Synthesis, and two photon absorption properties of 7,7′-(iminundecahydro-*closo*-dodecaborate)-9,9′-(dihexyl)-2,2′-bifluorene†

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Hybrid organic–inorganic bis-tetrabutylammonium-7,7′-(iminundecahydro-*closo*-dodecaborate)-9,9′-(dihexyl)-2,2′bifluorene (5) was prepared, and the influence of the *closo*-dodecaborate cluster on the two-photon absorption properties of bi-fluorene derivatives was demonstrated.

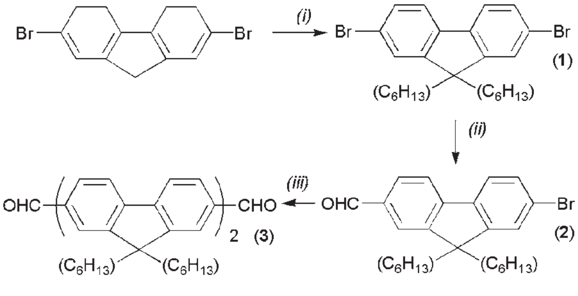
For several years, two photon absorption (TPA) based applications have developed in various domains, like optical power limiting,[1,2] 3D microfabrication,[3,4] photodynamic therapy,[5,6] or two-photon exited fluorescence microscopy.[7] The expansion in these spheres of activity requires important work in the domain of molecular engineering, in order to elaborate materials with high TPA properties. For that purpose, various π-conjugated chromophores have been investigated, including centrosymmetric or non-centrosymmetric linear or multi-branched compounds.[8] An original approach consists of the use of an oligofluorene derivative for which TPA results from dipolar coupling effect.[9] Recently, the potential of *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$ as a donor group for two-photon absorption was demonstrated in the case of non-centrosymmetric π-conjugated systems.[10] The use of the B_{12} cluster could be interesting namely for photodynamic therapy due to its low toxicity. We report in this paper the synthesis and the two-photon absorption properties in the visible range of anionic 7,7′-(iminundecahydro-*closo*-dodecaborate)-9,9′-(dihexyl)-2,2′-bifluorene (5), in order to evaluate the influence of the boron cluster on the TPA properties of the optically active bifluorene.[11]

The synthesis of bis-tetrabutylamonium-7,7′-(iminundecahydro-*closo*-dodecaborate)-9,9′-(dihexyl)-2,2′-bifluorene (5) was conducted step by step (Scheme 1). First, in order to increase the solubility in the usual organic solvent, 2,7-dibromo-9,9-dihexylfluorene (1) was prepared by dialkylation of the commercially available 2,7-dibromofluorene with 1-bromohexane in the presence of a sodium hydroxide aqueous solution and triethylbenzylammonium chloride.[12] This method was previously reported for other fluorene derivatives.[13–15] Intermediates **2** and **3** were previously described by C. Van der Pol *et al.*[16] 2-bromo-7-formyl-9,9-dihexyl-fluorene (**2**) was then obtained from **1**, butyllithium and dimethylformamide.[17,18] Then 7,7′-(formyl)-9,9′-(dihexyl)-2,2′-bifluorene (**3**) was obtained *via* the Yamamoto homocoupling reaction using a nickel catalyst (Scheme 1).[19,20]

Parallel to this work, tetrabutylammonium ammoniaundecahydro-*closo*-dodecaborate (**4**) was prepared from commercially available dodecahydro-*closo*-dodecaborate and hydroxylamine-*o*-sulfonic acid.[21] The bis-tetrabutylamonium-7,7′-(iminundecahydro-*closo*-dodecaborate)-9,9′-(dihexyl)-2,2′-bifluorene (**5**) was obtained, in the last step, from the diformyl-bifluorene derivative (**3**) and the tetrabutylammonium ammoniaundecahydro-*closo*-dodecaborate (**4**) in the presence of a catalytic amount of sodium hydroxide, according to the procedure initially reported by I. B. Sivaev *et al.* (Scheme 2).[22]

All compounds were characterized by NMR spectroscopy, elemental analysis or mass spectrometry and correspond to the expected structures (Fig. 1 and Fig. 2).

To the best of our knowledge, no examples of centrosymmetric bifluorenes for nonlinear applications using the TPA process are reported in the literature. In this context, the linear absorption and the TPA spectrum of compound **5** was compared to the one of 2,2′-(9,9′-dihexyl)-bifluorene (DHF) in order to evaluate the influence of the boron cluster on the optical properties of such derivatives. The results are reported in Table 1. The linear absorption spectrum of compound **5** in acetonitrile, shows an intense absorption band at 403 nm (ε_{max} = 105 235 L mol^{-1} cm^{-1}) (Fig. 3). The bathochromic and hyperchromic effects observed compared to DHF (Fig. 1), which presents an absorption band at 330 nm



(i) aqueous NaOH, Net3PhCl cat., DMSO, 2h, 60°C, 96%; (ii), 1/nBuLi, 2/DMF, THF, -78°C, 4h, 80%; (iii) Ni(PPh3)2Cl2, PPh3, Zn, 80°C, 20 h, 51%

Scheme 1 Synthesis of 7,7′-(formyl)-9,9′-(dihexyl)-2,2′-bifluorene (**3**).†

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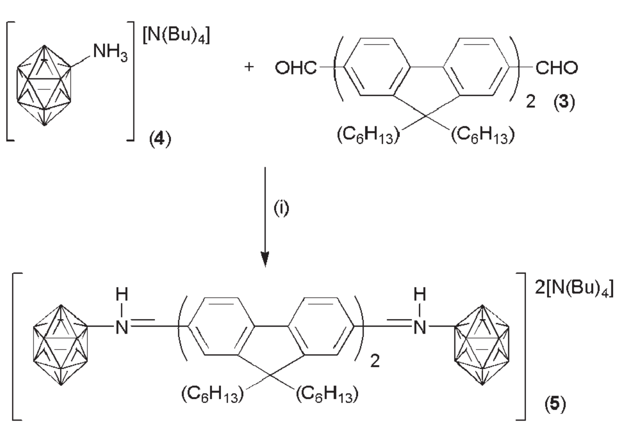

(i) (B12H11NH3)(NBu4)2, aqueous NaOH cat., DMF, 12h, rt, 55%.

Scheme 2 Synthesis B_{12}-bifluorene derivative **5**.†

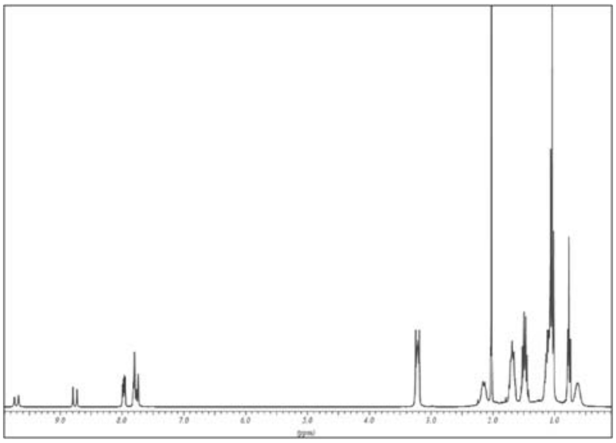

Fig. 1 ^1H NMR spectrum of **5**.

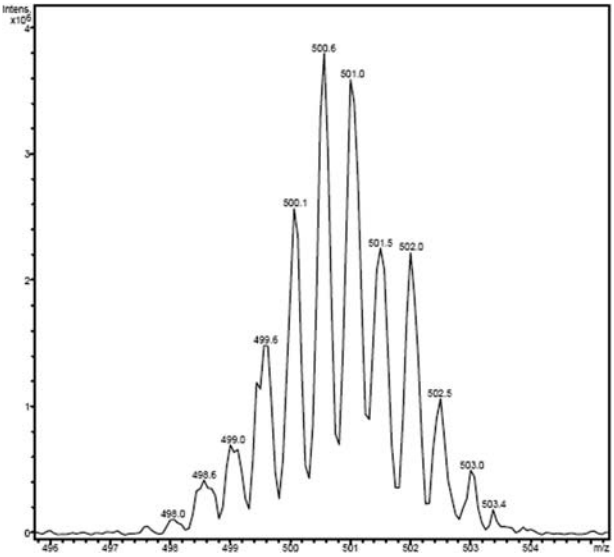

Fig. 2 Mass spectrometry of **5**.

(ε_{max} = 53 570 L mol^{-1} cm^{-1}), were attributed to the donor effect of the $NHB_{12}H_{11}$ group.

Table 1 Experimental single-photon maxima wavelength (λ_{max}), molar extinction coefficient (ε), wavelength for TPA absorption maxima (λ_{TPA}) and two-photon excitation cross-section (σ_{TPA})

Product	λ_{max}/nm	ε/L mol^{-1} cm^{-1}	λ_{TPA}/nm	σ_{TPA}/GM[a]
DHF[11]	330	53 570	534	60
5	403	105 235	725	1040

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

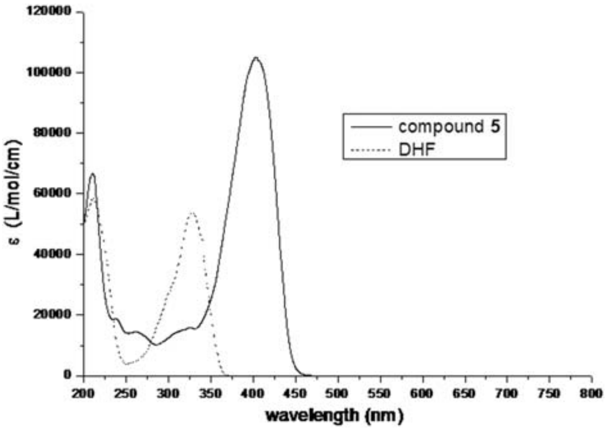

Fig. 3 Linear absorption of compound **5**, and DHF, in acetonitrile solution.

Due to the low solubility of compound **5** in chloroform, the two photon spectrum was recorded in acetonitrile. However, no solvatochromic effect was observed for 2,2′-(9,9′-dihexyl)-bifluorene, so it was possible to compare results obtained with compound **5** and for the DHF recorded in chloroform.[11] The fluorescence quantum yield of compound **5** was determined from the fluorescence emission spectra using *p*-bis-(*o*-methylstyryl)benzene (MSB) as a reference. The spectrum was recorded using an excitation wavelength of 340 nm, with an optical density of 0.05. The measured fluorescence quantum yield is 49% compared to MSB. The TPA spectrum of compound **5** was obtained by up-conversion fluorescence measurements using a Nd:YAG pumped optical paramagnetic oscillator producing 2.6 ns (full width at half maximum) in the range of 550 to 650 nm and using a Ti:sapphire femtosecond laser in the range of 700–950 nm. The excitation beam is collimated over a cell length (5 mm). The fluorescence is collected at 90° to the excitation beam and focused into an optical fibre connected to a spectrometer. The TPA cross section was determined at 720 nm using *p*-bis-(*o*-methylstyryl)-benzene as a reference standard for which σ_{TPA} = 1.6 × 10^{-50} cm^4 s per photon-molecule.[23] The TPA spectrum obtained with the nanosecond laser beam (550–650 nm) is expressed in arbitrary units without any calibration. This spectrum was just recorded in order to check the decrease of σ_{TPA} for lower wavelength (Fig. 4).

The TPA spectrum of compound **5** shows a strong resonance at 725 nm with a cross section σ_{TPA} = 1040 × 10^{-50} cm^4 s per photon-molecule. The absorption band is red shifted compared to the one of DHF (534 nm) and at this

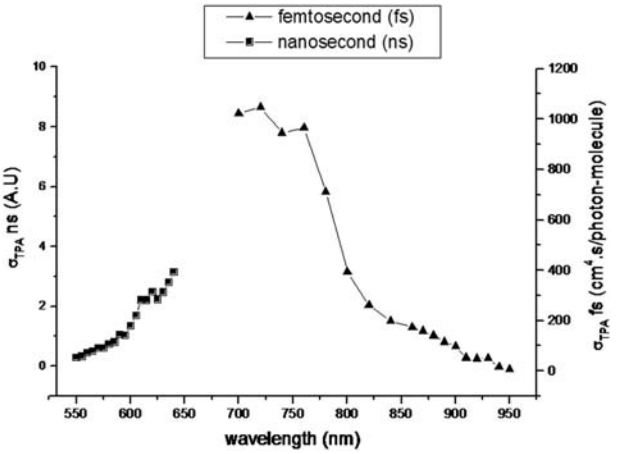

Fig. 4 Two-photon absorption spectrum of **5** in acetonitrile solution.

wavelength the corresponding σ_{TPA} is also increased (60×10^{-50} cm^4 s per photon-molecule for DHF).[11]

Compound **5** is the first example of a centrosymmetric bifluorene derivative containing a *closo*-dodecaborate cluster as the donor group. The interest of such compounds for two-photon processes was evidenced by the increase of the σ_{TPA} value compared to 2,2′-(9,9′-dihexyl)-bifluorene). Other similar bifluorene derivatives including different donor groups instead of the B_{12} cluster will be synthetized in order to evaluate the role of the boron cluster. Synthesis of longer oligofluorenes including the B_{12} cluster could be prepared in order to confirm the optical effect observed. The influence in the area of two photon absorption of a new type of boron-cluster was demonstrated, which opens the way to further developments in polyhedral boron chemistry. This study could be extended to monocarborane $CB_{11}H_{12}$, which is able to generate a whole variety of neutral systems as demonstrated by I. B. Sivaev *et al.* or A. Franken *et al.*[24,25]

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