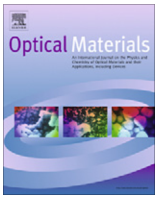
Optical Materials 35 (2013) 467–471

Contents lists available at SciVerse ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



# Linear and nonlinear optical properties of two novel D–$\pi$–A–$\pi$–D type conjugated oligomers with different donors

Tian-Hao Huang [a], Dan Yang [a], Zhi-Hui Kang [a], Er-Long Miao [c], Ran Lu [b,*], Hui-Peng Zhou [b], Fei Wang [c], Gao-Wen Wang [c], Peng-Fei Cheng [a], Ying-Hui Wang [a,*], Han-Zhuang Zhang [a,*]

[a] College of Physics, Jilin University, Changchun 130012, China
[b] College of Chemistry, Jilin University, Changchun 130012, China
[c] State Key Lab of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

ARTICLE INFO

*Article history:*
Received 25 July 2012
Received in revised form 26 September 2012
Accepted 26 September 2012
Available online 2 November 2012

*Keywords:*
Two-photon absorption
*z*-Scan
Linear conjugated oligomer

ABSTRACT

Experimental and theoretical studies on the donor-dependent optical characteristics of two D–$\pi$–A–$\pi$–D type linear fluorenone-based conjugated oligomers are presented, where fluorene and triphenylamine act as the donors, respectively. Because of the strong electron-donating ability, the triphenylamine chromophores lead to red-shifts of spectral features, shorten the excited state lifetime, and enhance the two-photon fluorescence efficiency and two-photon absorption cross-section in comparison with fluorene groups. Quantum chemical calculations provide complementary information regarding the molecular structures and the frontier orbitals, which can provide a deep insight into the electronic structure and properties of oligomers.

## 1. Introduction

Donor–acceptor (D–A) type $\pi$-conjugated organic oligomers have attracted much attention [1–6], because of their strong nonlinear optical properties, which can be used in the fields of two-photon fluorescence microscopy [7], three-dimensional (3D) optical data storage and fabrication [8–10], optical limiting [11], and photodynamic therapy [12], etc. Over the past two decades, organic molecules with excellent two-photon properties have developed significantly [13,14]. Mono-dispersed $\pi$-conjugated oligomer is one of the important model molecules that could be used to understand the structure–property relationship of organic materials [15,16]. It has been recognized that the two-photon optical properties of materials should be affected by the donor–acceptor strength, the molecular structure, the conjugation length and the intramolecular charge transfer (ICT), etc. [17–19]. The D–A $\pi$-conjugated oligomers usually have two types of molecular structures: asymmetrical D–$\pi$–A type and symmetrical D–$\pi$–A–$\pi$–D or A–$\pi$–D–$\pi$–A type, and their corresponding optical properties can be easily tuned by the introduction of different donor or acceptor moieties. A variety of functional donors (such as dimethylamino, diphenylamino, carbazoles, pyrroles, and dialkylamino) and acceptors (such as ketone, nitro, pyridine, and benzothiazole) have been chosen to synthesize molecules with strong nonlinear properties [20–22]. It has been reported that through introducing donors with strong electron-donating ability, the nonlinear optical parameters of molecules can be improved [23,24]. Additionally, symmetrical $\pi$-conjugated motifs bearing strong electron donor groups have revealed efficient two-photon absorption (TPA) properties [25,26] due to the facilitation of charge transfer between the donor substituents and the acceptor center. Therefore, further investigation on the symmetrical D–A linear oligomers with different donor groups is essential.

In this study, we compare the effects of donors on the linear and nonlinear optical characteristics of two novel D–$\pi$–A–$\pi$–D type fluorenone-based conjugated oligomers with fluorene [27] and triphenylamine as the donors (Fig. 1) by using various optical measurement techniques, including steady-state spectral measurement, time-correlated single-photon counting (TCSPC) technique, two-photon fluorescence (TPF) and femtosecond open aperture *z*-scan technique. We observe that the triphenylamine group with strong electron-donating capability may lead to red-shifts of spectral features through lowering the $\pi$–$\pi^*$ transition energy and increase the Stokes shift due to the enhancement of ICT, which are in good agreement with the theoretical calculation. Meanwhile, the triphenylamine group could improve the TPF efficiency and TPA cross-section of these $\pi$-conjugated oligomers.

## 2. Materials and optical measurements

The oligomers were synthesized via Heck reaction [28]. For **F–FO–F**, a mixture of **E–OFV1** [29] (1.36 g, 3.26 mmol), 2,7-dibromo

---

* Corresponding authors. Tel.: +86 431 85167378; fax: +86 431 85166112 (H.-Z. Zhang).

*E-mail addresses:* luran@mail.jlu.edu.cn (R. Lu), yinghui_wang@jlu.edu.cn (Y.-H. Wang), zhanghz@jlu.edu.cn (H.-Z. Zhang).

0925-3467/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.optmat.2012.09.032

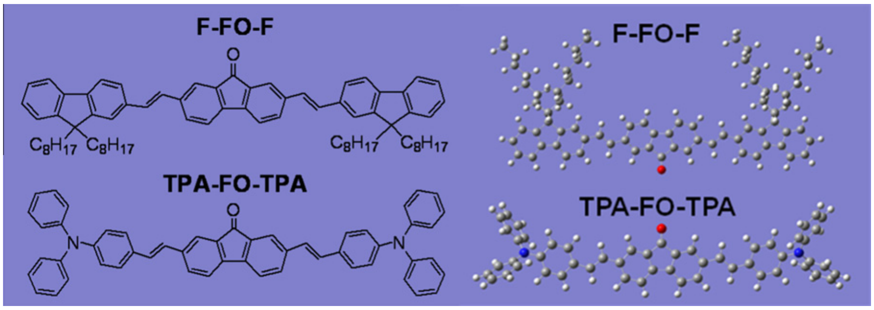


**Fig. 1.** Molecular structures of **F–FO–F** and **TPA–FO–TPA**, together with their optimized ground state geometries as predicted by quantum chemical calculation.

fluorenone (0.51 g, 1.50 mmol), tetrabutylammonium bromide (1.10 g, 3.20 mmol), anhydrous potassium carbonate (0.90 g, 6.50 mmol) and Pd $(OAc)_2$ (20 mg, 0.089 mmol) was added into 10 mL anhydrous DMF. The mixture was heated at 110 °C for 10 h under nitrogen atmosphere. After being poured into 400 mL water, the mixture was extracted with $CH_2Cl_2$ ($3 \times 50$ mL). The organic liquid was washed with brine and then dried with anhydrous $MgSO_4$. After the solvent was removed, the crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 5:1) and recrystallized from ethanol/THF to give red powder. Yield: 76%. Mp: 118–120 °C. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.91 (s, 2H), 7.71–7.65 (m, 4H), 7.60 (d, $J = 7.7$ Hz, 2H), 7.53–7.46 (m, 6H), 7.36–7.32 (m, 3H), 7.31–7.26 (m, 5H), 7.16 (d, $J = 16.2$ Hz, 2H), 2.04–1.95 (m, 8H), 1.21–1.03 (m, 40H), 0.81 (t, $J = 7.1$ Hz, 12H), 0.69–0.60 (m, 8H). IR (KBr, $cm^{-1}$): 2954, 2926, 2853, 1713, 1637, 1465, 1385, 962, 740. Elemental analysis calculated for $C_{75}H_{92}O$: C, 89.23; H, 9.19; O, 1.58. Found: C, 89.32; H, 9.02. MS, $m/z$: cal: 1009.5, found: 1009.7. **TPA–FO–TPA** was obtained from N-phenyl-N-(4-vinylphenyl) benzenamine [30] and 2,7-dibromo fluorenone following the general procedure for **F–FO–F**. The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 7:2) and recrystallized from ethanol/THF to give dark red powder. Yield: 77%. Mp: >200 °C. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.82 (s, 2H), 7.51 (d, $J = 9.3$ Hz, 2H), 7.44 (d, $J = 7.7$ Hz, 2H), 7.38 (d, $J = 8.7$ Hz, 4H), 7.30–7.26 (m, 6H), 7.26 (s, 2H), 7.14–7.10 (m, 10H), 7.07–7.02 (m, 8H), 6.97 (d, $J = 16.2$ Hz, 2H). IR (KBr, $cm^{-1}$): 2958, 2923, 2855, 1715, 1635, 1463, 1385, 1281, 964, 754. Elemental analysis calculated for $C_{53}H_{38}N_2O$: C, 88.55; H, 5.33; N, 3.90; O, 2.23. Found: C, 88.62; H, 5.26; N, 3.86. MS, $m/z$: cal: 718.9, found: 718.9.

Both oligomers were dissolved in toluene solution with concentrations of $5 \times 10^{-5}$ and $5 \times 10^{-4}$ M, for linear and nonlinear optical measurements, respectively. The samples were placed in a 2 mm thick quartz cuvette for the optical measurements. Steady-state absorption spectra were measured with a UV–Vis spectrophotometer (Purkinje, TU-1810PC). One and two-photon fluorescence measurements were carried out by using a CCD detector (Ocean Optics, USB4000). Time-dependent fluorescence kinetics at 600 nm was detected by a time-correlated single-photon counting spectrometer (Edinburgh, mini-$\tau$), with the excitation wavelength of 405 nm (Edinburgh, EPL-405). A mode-lock Ti:sapphire femtosecond laser (Coherent) was used for nonlinear optical measurements. The amplified pulses were obtained at 1 kHz, 800 nm, 130 fs, and 2.2 mJ. TPA cross-section measurements were carried out by employing the open aperture $z$-scan technique with a focal length of lens of 100 mm, a pulse energy of ~250 nJ, and the laser beam was modulated with an optical chopper at a rate of ~500 Hz. The signals were measured by a photodiode and then travel through a lock-in amplifier (SR830, DSP), which is able to obviously suppress noise outside a narrow frequency interval, before they reach the computer.

## 3. Results and discussion

Fig. 2 shows the steady-state absorption and one-photon fluorescence (OPF) spectra of oligomers in toluene ($5 \times 10^{-5}$ M). The absorption spectra of each oligomer is characterized by two bands. The high-energy absorption band at around 400 nm can be assigned to the $\pi$–$\pi^*$ electronic transitions of conjugated molecules, and the less intense one in the low-energy region could be attributed to the charge transfer (CT) processes [31,32]. The absorption peaks of **F–FO–F** appear at 392 and 483 nm, and those of **TPA–FO–TPA** are at 409 and 496 nm, respectively. Apparently, the absorption peaks of triphenylamine end-capped oligomer red-shift about 17 and 13 nm respectively, in comparison with those of fluorene end-capped oligomer, through lowering the $\pi$–$\pi^*$ transition energy and enhancing the intramolecular CT character [33]. Similar to the absorption spectra, the OPF spectra of **TPA–FO–TPA** also exhibits a red-shifted spectral feature compared to that of **F–FO–F**. According to the absorption and OPF spectra, we observe that the Stokes shift of **TPA–FO–TPA** is 10 nm larger than that of **F–FO–F**, indicating an enhanced ICT character [34] occurs in **TPA–FO–TPA**. In order to further understand the information of oligomers in excited state, TCSPC technique has been performed to detect the OPF kinetics of **F–FO–F** and **TPA–FO–TPA**. Photoexcitation is carried out at 405 nm, corresponding to the lowest energy $\pi$–$\pi^*$ transition [35], and the corresponding OPF relaxation curves at 600 nm are presented in Fig. 3, which exhibit mono-exponential decay. Through fitting the experimental data, we obtain lifetimes

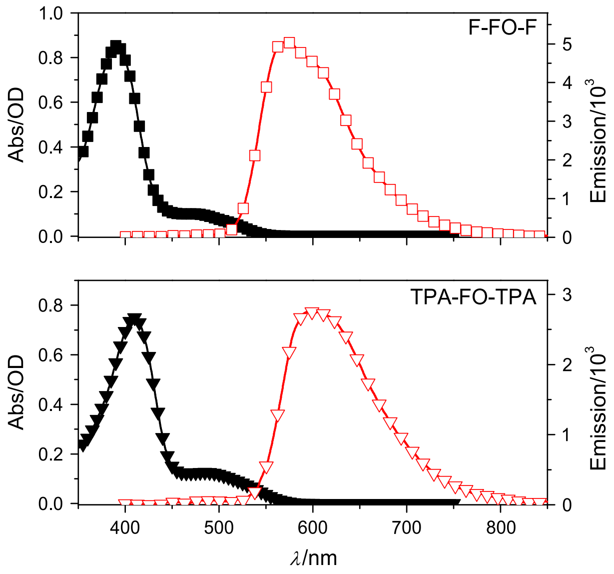


**Fig. 2.** Absorption and emission spectra of **F–FO–F** and **TPA–FO–TPA** ($5 \times 10^{-5}$ M).

of 3.0 and 1.9 ns for **F–FO–F** and **TPA–FO–TPA**, respectively. It suggests that the triphenylamine group, which bears a stronger electron-donating ability than fluorene group, is able to shorten the fluorescence lifetime.

Under the excitation of femtosecond laser pulses at 800 nm, an intense photoluminescence (PL) was observed in the oligomer solution with concentration of $5 \times 10^{-4}$ M. As seen in Fig. 4A, The emission maximums are located at 575 and 605 nm for **F–FO–F** and **TPA–FO–TPA**, respectively. Thus, compared to OPF spectra, the emission peaks in PL spectra excited with 800 nm femtosecond laser are red-shifted by 5 and 8 nm. This phenomenon could be explained by a volume reabsorption effect, as the concentration of solutions used in the multi-photon excitation is much higher [36]. The integral intensity of multi-photon fluorescence is linearly dependent on the square of the excitation intensity, as shown in Fig. 4B, thereby confirming the TPA process. It is obvious that the linear fitted line of **TPA–FO–TPA** shows a larger slope than that of **F–FO–F**, indicating that the triphenylamine group is able to enhance the TPF efficiency, and the TPF efficiency of **TPA–FO–TPA** is calculated to be almost 1.8 times higher than **F–FO–F**.

The nonlinear absorption coefficients were measured by the femtosecond open aperture *z*-scan technique at 800 nm, and the results are shown in Fig. 5. Nonlinear optical measurements were made under nonresonant excitation since the absorption bands of two oligomers are located in the range between 350 and 580 nm, being transparent in the near infrared region [37]. The curves exhibit a decrease of transmittance at positions (Z) near the focus, which is attributed to the TPA effect. Besides, we also took a measurement on neat toluene with an energy of 245 nJ, and the result shows that there is no effect of the laser beam on the solvent as seen in Fig. 5. Therefore, the influence of the solvent nonlinearity could be excluded. The TPA coefficient $\beta$ of two fluorenone-based oligomers can be obtained by fitting the experimental results with equation [38]:

$$T(z, S=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} \qquad (1)$$

where $q_0(z) = \beta I_0/(1+z^2/z_0^2), z_0 = k\omega_0^2/2$ is the Rayleigh length, $k = 2\pi/\lambda$ is the wave vector, $\omega_0$ is beam waist radius of Gaussian pulse, and $I_0$ is the pulse irradiance. The obtained values are summarized in Table 1. The TPA cross-section $\sigma$ can be calculated using $\sigma = h\nu\beta/N$, where $N$ is the number of molecules per cm$^3$, and $\sigma$ is expressed in Göppert-Mayer units (GM), with 1 GM = $1 \times 10^{-50}$ cm$^4$ s molecule$^{-1}$ photon$^{-1}$. Both the oligomers show considerable TPA cross-sections, the calculated $\sigma$ values of **F–FO–F** and **TPA–FO–TPA** are 626 and 884 GM, respectively, and the latter is almost 1.4 times larger than the former. This result indicates that the triphenylamine unit acting as a more electron-rich moiety is benefit for the enhancement of TPA cross-section.

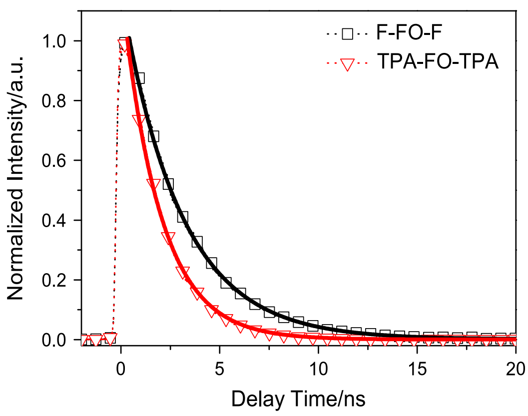


**Fig. 3.** Fluorescence dynamics (dot lines) and exponentially fitted lines (solid) of **F–FO–F** and **TPA–FO–TPA** ($5 \times 10^{-5}$ M).

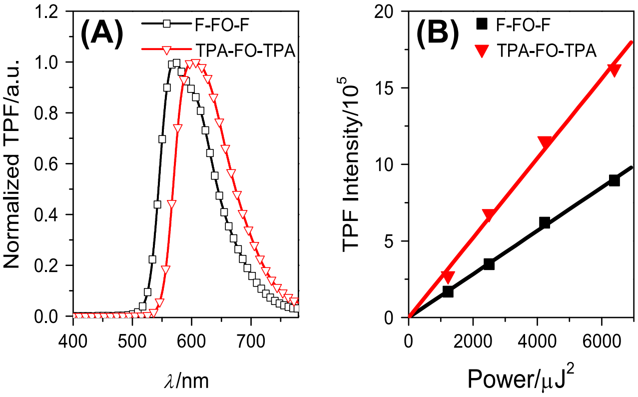


**Fig. 4.** (A) Normalized two-photon fluorescence spectra of **F–FO–F** and **TPA–FO–TPA** ($5 \times 10^{-4}$ M) and (B) two-photon induced fluorescence measurements as a function of laser power.

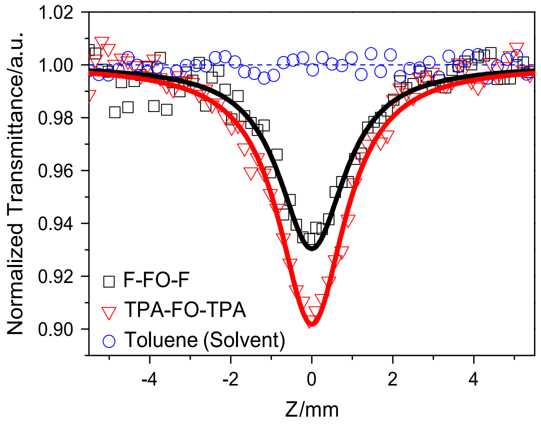


**Fig. 5.** Open aperture *z*-scan curves for **F–FO–F** and **TPA–FO–TPA**. ($5 \times 10^{-4}$ M).

In an effort to understand the basic photo-physical properties of these two conjugated oligomers at the molecular level, quantum chemical calculations based on density functional theory (DFT) were used to calculate the electronic structures and investigate the ground to excited state transitions. Fig. 1 shows the optimized ground state geometries of **F–FO–F** and **TPA–FO–TPA** obtained with the B3LYP/3-21G basis set [39–41]. Apparently, both oligomers show a good coplanarity between the fluorenone subunit and the donor moieties according to the quantum chemical calculation results, indicating that $\pi$-electrons in the two oligomers could be delocalized throughout the molecules, due to their $\pi$-conjugated system. Fig. 6 shows the plots of the representative frontier molecular orbitals in the ground states of **F–FO–F** and **TPA–FO–TPA**. In both molecules, the LUMO levels are nearly completely localized on the fluorenone moiety, while the HOMO levels are almost delocalized over the whole molecules. This indicates that the HOMO–LUMO transitions involve a significant ICT character besides the $\pi$–$\pi^*$ transitions. Because of the strong electron-donating capability, the electron density in HOMO of **TPA–FO–TPA** is much richer than that of **F–FO–F**, this characteristic may be used to understand the red-shift spectral behavior in the absorption and OPF spectra.

The calculated LUMO levels for compounds **F–FO–F** and **TPA–FO–TPA** are −2.412 and −2.324 eV, respectively, which are close to that of fluorenone unit (−2.518 eV). The HOMO levels for them

**Table 1**
Photo-physical parameters of two novel oligomers in toluene.

| Oligomers | $\lambda_{max}^{abs}$/nm | $\lambda_{max}^{em}$/nm | $E_g^{opt}$/eV | Stokes shift/ nm | β/ $10^{-2}$ cm $GW^{-1}$ | σ/ GM |
|---|---|---|---|---|---|---|
| **F–FO–F** | 392 | 570 | 2.397 | 178 | 0.76 | 626 |
| **TPA–FO–TPA** | 409 | 597 | 2.299 | 188 | 1.07 | 884 |

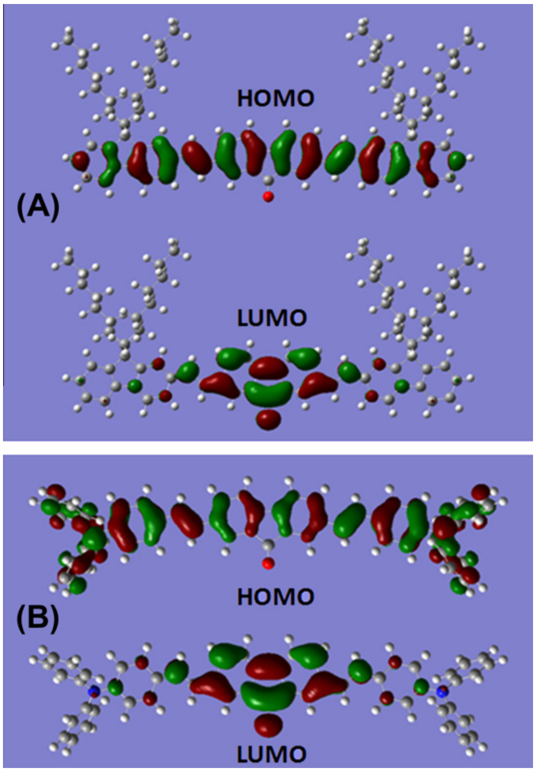


**Fig. 6.** HOMO and LUMO orbitals in the optimized ground state structure of (A) **F–FO–F** and (B) **TPA–FO–TPA**.

are −5.209 and −4.847 eV, indicating that the triphenylamine unit is able to obviously increase the position of HOMO level. This implies that variation of photo-physical properties of total oligomers can be determined by donor group. The calculated HOMO–LUMO gaps ($E_g$) for π-electron conjugative molecules **F–FO–F** and **TPA–FO–TPA** are 2.797 and 2.523 eV, respectively, and the variation trend of $E_g$ is in agreement with that of the experimental data $\left(E_g^{opt}\right)$ shown in Table 1, which were determined from the intersection of normalized absorption and emission spectra. The results indicate that the HOMO–LUMO gap of the D–A type oligomers could decrease with the increasing electron-donating capability, that is to say, the triphenylamine donors can lead to a larger electron delocalization effect. Overall, the DFT calculations on the two oligomers discussed above provide deep insight into their electronic structures and properties.

## 4. Conclusion

We have studied the donor-dependent photo-physical properties of two D–π–A–π–D type fluorenone-based conjugated oligomers in detail. The experimental results show that the triphenylamine groups acting as strong electron donors could lead to red-shifts of spectral features by lowering the $\pi$–$\pi^*$transition energy, and increase the Stokes shift due to the enhancement of ICT. Meanwhile, the triphenylamine groups can also improve the two-photon optical properties involving TPF efficiency and TPA cross-section. What's more, DFT calculations could offer a better understanding of the electronic structure and properties of oligomers. In a word, this study would be helpful for the easy adjustment of optical properties of oligomers and the better exploration of novel compounds with strong nonlinear behavior.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 10974071, 10774060 and 21103161), the Jilin Province Natural Science Foundation of China (No. 20070512), the National Found for Fostering Talents of Basic Science (No. J1103202) and the China Postdoctoral Science Foundation (No. 2011M500927). The calculations with the Gaussian 09 program were performed at the State Key Laboratory of Supramolecular Structure and Materials, Jilin University, China.

## References

[1] A.R. Morales, K.D. Belfield, J.M. Hales, E.W. Van Stryland, D.J. Hagan, Chem. Mater. 18 (2006) 4972.
[2] Z.J. Liu, T. Chen, B. Liu, Z.L. Huang, T. Huang, S.Y. Li, J.G. Qin, J. Mater. Chem. 17 (2007) 4685.
[3] Y.H. Jiang, Y.C. Wang, J.L. Hua, S.Y. Qu, S.Q. Qian, H. Tian, J. Polym. Sci. Part A: Polym. Chem. 47 (2009) 4400.
[4] L.L. Xue, J.T. He, X. Gu, Z.F. Yang, B. Xu, W.J. Tian, J. Phys. Chem. C. 113 (2009) 12911.
[5] J.L. Wang, Q. Xiao, J. Pei, Org. Lett. 12 (2010) 4164.
[6] V. Hrobáriková, P. Hrobárik, P. Gajdoš, I. Fitilis, M. Fakis, P. Persephonis, P. Zahradník, J. Org. Chem. 75 (2010) 3053.
[7] M.C. Skala, J.M. Squirrell, K.M. Vrotsos, V.C. Eickhoff, A. Gendron-Fitzpatrick, K.W. Eliceiri, N. Ramanujam, Cancer Res. 65 (2005) 1180.
[8] D.A. Parthenopoulos, P.M. Rentzepis, Science 245 (1989) 843.
[9] S. Kawata, H.-B. Sun, T. Tanaka, K. Takada, Nature 412 (2001) 697.
[10] W. Zhou, S.M. Kuebler, K.L. Braun, T. Yu, J.K. Cammack, C.K. Ober, J.W. Perry, S.R. Marder, Science 296 (2002) 1106.
[11] I. Fuks-Janczarek, J. Ebothe, R. Miedzinski, R. Gabanski, A.H. Reshak, M. Lapkowski, R. Motyka, I.V. Kityk, J. Suwinski, Laser Phys. 18 (2008) 1056.
[12] D. Gao, R.R. Agayan, H. Xu, M.A. Philbert, R. Kopelman, Nano Lett. 6 (2006) 2383.
[13] S.R. Marder, D.N. Beratan, L.T. Cheng, Science 252 (1991) 103.
[14] D.R. Kanis, M.A. Ratner, T.J. Marks, Science 94 (1994) 195.
[15] S.S. Zade, M. Bendikov, Org. Lett. 8 (2006) 5243.
[16] K.M. Knoblock, C.J. Silvestri, D.M. Collard, J. Am. Chem. Soc. 128 (2006) 13680.
[17] H.M. Kim, M.S. Seo, S.-J. Jeon, B.R. Cho, Chem. Commun. 47 (2009) 7422.
[18] B.A. Reinhardt, L.L. Brott, S.J. Clarson, A.G. Dillard, J.C. Bhatt, R. Kannan, L.X. Yuan, G.S. He, P.N. Prasad, Chem. Mater. 10 (1998) 1863.
[19] D. Beljonne, W. Wenseleers, E. Zojer, Z. Shuai, H. Vogel, S.J.K. Pond, J.W. Perry, S.R. Marder, J.-L. Bredas, Adv. Funct. Mater. 12 (2002) 631.
[20] G.S. He, L.-S. Tan, Q.D. Zheng, P.N. Prasad, Chem. Rev. 108 (2008) 1245.
[21] N. Pucher, A. Rosspeintner, V. Satzinger, V. Schmidt, G. Gescheidt, J. Stampfl, R. Liska, Macromolecules 42 (2009) 6519.
[22] Z.Q. Li, M. Siklos, N. Pucher, K. Cicha, A. Ajami, W. Husinsky, A. Rosspeintner, E. Vauthey, G. Gescheidt, J. Stampfl, R. Liska, J. Polym. Sci. A Polym. Chem. 49 (2011) 3688.
[23] O. Mongin, L. Porrès, M. Charlot, C. Katan, M. Blanchard-Desce, Chem. Eur. J. 13 (2007) 1481.
[24] W.J. Yang, D.Y. Kim, M.-Y. Jeong, H.M. Kim, Y.K. Lee, X.Z. Fang, S.-J. Jeon, B.R. Cho, Chem. Eur. J. 11 (2005) 4191.
[25] M. Fakis, I. Fitilis, S. Stefanatos, P. Vellis, J. Mikroyannidis, V. Giannetas, P. Persephonis, Dyes Pigm. 81 (2009) 63.
[26] J.-Z. Cheng, C.-C. Lin, P.-T. Chou, A. Chaskar, K.-T. Wong, Tetrahedron 67 (2011) 734.
[27] F. Jaramillo-Isaza, M.L. Turner, J. Mater. Chem. 16 (2006) 83.
[28] H.F. Heck, J.P. Nolley, J. Org. Chem. 37 (1972) 2320.
[29] H.P. Zhou, R. Lu, X. Zhao, X.P. Qiu, P.C. Xue, X.L. Liu, X.F. Zhang, Tetrahedron Lett. 51 (2010) 5287.
[30] H.P. Zhou, P.C. Xue, Y. Zhang, X. Zhao, J.H. Jia, X.F. Zhang, X.L. Liu, R. Lu, Tetrahedron 67 (2011) 8477.
[31] S.A. Jenekhe, L.D. Lu, M.M. Alam, Macromolecules 34 (2001) 7315.
[32] G. Ramakrishna, A. Bhaskar, T. Goodson, J. Phys. Chem. B 110 (2006) 20872.
[33] T. Gunnlaugsson, H.D.P. Ali, M. Glynn, P.E. Kruger, G.M. Hussey, F.M. Pfeffer, C.M.G. dos Santos, J. Tierney, J. Fluoresc. 15 (2005) 287.
[34] A. Bhaskar, G. Ramakrishna, Z.K. Lu, R. Twieg, J.M. Hales, D.J. Hagan, E. Van Stryland, T. Goodson, J. Am. Chem. Soc. 128 (2006) 11840.
[35] R. Siebert, D. Akimov, M. Schmitt, A. Winter, U.S. Schubert, B. Dietzek, J. Popp, ChemPhysChem 10 (2009) 910.
[36] L.Z. Wu, X.J. Tang, M.H. Jiang, C.H. Tung, Chem. Phys. Lett. 315 (1999) 379.

[37] L. De Boni, J.J. Rodrigues Jr., D.S. dos Santos Jr., C.H.T.P. Silva, D.T. Balogh, O.N. Oliveira Jr., S.C. Zilio, L. Misoguti, C.R. Mendonça, Chem. Phys. Lett. 361 (2002) 209.
[38] M. Sheik-Bahae, A.A. Said, T.-H. Wei, D.J. Hagan, E.W. Van Stryland, IEEE J. Quantum Electron. 26 (1990) 760.
[39] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[40] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B. 37 (1988) 785.
[41] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200.