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Synthesis and properties of thieno[2,3-*d*:5,4-*d'*]bisthiazoles and their oxidized derivatives: Thionyl chloride as a sulfurative ring-fusing reagent towards thiophene-based ring-fused heteroaromatic compounds

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ABSTRACT

A new route to thiophene-ring-fused compounds with thionyl chloride as a sulfur source was developed. Use of an excess amount thionyl chloride directly gave the corresponding thiophene-ring-fused compound via further reduction of generated thiophene-*S*-oxide with excess thionyl chloride in some cases. One-pot reduction with tributylphosphine also gave thiophene-ring-fused compounds in good yields, and oxidation with $NaClO \cdot 5H_2O$ gave *S*-dioxides. In addition, one of the obtained thiazole-thiophene ring-fused compounds showed some unexpected mechanochromism behavior.

1. Introduction

Acenes [1,2] and picenes [3,4] are widely found in functional materials, thanks to their high highest occupied molecular orbital (HOMO) and low lowest unoccupied molecular orbital (LUMO), as well as strong intermolecular interactions (i.e., π … π, π … H) due to their ring-fused structural features. However, their main frames consist only of carbon atoms, and it is hard to control their fundamental properties. Recently, ladder-type heteroaromatic ring-fused compounds, heteroacenes, have attracted significant attention since the introduction of heteroatoms can endow materials with spectacular functions [5]. For example, the introduction of heavier main group atoms such as sulfur atoms usually raises HOMO and lowers LUMO, which leads to a narrow HOMO-LUMO gap to give a red shift of their absorption and emission wavelengths, which is similar to the effect of the extension of π-systems in acenes and picenes. Also, the intermolecular interaction of these compounds usually increases due to the effect of these elements. Therefore, the development of methods for the construction of such heteroacenes, in particular, sulfur-containing ring-fused

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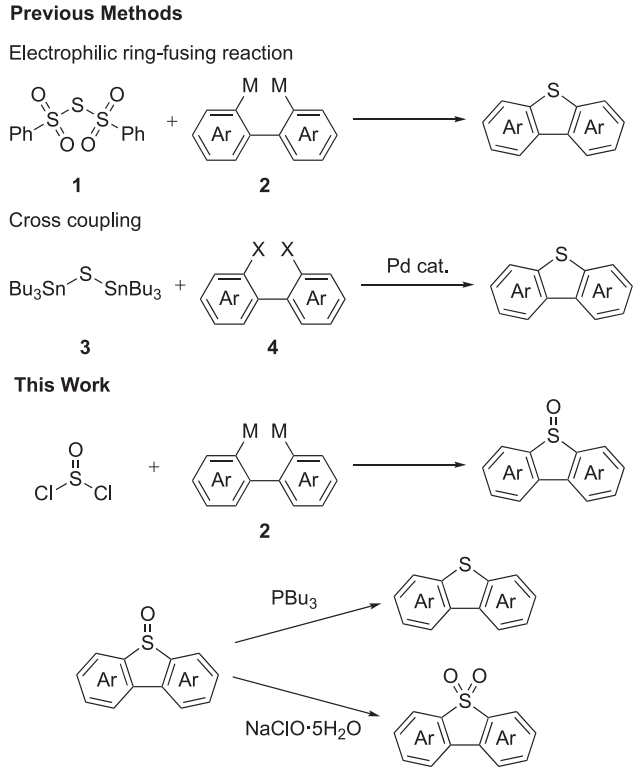
heteroacenes, thiophene-based ladder-type compounds is becoming increasingly important.

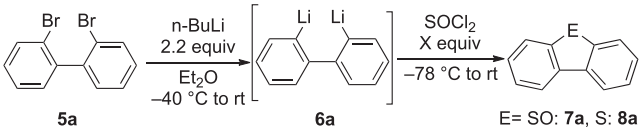


Previously, such thiophene-based ladder-type compounds were usually constructed by the reaction of an electrophilic sulfurizing reagent **1** and the corresponding biaryl dianion **2** [6]. Alternatively, formal nucleophilic sulfurizing reagent **3** could also be used in a cross-coupling-type reaction with dihalobiaryls **4** [7]. However, these methods needed rather uncommon sulfur compounds. It should be noted that the sulfurizing reagent compound **1** has recently become less available due to regulations regarding a "chemical weapon convention" for the raw material SCl_2 [8], and thus, the development of a substitute for such electrophilic sulfurizing reagent is highly desired. In this regard, readily available thionyl chloride is a very common electrophilic sulfur species. However, thionyl chloride has not been used as a sulfurizing reagent in such sulfurative ring-fusing reaction [9]. Herein we report a method for the synthesis of several oxidation levels of thiophene-based ladder-type compounds with thionyl chloride. Also, we found that one of the products, a thiazole-thiophene ring-fused compound, exhibited unexpected luminescent behavior, i.e., mechanochromism.

2. Results and discussions

First, we investigated the ring-fusing reaction of 2,2′-dibromobiphenyl (**5a**) as a substrate with thionyl chloride (Table 1). The biphenyl **5a** was treated with *n*-BuLi (2 equiv) in ether at −40 °C and then the mixture was allowed to warm to 0 °C. The resulting solution of dilithiated biphenyl **6a** was cooled to −78 °C. To this solution was added thionyl chloride (1 equiv) in one portion. Finally, the cool bath was gradually warmed to room temperature, and the resulting reaction mixture was quenched with water to give the corresponding ring-fused compound dibenzothiophene *S*-oxide (sulfoxide) **7a** in 42% yield, whereas the corresponding reduced dibenzothiophene (sulfide) **8a** was also obtained in 32% yield (entry 1). This result implied that the thionyl chloride acted as a reductant to give the reduced **8a** after formation of **7a**. In fact, the use of 2 equiv of thionyl chloride significantly improved the yield of **8a**, and **7a** was not detected in the reaction mixture (entry 2). In addition, treatment of quenched reaction mixture under conditions identical to those in entry 1 with thionyl chloride (1 equiv for the biphenyl skeleton) promoted the reduction to give sulfide **8a** as a sole product. On the other hand, slow addition of diluted thionyl chloride (1 equiv in Et_2O; 2.6 M) suppressed formation of the reduced product **8a**, and **7a** was obtained in 66% yield. Butylation of the lithiated compound **6a** proceeded in THF solution over ca. −30 °C prior to the reaction of thionyl chloride. In fact, quenching the reaction with water at that temperature before addition of thionyl chloride gave the butylated product in a similar yield. In addition, the ring-fusing reaction scarcely proceeded even if lithiation and the addition of thionyl chloride were carried out below −30 °C.

Table 1
Initial investigations of ring-fusing reaction of 2,2′-dibromobiphenyl.



Entry	X	Yields(%)[b]	
		7[a]	8a
1	1	42	32
2	2	N.D.	86
3	1[c]	66	13
4[d]	1	N.D.	N.D.

N.D.: not detected.
[a] The reaction was carried out in 0.1 M Et_2O solution.
[b] Isolated yield.
[c] Slow addition of diluted thionyl chloride in Et_2O (2.6 M).
[d] THF was used as a solvent instead of Et_2O. A large amount of butyl-containing compounds was observed in a complex mixture.

With these observations in mind, we applied this procedure to several dibromobiaryls (Fig. 1). Although the total yields of **7** and **8** were good to high, the ratio of sulfoxide **7** to sulfide **8** sensitively

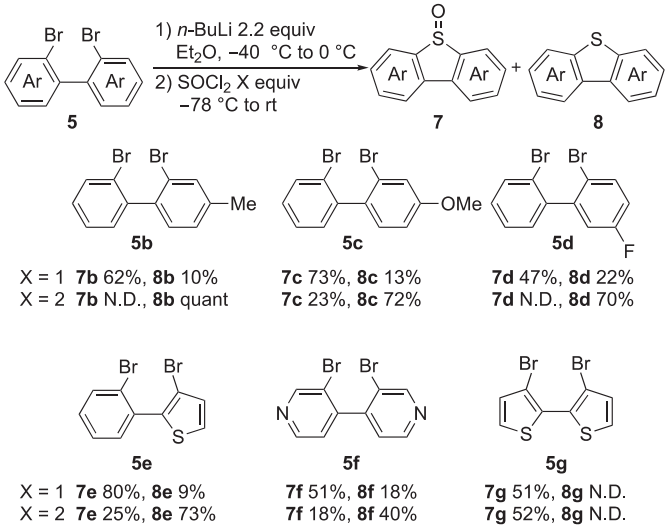


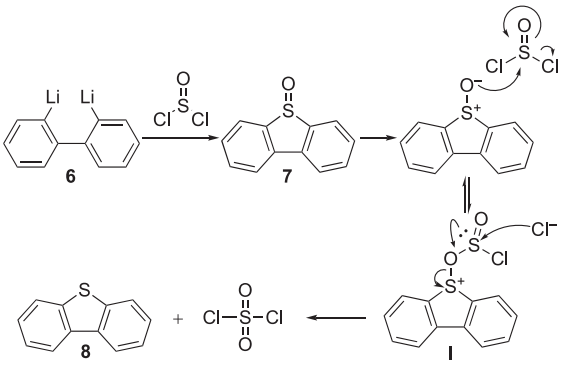
Fig. 1. Examples of ring-fusing reaction with thionyl chloride. Slow addition of diluted thionyl chloride (in Et_2O; *ca* 1 M) was applied to the reaction of X = 1. Neat thionyl chloride was used in the reaction of X = 2.

changed with the electron density of the aryl moieties. The reaction of biaryl bearing a relatively electron-donating methyl group (**5b**) and methoxy group (**5c**) with 1 equiv of thionyl chloride (slow addition of ca. 1 M Et_2O solution), mainly gave the corresponding sulfoxide **7b** and **7c** in respective yields of 62% and 73%. On the other hand, the biaryl bearing relatively electron-withdrawing fluorine (**5d**) underwent the reaction whereas further reduction of the generated sulfoxide took place to reduce the yield of **7d**. Relatively electron-rich phenylthiophene **5e** showed a tendency similar to that in the reactions of **5b** and **5c**. In all cases, the use of 2 equiv of thionyl chloride, which was added neat in one portion, improved the yield of sulfide **8b-e**. Meanwhile, in sharp contrast, electron-rich 2,2′-bithiophene **5g** did not give sulfide **8g** even with the use of an excess amount of thionyl chloride.

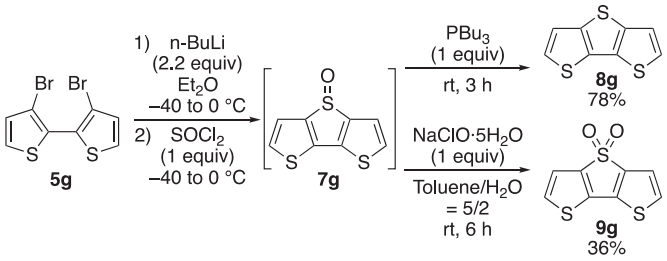
A proposed reaction pathway is shown in Scheme 1. Initially, the simple ring-fusing reaction of biaryl dianion and thionyl chloride takes place to give **7**. Meanwhile, the sulfoxide reversibly reacts with thionyl chloride to give intermediate **I**, and then attack of sulfur by chloride induces the elimination of sulfuryl dichloride (reduction of sulfoxide) to give the reduced compound, sulfide **8**. This reduction may proceed more easily with an electron-deficient skeleton due to the stability of the reduced form **8**, which can explain the decrease in the yield of **7d** and **7f** in the reaction with 1 equiv of thionyl chloride. Also, electron-rich **7g** was hardly reduced with an excess amount of thionyl chloride.

On the other hand, use of the high oxo-philicity of electron-rich phosphine, the product **7g** can be readily reduced to the corresponding sulfide **8g** by treatment with tributylphosphine as a reductant, and this cyclization and reduction could be carried out in a one-pot procedure without any quenching process in the first step (Scheme 2, upper). Also, treatment of **7g** with $NaClO \cdot 5H_2O$ [10] as an oxidant gave the corresponding sulfones **9g**; this reaction can also be carried out in a one-pot procedure, although water-quenching of the mixture is needed in the first step (Scheme 2, lower). In addition, **9g** was not produced at all when sulfuryl chloride (SO_2Cl_2) was used instead of thionyl chloride.

We then synthesized thioazole-thiophene ring-fused compounds **10a**-**12a** with the present methods, since we were interested in the properties of this structure regarding derivatives of thiazole-ring-fused compounds [7]. Short alkyl chains were introduced to the compounds to improve the solubility of the resulting products. Density functional theory (DFT) calculations for the model compounds [11] showed that the introduction of oxygen atoms to the central sulfur atom greatly influences their LUMO levels (Fig. 2) [12], which should significantly affect their properties. The dibrominated substrate **15** was prepared via oxidative homocoupling of 2-alkylarylthiazoles **13** [13] followed by bromination of resulting **14**. This bromination hardly proceeded, probably



Scheme 1. Proposed reaction pathway.



Scheme 2. One-pot procedure for formation of several oxidation levels of dithienothiophene.

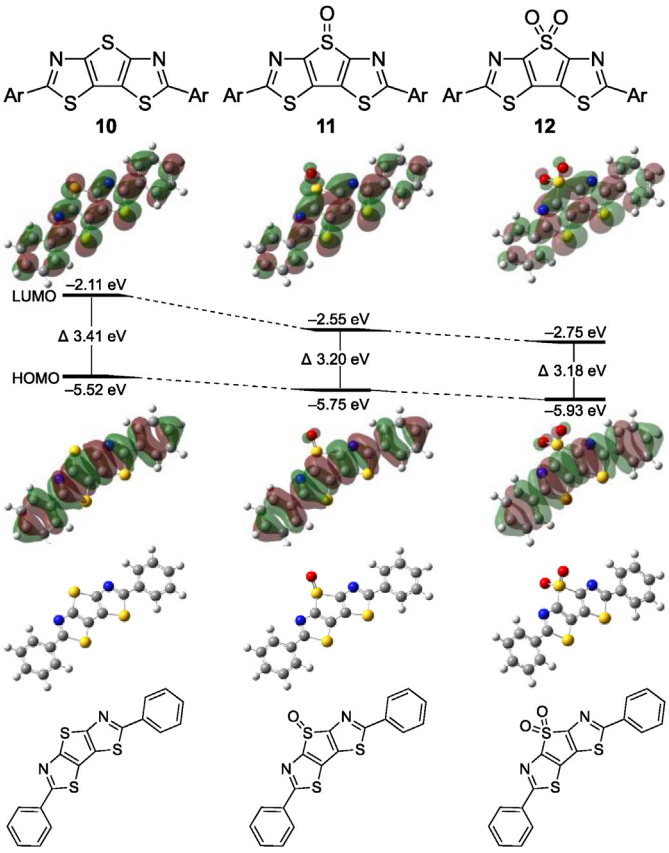
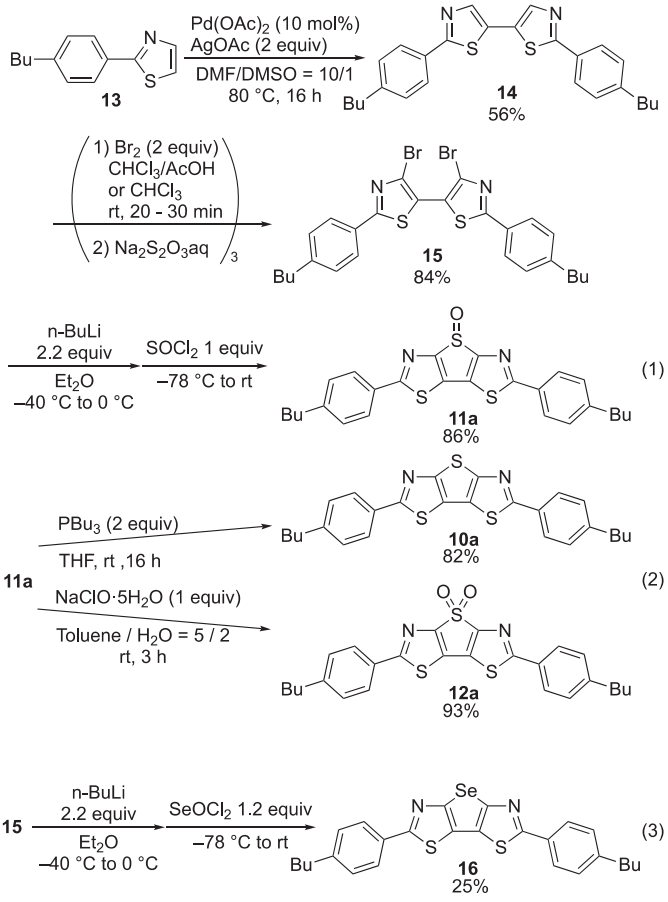


Fig. 2. DFT calculations for compounds **10**–**12** at the B3LYP//6-31G(d,p) level.

due to randomly occurring competitive bromination at the sulfur atom that significantly reduced the π-nucleophilicity of the thiazole ring. However, repeated treatment of the quenched crude mixture with bromine achieved full conversion. The present ring-fusing reactions with thionyl chloride furnished compounds **11a** in 86% yield (eq 1). The obtained **11a** could be readily converted to the corresponding **10a** and **12a** in high efficiency by the respective reactions described above (eq 2). Although **10a** and **12a** were robust under ambient conditions even in the solutions, **11a** was relatively unstable and some decomposition was observed in solution for measurement of photophysical properties (*vide infra*) and stored sample after a couple of weeks. Notably, the use of seleninyl chloride instead of thionyl chloride for the ring-fusing reaction also gave the corresponding **16** in a similar manner (eq 3). The yield of **16** did not significantly change with the amount of seleninyl chloride used. In this case, the corresponding firstly generated selenophene oxide may be easily decompose or reduced by unreacted

$SeOCl_2$ resulting in **16** as a sole product because of its stability.



The photophysical properties of obtained **10a**-**12a** were measured (Figs. 3 and 4 and Table 2). UV/vis absorptions of these compounds in chloroform solutions showed a large red-shift of the absorption on oxidized compounds **11a** and **12a**, comparable to the results of the DFT calculations. The fluorescence of these compounds in solution also showed a similar tendency, though the emission efficiency (quantum yield) significantly improved at higher oxidation levels. On the other hand, measurements in the solid phase (crystallization from $CHCl_3$ solution by evaporation) showed different absorption and emission behaviors. Broad absorptions were observed with all the compounds, and red-shifted emissions were also observed, in particular with sulfide **10a**. The emission efficiency of **12a** in the solid phase reached $\Phi = 0.59$.

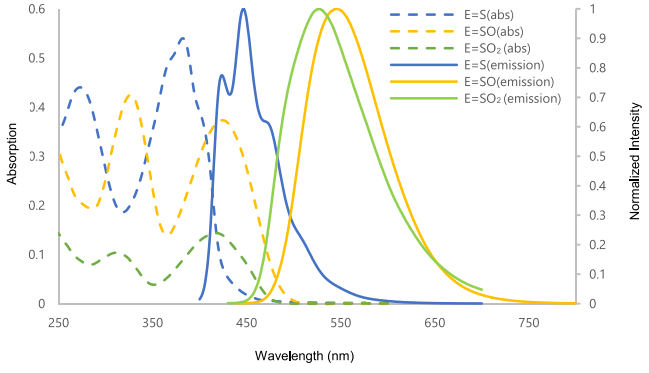


Fig. 3. UV/Vis absorption and fluorescence of compounds **10**–**12** in solution (in $CHCl_3$).

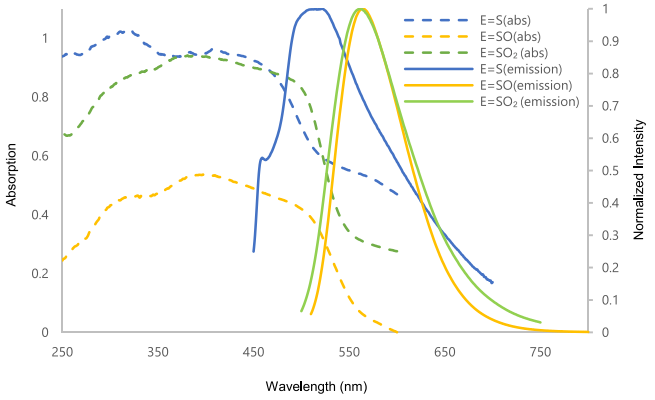
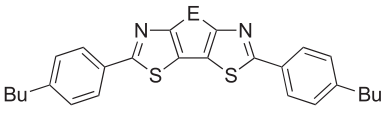


Fig. 4. UV/Vis absorption and fluorescence of compounds **10**–**12** in the solid phase. Dashed lines indicate absorption spectra and solid lines indicate emission spectra.

Table 2
UV/Vis absorption and fluorescence of compounds **10**–**12** in $CHCl_3$ solution[a] and solid phases.



entry	E	condition	UV–vis		fluorescence	
			λ_{abs}(nm)	log ε	λ_{em}(nm)	Φ_F[b]
1	S	10^{-5} M	273	4.64	424	0.35
	10a		382	4.73	447	
					471	
2		solid	318		505	0.15
			361		508	
			384		509	
			411			
3	SO	10^{-5} M	327	4.63	546	0.71
	11a		424	4.57		
4		solid	322		563	0.24
			399		565	
			489			
5	SO_2	10^{-5} M	312	4.02	527	0.84
	12a		417	4.12		
6		solid	327		560	0.59
			381		563	
			496			

[a] Measured in 1×10^{-5} M $CHCl_3$ solution.
[b] Absolute quantum yields.

Meanwhile, we thought that the diverse aggregation of molecules in the solid phase could account for the broad absorption. In fact, compound **10a** showed absorption and emission color change under the application of a physical stimulus (mechanochromism). A significant blue shift (ca. 50 nm) of the emission was observed with **10a** after grinding (Fig. 5) along with the disappearance of diffraction peaks in powder X-ray analysis (Fig. 6). Both the absorption and emission wavelengths got closer to those in the solution phase, and those peaks partly fitted the shoulder peaks in the solution phase. These observations implied that the emission mechanism of the amorphous phase of the compound got closer to that in the solution phase. Some of the intermolecular interactions, i.e., π … π and/or π … H, probably induced excimer emission in the unground solid phase. We did not obtain single crystals of compounds **10**–**12** that were suitable for X-ray structure analysis, and the packing pattern and structure still remain unknown to discuss the interaction. Further investigations of the photophysical

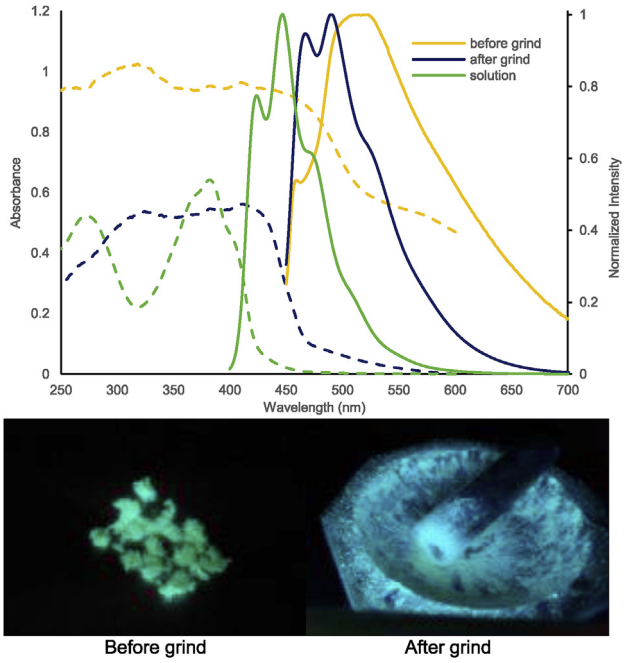


Fig. 5. Fluorescence of **10a** in the solid phase before and after grinding. Dashed lines indicate absorption spectra and solid lines indicate emission spectra. Images of fluorescencewere obtained under irradiation at 365 nm using handy UV light.

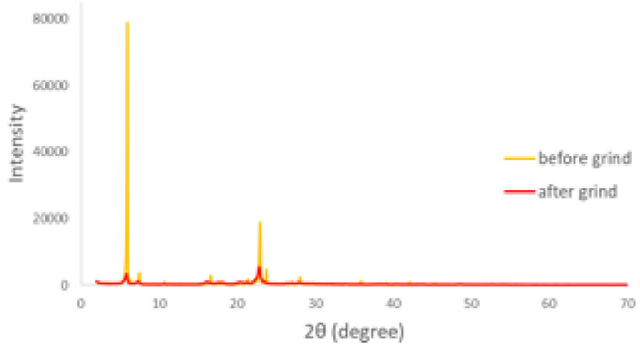


Fig. 6. Powder X-ray diffraction of **10a** before and after grinding.

behaviors of the thiazole–thiophene ring-fused compounds are underway by our group.

3. Conclusion

In conclusion, we developed a new route to thiophene-ring-fused compounds with thionyl chloride as a sulfur source. Use of an excess amount of thionyl chloride directly gave the corresponding thiophene-ring-fused compound via further reduction of the initially generated thiophene-*S*-oxide with excess thionyl chloride in some cases. Thionyl chloride costs ca. 1/6000 the cost of a conventional sulfur source, bis(phenylsulfonyl)sulfide (**1**) ($52,250/mol for compound **1** vs $9/mol for thionyl chloride; Aldrich catalog prices in 2020). Thus, even with the use of an excess amount of thionyl chloride, the cost of the sulfur source can be significantly reduced. In addition, the obtained thiazole-thiophene ring-fused compounds showed some unexpected photophysical behavior. Studies on the origin of such unexpected behavior and the application of **10**–**12** in functional materials such as organic semiconducting material and photovoltaic devices are underway by our group.

4. Experimental

4.1. General procedure A: synthesis of 2,2′-Dibromobiphenyls *5b*–*5d*

An oven-dried flask was charged with 2-bromoarylboronic acid (1.1 equiv), $Pd(PPh_3)_4$ (5 mol %), and Na_2CO_3 (2 equiv). After the flask was degassed and filled with Ar, substituted 1-bromo-2-iodobenzene (2 mmol), toluene (8 mL), ethanol (4 mL) and H_2O (4 mL) were added via syringe. The mixture was stirred at 110 °C. After the reaction was complete (monitored by TLC) and the mixture was cooled to room temperature, Et_2O was added. The organic layer was separated, washed with brine, and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by silica gel chromatography (hexane).

4.2. 2,2′-dibromo-4-methyl-1,1′-biphenyl (*5b*) [14]

This compound was synthesized according to the general procedure, using 2-bromophenylboronic acid (0.44 g, 2.2 mmol) and 3-bromo-4-iodotoluene (0.29 mL, 2 mmol). The title compound was isolated as a colorless oil (0.67 g, quant). Rf = 0.50 (Hexane); ^{1}H NMR ($CDCl_3$) δ 7.66–7.44 (m, 1H, Ar), 7.49 (s, 1H, Ar), 7.35 (dt, *J* = 7.1, 1.2 Hz, 1H, Ar), 7.25–7.21 (m, 2H, Ar), 7.17 (dd, *J* = 7.7, 0.9 Hz, 1H, Ar), 7.11 (d, *J* = 7.7 Hz, 1H, Ar), 2.38 (s, 3H, $C\underline{H}_3$).

4.3. 2,2′-dibromo-4-methoxy-1,1′-biphenyl (*5c*)

This compound was synthesized according to the general procedure, using 2-bromophenylboronic acid (0.44 g, 2.2 mmol) and 2-bromo-1-iodo-4-methoxybenzene (0.30 mL, 2 mmol). The title compound was isolated as a colorless solid (0.72 g, quant). Rf = 0.33 (Hexane). ^{1}H NMR ($CDCl_3$) δ 7.67–7.64 (m, 1H, Ar), 7.35 (dt, *J* = 7.6, 1.4 Hz, 1H, Ar), 7.25–7.21 (m, 3H, Ar), 7.15 (d, *J* = 8.5 Hz, 1H, Ar), 6.92 (dd, *J* = 8.5, 2.7 Hz, 1H, Ar), 3.85 (s, 3H, $OC\underline{H}_3$). ^{13}C NMR δ 159.7, 141.9, 134.6, 132.6, 131.6, 131.5, 129.3, 127.2, 124.3, 123.8, 117.7, 113.4, 55.7. HRMS (EI) Calcd for $C_{13}H_{10}^{79}Br_2O$: 339.9098, found: 339.9104.

4.4. 2,2′-dibromo-5-fluoro-1,1′-biphenyl (*5d*) [14]

This compound was synthesized according to the general procedure, using 2-bromophenylboronic acid (0.44 g, 2.2 mmol) and 1-bromo-4-fluoro-2-iodobenzene (0.26 mL, 2 mmol). The title compound was isolated as a colorless oil (0.71 g, quant); Rf = 0.50 (Hexane). ^{1} H NMR ($CDCl_3$) δ 7.67 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar), 7.63–7.59 (m, 1H, Ar), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H, Ar), 7.30–7.21 (m, 2H, Ar), 7.02–6.98 (m, 2H, Ar).

4.5. 3-Bromo-2-(2-bromophenyl)thiophene (*5e*) [15]

An oven-dried flask was charged with (2-bromophenyl)boronic acid (0.66 g, 3.3 mmol), $Pd(PPh_3)_4$ (0.19 g, 0.15 mmol), and Na_2CO_3 (0.64 g, 6 mmol). After the flask was degassed and filled with Ar, 2,3-dibromothiophene (0.72 g, 3 mmol), 1,4-dioxane (8 mL) and H_2O (2 mL) were added via syringe. The mixture was stirred at 100 °C for 14 h. After the reaction was complete (monitored by TLC) and cooled to room temperature, Et_2O was added. The organic layer was separated, washed with brine, and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by silica gel chromatography (hexane) to give the title compound (0.86 g, 88%) as a colorless solid. Rf = 0.5 (Hexane). ^{1}H NMR ($CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 1H, thiophene), 7.42–7.34 (m, 3H, Ar), 7.28 (ddd, *J* = 8.0, 6.7, 2.5 Hz, 1H, Ar), 7.07 (d, *J* = 5.3 Hz, 1H,

thiophene).

4.6. 3,3′-dibromo-4,4′-bipyridine (**5f**) [16]

To a solution of lithium diisopropylamide (15 mmol) in tetrahydrofuran (50 mL), 3-bromopyridine (2.4 g, 15 mmol) was added dropwise at −98 °C. The orange suspension was stirred for 1 h at that temperature and $CuCl_2$ (4.9 g, 36 mmol) was added. The resulting mixture was allowed to warm to room temperature, the reaction flask was backfilled with Ar, and stirring was continued overnight. The volatiles were removed under reduced pressure and the brown solid was taken up in H_2O (30 mL), 25%NH_4OHaq (15 mL) and sat. NH_4Cl (15 mL). This mixture was extracted three times with chloroform, and the combined organic layer was dried over Na_2SO_4 and concentrated to give a brown oil, which was purified by column chromatography (hexane: EtOAc = 2:1) to give the title product (1.3 g, 53%) as an off-white powder. Rf = 0.3 (Hexane: EtOAc = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 8.85 (s, 2H, Ar), 8.62 (d, J = 4.9 Hz, 2H, pyridine), 7.16 (d, J = 4.9 Hz, 2H, pyridine).

4.7. General procedure for the synthesis of ring-fused compounds using thionyl chloride

A suspension of dibromobiaryl in Et_2O was cooled to −40 °C. To this suspension was slowly added *n*-BuLi (2.2 equiv) dropwise. The mixture was gradually warmed to 0 °C, and then cooled again to −78 °C. After the mixture was stirred for 10 min, thionyl chloride was added in one portion or dropwise as a diluted solution in Et_2O. The mixture was gradually warmed to room temperature, and the resulting residue was quenched with sat. $NaHCO_3$aq and extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography to give thiophene and/or thiophene-oxide.

4.8. Dibenzo[b,d]thiophene-5-oxide (**7a**) [17]

This compound was synthesized according to the general procedure, using 2,2′-dibromo-1,1′-biphenyl (0.16 g, 0.5 mmol), *n*-BuLi (1.6 M in hexane, 0.7 mL, 1.1 mmol), and diluted thionyl chloride (2.7 M in Et_2O, 0.19 mL, 0.5 mmol), in Et_2O (5 mL). The title compound was isolated as a colorless solid (0.066 g, 66%). Rf = 0.12 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 7.6 Hz, 2H, Ar), 7.80 (d, J = 7.7 Hz, 2H, Ar), 7.59 (td, J = 7.6, 0.9 Hz, 2H, Ar), 7.49 (td, J = 7.6, 0.9 Hz, 2H, Ar).

4.9. Dibenzo[b,d]thiophene (**8a**) [18]

This compound was synthesized according to the general procedure, using 2,2′-dibromo-1,1′-biphenyl (0.16 g, 0.5 mmol), *n*-BuLi (1.6 M in hexane, 0.7 mL, 1.1 mmol), and neat thionyl chloride (0.08 mL, 1 mmol), in Et_2O (5 mL). The title compound was isolated as a colorless solid (0.079 g, 86%). Rf = 0.75 (Hexane: CH_2Cl_2 = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 8.17−8.15 (m, 2H, Ar), 7.87−7.84 (m, 2H, Ar), 7.47−7.44 (m, 4H, Ar).

4.10. 3-Methyldibenzo[b,d]thiophene-5-oxide (**7b**)

This compound was synthesized according to the general procedure, using 2,2′-dibromo-4-methyl-1,1′-biphenyl (0.17 g, 1.0 mmol), *n*-BuLi (1.6 M in hexane, 0.69 mL, 1.1 mmol), and diluted thionyl chloride (2.7 M in Et_2O, 0.19 mL, 1.0 mmol), in Et_2O (5 mL). The title compound was isolated as a white solid (0.069 g, 62%). Rf = 0.10 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 1H, Ar), 7.78 (s, 1H, Ar), 7.74 (d, J = 7.6 Hz, 1H, Ar), 7.67 (d, J = 8.1 Hz, 1H, Ar), 7. 57 (t, J = 7.6 Hz, 1H, Ar), 7.45 (d, J = 7.6 Hz, 1H, Ar), 7.38 (d, J = 8.1 Hz, 1H, Ar), 2.46 (s, 3H, $C\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 145.3, 145.0, 140.2, 137.3, 134.5, 133.4, 132.6, 129.1, 128.0, 127.5, 121.8, 121.7, 21.5. HRMS (EI) Calcd for $C_{13}H_{10}OS$:214.0452, found: 214.0452.

4.11. 3-Methyldibenzo[b,d]thiophene (**8b**) [19]

This compound was synthesized according to the general procedure, using 2,2′-dibromo-4-methyl-1,1′-biphenyl (0.20 mL, 1.0 mmol), *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol), and neat thionyl chloride (0.16 mL, 2.0 mmol), in Et_2O (10 mL). The title compound was isolated as a colorless solid (0.19 g, quant). Rf = 0.75 (Hexane: EtOAc = 4 : 1). ^{1}H NMR ($CDCl_3$) δ 8.02 (m, 1H, Ar), 7.95 (d, J = 8.0 Hz, 1H, Ar), 7.75 (m, 1H, Ar), 7.57 (s, 1H, Ar), 7.35 (m, 2H, Ar), 7.19 (d, J = 8.0 Hz, 1H, Ar), 2.43 (s, 3H, $C\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 142.2, 139.8, 139.3, 137.0, 135.7, 133.3, 129.4, 126.4, 126.0, 124.4, 122.9, 121.3 (Ar), 21.8 ($C\underline{H}_3$).

4.12. 3-Methoxydibenzo[b,d]thiophene-5-oxide (**7c**)

This compound was synthesized according to the general procedure, using 2,2′-dibromo-4-methoxy-1,1′-biphenyl (0.34 g, 1.0 mmol), *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol), and diluted thionyl chloride (1.3 M in Et_2O, 0.78 mL, 1.0 mmol), in Et_2O (10 mL). The title compound was isolated as a colorless solid (0.17 g, 73%). Rf = 0.050 (CH_2Cl_2).; mp 119.4 °C(dec). IR (KBr) 3459, 2933, 1599, 1451, 1430, 1302, 1250, 1215, 847, 770, 711, 583, 554, 486 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 1H, Ar), 7.70 (d, J = 8.5 Hz, 2H, Ar), 7.56 (d, J = 7.6 Hz, 1H, Ar), 7.51 (d, J = 2.2 Hz, 1H, Ar), 7.11 (dd, J = 8.1, 2.2 Hz, 2H, Ar), 3.91 (s, 3H, $OC\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 161.8, 146.7, 144.6, 137.3, 132.7, 129.6, 128.3, 127.5, 122.9, 121.2, 119.5, 111.9 (Ar), 56.0 ($OC\underline{H}_3$). MS (EI) *m/z* 230 (26, M+), 214 (18, $[M - O]^+$). HRMS (EI) Calcd for $C_{13}H_{10}OS$: 230.0402, found: 230.0407.

4.13. 3-Methoxydibenzo[b,d]thiophene (**8c**) [19]

This compound was synthesized according to the general procedure, using 2,2′-dibromo-4-methoxy-1,1′-biphenyl (0.27 g, 0.8 mmol), *n*-BuLi (1.6 M in hexane, 1.1 mL, 1.8 mmol), and neat thionyl chloride (0.12 mL, 1.6 mmol) in Et_2O (10 mL). The title compound was isolated as a colorless solid (0.12 g, 72%). Rf = 0.73 (Hexane: CH_2Cl_2 = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 8.06−8.01 (m, 2H), 7.80 (td, J = 7.8, 1.1 Hz, 1H), 7.39 (m, 3H), 7.05 (dd, J = 8.7, 2.4 Hz, 1H), 3.91 (s, 3H, $OC\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 159.2, 141.1, 138.7, 135.6, 129.2, 125.6, 124.5, 122.8, 122.4, 120.9, 113.5, 106.0 (Ar), 56.0 ($OC\underline{H}_3$).

4.14. 2-Fluorodibenzo[b,d]thiophene-5-oxide (**7d**)

This compound was synthesized according to the general procedure, using 2,2′-dibromo-5-fluoro-1,1′-biphenyl (0.17 g, 0.5 mmol), *n*-BuLi (1.6 M in hexane, 0.69 mL, 1.1 mmol), and diluted thionyl chloride (2.7 M in Et_2O, 0.19 mL, 1 mmol), in Et_2O (5 mL). The title compound was isolated as a colorless solid (0.053 g, 47%). Rf = 0.10 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.01−7.95 (m, 2H, Ar), 7.77 (d, J = 7.6 Hz, 1H, Ar), 7.63 (td, J = 7.6, 0.9 Hz, 1H, Ar), 7.54 (td, J = 7.6, 0.9 Hz, 1H, Ar), 7.48 (dd, J = 8.5, 2.7 Hz, 1H, Ar), 7.19 (td, 8.5, 2.7 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$) δ 165.8 (d, J = 254.3 Hz), 146.3, 140.8, 140.2, 136.1, 132.8, 130.3129.6 (d, J = 11.6 Hz), 127.7, 122.3, 116.8 (d, J = 23.1 Hz), 109.5 (d, J = 26.0 Hz). HRMS (EI) Calcd for $C_{12}H_7FOS$: 218.0202, found: 218.0201.

4.15. 2-Fluorodibenzo[b,d]thiophene (**8d**) [19]

This compound was synthesized according to the general procedure, using 2,2′-dibromo-5-fluoro-1,1′-biphenyl (0.19 mL,

1.0 mmol), *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol), and neat thionyl chloride (0.075 mL, 1.0 mmol), in Et_2O (10 mL). The title compound was isolated as a colorless solid (0.14 g, 70%). Rf = 0.70 (Hexane: EtOAc = 4 : 1). ^{1}H NMR ($CDCl_3$) δ 8.03–8.01 (m, 1H, Ar), 7.79–7.69 (m, 3H, Ar), 7.41 (td, *J* = 2.75 Hz, 2H, Ar), 7.14 (td, *J* = 2.75 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$) δ 161.1, (*J* = 242.4 Hz), 140.8, 137.0, 136.1, 134.6, 127.3, 124.5, 123.9 (*J* = 9.4 Hz), 123.1, 121.9, 115.1 (*J* = 24.4 Hz), 107.9, (*J* = 23.5 Hz). ^{19}F NMR ($CDCl_3$) δ −118.

4.16. Benzo[b]thieno[2,3-d]thiophene-4-oxide (**7e**) [9]

This compound was synthesized according to the general procedure, using 3-bromo-2-(2-bromophenyl)thiophene (0.32 g, 1 mmol), *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol), and diluted thionyl chloride (1.3 M in Et_2O, 0.78 mL, 1 mmol) in Et_2O (10 mL). The title compound was isolated as a colorless solid (0.16 g, 80%). Rf = 0.05 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.98 (d, *J* = 3.2 Hz, 1H, thiophene), 7.50 (d, 2H, *J* = 4.94 Hz, Ar), 7.31–7.43 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$) δ 149.6, 146.1, 145.4, 133.1, 132.5, 130.1, 128.4, 127.5, 123.8, 121.4.

4.17. Benzo[b]thieno[2,3-d]thiophene (**8e**) [9]

This compound was synthesized according to the general procedure, using 3-bromo-2-(2-bromophenyl)thiophene (0.16 g, 0.50 mmol), *n*-BuLi (1.5 M in hexane, 0.73 mL, 1.1 mmol), and thionyl chloride (0.038 mL, 0.50 mmol), in Et_2O (8 mL). The title compound was isolated as a white solid (0.060 g, 63%). Rf = 0.85 (Hexane: CH_2Cl_2 = 1 : 1). ^{1}H NMR ($CDCl_3$) δ 7.86–7.84 (d, 2H, *J* = 8.1, 0.9 Hz, Ar), 7.50 (d, 1H, *J* = 4.94 Hz, Ar), 7.31–7.43 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$) 142.8, 138.1, 135.0, 132.7, 128.1, 124.8, 124.5, 124.0, 121.9, 120.4.

4.18. Thieno[2,3-c:5,4-c']dipyridine-9-oxide (**7f**)

This compound was synthesized according to the general procedure, using 3,3′-dibromo-4,4′-bipyridine (0.32 g, 1 mmol), *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol), and diluted thionyl chloride (1.3 M in Et_2O, 0.78 mL, 1 mmol) in Et_2O (10 mL). The title compound was isolated as a brown solid (0.10 g, 51%). Rf = 0.03 (CH_2Cl_2: MeOH = 100 : 1). mp 189.2 °C(dec). IR (KBr) 3428, 3058, 2924, 2359, 1805, 1713, 1571, 1555, 1470, 1414, 1103, 1035, 854, 730, 622, 568, 453, 414 cm^{-1}. ^{1}HNMR ($CDCl_3$) δ 9.32 (s, 2H, pyridine), 8.97 (d, *J* = 5.0 Hz, 2H, pyridene), 7.84 (d, *J* = 5.0 Hz, 2H, pyridene). ^{13}C NMR ($CDCl_3$) δ 153.8, 149.2, 142.9, 141.4, 117.6. MS (EI) *m*/*z* 202 (27, M^+), 186 (46, $[M-O]^+$). HRMS (EI) Calcd for $C_{10}H_6N_2OS$: 202.0201, found: 202.0205.

4.19. Thieno[2,3-c:5,4-c']dipyridine (**8f**) [9]

This compound was synthesized according to the general procedure, using 3,3′-dibromo-4,4′-bipyridine **5f** (0.10 g, 0.33 mmol), *n*-BuLi (1.6 M in hexane, 0.45 mL, 0.72 mmol), and neat thionyl chloride (0.025 mL, 0.33 mmol) in Et_2O (8.0 mL). The title compound was isolated as a brown solid (0.034 g, 51%). Rf = 0.08 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 9.28 (s, 2H, Ar), 8.75 (d, *J* = 5.2 Hz, 2H, Ar), 8.11 (d, *J* = 5.2 Hz, 2H, Ar).

4.20. Dithieno[3,2-b:2′,3′-d]thiophene-4-oxide (**7g**)

This compound was synthesized according to the general procedure, using 3,3′-dibromo-2,2′-bithiophene **5g** (0.32 g, 1.0 mmol), *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol), and neat thionyl chloride (0.08 mL, 1 mmol) in Et_2O (10 mL). The title compound was isolated as a yellow solid (0.10 g, 50%). Rf = 0.10 (CH_2Cl_2). mp 134 °C(dec). IR (KBr) 3426, 3118, 3101, 3063, 1295, 1182, 1168, 1033, 879, 796, 706, 651, 632, 483, 452 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.39 (d, *J* = 5.0 Hz, 2H, thiophene), 7.33 (d, *J* = 5.0 Hz, 2H, thiophene). ^{13}C NMR ($CDCl_3$) δ 150.2, 138.6, 128.5, 124.0. HRMS (EI) Calcd for $C_7H_4OS_3$: 211.9424, found: 211.9418.

4.21. Dithieno[3,2-b:2′,3′-d]thiophene (**8g**) [20]

A suspension of 3,3′-dibromo-2,2′-bithiophene **5g** (0.16 g, 0.50 mmol) in Et_2O (5 mL) was cooled to −40 °C. To this suspension was added *n*-BuLi (1.6 M in hexane, 0.7 mL, 1.1 mmol). The mixture was gradually warmed to 0 °C, and then cooled again to −78 °C. After the mixture was stirred for 10 min, thionyl chloride was added. The mixture was gradually warmed to room temperature, and to this was added PBu_3 (0.15 mL, 0.5 mmol). After the mixture was stirred for 3 h, the resulting residue was quenched with sat. $NaHCO_3$aq. and extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (CH_2Cl_2) to give the title compound (0.078 g, 78%) as a colorless solid. Rf = 0.9 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.36 (d, *J* = 5.4 Hz, 2H, thiophene), 7.16 (d, *J* = 5.4 Hz, 2H, thiophene).

4.22. Dithieno[3,2-b:2′,3′-d]thiophene-4,4-dioxide (**9g**) [21]

A suspension of 3,3′-dibromo-2,2′-bithiophene **5g** (0.16 g, 0.5 mmol) in Et_2O (5 mL) was cooled to −40 °C. To this suspension was added *n*-BuLi (1.6 M in hexane, 0.7 mL, 1.1 mmol). The mixture was gradually warmed to 0 °C, then cooled again to −78 °C. After the mixture was stirred for 10 min, neat thionyl chloride was added. The mixture was gradually warmed to room temperature, and the resulting residue was quenched with $NaHCO_3$ aq. and extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. To the resulting residue were added toluene, H_2O and NaOCl. $5H_2O$ (83 mg, 0.5 mmol) and the mixture was stirred for 6 h. The resulting residue was quenched with $NaHCO_3$aq. and extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2) to give the title compound (41 mg, 36%) as a yellow solid. Rf = 0.5 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.36 (d, *J* = 4.9 Hz, 2H, thiophene), 7.23 (d, *J* = 4.9 Hz, 2H, thiophene).

4.23. 2-(4-Butylphenyl)thiazole (**13**)

To a solution of 4-butyliodobenzene (5.2 g, 20 mmol) in DMF (40 mL) was added $Pd(OAc)_2$ (0.23 g, 1 mmol), CuI (7.6 g, 40 mmol) and thiazole (2.8 mL, 40 mmol). The mixture was stirred at 140 °C for 40 h. After the reaction mixture was cooled to room temperature, the mixture was passed through a silica gel pad with EtOAc as an eluent and filtrate was concentrated *in vacuo*. The residue was extracted with Et_2O and NH_3OHaq. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was roughly purified by flash column chromatography on silica gel (hexane: EtOAc = 30 : 1) to give the title compound (2.9 g, 67%) as a yellow oil with a small amount of impurities. This compound was used in the next reaction without further purification. ^{1}H NMR ($CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H, Ar), 7.84 (d, *J* = 3.4 Hz, 1H, thiazole), 7.28 (d, *J* = 3.4 Hz, 1H, thiazole), 7.25 (d, *J* = 8.2 Hz, 2H, Ar), 2.58 (t, *J* = 7.2 Hz, 2H, Ar-C$\underline{H}_2$), 1.55 (quint, *J* = 7.2 Hz, 2H, Ar−CH_2−C$\underline{H}_2$), 1.30 (sext, *J* = 7.2 Hz, 2H, C$\underline{H}_2$−CH_3), 0.86 (t, *J* = 7.2 Hz, 3H, C$\underline{H}_3$).

*4.24. 2,2′-Bis(4-butylphenyl)-5,5′-bithiazole (**14**)*

To a solution of 2-(4-butylphenyl)thiazole **13** (6.5 g, 30 mmol) in DMF (90 mL) and DMSO (9 mL) were added $Pd(OAc)_2$ (0.67 g, 3 mmol) and AgOAc (10 g, 60 mmol). The mixture was stirred at 80 °C for 16 h, and then the mixture was filtered through a Celite pad and filtrate was concentrated *in vacuo*. The residue was washed with hexane and EtOAc to give the title compound (3.7 g, 56%) as a yellow solid. Rf = 0.04 (hexane: CH_2Cl_2 = 1 : 2). IR(KBr) 2955, 2924, 2854, 2359, 1478, 1421, 1409, 973, 847, 749, 665, 628, 495 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.90 (s, 2H, thiazole), 7.87 (d, *J* = 8.2 Hz, 4H, Ar), 7.28 (d, *J* = 8.2 Hz, 4H, Ar), 2.67 (t, *J* = 7.3 Hz, 4H, Ar-C$\underline{H}_2$), 1.63 (quint, *J* = 7.3 Hz, 4H, Ar-CH_2-C$\underline{H}_2$), 1.38 (sext, *J* = 7.3 Hz, 4H, C$\underline{H}_2$−CH_3), 0.95 (t, *J* = 7.3 Hz, 6H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 167.8, 145.9, 141.0, 130.8, 129.2, 128.1, 126.5 (Ar), 35.7, 33.5, 22.4, 14.0 (butyl). MS (EI) *m*/*z* 432 (M^+). HRMS (EI) Calcd for $C_{26}H_{28}N_2S_2$: 432.1694, found: 432.1681.

*4.25. 4,4′-dibromo-2,2′-bis(4-butylphenyl)-5,5′-bithiazole (**15**)*

To a solution of 2,2′-bis(4-butylphenyl)-5,5′-bithiazole **14** (0.93 g, 2 mmol) in $CHCl_3$ (21 mL) and AcOH (7 mL) was added Br_2 (0.2 mL, 4 mmol, 2 equiv). The mixture was stirred at room temperature for 20 min and then quenched with sat. $Na_2S_2O_3$aq and extracted with $CHCl_3$. The combined organic layer was concentrated *in vacuo*. These processes were repeated 3 times, and the resulting residue was purified by flash column chromatography on silica gel (CH_2Cl_2: hexane = 2 : 1) to give 4,4′-dibromo-2,2′-bis(4-butylphenyl)-5,5′-bithiazole (1.1 g, 84%) as a yellow viscous oil. Rf = 0.68 (hexane: CH_2Cl_2 = 1 : 1). IR(KBr) 3426, 3020, 2948, 2866, 1604, 1512, 1452, 1408, 1379, 1302, 1263, 987, 889, 839, 815, 780, 722, 643, 592, 531 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 4H, Ar), 7.28 (d, *J* = 8.2 Hz, 4H, Ar), 2.67 (t, *J* = 7.3 Hz, 4H, Ar-C$\underline{H}_2$), 1.64 (quint, *J* = 7.2 Hz, 4H, Ar−CH_2−C$\underline{H}_2$), 1.38 (sext, *J* = 7.2 Hz, 4H, C$\underline{H}_2$−CH_3), 0.95 (t, *J* = 7.2 Hz, 6H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 168.9, 146.8, 129.8, 129.3, 128.2, 126.5, 121.7 (Ar), 35.7, 33.4, 22.4, 14.0 (butyl). MS (EI) *m*/*z* 592 (50, M($2^{81}Br$)$^+$), 590 (100, M(^{79}Br+^{81}Br)$^+$), 588 (50, M($2^{79}Br$)). HRMS (EI) Calcd for $C_{26}H_{26}^{79}Br_2N_2S_2$: 587.9904, found: 587.9907.

*4.26. 2,6-Bis(4-butylphenyl)thieno[2,3-d:5,4-d']bisthiazole-4-oxide (**11a**)*

This compound was synthesized according to the general procedure, using 4,4′-dibromo-2,2′-bis(4-buyhylphenyl)-5,5′-bithiazole (0.31 g, 0.5 mmol), *n*-BuLi (1.5 M in hexane, 0.7 mL, 1.1 mmol), and neat thionyl chloride (0.036 mL, 0.5 mmol) in Et_2O (10 mL). The title compound was isolated as an orange solid (0.21 g, 86%). Rf = 0.25 (CH_2Cl_2). mp 191−193 °C (dec.). IR (KBr) 3436, 2955, 2926, 2856, 1607, 1514, 1455, 1408, 1215, 981, 886, 829, 681, 568, 507 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 4H, Ar), 7.29 (d, *J* = 8.2 Hz, 4H, Ar), 2.67 (t, *J* = 7.3 Hz, 4H, Ar-C$\underline{H}_2$), 1.64 (quint, *J* = 7.3 Hz, 4H, Ar−CH_2−C$\underline{H}_2$), 1.38 (sext, *J* = 7.3 Hz, 4H, C$\underline{H}_2$−CH_3), 0.95 (t., *J* = 7.3 Hz, 6H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 171.3, 163.4, 147.0, 130.2, 129.7, 129.4, 126.7 (Ar), 35.7, 33.3, 22.4, 14.0 (butyl). MS (EI) *m*/*z* 478 (6, M^+), 462 (100, $[M-O]^+$). HRMS (EI) Calcd for $C_{26}H_{26}N_2OS_3$: 478.1207, found: 478.1198.

*4.27. 2,6-Bis(4-butylphenyl)thieno[2,3-d:5,4-d']bisthiazole (**10a**)*

To a suspension of 2,6-bis(4-butylphenyl)thieno[2,3-*d*:5,4-*d'*] bisthiazole-4-oxide **11a** (0.19 g, 0.4 mmol) in degassed THF, PBu_3 (0.25 mL, 0.8 mmol) was added via syringe. After the mixture was stirred for 19 h, the reaction was completed (monitored by TLC), and the mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2) to give the title compound (0.15 g, 82%) as a yellow solid. Rf = 0.30 (hexane: CH_2Cl_2 = 1 : 2). mp 221−223 °C. IR(KBr) 3425, 2957, 2924, 2924, 2854, 1606, 1514, 1448, 1410, 1287, 960, 828, 681, 645, 574, 494 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 4H, Ar), 7.29 (d, *J* = 8.2 Hz, 4H, Ar), 2.67 (t, *J* = 7.3 Hz, 4H, Ar-C$\underline{H}_2$), 1.64 (quint, *J* = 7.3 Hz, 4H, Ar−CH_2−C$\underline{H}_2$), 1.38 (sext, *J* = 7.3 Hz, 4H, C$\underline{H}_2$−CH_3), 0.95 (t, *J* = 7.3 Hz, 6H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 168.6, 156.5, 146.0, 131.1, 129.2, 126.4, 121.6 (Ar) 35.6, 33.4, 22.3, 13.9 (butyl). MS (EI) *m*/*z* 462 (54, M^+). HRMS (EI) Calcd for $C_{26}H_{26}N_2S_3$: 462.1258, found: 462.1256.

*4.28. 2,6-Bis(4-butylphenyl)thieno[2,3-d:5,4-d']bisthiazole-4,4-dioxide (**12a**)*

To a suspension of 2,6-bis(4-butylphenyl)thieno[2,3-*d*:5,4-*d'*] bisthiazole-4-oxide(**11a**) (0.19 g, 0.4 mmol) in toluene and water (5/2, 2 mL) was added NaOCl. $5H_2O$ (66 mg, 0.4 mmol). The mixture was stirred for 3 h and then extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane: CH_2Cl_2 = 1 : 1) to give the title compound (0.18 g, 93%) as a yellow solid. Rf = 0.75 (hexane: CH_2Cl_2 = 1 : 2). mp 266−268 °C. IR (KBr) 3426, 2955, 2926, 2854, 2359, 1451, 1407, 1317, 1219, 1140, 984, 829, 687, 603, 561 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 4H, Ar), 7.29 (d, *J* = 8.2 Hz, 4H, Ar), 2.68 (t, *J* = 7.7 Hz, 4H, Ar-C$\underline{H}_2$), 1.62 (quint, *J* = 7.3 Hz, 4H, Ar−CH_2−C$\underline{H}_2$), 1.38 (sext, *J* = 7.3 Hz, 4H, C$\underline{H}_2$−CH_3), 0.96 (t, *J* = 7.3 Hz, 6H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 172.4, 153.8, 147.5, 129.6, 129.4, 126.8, 126.7 (Ar) 35.6, 33.3, 22.3, 13.9 (butyl). MS (EI) *m*/*z* 494 (41, M^+). HRMS (EI) Calcd for $C_{26}H_{26}N_2O_2S_3$: 494.1156, found: 494.1144.

*4.29. 2,6-Bis(4-butylphenyl)selenopheno[2,3-d:5,4-d']bisthiazole (**16**)*

This compound was synthesized according to the general procedure, using 4,4′-dibromo-2,2′-bis(4-buyhylphenyl)-5,5′-bithiazole (0.31 g, 0.5 mmol), *n*-BuLi (1.6 M in hexane, 0.7 mL, 1.1 mmol), and neat SeOCl (0.113 mL, 0.6 mmol) in Et_2O (10 mL). The title compound was isolated as an orange solid (64 mg, 25%). Rf = 0.40 (hexane: CH_2Cl_2 = 4 : 1). ^1H NMR ($CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 4H, Ar), 7.29 (d, *J* = 8.2 Hz, 4H, Ar), 2.67 (t, *J* = 7.3 Hz, 4H, Ar-C$\underline{H}_2$), 1.64 (quint, *J* = 7.3 Hz, 4H, Ar−CH_2−C$\underline{H}_2$), 1.38 (sext, *J* = 7.3 Hz, 4H, C$\underline{H}_2$−CH_3), 0.95 (t, *J* = 7.3 Hz, 6H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 168.4, 156.0, 146.0, 131.1, 129.3, 126.5, 123.0 (Ar), 35.7, 33.4, 22.4, 14.0 (butyl). HRMS (EI) Calcd for $C_{26}H_{26}N_2S_2Se$: 510.0703, found: 510.0702.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.131978.

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