Synthesis and Optical Properties of Pyridino End-Capped Oligothiophenes

Yong-Mook Hwang,[1] Joji Ohshita,*[1] Tomonobu Mizumo,[1] Hiroto Yoshida,[1] Yoshihito Kunugi,[2] and Takashi Sugioka[3]

[1]Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8527

[2]Department of Applied Chemistry, Faculty of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292

[3]Synthesis Research Laboratory, Kurashiki Research Center, Kuraray Co., Ltd., 2045-1 Sakazu, Kurashiki, Okayama 710-0801

Received June 1, 2011; E-mail: jo@hiroshima-u.ac.jp

Oligothiophenes end-capped with fused pyridino units were synthesized by means of the Stille coupling and their optical properties were studied. These compounds show absorption maxima and edges at 324–374 nm and 3.10–2.76 eV, respectively, depending on the oligothiophene chain lengths. DFT calculations indicate that both the HOMO and LUMO levels are lowered by the introduction of the pyridino units.

Oligo- and polythiophenes are of current interest, as promising organic materials that can be used for organic devices, such as organic thin film transistors and organic photovoltaic cells.[1] High planarity of oligo- and polythiophenes leads to enhanced conjugation, and the rather strong intermolecular interaction originating from the high polarizability of the sulfur electrons facilitates the intermolecular hopping mobility. However, there is still a need to improve the properties of oligo- and polythiophenes, including carrier mobility, film forming properties, thermal and chemical stability, etc.

The introduction of end-capping aromatic substituents has been often studied to tune the electronic states of oligo- and polythiophenes and also to avoid oxidation and polymerization, upon fabrication of the devices. For example, phenyl,[2] fluorenyl,[3] styryl,[4] and naphthyl[5] end-capped oligothiophenes were prepared as high-performance semiconductors with good carrier mobility and high device stability. Fused end-capping units have been also examined and benzo and naphtho end-capped oligothiophenes were reported to show moderate to high mobility in their vapor-deposited films.[6] In this paper, we report the first synthesis of pyridino end-capped oligothiophenes and their optical properties. In these compounds, polar pyridino units would enhance the intermolecular interaction in the solid states, and their electron-withdrawing properties would lead to the effective intramolecular interaction with the electron-donating oligothiophene units, enhancing the conjugation.

Results and Discussion

Pyridino end-capped oligothiophenes were prepared as shown in Scheme 1. Ring constructing reaction of benzenesulfonyl cyanide with (3-methylthien-2-ylmethylene)aniline, followed by bromination gave (benzenesulfonyl)bromothienopyridine, which was then treated with sodium alkoxide to give alkoxybromothienopyridine **1**. Oxidative coupling of methoxythienopyridinyllithium prepared from **1a** with $CuCl_2$ gave bi(thienopyridine) **2a** in 41% yield, while the Stille coupling reactions of **1** with bis(tributylstannyl)thiophene and -bithiophene catalyzed by $[Pd(PPh_3)_4]$ afforded pyridino end-capped oligothiophenes **3** and **4** in 35–45% yield (Scheme 1). Similar coupling with bis(tributylstannyl)benzene gave phenylene-linked thienopyridine **3a′** in 75% yield.

Some properties of the present oligothiophenes are summarized in Table 1. They are orange solids that melt without decomposition and are soluble in common organic solvents, such as toluene, THF, and chloroform. The absorption and emission maxima of the compounds are little affected by the substituents (R = Me, *n*-Bu, or *n*-Hex) and move to longer wavelength as elongating the oligothiophene chain from **2** to **4**, as presented in Figure 1. Compounds **2a** and **3a′** are not emissive in chloroform. Phenylene-bridged compound **3a′** exhibits a shorter absorption λ_{max} by 10 nm than **3a**. The UV spectrum of **4a** was measured also as a vapor-deposited film, which reveals the longer absorption maximum by 16 nm than that in chloroform, clearly indicating the close packing of the molecules in the solid state leading to the highly planar structure and/or the strong intermolecular π–π interaction. Optical properties of benzo[6] and hexyl end-capped oligothiophenes[7] shown in Scheme 2 were reported previously. Dihexylquaterthiophene **4H** shows the absorption band at $\lambda_{max} = 402$ nm red-shifted from that of **4a**–**4c** (374 nm), while the absorption edges (E_g) are only slightly red shifted on going from **4a**–**4c** (450 nm, 2.76 eV) to **4H** (460 nm, 2.70 eV).[7,8] The absorption maximum of **4B** is reported only for its film ($\lambda_{max} = 344$ nm),[6] which is at higher energy than that of **4a** (390 nm).

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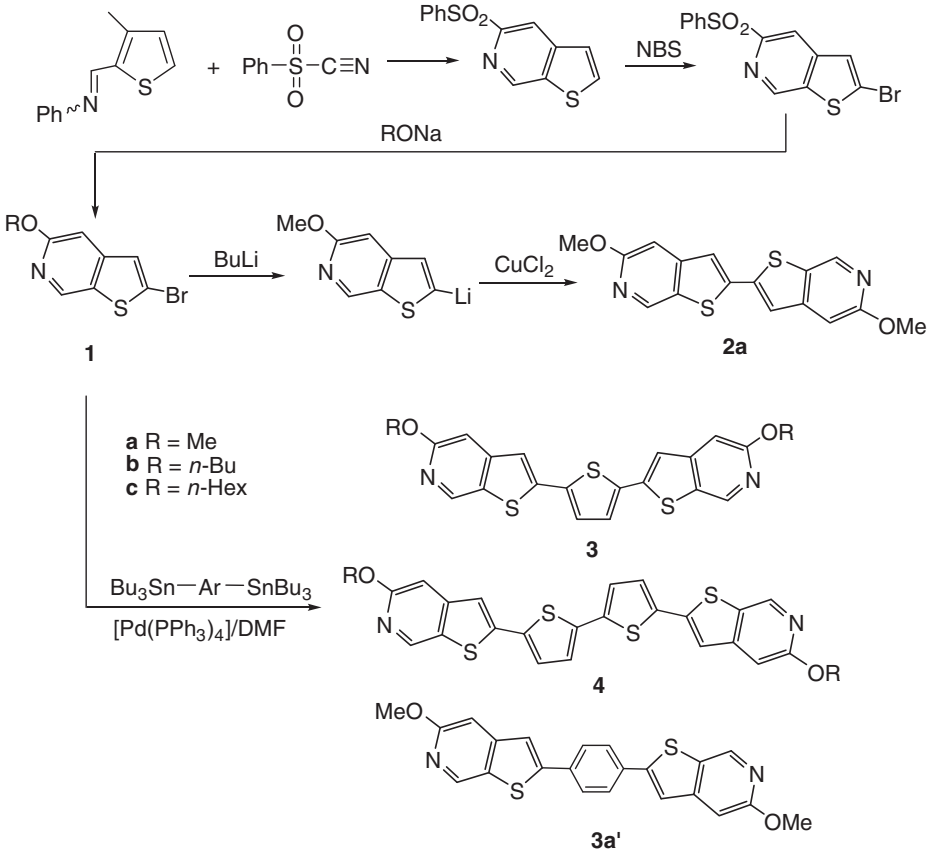


Scheme 1. Preparation of pyridino end-capped oligothiophenes.

Table 1. Synthesis and Properties of Pyridino End-Capped Oligothiophenes

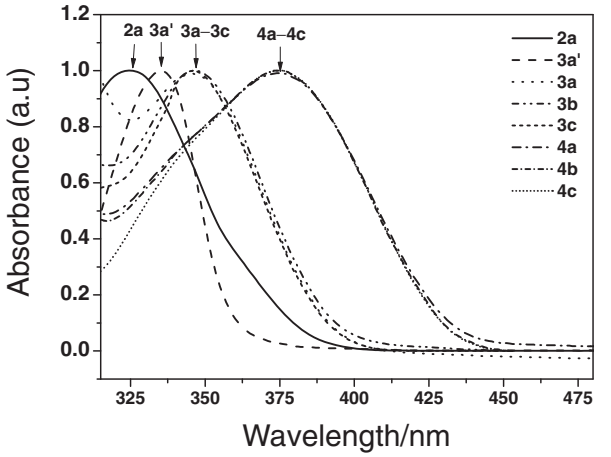
Compound	Yield /%	Mp /°C	UV–vis absorption[a)]		Emission[a)]	
			λ_{max}/nm	E_g/eV	λ_{em}/nm	Φ_f[b)]
2a	41	258	324	3.10	nd[c)]	nd[c)]
3a	35	196	344	3.00	428	0.12
3b	40	170	345	3.00	429	0.12
3c	41	165	346	3.00	430	0.12
3a′	75	205	334	3.22	nd[c)]	nd[c)]
4a	35	246	374	2.76	472	0.22
4b	42	206	374	2.76	473	0.22
4c	45	198	374	2.76	474	0.22

a) In chloroform, with [substrate] $= 2.0 \times 10^{-5}$ M. b) Absolute quantum efficiency, determined in an integration sphere. c) No emission detected.

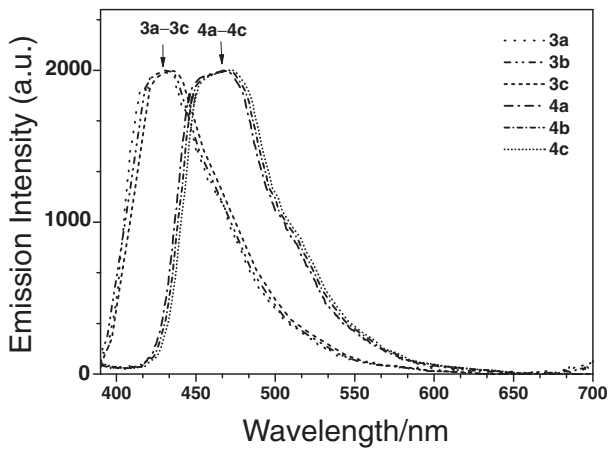
Since the absorption maxima reflect the average of the electronic states of conformers, it is likely that the larger difference of the absorption maxima between **4a**–**4c** and **4H** than that of the edges is due to the higher degree of the population of twisted conformers with respect to the thiophene–thiophene single bond rotation for **4a**–**4c**. This is supported also by the larger Stokes shifts for **4a**–**4c** than **4H**. Quaterthiophene **4H** was reported to show two emission maxima at 463 and 492 nm,[7] thus $\lambda_{em} - \lambda_{max} = 61$, 90 nm, both of which are smaller than those of **4a**–**4c** ($\lambda_{em} - \lambda_{max} =$ 98–100 nm).

Similar optical tendency is observed also for terthiophene derivatives (**3a**–**3c**: $\lambda_{max} = 344$–346 nm, $E_g = 2.95$ eV; **3H**: $\lambda_{max} = 374$ nm, $E_g = 2.91$ eV). For bithiophenes, however, both λ_{max} and E_g indicated rather enhanced conjugation for **2a** ($\lambda_{max} = 324$ nm, $E_g = 3.10$ eV) over **2H** ($\lambda_{max} = 316$ nm, $E_g = 3.43$ eV). For bithiophenes bearing only one interring bond, the effects of the conformer population are not very important and essentially pyridine end-capped oligothiophenes should possess better conjugation than the corresponding hexyl end-capped ones. The intramolecular charge-transfer (CT) interaction in these pyridino end-capped oligothiophenes would be considered. Indeed, the UV absorption band of **4a** moved to 382 nm in DMSO. However the shift is small (6 nm) and such CT interaction is not remarkably operative if it is involved.

To know more about the electronic states of these oligothiophenes, we carried out DFT calculations on simplified models and **4a** (Scheme 3) at the B3LYP/6-31G(d,p) level and the results are depicted in Figure 2.[9] The optimized geometries of these compounds exhibit high planarity of the systems, retaining all the ring atoms in one plane. Smaller HOMO–LUMO energy gaps are obtained for pyridino end-capped **2m** and **4m** than for **2Hm** and **4Hm**, respectively. Interestingly, pyridino annulation causes slight changes in bond angles and lengths in the annulated thiophene rings to shorten the intramolecular non bonding H–S contacts as shown in Scheme 3, which may increase the population of twisted conformers for pyridino end-capped quaterthiophenes, being

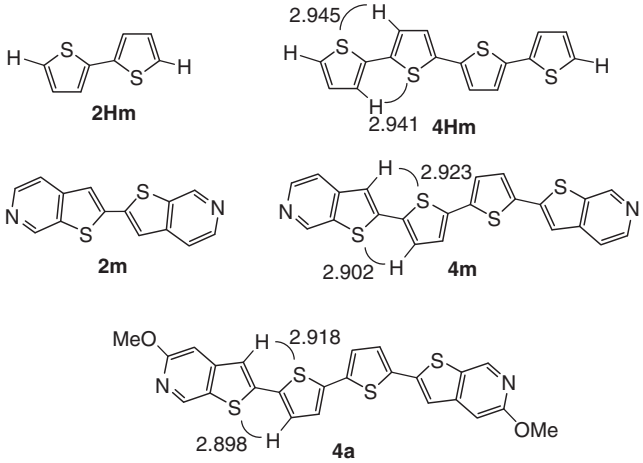


(a)



(b)

Figure 1. UV–vis absorption (a) and emission (b) spectra of pyridino end-capped oligothiophenes in chloroform.



Scheme 3. Model compounds and **4a** for DFT calculations. Numbers indicate the H–S contacts (Å) in the optimized geometries, derived from the calculations.

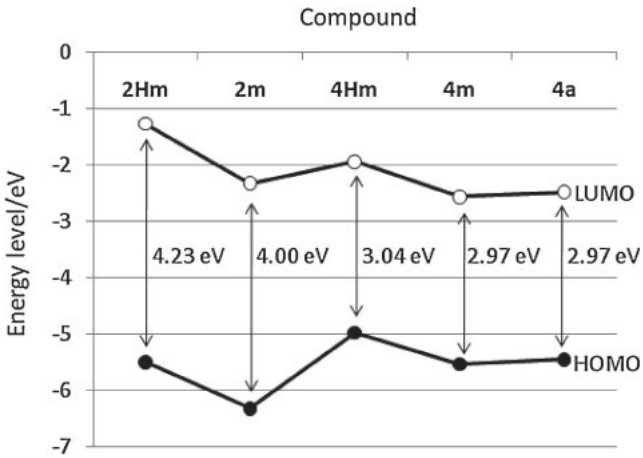
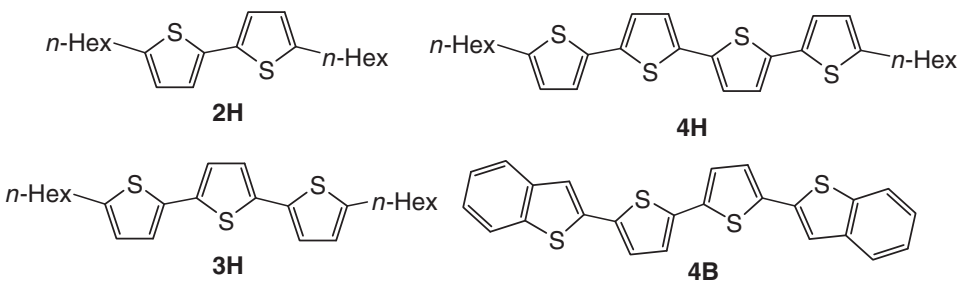


Figure 2. HOMO and LUMO energy levels of model compounds, derived from DFT calculations at the B3LYP/6-31G(d,p) level.



Scheme 2. Hexyl and benzo end-capped oligothiophenes (Refs. 6 and 7).

responsible for their blue-shifted absorptions relative to those of dihexyl analogs. It is also noteworthy that the introduction of pyridino groups at the ends lowers both the HOMO and LUMO levels significantly, and reduces the HOMO–LUMO energy gaps to an extent. One may consider the substitution effects, but the introduction of methoxy groups on **4m** elevates HOMO and LUMO energy levels only slightly, and exerts no significant influence on the energy gap.

Conclusion

In conclusion, we prepared pyridino end-capped oligothiophenes and demonstrated efficient conjugation in the system based on optical studies. The low-lying HOMOs and LUMOs of this type of compounds seem to provide opportunities to utilize them as organic device materials such as electron-transporting materials for organic light-emitting diodes, and host materials for photovoltaic cells with large V_{oc} (open circuit

voltage) and bipolar thin film transistor materials with stability toward oxidation. Studies to explore the applications of the present pyridino end-capped oligothiophenes are in progress.

Experimental

General Procedure. All reactions were carried out in dry nitrogen. Tetrahydrofuran (THF) and dimethylformamide (DMF) were distilled from sodium/benzophenone and calcium hydride, respectively, and were stored over activated molecular sieves until use. NMR spectra were recorded on JEOL Model LA-400 and EX-270 spectrometers. Mass spectra were measured on a SHIMADZU QP-5050A spectrometer, while HR-ESI-mass spectra were obtained on a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. UV and emission spectra were measured on Shimadzu UV-3150 and RF-5000 spectrophotometers, respectively. Emission quantum yields were determined in an integration sphere attached to a Hamamatsu Photonics C7473 Multi-Channel Analyzer. The usual workup mentioned bellow includes hydrolysis of the reaction mixture with water, extraction of organic products with chloroform, washing the extract with water, drying the washed extract over anhydrous magnesium sulfate, and evaporation of the solvent, in that order.

5-(Benzenesulfonyl)thieno[2,3-*c*]pyridine. A mixture of 3.77 g (22.6 mmol) of benzenesulfonyl cyanide and 3.08 g (22.6 mmol) of isobutyl chloroformate in 100 mL of xylene was heated to reflux. To this was added dropwise 3.03 g (15.0 mmol) of (3-methylthien-2-ylmethylene)aniline over a period of 30 min. The mixture was refluxed for an additional 1 h. After usual workup, the residue was chromatographed on silica gel to give 10.1 g (67% yield) of the title compound. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.48–7.62 (m, 4H), 7.90 (d, $J = 4.86$ Hz, 1H), 8.08–8.13 (m, 2H), 8.66 (d, $J = 1.1$ Hz, 1H), 9.16 (d, $J = 1.1$ Hz, 1H). MS: m/z 275 [M^+].

5-(Benzenesulfonyl)-2-bromothieno[2,3-*c*]pyridine. A mixture of 2.37 g (8.60 mmol) of 5-(benzenesulfonyl)thieno-[2,3-*c*]pyridine and 4.60 g (25.8 mmol) of NBS in 30 mL of acetonitrile was stirred at 70 °C for 6 h. To this were added 100 mL of acetic acid and 100 mL of water. After usual workup, the residue was recrystallized from toluene/ethyl acetate to give 2.49 g (81% yield) of the title compound. Mp 205 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.50–7.63 (m, 3H), 7.86 (s, 1H), 8.10–8.14 (m, 2H), 8.65 (d, $J = 0.8$ Hz, 1H), 9.13 (d, $J = 0.8$ Hz, 1H). MS: m/z 353 [M^+ for ^{79}Br].

5-Alkoxy-2-bromothieno[2,3-*c*]pyridine 1a–1c. A solution of 2-bromo-5-(benzenesulfonyl)thieno[2,3-*c*]pyridine (1.00 g, 2.82 mmol) and MeONa/MeOH prepared from sodium metal (2.5 g) and methanol (70 mL) in 30 mL of THF was heated to reflux overnight. After usual workup, the residue was subjected to column chromatography on silica gel (5% EtOAc in hexane as eluent) to yield **1a** as an orange solid (74%). Mp 117 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.02 (s, 3H), 7.10 (s, 1H), 7.63 (s, 1H), 8.68 (s, 1H). MS: m/z 245 [M^+]. Compounds **1b** and **1c** were obtained as orange solids in a fashion similar to that above, using *n*-BuONa/*n*-BuOH and *n*-HexONa/*n*-HexOH instead of MeONa/MeOH for **1b** and **1c**, respectively. Data for **1b**: 75% yield. Mp 55 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.99 (t, $J = 7.2$ Hz, 3H), 1.51–1.56 (m, 2H), 1.78–1.84 (m, 2H), 4.34 (t, $J = 6.5$ Hz, 2H), 7.09 (s, 1H), 7.62 (s, 1H), 8.67 (s, 1H). MS: m/z 287 [M^+]. Data for **1c**: 71% yield. Mp 42 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, $J = 6.8$ Hz, 3H), 1.33–1.37 (m, 4H), 1.45–1.53 (m, 2H), 1.78–1.86 (m, 2H), 4.32 (t, $J = 6.5$ Hz, 2H), 7.09 (s, 1H), 7.62 (s, 1H), 8.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.09, 22.65, 25.77, 29.18, 31.63, 67.06, 101.68, 106.24, 128.31, 130.21, 141.85, 146.87, 162.21. MS: m/z 315 [M^+].

2,2′-Bi(5-methoxythieno[2,3-*c*]pyridine) (2a). To a THF (15 mL) solution of (5-methoxythieno[2,3-*c*]pyridin-2-yl)lithium prepared by treating 0.400 g (1.64 mmol) of **1a** with 1.28 mL (2.13 mmol) of 1.66 M *n*-BuLi/hexane at −78 °C was added slowly 0.264 g (1.97 mmol) of $CuCl_2$ at the same temperature. After being stirred at −78 °C for 1 h, the mixture was hydrolyzed with dil. HCl. The organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and washed with dil. HCl to remove residual $CuCl_2$ then with water. After drying over anhydrous magnesium sulfate, the solvent was evaporated and the residue was subjected to column chromatography on silica gel (5% EtOAc in hexane as eluent) to yield **2a** as an orange solid (41% yield). Mp 258 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.00 (s, 6H), 7.02 (s, 2H), 7.76 (s, 2H), 8.78 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.1, 102.2, 120.9, 129.5, 141.1, 143.1, 148.7, 162.0. MS: m/z 328 [M^+]. HR-ESI-MS: m/z 329.0413 [$M + H^+$] (calcd for $C_{16}H_{13}O_2N_2S_2$, 329.0413).

Bis(5-alkoxythieno[2,3-*c*]pyridin-2-yl)thiophene 3a–3c and -bithiophene 4a–4c. A mixture of **1a** (200 mg, 0.819 mmol), 2,5-bis(tributylstannyl)thiophene (271 mg, 0.41 mmol), and [$Pd(PPh_3)_4$] (48 mg, 0.039 mmol) in DMF (15 mL) was stirred at 50 °C for 2 days. After usual workup, the residue was subjected to column chromatography on silica gel (20% ether in hexane as eluent) to yield **3a** as an orange solid (35% yield). Mp 196 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.04 (s, 6H), 7.38 (s, 2H), 7.47 (s, 2H), 7.78 (s, 2H), 8.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.24, 101.91, 125.75, 128.92, 130.49, 130.70, 135.79, 141.88, 146.20. MS: m/z 410 [M^+]. Anal. Calcd for $C_{20}H_{14}N_2O_2S_3$: C, 58.51; H, 3.44; N, 6.82%. Found: C, 58.59; H, 3.09; N, 6.65%. Compounds **3b**, **3c**, and **4a**–**4c** were obtained in a fashion similar to that above. Data for **4a**, purified by column chromatography on silica gel (10% EtOAc in hexane as eluent): 35% yield. Mp 246 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 (s, 6H), 7.26 (d, $J = 3.9$ Hz, 2H), 7.28 (d, $J = 3.9$ Hz, 2H), 7.47 (s, 2H), 7.74 (s, 2H), 8.74 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.2, 101.9, 124.3, 125.9, 128.9, 130.2, 130.7, 135.2, 136.5, 141.8, 146.1, 162.2. MS: m/z 492 [M^+]. Anal. Calcd for $C_{24}H_{16}N_2O_2S_4$: C, 58.51; H, 3.27; N, 5.69%. Found: C, 58.24; H, 3.09; N, 5.53%. Data for **3b**, purified by column chromatography on silica gel (10% ether in hexane as eluent): 40% yield. Mp 170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, $J = 7.2$ Hz, 6H), 1.47–1.55 (m, 4H), 1.77–1.85 (m, 4H), 4.35 (t, $J = 6.5$ Hz, 4H), 7.38 (s, 2H), 7.44 (s, 2H), 7.76 (s, 2H), 8.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.93, 19.31, 31.34, 66.63, 102.06, 125.79, 128.96, 130.37, 130.46, 135.80, 141.92, 146.23, 162.1. MS: m/z 494 [M^+]. Anal. Calcd for $C_{26}H_{26}N_2O_2S_3$: C, 63.13; H, 5.30; N, 5.66%. Found: C, 62.99; H, 5.13; N, 5.42%. Data for **4b**, purified by column chromatography on silica gel (10% EtOAc

in hexane as eluent): 42% yield. Mp 206 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, $J = 7.2$ Hz, 6H), 1.50–1.56 (m, 4H), 1.78–1.84 (m, 4H), 4.60 (t, $J = 6.5$ Hz, 4H), 7.26 (d, $J = 3.9$ Hz, 2H), 7.28 (d, $J = 3.9$ Hz, 2H), 7.45 (s, 2H), 7.73 (s, 2H), 8.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.92, 19.30, 31.34, 66.63, 102.09, 124.37, 125.96, 128.96, 130.18, 130.45, 135.29, 136.57, 141.89, 146.15, 162.09. MS: m/z 576 [M^+]. Anal. Calcd for $C_{30}H_{28}N_2O_2S_4$: C, 62.47; H, 4.89; N, 4.86%. Found: C, 62.30; H, 4.72; N, 4.78%. Data for **3c**, purified by column chromatography on silica gel (10% ether in hexane as eluent): 41% yield. Mp 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, $J = 7.2$ Hz, 6H), 1.33–1.37 (m, 8H), 1.45–1.52 (m, 4H), 1.78–1.85 (m, 4H), 4.35 (t, $J = 6.5$ Hz, 4H), 7.37 (s, 2H), 7.45 (s, 2H), 7.74 (s, 2H), 8.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.06, 22.62, 25.76, 29.21, 31.62, 66.91, 102.00, 125.75, 128.93, 130.32, 130.41, 135.75, 141.89, 146.18, 162.06. MS m/z: 550 [M^+]. HR-ESI-MS: m/z 551.1857 [$M + H^+$] (calcd for $C_{30}H_{35}O_2N_2S_3$, 551.1855). Data for **4c**, purified by column chromatography on silica gel (10% EtOAc in hexane as eluent): 45% yield. Mp 198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, $J = 7.2$ Hz, 6H), 1.33–1.37 (m, 8H), 1.45–1.51 (m, 4H), 1.79–1.86 (m, 4H), 4.35 (t, $J = 6.5$ Hz, 4H), 7.26 (d, $J = 3.9$ Hz, 2H), 7.28 (d, $J = 3.9$ Hz, 2H), 7.45 s, 2H), 7.73 (s, 2H), 8.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 22.64, 25.77, 29.23, 31.64, 66.94, 102.06, 124.37, 125.96, 128.96, 130.19, 130.43, 135.27, 136.56, 141.90, 146.12, 162.06. MS: m/z 632 [M^+]. Anal. Calcd for $C_{34}H_{36}N_2O_2S_4$: C, 64.52; H, 5.73; N, 4.43%. Found: C, 64.60; H, 5.69; N, 4.40%.

1,4-Bis(5-methoxythieno[2,3-*c*]pyridin-2-yl)benzene (3a′). A mixture of **1a** (0.771 g, 1.70 mmol), 1,4-bis(tributylstannyl)-benzene (0.280 g, 0.849 mmol), [$Pd(PPh_3)_4$] (49 mg, 0.040 mmol), CuI (16.2 mg, 0.085 mmol), and CsF (0.257 mg, 1.7 mmol) in 10 mL of DMF was stirred at 100 °C for 24 h. After usual workup, the residue was subjected to column chromatography on silica gel (10% EtOAc in hexane as eluent) to give **3a′** (75% yield). Mp 205 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 (s, 6H), 7.29 (s, 2H), 7.68 (s, 6H), 8.77 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.19, 101.63, 127.54, 128.81, 130.47, 130.97, 134.36, 136.03, 141.88, 146.88, 162.06. MS m/z: 404 [M^+]. HR-ESI-MS: m/z 405.0726 [$M + H^+$] (calcd for $C_{22}H_{17}O_2N_2S_2$, 405.0726).

Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **2a**, **3c**, and **3a′**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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