-harmonic spectra at various fundamental pumping powers are shown in figure 4(a). As indicated in figure 4(b), the detected signal of the second-harmonic generation was relatively measured to be dependent on the pumping power with a relation $\mathcal{P}_2 \propto \mathcal{P}^2$, which agreed well with the above theoretical analysis for the second-harmonic generation of a tightly focused fundamental Gaussian beam.

Observation of the macroscopic second-harmonics implied that there existed noncentrosymmetric alignment of the PDSBpy–Ru molecules. The glass substrate has acidic Si–O–H groups, and 2,2'-bipyridine, the unit component of the PDSBpy–Ru, is known to coordinate acidic H to form the s-cis conformation, in spite of the s-trans conformation in the ordinary state [7]. As shown in figure 5, the alignment of the dipolar chromophores at the interface came from the coordination of the PDSBpy–Ru molecules to the surface Si–O–H groups. The macroscopic second-order nonlinearities were assumed to have arisen from the coordination-induced alignment of the first PDSBpy–Ru layer neighbouring the glass
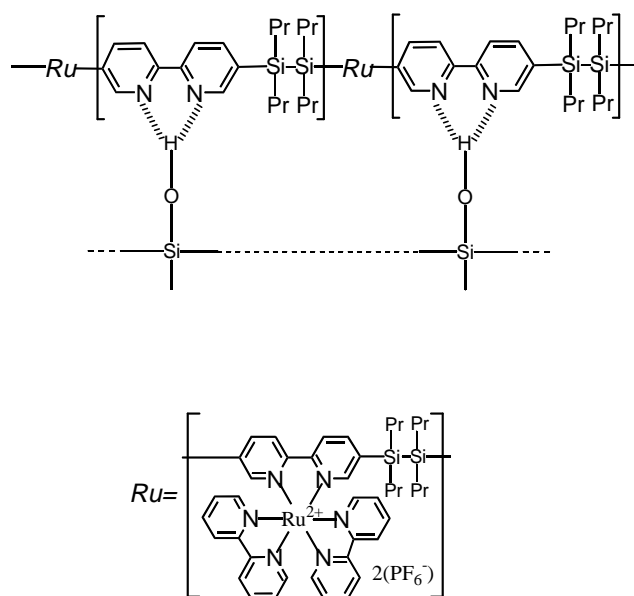
Figure 5. Coordination of PDSBpy–Ru molecules to the Si–O–H group, which gives rise to the alignment of PDSBpy–Ru molecules along the direction of the surface of the glass substrate.

substrate. However, the upper molecular layers above the first layer may be aligned along different directions [15]. We note that the observed signals of the second-harmonics were small, which meant that the effective second-order susceptibility $\chi^{(2)}$ was small. This may be due to the partly macroscopic poling of the PDSBpy–Ru molecules. Moreover, though there was an absorption valley near 400 nm in the UV-vis absorption spectrum, there still existed observable reabsorption and loss of the second-harmonic generation (near 400 nm), in particular in our measurement with reflective configuration. Loss of the fundamental laser beam due to two-photon absorption also affected the second-harmonics signals.

Interestingly, by scanning the film with the x–y–z micro-translation stage, we found that the second-harmonic signals at different positions were approximately of the same amplitudes. Figure 6 presents the second-harmonic signals scanned along two perpendicular directions. This indicated nearly homogeneous alignment of the dipolar chromophores, and PDSBpy–Ru molecules as well. It may be postulated that alignment of several rigidly linear PDSBpy– Ru molecules caused alignment of other molecules, which ensured a nearly homogeneous molecular orientation over a relatively large lateral range. However, there were still many ways to cause fluctuations of the observed signals, such as the inhomogeneity of the PDSBpy– Ru thin film itself, and the scattering of the fundamental beam.

In summary, scanning second-harmonic microscopy was used to study the spatial variation of the second-order nonlinear optical response of a σ–π copolymer (PDSBpy–Ru) thin film on a glass substrate. The 2,2'-bipyridines coordinated the acidic H in the surface Si–O–H groups of the glass substrate, which produced homogeneous orientation of the dipolar chromophores of the PDSBpy–Ru thin film, and therefore noncentrosymmetric alignments of the PDSBpy–Ru molecules. The second-harmonic generation was demonstrated to accompany the multiphoton MLCT excitations of the aligned PDSBpy–Ru molecules. Spatial homogeneity of the second-harmonic generation was observed, which indicated that the coordination-induced poling produced homogeneously poled thin films of PDSBpy–Ru on glass substrates. Furthermore,
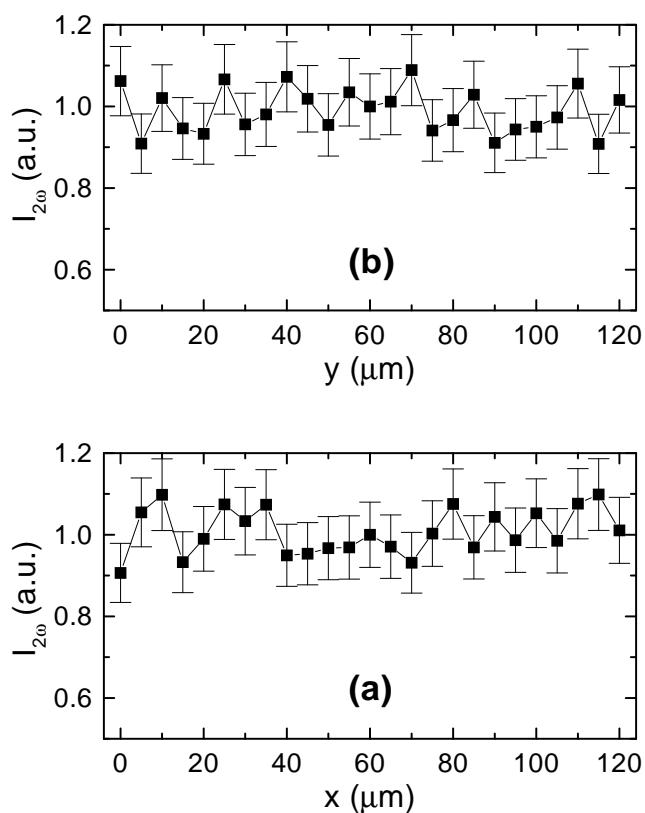
Figure 6. Lateral distributions of the second-harmonics in a PDSBpy–Ru thin film measured with scanning second-harmonic microscopy along two perpendicular directions x (a) and y (b).

PDSBpy–Ru molecules were chemically stable under the investigated irradiation conditions. The characteristic UV-vis absorption spectra remained unchanged after continuous laser irradiation for more than ten hours [8]. Interestingly, each component of such a $\sigma-\pi$ copolymer can be optimized for specific function of applications without affecting the optical responses by intelligent molecular designs. This may offer a novel type of high-performance nonlinear optical and optoelectronic material.

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