COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Trivalent boron as acceptor in D–π-A chromophores: synthesis, structure and fluorescence following single- and two-photon excitation†

Zhi-qiang Liu, Qi Fang,* Dong Wang, Gang Xue, Wen-tao Yu, Zong-shu Shao and Min-hua Jiang
State Key Laboratory of Crystal Materials, Shandong University, 250100 Jinan, P. R. China.
E-mail: fangqi@icm.sdu.edu.cn

Received (in Cambridge, UK) 24th July 2002, Accepted 23rd October 2002
First published as an Advance Article on the web 5th November 2002

A series of new donor–π-acceptor type compounds with trivalent boron as acceptor which show strong two-photon excited up-conversion fluorescence have been synthesized and one crystal structure described.

In a common molecular fluorescence process, excitation is caused by the absorption of a single photon which has higher energy compared to the molecular energy level. However, when certain lasers are used as the pump source, some molecules can simultaneously absorb two photons which have lower energy individually, and then the emission of frequency up-converted fluorescence may occur. This is known as two-photon excited fluorescence (TPEF).[1] Because of several advantages of two-photon absorption (TPA) and TPEF,[2] including intrinsic high three-dimensional resolution and the penetrating ability of the excitation light, this field has attracted great research interest and acquired several applications such as in two-photon laser scanning fluorescence microscopy.[1] Basically, two kinds of stratagies in designing TPA based fluorophores have been approached, namely symmetrical intramolecular charge transfer D–π-D or A–π-A systems and asymmetrical D–π-A systems, inducing series of compounds with large TPA as well as TPEF cross sections.[2–5]

While amine-based π electron donors have been widely adopted in opto-electronic materials, relatively few reports about organoboron compounds in this field can be found. Among the interesting photophysical properties exhibited in reported three-coordinate organoboron compounds are single-photon excited fluorescence (SPEF), second- and third-order nonlinear properties, and so on.[6–9] To our knowledge, up to now, there has been no report about TPEF properties of trivalent organoboron compounds.

Trivalent boron is a well known electron-deficient Lewis acid. Owing to its vacant p-orbital which is similar to the case of a carbonium ion, it should be able to receive part of the negative charge from an electron donor *via* certain delocalized π-bridges, and the trivalent boron containing group should be a good π-electron acceptor. Unfortunately, most organoboron compounds are not stable. Thus some bulky groups must be attached to protect the boron from attack from oxygen.[7–9] The Hammet substituent constant σ_H is a useful parameter to measure the electron-withdrawing ability of an acceptor group. Glogoweki and Williams have measured $\sigma_{UV,\,H} = 0.65$ for the dimesitylboryl group based on a spectroscopy correlation method,[10] and the electron-withdrawing ability of the $-B(Mes)_2$ group may be between that of –CN and $-NO_2$.

Besides the adoption of trivalent boron as an acceptor, we introduced the thiophene group as a π-electron reservoir because this aromatic system may be more rich in electronic density compared to a benzene ring. In this communication, we mainly describe the synthesis, structure, SPEF and TPEF properties of four compounds **1**–**4** (shown in Fig. 1), all of which exhibit large quantum yield *Φ* and TPEF cross section.

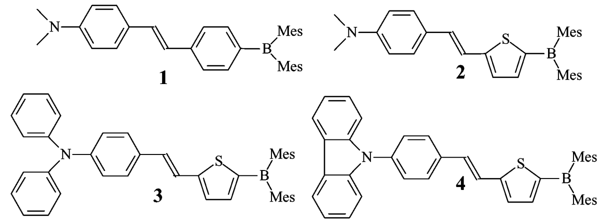

Fig. 1 Molecular structures of compounds **1**–**4** (Mes = 2,4,6-trimethylphenyl).

Compounds **2**–**4** were synthesized using different 4′-aminostyrylthiophenes as precursors,† and **1** was prepared referring the literature.[6] All are stable in air and in common organic solvents due to the steric protection. Single crystals of **1**, **2** and **4** were obtained and the structure of **2** was satisfatorily determined (with $R_1 = 0.0582$) by single crystal X-ray diffraction.‡ As shown in Fig. 2, the central boron and its three bonded carbons (C14, C15, C24) are perfectly co-planar forming a trigonal plane. Two mesityl groups, which have effectively protected the trivalent boron, are arranged in a propeller-like fashion with dihedral angles between the boron plane and the two mesityl planes of 57.20 and 59.30°. The dihedral angle between the thiophene ring and the benzene ring is only 10.86°, and the linkage between these two rings is quite conjugated with bond lengths of C6–C9 [1.454(4) Å], C9=C10 [1.335(4) Å] and C10–C11 [1.443(4) Å]. These structural features suggest that all non-hydrogen atoms between nitrogen and boron are highly conjugated, leading to a π-bridge for the charge transfer from nitrogen to boron. The bond lengths of B1–C15 and B1–C24 are 1.571(5) and 1.585(4) Å, but that of B1–C14 is reduced to 1.544(5) Å, this strengthened bonding also indicates that the p orbital of boron been partially occupied by transferred charge.

The photophysical properties of these compounds are summarized in Table 1. For each compound, with the increase of the polarity of the solvent, the absorption peaks show no obvious change, but the emission peaks clearly show a red-shift, and the fluorescent lifetimes are lenghthened. This means that the excited state of these compounds may possess higher polarity than that of the ground state, for the solvatochromism is associated with the energy level lowering. Increased dipole–

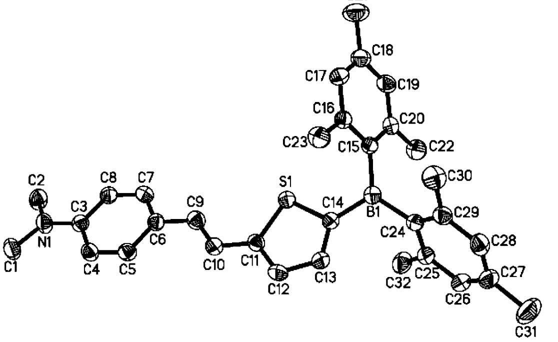

Fig. 2 ORTEP drawing of compound **2**.

---

† Electronic supplementary information (ESI) available: experimental: 1, synthesis and characterization; 2, the set up for measurement of photophysical properties. See http://www.rsc.org/suppdata/cc/b2/b207210f/

DOI: 10.1039/b207210f

Table 1 The linear and nonlinear properties of compound **1–4**

	UV–vis linear absorption[ad]			Single photon excited fluorescence (SPEF)[a]			Two-photon excited fluorescence (TPEF)[e]	
	Solvent	λ_{max}/nm	$\varepsilon/10^4$	λ_{max}/nm[b]	Φ[c]	τ/ns	λ_{max}/nm	$\sigma_2\Phi'$[f]
1	Toluene	403	2.08	492	0.32	1.13		
	THF	403	2.59	538	0.55	1.95	540	1.8
	CH_3CN	402	3.62	580	0.72	2.58		
2	Toluene	431	4.05	522	0.30	1.03		
	THF	431	3.98	558	0.35	1.60	559	0.9
	CH_3CN	434	3.77	602	0.47	2.04		
3	Toluene	432	4.99	502	0.91	1.73	519	3.5
	THF	428	4.97	536	0.82	2.18	540	2.6
	CH_3CN	427	4.61	580	0.65	2.82		
4	Toluene	399	4.67	454	0.93	1.61	476	4.3
	THF	397	5.12	484	0.84	1.95	484	2.5
	CH_3CN	393	5.33	512	0.74	2.67		

[a] Only the longest absorption maxima are tabulated. [b] Emission maximum wavelength excited at the absorption maximum. [c] Determined using fluorescein as the standard. [d] All the single-photon properties were measured at 1×10^{-5} M. [e] TPEF properties were measured at 5×10^{-3} M. [f] The relative value of TPEF cross section by assigning that of fluorescein as equal to 1.

dipole interaction between the solute and solvent leads to greater energy level lowering. Comparing **1** with **2**, the replacement of the phenyl by the thiophene group resulted in a red-shift of the absorption peaks and the emission peaks by about 20 nm. This may provide evidence for the higher electronic density of **2**. However, comparing **2** and **4**, by changing the alkylamino with arylamino, there is a large blue-shift in both absorption and emission spectra. The lone pair electrons on the nitrogen of **4** may have delocalized onto the teminal phenyls, which may have an effect of reducing charge transfer and the molecular polarity, especially for the excited state.

As shown in Table 1, the peak positions of TPEF spectra§ of **1–4** have no obvious shift compared to that of the corresponding SPEF in THF solution. However, in toluene, TPEF peak positions show a red shift of about 20 nm compared to that of SPEF, for instance, the SPEF maximum of **3** is 502 nm, but the TPEF maximum is 519 nm. This can be explained by the effect of reabsorption for, as shown in Fig. 3, the linear absorption band has a slight overlap with the emission band and our TPEF experiments were carried out on concentrated solutions which made reabsorption significant. In THF solution, however, the Stokes' shift, such as that of **3**, is large enough to make reabsorption negligible. As shown in Fig. 3(d), the scatter-point graph is the two photon fluorescence excitation spectrum, in which the peak wavelength is slightly less than the twice of that of the corresponding linear absorption peak. In addition to other similarities between SPEF and TPEF, the TPEF peak positons are also independent of the laser wavelength used. Thus although the electrons can be pumped to the different excited states by linear absorption or TPA due to the different selection rules, they would finally relax to the same lowest excited state *via* internal conversion and/or vibrational relaxation.

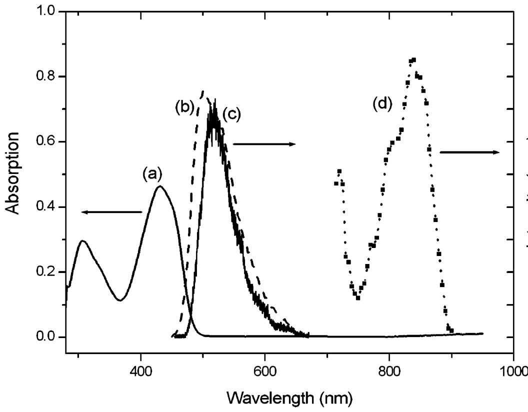

Fig. 3 Absorption and fluorescence spectra of **3** (a) linear absorption with $C = 1 \times 10^{-5}$ M in toluene, (b) SPEF with $C = 1 \times 10^{-5}$ M in toluene, (c) TPEF with $C = 5 \times 10^{-3}$ M in toluene and (d) two-photon excitation spectrum with $C = 5 \times 10^{-3}$ M in THF.

The TPEF cross section can be supposed to be proportional to the product of $\sigma_2\Phi'$, where σ_2 and Φ'stand for the TPA cross section and TPEF quantum yield respectively.[11] By comparison of the TPEF intensities of our compounds with that of fluorescein (as a standard compound) under exactly the same experimental conditions, we have obtained the relative TPEF cross sections which are listed in the last column of Table 1. Compound **4** in toluene solution shows the largest $\sigma_2\Phi'$ when it was pumped at 800 nm. The photophysical properties of all the precursors of **1–4** without boron have also been examined, their SPEF and TPEF are very weak compared to the boron-containing target compounds.

We acknowledge the grant of State Key Program of China and the National Natural Science Foundation of China (No. 20172034) for financial support.

Notes and references

‡ *Crystal data* for **2**: $C_{32}H_{36}BNS$, $M = 477.49$, triclinic, space group $P\bar{1}$, $a = 8.0588(12)$, $b = 10.4341(14)$, $c = 17.705(3)$ Å, $\alpha = 74.182(12)$, $\beta = 86.993(9)$, $\gamma = 79.471(11)°$, $V = 1408.2(4)$ Å^3, $Z = 2$, $T = 293(2)$ K, $D_c = 1.126$ g cm^{-3}, $R_1 = 0.0582$, $wR_2 = 0.1602$ for $I > 2\sigma(I)$. CCDC 190316. See http://www.rsc.org/suppdata/cc/b2/b207210f/ for crystallographic data in CIF or other electronic format.

§ *Measurement of TPEF properties*: a Coherent Mira 900 Ti:sapphire laser was used as the excitation source and a streak camera (Hamamastsu model C5680) was used as the detector.

1 W. Denk, J. H. Strickler and W. W. Webb, *Science*, 1990, **248**, 73.
2 M. Albota, D. Beljonne, J.-L. Bredas, J. E. Ehrlich, J.-Y. Fu, A. C. Maughon, J. W. Perry, H. Rockel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu and C. Xu, *Science*, 1998, **281**, 1653.
3 L. Ventelon, L. Moreaux, J. Mertz and M. Blanchard-Desce, *Chem. Commun.*, 1999, 2055.
4 B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He and P. N. Prasad, *Chem. Mater.*, 1998, **10**, 1863.
5 O.-K. Kim, K.-s. Lee, H. Y. Woo, K.-S. Kim, G. S. He, J. Swiatkiewicz and P. N. Prasad, *Chem. Mater.*, 2000, **12**, 2838.
6 M. Lequan, R. M. Lequan, K. Chane-Ching and A. C. Callier, *Adv. Mater. Opt. Electron.*, 1992, **1**, 243.
7 S. Yamaguchi, T. Shirasaka and K. Tamao, *Org. Lett.*, 2000, **2**, 4129.
8 Z. Yuan, J. C. Collings, N. J. Taylor, T. B. Marder, C. Jardin and J. F. Hale, *J. Solid State Chem.*, 2000, **154**, 5.
9 C. D. Entwistle and T. B. Marder, *Angew. Chem., Int. Ed.*, 2002, **41**, 2927–2931.
10 M. E. Glogowski and J. L. R. Williams, *J. Organomet. Chem.*, 1981, **218**, 137–146.
11 C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481.