

Two-Photon Absorption-Related Properties of Functionalized BODIPY Dyes in the Infrared Range up to Telecommunication Wavelengths

By Pierre-Antoine Bouit, Kenji Kamada, Patrick Feneyrou, Gérard Berginc, Loïc Toupet, Olivier Maury, and Chantal Andraud*

Two-photon absorption (TPA) is a resonant third-order nonlinear optical (NLO) process in which an electron is promoted from its ground state to an excited state by simultaneous absorption of two photons of half-energy in an intense focused light beam such as that generated by a laser source. This phenomenon, theoretically predicted in 1929 by Göppert-Mayer,^[1] was experimentally evidenced in 1961 in a TPA-induced fluorescence of Eu²⁺-doped CaF₂ crystals under ruby-laser irradiation.^[2] Since then, the intrinsic advantages of TPA excitation, that is, long wavelength and confocal 3D-resolved absorption, led to numerous applications in the fields of material sciences and biology following the availability of tunable laser sources. In particular, the development of femtosecond (fs)-Ti-sapphire lasers triggered numerous studies in the 700–1000 nm spectral range. For instance, TPA was successfully involved in the fabrication of microstructures^[3,4] or high-density optical memories^[5] with a 3D sub-micrometer resolution, in signal processing, or for the design of optical limiting devices devoted to the protection of sensors against laser damages.^[6,7] In life sciences, the long-wavelength TPA excitation is located in the biologically transparent spectral range (800–1000 nm), and is therefore able to penetrate more deeply into biological tissues. Combined with the above mentioned spatial resolution, TPA found exciting applications for bioimaging using nonlinear microscopy,^[8] and also for drug delivery or dynamic

phototherapy.^[9] All these applications encouraged the scientific community to design a large variety of chromophores with optimized two-photon cross-sections (σ_2) in this 700–1000 nm spectral range, such as organic dyes, organometallic or coordination complexes, polymers, dendrimers, or nanoparticles and quantum-dots, compiled in a recent exhaustive review.^[10] However, the near-infrared (NIR) spectral range has been less studied, and in particular the telecommunications-wavelengths spectral range (1.3–1.55 μm), where applications in signal processing (optical power stabilization, pulse suppression, optical limiting) are very attractive. Since 2005, inspired by the Marder–Van Stryland and Osuka–Kim groups, there is a great interest in the design of chromophores exhibiting strong TPA properties in the NIR. Maximal TPA cross-section of ca. 1500 GM at 1.44 μm and 1600 GM at 1.3 μm have been reported for dipolar and quadrupolar squarine-type chromophores, respectively,^[11,12] whereas nickel (bisdithiolene) complexes^[13] and singlet diradical systems^[14] exhibit significant σ_2 over the entire telecommunication range. On the other hand, numerous fused-, extended-, or organized-porphyrin complexes have been reported with very large TPA cross-sections ranging from 10³ to 10⁴ GM.^[15–19] Finally, we reported the TPA properties of cyanine-type chromophores (σ_2 of 750 GM at 1450 nm) that present enough solubility to carry out additional nonlinear transmittance experiments at telecommunications wavelengths.^[20] Herein, we report the synthesis and X-ray structures of aza boron-dipyrromethane (Bodipy) NIR dyes functionalized in the α position by donor- π -conjugated systems, and their TPA and nonlinear transmittance properties in the 1.2–1.6 μm spectral range.

It is worth noting that Bodipy dyes are a versatile class of chromophores^[21–22] largely studied for its exceptional luminescence properties, and are used as biomolecular labels, sensors (pH, NO, Hg²⁺, toxin...), or photonic therapeutic agents.^[21–26] Great efforts have been recently devoted to shift their spectroscopic properties to the NIR spectral range by i) introduction of electron-donating moieties,^[27] ii) rigidification of the structure,^[28] or iii) replacement of the meso-carbon by a nitrogen atom (the “aza”-Bodipy).^[29–31] But surprisingly, whereas water-soluble conventional Bodipy dyes featuring low two-photon cross-sections were used for two-photon imaging microscopy,^[32,33] these compounds were not fully optimized for TPA applications. To the best of our knowledge, only multi-chromophoric dyes containing two or three Bodipy units and exhibiting rather modest σ_2 values (75 GM at 990 nm) in the visible were described in the literature.^[34]

The synthesis of the target chromophores **B^{I-2}** (Scheme 1), featuring an extended π -conjugated skeleton, involves as key step

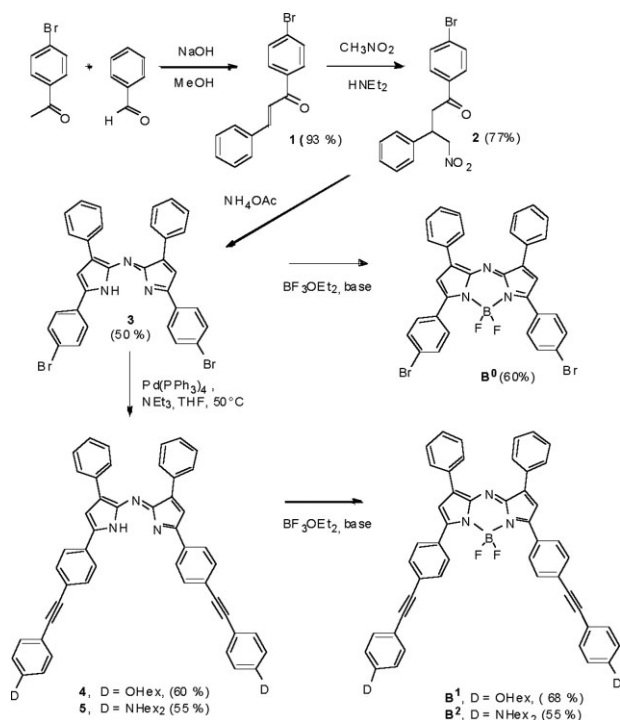
[*] Dr. C. Andraud, P.-A. Bouit, Dr. O. Maury
Université de Lyon, ICL
CNRS – Ecole Normale Supérieure de Lyon
46 allée d'Italie, Lyon 69007 (France)
E-mail: chantal.andraud@ens-lyon.fr

Dr. K. Kamada
Photonics Research Institute
National Institute of Advanced Industrial Science and Technology (AIST)
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577 (Japan)

Dr. P. Feneyrou
Thales Research & Technology France
Route Départementale 128
91767 Palaiseau cedex (France)

Dr. G. Berginc
Thales Optronique SABP 55
rue Guynemer, 78283 Guyancourt (France)

Dr. L. Toupet
Groupe de la Matière Condensée et Matériaux
UMR 6626 CNRS-Université de Rennes 1
Campus de Beaulieu, 35042 Rennes cedex (France)



Scheme 1. Synthesis of chromophores.

a copper-free Sonogashira cross-coupling using $\text{Pd}(\text{PPh}_3)_4$ as catalyst between bromo-functionalized aza-dipyrromethene^[35] and various donor-phenylethynyl derivatives ($D = \text{OHex}$, $D = \text{NHex}_2$), followed by classical complexation with boron trifluoride etherate in basic media (Scheme 1). The intermediate synthon three and the corresponding complex B^0 are prepared using the procedure described by O'Shea and co-workers.^[36] Synthetic details and complete characterization are compiled in the Supporting Information. It is important to note that the synthesis of B^{0-2} was carried out at a gram scale, and B^2 is soluble enough in chlorinated solvents to envisage further nonlinear transmittance experiments.^[20] Crystals of B^0 suitable for X-ray diffraction analysis were obtained by slow diffusion of diethylether into a dichloromethane solution. As already observed for other aza-Bodipy dyes,^[31,35,37,38] the structure (Fig. S1 in Supporting Information) shows three very planar central fused rings and four twisted peripheral phenyl groups (twist angle of $12\text{--}43^\circ$); the boron atom lies in an almost perfect tetrahedral environment, and the C–N bond lengths between bridging nitrogen N2 and the two pyrroles C4 and C5 are identical ($1.322(3)$ and $1.326(3)$ Å, respectively), showing the conjugated nature of the chromophore.

All the linear and nonlinear properties were studied in dichloromethane solution, and are summarized in Table 1. The absorption spectrum (Fig. 1) of B^0 is characteristic of aza-Bodipy dyes, with an intense sharp transition ($\omega_{1/2} = 1270\text{ cm}^{-1}$) exhibiting a shoulder at higher energy. The extended π -conjugated $\text{B}^{1,2}$ compounds present transitions whose red shift increases with the strength of the donor group ($\Delta\lambda = 37$ and 87 nm for B^1 and B^2 , respectively). It is worth noting that this shift is accompanied by a significant broadening of the absorption

Table 1. Photophysical data and nonlinear transmittance data in DCM solution

Compounds	B^0	B^1	B^2
$\lambda_{\text{abs}}/\text{nm}$	658	695	745
$\epsilon_{\text{max}}/\text{L mol}^{-1}\text{ cm}^{-1}$	83 000	80 000	57 000
$\lambda_{\text{TPA}}^{\text{max}}/\text{nm}$	–	1440	1220
$\sigma_2^{\text{max}}/\text{GM}$	<20	80 ± 10	1070 ± 100
$\alpha_2^{\text{calcd}}(\lambda)/\text{cm}^3\cdot\text{GW}^{-2}$ [a]	–	–	2.8 (1350)
$\alpha^3(\lambda)/\text{cm}^3\cdot\text{GW}^{-2}$ [b]	–	–	620 (1350)

[a] Deduced from fs-Z-scan experiments for a concentration of 106 g L^{-1} .

[b] Deduced from ns-nonlinear transmittance experiments for a concentration of 106 g L^{-1} .

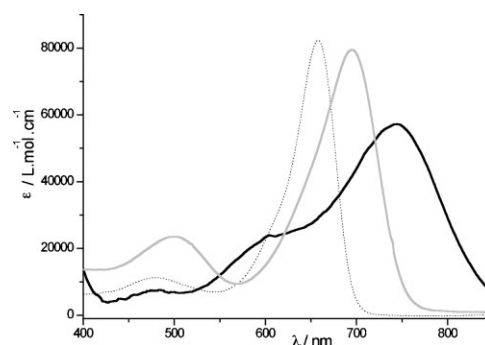
band ($\omega_{1/2} = 2850\text{ cm}^{-1}$ for the amino derivative). Open-aperture Z-scan measurements were performed in the $1200\text{--}1600\text{ nm}$ spectral range using a fs-optical parametric amplifier pumped by a Ti:sapphire source. At such short pulse durations (130 fs), only the TPA process is considered, and the propagation equation can be simplified as:

$$dI/dz = -\alpha_2 I^2 \quad (1)$$

where I represents the light intensity, z the propagation axis, and α_2 the TPA coefficient. As described previously,^[20] the α_2 coefficient can be determined from the molecular two-photon cross-section σ_2 by:

$$\sigma_2 = h\nu\alpha_2/N \quad (2)$$

Carrying these fs-Z-scan experiments at various wavelengths allowed the determination of the TPA spectra of $\text{B}^{0,1,2}$ over the entire $1200\text{--}1600\text{ nm}$ spectral range (Fig. 2). As expected for non-centrosymmetric compounds, each TPA spectrum matches the wavelength-doubled linear one, indicating that the same transition is one- and two-photon allowed. At these wavelengths, the unfunctionalized B^0 chromophore does not present any TPA response, in contrast to the donor- π -conjugated substituted systems $\text{B}^{1,2}$ (Table 1). While B^1 presents a rather small NLO activity, B^2 shows significant σ_2 values (around 600 GM) over the broad $1300\text{--}1450\text{ nm}$ spectral range. Furthermore, at lower wavelengths, a significant increase is observed with a maximal

Figure 1. Absorption spectra of B^0 (dashed), B^1 (gray), and B^2 (bold).

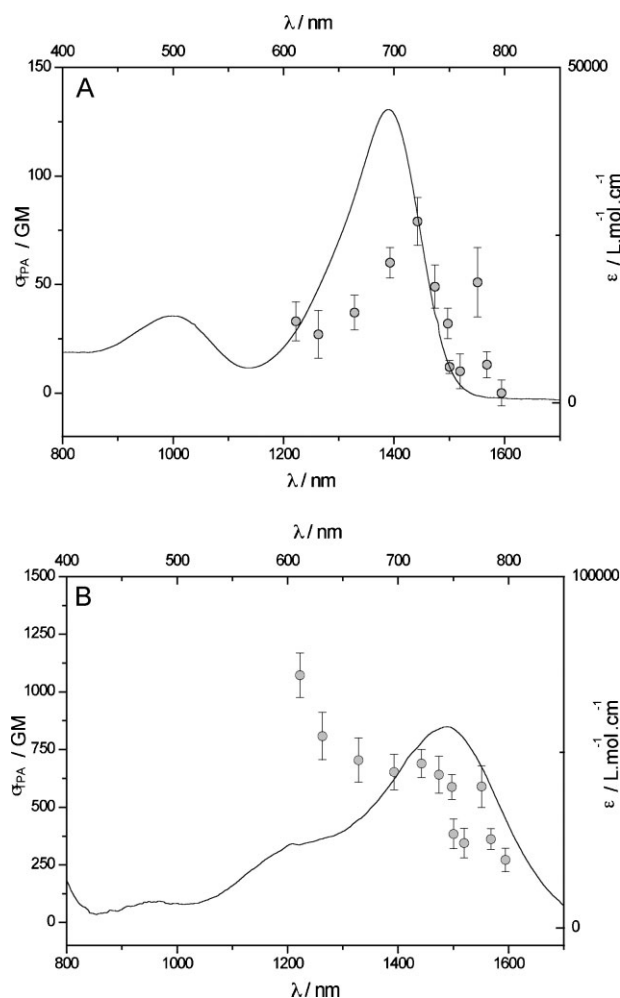


Figure 2. TPA spectra measured by fs-Z-Scan method (filled circle) and linear absorption spectra in upper abscissa (—) for **B**¹ (up) and **B**² (bottom).

two-photon cross-section σ_2^{\max} of 1070 GM at 1220 nm. This value is close to that of cyanine compounds,^[20] and in the same order of magnitude than that of dipolar or quadrupolar derivatives.^[11,12] In addition to the high solubility, exceptional thermal stability (T_{d10} about 360 °C) and the large-scale availability of **B**² allowed us to perform nonlinear transmittance experiments in the telecommunication spectral range. Such experiments were carried out for **B**² in a highly concentrated solution ($c = 0.1 \text{ mol L}^{-1}$) using a nanosecond (ns) optical parametric oscillator (OPO) pumped by a frequency-tripled Nd/YAG laser source.^[20] Over the 1350–1500 nm range, the nonlinear transmittance curves versus the laser fluence present characteristic nonlinear transmission properties; this behavior is illustrated at 1350 nm in Figure 3: a good transmission is observed at low energy ($T > 0.9$), whereas beyond the nonlinear transmission threshold observed for a fluence of 0.7 J cm^{-2} , the laser-beam intensity is strongly attenuated, up to 60% at a fluence of 7 J cm^{-2} . Due to the longer pulse duration (7 ns), the simulation of the experimental curves based only on a TPA process failed (dashed line, Fig. 3), and a higher-order effect related to a three-photon absorption, such as a

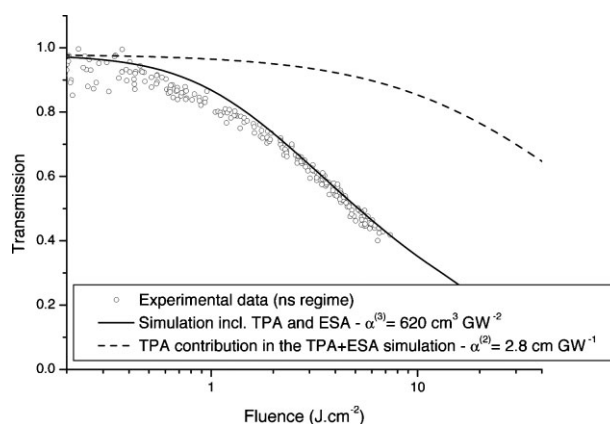


Figure 3. Transmittance variations with the laser fluence in a DCM solution of **B**² at a concentration of 106 g L^{-1} ; experimental data points (circles), theoretical simulation using complete model including TPA and ESA contribution (solid line), and including only the TPA contribution within this latter hypothesis (dashed line).

TPA-induced excited-state absorption (ESA) was taken into account. Consequently, as already observed in the NIR for cyanine dyes^[20] or in the visible,^[39,40] the propagation in Equation 1 becomes

$$dI/dz = -\alpha_2 I^2 - \alpha_3 I^3 \quad (3)$$

where α_3 is the three-photon absorption coefficient. The numerical resolution of Equation 3, for temporally and spatially Gaussian incident pulses and using the TPA coefficient previously measured by fs-Z-scan, allowed the determination of a α_3 coefficient of $620 \text{ cm}^3 \text{ GW}^{-2}$ at 1350 nm (Table 1). This value corresponds to a two-fold increase compared to that of cyanine dyes measured in the same condition of concentration ($230 \text{ cm}^3 \text{ GW}^{-2}$ at 1520 nm).^[20] This enhancement, which cannot be interpreted only as a stronger TPA efficiency, could be explained by a strong ESA contribution. This is illustrated in Figure S1 in Supporting Information, by the comparison of the spectral distribution of α_2 and α_3 between 1350 and 1500 nm: α_3 decreases from 600 to $300 \text{ cm}^3 \text{ GW}^{-2}$, while α_2 remains nearly constant.

In conclusion, this study clearly underlines the high potentialities of functionalized aza-Bodipy dyes for TPA-related applications in the telecommunications spectral range, and in particular for nonlinear transmission. The versatile nature of this class of chromophores opens the way for fine chemical engineering, in order to optimize the TPA properties in the NIR by additional functionalization of the β position or by rigidification of the lateral π -skeleton, for example.

Experimental

CCDC-668638 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors thank the Direction Générale de l'Armement for a grant to PAB. Supporting Information is available online from Wiley InterScience or from the author.

Received: June 25, 2008

Revised: September 14, 2008

Published online: February 19, 2009

- [1] M. Göppert-Mayer, *Naturwissenschaften* **1929**, 17, 932.
- [2] W. Kaiser, C. G. B. Garret, *Phys. Rev. Lett.* **1961**, 7, 229.
- [3] I. Wang, M. Bouriau, P. L. Baldeck, C. Martineau, C. Andraud, *Opt. Lett.* **2002**, 27, 1348.
- [4] K.-S. Lee, D.-Y. Yang, S. H. Park, R. H. Kim, *Polym. Adv. Technol.* **2006**, 17, 72.
- [5] S. Kawata, H.-B. Sun, T. Tanaka, K. Takada, *Nature* **2001**, 412, 697.
- [6] C. W. Spangler, *J. Mater. Chem.* **1999**, 9, 2013.
- [7] Y. Morel, A. Irimia, P. Najechalski, O. Stephan, P. L. Baldeck, C. Andraud, *J. Chem. Phys.* **2001**, 114, 5391.
- [8] A. Picot, A. D'Aléo, P. L. Baldeck, A. Grishine, A. Duperray, C. Andraud, O. Maury, *J. Am. Chem. Soc.* **2008**, 130, 1532.
- [9] W. R. Ziepfel, R. M. Williams, W. W. Webb, *Nat. Biotech.* **2003**, 21, 1369.
- [10] G. S. He, L.-S. Tan, Q. Zheng, P. N. Prasad, *Chem. Rev.* **2008**, 108, 1245.
- [11] L. Beverina, J. Fu, A. Leclercq, E. Zojer, P. Pacher, S. Barlow, E. W. Van Stryland, D. J. Hagan, J.-L. Brédas, S. R. Marder, *J. Am. Chem. Soc.* **2005**, 127, 7282.
- [12] S. J. Chung, S. Zheng, T. Odani, L. Beverina, J. Fu, L. A. Padilha, A. Biesso, J. M. Hales, X. Zhan, K. Schmidt, A. Ye, E. Zojer, S. Barlow, D. J. Hagan, E. W. Van Stryland, Y. Yi, Z. Shuai, G. A. Pagani, J.-L. Brédas, J. W. Perry, S. R. Marder, *J. Am. Chem. Soc.* **2006**, 128, 14444.
- [13] J.-Y. Cho, S. Barlow, S. R. Marder, J. Fu, L. A. Padilha, E. W. Van Stryland, D. J. Hagan, M. Bishop, *Opt. Lett.* **2007**, 32, 671.
- [14] K. Kamada, K. Ohta, T. Kubo, A. Shimizu, Y. Morita, K. Nakasuji, R. Kishi, S. Ohta, S. Furukawa, H. Takahashi, M. Nakano, *Angew. Chem. Int. Ed.* **2007**, 46, 3544.
- [15] Y. Inokuma, N. Ono, H. Uno, D. Y. Kim, S. B. Noh, D. Kim, A. Osuka, *Chem. Commun.* **2005**, 3782.
- [16] K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2006**, 45, 3944.
- [17] S. Mori, K. S. Kim, Z. S. Yoon, S. B. Noh, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2007**, 129, 11344.
- [18] Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2008**, 47, 681.
- [19] M. Drobizhev, Y. Stepanenko, A. Rebane, C. J. Wilson, T. E. O. Screen, H. L. Anderson, *J. Am. Chem. Soc.* **2006**, 128, 12432.
- [20] P.-A. Bouit, G. Wetzel, G. Berginc, L. Toupet, P. Feneyrou, Y. Bretonnière, O. Maury, C. Andraud, *Chem. Mater.* **2007**, 19, 5325.
- [21] A. Loudet, K. Burgess, *Chem. Rev.* **2007**, 107, 4891.
- [22] G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem. Int. Ed.* **2007**, 46, 2.
- [23] Y. Gabe, Y. Urano, K. Kikuchi, H. Kojima, T. Nagano, *J. Am. Chem. Soc.* **2004**, 126, 3357.
- [24] R. E. Gawley, H. Mao, M. M. Haque, J. B. Thorne, J. S. Pharr, *J. Org. Chem.* **2007**, 72, 2187.
- [25] A. Coskun, M. D. Yilmaz, E. U. Akkaya, *Org. Lett.* **2007**, 9, 607.
- [26] S. O. McDonnell, M. J. Hall, L. T. Allen, A. Byrne, W. M. Gallagher, D. F. O'Shea, *J. Am. Chem. Soc.* **2005**, 127, 16360.
- [27] Y.-H. Yu, A. B. Descalzo, Z. Shen, H. Röhr, Q. Liu, Y.-W. Wang, M. Spieles, Y.-Z. Li, K. Rurack, X.-Z. You, *Chem. Asian J.* **2006**, 1, 176.
- [28] W. Zhao, E. M. Carreira, *Angew. Chem. Int. Ed.* **2005**, 44, 1677.
- [29] W. Zhao, E. M. Carreira, *Chem. Eur. J.* **2006**, 12, 7254.
- [30] K. Umezawa, Y. Nakamura, H. Makino, D. Citterio, K. Suzuki, *J. Am. Chem. Soc.* **2008**, 130, 1550.
- [31] S. O. McDonnell, D. F. O'Shea, *Org. Lett.* **2006**, 8, 3493.
- [32] C. Nicoli, J. Baranski, S. Schlummer, J. Palomo, M. Lumbierres-Burgues, M. Kahms, J. Kuhlmann, S. Sanchez, E. Gratton, H. Waldmann, R. Winter, *J. Am. Chem. Soc.* **2006**, 128, 192.
- [33] F. Bestvater, E. Spiess, G. Stobrawa, M. Hacker, T. Feurer, T. Porwol, U. Berchner-Pfannschmidt, C. Wostlaw, H. Acker, *J. Microsc.* **2002**, 208, 108.
- [34] L. Porres, O. Mongin, M. Blanchard-Desce, *Tetrahedron Lett.* **2006**, 47, 1913.
- [35] A. Loudet, R. Bandichhor, L. Wu, K. Tetrahedron. Burgess, **2008**, 64, 3642.
- [36] A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher, D. F. O'Shea, *J. Am. Chem. Soc.* **2004**, 126, 10619.
- [37] J. Killoran, L. Allen, J. F. Gallagher, W. M. Gallagher, D. F. O'Shea, *Chem. Commun.* **2002**, 1862.
- [38] J. Killoran, S. O. McDonnell, J. F. Gallagher, D. F. O'Shea, *New, J. Chem.* **2008**, 32, 483.
- [39] R. Anémian, Y. Morel, P. L. Baldeck, B. Paci, K. Kretsch, J.-M. Nunzi, C. Andraud, *J. Mater. Chem.* **2003**, 13, 2157.
- [40] C. Girardot, B. Cao, J.-C. Mulatier, P. L. Baldeck, J. Chauvin, D. Rhiel, J. A. Delaire, C. Andraud, G. Lemerrier, *Chem. Phys. Chem.* **2008**, 9, 1531.