

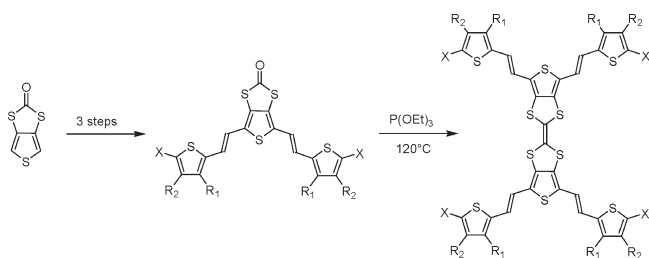
Synthesis of Trithienylenevinylenes Bearing Dithiocarbonate Groups and Their Dithiophene–Tetrathiafulvalene Derivatives

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A series of conjugated trithienylenevinylene compounds bearing dithiocarbonate groups were prepared by Wittig reactions. Dithiophene–tetrathiafulvalene (DT–TTF) derivatives can be readily prepared through trialkylphosphite-mediated coupling reactions of these trithienylenevinylene materials. All compounds were characterized by NMR, FT-IR, UV–vis, and mass spectroscopy.

Thienylenevinylene oligomers are still of great interest as conductive materials due to their unique electronic, electrochemical, and optical properties.^{1–4} Monodisperse oligomers not only provide the possibility for precise understanding of the structure–property relationship of conjugated materials, therefore extending to those of polydisperse polythienylenevinylene (PTV) derivatives,^{5–8} but also have been widely studied as processable organic electronic materials. Thieno[3,4-*d*]-1,3-dithiole-2-one (**1**) emerged as an

ideal building block for the synthesis of 2-D conductive polymer or metallopolymer owing to its unique structure.⁹ First, the dithiocarbonate group, which is formally named 1,3-dithiole-2-one, can be readily converted into dithiolate ligands through hydrolysis under basic conditions to form a metal–bis-1,2-dithiolene complex.^{10,11} Metal–bis-1,2-dithiolene complexes, such as M(dmit)₂ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate)^{12–15} and M(mnt)₂ (mnt = maleonitriledithiolate),^{16,17} are one class of the most extensively studied hybrid materials as potential organic superconductors.^{18–20} Another important feature of compound **1** is the possibility of forming dithiophene–tetrathiafulvalene (DT–TTF)-like compounds through trialkylphosphite-mediated coupling reactions.²¹ TTF charge-transfer salts have been well-known as good candidates for conductive and/or superconductive materials.^{22–24} Therefore, incorporation of TTF linkages into conjugated polymer systems would not only yield unique hybrid architectures, but also show some promising application fields such as organic solar cell devices.^{25,26}

This report describes the synthesis and characterization of a series of conjugated thiophene-based trithienylenevinylene compounds bearing dithiocarbonate groups through Wittig reactions, and followed by synthesis of DT–TTF derivatives resulting from trialkylphosphite-mediated coupling reactions. Our objectives are the preparation and characterization of soluble oligothiophenevinylenes. Maintaining dithiocarbonate groups in these trithienylenevinylene compounds would readily afford conjugated oligothiophenevinylene derivatives cross-linked by DT–TTF bridges, and also provide further opportunities to prepare metal–bis-1,2-dithiolene complexes.

Alkylthiophenecarboxaldehydes and alkylthiophenedicarboxaldehydes were prepared via Vilsmeier formylation with fairly good yields. Thieno[3,4-*d*]-1,3-dithiole-2-one (**1**)

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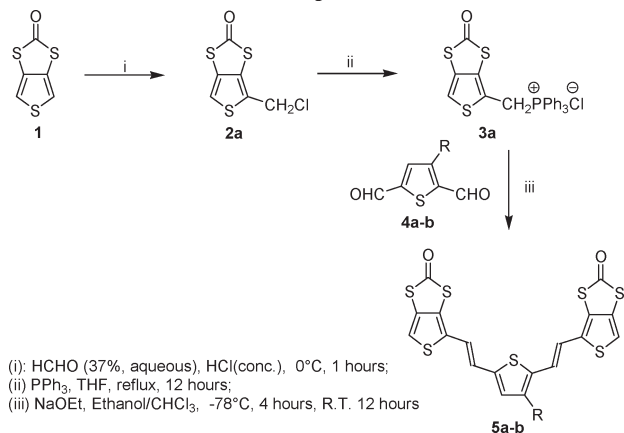
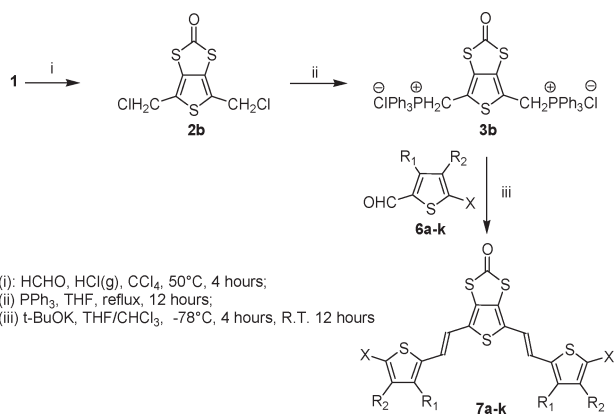
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SCHEME 1. Synthesis of Trithienylenevinylene Compounds with Two Dithiocarbonate Groups

SCHEME 2. Synthesis of Trithienylenevinylenes Bearing One Dithiocarbonate Group


was synthesized from a modified one-pot approach with 3,4-dibromothiophene as starting material.^{27–30} 3,4-Dibromothiophene was consecutively treated twice with butyllithium (1.0 equiv) followed by the addition of elemental sulfur to afford dilithium thiophene-3,4-dithiolate as an intermediate. Without further purification, the reaction mixture was allowed to react with phosgene in aqueous alkaline solution to afford compound **1**.

Preparations of trithienylenevinylene compounds with dithiocarbonate group(s) are outlined in Schemes 1 and 2. Triphenyl phosphonium ylides (**3a** and **3b**) were prepared by chloromethylation reactions of compound **1**, followed by treatment with triphenylphosphine in THF under mild reflux. The experimental data of trithienylenevinylene compounds are summarized in Tables 1 and 2. Compared with **7b** and **7c**, relatively lower yields of compounds **7f** (18%) and **7g** (23%) clearly demonstrated that alkyl substitution at the 3 position produces more steric resistance than that at the 4 position.

¹H NMR spectra of all trithienylenevinylene compounds show typical vinyl doublets with coupling constants of

TABLE 1. Experimental Data of Trithienylenevinylene Compounds 5a and 5b^a

entry	R	yield (%)	mp (°C)	$\lambda_{\max}^{\text{abs}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	Stokes shift (nm)
5a	butyl	35	138–139	443	533	90
5b	octyl	32	145–146	442	526	84

^a $\lambda_{\max}^{\text{abs}}$ and $\lambda_{\max}^{\text{em}}$ were obtained in CH₂Cl₂ solution. The excitation wavelength is 10 nm less than its $\lambda_{\max}^{\text{abs}}$ for each sample.

15.8 Hz, which indicated *trans* vinyl formations and the *trans* vinyl structures were further confirmed by the presence of strong absorptions at 913–921 cm⁻¹ region in the FT-IR spectra.

Triethylphosphite-mediated coupling reactions to obtain DT-TTF derivatives are illustrated in Scheme 3. Results and spectrum data of DT-TTF derivatives are summarized in Table 3. NMR and FT-IR spectra show *trans* vinyl formations were maintained in all conjugated DT-TTF derivatives. Compound **8h** and **8i** gave fairly higher yields than expected. At the melting points, both compounds immediately turned into shining metallic black from red, which might be explained as Br₂-doped conjugated polymer resulting from thermal elimination and coupling reactions. This type of solid state polymerization has been reported with other halogenated thiophene derivatives by several research groups.^{31,32} UV-vis spectra show the maximum absorption wavelengths of all DT-TTF derivatives are around 430 nm, representing extended π -conjugation, which are very close to those of their trithienylenevinylene counterparts. Photoluminescence results indicate large excitation and emission energy differences for DT-TTF derivatives in solution with Stokes shifts ranging from 156 to 168 nm.

The oxidation potentials of DT-TTF derivatives are listed in Table 4. Bromination at the α position gave higher $E_{\text{pa}}(2) - E_{\text{pa}}(1)$ values, which indicate stronger Coulombic repulsion between positive charges in the dication for **8h** and **8i**.³³ Compared with octyl-substituted analogues, slightly lower E_{pa} values for butyl-substituted DT-TTF derivatives were observed.

In summary, a series trithienylenevinylene compounds with dithiocarbonate group(s) were successfully synthesized via Wittig reactions, and triethylphosphite-mediated coupling reactions were applied to obtain some symmetric DT-TTF derivatives. All compounds were fully characterized by NMR, FT-IR, UV-vis, and mass spectrometry. Polymerization of these DT-TTF derivatives to obtain conjugated polythienylenevinylenes cross-linked by DT-TTF is still under investigation in our lab, and those projected hybrid structures might possess some unique electronic properties.

Experimental Section

General Procedure for the Synthesis of Trithienylenevinylenes with Two Dithiocarbonate Groups. A solution of 1 mmol of phosphonium salt **3a** and 1.2 mmol of alkylthiophenedicarboxaldehydes in 30 mL of anhydrous ethanol/CHCl₃ (1:1 v/v) was stirred and cooled to -78 °C under argon for 15 min, then 15 mL

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TABLE 2. Experimental Data of Trithienylenevinylene Compounds 7a–k^a

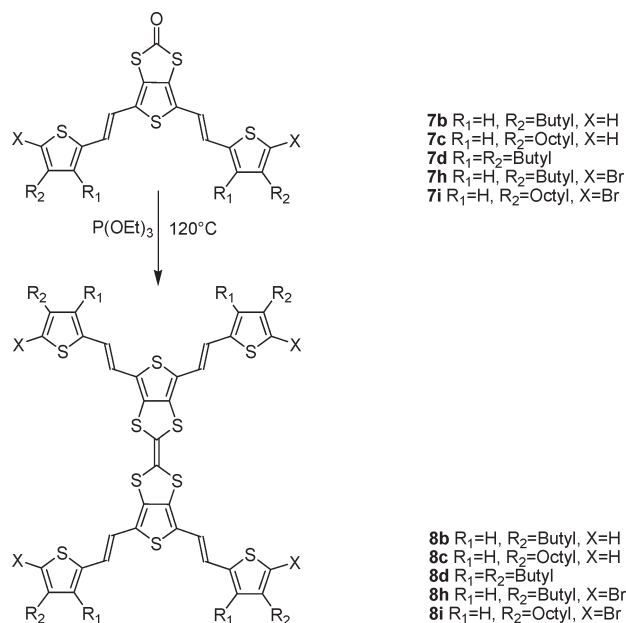
entry	R ₁	R ₂	X	yield (%)	mp (°C)	λ _{max} ^{abs} (nm)	λ _{max} ^{em} (nm)	Stokes shift (nm)
7a	H	H	H	31	169–170	427	509	82
7b	H	butyl	H	45	105–106	436	516	80
7c	H	octyl	H	37	102–103	439	520	81
7d	butyl	butyl	H	24	111–113	440	502	62
7e	R ₁ = R ₂ = –OCH ₂ CH ₂ O–		H	38	230–232	448	504	56
7f	butyl	H	H	18	87–88	438	497	59
7g	octyl	H	H	23	92–93	437	498	61
7h	H	butyl	Br	52	148–149	444	526	82
7i	H	octyl	Br	48	109–110	444	523	80
7j	butyl	butyl	Br	38	105–106	454	509	55
7k	R ₁ = R ₂ = –OCH ₂ CH ₂ O–		Br	43	> 250	455	512	57

^aλ_{max}^{abs} and λ_{max}^{em} were obtained in CH₂Cl₂ solution. The excitation wavelength is 10 nm less than its λ_{max}^{abs} for each sample.

TABLE 3. Experimental Data of Conjugated DT-TTF Derivatives

entry	R ₁	R ₂	X	yield (%)	mp (°C)	λ _{max} ^{abs} (nm) ^a	ε (M ⁻¹ ·cm ⁻¹)	λ _{max} ^{em} (nm) ^b	Stokes shift (nm)
8b	H	butyl	H	48	221–222	431	88300	598	167
8c	H	octyl	H	42	147–148	433	76800	599	166
8d	butyl	butyl	H	28	223–225	440	61100	596	156
8h	H	butyl	Br	71	211–212	438	126800	609	168
8i	H	octyl	Br	73	155–157	448	32100	611	163

^aUV–vis spectra were obtained in CH₂Cl₂ at a concentration around 1 × 10⁻⁵ M. ^bThe maximum wavelength of photoluminescence (λ_{max}^{em}) was obtained in CH₂Cl₂ (1 × 10⁻⁵ M) with excitation wavelength corresponding to 10 nm less than its λ_{max}^{abs}.

SCHEME 3. Preparation of DT-TTF Derivatives from Trithienylenevinylene Compounds

of 0.1 M sodium ethoxide ethanol solution was added slowly by syringe. After addition of sodium ethoxide, the reaction mixture was stirred in a dry ice acetone bath for 4 h, then allowed to warm to room temperature and kept for another 12 h. The reaction was quenched with glacial acetic acid and extracted with CH₂Cl₂. Organic layers were combined, washed with water and brine, and dried over MgSO₄. Crude products were concentrated under vacuum followed by column chromatography on silica gel. Further purification can be achieved by precipitating product solution (chloroform) in methanol.

General Procedure for the Synthesis of Trithienylenevinylenes Bearing One Dithiocarbonate Group. A solution of 1 mmol of phosphonium salt **3b** and 2.2 mmol of alkylthiophenecarboxaldehyde in 30 mL of anhydrous THF/CHCl₃ (1:1 v/v) was

TABLE 4. Peak Potentials for the Oxidation of Conjugated DT-TTF Derivatives^a

entry	E _{pa} (1) (V)	E _{pa} (2) (V)	E _{pa} (2) – E _{pa} (1) (V)
8b	0.78	1.22	0.44
8c	0.87	1.17	0.30
8d	0.97	1.32	0.35
8h	0.86	1.46	0.60
8i	0.90	1.52	0.62

^aDetermined by cyclic voltammetry of 3.0 × 10⁻⁵ M DT-TTF derivatives in CH₂Cl₂ with 0.1 M TBAHFP as supporting electrolyte, glassy carbon (working) and Pt wire (counter) electrodes, versus a nonleak Ag/AgCl reference electrode. Scan rate 50 mV/s.

stirred and cooled to –78 °C under argon for 15 min, then 15 mL of a 0.2 M potassium *tert*-butoxide THF solution was added slowly via syringe. After addition of the base, the reaction mixture was kept at –78 °C for another 4 h, then allowed to warm to room temperature, and stirred for an additional 12 h. The reaction was quenched with glacial acetic acid and extracted with dichloromethane. Organic layers were collected, washed with water and brine, dried over MgSO₄, and concentrated under vacuum. Crude products were purified by column chromatography on silica gel with EtOAc/hexanes as eluent solvents.

General Procedure for the Synthesis of DT-TTF Derivatives. To a dry flask equipped with a condenser were added 0.5 mmol of trithienylenevinylene and 4 g of triethylphosphite (excess), then the mixture was stirred at 120 °C for 8 h under argon protection. After cooling to room temperature, the reaction mixture was filtered, then the solid portion was collected and washed with a small amount of diethyl ether and hexanes and dried in a vacuum oven at 60 °C for 24 h to afford DT-TTF derivatives.

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Supporting Information Available: Experimental details and characterization data for all trithienylenevinylenes and their DT-TTF derivatives. This material is available free of charge via the Internet at <http://pubs.acs.org>.