Dyes and Pigments 107 (2014) 60–68

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Triarylborane-terminalized branched π-conjugative dyes: Synthesis, structure and optoelectronic properties

Mao-Sen Yuan [a,b,1], Dong-En Wang [a,1], Tian-Bao Li [a], Yongqian Xu [a], Wen-Ji Wang [a], Qin Tu [a], Yanrong Zhang [a], Manlin Li [a], Jinyi Wang [a,*]

[a] College of Science, Northwest A&F University, Yangling 712100, PR China
[b] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China

ARTICLE INFO

Article history:
Received 19 January 2014
Received in revised form
9 March 2014
Accepted 10 March 2014
Available online 18 March 2014

Keywords:
Triarylborane
Charge-transfer
Crystal structure
Optoelectronic properties
Solid-state fluorescence
Truxene

ABSTRACT

Organic optoelectronic materials with high fluorescence quantum yield, both in solution and in the solid state, have attracted considerable interest in recent years. In this work, we designed and synthesized three triarylborane-terminalized branched π-conjugative compounds, including two C_3-symmetric π-3A(acceptor) triarylboron dyes: 2,7,12-tri(5-(dimesitylboryl)thiophen-2-yl)-5,5′,10,10′,15,15′-hexaethyltruxene and 2,7,12-tri((5-(dimesitylboryl)thiophen-2-yl)ethynyl)-5,5′,10,10′,15,15′-hexaethyltruxene, and a 2D(donor)-π-A asymmetric dye: 2,7-di(*N*,*N*-diphenylamino)-12-(5-(dimesitylboryl)thiophen-2-yl)-5,5′,10,10′,15,15′-hexaethyltruxene. The three compounds displayed prominent optical properties. The ethynyl spaced thiophene analogue emitted intense fluorescence both in the THF solution and in the solid state with excellent quantum yields. Interestingly, their solid powders showed a very different fluorescence colour from their respective THF solution. The results of theoretical calculations were in good agreement with the experimental absorption and CV spectra. The high reversibility of the three boron-containing dyes in their redox process indicates substantial stability of the produced species, which make them promising light-emitting materials.

1. Introduction

Three-coordinate organoboron, with a vacant p_z orbital, is an excellent π-electronic acceptor when connected to a π-conjugated system. In recent years, three-coordinate organoboron compounds have attracted a great deal of attention because of their excellent photophysical and electronic properties [1]. Meanwhile, the availability of the empty p_z orbital makes three-coordinate organoboron compounds highly susceptible to the addition by Lewis bases, resulting in their relatively poor stability. An effective method of improving the stability is to utilize the aromatic substituents, which arise from bulky aryl groups to provide protection for the central boron atom by blocking the approach of nucleophiles [1a,2]. In the last decade, stable triarylboron compounds (triarylboranes) have been exploited extensively in a wide range of applications as optoelectronic materials, such as nonlinear optical materials [3], transporting and emissive materials in organic light-emitting devices (OLEDs) [4], two-photon absorption and emission materials [5] as well as selective chemosensors for fluoride and cyanide anions [6] and heat-sensitive materials [7]. For practical application, having enough high solid-state fluorescence efficiency is a fundamental issue for luminescent materials. However, most triarylboranes are highly emissive only in dilute solution and tend to show a decrease of fluorescence efficiency in the solid state due to the aggregation-caused quenching (ACQ) effect. The successful examples of stable and highly emissive triarylboranes in both solution and the solid state with a fluorescence quantum yield close to unity are still quite limited [8].

An effective strategy of molecular design to achieve an intense emissive organic compound in both solution and the solid-state is the construction of a multibranched π-conjugated framework with large building blocks [9]. The branched steric bulkiness will inherently reduce the intermolecular dipole–dipole interaction and π···π stacking, which will generally result in drastic fluorescence self-quenching in the aggregation state. In addition, in comparison to the linear molecules and polymers, branched π-conjugated molecules have a number of advantages for applications in optoelectronic devices, for example, the two- or three-

---

* Corresponding author. Tel./fax: +86 29 87082520.
E-mail addresses: jywang@nwsuaf.edu.cn, jinyiwangpharm@gmail.com (J. Wang).

[1] These two authors contributed equally to this work.

http://dx.doi.org/10.1016/j.dyepig.2014.03.014
0143-7208/© 2014 Elsevier Ltd. All rights reserved.

dimensional architectures, the well-defined molecular structure and good film-forming processing [10]. In this context, it is of particular interest to develop triarylborane-containing branched π-conjugated organic emissive materials exhibiting high fluorescence efficiency in both solution and the solid state.

As far as this issue is concerned, truxene (10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene), a heptacyclic polyarene, was chosen to construct the branched framework. Due to its C_3-symmetric skeleton and three-dimensional topology, the truxene unit has been intensively developed as a π-conjugated central core to fabricate star-shaped optoelectronic molecules, such as OLEDs [11], organic field-effect transistors (OFETs) [12], liquid crystals [13] and two-photon absorption materials [14]. Considering the good thermal and chemical stability, 2-thienyl and 2-thienyl-ethynyl were respectively used as the π-bridge to connect the 2, 7, 12-positions of truxene [15]. As for the termini of the branches, to continue our effort in the development of highly emissive materials utilizing the boron element, dimesitylboron (mesityl = 2,4,6-trimethylphenyl) group is a favourable choice for our proposed design principle: this bulky unit can suppress the π···π stacking and the strong electron-withdrawing ability can facilitate intramolecular/intermolecular charge transfer. Herein, we report three boron-containing branched π-conjugative compounds, including two C_3-symmetric π-3A(acceptor) triarylboron dyes: 2,7,12-tri(5-(dimesitylboryl)thiophen-2-yl)-5,5′,10,10′,15,15′-hexaethyltruxene (**S3B3**) and 2,7,12-tri((5-(dimesitylboryl)thiophen-2-yl)ethynyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**C3B3**), and a 2D(donor)-π-A asymmetric dye: 2,7-di(*N*,*N*-diphenylamino)-12-(5-(dimesitylboryl)thiophen-2-yl)-5,5′,10,10′,15,15′-hexaethyltruxene (**N2SB**). Their photophysical properties in both solution and the solid state, theoretical calculations, electrochemical properties, as well as the X-ray single-crystal structures of their precursors, have been comprehensively studied.

2. Experimental section

2.1. Synthesis and characterizations of the subject compounds

Solvents for reactions and spectral measurements were dried and distilled before use. The reagents used for reactions were purchased from J&K Scientific Ltd. ^{1}H NMR spectra were recorded at 25 °C on Bruker Avance 500 MHz spectrometer using $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded at 25 °C on Bruker Avance 125 MHz spectrometer using $CDCl_3$ as solvent. Element analyses (C, H, S) were performed using a PE 2400 autoanalyser. Mass spectrometry analyses were performed by a Bruker Biflex III matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometer.

Compounds **1**–**5** were synthesized according to literature methods [6h] and compounds **S3** and **C3** were synthesized following the literature [6i,14c].

2.1.1. Synthesis of compound N2S

A mixture of compound **5** (0.50 g, 0.54 mmol), 2-thiopheneboronic acid (0.10 g, 0.78 mmol), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), toluene (30 mL), ethanol (8 mL) and 2 M aqueous K_2CO_3 solution (2 mL) was heated and stirred at 80 °C under a nitrogen atmosphere for 24 h. The mixture were cooled to room temperature and poured into water (100 mL). After extraction with dichloromethane (DCM), the organic phase was dried over Na_2SO_4. The solvent was removed and the residue was purified by column chromatography on silica gel using DCM-hexane (1: 20) as the eluent to get compound **N2S** (0.16 g, 31.9%). **N2S**: a yellow powder, m.p. 156–158 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.21–0.28 (m, 18H), 1.89–2.15 (m, 6H), 2.84–2.99 (m, 6H), 7.02–7.12 (m, 6H), 7.32–7.33 (m, 3H), 7.46–7.49 (m, 2H), 7.55–7.58 (m, 16H), 7.57–7.67 (m, 2H), 8.09–8.27 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ154.22, 153.67, 152.67, 147.96, 129.24, 129.05, 128.24, 128.09, 126.35, 126.04, 125.31, 124.92, 124.59, 124.21, 122.95, 122.88, 122.69, 122.27, 121.98, 119.47, 117.66, 67.98, 56.65, 29.40, 29.19, 25.63, 21.46, 8.69, 8.65, 8.61. MALDI-TOF: *m*/*z* 927.3 [M$^+$], 898.9 [M-29]$^+$. Elemental Anal. Calcd. for $C_{67}H_{62}N_2S$: C, 86.78; H, 6.74; S, 3.46. Found: C, 86.71; H, 6.84; S, 3.35.

2.1.2. Synthesis of compound S3B3

n-BuLi (2.4 M solution in *n*-hexane, 0.20 mL, 0.48 mmol) was added to a stirred solution of compound **S3** (100 mg, 0.13 mmol) in THF (10 mL) under nitrogen at −78 °C over 5 min, and followed by warming to room temperature naturally. After reacting for further 4 h, the reactants were cooled to −78 °C again, and dimesitylboron fluoride (0.20 g, 0.74 mmol) in THF (5 mL) was injected over 5 min. The temperature was allowed to naturally rise to room temperature and the mixture continuously stirred for two days. Then the reactants were diluted with ethyl acetate, washed with water and dried over magnesium sulfate. After removal of the solvents, the crude product was obtained. After purification by column chromatography on silica gel, eluting with dichloromethane-petroleum ether (1:5), compound **S3B3** was obtained (58 mg, 29%). **S3B3**: a yellowish-green powder, m.p. 201–203 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.19–0.22 (t, *J* = 7.5 Hz, 18H), 1.52–2.06 (m, 42H), 2.32 (s, 18H), 2.94–2.98 (m, 18H), 6.85 (s, 12H), 7.38–7.41 (m, 6H), 7.51–7.53 (d, *J* = 10 Hz, 3H), 7.58 (s, 3H), 8.29–8.31 (d, *J* = 10 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 157.4, 153.6, 144.8, 144.3, 141.9, 140.9, 140.0, 138.5, 132.8, 132.4, 128.2, 125.4, 124.7, 124.3, 123.0, 119.5, 56.9, 29.7, 23.5, 21.3, 8.6. MALDI-TOF: *m*/*z* 1501.4 [*M*$^+$], 1472.8 [*M*-29]$^+$. Elemental Anal. Calcd. for $C_{105}H_{111}B_3S_3$: C, 83.98; H, 7.45; S, 6.41. Found: C, 83.91; H, 7.12; S, 6.42.

2.1.3. Synthesis of compound C3B3

A similar synthetic and purification procedure as for **C3B3** was followed for **S3B3** using compound **C3** as the precursor. Then compound **C3B3** (41.5%) was obtained. **C3B3:** a light green powder, m.p. 222–224 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.22–0.25 (t, *J* = 7.5 Hz, 18H), 2.10–2.32 (m, 42H), 2.35 (s, 18H), 2.97–3.02 (m, 6H), 6.88 (s, 12H), 7.41–7.43 (d, *J* = 10 Hz, 6H), 7.54–7.56 (d, *J* = 10 Hz, 3H), 7.61 (s, 3H), 8.32–8.34 (d, *J* = 10 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 152.9, 145.3, 141.1, 140.9, 140.1, 138.8, 138.5, 135.3, 133.6, 129.8, 128.2, 125.3, 124.6, 120.7, 97.6, 83.6, 57.0, 29.5, 23.5, 21.3, 8.5. MALDI-TOF: *m*/*z* 1572.7 [M$^+$], 1543.6 [M-29]$^+$. Elemental Anal. Calcd. for $C_{111}H_{111}B_3S_3$: C, 84.72; H, 7.11; S, 6.11. Found: C, 84.91; H, 7.02; S, 6.12.

2.1.4. Synthesis of compound N2SB

A similar synthetic and purification procedure as for **N2SB** was followed for **S3B3** using compound **N2S** as the precursor. Then compound **N2SB** (30.9%) was obtained. **N2SB:** a light green powder, m.p. 188–190 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.23–0.27 (m, 18H), 1.89–2.18 (m, 18H), 2.33 (s, 6H), 2.87–2.97 (m, 6H), 6.86 (s, 6H), 7.00–7.05 (m, 6H), 7.18–7.19 (m, 6H), 7.27–7.30 (m, 6H), 7.46–7.47 (m, 1H), 7.56–7.57 (m, 1H), 7.69–7.71 (d, *J* = 10 Hz, 6H), 8.08–8.10 (d, *J* = 10 Hz, 1H), 8.14–8.16 (d, *J* = 10 Hz, 1H), 8.24–8.26 (d, *J* = 10 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 157.6, 154.2, 153.8, 147.9, 146.5, 143.2, 141.9, 141.4, 140.9, 138.6, 138.5, 135.3, 129.3, 128.2, 125.2, 124.9, 124.3, 122.8, 120.0, 119.7, 117.6, 56.8, 56.7, 29.5, 29.4, 29.2, 23.5, 21.3, 8.7, 8.6. MALDI-TOF: *m*/*z* 1173.9 [M$^+$], 1144.8 [M-29]$^+$. Elemental Anal. Calcd. for $C_{85}H_{83}BN_2S$: C, 86.85; H, 7.12; N, 2.38; S, 2.73. Found: C, 86.67; H, 7.02; N, 2.37; S, 2.65.

2.2. Single crystal X-ray diffraction

The single crystals of compounds **S3** and **N2S** were firstly obtained by the slow diffusion of their respective $CHCl_3$: cyclohexane