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Novel multi-branched two-photon polymerization initiators of ketocoumarin derivatives

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Abstract

Novel multi-branched two-photon absorbing dyes containing highly efficient UV–vis curing initiator, ketocoumarin (3-acetyl-7-diethylaminocoumarin), were synthesized. There linear and non-linear optical properties were studied and the cooperatively enhanced two-photon absorption of two- and three-branched dyes were confirmed by femtosecond laser pulses. The largest two-photon absorption cross-section was obtained as 1117 GM. The results of photobleaching experiments showed that all dyes had very fast electron transferring speed with the commercial coinitiator *o*-Cl-hexaarylbisimidazoles (HABI). The two-photon polymerization initiated by a bimolecular system composed of the two-branched dye and HABI was investigated. This photopolymer system presented high photoinitiating efficiency. The single-shot two-photon exposure of the resin film was achieved with a threshold as 1 TW/cm^2 at 800 nm.

Keywords: Two-photon absorption; Ketocoumarin derivatives; Photobleaching; Photopolymerization

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1. Introduction

Research on two-photon absorbing compounds has been paid much attention for their potential applications in two-photon excited fluorescence microscopy [1], high-density optical data storage [2,3], three-dimensional microfabrication [4,5], two-photon up-converted lasing [6] and photodynamic therapy [7]. For all these applications, a large two-photon absorption (TPA) cross-section of compounds is required as the first key issue. Many design strategies were presented by pioneering researchers to explore the relationship of molecular structures and TPA properties [8–22]. For one-dimensional dipolar or quadrupolar systems, one point is clear for molecular design, to elongate the conjugated system for charge transfer will increase the TPA properties of compounds [8,9]. Since Prasad and co-workers firstly reported the cooperative enhancement of TPA in multi-branched structures [15], a large amount of octupolar, multi-branched or dendrimeric systems were investigated [16–22]. However, till now, the mechanism of the enhancement is not very clear. Though most data supported the cooperative enhancement, their enhanced extents were quite different. In addition, some reported data did not show such enhancement, especially which measured by femtosecond laser pulses [22,23]. Evidently, more efforts are needed on this study. On the other hand, we noticed, though lots of multi-branched compounds were studied for large TPA properties, none of them was designed specially for two-photon polymerization (TPP). Except the large TPA cross-section (δ), for TPP, a high initiating efficiency is also necessary as another key issue.

In this paper, for the first time, we incorporated a highly efficient UV curing initiator, ketocoumarin (3-acetyl-7-diethylaminocoumarin) into multi-branched molecular structures (Scheme 1), and investigated their TPA properties using

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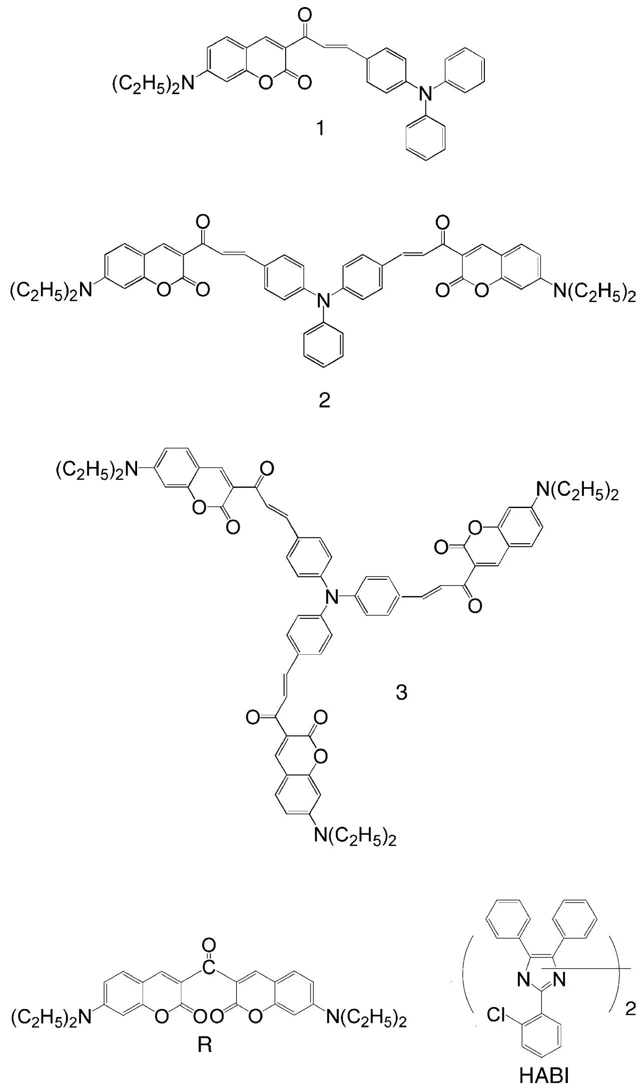

Scheme 1. Structural formulas of compounds.

femtosecond laser pulses. In addition, their polymerization initiating efficiency was studied by photobleaching and photopolymerization experiments.

2. Experimental

2.1. Materials

Ketocoumarin (3-acetyl-7-diethylaminocoumarin) and 3,3′-bis (7-diethylamino)-ketocoumarin (**R**) were prepared according to the literature [24]. Benzaldehyde derivatives were synthesized according to the literature [25]. *o*-Cl-hexaarylbisimidazoles (HABI, from TIC Co. Ltd.), cellulose acetate butyrate (CAB, form Acro Co. Ltd.), 2-phenoxyethyl acrylate (POEA, form Sartomer Co. Ltd.) and *N*-vinyl carbzole (NVC, form Acro Co. Ltd.) were used as received. Other A.R. grade solvents were used after purification and dry with common methods.

Compounds **1**–**3** were synthesized by an aldol condensation reaction of ketocoumarin and appropriate benzaldehyde derivatives with a catalytic amount of piperidine in ethanol/acetonitril (for **1** and **2**) and toluene (for **3**). The final products were purified by column chromatography and characterized by ^{1}H NMR, mass and elemental analysis [26].

2.2. Methods

TPA cross-section (δ) values of the three compounds in chloroform solution (10^{-4}–10^{-5} mol/L) were determined using the two-photon-excited fluorescence (TPEF) measurement technique with femtosecond laser pulses (from a mode-locked Tsunami Ti:sapphire, 740–880 nm, 80 MHz, <130 fs) following the experimental protocol described in detail by Xu and Webb [27]. To avoid any cumulative effect from photophysical/photochemical processes of solute molecules and contribution from other non-linear effects, the intensity of input pulses were adjusted to proper regimes to ensure a quadratic dependence of the fluorescence intensity versus excitation pulse energy was measured for each compound. Rhodamine B in methanol solution ($\sim 10^{-4}$ mol/L) was used as reference to calibrate our measurement [27]. The experimental uncertainty amounts to ±10%.

The light source for photobleaching experiments was 400 W Xenon lamps, light below 300 nm was filtered off with pyrex glass and the intensity of irradiation was 25 mW/cm^2. The typical high efficient triplet photosensitizer **R** was used as reference. The dye/HABI solution was bubbled with high purity nitrogen for 30 min to get rid of oxygen in solution before exposed under light. A regeneratively amplified Ti:sapphire system (Spitfire F-1K, 800 nm, 1000 Hz, ~130 fs) was used for photopolymerization experiments. The photocurable resin films were prepared by coating the mixed resin solution containing cellulose acetate butyrate/2-phenoxyethyl acrylate/*N*-vinyl carbzole as monomer, dyes 2 as sensitizer, HABI as coinitiator and chloroform as solvent onto glass substrates and dried in vacuum oven for 48 h for evaporating off all chloroform. The film thickness was controlled to be about 50 μm.

3. Results and discussions

3.1. Linear and non-linear optical properties

The absorption spectra and the fluorescence spectra of **1**–**3** in chloroform solution are shown in Fig. 1. Compared to the one-photon absorption peak ($\lambda_{\max}^{(1)}$) of **1**, the $\lambda_{\max}^{(1)}$ of **2** and **3** red-shift 13 and 11.5 nm, respectively, which indicates that the central triphenylamine moiety participate in the conjugation. It is worth to note that the absorption peak of **2** is obviously broader than those of **1** and **3**, and presents a shoulder peak near to the maximum one at 485.5 nm. It is considered that the stereo configurations of two branch chromophores of **2** are different, in addition the two moieties could

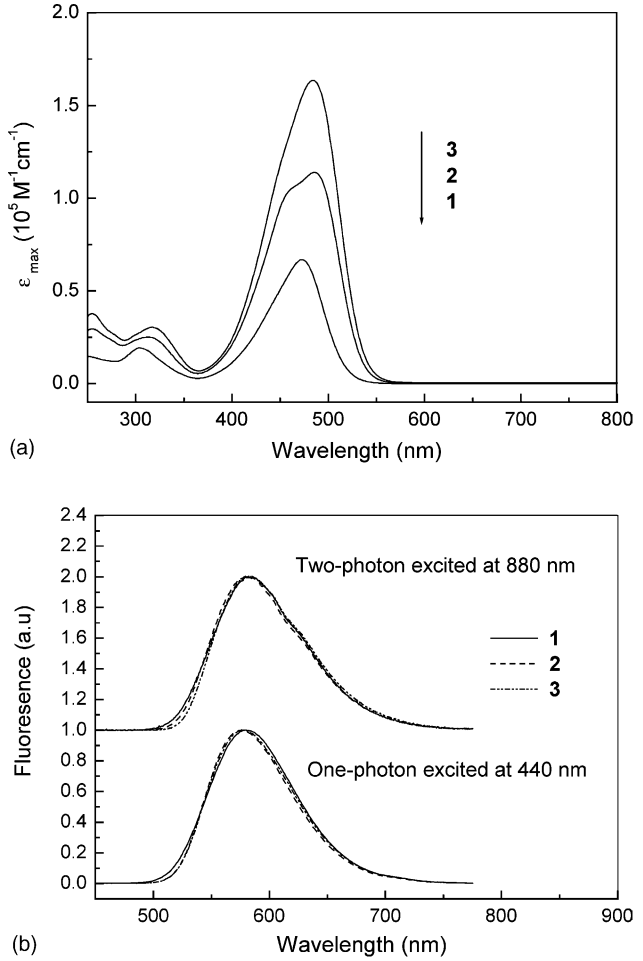

Fig. 1. (a) One-photon absorption spectra of compounds **1**–**3** in chloroform and (b) normalized fluorescence spectra of compounds **1**–**3** in chloroform excited by one-photon absorption at 440 nm and two-photon absorption at 880 nm.

have stronger intramolecular interaction than that of **3**, which induces the $\lambda^{(1)}_{max}$ of **2** even has a 1.5 nm red-shift to $\lambda^{(1)}_{max}$ of **3**. Though the $\lambda^{(1)}_{max}$ of three compounds are different, their fluorescence emission peaks (λ^{fl}_{max}) are almost exactly same. For the decrease of the Stokes shifts from **1** to **2** and **3** (Table 1), it could be due to cross-conjugation effect, which decreases the electron donating ability of triphenylamine from **1** to **2** and **3**, and thus diminishes the excited state charge transfer. For each compound, the fluorescence spectra are same for both one- and two-photon excitation in a same concentrated solution, indicating the fluorescence emission is independent on excitation process.

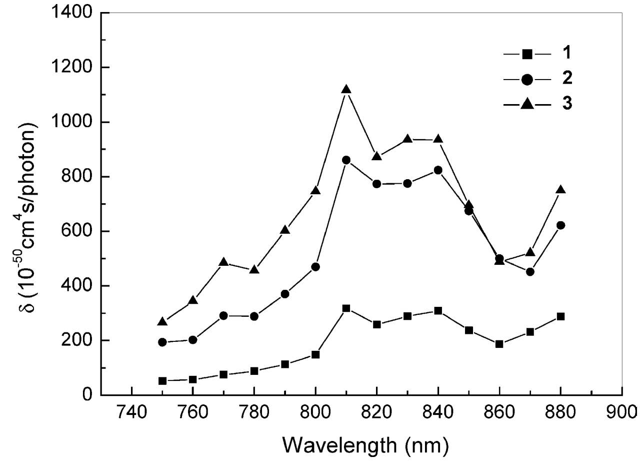

Fig. 2. Two-photon excitation spectra of compounds **1**–**3** in chloroform.

The fluorescence quantum yield (Φ) of **1**–**3** was measured in chloroform solutions. Rhodamine B in methanol was used as a standard ($\Phi = 0.70$) and refeactive index correction was performed [28]. Three compounds all showed strong fluorescence and high Φ as 0.49, 0.55 and 0.58, respectively. The increase of Φ could be also due to the decreasing of the excited state charge transfer from **1** to **2** and **3** as mentioned before.

The measurement results of three compounds' TPA cross-sections at 740–880 nm are shown in Fig. 2. Their two-photon absorption peaks ($\lambda^{(2)}_{max}$) are all located at 810 nm, which has a blue-shift about 150 nm compared to the double wavelength of their linear absorption peaks, 472.5–485.5 nm, indicating this two-photon absorption peak should correspond to electron transition of ground state (S_0) to second excited state (S_2) or even higher states. Except the absorption peak at 810 nm, it is shown that another absorption peak could exist in red side of 880 nm for each compound. Due to the non-centrosymmetric structures of these molecules, the allowed electron transition of $S_0 \rightarrow S_1$ may explain the appearance of this peak. Compared to centrosymmtric molecular systems, these dyes can match broader wavelength scope of laser pulses, and would have advantages for further applications.

All three compounds, especially **2** and **3**, showed quite large TPA cross-sections (10^{-48}–10^{-47} cm^4/s/photon) compared to commercial coumarin dyes [29,30]. The ratio of the relative δ_{max} values of **1**:**2**:**3** is 1:2.7:3.5 (for each branch chromophore in **1**–**3**, the ratio is 1:1.35:1.17). Obviously, both of **2** and **3** presented an enhancement for their TPA compared to **1**. In addition, it was interesting to note that **2** showed

Table 1
One- and two-photon optical properties of **1**–**3** in chloroform

Compound	$\lambda^{(1)}_{max}$ (nm)	ε_{max} (10^5 M^{-1} cm^{-1})	λ^{fl}_{max}[a] (nm)	$\Delta\nu$ (cm^{-1})	Φ	$\lambda^{(2)}_{max}$ (nm)	δ_{max} (GM)[b]
1	472.5	0.67	580/579	3923	0.49	810	318
2	485.5	1.14	576/579	3236	0.55	810	860
3	484	1.64	578/580	3336	0.58	810	1117

[a] The left data is from one-photon excitation spectra, the right one is from two-photon excitation spectra.

[b] 1 GM = 10^{-50} cm^4 s/photon.

more efficient cooperative effect than **3** within the whole measured regime. From linear optical properties of compounds, it was presented that the cross-conjugation of triphenylamine center increased effective conjugation length of molecules, but decreased the charge transfer of excited state within each branch, which are two reverse effects on TPA of compounds. On the other hand, in mutli-branched molecules, the inevitable intramolecular chromophore–chromophore interaction will enlarge the density of molecules' energy states, which has a positive effect on TPA of compounds. Thus, the enhancement of compounds' TPA will be determined by the cooperative effect from the cross-conjugation and the intramolecular interaction of different branches. In earlier discussion, we mentioned that **2** has broader linear absorption peak and considered it due to its stronger chromophore–chromophore interaction. Here, the stronger cooperative enhancement of its TPA could be also accord to the same reason.

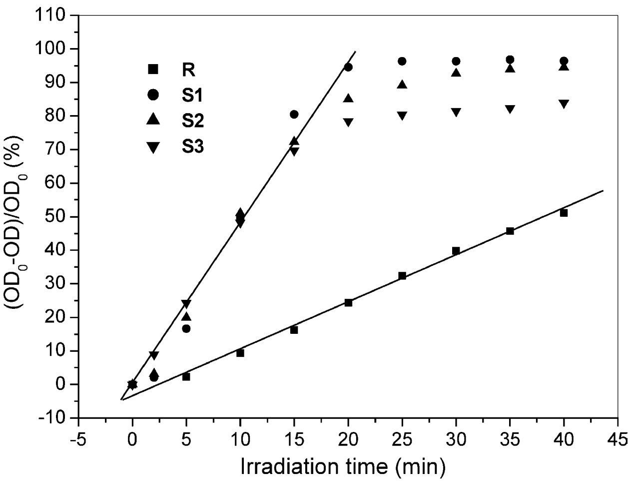

Fig. 3. Photobleaching of different dyes with HABI, $[\text{dye}] = 1 \times 10^{-5}$ mol/L, $[\text{HABI}] = 8 \times 10^{-5}$ mol/L, in chloroform, in N_2.

3.2. Photobleaching and photopolymerization

In UV photopolymerization, coumarin dyes are generally combined with coinitiators HABI or diphenyliodinium hexafluorophosphate as high efficient initiating composites. After dyes absorb photons and arrive to their excited states, the following reaction processes are same for both one- and two-photon polymerization. Thus, we use common photobleaching method to study the primary photoreaction between dyes **1**–**3** and HABI. When the dye/HABI combination system was exposed to light, due to the photoinduced electron transferring from dye to HABI, the dye would be oxidized and its absorption peak would decrease with irradiation time. In our contrastive experiments, in the absence of HABI, the absorption of dye was stable, which demonstrated that the decrease of dye's absorption in photobleaching experiments was according to its photooxidation. The photobleaching speed of dyes is determined by the speed of electron transfer between dye and HABI. The photoreaction kinetic study was carried out by monitoring the relative change of the optical density (OD) at dye's absorption maximum with irradiation time. In Fig. 3, the photobleaching of dye **1**–**3** and **R** were carried out under the same experimental condition. It is shown that the photobleaching rates R_b ($R_b = (\mathrm{OD}_0 - \mathrm{OD})/(\mathrm{OD}_0 \times t)$) of three dyes are all nearly three times of that of **R** in first 20 min with enough HABI. Twenty minute later, dyes were almost used up, so their absorption spectra became stable. The results indicate that dye **1**–**3** can match with commercial coinitiator HABI very well.

To investigate the initiating efficient of dye **2**/HABI in two-photon polymerization, a mixed resin film was prepared and single-shot exposure were carried out. 800 nm laser pulses were focused into the sample with a lens ($f = 15$ mm) and the focus size was ~32 μm. Fig. 4 shows the optical micrograph of exposed points under different pulse's energies. Due to different refractive index of materials exposed and unexposed, the polymerized points were observed very clear under optical microscope. When the energy of the single pulse was lower than 1 μJ, we did not observe polymerization dots. Thus, we determined that the threshold for this two-photon exposure is 1 TW/cm^2. Considering the threshold of a polymerization system is determined by many factors, except dyes, other factors, such as coinitiators, monomers, the width of pulses, the size of focus point and even the resolution of microscope all have effect on it, there is still a significant room for decreasing this threshold. When the pulse's energy was higher than 3 μJ, the size of exposed point became sta-

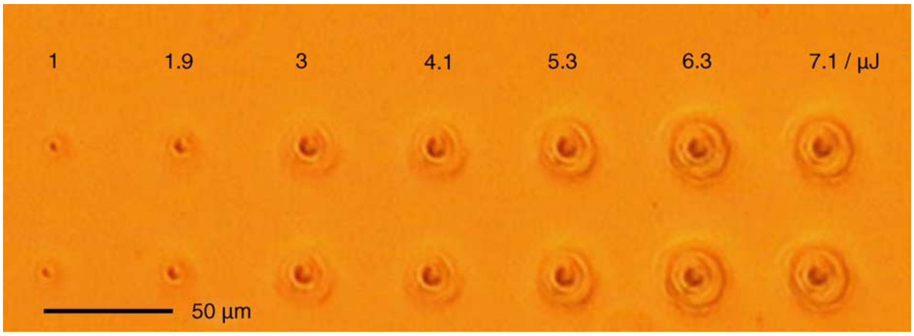

Fig. 4. Polymerized points under different exposure energy of laser pulses.

ble around 7–8 μm, but its surround area became more and more clear. We think it is due to two reasons, the shrinkage of exposed region and the partial polymerization happened within areas around exposed points due to heating effect when the energy of pluses is higher than some limitation. With 1 μJ pulse energy, the diameter of exposed dot is 2–3 μm, which is only tenth of the focus's size. It can be imagined that this resin would be applied for high-density optical storage and microfabrication with tightly focused optical systems.

4. Conclusion

We reported the synthesis of novel multi-branched TPA dyes of ketocoumarin derivatives, and observed a cooperative effect of TPA in two and three-branched dyes **2** and **3** with femtosecond laser pulses. All three compounds presented quite large TPA cross-sections compared to commercial coumarin dyes. The photobleaching results showed that all three dyes had very fast electron transferring speed to coinitiator HABI. A low threshold of 1 TW/cm^2 was obtained in a resin film containing dye **2**/HABI as two-photon initiator. For their large TPA cross-section and high initiating efficient, these ketocoumarin derivatives would have large potentialities in two-photon polymerization.

Acknowledgement

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References

[1] W. Denk, J.H. Strickler, W.W. Webb, Science 248 (1990) 73.

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

[3] A.S. Dvornikow, Y. Liang, C.S. Cruse, P.M. Rentzepis, J. Phys. Chem. B 108 (2004) 8652.

[4] H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Heikal, S.M. Kuebler, I.-Y.S. Lee, D. McCord-Maughon, J.Q. Qin, H. Rockel, M. Rumi, X.-L. Wu, S.R. Marder, J.W. Perry, Nature 398 (1999) 51.

[5] S. Kawata, H.-B. Sun, T. Tanaka, K. Takada, Nature 412 (2001) 697.

[6] J.D. Bhawalkar, G.S. He, C.-K. Park, C.F. Zhao, G. Ruland, P.N. Prasad, Opt. Commun. 124 (1996) 33.

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

[8] G.S. He, L. Yuan, N. Cheng, J.D. Bhawalkar, P.N. Prasad, L.L. Brott, S.J. Clarson, B.A. Reinhardt, J. Opt. Soc. Am. B 14 (1997) 1079.

[9] M. Albota, D. Beljonne, J.-L. Bredas, J.E. Ehrlich, J.-Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. Levin, S.R. Marder, D. McCord-Maughon, J.W. Perry, H. Rockel, M. Rumi, G. Subramaniam, W.W. Webb, X.-L. Wu, C. Xu, Science 281 (1998) 1653.

[10] K.D. Belfield, D.J. Hagan, E.W. Van Stryland, K.J. Schafer, R.A. Negres, Org. Lett. 1 (1999) 1575.

[11] L. Ventelon, S. Charier, L. Moreaux, J. Mertz, M. Blanchard-Desce, Angew. Chem. Int. Ed. 40 (2001) 2098.

[12] O. Mongin, L. Porre‘s, L. Moreaux, J. Mertz, M. Blanchard-Desce, Org. Lett. 4 (2002) 719.

[13] K.J. Schafer, J.M. Hales, M. Balu, K.D. Belfield, E.W. Van Stryland, D.J. Hagan, J. Photochem. Photobiol. A: Chem. 162 (2004) 497.

[14] K.D. Belfield, M.V. Bondar, O.V. Przhonska, K.J. Schafer, J. Photochem. Photobiol. A: Chem. 162 (2004) 489.

[15] S.-J. Chung, K.-S. Kim, T.-C. Lin, G.S. He, J. Swiatkiewicz, P.N. Prasad, J. Phys. Chem. 103 (1999) 10741.

[16] A. Adronov, J.M.J. Fréchet, G.S. He, K.-S. Kim, S.-J. Chung, J. Swiatkiewicz, P.N. Prasad, Chem. Mater. 12 (2000) 2838.

[17] B.R. Cho, K.H. Son, H.L. Sang, Y.-S. Song, Y.-K. Lee, S.-J. Jeon, J.H. Choi, H. Lee, M. Cho, J. Am. Chem. Soc. 123 (2001) 10039.

[18] S.-J. Chung, T.-C. Lin, K.-S. Kim, G.S. He, J. Swiatkiewicz, P.N. Prasad, G.A. Baker, F.V. Bright, Chem. Mater. 13 (2001) 4071.

[19] J. Yoo, S.K. Yang, M.-Y. Jeong, H.C. Ahn, S.-J. Jeon, B.R. Cho, Org. Lett. 5 (2003) 645.

[20] M. Drobizhev, A. Karotki, Y. Dzenis, A. Rebane, Z. Suo, C.W. Spangler, J. Phys. Chem. B 107 (2003) 7540.

[21] O. Mongin, J. Brunel, L. Porre‘s, M. Blanchard-Desce, Tetrahedron Lett. 44 (2003) 2813.

[22] B.J. Zhang, S.-J. Jeon, Chem. Phys. Lett. 377 (2003) 210.

[23] L. Porrès, C. Katan, O. Mongin, T. Pons, J. Mertz, M. Blanchard-Desce, J. Mol. Struct. 704 (2004) 17.

[24] D.P. Specht, P.A. Martic, S. Farid, Tetrahydron 38 (1982) 1203.

[25] H.J. Lee, J. Sohn, J. Hwang, S.Y. Park, H. Choi, M. Cha, Chem. Mater. 16 (2004) 456.

[26] Data for 1C: Anal. Calcd (%) for $C_{34}H_{30}N_2O_3$: C, 79.35; H, 5.88; N, 5.44. Found: C, 79.54; H, 5.79; N, 5.10. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.02 (d, $J = 15.7$, 1H), 7.81 (d, $J = 15.7$, 1H), 7.54 (d, $J = 8.6$, 2H), 7.44 (d, $J = 8.8$, 1H), 7.30 (t, $J = 7.7$, 4H), 7.14 (d, $J = 8.0$, 4H), 7.09 (t, $J = 7.4$, 2H), 7.02 (d, $J = 8.6$, 2H), 6.65 (dd, $J_1 = 8.8$, J_2=2.1, 1H), 6.51(d, $J = 2.1$, 1H), 3.47 (q, $J = 6.9$, 4H), 1.25 (t, $J = 6.9$, 6H). HR-MS: m/z 515.2326 [$M + \mathrm{H}$], 537.2156 [$M + \mathrm{Na}$]. Data for 2C: Anal. Calcd (%) for $C_{50}H_{45}N_3O_6$: C, 76.61; H, 5.79; N, 5.36. Found: C, 76.53; H, 6.02; N, 5.21. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 2H), 8.05 (d, $J = 15.7$, 2H), 7.81 (d, $J = 15.7$, 2H), 7.59 (d, $J = 8.5$, 4H), 7.45 (d, $J = 8.9$, 2H), 7.34 (t, $J = 7.8$, 2H), 7.16 (m, 3H), 7.10 (d, $J = 8.5$, 4H), 6.68 (dd, $J_1 = 8.9$, $J_2 = 2.1$, 2H), 6.54(d, $J = 2.1$, 2H), 3.48 (q, $J = 6.9$, 8H), 1.26 (t, $J = 6.9$, 12H). MALDI-TOF: m/z 784.6 [$M + \mathrm{H}$], 806.6 [$M + \mathrm{Na}$]. Data for 3C: Anal. Calcd (%) for $C_{66}H_{60}N_4O_9$: C, 75.27; H, 5.74; N, 5.32. Found: C, 74.95; H, 5.93; N, 5.27. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 3H), 8.07 (d, $J = 15.8$, 3H), 7.82 (d, $J = 15.8$, 3H), 7.62 (d, $J = 8.2$, 6H), 7.46 (d, $J = 8.8$, 3H), 7.14 (d, $J = 8.2$, 6H), 6.70 (d, $J = 8.9$, 3H), 6.56(s, 3H), 3.48 (q, $J = 6.9$, 12H), 1.26 (t, $J = 6.9$, 18H). MALDI-TOF: m/z 1053.8 [$M + \mathrm{H}$], 1075.8 [$M + \mathrm{Na}$].

[27] C. Xu, W.W. Webb, J. Opt. Soc. Am. B 13 (1996) 481.

[28] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.

[29] A. Fischer, C. Cremer, E.H.K. Stelzer, Appl. Opt. 34 (1995) 1989.

[30] C.-D. Li, L. Luo, S.-F. Wang, W.-T. Huang, Q.-H. Gong, Y.-Y. Yang, S.-J. Feng, Chem. Phys. Lett. 340 (2001) 444.