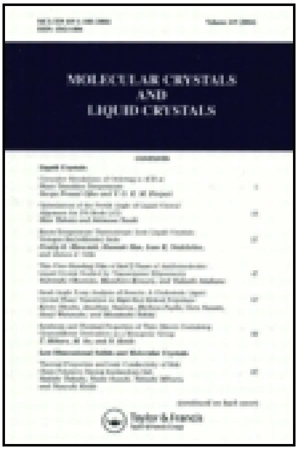

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Synthesis and Characterization of Two-Photon Absorbing Dithienothiophene Derivative with Silyl End Group

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Efficient two-photon absorbing chromophore based on dithienothiophene has been synthesized and its two-photon absorption cross section (σ_2) was evaluated by two-photon induced fluorescence excitation spectroscopy. The chromophore obtained shows a sizable two-photon absorption cross section value of 618 GM at 700 nm. By using one- and two-photon spectroscopic experiment, two-photon absorption properties of the chromophore with the electronic transition dipole moment and one- and two-photon transition energies were evaluated. Besides, we have demonstrated the successful application of this compound in fabrication of 2D and 3D microobjects by using two-photon microfabrication technique.

Keywords: 3D microfabrication; dithienothiophene; two-photon absorption

INTRODUCTION

Two-photon absorbing organic molecules are of great interest due to their great potential applications in various fields such as photodynamic therapy [1–3], three-dimensional (3D) optical data storage [4,5], optical power limiting [6–8] and 3D microfabrication [9,10]. To date, numerous two-photon absorption (TPA) materials have been synthesized in order to increase the appropriate two-photon absorbing

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activities required to different applications as mentioned above. It has been well known that TPA activity is strongly responsible for the type of π-bridge, the strength of donor and acceptor, the conformational changes of molecules, the symmetry of the systems and the conjugation length of systems. The thiophene rings have attracted considerable attention as new functional materials because of their effective π-conjugation of the molecular chains. Especially, the dithieno[3,2-*b*: 2A,3A-*d*]thiophene (DTT) has been appeared for a variety of optoelectronic materials that involve, one and two-photon absorption [11], excited fluorescence [12], photochromic materials [13] and non-linear optical chromophores [14]. Despite good electronic and optical properties, thiophene derivatives are insoluble in common organic solvents and are therefore difficult to process. Particularly, the use of DTT based π-conjugated systems has been limited due to their poor solubility. To address this issue, we prepared the new organic TPA molecules having DTT moiety as a π-center with symmetrically substituted fluorene containing trimethylsilyl group. The DTT moiety can delocalize electrons and possess the decreased rotational degree of freedom due to the presence of a fused ring structure. Here we report the synthesis and optical properties of novel TPA chromophore based on DTT and fluorene with high two-photon absorption efficiency as well as good solubility in commom organic solvent which is miscible with photocurable resin for successful 3D microfabrication.

EXPERIMENTAL

Chemicals

Dichloromethane, *N,N*-dimethylfromamide (DMF) and tetrahydrofuran (THF) were dried under calcium hydride and distilled. Other solvents (reagent grade) were used without any purification. All reactions were conducted under nitrogen atmosphere. All chromatographic separations were performed on silica gel (60 M, 230–400 mesh).

Synthesis

2,6-Dibromodithieno[3,2-b2′,3′-d]thiophene (**DTT-2Br**) were synthesized as reported in literature [12].

2,7-Dibromo-9,9-bis(2-ethylhexyl)fluorene (DBF-EH). To a mixture of 2,7-dibromo-9*H*-fluorene (2 g, 6.17 mmol) and *t*-BuOK (1.7 g, 15.42 mmol) in 10 mL of DMF, 2-ethlyhexyl bromide (2.47 mL, 13.57 mmol) wad added. The reaction mixture was stirred at 40°C for 18 hr before 40 mL of H_2O was added. The solution was then extracted twice with 50 mL of diethyl ether. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, followed by removal of excess 2-ethylhexylbromide by distillation under vacuum. The crude product was purified by column chromatography using hexane as eluent to yield a light yellowish oil, **DBF-EH** (yield: 95%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.4–0.6 (s, 9H), 0.62–0.98 (m, 27H), 1.87–1.98(d, 4H $J = 9.5$ Hz), 7.42–7.58 (m, 6H); GC/MS, m/z: 324 (100%, M^+).

2-Bromo-7-trimethylsily-9,9-bis(2-ethylhexyl)fluorene (BSF-EH). Into a solution of **DBF-EH** (11.1 g, 23.9 mmol) in anhydrous THF (150 mL) was added n-BuLi (2.5 M in hexane, 9.8 mL, 24.5 mmol) at −78°C for 30 min. The reaction mixture was stirred for 1 h, then chlorotrimethylsilane (3.4 mL, 26.8 mmol) was added. The mixture was warmed to room temperature, stirred for 30 min and poured into a large amount of water for extraction with petroleum ether. The organic extracts were washed with brine and dried over $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel using petroleum ether as the eluent to yield of 11 g **BSF-EH** (yield: 91%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.3–0.39 (s, 9H), 0.4–0.59 (m, 9H), 0.61–0.98 (m, 26H), 1.82–2.1 (m, 4H), 7.42–7.71(m, 6H); GC/MS, m/z: 541 (100%, M^+).

2-Trimethylsilyl-9,9-bis(2-ethylhexyl)fluoren-7-yl-bronic acid (SFB-EH). Into a solution of **BSF-EH** (0.45 g, 8.30 mmol) in anhydrous THF (25 mL) was added n-BuLi (2.5 M in hexane 3.6 mL, 9.04 mmol) at −78°C. The reaction mixture was stirred for 1 hr before triisopropyl borate (0.5 mL, 11.90 mmol) was added in one portion. The reaction mixture was stirred overnight at room temperature and poured into a large amount of water and extracted with ethyl ether. The organic extracts were washed with brine and dried over $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to yield **SFB-EH** (0.23 g, 52%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.3–0.3.9 (s, 9H), 0.45–1.1 (m, 38H), 2.03–2.21 (m, 4H), 7.55–7.58 (d, 1H $J = 7.42$ Hz), 7.65 (s, 1H), 7.79–7.86 (d, 1H $J = 7.42$ Hz), 7.89–7.94 (d, 1H $J = 7.7$ Hz), 8.28–8.36 (d, 2H $J = 8.52$ Hz).

Synthesis of SF-DTT-SF. Mixture of **DTT-2Br** (0.56445 g, 1.594 mmol), **SFB-EH** (2.346 g, 3.985 mmol) and $Pd(PPh_3)_4$ (30 mg, 2.6 mmol) in a 25 mL flask were dissolved into toluene (20 mL) and 2.0 M Na_2CO_3 solution (6.0 mL, 12.0 mmol) was added. The reaction mixture was stirred at 90°C for a day. After cooling, the product was extracted with dichloromethane, washed with water and dried over

$MgSO_4$. The solvent was evaporated off affording the crude mixture. After column chromatography with silica gel eluting with petroleum ether/dichloromethane, pure compound **SF-DTT-SF** (1.31 g, 74%) was obtained as a white yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.3–0.3.9 (s, 18H), 0.5–0.98 (m, 60H), 1.98–2.12 (m, 8H), 7.42 (s, 2H), 7.50 (d, 2H, $J = 7.7$ Hz), 7.58 (s, 8H), 7.63 (d, 4H, $J = 7.97$ Hz), 7.68 (d, 4H, $J = 7.42$ Hz), 7.72 (d, 4H, $J = 7.69$ Hz). MALDI-TOF: *m/z*: 1116 (M^+, 100%). Anal. Calcd. For $C_{72}H_{100}S_3$: C, 77.35; H, 9.02; S, 8.60. Found: C, 77.62, H, 9.30, S, 8.77.

Measurements

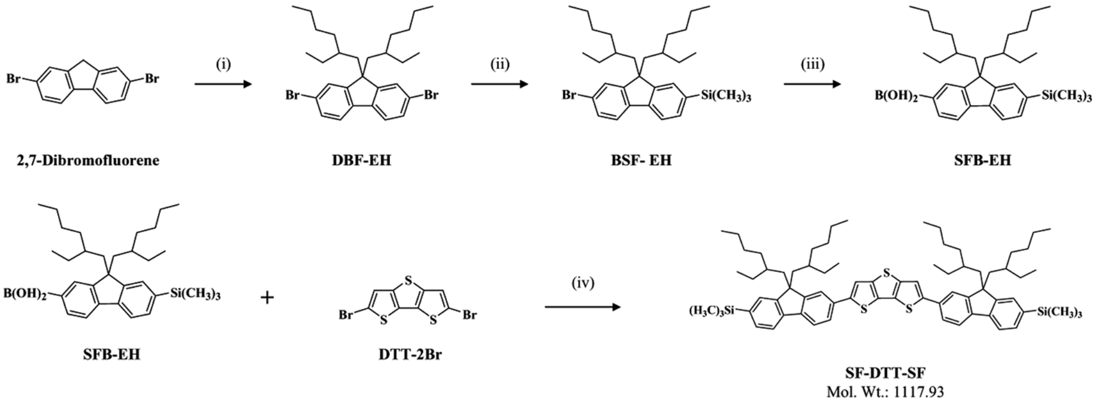
The linear absorption spectrum was recorded on a spectrophotometer (Perkin Elmer, Lambda 14) in diluted solutions, 1.0×10^{-6} M in THF. The fluorescence mearsurement was conducted with 1×10^{-6} M in THF using a Jobin-Ynon Fluorog FL-311 spectrofluorimeter. Mass spectroscopic data were obtained with a MALDI-TOF of Voyager-DETM STR Biospectrometry Workstation model. The TPA cross section was obtained by two-photon induced fluorescence (TPIF) method according to the method described in the literature [15]. Using this method fluorescence intensities obtained from two-photon excitation of unknown and reference molecules at the same conditions are compared over a range of frequencies. Mode-locked Ti-sapphire 100 femtosecond (fs) pulse laser was employed with a repetition rate of 90 MHz. The study was carried out in the range of 700 to 940 nm regime using fluorescein as a reference fluorophore.

RESULTS AND DISCUSSION

Synthesis and Photophysical Properties

The synthetic route for DTT-based two-photon absorbing chromophore (**SF-DTT-SF**) is displayed in Scheme 1. The **SF-DTT-SF** was synthesized by Suzuki coupling reaction between 2,6-dibromo-dithieno[3, 2-b2′,3′-d]thiophene (**DTT-2Br**) and 2-trimethylsilyl-9,9-bis(2-ethylhexyl)fluoren-7-yl-bronic acid (**SFB-EH**). 2,6-Dibromodithieno[3, 2-b2′,3′-d]thiophene (**DTT-2Br**) were synthesized as reported in literature [12]. All reaction intermediates and final product were carefully purified by chromatography and recrystallization and its chemical structure and purity were confirmed by NMR, MALDI-TOF and HPLC.

Figure 1 shows linear absorption and emission spectrum of **SF-DTT-SF**and its photophysical properties are summarized in Table 1. The absorption spectrum of **SF-DTT-SF** shows two characteristic



Scheme 1 Reagents and conditions: (i) *t*-BuOk, 2-Ethylhexylbromide, DMF; (ii) n-BuLi, Me_3SiCl, THF; (iii) *n*-BuLi, Tri-isopropyl borate, THF; (iv) $Pd(PPh_3)_4$, Na_2CO_3, Toluene

SCHEME 1 Synthetic route of TPA chromophore SF-DTT-SF.

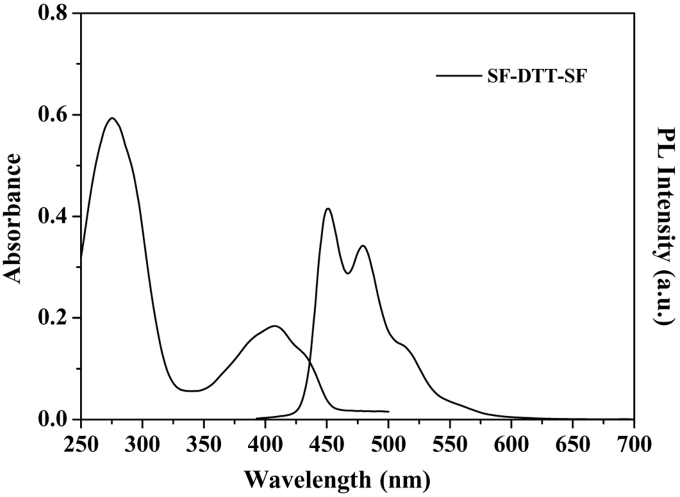


FIGURE 1 One-photon absorption and photoluminescence spectra of SF-DTT-SF.

absorption peaks with the higher energy band at 285 nm and the lower energy band at 415 nm in THF. Emission maximum of **SF-DTT-SF** was found to be at 450 nm with a quantum yield of 0.28. In the absorption spectrum we quantified the transition energy between the ground state and the one-photon allowed excited state (E_{ge}), the oscillator strength (f_{ge}), and the transition dipole moment (M_{ge}) of the lowest

TABLE 1 Photophysical Date of TPA Chromophore **SF-DTT-SF**

Compound	λ_{abs} (nm)	ε (M^{-1} cm^{-1})[a]	E_{ge}[b]	Γ_1[c] (cm^{-1})	f_{ge}[d]	M_{ge}[e] (D)	λ_{flu} (nm)	Φ[f]	σ_2 (GM)[g]
SF-DTT-SF	408	184000	3.06	4936	0.495	5.9	451	0.28	618 6 (at 700 nm)

All data in this table was measured in THF.

[a] Molar extinction coefficient.

[b] Energy of the transitions between the ground state and the one-photon allowed excited state.

[c] Band width (FWHM).

[d] Oscillator strength.

[e] Transition dipole moment.

[f] Fluorescence quantum yield.

[g] Two-photon absorption cross section ($1\,GM = 1 \times 10^{-50}\,cm^4\,s\,photon^{-1}\,molecule^{-1}$). Experimental uncertainty: ±15 %.

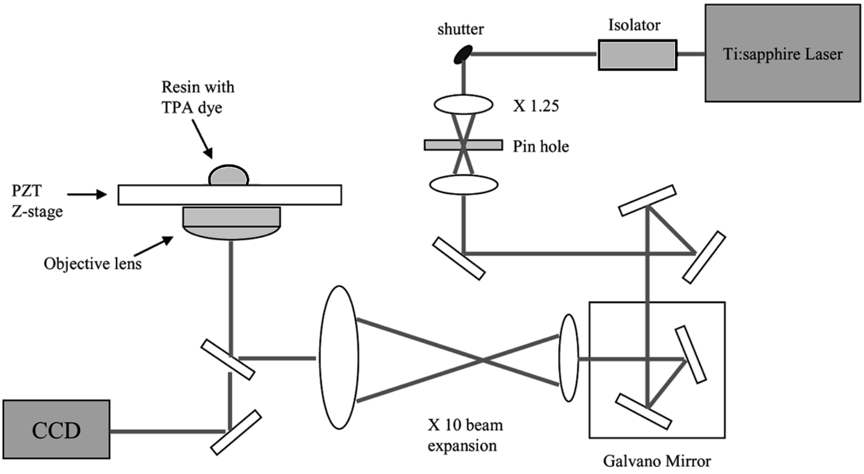


FIGURE 2 Schemetic diagram of nano-stereolithography set-up.

band of the **SF-DTT-SF**. The oscillator strength using a simplified equation for Gaussian shape was calculated as following Eq. (1) [16]:

$$f_{ge} = \frac{4.4 \times 10^{-9}}{n} \int \varepsilon d\nu = 4.6 \times 10^{-9} \frac{\varepsilon_{\max} \Gamma_1}{n} \tag{1}$$

where n is the refractive index of solution, ν is the frequency in cm^{-1}, Γ_1 is the full width at half maximum in cm^{-1} and $\varepsilon_{\max}$ is the maximum extinction coefficient. The transition dipole moment M_{ge} can be calculated from linear absorption spectrum according to Eq. (2) [16]:

$$|M_{ge}|^2 = \frac{f_{ge}}{4.7 \times 10^{29} \nu_{\max} G} \tag{2}$$

where $\nu_{\max}$ is the mean wavenumber of the band and G is the multiplicity weight factor.

The M_{ge} value of SF-DTT-SF was 5.9 D, which is effective value for the TPA cross section. It is well known that the transition dipole moment for g→e and e→e′ plays a crucial role in the two-photon transition, which is shown in Eq. (3) [17]:

$$\sigma_2 \propto \frac{M_{ge}^2 M_{ee'}^2}{(E_{ge} - E_{ge'}/2)^2 \Gamma} \tag{3}$$

where M_{ij} and E_{ij} are the transition dipole moment and the energy of the transitions of the state i and j, respectively. Γ is the damping factor. Another important factor is detuning energy, E_{ge}–$E_{\mathrm{ge'}}/2$, which

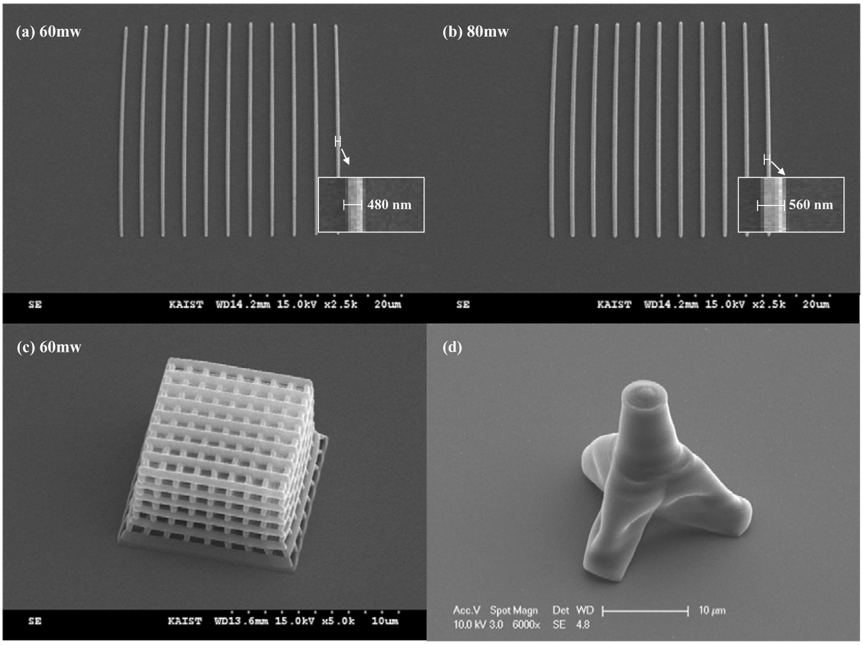


FIGURE 3 SEM images of the line pattern and 3-D structures fabricated by two-photon lithography; (a) a power of 60 mW with an exposure time of 2 ms, (b) a power of 80 mW with an exposure time of 2 ms, (c) and (d) 3D woodpile and tetraport structures fabricated at a laser power of 60 mW with an exposure time of 2 ms.

can be calculated from the one- and two-photon spectra, but we could not obtain this value because of limitation of excitation laser frequency of laser setup. In the further work we will measure $M_{ee'}$ by the experiment of excited state transient absorption spectroscopy.

TPA cross section was evaluated by using Mode-locked Ti-sapphire 100 fs pulse laser with a repetition rate of 90 MHz. TPA cross-section value (σ_2) was found to be 618 GM at 700 nm as shown in Table 1. The TPA was increased at shorter wavelengths, thus it could have larger value at the actual maximum. The strong TPA value is mainly because the DTT as a π-center has exceptionally electron rich properties and fluorene behaves like a weak acceptor, which allows efficient intramolecular charge transfer from DTT to the fluorene moieties. This result shows that the efficient charge transfer is effective in enhancing the TPA cross section, and DTT based on TPA chromophore is therefore expected to be an excellent candidate for two-photon absorbing materials.

TPA Polymerization for 3-d Patterning

To investigate the dependence of the resolution of TPA microfabrication on the various optical factors, line patterns have been fabricated on the glass substrate by using **SF-DTT-SF** as a photosensitizer in 0.1 wt% mixed with a urethane acrylate resin, SCR500 supplied by JCR. A mode-locked Ti:Sapphire laser has been employed as a light source and the central wavelength of 780 nm with a pulse width of 160 fs and a repetition rate of 80 MHz. The laser power was 60 mW and the exposure time was 1 ms. Scanning proceeded in on-and-off method and the speed was 30 nm/1 ms. The laser setup for TPA micropatterning was shown in Figure 2 [18]. Under this condition, fine line patterns were successfully obtained by TPP microfabrication using **SF-DTT-SF** (Fig. 3). There are many factors to influence the line width of TPP fabricated nano patterns such as laser power, exposure time, radical quenchers, numerical aperture of lens and other optical profiles. When the condition were differ in laser power and other things being equal, the resulting line width was measured to be 480 nm at 60 mw and to be 560 nm at 80 mw (Figure 3a and 3b). This result suggests that the laser power is associated with the line width. Following the line patterning, we were able to fabricate a 3D woodpile structure by adding the SF-DTT-SF chromophore as displayed in Figure 2c. The dimension of the woodpile pattern obtained was 10 × 10 × 10 μm. The fabrication of the finer patterns will be enable us to make complex 3D structures with widespread applications in a number of field like MEMS deviecs. As shown in Figure 2d, real 3D microstructure of tetrapot with the resolution of 230 nm could be fabricated. The diameter of the pillars is 5.5 μm, and the height of the structure is 15 μm. Since the single contour scanning method was employed for fast fabrication, only the contours are polymerized and inside the structure is still liquid state. The small distortion like the bottom pillar can be occurred due to the high surface tension during developing process. This problem might be solved by multi-path scanning method developed by us [19]. We are currently working on solving this problem.

CONCLUSIONS

In this paper, we report synthesis and photophysical properties of novel TPA chromophores based on DTT and fluorene by one- and two-photon absorption spectroscopy. In our experiment, we studied the relationship between TPA cross section and ground- and excited-state one-photon absorption parameters such as oscillator strength and transition dipole moment. **SF-DTT-SF** shows sizable TPA efficiency with electron rich DTT moiety facilitating intramolecular charge transfer from DTT to fluorene building block. For the application of TPP microfabrication, we used **SF-DTT-SF** as a two-photon photosensitizer with acrylate resin, and consequently 3D microstructures were successfully fabricated with high resolution.

REFERENCES

[1] Bhawalkar, J. D., Kumar, N. D., Zhao, C. F., & Prasad, P. N. (1997). *J. Clin. Laser Med. Surg.*, *15*, 201.

[2] Fisher, W. G., Partridge Jr, W. P., Dees, C., & Wachter, E. A. (1997). *Photochem. Photobiol.* *66*, 141.

[3] Frederiksen, P. K., Jorgensen, M., & Ogilby, P. R. (2001). *J. Am. Chem. Soc.*, *123*, 1215.

[4] Cumpston, B. H., Ananthavel, S. P., Barlow, S., Dyer, D. L., Ehrlich, J. E., Erskine, L. L., Heikal, A. A., Kuebler, S. M., Lee, I. Y. S., & McCord-Maughon, D. (1999). *Nature*, *398*, 51.

[5] Parthenopoulos, D. A. & Rentzepis, P. M. (1989). *Science*, *245*, 843.

[6] Silly, M. G., Porrès, L., Mongin, O., Chollet, P.-A., & Blanchard-Desce, M. (2003). *Chem. Phys. Lett.*, *379*, 74.

[7] Spangler, C. W. (1999). *J. Mater. Chem.*, *9*, 2013.

[8] Zhou, G., Wang, X., Wang, D., Shao, Z., & Jiang, M. (2002). *Appl. Opt.*, *41*, 1120.

[9] Kawata, S., Sun, H. B., Tanaka, T., & Takada, K. (2001). *Nature*, *412*, 697.

[10] Zhou, W., Kuebler, S. M., Braun, K. L., Yu, T., Cammack, J. K., Ober, C. K., Perry, J. W. & Marder, S. R. (2002). *Science*, *296*, 1106.

[11] Kim, O.-K., Lee, K.-S., Woo, H., Kim, K. S., He, G. S., Swiatkiewicz, J., & Prasad, P. N. (2000). *Chem. Mater.*, *12*, 284.

[12] Ventelon, L., Blanchard-Desce, M., Moreaux, L., & Mertz, J. (1999). *Chem. Comm.*, 2055.

[13] Tsivgoulis, G. M. & Lehn, J.-M. (1995). *Angew. Chem. Int. Ed.*, *34*, 1119.

[14] Kim, O.-K., Fort, A., Barzoukas, M., Blanchard-Desce, M., & Lehn, J. M. (1999). *J. Mater. Chem.*, *9*, 2227.

[15] Morel, Y., Irimia, A., Najechalski, P., Kervella, Y., Stephan, O., Baldeck, P. L., & Andraud, C. (2001). *J. Chem. Phys.*, *114*, 5391.

[16] Drobizhev, M., Makarov, N. S., Stepanenko, Y., & Rebane, A. (2006). *J. Chem. Phys.*, *124*, 224701.

[17] Rumi, M., Ehrlich, J. E., Heikal, A. A., Perry, J. W., Barlow, S., Hu, Z., McCord-Maughon, D., Parker, T. C., Rockel, H., & Thayumanavan, S. (2000). *J. Am. Chem. Soc.*, *122*, 9500.

[18] Park, S. H., Lim, T. W., Yang, D. Y., Cho, N. C., & Lee, K.-S. (2006). *Appl. Phys. Lett.*, *89*, 173133.

[19] Yang, D. Y., Park, S. H., Lim, T. W., Kong, H. J., Yi, S. W., Yang, H. K., & Lee, K.-S. (2007). *Appl. Phys. Lett.*, *90*, 013113.