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CyanobenzeneTTF-type donors; synthesis and characterization

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ABSTRACT

Two cyanobenzeneTTF-type electron donors, which are also dithiolene ligand precursors, cyanobenzenedicyanoethylthiotetrathiafulvalene, (cbdc-TTF) and dicyanobenzenedicyanoethylthiotetrathiafulvalene, (dcbdc-TTF), were obtained through cross-coupling reactions with triethyl phosphite between 4,5-bis (2-cyanoethylthio)-1,3-dithiole-2-one and 4,cyanobenzene-1,3-dithiole-2-thione or dicyanobenzene-1,3-dithiole-2-thione, respectively. These reactions also yield 2,3,6,7-tetrakis(2-cyanoethylthio)-TTF and the corresponding symmetric cyanobenzene TTF derivatives dicyanodibenzeneterathiafulvalene (dcdb-TTF) and tetracyanodibenzotetrathiafulvalene (TCN-DBTTF) resulting from the self-coupling reactions of the ketone and the thiones. Compound dcdb-TTF was also synthesized by homo-coupling reaction of the cyanobenzene-1,3-dithiole-2-ketone with triethyl phosphite. These compounds were characterized namely by single crystal X-ray diffraction and cyclic voltammetry.

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The large majority of organic metals and superconductors that have been developed during the last decades have been based on derivatives from tetrathiafulvalene molecule (TTF).¹ Their success as building blocks for conducting materials is due to unique π -donor properties of TTF and the possibility of extending the delocalized π -system by incorporation of additional sulfur or other hetero atoms in the molecular periphery and chemical functionalization. The exploration of different TTF derivatives in this context has been based on two guide lines. First, the extension of the π -system in general renders more accessible the different oxidation states, and maximizes the intermolecular interactions between planar molecules that tend to be organized as stacks in the solid state. Second, the incorporation of additional sulfur and other hetero atoms to the molecular periphery promotes the side intermolecular interactions along the molecular plane, allowing a possible 2D or 3D character to the electronic interactions.

Some extended TTF derivatives have also been used in the last decade as dithiolene ligands, to prepare extended transition metal bisdithiolene complexes.² These complexes deserved special attention since some of them, in their neutral state, were found to lead metallic behavior, the so called single component molecular metals.³

More recently there has been increasing interest in TTF derivatives containing N atoms in their periphery. Such compounds, while retaining the electroactive behavior of TTF could in addition be able to coordinate transition metals.⁴ Aiming at enlarging this type of complexes we decided to explore new extended dithiolene ligands that incorporate not only TTF, but also N containing units. Along this line we recently reported the synthesis of the pzdc-TTF, an extended TTF fused with a pyrazine moiety.⁵ Cyano groups incorporated into TTF type donors, which besides possible metal coordination can be engaged in weak intermolecular interactions such as hydrogen and halogen bonding, have been however a lot less explored. Literature examples are mostly restricted to salts of 3-cyano-3',4'-ethylenedithiotetrathiafulvalene (EDT-TTF-CN).⁶

In this Letter, we report the synthesis and characterization⁷ of two new extended TTF-type donors fused with cyanobenzene and dicyanobenzene moieties, the cyanobenzenedicyanoethylthiotet-rathiafulvalene, (cbdc-TTF) (1a)⁸ and the dicyanobenzenedicyanoethylthiotetrathiafulvalene (dcbdc-TTF) (1b),⁹ which are also precursors for the preparation of new extended cyano-TTF fused dithiolene ligands. A new symmetric cyanobenzene fused TTF-based donor molecule, the dicyanodibenzenetetrathiafulvalene (dcdb-TTF) (2a),¹⁰ is also reported.

The key compounds for the synthesis of the cyanobenzene substituted compounds (new extended TTF-type donors and symmetric TTF-type donors) are the thiones **Ia** (cyanobenzene-1,3-dithiole-2-thione) and **Ib** (dicyanobenzene-1,3-dithiole-2-thione).







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Scheme 1. Reagents and conditions: (i) K_2S , CS_2 , DMF; (ii) P(OEt)₃, toluene, 110 °C; (iii) Hg(OAc)₂, AcOH, DCM; (iv) P(OEt)₃, toluene, 110 °C.

Thione **Ia** was recently described by us¹¹ and thione **Ib**¹² was prepared in 59% yield following a similar procedure based on the reaction of 2,3-dichlorocyanobenzene with potassium trithiocarbonate. The corresponding ketones **IIa**¹³ and **IIb**¹⁴ (cyanobenzene-1,3dithiole-2-one and dicyanobenzene-1,3-dithiole-2-one), were used to prepare the symmetric donors **2a** and **2b** by homocoupling reactions. These ketones were obtained from a regular transchalcogenation reaction of the corresponding thiones, accomplished with mercuric acetate in dichloromethane and glacial acetic acid to give **IIa** and **IIb** in 81% and 64% yields, respectively.

The TTF-based donors **1a** and **1b** were obtained following a synthetic route first used by Underhill and co-workers² involving the coupling with triethyl phosphite between thiones and ketones

Table 1								
Crystallographic details	for	compounds	Ia,	Ib,	IIa,	IIb,	and	1b

(Scheme 1). Although similar results are expected to be achieved from a reaction between ketones only, such route was not explored.

The hetero-coupling reactions leading to the compounds 1a and 1b also yielded other by-products (2a, 2b, and 3), resulting from the self-coupling of the corresponding thiones (Ia and Ib) and ketone (III). Dicyanodibenzenetetrathiafulvalene (dcdb-TTF) (2a) and TCN-DBTTF (2b) result from the self-coupling of thiones Ia and Ib. However, due to the insolubility in common organic solvents of these compounds, this synthetic pathway is not a valuable option to isolate 2a or 2b in large yields. Their insolubility prevents the direct purification by column chromatography and a previous purification by Soxhlet extraction is required. One test in a small scale was performed and **2a** and **2b** were isolated in 25% and 18% yields, respectively. Both coupling reactions yield also to 2,3,6,7-tetrakis(2cvanoethylthio)TTF (**3**) resulting from the self-coupling of ketone **III.**¹⁵ with a 21% and 14% yield, as a by-product of the preparation of **1a** or **1b**, respectively. In alternative, compounds **2a** (76% yield) and 2b can be obtained in better yields by homo-coupling reactions as previous reported by Decurtins et al.¹⁶ for **2b**. Besides the products from the self-coupling of the thiones and ketones, reasonable yields of 37% and 34% were achieved for 1a and 1b, respectively, after column separation, using DCM/MeOH (v:v = 50:1) as eluent.

Compounds **Ia**, **Ib**, **IIa**, **IIb**, and **1b** were easily recrystallized affording single crystals suitable for their structural refinement based on single crystal X-ray diffraction (Table 1).¹⁷

Thione **Ia** crystallizes in the Monoclinic system, space group P2(1)/c, while thione **Ib** crystallizes in the Orthorhombic system, space group *Pbca*. Both asymmetric units contain one independent molecule in a general position.

Ketones **IIa** and **IIb** crystallize in the Orthorhombic system, space group *Pna2*(1) and *Pca2*(1), respectively, with both asymmetric units containing one independent molecule in a general position. Figure 1 shows the ORTEP diagrams of **Ia**, **Ib**, **IIa**, and **IIb** with the corresponding atomic numbering scheme. The thiones (**Ia** and **Ib**) and ketones (**IIa** and **IIb**) are essentially planar (Rms deviation of the fitted atoms: 0.0274 Å, 0.0196 Å, 0.0610 Å, and 0.0748 Å, respectively).

In the crystal structure of **Ia** and **IIb** the molecules are stacked head to head in regular columns along the *b* axis (Fig. 2a1 and b1, respectively) tilted approximately 24° and 21° , respectively, toward the staking axis *b*. The shorter contacts, clearly below the sum of van der Waals radii, are between neighboring columns, either hydrogen bonds or S...S contacts (Table 2), establishing layers of closely connected molecules parallel to the *a*, *c* plane.

	(Ia)	(Ib)	(IIa)	(IIb)	(1b)
Crystal size (mm)	$0.60 \times 0.10 \times 0.03$	$0.30 \times 0.18 \times 0.03$	$0.30 \times 0.28 \times 0.10$	$0.20 \times 0.20 \times 0.06$	$0.20 \times 0.18 \times 0.10$
Crystal color and shape	Yellow plate	Yellow plate	Colorless prism	Colorless plate	Orange block
Empirical formula	$C_8H_3NS_3$	$C_9H_2N_2S_3$	C ₈ H ₃ NOS ₂	$C_9H_2N_2OS_2$	$C_{18}H_{10}N_4S_6$
Molecular mass	209.29	234.31	193.23	218.25	474.66
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	P2(1)/c	Pbca	Pna2(1)	Pca2(1)	P-1
a (Å)	15.8538(11)	7.8700(5)	7.3555(2)	16.2207(9)	7.1703(2)
b (Å)	3.8896(2)	14.3785(8)	12.3095(1)	3.8093(2)	8.2429(2)
<i>c</i> (Å)	15.5207(10)	16.5094(10)	8.5265(2)	13.9027(9)	17.2712(4)
α (°)	90.00	90.00	90.00	90.00	93.4710(10)
β(°)	118.032(2)	90.00	90.00	90.00	98.4740(10)
γ (°)	90.00	90.00	90.00	90.00	105.115(2)
V (Å ³)	844.80(9)	1868.18(19)	772.01(3)	859.04(9)	969.47(4)
Z, D_{calcd} (mg/m ³)	4, 1.646	8, 1.666	4, 1.663	4, 1.687	2, 1.626
μ , (mm ⁻¹)	0.809	0.745	0.627	0.578	0.719
F (000)	424	944	392	440	484
Index range (h, k, l)	-18/19; -3/4: -18/18	-9/9; -16/17; -19/20	-9/9; -15/15; -10/10	-20/18; -4/4; -17/17	-8/8; -10/10; -21/21
T _{max/min}	0.9761/0.6423	0.9780/0.8074	0.9400/0.8342	0.9662/0.8834	0.9316/0.8696
Final R_1 , $[I > 2\sigma(I)]$, wR_2	0.0290, 0.0759	0.0349, 0.0831	0.0222, 0.0539	0.0259, 0.0259	0.0296, 0.0697



Figure 1. ORTEP diagrams of: compounds **Ia** (a), **Ib** (b), **IIa** (c), and **IIb** (d), drawn at 30% probability level with the atomic numbering scheme.



Figure 2. Crystal structure of compounds **Ia** and **IIb** viewed along b axis (a1 and b1) and along c axis (a2) and a axis (b1), respectively.

Figure 2a2 and b2 shows these layers along the c and a axis, respectively.

The crystal structure of **Ib** (Fig. 3a1 and a2) is composed by head to tail slightly dimerized stacks of planar molecules connected along the *a*-axis by short contacts ($C1\cdots S1$; $C1\cdots S2$; $C3\cdots S1$).

The molecules are tilted toward the stacking axis by 60.4°. In the unit cell there are 8 molecules arranged in four stacks with different orientations connected through several short contacts (Table 2). Molecules in different stacks make an angle of 120.8°. The crystal structure of **IIa** is made of head to head regular stacks of molecules along the *a*-axis with cyano groups alternating in different directions (Fig. 3b1 and b2). The molecules along these stacks are connected by short contacts (C5…C6) and tilted 68.4° toward the *a*-axis. In the unit cell there are two chains of molecules making an angle of 43.1° and connected by several short contacts listed in Table 2.

The compound **1b** crystallizes in the triclinic system, space group P-1. Figure 4 shows ORTEP diagrams with the corresponding atomic numbering scheme. The asymmetric unit contains one independent dcbdc-TTF molecule located in a general position. The central TTF core and the dicyanobenzene unit are essentially planar (Rms deviation of fitted atoms: 0.0378 Å) while the chains containing the cyanoethyl groups are drastically deviated from the central molecular plane. Bond lengths and angles in the TTF moiety are in the range expected for the neutral TTF derivatives.¹⁸

The crystal structure of **1b** is composed by head to tail stacks of dcbdc-TTF molecules along *b* (Fig. 5). These stacks are arranged with molecules in the same orientation, making layers of cyanoethyl groups segregated from the TTF cores, which alternate along *c* in layers parallel to the *a*,*b* plane. Molecules parallel to each other are connected by short contacts and hydrogen bonds (C10···C9; C8···S5; C16–H16A···N1; C16–H16A···N1) as listed in Table 2 and shown in Figure 5b.

The electrochemical behavior of these new donors was studied by cyclic voltammetry.¹⁹ In each case, the two standard one-electron quasi-reversible redox waves typical of TTF donors were observed at potentials listed in Table 3. The redox potentials of the donors **1a** and **1b** were measured in dimethylformamide. Due to poor solubility of donor **2a** the solvent was in this case replaced by benzonitrile. Donors **1a**, **1b**, and **2a** show the typical two redox processes of TTF-based donors. At lower potentials there is a quasi-reversible process, at 0.38 V, 0.42 V, and 0.27 V, respectively, corresponding to the formation of the cationic species and a second irreversible process at 0.54 V, 0.59 V, and 0.60 V, due to the formation of the dicationic species.

Comparing the redox potentials of the two new extended TTF donors (**1a** and **1b**) we can conclude that, as expected, the additional cyano substituent group reduces the donor properties, shifting the redox potentials to higher values due to the electron-withdrawing effect of the cyano groups.²¹

 Table 2
 Selected short contacts and hydrogen bonds in the crystal structure of Ia, Ib, IIa, IIb, and 1b

Ia		IIb		1b	
C6–H6···S1 (#a)	2.928 Å	C4−H4····N2 (#h)	2.578 Å	C10···C9 (#1)	3.387 Å
C3−H3····N1 (#b)	2.636 Å	S1····N2 (#i)	3.273 Å	C8···S5 (#2)	3.481 Å
C7–H7···N1 (#c)	2.668 Å	C4···O1 (#j)	2.981 Å	C16-H16A···N1 (#1)	2.617 Å
S1···S1 (#d)	3.519 Å	S2···N1 (# <i>l</i>)	3.179 Å	C17–H17A···N2 (#1)	2.707 Å
S3···S3 (#f), (#g)	3.443 Å	S2···N2 (#m)	3.273 Å	S5···N3 (#3)	3.178 Å
		C5−H5···N1 (#n)	2.692 Å	C18···C18 (#4)	3.280 Å
				C13−H13B…N4 (#3)	2.457 Å
Ib				Пр	
C1S2 (#j)	3.491 Å	S3····N1 (#p)	3.097 Å	O1···C8 (#j)	3.213 Å
C1···S1 (#j)	3.495 Å	N1···S2 $(#q)$	3.326 Å	C5···C6 (#j)	3.369 Å
C3···S1 (#j)	3.497 Å	N2···S2 $(\#r)$	3.249 Å	S2···N1 (#j)	3.272 Å
C5···C9 (#j)	3.394 Å	C3–H3····N2 (#h)	2.736 Å	C7−H7···O1 (#h)	2.535 Å
N2···S1 (#o)	3.238 Å	C6−H8···N1 (#x)	2.567 Å	C5–H5····N1 (#h)	2.497 Å
$(0, S1(\#_0))$	3 111 Å				

 $\begin{array}{l} \#a=x, -\frac{1}{2}-y, \frac{1}{2}+z; \ \#b=2-x, 1-y, 2-z; \ \#c=2-x, -\frac{1}{2}+y, 2.5-z; \ \#d=1-x, -1-y, 1-z; \ \#f=1-x, -\frac{1}{2}+y, 1.5-z; \ \#g=1-x, \frac{1}{2}+y, 1.5-z; \ \#b=\frac{1}{2}+x, 1-y, z; \ \#i=\frac{1}{2}+x, 1-y, z; \ \#i=2-x, -\frac{1}{2}+y, -\frac{1}{2}+z; \ \#i=1.5-x, -1+y, -\frac{1}{2}+z; \ \#i=1.5-x, -1+y, -\frac{1}{2}+z; \ \#i=1.5-x, 1-y, 1-z; \ \#i=1.5-x, 1-z; \ \#i=1.5-x, 1$



Figure 3. Crystal structure of compounds **Ib** viewed along a axis (a1) and along c axis (a2) and of compound **IIa** viewed along a axis (b1) and b axis (b2).



Figure 4. ORTEP diagrams of compound **1b** drawn at 30% probability level, showing the atomic numbering scheme in the top (a) and lateral (b) molecular views.

In conclusion we have prepared a variety of new extended TTFtype symmetric and asymmetric donors fused with cyanobenzene and dicyanobenzene moieties. The crystal structures of these donors are dominated by a large number of S mediated contacts. The crystal structure of compound **1b** presents a strong segregation of the ethyl cyano groups and the TTF cores in alternated layers. These new molecules are expected to be used directly as electroactive donors or as precursors for the preparation of new extended cyano-TTF fused dithiolene ligands with the potential to provide solids with interesting electrical and magnetic properties. In particular these molecules will allow to further explore the possible role of the cyano groups in crystal engineering, either coordinating to transition metals or promoting weak intermolecular interactions such as hydrogen and halogen bonding with halogenated anions.



Figure 5. Crystal structure of **1b**: (a) viewed along *b* axis, and (b) side view of one column.

Table 3

Redox potentials (vs Ag/Ag⁺) of the TTF-type donors **1a**, **1b**, **2a**, and **3** as well as of related donors (Half wave potentials $E_{1/2}$ except * where anodic peak values are given instead)

Donor	Solvent	${}^{1}E_{1/2}(V)$	${}^{2}\boldsymbol{E}_{1/2}(V)$
1a	DMF	0.38	0.54*
1b	DFM	0.42	0.59*
2a	Benzonitrile	0.27	0.60*
3 ^{18d}	DMF	0.64	0.84
DCET-BzTTF ²⁰	DCM	0.742	1.152
pzdc-TTF ⁵	DMF	0.43	0.63

* Anodic peak potentials.

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Supplementary data

Supplementary data (crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1015265-1015269 for compounds 1a, Ia, Ib, IIa, Ibb) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.10.111. These data include MOL files and InChiKeys of the most important compounds described in this article.

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- 7. Whenever required, the solvents were dried and purified by standard procedures,²² freshly distilled, and saturated with nitrogen prior to use. All starting reagents were purchased from commercial sources and used without further purification or synthesized from published methods. The thione **Ia** was prepared as previously described.¹¹ The ketone **III** was obtained after a regular S to O exchange reaction of the 4,5-cyanoethylthio)-1,3-dithiole-2-thione.¹⁵ Other chemicals were commercially obtained and used without further purification. Yields were calculated for the pure compounds. Column chromatography was carried out using silica gel (0.063 ± 0.2 mm) from SDS. IR spectra were obtained on a Perkin–Elmer 577 spectrophotometer. ¹H and ¹³C NMR spectra were recorded with an Oxford Varian Unity 300 with DMSO-d₆ as solvent and using TMS as internal reference. Elemental analyses of the isolated compounds were performed at CTN analytical services using an EA 110 CE Instruments automatic analyzer. Melting points were performed on a Stuart Scientific SMP2.
- 8. Cyanobenzenedicyanoethylthiotetrathiafulvalene, cbdc-TTF (1a): Compound Ia (0.55 g; 2.62 mmol) and III (0.8 g; 2.77 mmol) were suspended in 10 mL of triethyl phosphite (P(OEt)₃). The mixture was heated up to 90 °C under nitrogen atmosphere and stirred for 16 h. During the reaction an orange precipitate was formed. Upon cooling to ambient temperature the precipitate was filtered off and washed with 3 × 10 mL of methanol and dried under vacuum.

The pure compound **1a** (0.436 g; 0.97 mmol, yield = 37%) was isolated as an orange solid after separation by silica gel column chromatography, using DCM/ MeOH (v:v = 50:1) as eluent. Mp 192 °C; R_f = 0.76. IR (KBr) = 3074 (Ar–H), 2960; 2923 (CH₂), 2252; 2225 (C=N), 1463; 1564 (C=C), 1120 (Ar–S), 582 (C–S) cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6 , 25 °C, TMS) δ = 8.07 (s, 1H), 7.786 (d, J = 8 Hz, 1H), 7.683 (d, J = 8 Hz, 1H), 3.112 (t, J = 6.6 Hz, 2H), 2.758 (t, J = 6.6 Hz, 2H), ¹³C (75.3373 MHz), DMSO- d_6 ; δ = 151.6, 142.9, 131.0, 128.0, 126.3, 124.0, 119.6, 118.0, 109.8, 31.6, 18.9. Anal. Calcd for C₁₇H₁₁N₃S₆: C 45.41; H 2.47; N 9.34; S 42.78. Found C 444.58; H 2.53; N 9.11; S 42.42.

It was possible to isolate one of the other two products of the coupling reaction resultant from the self-coupling of the reactants: compound **3**, 0.3169 g; 0.582 mmol; yield = 21%; Mp 189 °C; R_f = 0.2. IR (KBr) = 2922 (CH₂), 2249 (C=N), 1590 (C=C), 1233 (C-C), 771 (C-S) cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6 , 25 °C, TMS) δ = 3.16 (t, J = 9 Hz, 2H), 2.87 (t, J = 9 Hz, 2H). ¹³C (75.3373 MHz), DMSO- d_6 ; δ = 127.62, 118.83, 109.47, 30.86, 18.23. Anal. Calcd for C₁₈H₁₆N₄S₈: C 39.99; H 2.96; N 10.28; S 47.08. Found C 39.51; H 3.12; N 10.63; S 47.16.

The poor solubility of 2a in common organic solvents did not allow the pure isolation of this compound using the procedure described above. The compound 2a stays at the top of the silica gel column chromatography, mixed with some silica gel (the crude mixture, before the chromatography separation, is mixed with some silica gel to facilitate the introduction of the crude in to the column). An alternative procedure was tested on a smaller scale. Before the column chromatography the crude product was purified by soxhlet extraction with hot DCM to isolate the insoluble compound 2a. The extracted DCM solution was evaporated to dryness and the mixture product was chromatographed, using DCM/MeOH (v:v = 50:1) as eluent.

The main purpose of this coupling reaction was the hetero coupling of the **Ia** and **III** with the synthesis of compound **1a** in a good yield, compounds **2a** and **3** were considered side products of the reaction result of the reactants homo coupling.

9. Dicyanobenzenedicyanoethylthiotetrathiafulvalene, dcbdc-TTF (1b): This compound was prepared using the same method described for 1a, using precursor lb (0.6 g; 2.56 mmol) instead of precursor la. The crude obtained was purified by column chromatography with DCM/MeOH (v:v = 50:1) as eluent. The pure compound 1b (0.413 g; 0.87 mmol, yield = 34%) was isolated as a red solid after column chromatography. Single crystals of 1b, suitable for RX measurements were obtained from slow evaporation of a refluxed chloroform

solution after cooling to ambient temperature. Mp 228–233 °C; R_f = 0.72. IR (KBr) = 3069; 3051 (Ar–H), 2981; 2937 (CH₂), 2252; 2230 (C=N), 1563 (C=C), 1123 (Ar–S), 522 (C–S) cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6 , 25 °C, TMS) δ = 8.320 (s, 1H), 3.176 (t, *J* = 6.6 Hz, 2H), 2.890 (t, *J* = 6.6 Hz, 2H). ¹³C (75.3373 MHz), DMSO- d_6 ; δ = 151.6, 143.9, 128.4, 127.4, 119.6, 116.2, 112.9, 109.4, 31.6, 18.9, Anal. Calcd for C₁₈H₁ON₄S₆: C 45.54; H 2.14; N 11.80; S 40.53. Found C 44.98, H 2.40, N 11.90, S 40.75.

It was possible to isolate one of the other two products of the coupling reaction resultant from the self-coupling of the reactants: compound **3**, 0.229 g; 0.0.42 mmol; yield = 15%; Mp 189 °C; R_f = 0.2. IR (KBr) = 2922 (CH₂), 2249 (C=N), 1590 (C=C), 1233 (C-C), 771 (C-S) cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6 , 25 °C, TMS) δ = 3.16 (t, *J* = 9 Hz, 2H), 2.27 (t, *J* = 9 Hz, 2H). ¹³C (75.3373 MHz), DMSO- d_6 ; δ = 127.62, 118.83, 109.47, 30.86, 18.23.

As in case of compound **2a**, also compound **2b** is insoluble in common organic solvents. The insolubility of **2b** did not allow the pure isolation of this compound. It stays at the top of the silica gel column chromatography.

10. Dicyanodibenzenetetrathiafulvalene, dcdb-TTF (2a): The compound IIa (0.79 g, 4.09 mmol) was suspended in the mixture of triethyl phosphite (10 mL) and toluene (10 mL). The mixture was heated up to 120 °C under nitrogen atmosphere and stirred for 3 h. During the reaction a yellow precipitate was formed. After cooling to room temperature, 20 mL of methanol was added to the reaction mixture to complete the precipitation. The product was isolated by filtration as a yellow powder, washed with methanol, and dried under vacuum (0.553 g, 1.56 mmol, yield = 76%). Mp >254 °C. IR (KBr pellet) = 3056 (Ar−S), 2227 (C≡N), 1577 (C=C), 1452 (C=C), 1122 (Ar−S), 582 (C−S); Anal. Calcd for C1₆H₆N₂S₄: C 54.21; H 1.71; N 7.90; S 36.18. Found C 54.67; H 1.87; N 7.76; S 36.24.

The insolubility in common organic solvents prevents further characterization of this compound by NMR techniques.

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- 4,5-Cyanobenzene-1,3-dithiole-2-thione (Ib): A mixture of potassium sulfide (43%. 3 g, 11.7 mmol), carbon disulfide (2 mL, 33 mmol) and dimethylformamide (8 mL) was stirred at room temperature for 3 h. To the resulting suspension of potassium trithiocarbonate, red 45dichlorophthalonitrile (1.97 g, 10 mmol) was added, and the mixture was further stirred for 24 h at 50 °C. The mixture was then poured into water (100 mL), filtered, dried in vacuum, and compound Ib (1.38 g, 5.9 mmol, yield = 59%) was isolated as a yellow solid after separation by silica gel column chromatography. Mp 247–250 °C; R_f =0.45 (CH₂Cl₂/hcxane, 3:1). IR (KBr) = 3076 (Ar–H), 2227 (C=N), 1568 (C=C), 1220 (C–C), 1120 (Ar–S), 1085 (C=S), 692 (C–S) cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6 , 25 °C, TMS): δ = 8.633 (s, 1H), ¹³C (75.3373 MHz, DMSO- d_6): δ = 113.6, 116.1, 128.4, 147.0, 213.0. Anal. Calcd for C9H2N2S3: C 46.13, H 0.86, N 11.96, S 41.05. Found C 46.00, H 0.59, N 11.45, S 39.38.
- 13. 4-Cyanobenzene-1,3-dithiole-2-one (IIa): Under Argon, a solution of mercuric acetate (1.54 g, 4.84 mmol) in acetic acid (30 mL) was drop wise added to a solution of 4-cyanobenzene-1,3-dithiole-2-thione (0.47 g, 2.2 mmol) in dichloromethane (125 mL) and stirred for 3 h. The resulting solution was filtered under Celite, washed with a saturated solution of NaHCO₃ (3 × 50 mL), H₂O (3 × 50 mL), and then dried with MgSO₄. The dichloromethane was evaporated and the light yellow residue was purified on a silica gel column using dichloromethane as eluent. After evaporating the solvent, the resulting pale yellow powder, compound IIa (0.346 g, 1.79 mmol, yield = 81.4%), was dried overnight under vacuum. Mp 179 °C; *R*₇ = 3.5 (CH₂Cl₂). IR (KBr) = 3083 (Ar−H), 2229 (C=N), 1680 (C=O), 1560 (C=C), 1199 (C−C), 1122 (Ar−S), 702 (C−S) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS) δ = 187.4, 138.2, 134.0, 129.9, 126.1, 123.6, 117.4, 111.0. Anal. Calcd for C₈H₃NoS₂: calcd C 49.73, H 1.56, N 7.25, S 33.18; found C 49.57, H 1.84, N 7.32, S 33.24.
- 14. *4,5-Cyanobenzene-1,3-dithiole-2-one* (**IIb**): Under anaerobic conditions, the mercuric acetate (1.16 g, 3.63 mmol) was added to a solution of 4,5-cyanobenzene-1,3-dithiole-2-thione (0.28 g, 1.21 mmol) in a mixture of chloroform and acetic acid (3:1) (45 mL) and stirred overnight. The resulting solution was filtered under celite, and washed firstly with a fraction of water (40 ml), then with a saturated solution of NaHCO₃ (40 ml) and to finish with other fraction of water (40 ml) and then dried with MgSO₄ (30 min). The solvent was evaporated and the resulting light yellow precipitated, compound **IIb** (0.17 g, 0.78 mmol, yield = 64.4%), was dried overnight under vacuum. Mp >247 °C; R_f = 3.0 (CH₂Cl₂). IR (KBr) 3086 (Ar—H), 2233 (C=N), 1692 (C=O), 1574 (C=C), 1218 (C=C), 1125 (Ar=S) cm⁻¹. ⁻¹ H NMR (400 MHz, CDCl₃): δ = 8.68 (s, 2H). ¹³C NMR (75.3373 MHz, DMSO-*d*₆): δ = 189.32, 139.28, 123.57, 129.39, 116.12, 113.1. Anal. Calcd for C₉H₂N₂OS₂: C 49.53; H 0.92; N 12.84; S 29.38. Found C 49.19; H 1.02; N 12.18; S. 28.24.
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- 17. The X-ray diffraction data for compounds Ia, Ib, IIa, IIb, and 1b were collected on a Bruker APEXII CCD diffractometer equipped with an Oxford Cryosystems low-temperature device at 150 K in the ω and φ scan mode. A semi empirical absorption correction was carried out using SADABS.²³ Data collection, cell refinement, and data reduction were done with the SMART and SAINT programs.²⁴ The structures were solved by direct methods using SIR97²⁵ and refined by full-matrix least-squares methods with the SHELXL97²⁶ program

using the WINGX²⁷ software package. Nonhydrogen 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 ORTEP3²⁸ and MERCURY 1.4.2.²⁹

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- 19. Cyclic voltammetry data were obtained using a BAS C3 Cell Stand. The measurements were performed at room temperature in dimethylformamide solutions, containing $[n-Bu_4]PF_6$ (0.1 M) as supporting electrolyte, with a scan rate of 100 mV/s using platinum wire working and counter electrodes and a Ag/Ag^+ reference electrode.
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