

A New Synthetic Strategy to Prepare a Polyphosphazene with Charge-Transporting Agents and Nonlinear Optical Chromophores as Side Chains

LI, Zhen^a(李振) QIN, Jin-Gui^{*a}(秦金贵) LI, Shao-Jun^b(李绍军) YE, Cheng^b(叶成)

^a Department of Chemistry, Wuhan University, Wuhan, Hubei 430072, China

^b Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

A new strategy, a post coupling method to develop the polyphosphazene (P2) functionalized with carbazolyl groups and nonlinear optical (NLO) chromophores, has been explored. P2 exhibits good solubility in common organic solvents. The poled film of P2 exhibits a resonant d_{33} value of 42 pm/V by second harmonic generation (SHG) measurements.

Keywords post coupling method, polyphosphazene, synthesis

Introduction

Polyphosphazene is an inorganic polymer with a backbone of alternating phosphorus and nitrogen atoms, and its properties mainly depend on the nature of two substituted side groups which are linked onto the phosphorus atoms. This backbone inherently possesses some unusual properties, such as a high thermo-oxidative and photolytic stability, optical transparency from 220 nm to 800 nm. Most polyphosphazenes have very high molecular weight, and they are usually amorphous, soluble, and easily prepared.¹⁻⁴ Due to these advantages, polyphosphazenes were considered as an preferential candidate for electro-optical (EO)⁵⁻⁷ and photorefractive applications.^{8,9}

In our previous work, the synthesis of polyphosphazene with functional side groups from a highly reactive macromolecular intermediate, poly(dichlorophosphazene), by direct nucleophilic substitution reaction was reported.^{8,9} In this paper, the synthesis and characterization of a new polyphosphazene by a post functional coupling method with the mild conditions are reported. The post azo coupling between the polymers and diazonium salts has been used to enable the introduction of nonlinear optical (NLO) chromophores, but never been applied to the synthesis of functional polyphosphazenes. Therefore, polyphosphazene (P1) with carbazolyl and aniline groups was first prepared by direct nucleophilic substitution reaction with poly(dichlorophosphazene). Then, polyphosphazene (P2) containing charge-transporting agents (carbazolyl groups)

and azo chromophores was synthesized via a post azo coupling reaction of P1 and *p*-Nitrobenzenediazonium fluoroborate in *N*-methylpyrrolidone (NMP) (Scheme 1). The structures of P1 and P2 are characterized, and the poled film of P2 reveals a resonant d_{33} value of 42 pm/V by second harmonic generation (SHG) measurements.

Experimental

Materials and measurements

Tetrahydrofuran (THF) and petroleum ether (60—90 °C) was dried and distilled from K-Na alloy under dry nitrogen atmosphere. *p*-Nitrobenzenediazonium fluoroborate was synthesized according the method reported.¹⁰ *N*-Methylpyrrolidone (NMP) was dried over and distilled from CaH₂ under dry nitrogen atmosphere. All other reagents were used as received. Poly(dichlorophosphazene) was obtained from thermal ring-opening polymerization of phosphonitrile chloride trimer.¹¹ *N*-Ethyl-*N*-(6-hydroxyhexanyl)aniline (4) was synthesized from *N*-ethylaniline and 6-bromohexanol.¹² Sodium hydride was weighted in the dry box. The substitution reactions of poly(dichlorophosphazene) were carried out under dry nitrogen atmosphere using Schlenk technique.

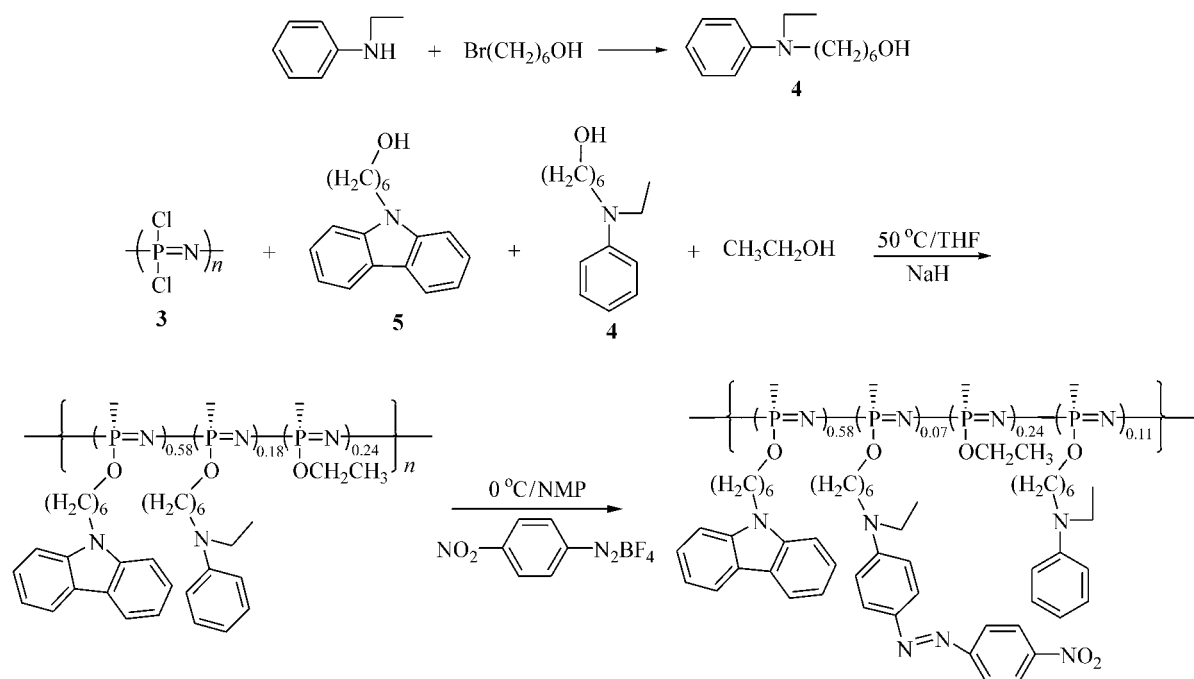
¹H NMR was measured with a Varian Mercury 300 spectrometer. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 spectrometer in the region of 3000—400 cm⁻¹ on KBr pellets. UV-vis spectra were obtained using a Shimadzu 160A spectrometer in DMF. Molecular weights were determined in THF by Waters 2960D separation Module containing Styragel HR1 THF column and Waters 2410 Refractive Index Detector with a calibration curve of polystyrene standards. Differential scanning calorimetry (DSC) was performed in a Rigaku Themoflex DSC8131 with a scan rate of 10 °C/min.

* E-mail: jgqin@whu.edu.cn; Tel.: +86-27-87684117; Fax: +86-27-87686757

Received December 10, 2002; revised and accepted June 5, 2003.

Project supported by the Education Ministry of China and Hubei Province (Nos. 2003ABA074, 2003 × 107).

Scheme 1



Synthesis of *N*-(6-hydroxyhexanyl)carbazole (5)

Potassium hydroxide (12 g) was stirred in DMF (150 mL) at room temperature for 15 min. Then carbazole (14 g) was added, and the resultant mixture was stirred at room temperature for 1 h. 6-Bromohexanol (13 mL) was added slowly, and the reaction was kept at room temperature for 24 h. The mixture was poured into water (2 L) and the white solid was filtered, washed with water, and dried under the reduced pressure at room temperature. The solid was recrystallized from ethanol/water (2:1) to obtain **5** (80%). $^1\text{H NMR}$ (CDCl_3) δ : 1.38–1.41 [m, 8H, $(\text{CH}_2)_4\text{CO}$], 3.6 (t, $J = 8$ Hz, 2H, OCH_2), 4.3 (t, $J = 8$ Hz, 2H, NCH_2), 7.22–7.27 (m, 2H, ArH), 7.40–7.49 (m, 4H, ArH), 8.12 (d, $J = 4$ Hz, 2H, ArH); FT-IR, (KBr) ν : 1593 (C=C), 1230 (C–N) cm^{-1} .

Synthesis of polyphosphazene (P1)

Compound **5** (2.2 g, 8 mmol) reacted with sodium hydride (0.19 g, 7.9 mmol) in THF (20 mL) at 50 °C for 10 h, then the solution was added to a solution of poly(dichlorophosphazene) (**3**, 0.92 g, 7.9 mmol) in 30 mL of THF. The mixture was stirred at 60 °C for two days. Then 50 mL of sodium salt of **4** [prepared from **4** (0.70 g, 3.1 mmol) and sodium hydride (0.072 g, 3.0 mmol) in 50 mL of THF] was added, and the mixture was stirred again at 60 °C for two days. Finally, 20 mL of the solution of $\text{NaOCH}_2\text{CH}_3$ [prepared from sodium (0.36 g, 15.6 mmol) and ethanol (0.8 g, 17.4 mmol) in 20 mL of THF] was added, and the reaction lasted for another three days at 60 °C. After most of THF was removed under vac-

uum, the mixture was poured into 1000 mL of water, and the white solid was filtered, washed with water, and air-dried. The solid was dissolved in THF, and the insoluble residue was filtered out. The filtrate was evaporated to remove most of THF. About 50 mL of methanol was added to precipitate the product, the product was purified by several dissolution and precipitations cycles in chloroform and methanol. The solid was dried under vacuum at 40 °C to yield white product (1.3 g, 41%). $^1\text{H NMR}$, (CDCl_3) δ : 7.80–8.20 (ArH), 7.00–7.70 (ArH), 6.40–6.70 (ArH), 3.00–4.40 (NCH_2 , OCH_2), 0.90–2.00 [$(\text{CH}_2)_4$, CH_3].

Preparation of polyphosphazene (P2)

Polyphosphazene (**P1**) (0.23 g) was dissolved in 1.5 mL of *N*-methylpyrrolidone (NMP), and then *p*-nitrobenzenediazonium fluoroborate (62 mg) was added at 0 °C. The color of the solution changed from colorless to red immediately. After stirring for 8 h at 0 °C, excessive anhydrous potassium carbonate was added and the mixture was stirred for another one hour, and then filtered. The residue was washed with THF and the filtrate was collected, and then THF was removed under reduced pressure. Some methanol was added dropwise to precipitate the polymer. The solid was dried under vacuum at 40 °C to yield 0.16 g red product **P2** (60%). $^1\text{H NMR}$ ($\text{DMSO}-d_6$) δ : 8.11–8.40 (ArH), 7.88–8.08 (ArH), 7.60–7.82 (ArH), 7.20–7.60 (ArH), 6.90–7.20 (ArH), 3.50–4.40 (NCH_2 , OCH_2), 0.60–1.80 [$(\text{CH}_2)_4$, CH_3].

Preparation of polymer film

P2 was dissolved in THF, and the solution (4 wt. %) was filtered through syringe filters. Polymer films were spin coated onto indium-tin-oxide- (ITO-) coated glass substrates which were cleaned by *N,N*-dimethylformide, acetone, distilled water and THF subsequently in ultrasonic bath. Residual solvent was removed by heating the films in a vacuum oven at 45 °C for two days. The film thickness (0.21 μm) was measured by TENCOR 500 Surface Profiler.

Characterization of poled films

The second-order optical nonlinearity of **P2** was determined by *in-situ* second harmonic generation (SHG) experiments by using a closed temperature-controlled oven with optical windows and three needle electrodes. The film, which was kept at 45° to the incident beam, was poled inside the oven, and SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature 90 °C, voltage 7.5 kV at the needle point, gap distance 0.8 cm. SHG measurements were carried out with an Nd:YAG laser operating with a 10 Hz of repetition rate and an 8 ns of pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

Results and discussion

Synthesis

Poly(dichlorophosphazene) (**3**) was prepared by thermal ring-opening polymerization of phosphonitrile chloride trimer.¹¹ Separation of phosphonitrile chloride trimer from poly(dichlorophosphazene) is very important. Petroleum ether (60–90 °C) was used to wash the un-polymerized trimer as poly(dichlorophosphazene) did not dissolve in petroleum ether. By comparison of the amount of the trimer before and after the polymerization, it could be easily known the quantity of poly(dichlorophosphazene) as reported in our previous paper.^{8,9,13}

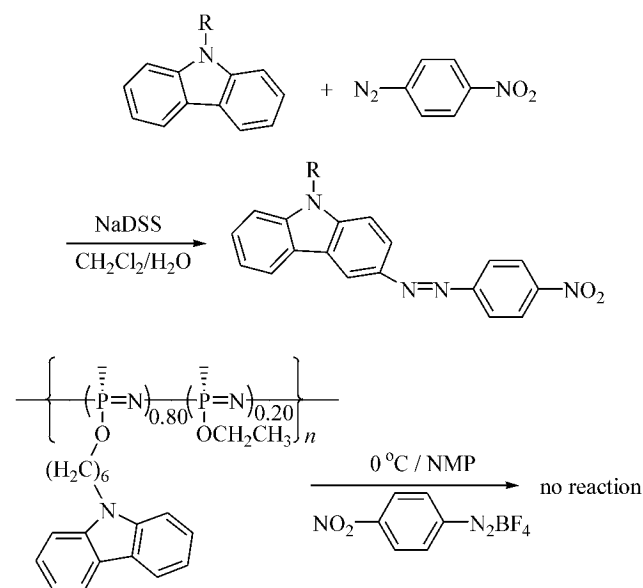
Carbazolyl and aniline groups can not react with all the chlorine atoms because of the steric shielding effect.¹⁴ However, if some chlorine atoms remain in the polymer backbone, cross-linking may take place and the polymer becomes insoluble when it is exposed to moisture or water. So an excess of NaOCH₂CH₃ was added into the reacting solution to replace all the remaining chlorine atoms.

The synthetic route of **P1** and **P2** was shown in Scheme 1. **P1** was obtained from the highly reactive macromolecular intermediate, poly(dichlorophosphazene) (**3**), by nucleophilic substitution reaction. **P2** was synthesized via a post azo coupling reaction, which has been recently utilized as a convenient method to introduce azo chromophores into the side chains of EO polymers. This method was first used by Katz¹⁵ to functionalize a copolymer of methyl methacrylate and methacrylate ester of *N*-

ethyl-*N*-(hydroxyethyl)aniline in acetic acid. As an acid medium was not a favorite solvent for most polymers, Tripathy¹⁶ developed this method by using polar organic solvent such as dimethylformamide or dimethylacetamide. In our previous studies, DR-1 containing polysilanes could be easily synthesized by the azo coupling reaction in *N*-methylpyrrolidone (NMP) with high yield.¹⁷ In this study, this method was further extended to synthesize **P2** with relatively high yield. The overall synthesis of **P2** was carried out through two steps. The synthetic route is simple, and the purification of the products is very easy. Also the yield was improved compared with the direct methods reported previously.^{8,9}

According to the literature¹⁸ and our previous experiments,^{9,19} the azo carbazole molecules could be synthesized by the reaction of the carbazole and the azo salt in the presence of a catalyst (Scheme 2). At the very beginning of this research, we worried if the *p*-nitrobenzenediazonium fluoroborate might attack the carbazolyl ring to form azo carbazolyl moieties though there was no catalyst. If it occurs, the structure of the product would be very complicated. To seek the answer of this question, a comparison experiment was conducted (Scheme 2): Another polyphosphazene (**P3**), which was prepared and reported,^{13a} was dissolved in NMP and reacted with *p*-nitrobenzenediazonium fluoroborate. The reaction conditions were the same as described in the preparation of **P2**. However, there was no absorption assigned to the azo carbazolyl chromophore in UV-vis spectroscopy of the product, and no absorption of the nitro groups appeared in IR spectroscopy. On the contrast, UV-vis, IR and NMR spectra were essentially the same as those of **P3**. These results demonstrated that the azo salts did not attack the carbazolyl ring in the side chain of **P3** in the absence of a catalyst under the same reaction conditions. Therefore, in the preparation of **P2**, the *p*-nitrobenzenediazonium fluoroborate would only attack the ani-

Scheme 2



line groups, and the structure of **P2** is just as shown in Scheme 1.

Structure characterization of **P1** and **P2**

The IR spectra of **P1** and **P2** were shown in Fig. 1. The 1250–1200 cm^{-1} bands were attributed to an intense P=N stretching vibration and the 750 cm^{-1} band to an in-phase P-N-P stretch. In addition, the absorbances for the carbazolyl ring are at 1598, 1458, 722 cm^{-1} . Two apparent new strong absorption bands appeared at 1517 and 1335 cm^{-1} in Fig. 1(b), which were assignable to the absorption of the nitro unit. This confirmed that *p*-nitrobenzediazonium fluoroborate had reacted with the aniline side groups and the nitro units were introduced into the polymer side chains.

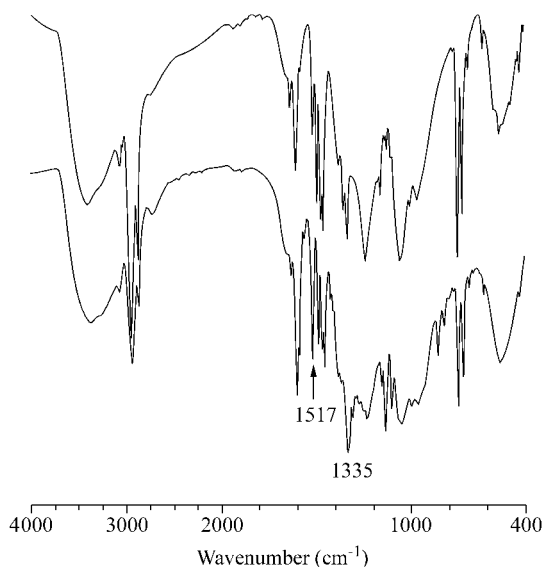


Fig. 1 IR spectra of **P1** (up) and **P2** (down).

The composition of the polymer could be calculated by ^1H NMR (Scheme 1). For **P1**, the composition could be calculated from the integration area of two phenyl protons of the carbazolyl group in the range of δ 7.80–8.20, two phenyl protons of the aniline moieties at δ 6.40–6.70, the protons of $-\text{NCH}_2$, $-\text{OCH}_2$ groups at δ 3.0–4.4, and the protons of $-(\text{CH}_2)_4-$ and methyl groups around δ 1.0. As the composition of carbazolyl and ethoxide groups in the polyphosphazene remained the same before and after the post azo coupling reaction, it was easy to estimate the component concentrations in **P2** by comparison the proton resonances in the downfield.

P1 and **P2** have good solubility in common organic solvents, such as CHCl_3 , THF, DMSO and DMF, *etc.* Fig. 2 showed UV-vis spectra of **P1** and **P2** in DMF. The absorption bands of **P1** and **P2** at 296, 333, 347 nm were attributed to the carbazolyl rings. After the post azo coupling reaction, a new strong absorption peak of π - π^* transition of chromophore appeared at about 503 nm. This further confirmed the success of the post coupling reaction.

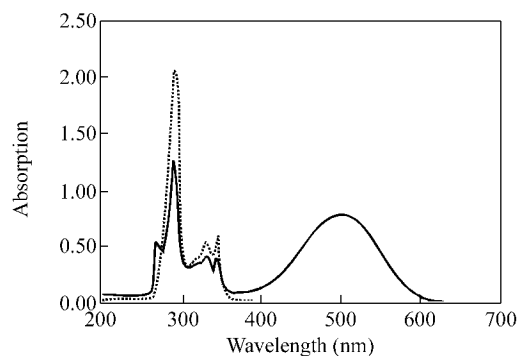


Fig. 2 UV-vis spectra of **P1** (dash line) and **P2** (solid line) in DMF.

There was no glass transition temperature detected from its DSC curve of **P2**. The molecular weights of **P2** were determined by gel permeation chromatography with refractive index detector. The M_n and M_w of **P2** were 3.5×10^4 and 1.1×10^5 , respectively.

To evaluate the NLO activity of the poled polymer films, thin films of **P2** were prepared for SHG measurement. As the T_g of **P2** was not known, the poling temperature of the thick film of **P2** changed from room temperature to 100 $^\circ\text{C}$ in SHG measurement as other conditions remaining the same, and it was found that 90 $^\circ\text{C}$ was the best poling temperature. Calculation of d_{33} value for the poled **P2** is based upon the Eq. (1),²⁰

$$\frac{d_{33s}}{d_{11q}} = \sqrt{\frac{I_s l_{c,q}}{I_q l_s}} F \quad (1)$$

where d_{11q} is d_{11} of the quartz crystals, which is 0.45 pm/V, I_s and I_q are SHG intensities of the sample and the quartz, respectively, $l_{c,q}$ the coherent length of the quartz, l_s the thickness of the polymeric films, and F the correction factors of the apparatus and equals 1.2 when $l_c \gg l_s$. The d_{33} value of **P2** was calculated to be 42 pm/V at 1064 nm. Generally, the photorefractive (PR) effect can occur in materials that simultaneously possess electro-optical activity and photoconductivity.^{21–23} Here in **P2**, almost every unit contains one carbazolyl group, therefore the carbazolyl groups are close enough in space due to its high density and the good flexibility of polyphosphazene backbone, and the charge carrier may transport between the carbazolyl moieties as they are good charge-transporting agents.^{22–23} As **P2** has demonstrated the second nonlinear property, and the photoconductive property of carbazole-based polymers has been shown,^{22–23} therefore, it is expected that **P2** could show PR effect. The PR properties of **P2** will be investigated in the near future.

References

- 1 Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.
- 2 Allcock, H. R. *Appl. Organomet. Chem.* **1998**, *12*, 659.
- 3 Li, Z.; Zhan, C.; Qin, J. *J. Funct. Polym.* **2000**, *13*,

- 240 (in Chinese).
- 4 Neilson, R. H. ; Neilson, P. W. *Chem. Rev.* **1988**, *88*, 541.
- 5 Allcock, H. R. ; Dembek, A. A. ; Kim, C. ; Devine, R. L. S. ; Shi, Y. ; Steier, W. H. ; Spangler, C. W. *Macromolecules* **1991**, *24*, 1000.
- 6 Allcock, H. R. ; Cameron, C. G. ; Skloss, T. W. ; Meyers, S. T. ; Haw, J. F. *Macromolecules* **1996**, *29*, 233.
- 7 Allcock, H. R. ; Ravikiran, R. ; Olshavsky, M. A. *Macromolecules* **1998**, *31*, 5206.
- 8 Li, Z. ; Luo, J. ; Li, J. ; Zhan, C. ; Qin, J. *Polym. Bull.* **2000**, *45*, 105.
- 9 Li, Z. ; Li, J. ; Qin, J. *React. Funct. Polym.* **2001**, *48*, 113.
- 10 Starkey, E. B. ; Smith, L. I. ; Ungnade, H. E. *Org. Synth.* **1943**, *2*, 225.
- 11 Allcock, H. R. ; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
- 12 VanSteenwinckel, D. ; Engels, C. ; Gubbelmans, E. ; Hendrickx, E. ; Samyn, C. ; Persoons, A. *Macromolecules* **2000**, *33*, 4074.
- 13 (a) Li, Z. ; Qin, J. ; Deng, X. ; Cao, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3428.
(b) Li, Z. ; Qin, J. ; Li, S. ; Ye, C. ; Luo, J. ; Cao, Y. *Macromolecules* **2002**, *35*, 9232.
- 14 Allcock, H. R. In *Comprehensive Polymer Science*, Eds.: Allen, S. G. ; Bevington, J. C., Pergamon, Oxford, **1989**, p. 525.
- 15 Schilling, M. L. ; Katz, H. E. ; Cox, D. I. *J. Org. Chem.* **1988**, *53*, 5538.
- 16 Wang, X. ; Kumar, J. ; Tripathy, S. K. ; Li, L. ; Chen, J. *Macromolecules* **1997**, *30*, 219.
- 17 Tang, H. ; Luo, J. ; Qin, J. ; Kang, H. ; Ye, C. *Macromol. Rapid Commun.* **2000**, *21*, 1125.
- 18 Ho, M. S. ; Barrett, C. ; Paterson, J. ; Esteghamatian, M. ; Natansohn, A. ; Rochon, P. *Macromolecules* **1996**, *29*, 4613.
- 19 Li, J. ; Li, Z. ; Zhan, C. ; Qin, J. ; Kippelen, B. ; Peyghambarian, N. ; Marder, S. R. *Proc. SPIE-Int. Soc. Opt. Eng.* **1998**, *3554*, 229.
- 20 Dalton, L. R. ; Xu, C. ; Harper, A. W. ; Ghosn, R. ; Wu, B. ; Liang, Z. ; Montgomery, R. ; Jen, A. K.-Y. *Nonlinear Opt.* **1995**, *10*, 383.
- 21 Ducharme, S. ; Scott, J. C. ; Twieg, R. J. ; Moerner, W. E. *Phys. Rev. Lett.* **1991**, *66*, 1846.
- 22 Moerner, W. E. ; Jepsen, A. G. ; Thompson, C. L. *Annu. Rev. Mater. Sci.* **1997**, *27*, 585.
- 23 Moerner, W. E. ; Silence, S. M. *Chem. Rev.* **1994**, *94*, 127.

(E0212107 SONG, J. P. ; LU, Z. S.)