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Facile synthesis of acetylene-substituted terthiophenes

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Abstract—A modified Horner–Emmons condensation reaction has been employed for the synthesis of acetylene-substituted terthiophenes in excellent yields. Conjugating 3′-aryl substituents to terthiophene using an ethyne rather than an ethene linker results in enhanced planarity of the resulting molecule as established by X-ray structural analysis of (2,2′:5′,2″-terthiophen-3′-yl)-4‴-pyridylethyne.

Since their discovery in 1977,[1,2] conjugated polymers and oligomers have been extensively investigated for use in applications such as solar cells, actuators, light emitting diodes and non-linear optical materials.[3] Prominent among the conjugated materials studied to date are the oligo- and polythiophenes. These materials have good chemical stability in both their oxidised and reduced states, and a wide variety of functionality can be readily incorporated into the polymers by functionalisation of the corresponding monomers whether thiophene, bithiophene, or terthiophene.[4–7]

The electronic properties of thiophene oligomers and polymers may be tuned by introducing functionality onto the polymer chain in the form of aromatic substituents. Thus, poly(3-arylthiophenes) have improved doping capacity and redox cycling characteristics when compared with polythiophene.[8,9] Aromatic substituents have also been attached to thiophene as styryl groups. Although electrochemical homopolymerisation of 3-styrylthiophene resulted in a nonconductive material, conductive polymers have been obtained by copolymerisation of styryl-substituted thiophenes with thiophenes.[10,11] However, whilst these copolymerisations undoubtedly lead to improvement in desired polymer properties, their irregular and random structure makes it difficult to deconvolute the role of the substituent.

An alternative approach to the formation of regioregular styryl-functionalised oligo- and polythiophenes is to polymerise styryl-substituted terthiophene monomers and towards this end we have reported a method for the synthesis of a range of terthiophenes functionalised at the 3′-position with styryl moieties.[12,4,5,13,6] The introduction of an ethene linker between the aryl substituent at the 3′ position of 2,2′:5′,2″-terthiophene allows the aryl and thiophene rings to assume a greater π orbital overlap than that present in 3′-phenyl-2,2′:5′2″-terthiophene,[5] giving rise to the possibility of tuning the optoelectronic properties of the 3′-substituted thiophenes by varying the aryl moiety. In 3′-phenyl-2,2′:5′2″-terthiophene the aryl ring is twisted at an angle of −116.7° with respect to the central thiophene ring,[14] while in (*E*)-1-((2′,2″:5″,2‴-terthiophene)-3″-yl)-2-(4⁗-cyanophenyl)ethene this angle is reduced to 26.5°.[5] The principal interaction preventing a smaller dihedral angle in the styryl terthiophene is most likely a steric repulsion between the vinyl hydrogen closest to the central thiophene ring and the sulfur atom on the outer thiophene ring closest to the styryl substituent. Replacement of the ethene by an ethyne linker should, therefore, result in a decrease in the above dihedral angle, with a concomitant further increase in the π-orbital overlap, and this was the objective of this work.

Typically, acetylene substitution of thiophene involves a Sonogashira coupling reaction or other metal-catalysed reactions from the appropriate bromothiophene.[15–20] However, this requires expensive metal catalysts, a

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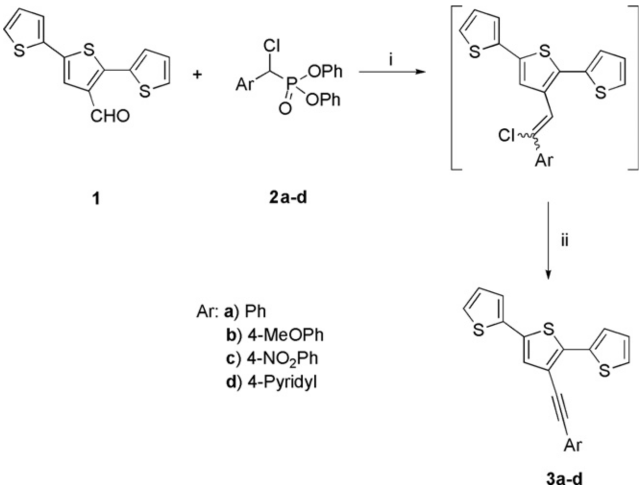
preformed acetylene precursor and somewhat harsh conditions (long reaction times and high boiling solvents). In contrast, the modified Horner–Emmons reaction, which has been used to synthesis a range of symmetrical and asymmetrical substituted diaryl acetylenes,[21–23] does not require a metal catalyst and can be carried out at low temperature in the presence of a variety of functionality. To our knowledge, however, this technique has never been applied to the introduction of acetylene substituents onto thiophenes.

The usual experimental procedure for the modified Horner–Emmons reaction (Scheme 1) involves equimolar amounts of reactants catalysed by 2 equiv of base. However, using this procedure for the reaction shown in Scheme 1 results in an incomplete conversion, in which the main product is the chlorovinyl intermediate, which is difficult to separate from the desired product. Increasing the concentration of base in a single step to drive the reaction to completion has the desired effect but results in a low yield of the final product. Carrying out the reaction in two steps, however, results—with the exception Ar = 4-nitrophenyl—in high product yields (see Table 1). First, slightly more than 2 equiv of base are added to a solution of terthiophene-3′-carboxaldehyde (**1**) and the appropriate phosphonate (**2a–d)** in tetrahydrofuran, the solution is left to stir for 3 h and then a further 10-fold excess of base is added.[24] The reaction of **1** with **2c** does not yield **3c** but results in the hydroxylated derivative **3e** substituted *ortho* to the nitro group of the benzene ring. Given that a deep red colour was observed on addition of butoxide to the reaction mixture, indicative of a Meisenheimer complex, it is possible that a vicarious nucleophilic substitution of hydrogen occurred leading to hydroxylation of the nitrobenzene ring.[25]



Scheme 1. Reagents and conditions: (i) THF, Bu^{t}OK (2 equiv), rt; (ii) THF, Bu^{t}OK (>10 equiv), rt.

Table 1. Product yields

Entry	Ar	Product	Yield (%)
1	Phenyl	**3a**	87
2	4-Methoxyphenyl	**3b**	88
3	4-Nitrophenyl	**3c**	0
4	4-Pyridyl	**3d**	98
5	3-Hydroxy-4-nitrophenyl	**3e**	31

Undertaking the same experimental procedure using thiophene-3-carboxaldehyde in place of 3′-formylterthiophene results in a quantitative yield of the desired product, illustrating that this is a general method for the synthesis of acetylene-functionalised thiophenes.

All the products were characterised using 1- and 2-D ^{1}H and ^{13}C NMR experiments as previously described for 3′-styryl-substituted terthiophenes.[5] The mass spectrometry and UV–visible spectroscopic data were consistent with the proposed structures.

Confirmation of the increased planarity induced by the acetylene linker was obtained from the X-ray structural analysis of **3d** (Fig. 1).[26] The X-ray data indicate that the outer thiophene rings exist as conformers with the general structure having the antiparallel orientation shown in Figure 1, that is, there is a flip type disorder that seems to be general for 3′-substituted terthiophenes.[5,14,27,28] The torsional angle between the central thiophene ring and the ring closest to the alkyne linker is 4.4(3)° [S(3)–C(10)–C(9)–C(8)] and the other torsional angle [S(1)–C(5)–C(6)–C(7)] is 3.6(3)°. The dihedral angle between the mean plane through the atoms of the central thiophene ring and the pyridine ring is 9.8(3)°. The corresponding three angles in (*E*)-1-((2′,2″:5″,2‴-terthiophene)-3″-yl)-2-(4⁗-cyanophenyl)ethene, that is, an ethene-linked terthiophene, are −148°, −151.2° and 26.5°.[5] Thus, the replacement of an alkene by an alkyne spacer results in a more planar structure that allows the aryl and thiophene rings to achieve a greater π-orbital overlap.

The effect on the electronic spectra of the conjugated 4-methoxyphenyl-substituted terthiophenes of changing the ethene linker for an ethyne group is shown in Figure 2. In (*E*)-1-((2′,2″:5″,2‴-terthiophene)-3″-yl)-

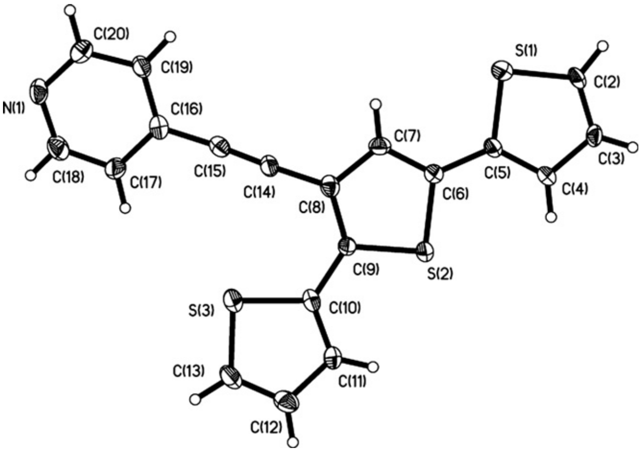


Figure 1. X-ray crystal structure of compound **3d**. The displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as small spheres of arbitrary radii.

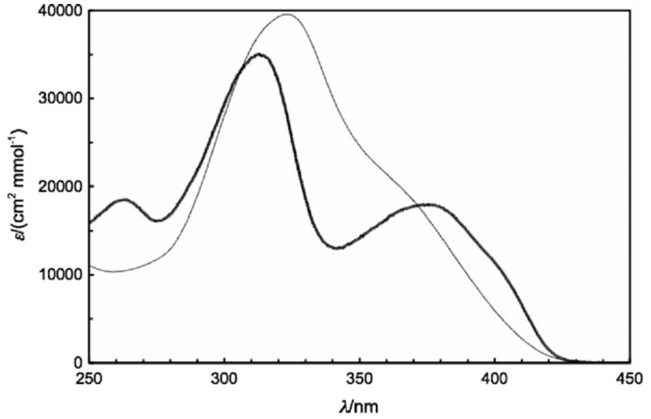


Figure 2. Electronic absorption spectra of (2,2′:5′,2″-terthiophene-3′-yl)-(4‴-methoxyphenyl)ethyne **3b** (thicker line) and (*E*)-1-((2′,2″:5″,2‴-terthiophene)-3″-yl)-2-(4⁗-methoxyphenyl)ethene as measured in DCM at 25 °C.

2-(4⁗-methoxyphenyl)ethene the more intense higher energy transition at 323 nm corresponds to the HOMO − LUMO + 1 transition and the shoulder at 362 nm to the HOMO − LUMO transition.[29] It is reasonable to assume that the transitions are similar in the ethyne-linked terthiophenes and therefore, in **3b** the HOMO − LUMO transition is red-shifted by 14 nm while the HOMO − LUMO + 1 is blue-shifted by 10 nm. The comparative red and blue shifts for the analogous phenyl-substituted ethene and ethyne (**3a**) terthiophenes are 23 nm and 3 nm.[29,17] A DFT study is being undertaken to explain these observations and the results will be published elsewhere.

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24. *Experimental procedure and spectroscopic data for compounds* **3b**, **d** *and* **e**. Spectroscopic data for compound **3a** can be found in Ref. 20. 2,2′:5′,2″-Terthiophen-3′-carboxaldehyde **1** (362 mg, 1 mmol) and the appropriate phosphonate **2b**–**d** (1.1 mmol) were dissolved in dry tetrahydrofuran (20 mL), and *t*-BuOK (253 mg, 2.26 mmol) was added. The resulting, usually coloured, mixture was stirred at room temperature for 3 h then a second batch of *t*-BuOK was added (2.000 g, 17.9 mmol), and the cloudy solution was stirred for an additional hour. After removal of the solvent by evaporation under reduced pressure at 60 °C, the residue was dissolved in diethyl ether (50 mL) and filtered through a pad of silica. The filtrate was evaporated to dryness under reduced pressure at 60 °C, and the resulting oily mass was purified on silica using a dichloromethane/hexane (1:2) mixture as eluent. The products were oils that solidified with time. Analytical samples were crystallised from ethanol. *(2,2′:5′,2″-Terthiophen-3′-yl)-(4‴-methoxyphenyl)ethyne* **3b**: Mp 80–81 °C irregular yellow crystals. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.54–7.52 (m, 2H, Ar-H), 7.50 (dd, 1H, $J = 1.0$ and 3.5 Hz, Th-H3), 7.32 (dd, 1H, $J = 1.0$ and 5.0 Hz, Th-H5), 7.25 (dd, 1H, $J = 1.0$ and 5.0 Hz, Th-H5″), 7.19 (dd, 1H, $J = 1.0$ and 3.5 Hz, Th-H3″), 7.18 (s, 1H, Th-H4′), 7.07 (dd, 1H, $J = 3.5$ and 5.0 Hz, Th-H4), 7.04 (dd, 1H, $J = 3.5$ and 5.0 Hz, Th-H4″), 6.93–6.90 (m, 2H, Ar-H), 3.84 (s, 3H, OCH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.8, 136.3, 136.0, 134.0, 133.0, 127.9, 127.2, 127.1, 127.0, 125.6, 125.3, 125.0, 124.1, 118.1, 115.3, 114.1, 94.4, 83.8, 55.3. *m*/*z* (FAB): 378 (22, M$^+$), 154 (100), 137 (57), 136 (70), 89 (23); HRMS (FAB): M$^+$ found 378.02068. C$_{21}$H$_{14}$OS$_3$ requires 378.02068. UV (CH$_2$Cl$_2$) λ_{max} nm (ε) 263 (18,600), 313 (35,100), 376 (18,000), 398 sh (12,100). *(2,2′:5′,2″-Terthiophen-3′-yl)-4‴-pyridylethyne* **3d**: Mp 104–106 °C yel-

low needles. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.63–8.62 (m, 2H, Pyr-H), 7.48 (dd, 1H, $J = 1.0$ and 3.5 Hz, Th-H3), 7.43–7.42 (m, 2H, Pyr-H), 7.37 (dd, 1H, $J = 1.0$ and 5.0 Hz, Th-H5), 7.27 (dd, 1H, $J = 1.0$ and 5.0 Hz, Th-H5″), 7.21 (dd, 1H, $J = 1.0$ and 3.5 Hz, Th-H3″), 7.19 (s, 1H, Th-H4′), 7.09 (dd, 1H, $J = 3.5$ and 5.0 Hz, Th-H4), 7.05 (dd, 1H, $J = 3.5$ and 5.0 Hz, Th-H4″). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 140.0, 135.9, 135.3, 134.6, 131.3, 128.0, 127.4, 126.7, 126.3, 126.0, 125.3, 125.2, 124.4, 116.6, 91.2, 89.6. *m*/*z* (FAB): 350 (7, M^++1), 349 (4, M^+), 154 (100), 137 (59), 136 (71), 89 (22); HRMS (FAB): M^+ found 349.00525. $C_{19}H_{11}NS_3$ requires 349.00536. UV (CH_2Cl_2) λ_{max} nm (ε) 300 sh (25,600), 312 (30,500), 366 (16,400). *(2,2′:5′,2″-Terthiophen-3′-yl)-(3‴-hydroxy-4‴-nitrophenyl)ethyne* **3e**: Mp 167–168 °C red blocks. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.68 (s, 1H, OH), 8.12 (d, 1H, $J = 8.5$ Hz, Ar-H5), 7.48 (dd, 1H, $J = 1.0$ and 3.5 Hz, Th-H3), 7.40 (dd, 1H, $J = 1.0$ and 5.0 Hz, Th-H5), 7.34 (d, 1H, $J = 1.7$ Hz, Ar-H2), 7.28 (dd, 1H, $J = 1.0$ and 5.0 Hz, Th-H5″), 7.21 (dd, 1H, $J = 1.0$ and 3.5 Hz, Th-H3″), 7.20 (s, 1H, Th-H4′), 7.15 (dd, 1H, $J = 1.7$ and 8.5 Hz, Ar-H6), 7.11 (dd, 1H, 3.5 and 5.0 Hz, H4), 7.05 (dd, 1H, $J = 3.5$ and 5.0 Hz, Th-H4″). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 135.8, 135.2, 132.9, 132.8, 128.0, 127.4, 126.6, 126.5, 126.2, 125.4, 125.3, 124.5, 123.0, 122.1, 119.7, 116.4. *m*/*z* (FAB): 409 (3, M^+), 154 (100), 137 (58), 136 (68), 124 (9), 120 (11); HRMS (FAB): M^+ found 408.99028. $C_{20}H_{11}NO_3S_3$ requires 408.99011. UV (CH_2Cl_2) λ_{max} nm (ε) 262 (12,900), 357 (32,500), 419 sh (10,300).

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