

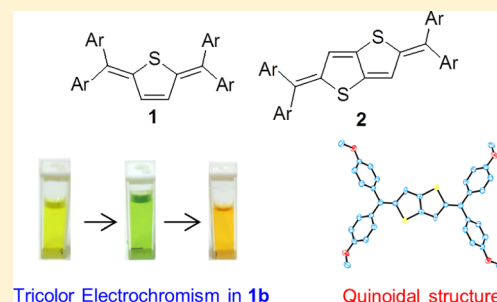
Preparation, Structure, and Redox Behavior of Bis(diarylmethylene)dihydrothiophene and Its π -Extended Analogues

Takashi Takeda* and Tomoyuki Akutagawa

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-8577, Japan

S Supporting Information

ABSTRACT: The preparation, X-ray structure, and optoelectronic properties of bis(diarylmethylene)dihydrothiophene **1** and its π -extended analogues **2** are described. The development of a simple, short-step synthetic route allowed us to prepare derivatives with different aryl units. X-ray crystallographic analysis of **1b** and **2b** revealed their quinoidal structures, which exhibit strong electronic absorption in the visible region. Cyclic voltammetry measurements revealed their strong electron-donating properties. **1b** showed two-step electrochromic behavior between the corresponding radical cation and dication.



Quinoidal compounds have attracted considerable attention with respect to their reactivity and diradical character. For example, *o*-quinodimethane, the simplest quinoidal molecule, shows high reactivity.¹ Recently, π -conjugated quinoidal molecules with diradical character have been reported to show low-energy light absorption that reached to the near-infrared (NIR) region.²

Polythiophene,³ thienothiophene, and their derivatives, such as P3HT⁴ and BTBT,⁵ have been extensively studied from the viewpoint of conducting organic materials in hole-transporting materials for use in organic field-effect transistors⁶ and bulk heterojunction solar cells.⁷ Polythiophene derivatives are characterized by strong electron-donating properties and a narrower HOMO–LUMO gap due to the long π -conjugation of electron-donating thiophene units. The relationships between the number of thiophene rings and photophysical and/or electronic properties have been extensively studied with oligothiophene derivatives.⁸

On the basis of the unique properties of quinoidal molecules and oligothiophene and/or thienothiophene, quinoidal oligothiophene should be an interesting structural motif with regard to its electronic, photonic, and diradical characteristics. In fact, quinoidal oligothiophene and thienothiophene with dicyanomethylene groups have been extensively studied as organic conductors,⁹ optical materials,¹⁰ and organic field-effect transistors.¹¹ For example, Otsubo et al. studied an oligothiophene with a dicyanomethylene group up to a hexamer and reported amphoteric redox behavior and the emergence of a diradical character with extension of the thienoquinoidal framework.¹² Dihydrothienothiophenes with dicyanomethylene units have also been prepared for examination of their photophysical and conductive properties.¹³ While quinoidal oligothiophenes and thienothiophene with electron-withdrawing dicyanomethylene units have been extensively

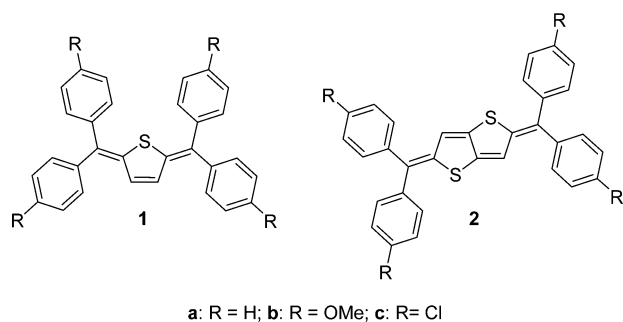
examined, little is known about those with electron-donating substituents. Although bis(diphenylmethylene)dihydrothiophene **1a** and its π -extended analogue have been reported sporadically,¹⁴ their molecular structures and their optical and electronic properties have not been well examined.

In this work, we prepared bis(diarylmethylene)dihydrothiophene **1** and its π -extended analogues **2** by a simple and versatile synthetic route. Because quinoidal bithiophene with diphenylmethylene groups has been reported to isomerize in solution,¹⁵ we chose thienothiophene instead to expand the thiophene core. X-ray structural analysis of **1** and **2** revealed their quinoidal molecular structure. Extension of a π -electron unit and the manipulation of electron-donating and -accepting groups on an aryl group strongly affect their absorption spectra. With regard to the electrochemistry of these derivatives, different redox behaviors were observed depending on the electron-donating and -accepting properties on the terminal aryl group. Compound **1b** with a simple molecular structure showed tricolor electrochromic behavior.

We first sought to identify an efficient synthetic route for **1** and **2**. It has been reported that fluorene-fused dihydrothienothiophene with a quinoidal molecular structure could be synthesized from the corresponding diol by dehydration in the solid state or in a photochemical reaction and from the corresponding dihydro derivative by deprotonation followed by oxidation.^{14c} However, some of these reactions require extreme reaction conditions. Nakayama et al. reported the preparation of **1a–c** from the corresponding dication species.^{14b} However, during the course of our studies, we found that these cations

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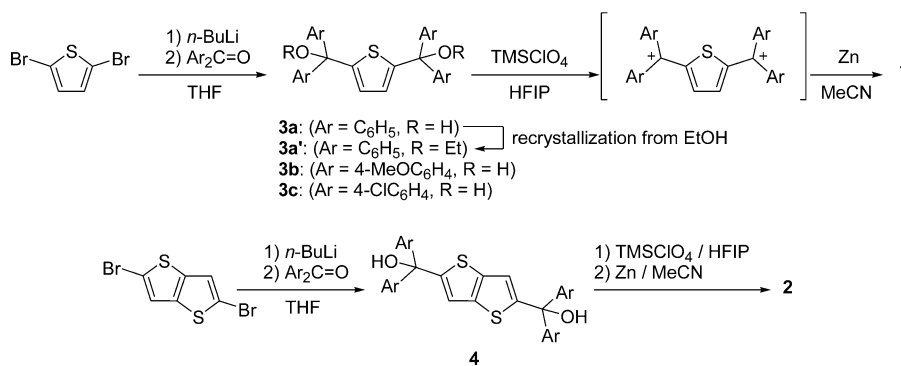
showed moderate instability toward moisture, which hampered their purification.

Thus, we developed a simple, versatile synthetic route for **1**, as summarized in Scheme 1. The addition of diarylketone to dilithiothiophene generated from dibromothiophene gave the corresponding diol **3**. Diols **3b** and **3c** were purified by silica gel column chromatography, whereas phenyl derivative **3a'** was isolated as an ethoxy derivative after recrystallization of the crude product from ethanol. In the previous paper,^{14b} the dication was generated from the corresponding diol by the reaction with Brønsted acidic medium consisting of aq HClO₄ in acetic anhydride, which cannot be easily removed because of the low volatility of the reagents. Thus, we chose a Lewis acid, TMSClO₄, with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as a solvent to generate the corresponding dicationic species, because all of the reagent and solvent could be removed by evaporation,¹⁶ which allowed us to reduce the dicationic species *in situ*. Treatment of the diol with TMSClO₄ in HFIP followed by reduction of the generated dicationic species with Zn in MeCN successfully gave the corresponding thienoquinoid **1**. The dication could also be obtained from ethoxy derivative **3a'**, which was reduced to give **1a**. The versatility of this route was demonstrated by the preparation of **1b**, **1c**, and **2a–c**, which have different aryl moieties and/or thiophene units. Electron-donating aryl moieties and an electron-deficient aryl group can be introduced by this method. Notably, the yield of **1c** was drastically improved from 6% with HClO₄ and Ac₂O^{14b} to 99% with TMSClO₄ and HFIP. While extension of the thiophene unit to thienothiophene was also successfully demonstrated, the introduction of a stronger electron-donating aryl unit such as Me₂NC₆H₄ and further extension of the thiophene spacer such as dithieno[3,2-*b*:2',3'-*d*]thiophene failed. Because of the strong electron-donating properties of **1b** and **2a** (*vide infra*), these quinoid compounds should be oxidized and decompose during workup and purification.

Single-crystal X-ray crystallographic analyses and DFT calculations were performed for neutral donors **1** and **2** and their respective dicationic states **1**²⁺ and **2**²⁺ to examine their molecular structures. Figure 1 shows ORTEP drawings of **1b** and **2b** and optimized structures for **1b**²⁺ and **2b**²⁺. Crystal data, data collection, and reduction parameters for crystals **1a**, **1b**, **2a**, and **2b** and selected bond lengths and torsion angles of **1a**, **1b**, and **2b** are summarized in Table 2 and Table S1 of the Supporting Information. The bond length was successfully determined with a high degree of accuracy in the crystal structures of **1a**, **1b**, and **2b**, which allowed us to examine the bonding characteristics of these compounds. Because disorder in the thienothiophene ring of **2a** made it difficult to determine the precise bond lengths, structural data for **2a** were excluded from the discussion. The C_A–C_B (**1** and **2**), C_C–C_{C'} (**1**), and C_C–C_D (**2**) bonds are shorter than the C_B–C_C bond, indicating the formation of a quinoidal structure, which is consistent with the optimized molecular structure obtained using DFT calculations (see Tables S2 and S3 of the Supporting Information). The terminal aryl moieties and central thiophene ring are twisted because of steric repulsion between hydrogens on the aryl group and hydrogen or sulfur on the thiophene ring. Dicationic species **1**²⁺ and **2**²⁺ are relatively unstable toward moisture, which made it difficult to grow a single crystal that was suitable for X-ray analysis. Thus, we performed DFT calculations at the B3LYP/6-31G(d) level of theory. In contrast to those of neutral donors **1** and **2**, the C_A–C_B bonds in dications **1**²⁺ and **2**²⁺ are longer than the C_B–C_C bonds (Table S4 of the Supporting Information), which reflects a benzenoid molecular structure. This switching of the quinoid–benzenoid structure based on electron transfer should be interesting with regard to the change in photophysical properties.

Next, we examined photophysical properties. Figure 2 shows UV–vis and fluorescence spectra of **1** and **2** in dichloromethane. Thienoquinoid **1a** showed strong absorption in the visible region at 422 nm, which can be assigned to the HOMO–LUMO transition of the thienoquinoid substructure, which was supported by DFT calculations [B3LYP/6-31G(d) (see Figure 3)]. Extension of the central π -electron unit from a thienoquinoid unit to a thienothienoquinoid unit caused a huge red shift of 44 nm for **2a** in contrast to that of **1a** due to narrowing of the HOMO–LUMO gap through the extension of π -conjugation. The absorption spectra of **1** and **2** were also strongly affected by the substituents on the terminal aryl moieties. The introduction of both electron-donating methoxy units and electron-accepting chloro atoms on phenyl moieties caused a red shift. Table 1 summarizes the energy levels of

Scheme 1. Preparation of **1** and **2** with Different Aryl Groups



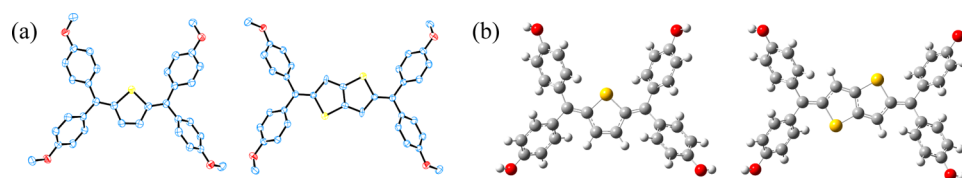


Figure 1. (a) ORTEP drawings of **1b** (left) and **2b** (right) and (b) optimized structures of **1b**²⁺ (left) and **2b**²⁺ (right).

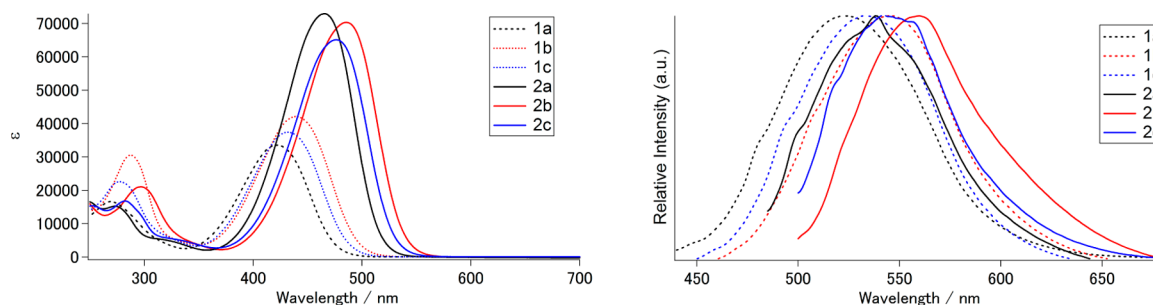


Figure 2. UV-vis (left) and fluorescence (right) spectra of **1** and **2** in CH₂Cl₂.

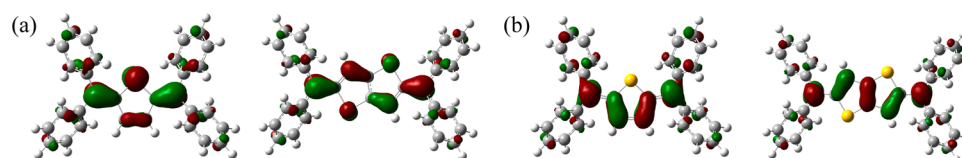


Figure 3. (a) HOMO and (b) LUMO of molecules **1a** (left) and **2a** (right).

Table 1. HOMO and LUMO Energy Levels of **1** and **2** Calculated at the B3LYP/6-31G* Level of Theory

	1a	1b	1c	2a	2b	2c
HOMO (eV ⁻¹)	-4.70	-4.37	-5.14	-4.58	-4.28	-4.98
LUMO (eV ⁻¹)	-1.84	-1.60	-2.34	-2.09	-1.87	-2.55

HOMO and LUMO for **1** and **2**. While the introduction of an electron-donating methoxy group increased the HOMO energy more than the LUMO energy, an electron-accepting chloro atom decreased the LUMO energy more than the HOMO energy. As a result, the HOMO-LUMO gap narrowed in both cases to cause a significant red shift in **1** and **2**. Compounds **1** and **2** exhibited weak fluorescence in solution. The tendency of the wavelength of emission maxima was in accord with that of absorption maxima. Thienoquinoid **1** showed fluorescence also in the solid state (Figure S4 of the Supporting Information).

Electrochemical properties were examined by cyclic voltammetry (CV). Figure S1 of the Supporting Information shows a CV chart for **1b** and **2b**. Both compounds showed reversible one-wave two-electron oxidation waves, which correspond to the generation of the dication species. The oxidation potentials of **1b** and **2b** were 0.64 and 0.56 V versus Ag/AgCl, respectively, which correspond to HOMO energies of -4.83 and -4.73 eV, respectively, which demonstrates strong electron-donating properties. The oxidation potential could be tuned by not only the length of the thienoquinoid π -system but also the substituents on the aryl group. The less electron-rich phenyl derivative and 4-chlorophenyl derivative showed irreversible one-wave oxidation waves at 0.98 (**1a**), 0.83 (**2a**), 1.13 (**1c**), and 0.94 V (**2c**), indicating the facile decomposition of cation radical species in an electron-poor cation radical intermediate. In addition to electron-donating properties, the conjugation effect of the methoxy group in **1b**

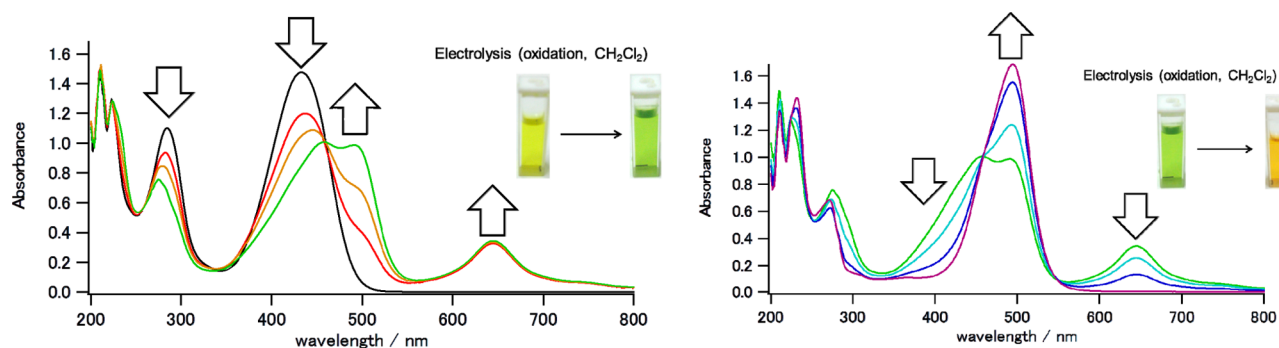


Figure 4. Change in the UV-vis spectrum of **1b** in MeCN containing 0.1 M Bu₄NBF₄ electrolyte upon constant-current electrolysis (20 μ A; every 4 min). The durations of oxidation for the spectra on the left and right were from 0 to 16 min and from 16 to 28 min, respectively.

Table 2. Crystal Data, Data Collection, and Reduction Parameters for Crystals 1a, 2a·CH₂Cl₂, 1b, and 2b

	1a	2a·CH ₂ Cl ₂	1b	2b
chemical formula	C ₃₀ H ₂₂ S	C ₃₂ H ₂₀ Cl ₂ S ₂	C ₃₄ H ₃₀ O ₄ S	C ₃₆ H ₃₀ O ₄ S ₂
formula weight	414.56	551.51	534.67	590.75
space group	P2 ₁ /n (No. 14)	P2 ₁ /n (No. 14)	P $\bar{1}$ (No. 2)	P2 ₁ /c (No. 14)
a (Å)	12.0374(5)	9.01922(16)	10.0009(3)	15.5917(2)
b (Å)	12.5139(4)	15.0820(3)	11.5470(3)	6.83809(10)
c (Å)	14.3361(5)	9.93380(18)	13.2679(4)	14.0291(2)
α (deg)			89.9142(16)	
β (deg)	99.098(3)	103.3317(9)	70.0107(13)	97.0284
γ (deg)			72.5011(13)	
V (Å ³)	2132.35(13)	1314.86(5)	1364.45(7)	1484.51(4)
Z	4	2	2	2
D _{calc} (g cm ⁻³)	1.291	1.393	1.301	1.321
μ (cm ⁻¹)	1.441	3.863	1.358	1.942
no. of reflections measured	23612	14443	14785	15175
no. of independent reflections	3852	2393	4867	2720
no. of reflections used	3852	2393	4867	2720
R ^a	0.0433	0.0683	0.0638	0.0489
R _w (F ²) ^b	0.1104	0.1967	0.1673	0.1415
goodness of fit	1.077	1.113	0.920	1.064

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega F_o^2]^{1/2}.$$

and **2b** might contribute to the improvement of the electron-donating properties of the molecules and the stabilization of the dicationic state.

We examined the electrochromic^{17,18} behavior of **1b**. Figure 4 shows changes in the UV–vis spectra of **1b** upon constant-current oxidation, where two-stage electrochromic behaviors were observed. In the early stage of oxidation, the absorption intensity corresponding to neutral species **1b** decreased, whereas the new long-wave absorption intensity at ~645 nm increased. The absorption intensity of a new low-energy absorption band remained constant even as electrolysis proceeded. In the later stage, this absorption was suppressed with a continuous decrease in the absorption intensity of the intermediate, whereas the intensity of a new strong absorption peak at ~500 nm increased. Because **1b**²⁺ was expected to show absorption at ~500 nm based on TDDFT calculations at the B3LYP/6-31G(d) level of theory, this change in the UV–vis spectrum should correspond to stepwise oxidation to dication **1b**²⁺ via cation radical intermediate **1b**^{•+}. It is interesting to compare the electrochromic behavior to that of bis[di(4-methoxyphenyl)ethenyl]thiophene, which has an additional conjugated carbon and shows bicolor electrochromism between the neutral state and dication state.¹⁹ The difference in electrochromic behavior could probably be ascribed to the difference in the degree of interaction between the terminal redox active diarylmethylene unit, which was directly connected to a thiophene π -spacer in **1b** and resulted in weak electronic coupling to show two-step electrochromism. On the other hand, diarylmethylene units were separated by two additional carbon units in bis[di(4-methoxyphenyl)ethenyl]thiophene, and the electronic coupling between terminal units was negligible for the achievement of bicolor electrochromism. A tricolor change could be triggered by two different mechanisms, i.e., a change in the electronic nature of the thienoquinoid π -unit and a change in the chromophore from thienoquinoid to triarylmethylum.

CONCLUSION

In summary, we have developed a versatile synthetic route for bis(diarylmethylene)dihydrothiophene **1**. The versatility of this method was demonstrated by the derivatization of aryl moieties and π -extension of a thiophene unit. X-ray crystallographic analysis of **1** and **2** revealed their quinoidal molecular structures. The electronic absorption spectra of compounds **1** and **2** were strongly affected by the π -conjugation length and the presence of electron-donating and/or electron-accepting substituents on the aryl groups. While electron-poor molecules **1a**, **2a**, **1c**, and **2c** were unstable toward electrochemical oxidation, molecules **1b** and **2b** with an electron-donating 4-methoxyphenyl group showed reversible redox behavior between dication species via the corresponding cation radical. This oxidation process can be monitored by UV–vis spectra to show tricolor electrochromic behavior. Redox active quinoidal molecules with switching ability²⁰ should be an interesting molecular system, which may be useful in optoelectronic materials.

EXPERIMENTAL SECTION

General Methods. All chemical reactions were performed under a nitrogen atmosphere. Commercially available reagents and solvents were used without further purification. TMSClO₄ in toluene was prepared according to a literature method.¹⁶ Chemical shifts (δ) in parts per million were referenced to an internal standard of tetramethylsilane or residual nondeuterated solvent (¹H at 5.32 ppm for CD₂Cl₂ and ¹³C at 77.0 ppm for CDCl₃). Mass spectra were obtained in EI mode with a magnetic sector mass spectrometer. Infrared (IR, 400–4000 cm⁻¹) spectra were measured on a KBr pellet with a resolution of 4 cm⁻¹.

X-ray Structural Analysis. Temperature-dependent crystallographic data (Table 2) were collected using a diffractometer equipped with a rotating anode fit with multilayer confocal optics using Cu K α (λ = 1.54187 Å) radiation. Structural refinements were conducted using the full-matrix least-squares method on F². Calculations were performed using the Crystal Structure and SHELEX software packages.²¹ Parameters were refined using anisotropic temperature factors except for the hydrogen atom.

Computational Methods. DFT calculations were performed with the Gaussian 09 program package.²² The geometries of the molecules

were optimized using the B3LYP/6-31G* basis set. Stationary points were assessed by a vibration frequency analysis.

Preparation of 3a'. To a solution of 2,5-dibromothiophene (1.0 mL, 8.85 mmol) in dry THF (100 mL) was added *n*-butyllithium (1.60 M in hexane, 12.0 mL, 19.2 mmol) at -78°C . The mixture was stirred at this temperature for 60 min. Benzophenone (3.55 g, 19.5 mmol) was then added in one portion. The mixture was allowed to gradually warm to room temperature and stirred for 19 h. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl . The mixture was extracted with CH_2Cl_2 . The combined organic layer was washed with brine and dried over MgSO_4 . The crude product was recrystallized from ethanol to give **3a'** (2.05 g, 46%) as a white solid. Mp: $100\text{--}102^{\circ}\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.52–7.47 (m, 8H), 7.31–7.19 (m, 12H), 6.76 (s, 2H), 3.23 (q, $J = 6.9$ Hz, 4H), 1.21 (t, $J = 6.9$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 148.9, 144.6, 127.9, 127.7, 127.1, 84.6, 59.8, 15.3. IR: 3085, 3056, 3023, 2970, 2921, 2884, 1597, 1490, 1444, 1389, 1315, 1226, 1212, 1176, 1155, 1138, 1114, 1067, 1031, 1003, 943, 920, 868, 803, 770, 754, 742, 701, 678, 646, 491 cm^{-1} . HRMS (EI): calcd for $\text{C}_{34}\text{H}_{32}\text{O}_2\text{S}$ m/z 504.2123 (M^+), found m/z 504.2123.

Preparation of 3b. To a mixture of 2,5-dibromothiophene (1.0 mL, 8.85 mmol) in dry THF (100 mL) was added *n*-BuLi (1.60 M in hexane, 12.0 mmol, 19.2 mmol) at -78°C . After the mixture was stirred for 50 min at this temperature, 4,4'-dimethoxybenzophenone (4.71 g, 19.4 mmol) was added. The mixture was allowed to gradually warm to room temperature and stirred for 17 h. After the addition of a saturated aqueous solution of NH_4Cl , the mixture was extracted with CH_2Cl_2 . The combined organic layer was washed with brine and dried over Na_2SO_4 . The crude product was subjected to silica gel column chromatography ($\text{CHCl}_3/\text{AcOEt} = 100/3$) to give **3b** (2.70 g, 54%) as a pale red solid. Mp: $78\text{--}79^{\circ}\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.26 (d, $J = 8.9$ Hz, 8H), 6.82 (d, $J = 8.9$ Hz, 8H), 6.52 (s, 2H), 3.79 (s, 12H), 2.76 (s, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 158.9, 152.6, 138.9, 128.5, 125.9, 113.2, 79.6, 55.3. IR: 3471, 3000, 2953, 2933, 2905, 2835, 1608, 1583, 1509, 1463, 1442, 1414, 1302, 1251, 1175, 1112, 1033, 909, 826, 792, 605, 575 cm^{-1} . HRMS (EI): calcd for $\text{C}_{34}\text{H}_{32}\text{O}_6\text{S}$ m/z 568.1920 (M^+), found m/z 568.1920.

Preparation of 3c. To a solution of 2,5-dibromothiophene (1.0 mL, 8.85 mmol) in dry THF (100 mL) was added *n*-BuLi (1.63 M in hexane, 11.8 mL, 19.2 mmol) at -78°C . After the mixture was stirred for 45 min at this temperature, 4,4'-dichlorobenzophenone (4.87 g, 19.4 mmol) was added. The mixture was allowed to gradually warm to room temperature and stirred for 18.5 h. After the addition of a saturated aqueous solution of NH_4Cl , the mixture was extracted with CH_2Cl_2 . The combined organic layer was washed with brine and dried over Na_2SO_4 . The crude product was subjected to silica gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2 = 3/1 \rightarrow 0/1$) to give **3c** (3.14 g, 61%) as a pale orange solid. Mp: $79\text{--}80^{\circ}\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.29 (s, 16H), 6.56 (s, 2H), 2.83 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 151.7, 144.2, 133.9, 128.5, 128.3, 126.5, 79.3. IR: 3561, 3452, 3069, 1592, 1575, 1489, 1400, 1316, 1227, 1180, 1137, 1093, 1013, 909, 811, 530, 507 cm^{-1} . HRMS (EI): calcd for $\text{C}_{30}\text{H}_{20}\text{Cl}_4\text{O}_2\text{S}$ m/z 583.9938 (M^+), found m/z 583.9937.

Preparation of 1a. To a mixture of **3a'** (496 mg, 983 μmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (10 mL) was added TMSClO_4 in toluene (0.74 M, 7.0 mL, 5.18 mmol). After the mixture was stirred for 2.5 h at room temperature, the volatile solvent and reagent were removed by evaporation. The obtained dicationic species was dissolved in dry MeCN (15 mL), and Zn powder (2.38 g, 36.4 mmol) was added. The mixture was stirred for 24 h, diluted with CH_2Cl_2 , and filtered on a Celite pad. The filtrate was washed with brine and dried over Na_2SO_4 . The crude product was subjected to silica gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2 = 1/3$) to give **1a** (373 mg, 92%) as a yellow solid. Mp: $199\text{--}200^{\circ}\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.40–7.20 (m, 20H), 6.83 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 142.4, 142.2, 141.7, 133.7, 131.8, 130.5, 129.6, 128.3, 128.2, 127.4, 127.2. IR: 3049, 3027, 1594, 1572, 1537, 1489, 1440, 1170, 1155, 1139, 1072, 1029, 999, 967, 924, 903, 856, 836, 824, 800, 789, 768, 757, 694, 662, 645, 624, 612, 573, 518, 420 cm^{-1} . HRMS (EI): calcd for $\text{C}_{30}\text{H}_{22}\text{S}$ m/z 414.1442 (M^+), found m/z 414.1442.

Preparation of 1b. To a mixture of **3b** (1.00 g, 2.82 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (10 mL) was added TMSClO_4 in toluene (0.74 M, 8.6 mL, 6.36 mmol). After the mixture was stirred for 13 h at room temperature, the volatile solvent and reagent were removed by evaporation. The obtained dicationic species was dissolved in dry MeCN (20 mL), and Zn powder (1.43 g, 20.5 mmol) was added. The mixture was stirred for 9 h, diluted with CH_2Cl_2 , and filtered. The filtrate was washed with brine and dried over Na_2SO_4 . The crude product was subjected to silica gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2 = 1/4$) to give **1b** (800 mg, 89%) as a yellow solid. Mp: $204\text{--}205^{\circ}\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.30 (d, $J = 8.0$ Hz, 4H), 7.14 (d, $J = 8.0$ Hz, 4H), 6.86 (d, $J = 8.6$ Hz, 4H), 6.82 (d, $J = 8.6$ Hz, 4H), 6.77 (s, 2H), 3.81 (s, 6H), 3.79 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 158.7, 140.8 (br), 135.1 (br), 134.6 (br), 133.0, 131.6, 131.0, 113.6, 113.5, 55.22, 55.17. IR: 3024, 2995, 2950, 2931, 2904, 2833, 1604, 1570, 1544, 1504, 1462, 1441, 1412, 1317, 1304, 1290, 1273, 1248, 1176, 1137, 1108, 1032, 969, 960, 939, 912, 837, 817, 810, 798, 772, 732, 689, 657, 623, 613, 605, 586, 572, 555, 539, 522, 438 cm^{-1} . HRMS (EI): calcd for $\text{C}_{34}\text{H}_{30}\text{O}_4\text{S}$ m/z 534.1865 (M^+), found m/z 534.1867.

Preparation of 1c. To a mixture of **3c** (503 mg, 858 μmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (10 mL) was added TMSClO_4 in toluene (0.74 M, 4.0 mL, 2.96 mmol). After the mixture was stirred for 6 h at room temperature, the volatile solvent and reagent were removed by evaporation. The obtained dicationic species was dissolved in dry MeCN (20 mL), and Zn powder (3.35 g, 51.2 mmol) was added. The mixture was stirred for 22 h, diluted with CH_2Cl_2 , and filtered on a Celite pad. The solvent of the filtrate was evaporated and then suspended with a small amount of CH_2Cl_2 . The insoluble solid was collected by filtration followed by washing with CH_2Cl_2 to give **1c** (240 mg) as a yellow solid. The filtrate was subjected to silica gel column chromatography to give additional **1c** (228 mg). The total yield was 99%. Mp: $173\text{--}174^{\circ}\text{C}$ dec. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.32 (d, $J = 8.6$ Hz, 4H), 7.28 (br d, 8H), 7.14 (d, $J = 8.6$ Hz, 4H), 6.81 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 142.9, 140.0, 139.5, 133.9, 133.58, 133.55, 131.64, 130.9, 129.9, 129.7, 128.6. IR: 1587, 1487, 1398, 1173, 1140, 1091, 1015, 912, 850, 832, 817, 797, 726, 711, 650, 612, 567, 525, 491, 438 cm^{-1} . HRMS (EI): calcd for $\text{C}_{30}\text{H}_{18}\text{Cl}_4\text{S}$ m/z 549.9883 (M^+), found m/z 549.9880.

Preparation of 4a. To a solution of 2,5-dibromothiopheno[3,2-*b*]thiophene (2.50 g, 8.39 mmol) in dry THF (80 mL) was added *n*-BuLi (1.55 M, 11.4 mL, 17.6 mmol) at -78°C . After the mixture was stirred at this temperature for 40 min, benzophenone (3.38 g, 18.5 mmol) was added. The mixture was allowed to gradually warm to room temperature and stirred overnight. After the addition of a saturated aqueous solution of NH_4Cl , the mixture was extracted with CH_2Cl_2 . The combined organic layer was washed with brine and dried over Na_2SO_4 . The crude product was suspended with a small amount of CHCl_3 , and the insoluble solid was collected by filtration to give **4a** (2.34 g, 55%) as a white solid. Mp: $218\text{--}220^{\circ}\text{C}$ dec. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42–7.37 (m, 8H), 7.36–7.29 (m, 12H), 3.00 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 154.0, 146.0, 138.3, 128.1, 127.3, 119.6, 80.6. IR: 3583, 3561, 3082, 3057, 3024, 1598, 1582, 1490, 1446, 1394, 1331, 1317, 1283, 1205, 1188, 1174, 1158, 1123, 1081, 1032, 1009, 925, 896, 838, 816, 769, 750, 701, 681, 657, 645, 586, 552, 511, 470, 406 cm^{-1} . HRMS (EI): calcd for $\text{C}_{32}\text{H}_{24}\text{O}_2\text{S}_2$ m/z 504.1218 (M^+), found m/z 504.1221.

Preparation of 4b. To a solution of 2,5-dibromothiopheno[3,2-*b*]thiophene (1.99 g, 6.68 mmol) in dry THF (60 mL) was added *n*-BuLi (1.60 M, 8.8 mL, 14.1 mmol) at -78°C . After the mixture was stirred at this temperature for 60 min, 4,4'-dimethoxybenzophenone (3.56 g, 14.7 mmol) was added. The mixture was allowed to gradually warm to room temperature and stirred for 17 h. After the addition of a saturated aqueous solution of NH_4Cl , the mixture was extracted with CH_2Cl_2 . The combined organic layer was washed with brine and dried over Na_2SO_4 . The crude product was suspended with a small amount of CH_2Cl_2 , and the insoluble solid was collected by filtration to give **4b** (1.90 g) as a pale red solid. The filtrate was subjected to silica gel column chromatography ($\text{CH}_2\text{Cl}_2/\text{AcOEt} = 95/5$) to give additional **4b** (414 mg). The total yield was 55%. Mp: $225\text{--}227^{\circ}\text{C}$ dec. ^1H

NMR (400 MHz, CDCl₃): δ 7.29 (d, J = 8.9 Hz, 8H), 6.85 (d, J = 8.9, 8H), 6.78 (s, 2H), 3.80 (s, 12H), 2.88 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 159.0, 154.7, 138.5, 138.2, 128.6, 119.3, 113.3, 80.0, 55.3. IR: 3491, 3002, 2956, 2934, 2906, 2836, 1608, 1584, 1509, 1461, 1441, 1414, 1331, 1298, 1253, 1177, 1111, 1032, 909, 832, 811, 781, 608, 579 cm⁻¹. HRMS (EI): calcd for C₃₆H₃₂O₆S₂ m/z 624.1640 (M⁺), found m/z 624.1641.

Preparation of 4c. To a solution of 2,5-dibromothiopheno[3,2-*b*]thiophene (2.50 g, 8.39 mmol) in dry THF (100 mL) was added *n*-BuLi (1.63 M, 10.8 mL, 17.6 mmol) at -78 °C. After the mixture was stirred at this temperature for 40 min, 4,4'-dichlorobenzophenone (4.75 g, 18.7 mmol) was added. The mixture was allowed to gradually warm to room temperature and stirred for 18.5 h. After the addition of a saturated aqueous solution of NH₄Cl, the mixture was extracted with CH₂Cl₂. The combined organic layer was washed with brine and dried over Na₂SO₄. The crude product was subjected to silica gel column chromatography (CH₂Cl₂) to give 4c (2.42 g, 43%) as a pale gray solid. Mp: 135–137 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.32 (br d, 16H), 6.81 (s, 2H), 3.00 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 153.5, 144.0, 138.5, 134.1, 128.7, 128.4, 119.7, 79.8. IR: 3560, 3441, 3083, 1592, 1575, 1489, 1400, 1336, 1318, 1179, 1123, 1094, 1014, 908, 827, 796, 738, 563, 528, 503, 465 cm⁻¹. HRMS (EI): calcd for C₃₂H₂₀Cl₄O₂S₂ m/z 639.9659 (M⁺), found m/z 639.9659.

Preparation of 2a. To a mixture of 4a (547 mg, 1.08 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (10 mL) was added TMSClO₄ in toluene (0.74 M, 7.0 mL, 5.18 mmol). After the mixture was stirred for 2.5 h at room temperature, the volatile solvent and reagent were removed by evaporation. The obtained dicationic species was dissolved in dry MeCN (15 mL), and Zn powder (2.56 g, 39.1 mmol) was added. The mixture was stirred for 24.5 h. After dilution with CH₂Cl₂, the suspension was filtered. The filtrate was washed with brine and dried over Na₂SO₄. The solvent was evaporated and then suspended with a small amount of CH₂Cl₂. The insoluble solid was collected by filtration followed by washing with CH₂Cl₂ to give 2a (266 mg) as a red solid. The filtrate was subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 1/3) to give additional 2a (98 mg). The total yield was 71%. Mp: 257–259 °C dec. ¹H NMR (400 MHz, CDCl₃): δ 7.41–7.25 (m, 20H), 6.53 (s, 2H). ¹³C NMR could not be measured because of the low solubility of 2a. IR: 3052, 3026, 1594, 1526, 1489, 1440, 1175, 1154, 1137, 1076, 1029, 1001, 931, 899, 811, 767, 748, 701, 666, 650, 634, 617, 586, 502, 447 cm⁻¹. HRMS (EI): calcd for C₃₂H₂₂S₂ m/z 470.1163 (M⁺), found m/z 470.1165.

Preparation of 2b. To a mixture of 4b (592 mg, 947 μ mol) in 1,1,1,3,3,3-hexafluoro-2-propanol (10 mL) was added TMSClO₄ in toluene (0.74 M, 4.0 mL, 2.96 mmol). After the mixture was stirred for 13.5 h at room temperature, the volatile solvent and reagent were removed by evaporation. The obtained dicationic species was dissolved in dry MeCN (20 mL), and Zn powder (1.39 g, 21.3 mmol) was added. The mixture was stirred for 10.5 h. After dilution with CH₂Cl₂, the suspension was filtered. The filtrate was washed with brine and dried over Na₂SO₄. The crude product was subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 1/4) to give 2b (461 mg, 85%) as a red solid. Mp: 282–283 °C dec. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.30 (d, J = 8.8 Hz, 4H), 7.17 (d, J = 8.8 Hz, 4H), 6.88 (d, J = 8.8 Hz, 4H), 6.87 (d, J = 8.8 Hz, 4H), 6.50 (s, 2H), 3.81 (s, 12H). ¹³C NMR (125 MHz, CD₂Cl₂): δ 159.8, 150.3, 145.0, 135.5, 135.0, 132.2, 131.8, 130.8, 117.0, 114.3, 55.9. IR: 1603, 1569, 1526, 1503, 1457, 1440, 1412, 1318, 1304, 1293, 1277, 1241, 1175, 1137, 1110, 1035, 1023, 964, 942, 923, 904, 834, 820, 809, 781, 765, 731, 715, 662, 630, 619, 595, 555, 533, 496, 471, 423 cm⁻¹. HRMS (EI): calcd for C₃₆H₃₀O₄S₂ m/z 590.1585 (M⁺), found m/z 590.1588.

Preparation of 2c. To a mixture of 4c (509 mg, 792 μ mol) in 1,1,1,3,3,3-hexafluoro-2-propanol (10 mL) was added TMSClO₄ in toluene (0.74 M, 4.0 mL, 2.96 mmol). After the mixture was stirred for 6.5 h at room temperature, the volatile solvent and reagent were removed by evaporation. The obtained dicationic species was dissolved in dry MeCN (20 mL), and Zn powder (5.21 g, 79.7 mmol) was added. The mixture was stirred for 10.5 h. After dilution with CH₂Cl₂, the suspension was filtered. The filtrate was washed with brine and then dried over Na₂SO₄. The solvent of the filtrate was evaporated and

then suspended with a small amount of CH₂Cl₂. The insoluble solid was collected by filtration followed by washing with CH₂Cl₂ to give 2c (436 mg, 100%) as a red solid. Mp: 176–178 °C dec. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.37–7.30 (m, 12H), 7.19 (d, J = 8.2 Hz, 4H), 6.53 (s, 2H). ¹³C NMR could not be measured because of the low solubility of 2c. IR: 1518, 1486, 1396, 1182, 1139, 1109, 1092, 1011, 961, 942, 924, 903, 826, 790, 708, 691, 648, 636, 627, 621, 524, 519, 473, 457, 414, 401 cm⁻¹. HRMS (EI): calcd for C₃₂H₁₈Cl₄S₂ m/z 605.9604 (M⁺), found m/z 605.9603.

■ ASSOCIATED CONTENT

📄 Supporting Information

Selected bond lengths and torsion angles in the optimized structures of 1, 1²⁺, 2 and 2²⁺ determined by X-ray analyses and DFT calculations, ORTEP drawings of 1a, 1b, 2a, and 2b, photo of the fluorescence of 1a–c in the solid state, ¹H and ¹³C NMR spectra of compounds 1–4, Cartesian coordinates for optimized structures, and CIF files of 1a, 1b, 2a, and 2b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

✉ Corresponding Author

*E-mail: takeda@tagen.tohoku.ac.jp.

Notes

The authors declare no competing financial interest.

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