Donor–acceptor complex of a new bis-TTF donor containing a pyridine diester spacer with TCNQ as the acceptor: a disappointing system

Lakhemici Kaboub,[a]‡ **Jean-Marc Fabre,**[a] **Laure Vendier**[b,c] **and Jean-Pierre Legros**[b,c]*

[a]Institut Charles Gerhardt, UMR CNRS 5253, AM2N, ENSCM, 8 rue de l'Ecole Normale, F-34296 Montpellier Cedex 5, France, [b]CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, F-31077 Toulouse, France, and [c]UPS, INPT, LCC, Université de Toulouse, F-31077 Toulouse, France
Correspondence e-mail: jean-pierre.legros@lcc-toulouse.fr

A new bis-TTF donor (TTF is tetrathiafulvalene) containing a pyridine diester spacer, namely bis{2-[(6,7-tetramethylene-3-methylsulfanyltetrathiafulvalen-2-yl)sulfanyl]ethyl} pyridine-2,6-dicarboxylate–tetracyanoquinodimethane–dichloromethane (2/1/2), $2C_{33}H_{33}NO_4S_{12} \cdot C_{12}H_4N_4 \cdot 2CH_2Cl_2$, has been synthesized and its electron-donating ability determined by cyclic voltammetry. The electrical conductivity and crystal structure of this donor–acceptor (DA) complex with TCNQ (tetracyanoquinodimethane) as the acceptor are presented. The TCNQ moiety lies across a crystallographic inversion centre. In the crystal structure, TTF and TCNQ entities are arranged in alternate stacks; this feature, together with the bond lengths of the TCNQ molecule, suggest that the expected charge transfer has not occurred and that the D and A entities are in the neutral state, in agreement with the poor conductivity of the material ($\sigma_{RT} = 2 \times 10^{-6}$ S cm^{-1}).

Comment

It is now clearly established that the metallic state observed in organic conducting materials of the TTF type (TTF is tetrathiafulvalene) (Fabre, 2002) can be strongly stabilized by increasing their structural and electronic dimensionality (Williams et al., 1992; Fabre, 2000). Such a result can be attained by introducing, on the TTF ring, a functional group able to provide supplementary molecular interactions (Batsanov et al., 1995; Heuzé et al., 2000; Legros et al., 2000; Lorcy et al., 2009). In the past decade, extended TTF systems have received much attention as building blocks potentially able to enhance the dimensionality in derived conducting

‡ Permanent address: Laboratoire de Chimie des Matériaux Organiques, Centre Universitaire de Tébessa, Route de Constantine, 12000 Tébessa, Algeria.

materials (Bryce, 1995; Iyoda, 2004; Lorcy et al., 2009). Following a similar strategy, we have developed a research programme based mainly on bis-TTF, in which the TTF cores are linked by various functionalized spacers (Bouguessa et al., 2003; Carcel et al., 2006; Kaboub et al., 2008; Kaboub, 2009). As part of this research programme, we have synthesized a new bis-TTF donor compound, (3) (see Scheme), in which ester functionalities have been introduced within the covalent spacer linking the two TTF units to give bis[(6,7-tetramethylene-3-methylsulfanyltetrathiafulvalenyl)-2-ethylsulfanyl]pyridine-2,6-dicarboxylate [abridged name hereinafter: bis-TTF(pyridine diester)]. Moreover, the presence of a pyridine ring in (3) can allow the coordination of paramagnetic metals, leading to potential precursors of magnetic conducting solids (Iwahori et al., 2001; Ouahab et al., 2003; Lorcy et al., 2009). In the present work, we describe the preparation and electrochemical behaviour of (3). Since the electrochemical properties of this new donor are promising (see Experimental), we have prepared the title donor–acceptor (DA) complex, (I), with (3) as the donor and TCNQ (tetracyanoquinodimethane) as the π-acceptor. The structural properties and electrical conductivity of this material are also discussed below.
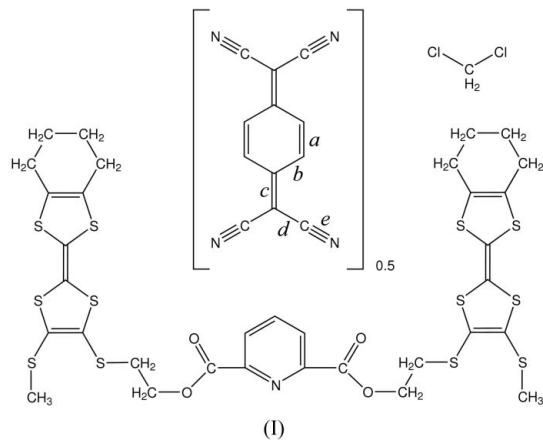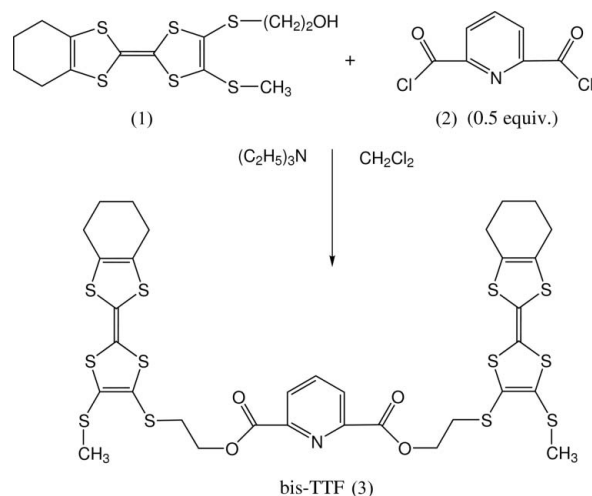
In the crystal structure of (I), the TCNQ acceptor lies on a centre of symmetry, with the donor and a solvent molecule occupying general positions. Thus, the content of the asym-
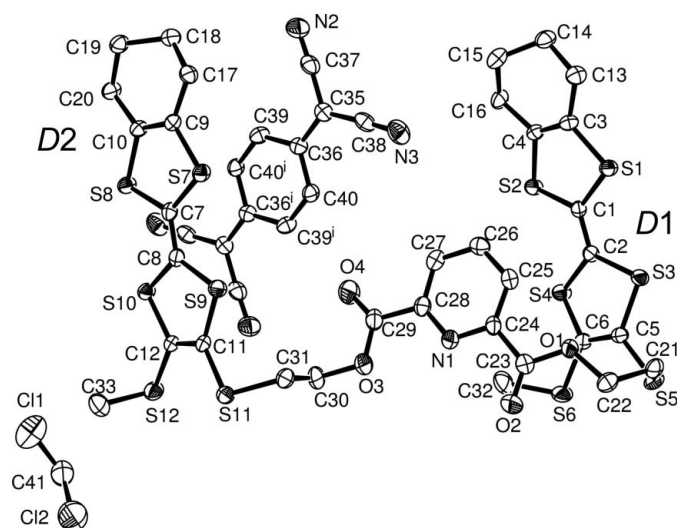
organic compounds

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. For clarity, the complete TCNQ molecule has been drawn and H atoms omitted. The symbols $D1$ and $D2$ denote the two TTF cores of the bis-TTF donor, as used in the *Comment*. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]
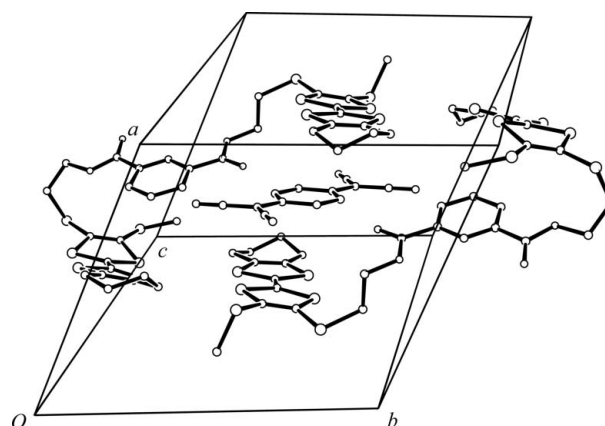

Figure 2
A perspective view of the stacking of [bis-TTF(pyridine diester)]$_2$-[TCNQ] in the unit cell of (I). H atoms and solvent molecules have been omitted for clarity.
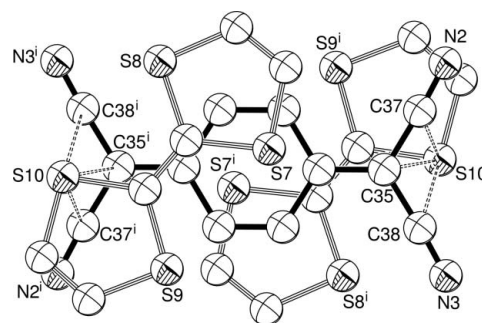

Figure 3
A projection of the repeat unit of a $D2$–A–$D2$ stack onto the molecular plane of TCNQ. Bonds in TCNQ are drawn in black. Short S$\cdots$C contacts (see *Comment*) are drawn as dashed lines. Only non-C atoms and atoms involved in the short S$\cdots$C contacts are labelled. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

metric unit is bis-TTF(pyridine diester)[TCNQ]$_{0.5}\cdot$CH$_2$Cl$_2$ (see Scheme). The atomic numbering is shown in Fig. 1.

Each TTF unit of the donor molecule of (I) bears a tetramethylene substituent at one end and a sulfanylmethyl substituent at the other. The two TTF cores, $D1$ and $D2$ (see Fig. 1), are connected by the pyridine diester spacer. $D1$ is not planar and shows a boat conformation, *i.e.* a curvature of the TTF core. The two C$_3$S$_2$ rings are folded around the S1$\cdots$S2 and S3$\cdots$S4 hinges. With respect to the central mean plane defined by S1/S2/S3/S4/C1/C2, the mean planes defined by S1/S2/C3/C4 and S3/S4/C5/C6 make dihedral angles of 7.30 (9) and 22.11 (5)°, respectively. $D2$ is closer to planarity but the two C$_3$S$_2$ rings of the TTF core are not in exactly the same plane because of a torsion angle of 3.96 (8)° around the central C7—C8 bond. The TCNQ molecule is almost planar [maximum deviation from its mean plane is 0.032 (3) Å for atom C39]. The mean planes and main axes of $D1$ and $D2$ are almost parallel [dihedral angle between the mean planes of $D1$ and $D2$ is 6.01 (4)°]. The mean plane of TCNQ makes dihedral angles of 12.26 (6) and 6.40 (7)° with the mean planes of $D1$ and $D2$, respectively.

In the crystal structure of (I), $D2$ and TCNQ are arranged in stacks along the [100] direction (Fig. 2) according to the pattern $\ldots D2$–A–$D2$–$D2$–A–$D2\ldots$, where A stands for TCNQ and each pair of $D2$ units is related by the centre of inversion located at the centre of the intervening A. Fig. 3 is a projection onto the molecular plane of TCNQ and shows a partial overlap of $D2$ and TCNQ. This packing induces three intermolecular contacts less than the sum of the relevant van der Waals radii (S$\cdots$C = 3.50 Å; Bondi, 1964): S10$\cdots$C35^i = 3.349 (4) Å, S10$\cdots$C37^i = 3.335 (4) Å and S10$\cdots$C38^i = 3.483 (4) Å [symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$].

The TTF moieties $D1$ are also stacked along the [100] direction, according to the pattern $\ldots D1$–$D1$–py–$D1$–$D1\ldots$, with the pyridine ring of the spacer being located half-way between $D1$–$D1$ stacks. In addition, there is only one intermolecular S$\cdots$S contact from the $D1$ core that is shorter than the sum of the van der Waals radii (3.7 Å; Bondi, 1964): S6$\cdots$S6^{ii} = 3.232 (2) Å [symmetry code: (ii) $-x$, $-y$, $-z + 2$].

Most of the DA compounds that crystallize with an alternate stacking of the D and A entities exhibit low electrical conductivity (Cassoux & Valade, 1996). Examples with TCNQ as the acceptor are given by Chasseau *et al.* (1982), Imaeda *et al.* (1991) and Legros *et al.* (2000). In addition, the lack of efficient overlap between the molecules of the stacks is another factor unfavourable to electronic delocalization. It is thus not surprising that the compound studied here exhibits a rather low conductivity of $\sigma_{RT} = 2 \times 10^{-6}$ S cm^{-1} [room-temperature measurement on a single crystal by a four-probe method (Coleman, 1975)]. An estimation of the charge on the TCNQ entity can be made by an analysis of bond lengths a–e (see Scheme) using the method of Flandrois & Chasseau (1977); this comparative study of a large number of TCNQ molecules shows lengthening of a, c and e and shortening of b

and d on going from $TCNQ^0$ to $TCNQ^-$. As no such changes are observed in the case of (I), we conclude that the TCNQ unit is in the neutral state, indicating that the expected charge transfer between the bis-TTF(pyridine diester) (3) and TCNQ has not occurred, in spite of the promising electrochemical properties of the new donor.

Experimental

The synthesis of the singly bridged symmetric bis-TTF(pyridine diester), (3), and the characterization of its electrochemical behaviour were carried out as follows. The synthesis is outlined in the scheme. Mono-hydroxy-TTF, (1), was obtained following a synthesis procedure described previously (Binet & Fabre, 1997; Legros *et al.*, 1999, 2000). To incorporate the two ester functions in the link between the TTF units, a reaction involving one equivalent of (1) and half an equivalent of pyridine-2,6-dicarbonyl dichloride, (2) (Aldrich), in dry CH_2Cl_2 in the presence of triethylamine was used (Bryce *et al.*, 1998, 2001; Griffiths *et al.*, 2003; Carcel *et al.*, 2006). The bi-functionalized bis-TTF(pyridine diester), (3) (m.p. 348 K), was isolated in 35% yield after purification by column chromatography (SiO_2, CH_2Cl_2–AcOEt 9:1 *v/v*) followed by recrystallization from CH_2Cl_2–MeOH (8:2 *v/v*).

The redox behavior of (3) was determined by cyclic voltammetry (CV) (Spanggaard *et al.*, 2000) and by square-wave voltammetry (SQW) (Carcel *et al.*, 2000; Bouguessa *et al.*, 2003) in a CH_2Cl_2–NBu_4PF_6 (0.1 *M*) solution on a Pt working electrode/SCE (scan rate 0.1 V s^{-1}). These measurements showed reversible redox waves by CV and two sharp bielectronic oxidation waves by SQW, indicating two independent TTF units in (3). The oxidation values found at $E_{ox1} = 600$ mV and $E_{ox2} = 1018$ mV for (3) are similar to those of BEDT-TTF ($E_{ox1} = 618$ mV and $E_{ox2} = 1004$ mV), a TTF-derived π-donor known to lead to many conducting and superconducting materials (Williams *et al.*, 1992).

The title donor–acceptor complex, (I), of bis-TTF, (3), with TCNQ was prepared by mixing boiling solutions of two equivalents each of TCNQ and (3) in equimolar CH_2Cl_2–CH_3CN mixtures. After one week of slow evaporation at room temperature, black single crystals of complex (I) were isolated and used for conductivity measurements and for structural study by single-crystal X-ray diffraction.

Crystal data

$2C_{33}H_{33}NO_4S_{12}·C_{12}H_4N_4·2CH_2Cl_2$	$\gamma = 71.257\,(12)°$
$M_r = 2158.70$	$V = 2321.2\,(5)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 11.3220\,(15)$ Å	Mo $K\alpha$ radiation
$b = 12.9538\,(16)$ Å	$\mu = 0.73$ mm^{-1}
$c = 17.659\,(2)$ Å	$T = 180$ K
$\alpha = 71.165\,(12)°$	$0.41 \times 0.23 \times 0.2$ mm
$\beta = 84.364\,(11)°$	

Data collection

Oxford Xcalibur diffractometer with a CCD detector	15734 measured reflections
	8164 independent reflections
Absorption correction: multi-scan (Blessing, 1995)	5879 reflections with $I > 2\sigma(I)$
$T_{min} = 0.737$, $T_{max} = 0.907$	$R_{int} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	550 parameters
$wR(F^2) = 0.151$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
8164 reflections	$\Delta\rho_{min} = -0.91$ e Å^{-3}

H atoms were positioned geometrically, with C—H = 0.97 (CH_2), 0.96 (CH_3) or 0.93 Å (aromatic), and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *CAMERON* (Watkin *et al.*, 1993) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Batsanov, A. S., Svenstrup, N., Lau, J., Becher, J., Bryce, M. R. & Howard, J. A. K. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1201–1202.
Binet, L. & Fabre, J.-M. (1997). *Synthesis*, pp. 1179–1184.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bouguessa, S., Hervé, K., Golhen, S., Ouahab, L. & Fabre, J.-M. (2003). *New J. Chem.* **27**, 560–564.
Bryce, M. R. (1995). *J. Mater. Chem.* **5**, 1481–1496.
Bryce, M. R., Cooke, G., Devonport, W., Duclairoir, M. A. & Rotello, V. M. (2001). *Tetrahedron Lett.* **42**, 4223–4226.
Bryce, M. R., Devonport, W., Goldenberg, L. M. & Changsheng, W. (1998). *Chem. Commun.* pp. 945–951.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII.* Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Carcel, C., Fabre, J.-M., Garreau de Bonneval, B. & Coulon, C. (2000). *New J. Chem.* **24**, 919–924.
Carcel, C., Kaboub, L., Gouasmia, A. K. & Fabre, J.-M. (2006). *Synth. Met.* **156**, 1271–1279.
Cassoux, P. & Valade, L. (1996). *Inorganic Materials*, 2nd ed., edited by D. W. Bruce & D. O'Hare, pp. 3–64. New York: John Wiley & Sons.
Chasseau, D., Gaultier, J., Fabre, J. M. & Giral, L. (1982). *Acta Cryst.* B**38**, 1632–1635.
Coleman, L. (1975). *Rev. Sci. Instrum.* **46**, 1125–1126.
Fabre, J.-M. (2000). *J. Phys. IV*, **10**, 3–19.
Fabre, J.-M. (2002). *J. Solid State Chem.* **168**, 367–383.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flandrois, S. & Chasseau, D. (1977). *Acta Cryst.* B**33**, 2744–2750.
Griffiths, J. P., Brown, R. J., Day, P., Matthews, C. J., Vital, B. & Wallis, J. D. (2003). *Tetrahedron Lett.* **44**, 3127–3131.
Heuzé, K., Fourmigué, M., Batail, P., Canadell, E. & Auban-Senzier, P. (2000). *Chem. Mater.* **12**, 1898–1904.
Imaeda, K., Mori, T., Nakano, C., Inokuchi, H., Iwazawa, N. & Saito, G. (1991). *Bull. Chem. Soc. Jpn*, **64**, 2159–2168.
Iwahori, F., Golhen, S., Ouahab, L., Carlier, R. & Sutter, J.-P. (2001). *Inorg. Chem.* **40**, 6541–6542.
Iyoda, M. (2004). *TTF Chemistry – Fundamentals and Applications of Tetrathiafulvalene*, edited by J. Yamada & T. Sugimoto, pp. 177–204. Tokyo: Kodansha and Springer.
Kaboub, L. (2009). PhD thesis, University of Montpellier, France.
Kaboub, L., Fabre, J.-M. & Legros, J.-P. (2008). *Acta Cryst.* E**64**, o2484–o2485.
Legros, J.-P., Dahan, F., Binet, L., Carcel, C. & Fabre, J.-M. (2000). *J. Mater. Chem.* **10**, 2685–2691.

organic compounds

Legros, J.-P., Dahan, F., Binet, L. & Fabre, J.-M. (1999). *Synth. Met.* **102**, 1632–1633.

Lorcy, D., Bellec, N., Fourmigué, M. & Avarvari, N. (2009). *Coord. Chem. Rev.* **253**, 1398–1438.

Ouahab, L., Iwahori, F., Golhen, S., Carlier, R. & Sutter, J.-P. (2003). *Synth. Met.* **133–134**, 505–507.

Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.31.5. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spanggaard, H., Prehn, J., Nielsen, M. B., Levillain, E., Allain, M. & Becher, J. (2000). *J. Am. Chem. Soc.* **122**, 9486–9494.

Watkin, D. M., Pearce, L. & Prout, C. K. A. (1993). *CAMERON*. University of Oxford, England.

Williams, J. M., Ferraro, J. R., Thorn, R. I., Carlson, K. D., Geiser, U., Wang, H. H. A. M., Kini, A. M. & Wangbo, M. H. (1992). *Organic Superconductors (including Fullerenes). Synthesis, Structure, Properties and Theory*. Englewood Cliffs, New Jersey: Prentice Hall.