# Synthesis, Characterization, and Non-Linear Optical Properties of Two New Symmetrical Two-Photon Photopolymerization Initiators

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Two new symmetrical two-photon free-radical photopolymerization initiators, 1,4-bis-{2-[4-(2-pyridin-4-ylvinyl)phenyl]vinyl}-2,5-bisdimethoxybenzene **6** and 1,4-bis-{2-[4-(2-pyridin-4-ylvinyl)phenyl]vinyl}-2,5-bisdodecyloxybenzene **7**, were synthesized using an efficient Wittig and Pd-catalyzed Heck coupling methodology. One-photon fluorescence, one-photon fluorescence quantum yields, one-photon fluorescence lifetimes, and two-photon fluorescence have been investigated. Experimental results show that both compounds were good two-photon absorbing chromophores and effective two-photon photopolymerization initiators. Two-photon polymerization microfabrication experiments have been studied and the possible photopolymerization mechanism is discussed.

Manuscript received: 26 June 2004. Final version: 9 November 2004.

# Introduction

Organic materials possessing large two-photon absorption (TPA) cross-sections have a variety of technical applications, such as optical power limiting,<sup>[1,2]</sup> two-photon fluorescence microscopy,<sup>[3]</sup> frequency-upconverted lasing,<sup>[4]</sup> threedimensional (3D) optical data storage, and microfabrication.<sup>[5-8]</sup> These applications take advantage of the fact that the TPA depends quadratically on the excitation intensity, so under tight-focussing conditions, absorption at the focus is confined to a volume in the order of  $\lambda^3$  (where  $\lambda$  is the excitation wavelength). Three-dimensional microfabrication has been demonstrated using two-photon-initiated polymerization of resins incorporating conventional ultravioletabsorbing initiators. However, the TPA cross-sections,  $\delta$ , of most initiators including commercial dyes are typically very small, and as a result they exhibit low two-photon sensitivity. Resins containing these initiators can be polymerized only by means of long exposure times and high excitation intensities that frequently result in damage to the structure of the polymerized resin.

Some approaches towards improving the photosensitivity of photointiator molecules are based on the idea of increasing their two-photon absorption cross-sections.<sup>[9]</sup> Several chromophores with large two-photon absorption cross-sections have been identified by theoretical and experimental studies.<sup>[10–14]</sup> Symmetrically substituted stilbene-type chromophores (D- $\pi$ -D) are the most widely investigated compounds in these studies, because their two-photon absorption cross-section values are larger than their respective asymmetric counterparts,<sup>[14]</sup> and because they have the advantage

of high transmission in the visible spectrum (400–800 nm). Although symmetrical molecules  $(D-\pi-D)$  show very small dipole moments in the ground state, quantum chemical calculations have confirmed that there is substantial change in both the transition dipole moment and quadrupole moment<sup>[10]</sup> upon excitation. Such changes assist intermolecular charge transfer, which increases the two-photon absorptivity. Therefore, the synthesis of this type of symmetric chromophore has practical application. Here we report two new symmetrically substituted stilbene-type chromophores 6 and 7 synthesized by means of an efficient Wittig and Pd-catalyzed Heck coupling methodology. Experimental results show that the two compounds are good two-photon absorbing chromophores and effective two-photon photopolymerization initiators. Both chromophores can be used as initiators to fabricate three-dimensional polymerized structures under irradiation of a Ti:sapphire femtosecond laser at 830 nm. The possible photopolymerization mechanism is discussed.

# Experimental

### Chemicals

4-Vinylpyridine (95%), palladium(II) acetate (47.5% Pd), and 4-bromobenzaldehyde were purchased from Acros Organics. Tri-*o*-tolylphosphine and 4-(N,N-diphenylamino)benzaldehyde were purchased from Tokyo Kasei Kogyo Co. These chemicals were used without further purification.

# Instrumentation

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Bruker AV600 spectrometer. Elemental analysis was carried out on a Perkin–Elmer PE 2400 elemental analyzer. UV-Vis–near-IR spectra were measured on a Hitachi



**Scheme 1.** Synthesis of two compounds: (*a*) PPh<sub>3</sub>/CCl<sub>4</sub>/BPO, reflux; (*b*) THF/4-bromobenzaldehyde, grind, room temp.; (*c*) THF/1/grind, room temp.; (*d*) vinylpyridine/tri-*o*-tolylphosphine/palladium(II) acetate/triethylamine, reflux.

U-3500 recording spectrophotometer. Melting points were measured on a Mettler-Toledo DSC822e differential calorimeter. Steady-state fluorescence spectra were measured on an Edinburgh FLS920 spectrofluorimeter with a 450 W X e arc lamp as the 400 nm excitation source. Spectra were recorded between 420 and 700 nm at a resolution of 0.1 nm using a photomultiplier tube detector in single-photon counting mode. The quartz cuvettes had a 1 cm path length.

#### Synthesis

The synthetic sequence for the preparation of our target molecules is shown in Scheme 1. Triphosphonium chloride **2** was synthesized in our laboratory. 4-Bromobenzyl(triphenyl)phosphonium bromide **1** and 2,5-bisdodecyloxybenzene-1,4-dicarbaldehyde **3** were synthesized according to reported methods.<sup>[15,16]</sup>

## 1,4-Bis-{2-[4-(2-pyridin-4-ylvinyl)phenyl]vinyl}-2,5bisdimethoxybenzene **6**

At room temperature, 4-bromobenzaldehyde (1.85 g, 0.01 mol), triphosphonium chloride 2 (3.16 g, 0.004 mol), NaOH (8.00 g, 0.2 mol), and tetrahydrofuran (2 mL) were placed in a mortar. After being ground for about 5 min, the mixture was poured into 200 mL distilled water, then neutralized with dilute hydrochloric acid, and extracted with dichloromethane. The organic layer thus obtained was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed from the solution at reduced pressure and the residue dissolved in dichloromethane. This solution was separated by chromatography on silica gel using ethyl acetate/petroleum ether (1:20) as eluent. The green crystals obtained were added to a mixture of tri-o-tolylphosphine (1.96 g, 6.44 mmol), vinylpyridine (3.48 mL, 32.24 mmol), palladium(II) acetate (0.18 g, 0.8 mmol), and redistilled triethylamine (100 mL). The mixture was refluxed in an oil bath under nitrogen. An orange product was obtained after heating and stirring for 36 h. The solvent was then removed under reduced pressure and the residue was dissolved in dichloromethane, washed three times with distilled water, dried with anhydrous magnesium sulfate, and then filtered and concentrated. The resulting solution was chromatographed on silica gel using ethyl acetate as eluent to produce a red compound in 34% yield. Found: C 84.0, H 6.0, N 5.2. Calc. for  $C_{38}H_{32}N_2O_2$ : C 83.2, H 5.8, N 5.1.  $\delta_H$  (CDCl<sub>3</sub>, 600 MHz) 8.58 (4H, q, *J* 5.2), 7.56 (3H, q, *J* 10.9), 7.44 (3H, t, *J* 7.6), 7.36 (7H, m), 7.15 (1H, t, *J* 9.1), 7.02 (4H, d, *J* 16.2), 6.80 (2H, d, *J* 7.3), 6.75 (2H, t, *J* 12.3), 6.66 (2H, t, *J* 12.8), 3.90 (3H, s), 3.54 (3H, s).  $\delta_C$  (600 MHz, CDCl<sub>3</sub>) 152.3, 151.6, 146.3, 146.1, 139.9, 139.6, 136.4, 134.5, 134.3, 131.3, 131.2, 131.0, 129.9, 128.9, 128.5, 128.3, 128.3, 127.8, 127.5, 127.4, 127.2, 127.1, 125.4, 122.3, 122.3, 114.8, 114.3, 110.3, 57.7, 57.4.

## 1,4-Bis{2-[4-(2-pyridin-4-ylvinyl)phenyl]vinyl}-2,5bisdodecyloxybenzene 7

The compound was obtained by a similar synthetic method as for compound **6** in 39% yield. Found: C 84.8, H 9.0, N 3.4. Calc. for C<sub>60</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub>: C 84.1, H 8.9, N 3.3.  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 600 MHz) 8.59 (4H, d, *J* 4.0), 7.57(10H, m), 7.41 (4H, d, *J* 4.7), 7.36 (1H, s), 7.33 (1H, s), 7.19 (1H, s), 7.15 (3H, d, *J* 2.2), 7.05 (2H, d, *J* 16.2), 4.09 (4H, t, *J* 6.4), 1.91 (4H, m), 1.58 (4H, m), 1.41 (32H, m), 0.88 (6H, t, *J* 6.8).  $\delta_{\rm C}$  (600 MHz, CDCl<sub>3</sub>) 151.3, 149.6, 138.7, 135.1, 133.3, 128.2, 127.5, 127.0, 125.4, 124.3, 120.9, 114.6, 114.4, 110.7, 69.6, 32.0, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 26.3, 22.7, 14.1.

#### **Results and Discussion**

#### Linear Absorption and Fluorescence Spectra

The photophysical properties of compounds **6** and **7** are summarized in Table 1. Linear absorption spectra were measured in solvents of different polarity at a concentration c of  $10^{-5}$  mol L<sup>-1</sup>. At this concentration, there is no influence of solvent on the spectra. The one-photon fluorescence spectra were measured at the same concentrations as for the linear absorption spectra. The maximum excitation wavelengths of **6** and **7** were 420 and 430 nm, respectively. Fig. 1 shows the

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| $\Phi$ is the one-photon quantum yield determined using coumarin 307 as the standard; <sup>[21]</sup> $\tau$ is the one-photon fluorescence lifetime;<br>$\varepsilon$ is the relative permittivity at 20°C; <sup>[22]</sup> $\varepsilon_{res}$ is the corresponding molar absorption coefficient |                                 |       |                              |                              |                              |        |      |                            |
|--|---------------------------------|-------|------------------------------|------------------------------|------------------------------|--------|------|----------------------------|
| Cpds   | Solvent                         | ε     | $\lambda_{\max}^{(1a)}$ [nm] | $\varepsilon_{\rm res}/10^4$ | $\lambda_{\max}^{(1f)}$ [nm] | τ [ns] | Φ    | $\lambda_{max}^{(2)}$ [nm] |
| 6  | DMF                             | 37.6  | 415                          | 4.36                         | 518                          | 1.67   | 0.66 |                            |
|  | Benzyl alcohol                  | 13.1  | 429                          | 5.51                         | 520                          | 1.42   | 0.76 |                            |
|  | THF                             | 7.58  | 420                          | 6.62                         | 510                          | 1.52   | 0.60 |                            |
|  | $CH_2Cl_2$                      | 9.1   | 419                          | 6.02                         | 512                          | 1.56   | 0.63 |                            |
|  | CHCl <sub>3</sub>               | 4.806 | 423                          | 5.78                         | 506                          | 1.41   | 0.66 | 525                        |
| 7  | DMF                             | 37.6  | 421                          | 3.52                         | 520                          | 1.65   | 0.65 |                            |
|  | Benzyl alcohol                  | 13.1  | 433                          | 4.87                         | 522                          | 1.52   | 0.75 |                            |
|  | THF                             | 7.58  | 426                          | 5.54                         | 512                          | 1.38   | 0.58 |                            |
|  | CH <sub>2</sub> Cl <sub>2</sub> | 9.1   | 425                          | 5.38                         | 514                          | 1.43   | 0.61 |                            |

5.00

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**Table 1.** Solvent effects on the absorption spectra and one- and two-photon fluorescence spectra of compounds 6 and 7  $\lambda_{\text{max}}^{(1a)}, \lambda_{\text{max}}^{(1f)}$ , and  $\lambda_{\text{max}}^{(2)}$  are one-photon absorption, one-photon fluorescence, and two-photon fluorescence maxima peaks, respectively.

CHCl<sub>3</sub> 4.806 428 linear absorption and one-photon fluorescence spectra of the two compounds in chloroform. Table 1 is organized such that the polarity of solvents decreases gradually from DMF (3.82 D) to CHCl<sub>3</sub> (1.01 D). Table 1 shows that for both compounds the maximum absorption peaks show a slight blue shift, the maximum fluorescence peaks show a clear red shift, and the fluorescence lifetimes are lengthened with an increase in solvent polarity, with the exception of benzyl alcohol. This effect can be explained by the fact that the excited state of two compounds may produce a higher polarity than that of the ground state, because the solvatochromism is associated with energy level lowering. An increased dipole-dipole interaction between the solute and solvent leads to a lowering of the energy level.<sup>[17,18]</sup> For benzyl alcohol, hydrogen bonding between the solvent and solute molecules decreases the excitation energy.<sup>[19]</sup> It is should noted that both the largest one-photon oscillator strength and the maximum two-photon absorption cross-section occur in the same excited state, the charge-transfer state, in the lower-energy region because of the symmetrical characteristics of the present molecules. Therefore, we studied the two-photon fluorescence spectra, as described in the following Section.

## Two-Photon Fluorescence Spectra

The two-photon fluorescence spectra of 6 and 7 in chloroform are also shown in Fig. 1 at concentrations c of the order of  $10^{-3}$  mol L<sup>-1</sup>. Spectra were recorded with a modelocked Ti:sapphire laser (Coherent Mira 900F) pump source with a 200 fs pulse duration, a repetition rate of 76 MHz, and a single-scan streak camera (Hamamatsu C5680-01) and monochromator. Excitation wavelengths for 6 and 7 were all 830 nm. Table 1 shows that the maximum peak of the two-photon fluorescence has a slight red shift compared with that of one-photon fluorescence in chloroform for each compound. This can be ascribed to the effect of reabsorption for the linear absorption band having a slight overlap with the emission band, and our two-photon fluorescence experiments were carried out on concentrated solutions that made reabsorption significant.<sup>[23]</sup> Table 1 also shows that the maximum peak positions in the absorption and fluorescence spectra of 7 show a red shift compared with those of 6. This can be explained by the fact that the electron donor strength of



1.35

0.63

Fig. 1. Absorption and fluorescence spectra of 6 and 7. The linear absorption and one-photon fluorescence spectra were measured in chloroform at a concentration of  $1 \times 10^{-5}$  mol L<sup>-1</sup>. Two-photon fluorescence spectra were measured in chloroform with the concentration of  $1 \times 10^{-5}$  mol L<sup>-1</sup>. Spectra **a**, **c**, and **e** are linear absorption and one- and two-photon fluorescence spectra of 6, respectively; spectra **b**, **d**, and **f** are linear absorption and one- and two-photon fluorescence spectra of 7, respectively.

dodecyl group linked to the O atom is larger than that of methyl linked to O.

In addition to the similarities between one-photon fluorescence and two-photon fluorescence, the two-photon fluorescence peak positions are also independent of the laser wavelength used. Thus, although the electrons can be pumped to the different excited states by linear absorption or twophoton absorption due to the different selection rules, they would finally relax to the same lowest excited state by internal conversion and/or vibrational relaxation.

#### Two-Photon Photopolymerization

Our two-photon initiating photopolymerization experiments have been accomplished using **6** or **7** as an initiator. The two-dimensional lattice was fabricated with negative resins system, which contained oligomers (bisphenyl A epoxide dimethylacylate) and **6** or **7** (5%) as an initiator and a small amount of dichloroethane (increasing the compatibility and controlling the viscosity). The 830 nm laser source from the mode-locked Ti:sapphire was tightly focussed through an objective lens ( $\times$ 40, NA 0.65) onto the sample film mounted on the *xy*-step monitorized stage controlled by a computer. The pulse energy after being focussed by the objective lens was approx. 10 mW. Unreacted liquid was washed out to obtain the polymerized grating shown in the micrograph in Fig. 2.

The photopolymerization mechanism of the two new initiators is still unclear. According to Cumpston et al.,<sup>[5]</sup> strong donor substituents would make the conjugated system electron rich, so that electrons may be transferred to relatively weak acceptor molecules after one- or two-photon excitation. This process may activate the polymerization reaction. In order to demonstrate this process, we performed ab initio calculations at time-dependent hybrid density functional theory B3LYP level in the *Gaussian* package for **6**, showing that the first excited state is the charge-transfer (CT) state with the excited energy  $\lambda$  of 493 nm. When the molecule is irradiated by 830 nm laser, it can be expected that the molecule will simultaneously absorb two photons and is excited to the first excited state (the CT state). For a better understanding of the charge-transfer process, we have plotted the charge



Fig. 2. Optical micrograph, obtained on an Olympus BX-51 microscope, of a grating fabricated by two-photon polymerization with compound 6 as an initiator.



**Fig. 3.** Density difference between the charge-transfer and ground states of compound **6** in the gas phase. Areas with chickenwire and dots represent the electron loss and gain, respectively, upon the excitation. The electron of pyridine side (acceptor) is lost and marked with chickenwire. The electrons of the central parts (donor) is gained and marked with dots.

density difference between the ground state and the CT state for molecule **6** in the gas phase (see Fig. 3) by the *Molekel* program.<sup>[25]</sup> It can be seen that upon excitation, charges are mainly transferred from the acceptor side (pyridine side) to the donor side (the central parts) of the molecule. In the CT state, there are more electrons on the central parts of the molecule, indicating that an electron may be more readily released from the molecule to the surroundings. This picture seems to support the conclusion of Cumpston et al.<sup>[5]</sup> However, whether the photo-induced electron-transfer reaction is energetically feasible needs further theoretical investigation.

# Conclusions

Two new symmetrical two-photon photopolymerization initiators, **6** and **7**, have been synthesized and characterized. The one-photon fluorescence quantum yields, lifetimes, and solvent effects of these initiators are presented in detail. Both compounds exhibit large delocalized  $\pi$ -electron conjugated systems. Experimental results show that the two compounds are good two-photon absorbing chromophores and effective two-photon photopolymerization initiators. A possible photopolymerization mechanism involving a charge-transfer process under laser irradiation is discussed.

# Acknowledgments

This work was supported by grants from the state National Natural Science Foundation of China (grant nos 50323006, 50325311, and 10274044) and the Swedish International Development Cooperation Agency (SIDA).

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