

Synthesis and photophysical properties of 1,4-bis(4,5-diarylimidazol) benzene dyes

Nan Xie, Yi Chen*

Laboratory of Organic Optoelectronic Functional Materials and Molecular Engineering, Technical Institute of Physics and Chemistry, The Chinese Academy of Science, Beijing 100080, China

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Abstract

A class of π -conjugated 1,4-bis(4,5-diarylimidazol)benzene dyes (**1–5**) are synthesized, and all dyes exhibit strong fluorescence in solution ($\phi_f = 0.96–0.45$, in DMSO). It is found that both absorption and fluorescence of dyes are influenced by molecular structures and electronic properties of substitute groups, but little influenced by the polarity of solvents and pH value. Besides, two-photon properties of dyes are also investigated. The largest two-photon absorption cross-section ($\sigma = 98 \text{ GM}$) for dye **4** is obtained with 700 nm in DMSO, and two-photon fluorescence emission is also observed with 740 nm excitation in solution.

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Keywords: 1,4-Bis(4,5-diarylimidazol)benzenes; Fluorescence; Two-photon absorption; Two-photon fluorescence

1. Introduction

The development of new molecular fluorophores for biologic analysis [1] and optical application [2] has emerged as an actively investigated research in recent years. Despite the multitude of available fluorophores [3], new fluorophoric systems with easy preparation and strong fluorescence are hotly sought for more challenging applications including two-photon fluorescence imaging [4], fluorescence sensor [5], fluorescence switching [6] and nondestructive readout [7]. Herein, we report a family of π -conjugated 1,4-bis(4,5-diarylimidazol)benzenes (**1–5**) (Scheme 1), which are obtained easily and exhibit very strong fluorescence in solution. Although some of them have been reported alone on synthesis and properties [8], that the photophysical properties of these dyes influenced by both molecular structures and electronic properties of substitute groups as well as the solvent polarity and pH value is, for the first time, reported in this paper. Beside, both two-photon absorption cross-section and two-photon fluorescence emission of these dyes are investigated for the first time, and the results are also presented in this paper.

2. Experimental

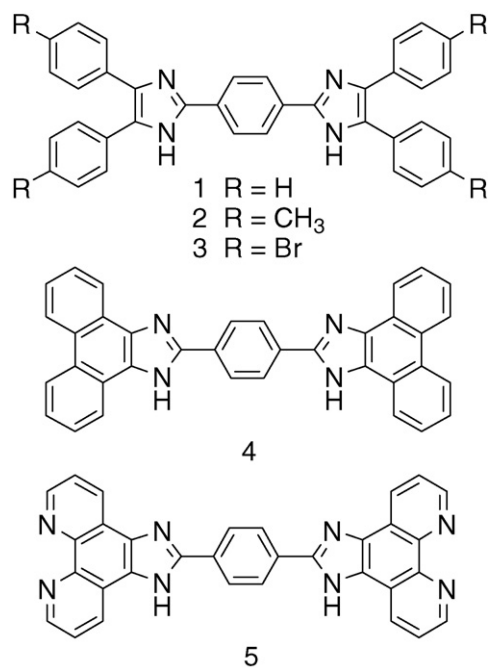
2.1. Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz with TMS as an internal reference and DMSO- d_6 as solvent. UV absorption spectra and fluorescence spectra were measured on an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (F-2500), respectively. Two-photon induced excited fluorescence spectra were recorded on SD2000 spectrometer (Ocean Optical), excited by mode-locked Ti:sapphire femtosecond laser (Tsunami, Spectra-Physics) which oscillating wavelength, pulse width and repetition rate were 780 nm, 80 fs and 82 MHz, respectively.

2.2. Chemicals

All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Compounds **1–5** were prepared as following: a vigorously stirred mixture of terephthalaldehyde (40 mg, 0.3 mmol), phenanthrenequinone (140 mg, 0.67 mmol), and ammonium acetate (300 mg, 3.9 mmol) in ethanol (50 ml) was refluxed for 10 h. During this time, the color gradually changed, and bright yellow precipitate was produced. The reaction mixture

* Corresponding author. Tel.: +86 10 82543595; fax: +86 10 62564049.
E-mail address: yichencas@yahoo.com.cn (Y. Chen).



Scheme 1. Chemical structures of 1,4-bis(4,5-diarylimidazol)benzenes.

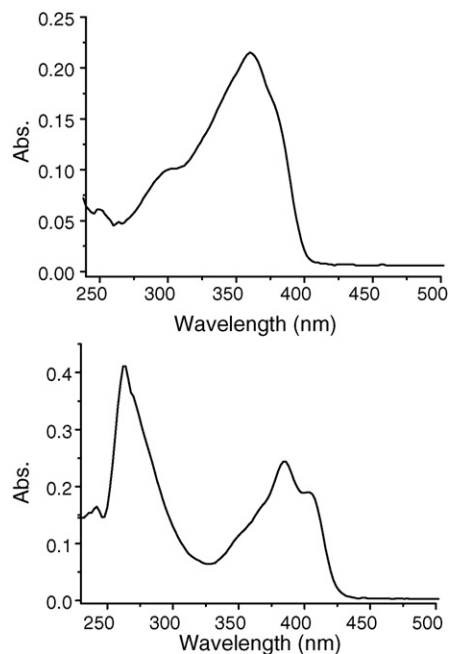
was cooled, and the yellow product was filtered off, washed with water and EtOH, pure **4** was obtained after vacuum-dried. Compounds **1–3** and **5** were prepared by the same procedures except that the starting material was replaced by benzil, benzil derivatives and 1,10-phenanthroline-5,6-dione, respectively.

(**1**) Yield 73%. mp > 300 °C. ¹H NMR: 12.76 (s, 2H), 8.19 (s, 4H), 7.58 (d, *J* = 7.4 Hz, 4H), 7.54 (d, *J* = 7.4 Hz, 4H), 7.46 (t, 4H), 7.39 (t, 2H), 7.32 (t, 4H), 7.24 (t, 2H). ¹³C NMR: 145.1, 137.4, 135.1, 131.0, 129.8, 128.7, 128.4, 128.3, 127.9, 127.2, 126.7, 125.4. FAB MS (*m/z*): [*M* + *H*]⁺ calcd. for C₃₆H₂₆N₄: 514.63. Found: 515. Anal. Calcd. for C₃₆H₂₆N₄: C, 84.02; H, 5.09; N, 10.89. Found: C, 84.04; H, 5.07; N, 10.92. (**2**) Yield 70%. mp > 300 °C. ¹H NMR: 12.63 (s, 2H), 8.15 (s, 4H), 7.46 (d, *J* = 8.0 Hz, 4H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.26 (d, *J* = 8.0 Hz, 4H), 7.13 (d, *J* = 8.0 Hz, 4H), 2.36 (s, 6H), 2.19 (s, 6H). ¹³C NMR: 144.8, 137.1, 135.7, 132.4, 129.8, 129.3, 128.8, 128.2, 127.1, 125.3, 20.8. FAB MS (*m/z*): [*M* + *H*]⁺ calcd. for C₄₀H₃₄N₄: 570.74, Found: 571. Anal. Calcd. for C₃₈H₃₄N₄: C, 84.18; H, 6.00; N, 9.82. Found: C, 84.21; H, 5.58; N, 9.86. (**3**) Yield 65%. mp > 300 °C. ¹H NMR: 12.91 (s, 2H), 8.17 (s, 4H), 7.86 (d, *J* = 2.2 Hz, 4H), 7.68 (d, *J* = 8.0 Hz, 4H), 7.55–7.46 (m, 8H). ¹³C NMR: 192.9, 136.7, 134.1, 132.6, 131.8, 131.7, 131.4, 131.2, 130.4, 130.1, 129.8, 129.2, 125.6, 119.9. FAB MS (*m/z*): [*M* + *H*]⁺ calcd. for C₃₆H₂₂Br₄N₄: 830.21, Found: 831. Anal. Calcd. for C₃₆H₂₂Br₄N₄: C, 52.08; H, 2.67; N, 6.75. Found: C, 52.11; H, 2.64; N, 6.78. (**4**) Yield 80%. mp > 300 °C. ¹H NMR: 13.61 (s, 2H), 8.91 (d, *J* = 8.4 Hz, 2H), 8.87 (d, *J* = 8.3 Hz, 2H), 8.66 (d, *J* = 7.8 Hz, 2H), 8.62 (d, *J* = 8.0 Hz, 2H), 8.54 (s, 4H), 7.81–7.74 (m, 4H), 7.69–7.65 (m, 4H). ¹³C NMR: 148.5, 137.3, 130.7, 127.9, 127.8, 127.7, 127.3, 127.2, 126.9, 126.6, 125.6, 125.4, 124.2, 123.8, 122.4, 122.1, 122.0. FAB MS (*m/z*): [*M* + *H*]⁺ calcd. for C₃₆H₂₂N₄: 510.60, Found: 511. Anal. Calcd. for C₃₆H₂₂N₄: C, 84.68; H, 4.34; N, 10.97. Found: C, 84.68; H,

4.31; N, 10.99. (**5**) Yield 78%. mp > 300 °C. ¹H NMR: 13.99 (s, 2H), 9.07 (d, *J* = 4.2 Hz, 4H), 8.99 (d, *J* = 8.0 Hz, 4H), 8.53 (s, 4H), 7.88–7.84 (m, 4H). FAB MS (*m/z*): [*M* + *H*]⁺ calcd. for C₃₂H₁₈N₈: 514.5502, Found: 515. Anal. Calcd. for C₃₂H₁₈N₈: C, 74.70; H, 3.52; N, 21.78. Found: C, 74.74; H, 3.50; N, 21.82.

3. Results and discussion

The absorption spectra of **1** and **4** in DMSO solution were presented in Fig. 1. The absorption peaks of **1** were at λ = 380 nm (should) (ε = 3.2 × 10⁴), 363 nm (ε = 4.2 × 10⁴), and 300 nm (ε = 2.0 × 10⁴), respectively. By comparison of the absorption spectrum of **1** with that of benzil, it is found that the longer peaks (380 and 363 nm) attribute to the absorption of the whole molecule **1**, while the shorter peak at 300 nm corresponds to the absorption of benzil group. Similar results were obtained when the absorption spectra of **4** was measured. As shown in Fig. 1 (down), The two longer absorption bands at λ_{max} = 410 nm (ε = 3.5 × 10⁴) and λ_{max} = 386 nm (ε = 4.4 × 10⁴), respectively, attribute to the absorption of the whole molecule **4**, while the absorption at λ_{max} = 272 nm (ε = 8.0 × 10⁴) corresponds to the absorption of phenanthrenequinone group. Investigating other dyes **2**, **3**, and **5** found that the results were similar to that of the above. The UV data of dyes **1–5** are listed in Table 1.

Fig. 1. Absorption spectra of **1** (up) and **4** (down) in DMSO (*c* = 5 × 10⁻⁶ M).Table 1
The UV data of dyes **1–5** in DMSO (5 × 10⁻⁶ M)

Dye	λ (nm)/ε (×10 ⁴)	λ (nm)/ε (×10 ⁴)	λ (nm)/ε (×10 ⁴)
1	380 (3.2)	363 (4.2)	300 (2.0)
2	395 (3.1)	370 (4.0)	305 (2.1)
3	289 (2.4)	368 (3.6)	287 (2.5)
4	410 (3.5)	386 (4.4)	272 (8.0)
5	398 (3.6)	378 (4.4)	284 (3.8)

Comparing the longer absorption wavelength of **4** and **5** with that of **1–3** found that the absorption wavelength of **4** or **5** is longer than that of compounds **1–3n** and it is probably due to the fact that the structure of **4** or **5** is more coplanar than that of **1–3** because of the inhibition of C–C single bonds rotation of **4** and **5**. It is also found that the absorption wavelength of **2** and **3** is longer than that of **1**, which probably results from intramolecular charge transfer (ICT) of dyes. ICT is stronger with electron-donating group (**2**) or electron-acceptor group (**3**) than that with H group (**1**). Both coplanar and intramolecular charge transfer result in the energy decreased in excited state and the absorption bands red-shifted.

The fluorescence spectra of dyes **1** and **4** in DMSO solution were presented in Fig. 2. There are two emission bands at $\lambda_{em} = 440$ nm and $\lambda_{em} = 410$ nm for **1**, and $\lambda_{em} = 460$ nm and $\lambda_{em} = 430$ nm for **4**, respectively. Both dyes exhibited very strong blue emission in DMSO with 375 and 400 nm, respectively, excitation wavelength. High fluorescence quantum yields ($\phi_f = 0.94$ for dye **1**, $\phi_f = 0.78$ for dye **4**) were obtained by using coumarin 307 ($\phi_f = 0.58$, in CH₃CN) as a reference.

Examining of other dyes found that the profiles of emission spectra of **2** and **3** were similar to that of **1**, and the profile of emission spectrum of **5** was similar to that of **4**. They also exhibited strong fluorescence emission ($\phi_f = 0.78$ – 0.96) except for **3**, in which the low value of ϕ_f is the result of competing S₁ → T₁ intersystem crossing because of “internal heavy-atom effect” and it is confirmed by the fluorescence lifetime of **3**, in which the τ_f of **3** is only half as long as that of **1** in the same condition.

The fluorescence data of **1–5** were listed in Table 2. Comparing the fluorescence of **1** and **4**, together with their structures found that fluorescence of **1** is stronger than that of **4**, but the

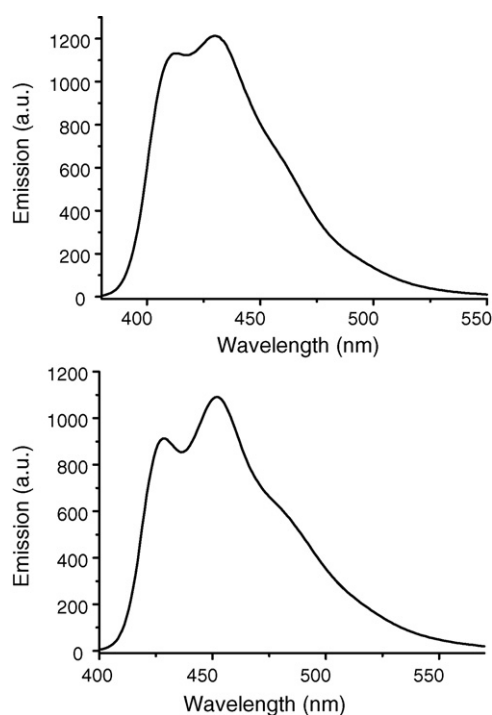


Fig. 2. Fluorescence spectra of **1** (up) and **4** (down) in DMSO ($c = 5 \times 10^{-6}$ M).

Table 2

The fluorescence data of **1–5** in DMSO (5×10^{-6} M)

Dye	λ_{em} (nm)	ϕ_f	τ_f (ns)
1	440, 410	0.94	1.05
2	445, 420	0.96	1.07
3	441, 413	0.49	0.55
4	460, 430	0.78	1.25
5	454, 426	0.84	1.36

emission band is shorter than the latter, which suggested that the co-planarity of the molecule is favor to red-shifted of emission band but not good to fluorescence emission.

The spectral characteristics of **4** in different solvents were also investigated and the spectroscopic data were listed in Table 3. It was found that no significant changes of absorption and emission were detected when **4** in different solvents. Besides, it was also found that no marked changes of the spectral characteristics of **4** was detected when **4** was in solvent (DMSO or EtOH) with different pH value (pH value was adjusted by HCl or NaOH). All indicated that both the polarity of solvents and pH value of solution have little influence on the spectral characteristics of **4**. Similar results were obtained when other dyes **1–3** and **5** were investigated in different solvents and different pH value of solution.

It is worth noting that both starting materials 1,4-benzenedicarboxaldehyde and benzil derivatives have no fluorescence emission, the condensation products, however, showed extremely strong fluorescence emission, and the large fluorescence quantum yields of compounds can be attributed to a substantial decrease in nonradiative relaxation to the ground state respect to the aromatic ring. Moreover, no significant changes of spectra characteristics were observed for all dyes **1–5** when they were in different solvents or solutions with different pH value. High fluorescence quantum yield and insensitive to solvent polarity and pH value may provide these fluorescence dyes potentially superior to conventional fluorophores in some applications to biological analysis and material science.

In addition, preliminary investigation of two-photon properties of dyes was also carried out. It is well known that one of the major drawbacks of one-photon fluorescence imaging for biological applications is that the excitation wavelengths are in the range of 350–560 nm, which may cause damage to the substrates [9]. The problem could be avoided if one develops two-photon fluorescence imaging, which allow visualization of ions, small molecules, or enzyme activity in living cells by employing two-photon-induced fluorescence microscopy that uses NIR photons as the excitation source. More importantly,

Table 3

Photophysical properties of dye **4** in different solvents (5×10^{-6} M)

Solvent	λ_{abs} (nm)	λ_{em} (nm)	ϕ_f
DMSO	410	460	0.78
CH ₂ Cl ₂	413	465	0.76
THF	411	456	0.79
CH ₃ CN	412	462	0.76
EtOH	410	461	0.77

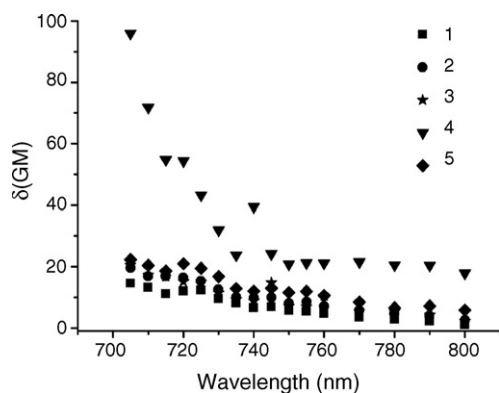


Fig. 3. Two-photon absorption cross-section of 1–5 with different wavelength in DMSO (1×10^{-4} M).

the two-photon confocal laser scanning microscopy would make it possible to determine the three-dimensional distribution of the guest molecules in the living cells in high resolution [10]. Figs. 3 and 4 represented two-photon absorption cross-section against different wavelengths and the fluorescence emission of 4 with two-photon excitation, respectively. The two-photon absorption cross-section of 1–5 were measured by the method of two-photon-induced fluorescence, and calculated in terms of the following equation [11], using coumarin 307 ($\delta = 19$ GM, $\lambda = 776$ nm) as a reference [12].

$$\delta_2 = \delta_1 \left(\frac{F_2}{F_1} \right) \left(\frac{\phi_1}{\phi_2} \right) \left(\frac{C_1}{C_2} \right)$$

δ_2 and δ_1 : two-photon absorption cross-section of sample and reference, respectively; F_2 and F_1 : two-photon induced fluorescence intensity of sample and reference, respectively; ϕ_2 and ϕ_1 : the fluorescence quantum yield of sample and reference, respectively; C_2 and C_1 : the concentration of sample and reference, respectively.

As demonstrated in Fig. 3, all compounds showed small two-photon absorption cross-section (TPACS) comparing to the large ones reported recently [13], the TPACS of 4 is, however, significantly higher than that of others and the largest TPACS ($\delta = 98$ GM) of 4 was obtained in DMSO with 700 nm excitation although the reason is not clear. In addition, upon excitation at 740 nm with a 80-fs pulse, 4 showed blue fluorescence, and the two-photon emission peaks in DMSO are red-shifted by 25

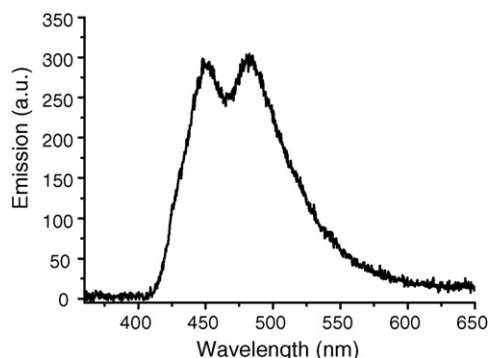


Fig. 4. Two-photon emission of 4 in DMSO (1×10^{-4} M) with 740 nm excitation.

and 10 nm, respectively, with respect to that of single-photon emission, which might be explained by a reabsorption effect [14].

4. Conclusions

A class of fluorescence dye has been synthesized and their photophysical properties were explored. These fluorophores can be characterized by the following advantages: (1) one-step preparation from commercially available materials, (2) inexpensive substrates, (3) high fluorescence quantum yield, and (4) insensitive to solvent polarity and pH value.

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References

- [1] (a) B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, New York, 2002; (b) W.T. Mason, *Fluorescent and Luminescent Probes for Biological Activity*, Academic Press, New York, 1999; (c) A.P. de Silva, H.W.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, *Chem. Rev.* 97 (1997) 1515; (d) V. Ntziachristos, J. Ripoll, L.H.V. Wang, R. Weissleder, *Nat. Biotechnol.* 23 (2005) 313; (e) M.J. Hall, L.T. Allen, D.F. O'Shea, *Org. Biomol. Chem.* 4 (2006) 776; (f) M.D. Bowman, M.M. Jacobson, H.E. Blackwell, *Org. Lett.* 8 (2006) 1645.
- [2] (a) R.F. Service, *Science* 310 (2005) 1762; (b) T. Mitsumori, M. Bendikov, O. Dautel, F. Wudl, T. Shioya, H. Sato, Y. Sato, *J. Am. Chem. Soc.* 126 (2004) 16793; (c) R. Mondal, B.K. Shah, D.C. Neckers, *J. Org. Chem.* 71 (2006) 4085; (d) T. Agou, J. Kobayashi, T. Kawashima, *Org. Lett.* 8 (2006) 2241; (e) C.-H. Chen, J.T. Lin, M.-C.P. Yeh, *Org. Lett.* 8 (2006) 2233.
- [3] (a) S. Selvi, S.-C. Pu, Y.-M. Cheng, J.-M. Fang, P.-T. Chou, *J. Org. Chem.* 69 (2004) 6674; (b) Y. Yamaguchi, T. Ochi, T. Wakamiya, Y. Matsubara, Z. Yoshida, *Org. Lett.* 8 (2006) 717; (c) D. Gryko, J. Piechowska, M. Tasiar, J. Waluk, G. Orzanowska, *Org. Lett.* 8 (2006) 4747; (d) Y. Xiao, F. Liu, X. Qian, J. Cui, *Chem. Commun.* (2005) 239; (e) H.-C. Yeh, W.-C. Wu, C.-T. Chen, *Chem. Commun.* (2003) 404.
- [4] (a) W. Denk, J.H. Strickler, W.W. Webb, *Science* (1990) 248; (b) R.H. Kohler, J. Cao, W.R. Zipfel, W.W. Webb, M.R. Hansen, *Science* 276 (1997) 2039; (c) C. Xu, W.R. Zipfel, J.B. Shear, R.M. Williams, W.W. Webb, *Proc. Natl. Acad. Sci. U.S.A.* 93 (1996) 10763; (d) W. Denk, *Proc. Natl. Acad. Sci. U.S.A.* 91 (1994) 6629; (e) J. Mertz, C. Xu, W.W. Webb, *Opt. Lett.* 20 (1995) 2532.
- [5] (a) R. Kramer, *Angew. Chem., Int. Ed.* 37 (1998) 772; (b) A. Torrado, G.K. Walkup, B. Imperiali, *J. Am. Chem. Soc.* 120 (1998) 609; (c) M.D. Shults, D.A. Pearce, B. Imperiali, *J. Am. Chem. Soc.* 125 (2003) 10591; (d) S.C. Burdette, C.J. Frederickson, W. Bu, S.J. Lippard, *J. Am. Chem. Soc.* 125 (2003) 1778; (e) J.L. Bricks, A. Kovalchuk, C. Triefinger, M. Nofz, M. Buschel, A.I. Tolmachev, J. Daub, K. Rurack, *J. Am. Chem. Soc.* 127 (2005) 13522.

- [6] (a) M.-Q. Zhu, L. Zhu, J.J. Han, W. Wu, J.K. Hurst, A.D.Q. Li, *J. Am. Chem. Soc.* 128 (2006) 4303;
(b) M. Heilemann, E. Margeat, R. Kasper, M. Sauer, P. Tinnefeld, *J. Am. Chem. Soc.* 127 (2005) 3801;
(c) Y. Shiraishi, Y. Tokitoh, G. Nishimura, T. Hirai, *Org. Lett.* 7 (2005) 2611;
(d) S. Abad, M. Kluciar, M.A. Miranda, U. Pischel, *J. Org. Chem.* 70 (2005) 10565;
(e) T. Fukaminato, T. Sasaki, T. Kanai, N. Tamai, M. Irie, *J. Am. Chem. Soc.* 126 (2004) 14843.
- [7] (a) T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, *J. Am. Chem. Soc.* 126 (2004) 14843;
(b) T.B. Norsten, N.R. Branda, *J. Am. Chem. Soc.* 123 (2001) 1784;
(c) G. Jiang, S. Wang, W. Yuan, L. Jiang, Y. Song, H. Tian, D. Zhu, *Chem. Mater.* 18 (2006) 235;
(d) S.-J. Lim, B.-K. An, S.D. Jung, M.-A. Chung, S.Y. Park, *Angew. Chem., Int. Ed.* 43 (2004) 6346;
(e) Y. Chen, N. Xie, *J. Mater. Chem.* 15 (2005) 3229.
- [8] (a) E. Amouyal, A. Homsy, J.-C. Chambron, J.-P. Sauvage, *J. Chem. Soc., Dalton Trans.* 1990 (1841);
(b) F.C. Krebs, L.R. Lindvold, M. Jorgensen, *Tetrahedron Lett.* 42 (2001) 6753;
(c) F.C. Krebs, H. Spanggaard, *J. Org. Chem.* 67 (2002) 7185.
- [9] (a) A. Ojida, Y. Mito-oka, M. Inoue, I. Hamchi, *J. Am. Chem. Soc.* 124 (2002) 6256;
(b) A. Minta, J.P.Y. Kao, R.Y. Tsien, *J. Biol. Chem.* 264 (1989) 8171.
- [10] (a) M.D. Cahalan, I. Parker, S.H. Wei, M.J. Miller, *Nature* 2 (2002) 872;
(b) T. Euler, P.B. Detwiller, W. Denk, *Nature* 418 (2002) 845;
(c) D.R. Larson, W.R. Zipfel, R.M. Williams, S.W. Clark, M.P. Bruchez, F.W. Wise, W.W. Webb, *Science* 300 (2003) 1434;
(d) M. Taki, J.L. Wolford, T.V. O'Halloran, *J. Am. Chem. Soc.* 126 (2004) 712.
- [11] Z. Chen, D.L. Kaplan, K. Yang, J. Kumar, K.A. Marx, S.K. Tripathy, *Appl. Opt.* 36 (1997) 1655.
- [12] C. Xu, W.W. Webb, *J. Opt. Soc. Am. B.* 13 (1996) 481.
- [13] (a) H. Rath, J. Sankar, V. Prabhuraja, T.K. Chandrashekar, A. Nag, D. Goswami, *J. Am. Chem. Soc.* 127 (2005) 11608;
(b) H. Rath, V. Prabhuraja, T.K. Chandrashekar, A. Nag, D. Goswami, B.S. Joshi, *Org. Lett.* 8 (2006) 2325;
(c) T.E.O. Screen, J.R.G. Thorne, R.G. Denning, D.G. Bucknall, H.L. Anderson, *J. Am. Chem. Soc.* 124 (2002) 9712;
(d) K.D. Belfield, D.J. Hagan, E.W. Van Stryland, K.J. Schafer, R.A. Negres, *Org. Lett.* 1 (1999) 1575.
- [14] T. Lin, G. He, P.N. Parasad, L. Tan, *J. Mater. Chem.* 14 (2004) 982.