Bulky 4-tritylphenylethynyl substituted boradiazaindacene: pure red emission, relatively large Stokes shift and inhibition of self-quenching†

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Received (in Cambridge, UK) 22nd May 2008, Accepted 30th June 2008
First published as an Advance Article on the web 6th August 2008
DOI: 10.1039/b808681h

Bulky 4-tritylphenylethynyl substituted boradiazaindacene with pure red emission, relatively large Stokes shift, high fluorescence quantum yield, and low self-quenching was efficiently synthesized and qualified as a potential EL dopant.

Fluorescent dyes based on boradiazaindacene (BODIPY or BDP),[1] show excellent optical properties and photostability, and play increasingly important roles in many fields such as molecular probes,[2] laser dyes,[3] and solar energy harvesters.[4] In addtion, because of their typically narrow emission spectra which may result in attractively high color purity, they are expected to demonstrate further application as potential emitters for organic light-emitting diodes (OLEDs).

However, there are few reports on the applications of BODIPY dyes as EL dopants.[5] It is a pity that most BODIPY dyes have rather weak fluorescence in the solid state due to their small Stokes shifts (5–20 nm, in most cases) which will lead to serious self-quenching at high concentration. Moreover, due to their high planarity in molecular structures, they have an inherent tendency to aggregate compactly in solid state, which further aggravates self-quenching. In the reported devices, the doping amounts of the BODIPY dye in the host materials were controlled to be very low ($<1\%$) in order to avoid self-quenching. It should be noted that lower doping concentrations may lead to not only the lower EL intensities, but also poor color purity because of the incompletely-quenched shorter wavelength emission from the host materials.

On the other hand, in OLED applications, red-emissive materials with good color purity, high efficiency and good stability have been in great demand while efficient blue- and green-emissive materials have been developed to meet the commercial applications. Red-emissive materials remain as the stumbling block in realizing full color OLED. We expect that BODIPY dyes can solve such a problem. First, we need to develop novel BODIPY derivatives with pure red emission, as most known BODIPY dyes are green emitters. Some red-emissive BODIPY dyes previously reported are "excessively red" (considerable emission spectra in the near infrared region), and might not be suitable candidates for display applications. Secondly, self-quenching should be avoided by both increasing the Stokes shift and inhibiting molecular aggregation. It is a challenge to develop fluorophores with relatively large Stokes shifts in combination with high fluorescence quantum yields and narrow emission spectra.[6] Although it is a good method to introduce bulky and rigid side chains to strengthen steric hindrance for inhibition of molecular aggregation, this strategy is rarely attempted on the BODIPY platform.[7]

With these considerations, we introduced two 4-tritylphenylethyl groups into the 2,6-positions of the BODIPY core (compound **3**). It is reasonable to expect that the extended conjugation will lead to a red shift of the emission maxima, and the bulkiness of the substituents will efficiently inhibit concentration quenching due to the reduction of π–π stacking. Additionally, with substituents on all the positions of BODIPY, our compounds were expected to have larger Stokes shifts than the reported 3,5-bisphenylethyl substituted BODIPY[8] which has no substituents on positions 1,2,6,7. According to previous experiences on BODIPY derivatives, steric hindrance effect and nonplanarity induced by higher substitution degree will lead to an increase in Stokes shift, due to the change in geometrical structure upon excitation.[5b]

The target compound **3** and the reference compound **4** were efficiently synthesized as shown in Scheme 1. Iodination of the precursor BODIPY **1** with excess *N*-iodosuccinimide (NIS) gives the 2,6-bisiodo-BODIPY **2** in high yield (70%) while 4-tritylphenylethyne was synthesized *via* a four-step route[9] from chlorotriphenylmethane. Sonogashira coupling reaction of the above two intermediates produced compound **3** with satisfactory yield (71%). Noticeably, this facile synthetic work, together with the previous reports,[8,10] confirmed that Pd-catalyzed Sonogashira coupling reactions were very efficient and versatile methods for developing new longer wavelength BODIPY derivatives.

The absorption and emission spectra of compounds **3** and **4** in dichloromethane were recorded in Fig. 1, and the data were listed in Table 1. Compared with the parent BODIPY **1** (λ_{abs} = 498 nm, λ_{flu} = 508 nm),[1a] compounds **3** and **4** exhibit significant red-shift in absorption and emission maxima, which indicates that the phenylethynyl groups extend conjugation efficiently. For compound **3**, the emission band peak at 610 nm has entered the red light region while compound **4** emits

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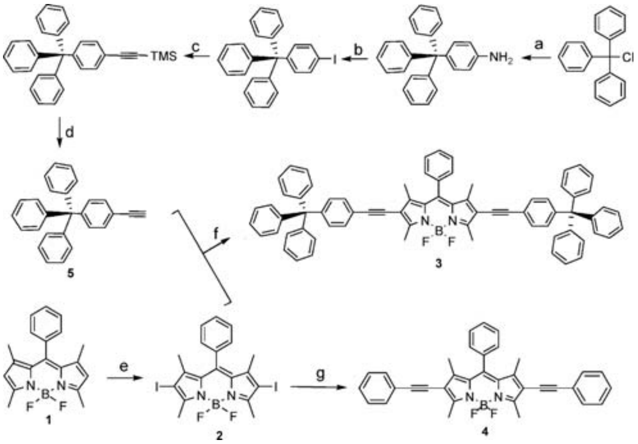
† Electronic supplementary information (ESI) available: Experimental section. CCDC 650117. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808681h



Scheme 1 Routes to 4-tritylphenylethyne and BODIPY derivatives **3** and **4**. *Reagents and conditions*: (a) aniline, 220 °C and reflux with 2 M HCl/MeOH, 95%; (b) $NaNO_2$, HCl, 0 °C and KI, acetone 60 °C, 70%; (c) ethynyltrimethylsilane, $Pd(PPh_3)_2Cl_2$, CuI, DMF–NEt_3 = 9 : 1, 85%; (d) 1 M NaOH, THF, 20 °C, 93%; (e) NIS, CH_2Cl_2, 70%; (f) CuI, Pd $(PPh_3)_4$, DMF–NEt_3 = 9 : 1, 65 °C, 71%, Sonogashira coupling with compound **5**; (g) Sonogashira coupling with ethynylbenzene, 76%.

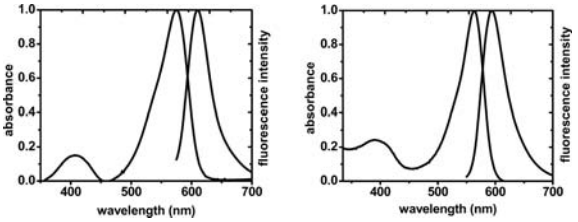


Fig. 1 Normalized UV-Vis absorption and photoluminescence spectra of compounds **3** (left) and **4** (right) in CH_2Cl_2.

orange–red light with an emission maximum at 594 nm. Both compounds inherit the characteristics of high molar extinction coefficients (ε) and high fluorescence quantum yields (Φ_F) from the BODIPY family. However, they exhibit larger Stokes shifts (35, 33 nm for compound **3** and **4**, respectively) than most BODIPY derivatives. Due to their relatively large Stokes shifts in combination with the narrow emission bands, there are smaller overlap areas between the absorption and emission spectra (Fig. 1), which is a distinct aspect compared with the very large spectra overlap areas observed in many other BODIPY dyes. This is beneficial to inhibit self-quenching.

The electronic states were investigated through cyclic voltammetry and theoretical calculation (B3LYP, 3-21G),[11] and the results were summarized in Table 2 (details in ESI†). Both studies show consistent results: the energy level of the LUMO for compound **3** is very close to that of compound **4**, while the energy level of the HOMO is a little higher than that of the latter. These data indicate that the trityl groups play a role to elevate the HOMO energy level without influencing the LUMO, and thus reduce the energy gap and lead to spectra red-shifts of compound **3** relative to compound **4**. Another important information from the above studies is that both compounds may be suitable for electroluminescence applications, because their LUMO levels match well with those of normal electron transfer layer materials (*e.g.* Alq_3, −3.0 eV) and HOMO levels match well with those of common hole transfer layer materials (*e.g.* NPB, −5.2 eV).[12]

Table 1 Optical properties of compounds **3** and **4**

Compound	λ_{abs}/nm	λ_{flu}/nm	ΔS[a]/nm (cm^{-1})	Φ_F[b]	ε/M^{-1} cm^{-1}
3	575	610	35 (998)	0.79	76 600
4	561	594	33 (990)	0.82	73 000

[a] Stokes shift calculated from the absorption and emission energies. [b] The reference system used was rhodamine 6G in ethanol (Φ_F = 0.95).

Table 2 Electronic states studies of compounds **3** and **4**

E_g[a]/eV	E_{onset}^{ox}[b]	E_p^{ox}	E_p^{red}[c]	HOMO/ LUMO[d]/eV	HOMO/ LUMO[e]/eV
2.01	0.73	1.07	−1.28	−5.13/−3.12	−5.23/−2.69
2.11	0.81	1.00	−1.30	−5.21/−3.10	−5.34/−2.67

[a] Energy band gap, determined from UV-Vis absorption spectra. [b] E_{onset}^{ox} = onset oxidation potential; E_p^{ox} = oxidation peak potential; potentials reported *vs.* ferrocene as internal standard, glassy carbon working electrode, Ag/$AgNO_3$ reference electrode, platinum counter electrode, 0.1 M Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV s^{-1} at 20 °C. [c] E_p^{red} = reduction peak potential. [d] HOMO = E_{onset}^{ox} + 4.4 eV; LUMO = HOMO − E_g. [e] Energy levels estimated from theoretical calculation.

X-Ray single crystal analysis revealed the nonplanar structure of compound **4**. The dihedral angle between the pyrrole plane and the phenyl moiety of phenylethynyl is 13.7° (shown in Fig. 2, center). It may be that fast changes in geometrical structures of the nonplanar fluorophore molecules upon excitation result in a large Stokes shift. One previous example is 3,5-dinaphthyl-BODIPY (λ_{abs} = 542 nm, λ_{flu} = 607 nm), in which the twist angle between the naphthyl moiety and the BODIPY core is up to 50°.[13] For this compound, a large Stokes shift (65 nm) is observed though its fluorescence quantum yield is relatively low (0.38 in $CHCl_3$). Obviously, larger Stokes shifts are accompanied with more non-emissive decay of excitation energy. For our BODIPY derivative **4**, the dihedral angle is apparent but not very large, so that it has an relatively large Stokes shift while maintaining a high fluorescence quantum yield. This explanation is also suitable for compound **3**, since it has the similar conjugation to compound **4**, although single crystals were not obtained, due to its amorphous nature induced by the tetraphenylmethane units.[14]

Although compounds **3** and **4** have similar Stokes shifts and fluorescence quantum yields in solution, their solid-state spectral

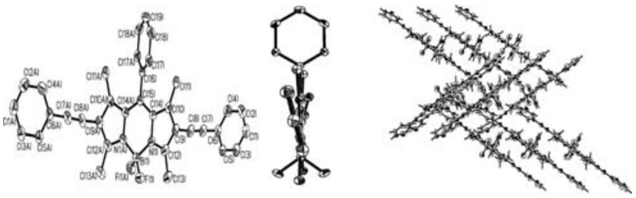


Fig. 2 Crystal structure of **4** with ellipsoids shown at the 30% probability level and all hydrogen atoms removed for the sake of clarity. Left: View perpendicular to the BODIPY main axis. Center: View from phenylethynyl to BODIPY core. Right: Crystal packing diagram.

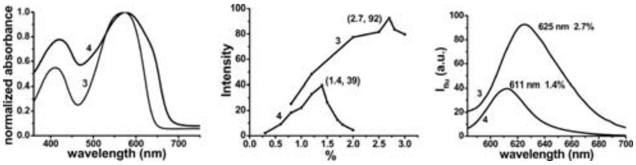


Fig. 3 UV-Vis absorption spectra of compounds **3** and **4** in the solid-state (left), intensity–doped concentration curves (centre) and emission intensity of compounds **3** and **4** on films under their maximum doped concentrations as dopants for SBS (right).

properties are quite different. As shown in Fig. 3, the solid absorption spectrum of compound **4** become very broad and considerably red-shifted compared with that in dichloromethane. Absorption of compound **3** however broadens only slightly, with a negligible shift. Further, the fluorescence concentration-quenching effect for compound **4** is very serious. The fluorescence intensity for compound **4** doped in SBS (styrene-butadiene block copolymer, M.W. = 200 000 g mol^{-1}, an inert polymer matrix) film reaches a maximum at a doping concentration of only 1.4% above which the fluorescence intensity decreases, a similar result to the reported doping concentration limit (1%) of another green emissive BODIPY dopant.[5a] However, for compound **3**, the doping concentration limit is increased to 2.7%. The maximum fluorescence intensity of compound **3** is about 2.4-fold higher than that of compound **4** (Fig. 3, right), which indicates that compound **3** is superior to compound **4** as a solid-state emitter. Molecules of compound **4** aggregate *via* forming compact π–π stacking, as is proved by the X-ray single crystal analysis (Fig. 2, right, the shortest distance between indacene and a benzene ring in another molecule is 3.389 Å), which explains its broadened absorption spectra and strong self-quenching effect. The tendency to form π–π stacking for molecules of compound **3** is counteracted by the steric hindrance from bulky trityl groups, so that the intermolecular interactions are weakened and self-quenching is inhibited to some extent.

As a preliminary work for OLED investigations, electroluminescence spectra (Fig. 4) of compounds **3** and **4** were measured in devices with a simple configuration without any optimization (details in ESI†). The configuration was ITO/PEDOT (30 nm)|BDP-PPV: 2% 3–4 (60 nm)|$\mathrm{Alq_3}$ (10 nm)|Al (100 nm), where ITO was the anode, PEDOT was used as a hole-injection layer, compounds **3** and **4** were doped into BDP-PPV as an emitting layer, $\mathrm{Alq_3}$ was used as an electron-transporting as well as a hole-blocking layer, and Al was used as the cathode. The devices show EL peaks at 620 nm with Commission Internationale de l'Eclairage (CIE) coordinates (0.65, 0.34) for **3** and 608 nm (0.65, 0.35) for **4**. The coordinates are accordant or comparable with (0.64, 0.34) and (0.64, 0.33) of the standard red CRT phosphors of the Society of Motion Picture and Television Engineers (SMPTE-C) and European Broadcasting Union (EBU), respectively.[15] Taking into account the pure red EL spectrum of compound **3**, as well as its other favorable characteristics introduced in this paper, we believe it is worthwhile to further optimize the device fabrication for higher performance.

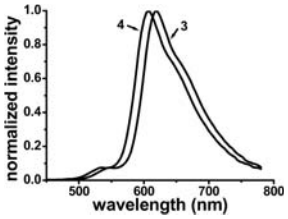


Fig. 4 EL spectra for compounds **3** and **4**.

In conclusion, Sonogashira coupling reactions on the 2,6-positions of the BODIPY core were utilized as an efficient method to develop novel derivatives with red-shifted spectra. With the bulky substituents, 2,6-di-(4-tritylphenylethynyl) BODIPY exhibited relative large Stokes shift, inhibition of self-quenching effect and a pure red EL spectrum, which qualified it as a potential candidate for red EL dopant.

This work was supported by National Natural Science Foundation of China (No. 20406004, 20572012, 20536010) and Program for Changjiang Scholars and Innovative Research Team in University (IRT0711).

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