Influence of the structure of electron-donating aromatic units in organosilicon luminophores based on 2,1,3-benzothiadiazole electron-withdrawing core on their absorption-luminescent properties

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ABSTRACT

A series of new linear π-conjugated oligomers consisting of five conjugated rings based on 2,1,3-benzothiadiazole (BTD) electron-withdrawing group and various combinations of 2,5-thiophene and 1,4-phenylene electron-donating units with terminal trimethylsilyl groups has been synthesized and characterized. Investigation of their absorption-luminescent properties revealed that all of them possess high photoluminescence (PL) quantum yield and large Stokes shift both in diluted solutions and polymer matrix, while in the solid state their PL efficiency decreases. It was found that the main factor influencing the optical properties of the molecules obtained is the type of aromatic fragment directly attached to the central BTD moiety. Changing the chemical structure of the donor aromatic fragments from 1,1′-biphenyl to 2,2′-bithiophene allows tuning the PL spectral maximum of the luminophores in wide range from 510 to 660 nm. It was shown that the presence of trimethylsilyl groups in these luminophores is responsible for their increased solubility, enhanced molar extinction coefficients and shortening the excited state lifetime without decreasing the PL efficiency.

1. Introduction

Luminophores as functional materials are successfully applied in many fields of science and technology. Great progress has been made in the development of various electronic devices based on organic materials such as displays [1,2], organic light-emitting transistors [3–5], luminescent down-shifting layers for photovoltaic [6]. 2,1,3-Benzothiadiazole (BTD) derivatives play an important role among such materials due to their unique optical and electronic properties. They are normally form efficient luminophores [7–11], characterized by high chemical and thermal stability, also widely used in organic photovoltaic materials as strong electron-withdrawing moiety [12,13]. In addition, compounds based on BTD due to their relatively high reduction potential and electron affinity are widely used as emissive layers in organic light-emitting diodes (OLEDs) [14,15].

Typically, BTD-based luminescent materials are symmetrical molecules composed by a donor − acceptor − donor (D-A-D) framework with an electron-poor benzothiadiazole central core connected to two electron-rich substituents. 4 and 7 positions of BTD unit are usually preferred for direct π-extension and has a very positive effect both on PL spectra and photostability [16,17]. More importantly, the absorption-luminescent properties of such molecules can be tuned by the electronic properties of the extended donor substituents [18–20].

On the one hand, high potential of luminescent BTDs derivatives was already demonstrated and recently reviewed [21]. However, there is very little information available about the interactions between the BTD acceptor and various donor substituents. On the other hand, σ-π interactions of the silylene group with the conjugated chromophores is well known [22,23]. Introduction of silicon atoms into conjugated organic compounds can lead to the following advantages: high thermal stability; high solubility in many organic solvents and therefore good processability from solutions, which is necessary for obtaining various devices of organic electronics by inexpensive printing methods; and the most important – the presence of specific electronic effects [24]. These include an increase in the conjugation due to direct influence of silicon on the conjugated system, which is the reason for an increase in the molar extinction coefficient and a shift of the optical spectra maxima to the long-wavelength region [25,26]. In addition, organosilicon
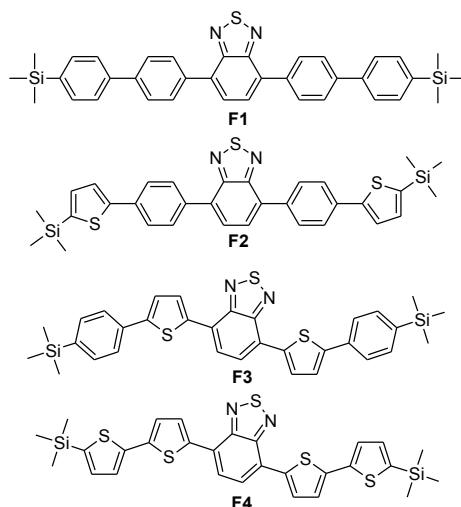
Fig. 1. Chemical structures of novel organosilicon luminophores based on 2,1,3-benzothiadiazole core synthesized and investigated in this work.

luminophores, in contrast to their non-silicon analogues, can exhibit an increased photoluminescence quantum yield (PLQY) [27]. Therefore, organosilicon derivatives of BTD-based luminophores are promising materials both from the fundamental and applied points of view. In this work the synthesis and systematic study of optical and thermal properties of four novel BTD-based luminophores, being linear conjugated oligomers with a conjugation length of five aromatic rings with the central BTD acceptor core containing various combinations of 1,4-phenylene and 2,5-thiophene units with terminal trimethylsilyl (TMS) groups are reported (Fig. 1). Influence of the TMS groups on physical properties of the luminophores was revealed by comparing compound **F1** with its full analogue **F1a** without TMS groups described earlier [18,19,28].

2. Experimental section

2.1. Materials

Hexane solutions of 1.6 M and 2.5 M *n*-butyllithium (CAUTION: solution can ignite in contact with water and carbon dioxide [29], this compound should be handled under nitrogen with special equipment [30]), trimethylchlorosilane (CAUTION: Reacts violently or explosively with water [31,32]), 2-bromothiophene, sodium carbonate, magnesium and 1,4-dibromobenzene were obtained from Acros organics; *tetrakis* (triphenylphosphine)palladium(0) Pd(PPh₃)₄, [1,1′-*bis*(diphenylphosphino)ferrocene] dichloropalladium(II), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB) were obtained from Sigma-Aldrich and used as received. 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)-thiophene (**2**) [33], (4′-bromobiphenyl-4-yl)(trimethyl)silane (**3**) [34], trimethyl[4-(2-thienyl)phenyl]silane (**5**), 2,2′-bithien-5-yl(trimethyl)silane (**6**) [35], trimethyl{4-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]phenyl}silane (**9**) [26] and 4,7-dibromo-2,1,3-benzothiadiazole (**11**) [8] were synthesized as described earlier. THF, diethyl ether, toluene and ethanol were dried and purified according to the standard techniques and then used as the solvents.

2.2. Characterization

The ¹H NMR spectra were recorded on a Bruker WP250 SY spectrometer (250.13 MHz) using the residual signal of CDCl₃ (δ 7.27 ppm) as the internal standard. The ¹³C and ²⁹Si NMR spectra were recorded on a Bruker Advance II 300 spectrometer at working frequencies 75 MHz and 60 MHz, respectively. In the case of ¹H NMR spectroscopy,

the compounds to be analyzed were taken in the form of 0.5% solutions in CDCl₃. In the case of ¹³C or ²⁹Si NMR spectroscopy, the compounds to be analyzed were taken in the form of 1–3% solutions in CDCl₃. The spectra were then processed on the computer using the ACD Labs software.

Elemental analysis of C, H, N elements was carried out using CHN automatic analyzer CE1106 (Italy). Experimental error is 0.30–0.50%. The burning was done in the Sheninger flask using alkaline solution of hydrogen peroxide as an absorbent. Spectrophotometry technique was used for the Si analysis.

Thermogravimetric analysis was carried out in dynamic mode in 30–800 °C interval using Mettler Toledo TG50 system equipped with M3 microbalance allowing measuring the weight of the samples in 1–150 mg range with 1 µg precision. Heating/cooling rate was chosen to be 20 °C/min. Every compound was studied twice: in air and under nitrogen flow of 200 mL/min.

GPC analysis was performed on a Shimadzu instrument with a RID10A^{VP} refractometer and a SPD-M10A^{VP} diode matrix as detectors using 7.8 × 300 mm² Phenomenex columns (USA) filled with the Phenogel sorbent with pore size of 500 Å and THF as the eluent. In the case of column chromatography, silica gel 60 ("Merck") was taken. For thin layer chromatography (TLC), "Sorbfil" (Russia) plates were used. The solvents were removed under vacuum (1 mBar) at 80 °C. All reactions, unless stated otherwise, were carried out in an inert atmosphere using anhydrous solvents.

The absorption spectra were recorded on a Shimadzu UV-2501PC (Japan) spectrophotometer in the standard 10 mm photometric quartz cuvette using THF solutions with the concentrations of 10^{-5} M. A scanning spectrofluorimeter ALS01 M (Russia) with registration in single photon counting mode at successive time intervals and automatic adjustment of the intensity of the measured emission was used for the registration of photoluminescence spectra (PL). Measurements were carried out for several optical densities in the range from 0.06 to 0.12 absorbance units in 10 mm cuvette, measurement geometry − 90°. Measurements of the PL spectra in polystyrene (PS) and polycrystalline thin films were carried out in the integrating sphere. The photoluminescence quantum yield (PLQY) was measured by comparing the integral PL intensity of 10^{-6} M diluted solutions of luminophores in THF with the integral PL intensity of the standard as described elsewhere [36]. As the standards in measuring the PLQY a solution of 1,4-*bis*(5-phenyloxazol-2-yl)benzene (POPOP) in cyclohexane (PLQY = 1) and a solution of rhodamine 6G in ethanol (PLQY = 1) were used. Measurements of the PL lifetime were made by the pulsed method in single photon counting mode on the Fluorolog-3 spectrofluorimeter (HORIBA Scientific).

Density functional theory (DFT) calculations were performed using the ORCA v. 4.0.1 software package using the B3LYP5/6-31G[d] approximation [37–39]. Optimization of the singlet ground state geometries was carried out without any restriction on their symmetry.

2.3. Synthesis

2.3.1. General procedure for the Suzuki coupling

A flask was charged with organoboron precursor, 4,7-dibromo-2,1,3-benzothiadiazole (**11**) and Pd(PPh₃)₄ (1–5 mol %). The mixture was degassed, toluene, an aqueous solution of Na₂CO₃ (2.0 M) and ethanol was added and heated to reflux until the reaction was complete. Completeness of the reaction was controlled by GPC analysis. After completion of the reaction, the mixture was cooled down to room temperature, the bottom aqueous phase was taken out by a syringe and organic phase was concentrated and filtrated over a thin pad of silica gel in toluene, which was evaporated by a Rotorvapour.

[5-(4-Bromophenyl)-2-thienyl] (trimethyl)silane (4). This compound was obtained by the general procedure for the Suzuki coupling using trimethyl[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]silane (**2**) (5.74 g, 20.3 mmol), 1,4-dibrombenzene (14.39 g,