Tetrathiafulvalene (TTF) derivatives have been intensely studied for over 30 years, since the discovery of the first organic metal tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). The charge-transfer salts of cationic radical TTF derivatives have generated a wide variety of molecular conductors and superconductors. The driving force in the crystallization of these salts is the \( \pi-\pi \) stacking, which permits, together with the S···S interactions, intermolecular electronic transfer, which is responsible for their transport properties. TTF derivatives have been used not only as building blocks of organic conductors, but also as components of molecular machines, organic magnets, electrochemical sensors, and solar cells.

Recently, TTF derivatives have also proved to be excellent semiconductors for use in organic field-effect transistors (OFETs). It has been shown that the best performing TTF OFETs have contained planar and symmetrical TTFs, and field-effect mobilities of the order of amorphous silicon have been achieved with these materials. More importantly, one major advantage of TTF semiconductors compared to acene and oligothiophene derivatives, which have been the benchmark in the field of OFETs, is that TTFs are generally soluble in various organic solvents. This not only allows for the synthesis of tailored materials, but also makes these materials compatible with low-cost processing techniques that are desirable for potential applications. To date, the highest performance TTF OFETs have been based on dithiophene-tetrathiafulvalene (DT-TTF), which exhibits the highest field-effect mobility (1.4 cm\(^2\)/Vs) found for a solution-processed material. However, the DT-TTF synthetic routes found in the literature are low yielding, which might inhibit employing these molecules in commercial applications. Herein we report a significantly improved high-yield route to prepare this extremely promising organic semiconductor.

The published synthetic routes of DT-TTF are either long or unreliable. All these synthetic routes are low yielding and proceed via thieno[3,4-\( d \)]-1,3-dithiole-2-thione (1) (Scheme 1). They involve the direct coupling of 1,3-dithiole-2-thione 1 (31% yield), the conversion of the thione into the toxic selone and subsequent coupling (yield from thione 48%), or the coupling of the [3,4-\( d \)]-1,3-dithiole-2-carbene formed by deprotonation of the thieno[3,4-\( d \)]-1,3-dithiolium cation with tertiary amine (yield from the thione 31%) (Scheme 1). The novel route to synthesize DT-TTF that we show here involves the coupling of the precursor 1,3-dithiol-2-one with trimethyl phosphate, and gives a significantly improved yield for the DT-TTF coupling reaction (70%).

The synthesis reported here was thus based on the coupling of thieno[3,4-\( d \)]-1,3-dithiol-2-one (8) (Scheme 2). The type of chalcogenene (ketone, thione, or selone) used often has a great influence on the yield of the self- or cross-coupling products. Some examples show that the coupling of 1,3-dithiol-2-ones to form TTFs proceed in higher yield than the coupling of the corresponding 2-thiones. However, the yields of the formation of 2-ones from the corresponding 2-thiones by the reaction with mercury(II) acetate vary. In the case of thieno[3,4-\( d \)]-1,3-dithiole-2-thione 1, this is only 30%. Hence, to improve the total reaction yield in the new synthesis reported here, cyclic dithiocarbonate 8 was formed directly by the cyclization of the \( \beta \)-keto-\( O \)-alkyl precursor 4 in the presence of sulfuric acid (Scheme 2). Similar reactions have been used for the synthesis of bisethylenethio-tetrathiaful-
valene (BET-TTF)\textsuperscript{10} and bisethylenedithio-tetrathiafulvalene (BEDT-TTF).\textsuperscript{10}

The synthesis of DT-TTF via 8 was carried out in seven high-yielding steps (Scheme 2). Although commercially available, potassium O-isopropyl dithiocarbonate (3) is easily formed by the reaction of propan-2-ol with carbon disulfide and potassium hydroxide as previously described.\textsuperscript{11} The reaction of 3 with 3-bromobutan-2-one led to the formation of O-isopropyl S-3-oxobutan-2-yl dithiocarbonate (4) through the elimination of potassium bromide.\textsuperscript{12} The preparation of 4,5-dimethyl-1,3-dithiol-2-one (5) was achieved by the cyclization of 4. Next, the bromination of 5 with N-bromosuccinimide and white light (500 W) in carbon tetrachloride afforded 4,5-bis(bromomethyl)-1,3-dithiol-2-one (6) as previously described.\textsuperscript{13} The cyclic dithiocarbonate 7 was formed by the reaction of the dibromo-substituted cyclic dithiocarbonate 6 with sodium sulfide. The aromatization of 7 to form 8 was carried out by refluxing 7 in 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. These two steps are similar to those reported for the formation of thiene[3,4-d]-1,3-dithiole-2-thione.\textsuperscript{14} Finally, the self-coupling of cyclic dithiocarbonate 8 by refluxing in trimethyl phosphate for eight hours gave DT-TTF in high yield (70%) (Scheme 2).\textsuperscript{8} The yield of this coupling reaction is much higher than that in any of the previously reported routes.

We also attempted to synthesize 8 directly in a one-flask reaction, adapting methods from the literature,\textsuperscript{3} and following the route shown in Scheme 3. 3,4-Dibromo-thiophene was treated twice with n-butyllithium (1 equiv) and elemental sulfur (1 equiv), to generate intermediate 9. Without isolation of this compound, the reaction mixture was allowed to react with 1,1'-carbonyldimidazole, to give 8 (Scheme 3). However, this reaction gave several side products and gave a maximum yield of 8%.

Scheme 2 The novel synthesis of DT-TTF. Reagents and conditions: (i) KOH, CS\textsubscript{2}; (ii) 3-bromobutan-2-one, acetone; (iii) H\textsubscript{2}SO\textsubscript{4}; (iv) NBS, CCl\textsubscript{4}; (v) Na\textsubscript{2}S·9H\textsubscript{2}O; (vi) DDQ, toluene; (vii) P(OMe)\textsubscript{3}.

Scheme 3 One-pot synthesis of ketone 8 in tetrahydrofuran. Reagents and conditions: (i) 1. n-BuLi (1 equiv); 2. S\textsubscript{8} (1 equiv); 3. n-BuLi (1 equiv); 4. S\textsubscript{8} (1 equiv).

In conclusion, the route presented for the formation of DT-TTF is reproducible and proceeds in high yield. The development of novel and easier TTF synthetic routes is vital if these materials are to be commercially exploited as organic electronic components.

All compounds were purchased from Aldrich and used without further purification, except for 3-bromobutan-2-one, which was purchased from Avocado. Melting points were determined on a Stuart Scientific BIBBY SMP10 apparatus. IR spectra were measured on a Perkin-Elmer Spectrum One Fourier transform spectrometer; samples were dispersed in KBr pellets. \textsuperscript{1}H (250 MHz) and \textsuperscript{13}C NMR (63 MHz) spectra were recorded on a Bruker Avance 250 spectrometer. MALDI-TOF MS was carried out in positive mode on a Maldi 2K-probe mass spectrometer from Kratos Analytical.

O-Isopropyl S-3-Oxobutan-2-yl Dithiocarbonate (4)

A solution of 3\textsuperscript{11} (4.53 g, 26 mmol) in anhyd acetone (130 mL) was added slowly to a solution of 3-bromobutan-2-one (4.0 g, 26 mmol) in anhyd acetone (50 mL). The resulting solution was stirred for 30 min and then poured into H\textsubscript{2}O (150 mL). The mixture was extracted with Et\textsubscript{2}O (3 × 50 mL), and the organic portions were combined, dried (MgSO\textsubscript{4}), and concentrated on a rotary evaporator to an emulsion, which was extracted with CH\textsubscript{2}Cl\textsubscript{2} (50 mL). Evaporation of the solvent yielded a yellow oil. Yield: 4.87 g (91%).

\textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): \( \delta = 1.35 (d, J = 6 Hz, 6 H, i-Pr CH) \), 1.42 (d, \( J = 7 Hz, 3 H, CH\textsubscript{3} \)), 2.27 (s, 3 H, CH\textsubscript{2}CO), 4.33 (q, \( J = 7 Hz, 1 H, CH\textsubscript{2} \)), 5.68 (sept, \( J = 6 Hz, 1 H, i-Pr CH \)).

4,5-Dimethyl-1,3-dithiol-2-one (5)

Compound 4 (5.76 g, 28 mmol) was slowly added to a solution of concd H\textsubscript{2}SO\textsubscript{4} (160 mL) that had been pre-cooled in an ice–salt bath. The resulting solution was stirred for 15 min, the ice–salt bath was removed, and the solution was stirred for an additional 90 min. This solution was cooled in an ice bath and slowly poured into ice-cooled H\textsubscript{2}O (400 mL). After stirring for 15 min, the solution was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 50 mL) to yield a dark red oil. The oil was purified by flash chromatography (silica gel, CH\textsubscript{2}Cl\textsubscript{2}). Yield: 3.90 g (93%); mp 46–47 °C.

IR (KBr): 2942, 2914, 1754, 1655, 1598, 1434, 1188, 1092, 940, 886, 756, 576, 425 cm\textsuperscript{–1}.

MALDI-TOF MS (positive mode): \( m/z = 146.5 \).
SHORT PAPER

Improved Synthesis of Dithiophene-Tetrathiafulvalene

4,6-Dihydrothieno[3,4-d][1,3]dithiol-2-one (7)

Solns of 6 (2.44 g, 8.1 mmol) in THF–EtOH (4:1, 250 mL) and Na₂S·9H₂O (1.93 g, 8.0 mmol) in THF–EtOH (4:1, 250 mL) were simultaneously and very slowly added to EtOH (200 mL) with vigorous stirring. After stirring overnight, the soln was concentrated to dryness on a rotary evaporator, and the residue was leached with CH₃Cl₂ (4 × 50 mL) and H₂O (150 mL). The aqueous phase was washed with CH₃Cl₂ (50 mL) and the organic layers were combined, dried (MgSO₄), and concentrated on a rotary evaporator to leave a beige solid. The stability of 7 in air was low, and therefore, after characterization by ¹H NMR spectroscopy, it was quickly used in the next step. Yield: 1.17 g (82%).

¹H NMR (250 MHz, CDCl₃): δ = 4.08 (s, CH₃).

Thieno[3,4-d][1,3]dithiol-2-one (8)

From 7: A soln of 7 (1.15 g, 0.0065 mol) and DDQ (3.06 g, 13.5 mol) in anhyd toluene (100 mL) was refluxed under argon for 3 h. The resulting soln was cooled, and concentrated to dryness on a rotary evaporator, and the product was extracted with CH₂Cl₂ (200 mL). This organic phase was washed with H₂O (150 mL) and dried (MgSO₄). After the soln had been washed with activated carbon, it was filtered on Celite, and the filtrate was concentrated on a rotary evaporator to yield a white crystalline compound. Prior to coupling to form DT-TTF, 8 was recrystallized from hexane. Yield: 0.93 g (82%). Spectroscopic data were in accordance with those previously reported.⁷

One-pot synthesis via 9: A soln of 3,4-dibromothiophene (1.0 g, 4.1 mmol) in anhyd THF (25 mL) was stirred and cooled to −78 °C. A 1.4 M soln of n-BuLi in hexane (3.2 mL, 4.5 mmol) was added by syringe and the soln was stirred for 30 min. Next, S₈ (0.137 g, 4.3 mmol) was added and the soln was stirred for a further 90 min. During this time, the soln turned yellow-orange. Then the mixture was treated again with n-BuLi (1 equiv) and S₈ (1 equiv). After the mixture had stirred for another 1 h, a suspension of carbonylbis(imidazolyl)thieno[3,4-d][1,3]dithiol-2-ylidene)thieno[3,4-c][1,3]dithiol-2-one (8)

A soln of 8 (0.660 g, 3.8 mmol) in freshly distilled P(OMe)₃ (4.7 mL) was stirred and cooled to −78 °C. A soln of 3,4-dibromothiophene (1.0 g, 4.1 mmol) was added, and the soln was stirred for a further 90 min. After stirring overnight, the soln was concentrated to dryness on a rotary evaporator to yield a white crystalline compound. Prior to coupling to form DT-TTF, 8 was recrystallized from hexane. Yield: 0.93 g (82%). Spectroscopic data were in accordance with those previously reported.⁷

Acknowledgment

The authors thank the EU for the support through the 6FP NAIMO Integrated Project No NMP4-CT-2004-500355 and DGI Spain (contract CTQ2006-06333/BQU). N.C. thanks the Ministerio de Ciencia y Tecnología for a PhD fellowship.

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