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Wavelength dependence of optical nonlinearity of terpyridine-based Zn(II)-coordinated rigid linear polymers

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We present the wavelength dependent optical nonlinearities of two terpyridine-based Zn(II)-coordinated rigid linear polymers. It is found that the polymers exhibit large saturable absorption behavior under resonant excitation, while strong and tunable 2-photon absorption behaviors are observed in the biological window of 700–900 nm. Interestingly, Z-scan results reveal that, the polymers also exhibit large positive nonlinear refraction at 1300 nm in the solutions even with a low concentration, accompanied by small 3-photon absorption. Our results suggest that the polymers will be promising in various photonic applications, such as mode locking, 2-photon biological imaging, and all-optical switching. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4767390>]

Because of the broad applications in military and civilian fields, including optical limiting, mode locking, biological imaging, and all-optical switching, nonlinear optical (NLO) materials have gained intense attention.¹ So far, significant NLO behaviors have been observed in a variety of materials, such as inorganic nanoparticles² and semiconductors³ and organic molecular and polymeric materials.⁴ Among these possible NLO materials, molecular engineering has been one of the major pathways that have been exploited to achieve strong optical nonlinearity, combined with molecular fast response time, and processibility.⁵

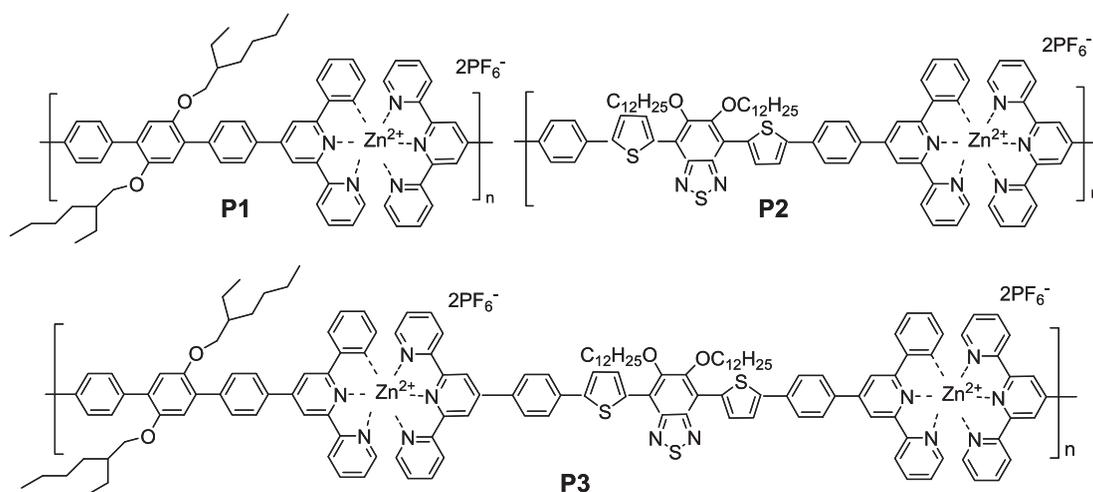
The last two decades have witnessed significant progress in the realm of metal-organic coordination compounds, due to their high yielding synthesis and superior physical and chemical stability.⁶ Extensive efforts have been devoted to fabricate various species with diverse topologies to correlate the relationship between the molecular structure and suitability for specific applications. The metal ions in the coordination compounds not only increase the molecular number density but also enhance the intramolecular charge-transfer process, which can be used to enhance optical nonlinearity. However, there are only few studies of the dependence of NLO properties on structure, although this is of crucial importance for optimizing their optical properties.⁷ Meanwhile, almost all the existing reports used small molecules as the research targets. Unfortunately, small molecules have the disadvantages of possible phase separation, crystallization, or the formation of concentration gradients when NLO chromophores are incorporated with high concentration, which will seriously limit their use in real applications. By contrast, the use of polymers can overcome these problems. In this letter, we have investigated the NLO properties of two terpyridine-based Zn(II)-coordinated rigid linear polymers in the visible to near-infrared regions. Wide spectral informa-

tion about their structure-dependent NLO mechanism, which is usually absent in previous reports, has been obtained. Based on the experimental results, we conclude that, due to their rigid structures, the polymers present large optical nonlinearity in the visible to near-infrared regions, indicating wide range of possible applications including as saturable absorbers, or in 2-photon biological imaging and all-optical switching.

The molecular structures for Zn(II)-terpyridine coordinated polymers **P2** and **P3** investigated in this letter, as well as polymer **P1** used for reference, are shown in Figure 1. The detailed synthesis of the polymers was published elsewhere.⁸ The use of terpyridine ligands in the polymers produced high binding constants by $d\pi \rightarrow p\pi^*$ bonding and induced the formation of distorted octahedral 2:1 ligand-complexes. The choice of Zn(II) was due to its thermodynamically stable bond and low cost. As shown in Figure 1, monomer of **P3** contains alternating monomers of **P1** (donor) and **P2** (acceptor), which allows the efficient energy transfer from donor to acceptor in **P3**. In this work, the optical nonlinearities were investigated using Z-scan experiments.⁹ The solutions were filled in 1-mm length quartz cells and were excited by 100 fs laser pulses, with a repetition rate of 1000 Hz.

In general, saturable absorption (SA) often occurs for resonant excitation. In our case, due to the large molar extinction coefficient in absorption band (UV-vis linear absorption spectrum is shown in supporting information, Figure S1 (Ref. 23)), we anticipated that at low power intensity, SA may be observed. As shown in Figure 2(a), open aperture Z-scan data for the dimethyl sulfoxide (DMSO) solutions of **P2** and **P3** at 500 nm, excited with the peak intensity of 7.5 GW/cm², indeed confirmed the occurrence of SA. The concentration for **P2** and **P3** was 5.4×10^{-4} and 3.5×10^{-4} M/l, respectively. It was found that pure DMSO did not show any nonlinear optical response under the same experimental conditions. The absorption coefficient in the case of two-level system possessing in homogeneously broadened

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FIG. 1. Molecular structures of linear metallopolymers **P1–P3**.

states can be written as $\alpha = \alpha_0 / (1 + I/I_s)^{0.5}$, where α_0 is linear absorption coefficient, I is incident power intensity, and I_s is saturable intensity.¹⁰ Linear absorption coefficients of **P2** and **P3** in DMSO at 500 nm were 12.5 cm^{-1} and 12.33 cm^{-1} , respectively. The SA coefficients were obtained as -0.39 cm/GW for **P2** and -0.91 cm/GW for **P3**, respectively. The solid lines in Figure 2(a) are the theoretical fits with $I_s = 9.9 \text{ GW/cm}^2$ for **P2** and $I_s = 1.67 \text{ GW/cm}^2$ for **P3**. Though we used relatively low concentration, the polymers presented low saturable intensity comparable to graphene

oxide.¹¹ Moreover, **P3** had stronger SA than **P2**, plausibly due to the energy transfer from donor to acceptor in **P3**. As shown in Figures 2(b) and 2(c), the polymers exhibited large SA behaviors around the absorption peak (470–510 nm). Though we did not measure the nonlinear absorption at other wavelengths, it was expected that the polymers should exhibit large SA behavior in the whole absorption band.

From the linear absorption spectra of polymers, it was expected that under the excitation of femtosecond pulses in the range of 700–900 nm, both **P2** and **P3** might exhibit 2-photon absorption (2PA) behaviors. Upon excitation at 765 nm, the polymers in DMSO, with a concentration of $1.25 \times 10^{-4} \text{ M}$, indeed exhibited bright photoluminescence (PL) emission even excited with low power intensity. The linear dependence of PL emission intensity on the square of the excitation intensity for **P2** and **P3**, as shown in the inset of Figure 3(a), confirms that 2PA is the main mechanism of strong PL emission.¹² Moreover, with 1- and 2-photon excitation, the temporal relaxation measurements of PL emission manifested the same single decay behavior, that is, with the decay constant 2.9 ns for **P2** and 3.8 ns for **P3**, respectively, further indicating the 2PA mechanism. Due to the wide applications of DMSO in cell culture,¹³ the polymers should have strong potential in biological imaging. In order to assess the effect of the molecular environment and solvent polarity on the 2PA properties, that is, the influence of intramolecular charge transfer,¹⁴ we also investigated the effect of the solvent polarity on 2PA properties. It was found that, with the addition of a solvent with moderate polarity, such as tetrahydrofuran (THF), the 2-photon emission from both **P2** and **P3** was enhanced greatly, without the expense of obvious shift of emission wavelength, as shown in Figures 3(b) and 3(c). The quantum yields for **P2** and **P3** in DMSO were 4.3% and 2.6%, respectively, while they were boosted up to 47% and 21% in the mixture of THF and DMSO (V: V = 80%: 20%). The 2PA cross-sections of polymers were then measured by using Z-scan technique.⁹ From the 2PA spectra presented in Figure 4(a), it can be seen that both **P2** and **P3** display good 2PA behavior in the range of 700–900 nm. For example, the maximum 2PA cross-sections (δ_{max}) for each repeat unit in DMSO were 495 GM for **P2**

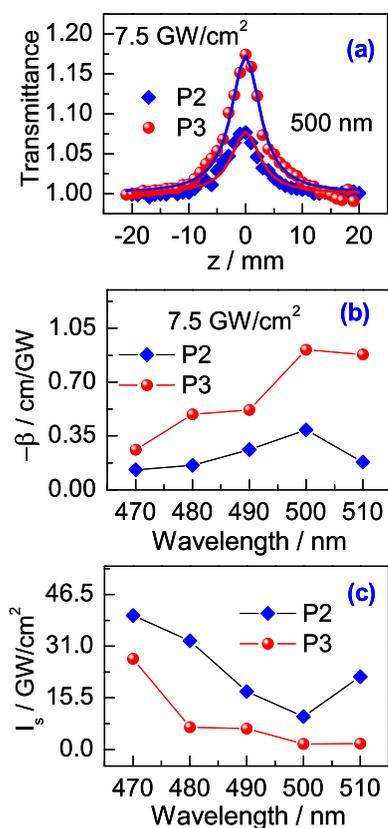


FIG. 2. (a) Open aperture Z-scan data for **P2** and **P3** at 500 nm with the power intensity of 7.5 GW/cm^2 . SA coefficient obtained with the excitation intensity of 7.5 GW/cm^2 (b) and saturable intensity (c) for **P2** and **P3** in the wavelength range of 470–510 nm.

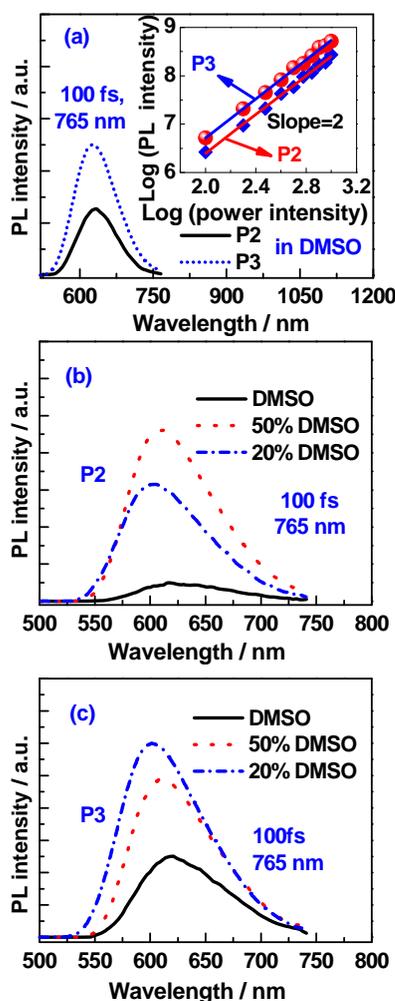


FIG. 3. (a) 2-photon excited emission spectra of **P2** and **P3** in DMSO at 765 nm. The inset is the emission intensity versus the square of the excitation power intensity. The log-log plot with slope value of around 2 indicates the nature of 2PA. 2-photon excited emission spectra for **P2** (b) and **P3** (c) in different solvents at 765 nm.

and 1542 GM for **P3**, respectively. Obviously, the δ_{\max} value for **P3** was much larger than that of **P2**, although the pure donor (**P1**) exhibited very small 2PA cross-sections. With the addition of THF, as shown in Figures 4(b) and 4(c), though the 2PA cross-sections decreased, the maximum 2PA action cross-sections for **P2** and **P3** largely increased. It is known that the solvent polarity can influence the magnitude of intramolecular charge transfer. With the addition of THF into DMSO, the mixed solvents strongly affected the electronic structure and the charge transfer separation of polymers in both ground state and excited states, which would thus influence their 2PA behaviors. The flexible tunable 2PA behaviors indicated that the polymers had the potential in 2-photon emission based applications.

NLO phenomena at 1300–1600 nm permit all-optical switching and signal processing, which require the materials to have large nonlinear refraction accompanied by minimal absorption losses.¹⁵ However, few organic materials reported to date satisfy these requirements.¹⁶ Considering the high conjugated length and the rigid structures of **P2** and **P3**, as well as short 1-photon absorption wavelength ($\lambda_{\max} \sim 490$ nm), large nonresonant nonlinear refraction may be expected at

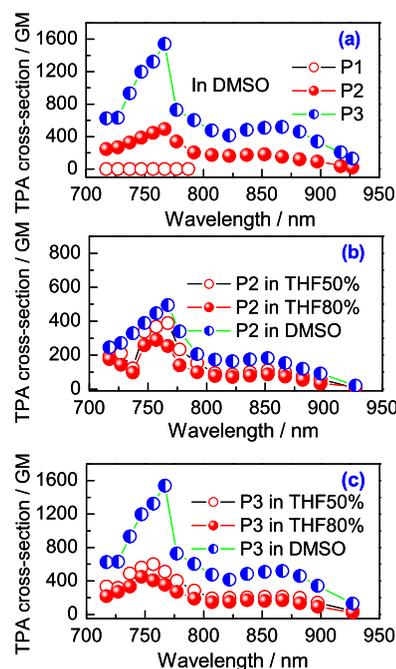


FIG. 4. (a) 2PA spectra of **P1-P3** in DMSO. 2PA spectra for **P2** (b) and **P3** (c) in different solvents.

1300 nm. It therefore motivated us to investigate their NLO properties and figures of merit at this wavelength. Prior to measurements on these samples, the system was carefully calibrated using CS_2 as a reference.⁹ The third-order nonlinear refractive index of CS_2 was evaluated to be $3.3 \times 10^{-6} \text{ cm}^2/\text{GW}$, which was in good agreement with previous measurements in this range of femtosecond pulse duration ($3.0 \times 10^{-6} \text{ cm}^2/\text{GW}$).¹⁷

In order to evaluate the figures of merit, we first investigated the nonlinear absorption behaviors of **P2** and **P3**. It was found that under the excitation of 1300 nm, both **P2** and **P3** presented 3-photon excited PL emission, as indicated in the inset of Figure 5(a). The 3-photon absorption (3PA) coefficients were obtained by using open aperture Z-scan measurements with a concentration $5 \times 10^{-4} \text{ M/l}$, as shown in Figure 5(b). By employing the analytical method described in Ref. 18, the 3PA coefficients, γ , for the polymers **P2** and **P3** were found to be 6.0×10^{-5} and $7.6 \times 10^{-5} \text{ cm}^3/\text{GW}^2$, respectively. Based on the 3PA coefficient and the data processing procedure described in Ref. 19, the 3PA cross-sections were calculated to be $80 \times 10^{-80} \text{ cm}^6 \text{ s}^2$ for **P2** and $101 \times 10^{-80} \text{ cm}^6 \text{ s}^2$ for **P3**, respectively. In order to calculate the contribution of solute to the measured total nonlinear refraction, measurement on the pure DMSO was also performed under the same measuring conditions. Figure 5(c) comparatively shows the closed aperture Z-scan data divided by corresponding open aperture data for DMSO solutions of **P1-P3**, pure DMSO, and CS_2 at the same power intensity of $85 \text{ GW}/\text{cm}^2$. The valley-to-peak configuration indicated all of them exhibited positive nonlinear refraction, i.e., self-focusing effect. By theoretical fitting using Z-scan theory, we extracted the nonlinear refractive index, n_2 . For both of the **P2** and **P3** solutions, n_2 was determined to be $1.1 \times 10^{-6} \text{ cm}^2/\text{GW}$, much larger than those of pure DMSO and **P1** ($n_2 = 4.5 \times 10^{-7} \text{ cm}^2/\text{GW}$ for both of them). **P2** and **P3** had

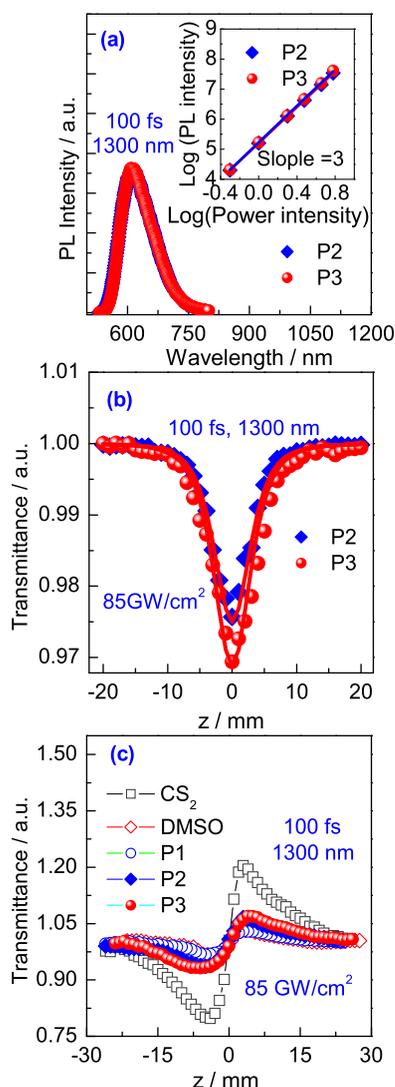


FIG. 5. (a) 3-photon excited emission spectra of **P2** and **P3** in DMSO. The inset is the emission intensity versus the cubic of the excitation intensity. The log-log plot with slope value of around 3 indicates the nature of 3PA. (b) Open aperture Z-scan data for **P2** and **P3** at 1300 nm. (c) Closed-aperture Z-scan data divided by corresponding open aperture data for CS₂, DMSO, and **P1-P3**.

almost the same nonlinear refraction due to less efficient energy transfer at 1300 nm. Considering the very low concentration we used, even though the nonlinear refraction of **P2** and **P3** was smaller than CS₂, much larger nonlinear refraction should be obtained if we use high concentration or polymer films. To evaluate the refractive nonlinearity of the solute, we assumed a solution of non-interacting particles. Moreover, the total nonlinear refraction of DMSO solution is given by $n_2(\text{solution}) = (1-f)n_2(\text{solvent}) + fn_2(\text{solute})$, where f is the mole fraction of solute, and $n_2(\text{solvent})$ and $n_2(\text{solute})$ are the nonlinear refractive indices of solvent and solute, respectively.²⁰ In our case, the value of f was 3.57×10^{-5} . The intrinsic nonlinear refractive index $n_2(\text{solute})$ was calculated as $1.82 \times 10^{-2} \text{ cm}^2/\text{GW}$. This value was extremely larger compared to many other small molecules.^{20,21} To evaluate the requirements for all-optical switching devices, we calculated two figures of merit W and V for **P2** and **P3**, where W and V were 1-photon and 3-photon figures of merit and defined as $W = n_2 I / (\alpha_0 \lambda)$,

TABLE I. Linear and nonlinear optical parameters for **P1-P3**.

	Solvent	Φ^a	τ^b	σ_2^c	$\Phi\sigma_2^d$	σ_3^e	n_2^f
P2	DMSO	4.3	2.9	495	21	80	1.1
	50% DMSO	50.0	...	390	195
P3	20% DMSO	47.0	...	290	136
	DMSO	2.6	3.8	1542	40	101	1.1
P3	50% DMSO	13.0	...	600	78
	20% DMSO	21.0	...	450	95

^aFluorescence quantum yields (%).

^bFluorescence lifetime (ns) under the excitation at 765 nm.

^cMaximum 2PA cross-section (GM) in the measurable range: $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$.

^dMaximum 2PA action cross-section (GM).

^e3PA cross-section at 1300 nm, in unit of $10^{-80} \text{ cm}^6 \text{ s}^2$.

^fNonlinear refractive index at 1300 nm, in unit of $10^{-6} \text{ cm}^2/\text{GW}$.

$V = \gamma \lambda I / (3n_2)$.²² The figures of merit were calculated to be $W > 1$, $V = 0.2$ for **P2** and $W > 1$, $V = 0.34$ for **P3**, which satisfied the requirements $W > 1$, $V < 0.68$ for all-optical switching. In Table I, we have summarized the linear and nonlinear parameters for **P2** and **P3**.

In conclusion, the broad spectral information about NLO properties of two terpyridine-based Zn(II)-coordinated rigid linear polymers has been investigated in detail. Due to the highly rigid structures of the backbone, **P2** and **P3** exhibit strong SA behaviors in absorption band and 2PA in the biological window of 700-900 nm, and large nonlinear refraction with minimal optical loss at 1300 nm, indicating ideal figures of merit for applications in mode locking, 2-photon biological imaging, and ultrafast all-optical switching.

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- ²³See supplementary material at <http://dx.doi.org/10.1063/1.4767390> for Figure S1: UV-vis absorption and photoluminescence spectra of metallo-polymers **P1-P3** in DMSO solution (1.00×10^{-5} M).