

Synthesis and characterization of the novel extended TTF-type donors with thiophenic units

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Abstract

Two new TTF-based donors that are dithiolene ligand precursors, 3-{5-[(2-cyanoethyl)thio]-2-(5,6-dihydrothieno[2,3-*d*][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl)thio}propanenitrile, dtdt (**1**) and 3-({5-[(2-cyanoethyl)thio]-2-thieno[2,3-*d*][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl)thio}propanenitrile, α -tdt (**2**), were synthesized and characterized. The electrochemical properties of these compounds were studied by cyclic voltammetry (CV) in acetonitrile. Compound **1** shows two reversible oxidation processes at $^1E_{1/2} = 0.639$ V and $^2E_{1/2} = 0.997$ V versus Ag/AgCl. This same processes occurs at $^1E_{1/2} = 0.612$ V and $^2E_{1/2} = 0.906$ V in the case of **2**. The crystal structures confirm the ability of these molecules to establish interactions with their neighbours through the peripheral sulfur atoms.

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1. Introduction

The TTF molecule, due to its unique π -donor properties, has been at the basis of many charge transfer salts with unique electronic and magnetic properties since its preparation [1] and the discovery of first organic conductors [2], more than 30 years ago. Its ability to form partially oxidized states gave rise to many molecular conductors [3], and in fact the large majority of organic metals and superconductors known so far are based on TTF derivatives. One of the trends in the preparation of new TTF derivatives for electronic materials is the search for molecules with, simultaneously, more extended π -systems and an

increasing number of sulfur atoms in the periphery, which can play a significant role in reducing the on-site Coulombic repulsion and increasing the strength and dimensionality of solid state interactions due to more S...S contacts. Indeed one of the most successful TTF derivatives is the [bis(ethylenedithio)tetrathiofulvalene], BEDT-TTF, which leads to an enormous number of radical-ion salts, showing a rich diversity of electronic behaviour, including circa 100 superconductors [4].

Following a similar approach, a series of donors based on TTF fused with thiophene moieties have also been explored leading to charge transfer salts with unique properties [5].

More recently, some extended TTF-based ligands were also used in the preparation of transition metal bisdithiolates obtained from cyanoethyl substituted TTF-dithiolates. One of the most interesting compounds obtained from these extended TTF dithiolene ligands, so far, is the neutral complex Ni(tmdt)₂, which at room temperature

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displays an electrical conductivity of 400 S/cm and transport properties typical of a metallic system [6].

In this paper, we report the synthesis and characterization of two new sulfur rich TTF-type donors fused with thiophene moieties, 3-{5-[(2-cyanoethyl)thio]-2-(5,6-dihydrothieno[2,3-*d*][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl)thio}propanenitrile, dtdt (**1**) and 3-({5-[(2-cyanoethyl)thio]-2-thieno[2,3-*d*][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl)thio}propanenitrile, α -tdt (**2**), which are also precursors for the preparation of new extended thiophene-TTF fused dithiolenes ligands.

2. Results and discussion

The preparation of the novel asymmetric TTF donors fused with thiophene moieties **1** and **2** was achieved following a synthetic route first used by Underhill and co-workers [7] involving the coupling with phosphorous methoxide between ketones **I** and **II** and thione **III** (Scheme 1).

Ketone **I**, 5,6-dihydrothieno[2,3-*d*]-1,3-dithiol-2-one was obtained, with low but reproducible yield, through a multi-step reaction previously described [8] and ketone **II**, 5,6-thieno[2,3-*d*]-1,3-dithiol-2-one was obtained, in a quantitative yield, by dehydrogenation of **I** using DDQ [9]. Thione **III**, 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione, was prepared as previously described [10] using bis-(tetraethylammonium)bis(2-thioxo-1,3-dithiole-4,5-dithiolate)zincate complex [11] as precursor, by a nucleophilic substitution reaction [7].

The coupling reaction of Scheme 1 leading to compounds **1** and **2** also gives rise to several by-products resulting mainly from the self-coupling of the reactants. However reasonable yields, 20% and 28% for **1** and **2**, respectively, were achieved after column purification, using dichloromethane as a solvent, and optimization of some reaction parameters, such as temperature, reaction time or solvent amount, to cause the precipitation of the formed TTF compounds, which were found critical for the final yield and purity. These compounds are soluble in usual organic solvents, such as dichloromethane and acetonitrile, and single crystals suitable for RX measurements were obtained from slowly cooling dichloromethane and saturated *n*-hexane solutions.

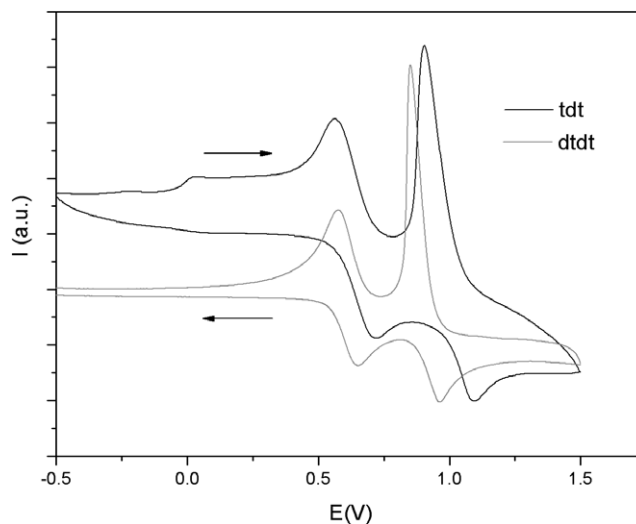
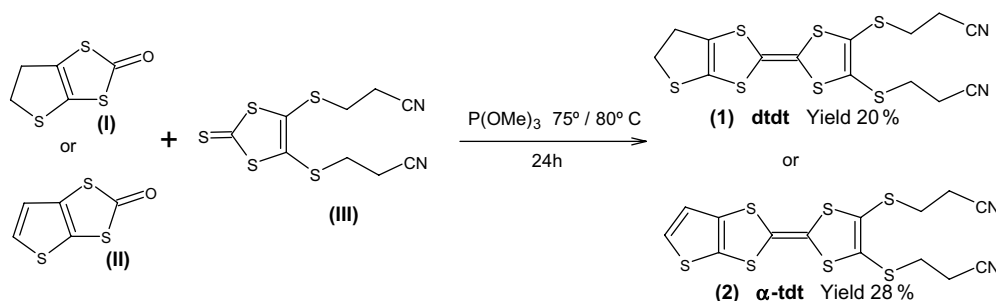


Fig. 1. Cyclic voltammograms of dtdt (grey) and α -tdt (black).

The electrochemical studies of **1** and **2** show two quasi reversible single electron oxidation processes typical of TTF-based donors (see Fig. 1). Cyclic voltammetry of α -tdt, in acetonitrile, shows a pair of asymmetric redox waves at (0.904, 1.090 V) 0.997 V versus Ag/AgCl, that correspond to the couple $[\alpha\text{-tdt}]^+ / [\alpha\text{-tdt}]^{2+}$. At lower potentials there is a pair of reversible waves centred at 0.639 V corresponding to the couple $[\alpha\text{-tdt}]^0 / [\alpha\text{-tdt}]^+$. For dtdt, the reversible waves that correspond to the $[\text{dtdt}]^0 / [\text{dtdt}]^+$ couple are observed at 0.612 V and a second, reversible but asymmetric, pair of redox waves is observed at (0.851, 0.962 V) 0.906 V that is ascribed to the $[\text{dtdt}]^+ / [\text{dtdt}]^{2+}$ couple. These same studies performed using DMF as a solvent show the same oxidation processes, at slightly lower potentials. The asymmetric nature of these last waves is typically due to the formation of a less soluble product that precipitates on the electrode. These electrochemical studies show that the non-aromatic compound is slightly easier to oxidize than the aromatic one, indicating that the aromatic thiophenic ring in α -tdt stabilizes the neutral state. The redox potential values obtained are comparable with those observed in the corresponding symmetric thiophenic-TTF-based donors, such as bis(ethylenethio)tetrathiafulvalene (BET-TTF) and α -dithiophenetetrathiathiophene (α -DT-TTF), sharing in a



Scheme 1.

Table 1
Electrochemical data of TTF derivatives **1** and **2** as well as of the related donors

Donor	Solvent	$^1E_{1/2}$ (V)	$^2E_{1/2}$ (V)
BET-TTF	MeCN [13]	0.39	0.66
	DMF [14]	0.43	0.58
α -DT-TTF	DMF [14]	0.50	0.67
TTF	MeCN [15]	0.37	0.75
	DMF [16]	0.39	0.62
(TCNEt-TTF) ^a	DMF	0.64	0.84
ddt	MeCN	0.61	0.91
	DMF	0.53	0.72
α -tdt	MeCN	0.64	1.00
	DMF	0.56	0.73

Potentials vs. Ag/AgCl; Pt working and counter electrodes.

^a 2,3,6,7-Tetrakis(2-cyanoethylthio)TTF obtained as a by-product of the synthesis reported in this work.

symmetrical fashion the same terminal thiophenic units and 2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene [12] (TCNEt-TTF), a TTF substitute with four cyanoethyl “arms”, obtained as by-product in the synthesis of **1**

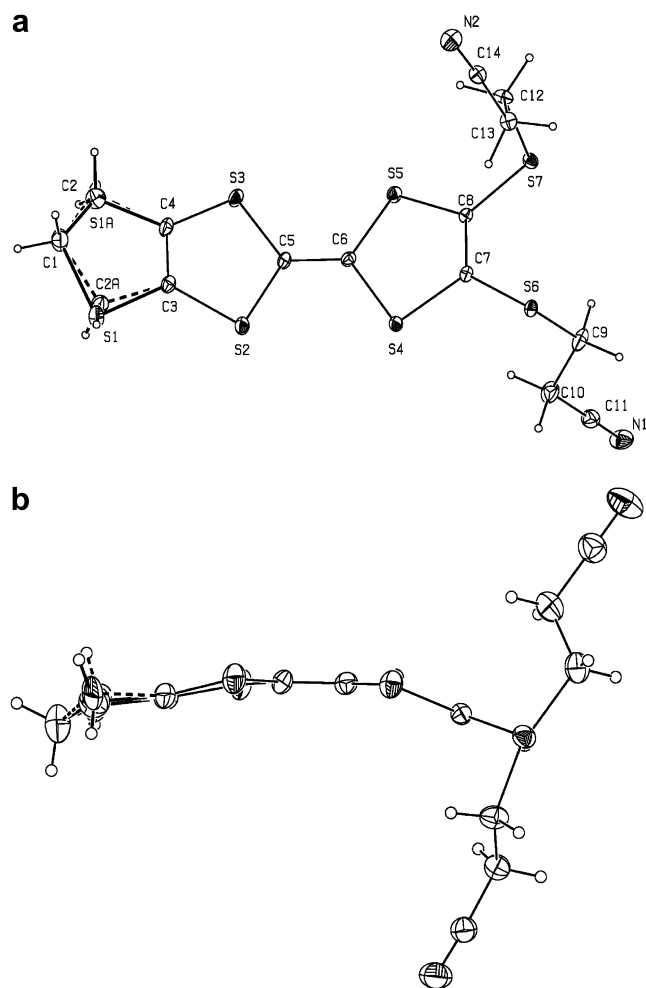


Fig. 2. ORTEP views and atomic numbering scheme of ddt (**1**) with thermal ellipsoids at 40% probability level.

and **2** (Table 1). From this comparison, we observe that the asymmetric fusion of the TTF core with only one thiophenic ring reduces the donor properties compared both with simple TTF and with TTF bisfused derivatives, BET-TTF and α -DT-TTF, but rises these donor properties when compared with TCNEt-TTF.

Compound **1** crystallizes in the orthorhombic system, space group $Pca2_1$, $Z = 4$, with unit cell parameters $a = 30.463(6)$ Å, $b = 9.0732(18)$ Å, $c = 7.0201(14)$ Å. The unit cell contains one independent ddt molecule in a general position, which presents a slight boat type distortion of the TTF core (Fig. 2). The terminal thiophenic sulfur atom presents an orientational disorder with occupation factors of 75% and 25% for S1 and S1A, respectively. The dihedral angle between the plane of the central core of the molecule (defined by the S5, S4, C5, C6, S3, S2 atoms) and the thiophenic ring is 10.7° , and between the plane defined by the atoms C7, C8, S7, S6 in the opposite end is 10.2° . The bond lengths of the molecule are within the expected range of values for neutral TTF derivatives [17].

The crystal structure is composed by head to tail stacks of ddt molecules along b . These stacks are made of molecules with their long axis in alternated orientations, making an angle of circa 45° (Fig. 3b), and are interlocked in such a way that the cyanoethyl “arms” are segregated from the TTF cores in alternated layers parallel to the a, c plane (Fig. 3a).

Molecules parallel to each other are connected by a short S4...S7 contact (Fig. 3b, Table 2). Molecules with their long axis tilted almost 45° (depicted in different shades

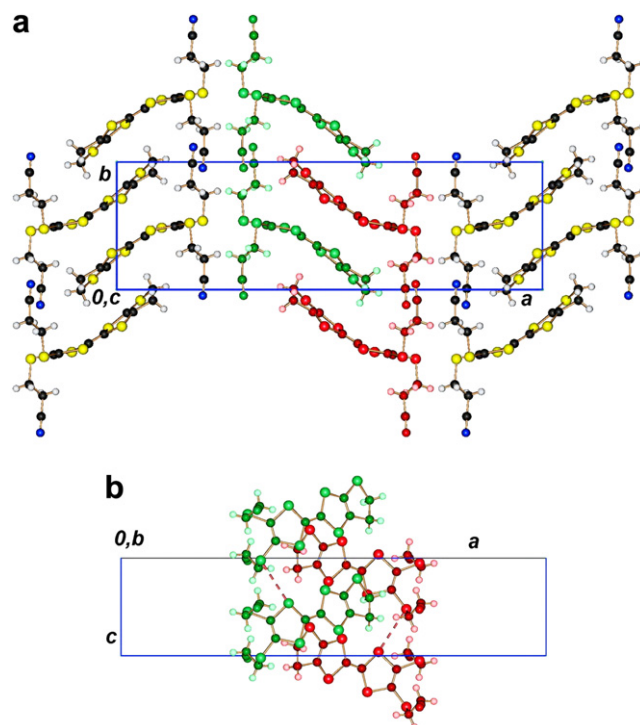


Fig. 3. Crystal structure of **1**: (a) viewed along c and (b) viewed along b .

Table 2
Hydrogen bonds and short contacts in the crystal structure of compound 1

	<i>d</i> (Å)	Angle (°)
S4...S7	3.687	
N2...H10b–C10	2.673	136
N2...H9b–C9	2.519	154
N1...H13a–C13	2.588	141

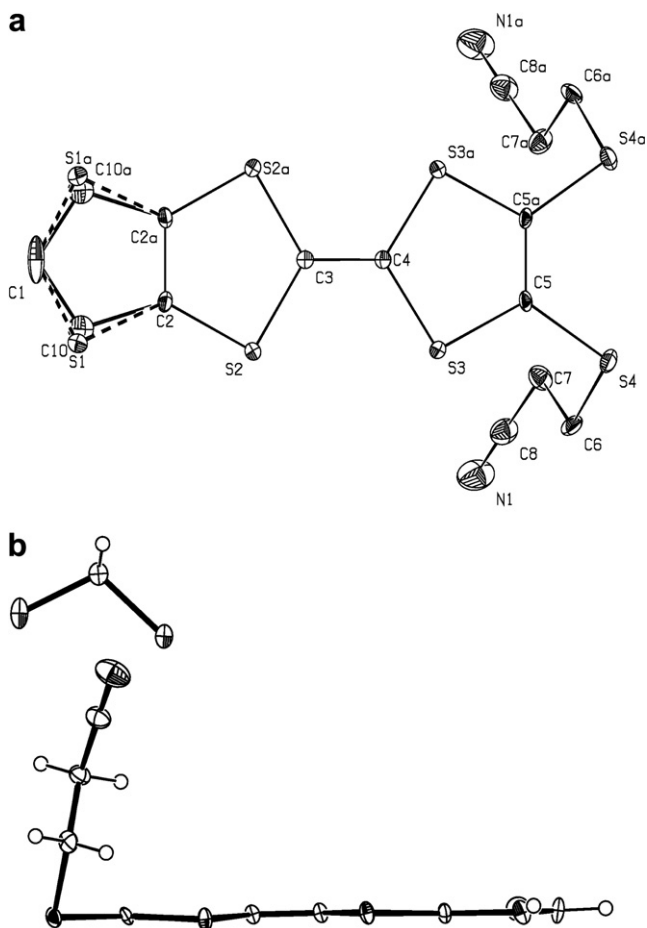


Fig. 4. ORTEP views and atomic numbering scheme of α -tdt \cdot CH₂Cl₂ (2) with thermal ellipsoids at 40% probability level.

in Fig. 3b) are connected by one short S...S contact (3.71 Å apart, only slightly above the S–S van der Waals radii sum). Some C–H...N hydrogen bonds are also bridging these two kinds of molecules (Table 2).

Along *a* the closest layers are connected by several C–H...N hydrogen bonds, involving the cyanoethyl “arms” (Table 2).

Compound 2 crystallizes in the monoclinic system, space group $P2_1/m$, $Z=2$, with unit cell parameters $a = 5.9780(13)$ Å, $b = 12.387(3)$ Å, $c = 13.933(3)$ Å and $\beta = 96.059(4)^\circ$. The unit cell contains one independent tdt molecule, positioned in a mirror plane containing C3 and C4 and perpendicular to the central TTF core, and one independent dichloromethane molecule also in a mirror plane (Fig. 4). The tdt molecule is planar with the exception

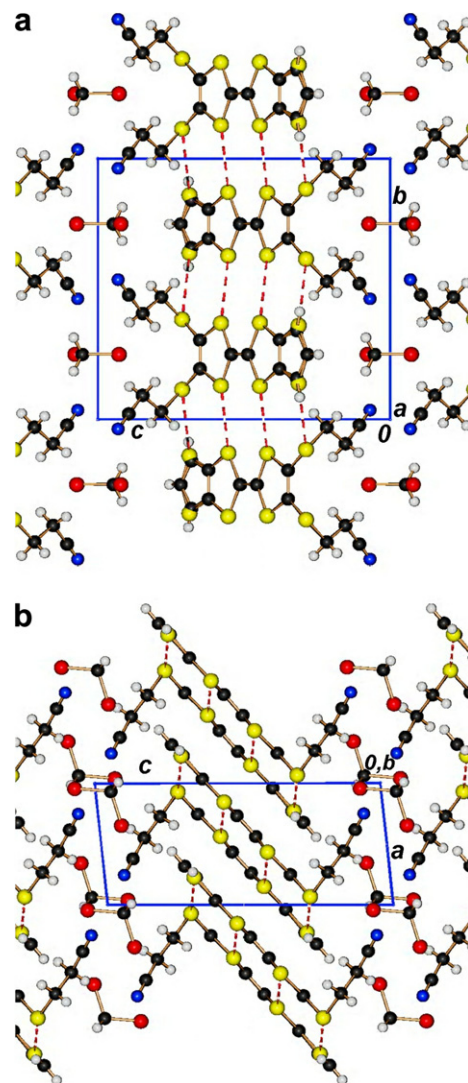


Fig. 5. Crystal structure of 2: (a) viewed along *a* and (b) viewed along *b*.

of the $-(\text{CH}_2)_2\text{-CN}$ “arms” which lie almost perpendicularly to the TTF core. Excluding these atoms, the atomic deviations from the average TTF plane are less than 0.069 Å. As imposed by the crystal symmetry the molecule presents 50% orientation disorder of the terminal thiophenic ring. The bond lengths of the molecule are within the expected range typical of neutral TTF [17].

The crystal structure consists of stacks along *a* of tdt molecules tilted toward this axis so that the angle between *a* and the normal of the TTF plane is 36.2° . The unit cell contains two stacks with parallel TTF planes but with opposite tail orientations. Again, as in the previous structure, there is a significant segregation of cyanoethyl groups and solvent molecules from the TTF cores in layers alternating along *c* (Fig. 5).

The overlap mode between molecules in a column is that of the thiophenic ring over TTF ring, with an interplanar distance of 3.53 Å and with a shortest S...S distance of 3.798 Å, slightly larger than the van der Waals radii sum. The molecules in the neighbouring columns interact

Table 3
Hydrogen bonds and short contacts in the crystal structure of compound **2**

	<i>d</i> (Å)	Angle (°)
S4···S1	3.618	
S3···S2	3.621	
N1···H9a–C9	2.352	149
Cl···H1–C1	2.763	134

through side-by-side S···S short contacts (Fig. 5a, Table 3). There are also several hydrogen bonds of the C–H···Cl and C–H···N type, between α -tdt and dichloromethane (Table 3).

These multi-sulfurated molecules tend to position themselves, side-by-side, in order to maximize the sulfur–sulfur interactions.

3. Conclusions

The convenient synthesis of two new TTF-based donors fused with thiophene moieties and substituted with dithiolenic precursors, 3-{5-[(2-cyanoethyl)thio]-2-(5,6-dihydrothieno[2,3-*d*][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl)thio}propanenitrile, dtdt (**1**) and 3-({5-[(2-cyanoethyl)thio]-2-thieno[2,3-*d*][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl)thio}propanenitrile, α -tdt (**2**), was achieved. These new molecules show reduced donor properties when compared with the corresponding symmetrically thiophene fused TTFs. As sulfur rich molecules they display a crystal structure dominated by several short S···S contacts. These TTF donors are also ligand precursors for preparing bisdithiolenic complexes with highly extended ligands, currently under study in our laboratory, and which will be reported in due course.

4. Experimental

4.1. General

All solvents were purified following standard procedures. 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione (**III**) and bis(tetraethylammonium)bis(2-thioxo-1,3-dithiole-4,5-dithiolate) zincate complex were prepared by an analogous procedure to that in Refs. [10,11] above, 5,6-dihydrothieno[2,3-*d*]-1,3-dithiol-2-one (**I**) and 5,6-thieno[2,3-*d*]-1,3-dithiol-2-one (**II**) were synthesized as previously described [8,9]. Other chemicals were commercially obtained and used without further purification. Column chromatography was carried out using silica gel (0.063 \pm 0.2 mm) from SDS. IR spectra were obtained on a Perkin–Elmer 577 spectrophotometer. ^1H NMR spectra were recorded on a Bruker Aspect 3000 (300 MHz for ^1H) and CDCl_3 was used as the solvent, TMS was the internal reference. MALDI mass spectra were obtained in time-of-flight negative linear mode on a Kratos Kompact Maldi 2K probe (KRATOS Analytical) that was operated with pulsed extraction of the ions. Cyclic voltammetry data were obtained using a EG&G PAR 263A potentiostat galvanostat with a cell equipped with a double KCl (3 M) bridge.

The measurements were performed at room temperature in acetonitrile and dimethylformamide that contained *n*-Bu₄PF₆ (10⁻¹ M) as the supporting electrolyte, with a scan rate of 100 mV/s, platinum wire working and counter electrodes and a Ag/AgCl reference electrode.

4.2. Synthesis

4.2.1. 3-{5-[(2-Cyanoethyl)thio]-2-(5,6-dihydrothieno[2,3-*d*][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl)thio}propanenitrile, dtdt (**1**)

Compound **I** (1.223 g, 6.94 mmol) and compound **III** (2.2 g, 7.22 mmol) were dissolved in 12 mL of P(OMe)₃ in a 50 mL round bottomed flask. The mixture is heated to 75 °C/80 °C for 24 h. Upon cooling, 60 mL of methanol was added and the mixture was cooled down to -15 °C, during 24 h. The precipitate was filtered off and washed with 3 \times 10 mL of methanol and dried under vacuum. This solid was purified by column chromatography, using CH₂Cl₂ as a solvent (rf = 0.35). Single crystals, suitable for RX measurements were obtained from cooling down a refluxed 3:1 *n*-hexane/CH₂Cl₂ solution. Yield 20% (592 mg); Elemental Anal. Calc. for C₁₄H₁₂N₂S₇: C, 38.86; H, 2.80; N, 6.47; S, 51.87. Found: C, 39.49; H, 2.51; N, 6.23; S, 51.35%. FT-IR (KBr), cm⁻¹: 2925 (m, -CH₂-), 2253 (m, -C \equiv N), 1617 and 1482 (m, C=C), 1425 (s, S-CH₂-R); H NMR (300 MHz, CDCl₃): δ = 3.781 (t, *J* = 8 Hz, 2H, -C2H₂-ClH₂-S1-); 3.084 (t, *J* = 7 Hz, 2H, -C4-C2H₂-C1H₂-); 2.876 (t, *J* = 8 Hz, 4H, S-CH₂-CH₂-CN); 2.738 (t, *J* = 7 Hz, 4H, S-CH₂-CH₂-CN) ppm; MS: *m/z* (%) = 431.9 (M⁺,100); M.p.: 129–130 °C.

4.2.2. 3-({5-[(2-Cyanoethyl)thio]-2-thieno[2,3-*d*][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio}propanenitrile, α -tdt (**2**)

This compound was prepared by using the same method described for **1**, using precursor **II** instead of precursor **I**. The solid obtained was purified by column chromatography with CH₂Cl₂ as a solvent (rf = 0.35). Single crystals suitable for RX measurements, were obtained from slowly cooled 3:1 *n*-hexane/CH₂Cl₂ solutions. Yield 28% (743 mg); Elemental Anal. Calc. for C₁₄H₁₀N₂S₇: C, 39.04; H, 2.34; N, 6.50; S, 52.12. Found: C, 39.65; H, 2.34; N, 6.47; S, 53.06%. FT-IR (KBr), cm⁻¹: 3077 (w, -C \equiv N), 2926 (m, -CH₂-), 2250 (m, -C \equiv N), 1634 and 1487 (w, -C=C-), 1416 (s, S-CH₂-R); H NMR (250 MHz, CDCl₃): δ = 7.30 (d, *J* = 5 Hz, 2H, -C10H-C1H-S1-); 6.84 (d, *J* = 5 Hz, 2H, -C1H-C10H-C2-); 3.11 (t, *J* = 7 Hz, 4H, -S4-C6H₂-C7H₂-CN); 2.74 (t, *J* = 7 Hz, 4H, -S4-C6H₂-C7H₂-CN) ppm; MS: *m/z* (%) = 429.7 (M⁺,100); M.p.: 137–138 °C.

5. X-ray crystallographic study

X-ray diffraction experiments were performed with a Bruker AXS APEX CCD detector diffractometer using grap-

Table 4
Crystallographic data and structure refinement results for dtdt (**1**) and α -tdt \cdot CH₂Cl₂ (**2** \cdot CH₂Cl₂)

Formula	C ₁₄ H ₁₂ N ₂ S ₇ (1)	C ₁₅ H ₁₂ Cl ₂ N ₂ S ₇ (2 \cdot CH ₂ Cl ₂)
Molecular weight	432.68	430.66
Crystal system	orthorhombic	monoclinic
Space group	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ / <i>m</i>
<i>T</i> (K)	295(2)	130(2)
<i>a</i> (Å)	30.453(6)	5.9780(10)
<i>b</i> (Å)	9.0732(18)	12.387(2)
<i>c</i> (Å)	7.0201(14)	13.933(2)
β (°)		96.059(3)
<i>V</i> (Å ³)	1939.7(7)	515.59
<i>Z</i>	4	2
λ (Å)	0.71073	0.71073
μ (Mo K α) (mm ⁻¹)	0.811	1.033
Crystal size (mm)	0.22 \times 0.16 \times 0.06	0.35 \times 0.25 \times 0.02
θ_{\max} (°)	23.42	27.10
<i>T</i> _{min} , <i>T</i> _{max}	0.8418/0.9530	0.7138/0.9796
Measured reflections	4534	4161
Independent reflections	2568	2360
<i>R</i> _{int}	0.0436	0.0475
Data/restraints/ parameters	2568/21/223	2360/8/153
<i>R</i> (<i>F</i> ²)[<i>F</i> ² > σ (<i>F</i> ²)]	0.0460	0.0490
<i>wR</i> (<i>F</i> ²)	0.0785	0.0907

hite monochromated Mo K α radiation ($\lambda = 0.71073$ Å), in the φ and ω scans mode. A semi empirical absorption correction was carried out using SADABS [18]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [19]. The structures were solved by direct methods using SIR97 [20] and refined by full-matrix least-squares methods using the program SHELXL97 [21] using the WINGX software package [22]. Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP3 [23]. A summary of the crystal data, structure solution and refinement is given in Table 4.

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Appendix A. Supplementary material

CCDC 626998 and 626999 contain the supplementary crystallographic data for **1** and **2** \cdot CH₂Cl₂. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: depos-

it@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.03.041.

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