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1. Introduction

Introduction of a heteroatom bridge, such as an organophosphorus,¹ -boron,² or -germanium unit,³ at the 3,3'-position of bithiophene forming fused tricyclic systems has been extensively studied. In these systems, better conjugation than that in the parent bithiophene is expected primarily by fixing the bithiophene π -electron system to be completely planar. In addition, the electronic effects of the bridging heteroatom often provide opportunities to manipulate the bithiophene properties and functionalities. In regard to this, we have introduced silicon-bridged dithienosilole (DTS) system, in which the bonding interaction between the silicon σ^* - and bithiophene π^* -orbital lowers the LUMO energy level, leading to even more enhanced conjugation.⁴ Currently, the DTS system attracts much attention as the donor-components of donoracceptor type π -conjugated photovoltaic polymers.⁵ We have recently studied the photoluminescent (PL) properties of DTS compounds, expecting that the rigid tricyclic system minimises the non-radiative decay based on molecular vibration and that the introduction of sterically bulky substituents on the ring silicon prevents the DTS chromophores from being stacked intermolecularly to suppress the concentration quenching. Furthermore, it has been demonstrated that the introduction of silicon substituents on a chromophore often

Synthesis of dithienosilole-based highly photoluminescent donor-acceptor type compounds

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Highly photoluminescent acceptor–donor–acceptor (A–D–A) and donor–acceptor (D–A) type compounds with a dithienosilole unit as the donor and perfluorotolyl or dimesitylboryl group(s) as the acceptor were prepared by the reaction of lithiated dithienosilole derivatives with perfluorotoluene or fluorodimesitylborane, respectively. The resulting A–D–A and D–A type compounds showed red-shifted UV absorption and PL bands compared to those of simple dithienosiloles having no acceptor units, reported previously, and were highly photoluminescent in the solid state as well as in solution. Solvatochromic behaviour that would arise from the intramolecular donor–acceptor interaction were observed for the D–A type compounds with respect to the UV absorption and PL spectra. In addition, it was found that bis(dimesitylboryl)dithienosilole and (dimesitylboryl)(methylthio)dithienosilole responded to coexisting fluoride anions, leading to clear UV absorption and PL spectral changes in solutions.

enhances the fluorescence properties.⁶ Indeed, we demonstrated that DTSs featuring phosphorus-substituents exhibited high PL quantum efficiencies in the range of $\Phi = 0.22-0.99$ and 0.33-0.79 as solutions and solids, respectively (Chart 1).⁷ Interestingly, **DTS1-P** showed a higher quantum yield as a solid than that in chloroform, while the PL quantum yields in solution were markedly improved by quenching the phosphorus lone pair electrons by oxidation and complex formation (**DTS1-PO**^{7*a*} and **DTS2-PAu**^{7*b*}). It was also found that vapour-deposited films of **DTS3-PO** exhibited electroluminescence properties in organic light emitting diode (OLED) systems, giving a blue-green emission.^{7*a*} However, those phosphorus-substituted DTSs showed high quantum yields

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Chart 1 Phosphorus-substituted dithienosiloles and their PL quantum yields.

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either in solution or as solids, and none of them exhibited efficient PL properties in the both phases.

On the other hand, recent attention has been focused on the development of fluorescence compounds with donoracceptor (D-A) type structures, in which intramolecular charge transfer (ICT) photoexcitation leads to strong UV absorption and PL properties. Applications of the D-A compounds as functional materials such as fluorescent probes, non-linear optics, chromic materials, sensitizing dyes for dye-sensitized solar cells, and two-photon absorption materials have been also explored.⁸⁻¹⁰ In the hope of obtaining materials with high PL properties based on the DTS system, we prepared A-D-A and D-A type DTSs that possessed electron-deficient perfluorotolyl and boryl substituents as the acceptor and relatively electron rich DTS and methylthio-DTS as the donor. As expected, the present DTS compounds were highly photoluminescent in the solid state as well as in solution, and the D-A type compounds showed clear solvatochromic behaviour. In addition, bis(dimesitylboryl)-DTS and (dimesitylboryl)(methylthio)-DTS were found to be ionochromic towards fluoride anion (F⁻), being potentially applicable to F⁻-sensing.

2. Experimental

2.1 General procedure

All reactions were carried out in dry argon. Diethyl ether used as the reaction solvent was distilled from sodium-benzophenone ketyl and stored over activated molecular sieves until use. Starting DTS compounds DTS1-Br,4a DTS2-Br,11 and DTS1-BrS¹² were prepared as reported in the literature. NMR spectra were recorded using Varian 400MR and System 500 spectrometers. BF₃·OEt₂ was used as the external reference for ^{11}B NMR spectroscopy. APCI, APPI, and ESI mass spectra were measured using a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer at the Natural Science Centre for Basic Research and Development (N-BARD), Hiroshima University, while DI-EI mass analysis was performed using a Shimadzu QP5050A spectrometer. UV absorption and PL spectra were measured using Shimadzu UV-3150 and Hitachi F4500 spectrophotometers, respectively. PL quantum yields were determined in an integration sphere attached to a Hamamatsu Photonics C7473 multi-channel analyzer. The usual workup mentioned below includes hydrolysis of the reaction mixture with water, extraction of the organic products with toluene, washing the extract with water, drying the washed extract over anhydrous magnesium sulfate, and evaporation of the solvent, in that order. The synthetic routes to A-D-A and D-A type DTSs are summarized in Scheme 1.

2.2 Preparation of DTS2-F

To a solution of 0.50 g (0.81 mmol) of **DTS2-Br** in 15 mL of diethyl ether was added 1.00 mL (1.57 mmol) of a 1.57 M hexane solution of *n*BuLi at -80 °C. After the mixture was stirred for 1 h at room temperature, 0.35 mL (2.5 mmol) of per-fluorotoluene was added to the mixture at -80 °C and the



Scheme 1 Synthesis of perfluorotolyl- and dimesitylboryl-substituted DTS derivatives.

mixture was stirred at room temperature for 10 h. After the usual workup, the residue was subjected to silica gel column chromatography eluting with hexane and the resulting crude solids were recrystallized from ethanol to give 0.10 g (14% yield) of DTS2-F as yellow fine needles: mp 204.2-206.1 °C; APCI-MS m/z 890 (M⁻); ¹H NMR (δ in CDCl₃) 0.91 (t, 6H, J = 7.2 Hz, CH₂CH₂CH₂CH₂CH₃), 1.34 (m, 4H, CH₂CH₂CH₂CH₃), 1.58 $(m, 4H, CH_2CH_2CH_2CH_3), 2.62$ (t, 4H, J = 8.0 Hz, CH₂CH₂CH₂CH₃), 7.23 (d, 4H, J = 8.0 Hz, m-Ph), 7.57 (d, 4H, J = 8.0 Hz, o-Ph), 7.92 (s, 2H, DTS ring H); ¹³C NMR (δ in CDCl₃) 13.94, 22.37, 33.44, 35.79, 118.33 (m), 119.48, 122.17, 126.54, 128.70, 128.94, 134.57 (t, J = 7.5 Hz), 135.44, 142.99, 143.38 (dm, J = 252 Hz), 144.59 (dm, J = 261 Hz), 146.16, 153.03 (m). Anal. Calcd for C₄₂H₂₈F₁₄S₂Si: C, 56.62; H, 3.17. Found: C, 56.85; H, 3.35. The chemical shifts and coupling patterns of the ¹³C NMR signals of the fluorocarbons are consistent with the literature data for perfluorotolyl-arenes.13

2.3 Preparation of DTS1-B

To a solution of 0.32 g (0.64 mmol) of DTS1-Br in 10 mL of diethyl ether was added 0.80 mL (1.3 mmol) of a 1.65 M hexane solution of nBuLi at -80 °C. After the mixture was stirred for 1 h at room temperature, 0.34 g (1.28 mmol) of fluorodimesitylborane was added to the mixture at -80 °C and the mixture was stirred at room temperature for 10 h. After usual workup, the residue was subjected to silica gel column chromatography eluting with hexane-chloroform = 3:1 to give 0.36 g (66% yield) of DTS1-B as yellow powders: mp 316.0–317.8 °C; ESI-MS m/z 865.4 ([M + Na]⁺); ¹H NMR (δ in CDCl₃) 2.14 (s, 24H, o-Me), 2.30 (s, 12H, p-Me), 6.82 (s, 8H, Mes ring H), 7.32-7.56 (m, 6H, m- and p-Ph), 7.57 (br m, 4H, o-Ph), 7.62 (s, 2H, DTS ring H); 13 C NMR (δ in CDCl₃) 21.24, 23.59, 128.16, 128.21, 130.43, 131.34, 135.40, 138.56, 140.79, 141.22, 143.97, 144.96, 154.77, 162.34; ¹¹B NMR (δ in CDCl₃) 67.47 (br). Anal. Calcd for C₅₆H₅₆B₂S₂Si: C, 79.80; H, 6.70. Found: C, 79.81; H, 6.72.

2.4 Preparation of DTS1-FS

To a solution of 0.20 g (0.42 mmol) of DTS1-BrS in 20 mL of diethyl ether was added 0.25 mL (0.41 mmol) of a 1.65 M hexane solution of *n*BuLi at -80 °C and the mixture was stirred at room temperature for 1 h. To this was added 0.20 mL (1.2 mmol) of perfluorotoluene at -80 °C and the resulting mixture was stirred at room temperature for 12 h. After the usual workup, the residue was subjected to silica gel column chromatography eluting with hexane-chloroform to give 0.070 g (27% yield) of DTS1-FS as yellow powders: mp 202.7-203.9 °C; ¹H NMR (δ in CDCl₃) 2.55 (s, 3H, SMe), 7.24 (s, 1H, HC=C(S)), 7.37-7.47 (m, 6H, m- and p-Ph), 7.62-7.65 (m, 4H, o-Ph), 7.89 (s, 1H, HC=C(C_7F_7)); ¹³C NMR (δ in CDCl₃) 22.44, 118.55 (m), 119.50, 122.24, 127.31, 128.40, 130.50, 130.76, 133.90, 134.43 (t, J = 7.5 Hz), 135.38, 139.89, 141.11, 142.41, 143.78 (dm, J = 256 Hz), 144.57 (dm, J = 257 Hz), 150.54, 154.63; Exact APPI-MS Calcd for C₂₈H₁₅F₇S₃Si (M⁺): 609.00661. Found: 609.00604.

2.5 Preparation of DTS1-BS

To a solution of 0.35 g (0.74 mmol) of DTS1-BrS in 20 mL of diethyl ether was added 0.45 mL (0.74 mmol) of a 1.65 M hexane solution of *n*-BuLi at -80 °C and the mixture was stirred at room temperature for 1 h. To this was added a solution of 0.20 g (0.75 mmol) of fluorodimesitylborane in 5 mL of ether at 0 °C and the resulting mixture was stirred at room temperature for 12 h. After the usual workup, the residue was subjected to silica gel column chromatography eluting with hexane-chloroform to give 0.082 g (18% yield) of DTS1-BS as yellow powders: mp 222.7–224.3 °C; ¹H NMR (δ in CDCl₃) 2.16 (s, 12H, o-Me), 2.30 (s, 6H, p-Me), 2.51 (s, 3H, SMe), 6.83 (s, 4H, Mes ring H), 7.21 (s, 1H, HC=C(S)), 7.33-7.43 (m, 6H, *m*- and *p*-Ph), 7.56–7.60 (m, 5H, *o*-Ph and HC=C(B)); ¹³C NMR (δ in CDCl₃) 21.23, 22.45, 23.57, 128.19, 128.21, 130.48, 131.23, 133.97, 135.38, 138.42, 141.17, 141.77, 143.41, 144.06, 151.71, 162.94; ¹¹B NMR (δ in CDCl₃ from BF₃·Et₂O) 66.81 (br); Exact APPI-MS Calcd for C₃₉H₃₇BS₃Si (M⁺): 640.19142. Found: 640.19141.

3. Results and discussion

3.1 Synthesis

As shown in Scheme 1, A–D–A type bis(perfluorotolyl)- and bis-(dimesitylboryl)-substituted dithienosiloles (**DTS1-F**, **DTS2-F**, and **DTS1-B**) were prepared by the reactions of dilithio-DTSs with perfluorotoluene¹⁴ and fluorodimesitylborane, respectively. The low yield of **DTS2-F** was ascribed to the formation of many unidentified by-products including non-volatile substances. We also attempted to prepare **DTS1-F** using a similar reaction. Although the GC-MS analysis of the reaction mixture indicated the formation of the expected product in approximately 20% yield, it could not be isolated in a pure form. Similar reactions of lithio(methylthio)dithienosilole prepared from **DTS1-BrS** gave unsymmetrical D–A type compounds **DTS1-FS** and **DTS1-BS**.

 Table 1
 Optical properties of perfluorotolyl- and dimesitylboryl-substituted

 DTS derivatives

Compound	abs $\lambda_{\max}/nm (\epsilon/10^4)$ in chloroform	Emission $\lambda_{\rm em}/{\rm nm}^a$ (Φ) in chloroform ^b	Solid
DTS2-F DTS1-B	410 (2.6), 430 (2.1) 342 (1.1), 418 (4.7), 441 (5.3)	462, 481 (0.67) 460, 481 (0.90)	531 (0.60) 496 (0.83)
DTS1-FS DTS1-BS DTS1	403 (2.8) 415 (2.6) 356 (1.0)	497 (0.84) 486 (0.83) 409 (0.71)	$511 (0.66) \\ 501 (0.58) \\ _^c$

 a Excited at absorption maxima. b Measured at [substrate] = 1.8–5.2 \times 10 $^{-6}$ M. c Not measured.



These A–D–A and D–A type compounds were obtained as stable yellow solids that could be handled under ambient conditions. They were soluble in common organic solvents and melted without decomposition.

3.2 Optical properties

Table 1 summarizes the optical properties of the DTS derivatives thus prepared. The UV absorption and emission bands were red-shifted from those of the phosphorus-substituted DTSs (Chart 1)⁷ that showed absorption and emission bands at λ_{max} (CHCl₃) = 361–380 nm, λ_{em} (CHCl₃) = 422–465 nm, and $\lambda_{\rm em}$ (powder) = 434–464 nm, and also from those of trimethylsilyl-substituted DTS1 (Chart 2 and Table 1), reported previously.^{4a} It was also noted that the present DTS compounds exhibited relatively high absorption coefficiencies, as compared to DTS1. Interestingly, they showed high PL quantum efficiencies in both solution and the solid state, in contrast to the phosphorus-substituted DTSs reported previously, which exhibited highly PL properties only in either the solution or the solid state. This is presumably ascribed to the D-A and A-D-A type structures of the present DTS compounds and also to the sterically large and rigid perfluorotolyl and dimesitylboryl groups that prevent the DTS chromophores from being stacked and minimize the molecular vibration in the solid state.

D-A type compounds **DTS1-FS** and **DTS1-BS** were solvatochromic, although A-D-A type **DTS2-F** and **DTS1-B** showed no evident UV absorption and PL spectral changes depending on the solvents. As shown in Fig. 1, the UV absorption and PL maxima of **DTS1-FS** moved to shorter and longer wavelength respectively, as the solvent polarity increased on going from chloroform ($\lambda_{em} = 403 \text{ nm}$, $\lambda_{em} = 497 \text{ nm}$) to DMSO ($\lambda_{em} =$ 369 nm, $\lambda_{em} = 532 \text{ nm}$). Compound **DTS1-BS** showed smaller red shifts with solvent polarity in the PL spectrum from $\lambda_{em} =$ 486 nm in chloroform to 509 nm in DMSO, and no obvious



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Fig. 1 UV absorption (a) and PL (b) spectra of DTS1-FS in different solvents.

changes in the UV absorption spectra. These chromic behaviours were probably due to the photo-induced intramolecular charge transfer (ICT) of **DTS1-FS** and **DTS1-BS**. In fact, the PL lifetimes were slightly but certainly extended from 2.5 and 2.6 ns in chloroform to 2.6 and 2.8 ns in DMSO for **DTS1-FS** and **DTS1-BS**, respectively, suggesting stabilization of the photo-excited states in relatively polar DMSO.

3.3 F⁻-sensing

Recently, triarylboranes have been studied as optical sensor materials for F^- ions,^{9,10} in which coordination of F^- to the Lewis acidic borane centre causes UV and/or PL spectral changes. Compound **DTS1-B** also responded to the presence of fluoride anions in solution. Thus, on addition of Bu₄NF as the F^- source to a THF solution of **DTS1-B**, the UV absorption spectra changed in two steps, as shown in Fig. 2a. When 0 to 10 equiv. of Bu₄NF was added to **DTS1-B**, the absorption bands were broadened a little and shifted to longer wavelengths, while further addition of Bu₄NF resulted in a decrease in the absorption intensity and blue shifts of the maxima. The PL spectra showed similar behaviors including red-shifts at low Bu₄NF concentration (0–10 equiv.) and a subsequent blue-shift of the maximum with an excess of Bu₄NF (Fig. 2b).

Complex formation between **DTS1-B** and F^- proceeds in two steps (**DTS1-B** \rightarrow **DTS1-B-F** \rightarrow **DTS1-B-F2**), and supporting evidence for this was provided by monitoring the process *via* ¹H NMR spectroscopy. As shown in Fig. 3, new signals (H^c-H^f), assignable to the unsymmetrical **DTS1-B-F** protons with a borane–DTS–borate structure appeared on addition of Bu₄NF, of which H^c and H^d were high-field shifted from others, reflecting the existence of the electron-rich borate unit. Further addition of Bu₄NF afforded two additional new signals for symmetrical borate–DTS–borate **DTS1-B-F2** (H^g and H^h) at even higher field. In these spectra, the integration ratios



Fig. 2 $\,$ UV absorption (a) and PL (b) spectral changes of DTS1-B in THF on addition of $Bu_4NF\text{-}THF.$



Fig. 3 ¹H NMR spectral changes of **DTS1-B** in CDCl₃ (aromatic region) on addition of 0 equiv. (*a*), 2.0 equiv. (*b*), 4.0 equiv. (*c*), and 30 equiv. (*d*) of Bu₄NF-THF (1.0 M). High field shifts of the signals in spectrum *d* compared to those of *c* are likely due to the increased THF content of the solvent from *ca.* 5% to 30%. Asterisks indicate ¹³C satellite bands.

always agreed with the assignments. The process was reversible and addition of CaCl₂ to the solution of **DTS1-B** and Bu₄NF led to recovery of the original ¹H NMR spectra, together



Fig. 4 HOMO (a) and LUMO (b) profiles of boryl and borate-substituted DTSs, derived from DFT calculations at the B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p) level. Hydrogen atoms are omitted for clarity.

with precipitation of CaF_2 from the solution, although some unidentified low intensity signals were also observed. In accordance with the ¹H NMR spectral changes, a borate signal appeared at about 4 ppm in the ¹¹B NMR spectra on the addition of Bu₄NF.

Usually, complex formation between triarylboranes and F⁻ suppresses $p-\pi$ interactions, leading to the blue-shift of the absorption bands.9 An exception to this is the ionochromism of bis(dimesitylboryl)arenes (R₂B-Ar-BR₂) towards F⁻, which showed two-step spectral changes involving red-shifts of the absorption bands followed by blue-shifts, similar to the present case.¹⁰ It was suggested by Müllen et al. that the R₂B-Ar-R₂BF⁻ structure permitted ICT type interactions between the boron and borate units, being responsible for the red-shifts of the absorption bands at the early stage of the F⁻ addition.^{10b} However, no quantum chemical approaches to this phenomenon have been conducted. To learn more about the ionochromic behaviour of DTS-B, we carried out DFT calculations at the level of B3LYP/6-31+G(d,p)//B3LYP/6-31G-(d,p)^{15,16} on model molecules **DTS0-B**, **DTS0-B-F**, and **DTS0-B-F2**, shown in Fig. 4. The HOMOs and LUMOs of these compounds originate from the DTS π -conjugated units featuring the boron and borate orbital and the gaps decrease in the order of DTS0-B-F2 (3.67 eV) > DTS0-B (3.28 eV) > DTS0-B-F (2.79 eV), in accordance with the experimental observation for DTS1-B described above. Clear $p-\pi$ interaction between the borane and DTS units is seen in the HOMO and LUMO profiles of DTS0-B. On the contrary, those of DTS0-B-F2 are rather localized on the DTS segment with only limited contribution of the borate orbital. For DTS0-B-F, the LUMO is localized on the borane-DTS fragment, while the HOMO is delocalized over the borane-DTS-borate unit, suggesting the ICT excited state as expected. These results qualitatively support the observed spectral behaviour presented in Fig. 2, including the clear spectral changes around the addition of 1 equiv. of Bu₄NF. However, the changes were not saturated upon addition of 2 equiv. of Bu₄NF, indicating that the coordination of F⁻ to the borane centre is not very strong and that they were at equilibrium.

The monoboryl compound **DTS1-BS** exhibited normal ionochromic changes in its UV and PL spectra as shown in Fig. 5,





Fig. 5 UV absorption (a) and PL (b) spectral changes of $\mbox{DTS1-BS}$ in THF on addition of $\mbox{Bu}_4\mbox{NF-THF}.$

including monotonous blue-shifts of the bands. We examined Job's plots to investigate the stoichiometry of complex formation. However, this was complicated, presumably due to the formation of aggregated complexes and the stoichiometry could not been determined.

4. Conclusions

In conclusion, we prepared new A–D–A and D–A type compounds with a DTS unit as the donor and perfluorotolyl or dimesitylboryl group(s) as the acceptor and demonstrated their high absorption coefficiencies in solution and also highly PL properties in the solid state as well as in solution. Of those, the D–A type compounds exhibited efficient photoexcited ICT, leading to the solvatochromic behaviour. We also found that the dimesitylboryl-DTS system is potentially useful for F[–] sensing, which is of importance in the both chemical and biological fields of research.⁹

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