Synthesis and Electrochemical Properties of Highly Extended and Sulfur-Rich Vinylogs of Tetrathiafulvalene

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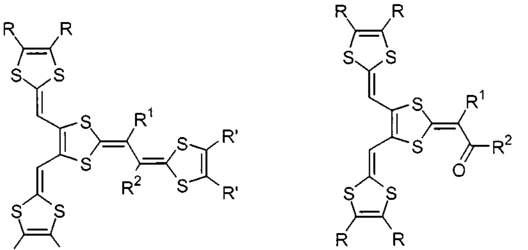
Using the reactivity of the carbonyl groups of 4,5-diformyl-1,3-dithiol-2-ylidene-substituted ethanals or ethanones with ylides or phosphonate anions, highly extended analogs of TTF **1** and **2** were synthesized by Wittig or Wittig–Horner reactions. Their excellent π-donor properties, as well as the possibility of obtaining polycationic states, were confirmed by cyclic voltammetry. The structural study of cation-radical salt **1bβγ·PF$_6$** reveals a two-dimensional network in the solid state.

Introduction

Owing to their high electrical conductivity and their unusual magnetic properties, the cation-radical salts (CRS) of the tetrathiafulvalene (TTF) series are the subject of considerable works.[1] While physicists and theoreticians aim for a better understanding and characterization of their physical behavior, chemists are focusing on improving the properties of these organic materials by developing new structures.[2,3] A lot of time has been invested in the design of new π-donors by modification of the TTF framework in order to increase the stability of the cation radical and/or to control the intermolecular architecture in the material.[4] The main objective is to enhance the dimensionality in the solid state in order to suppress the Peierls transition resulting from electron−phonon coupling inherent to monodimensional materials. A trend in this area involves the building of highly extended and sulfur-rich π-donors.[5] For the molecule, a better stability of oxidized states is expected due to the larger delocalization of the positive charge in the cation radical and the weaker intramolecular coulombic repulsion in the polycationic states.[6] Moreover, both the increase in the π-interactions and sulfur−sulfur contacts may allow better intra- and inter-chain contacts between the donors, and may increase the dimensionality of the corresponding CRS. Based on these considerations, our group has shown that extended tetrathiafulvalenes built from a TTF core bearing 1,4-dithiafulven-6-yl groups as substituents leads to an original material with a significant 2D character.[7] Mori and Misaki have equally obtained a new superconducting CRS from a fused TTF with an ethylenic spacer.[8] Compounds **1** combine these two approaches[9] by possessing a TTF vinylog framework grafted with two dithiafulvene arms. In this article, the synthesis and the electrochemical behavior of molecules **1** and their precursors, **2** are described (Scheme 1), as well as the structure of a cation radical salt derived from **1**.



1 **a** : R^1 = Ph, R^2 = H
b : R^1 = pMePh, R^2 = H
c : R^1 = Me, R^2 = Me

β : R'-R' = -(CH=CH)$_2$-
γ : R'-R' = -SCH$_2$-CH$_2$S-
δ : R-R = -(CH$_2$)$_4$-

2 **a** : R^1 = Ph, R^2 = H
b : R^1 = pMePh, R^2 = H
c : R^1 = Me, R^2 = Me
d : R^1 = H, R^2 = pMePh

α : R = CO$_2$Me
β : R-R = -(CH=CH)$_2$-
γ : R-R = -SCH$_2$-CH$_2$S-
δ : R-R = -(CH$_2$)$_4$-

Scheme 1

Results and Discussion

The retrosynthetic strategy involves a triple Wittig or Wittig−Horner olefination from 4,5-diformyl-1,3-dithiol-2-ylidene-substituted ethanals or ethanones **3** with Akiba's reagents **W** or **P**, bearing the adequately 4,5-disubstituted 1,3-dithiol-2-ylidene moiety (Scheme 2).[10] Compounds **3** with varied substituents R^1 and R^2 are obtained from the mono(diethyl) acetal of acetylenedicarbaldehyde and a 3-thioxo-1,2-dithiole as previously described.[11]

Several attempts to obtain **1** directly from **3** and phosphorus ylides **W**, which are easier to handle than corresponding phosphonates anions **P**, were unsuccessful. These reaction always stopped at the stage of bis(olefination) of

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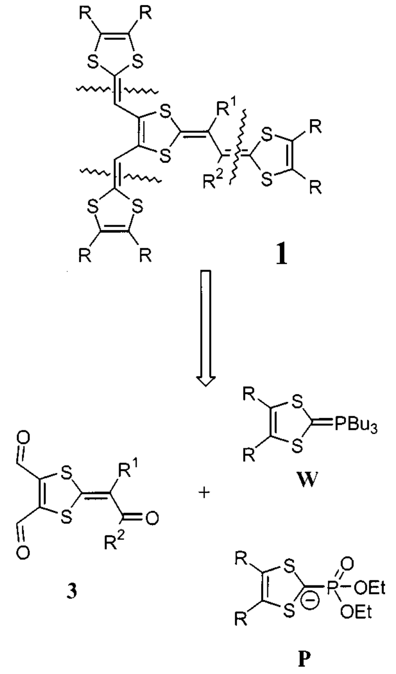
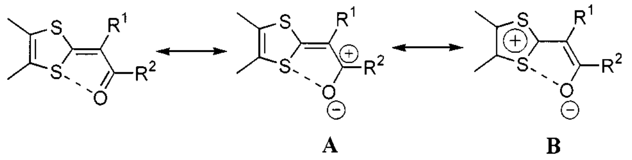


Scheme 2

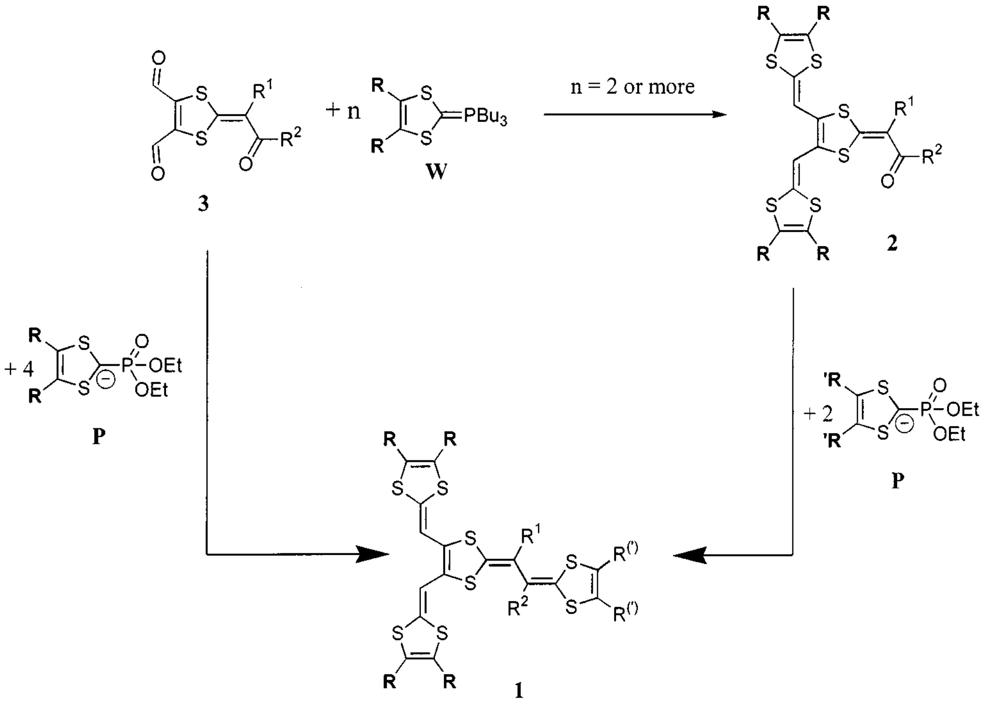


Scheme 4

the vicinal aldehyde functionalities, thus leading to compounds **2** (Scheme 3), even in the presence of a very large excess of **W**. This failure can be explained by both electronic and structural effects that contribute to a decrease in the reactivity of the remaining carbonyl group. As shown in Scheme 4, the weight of the mesomeric form **B**, which decreases the electrophilicity of this carbonyl group, is enhanced by the aromatic character of the dithiolium cation. Moreover, in the case of compounds **2**, the presence of the strongly releasing dithiafulvalenyl groups grafted in the 4,5-positions of the dithiole ring confers an additional importance to the poorly reactive form **B**. Additionally, we should keep in mind that compounds **3** present a δ-*cis* conformation, stabilized by a strong S···O intramolecular interaction,[12] which contributes to enhance the activation energy of the olefination reaction.

Except in the case of the aromatic ketone **2d** (R^2 = Ar), the olefination of compounds **2** could be carried out by using an excess (2 equiv.) of the more nucleophilic anion **P**. This anion was generated from the corresponding phosphonate by treatment with BuLi in the presence of the carbonyl compound **2** at 0−10 °C. This unconventional procedure was also effective starting from **3** by adding 4 equiv. of **P**, thus giving rise directly to **1** in one step. As indicated in Scheme 3, playing with the various reactivity of the carbonyl groups of compounds **3** with Akiba's reagents **W** and **P**, we have synthesized several products **1** that are substituted with different (from **2**) or identical groups R and R′. The procedure, the yield, and the numeration adopted for the compounds **1** and **2** synthesized are summarized in Table 1.

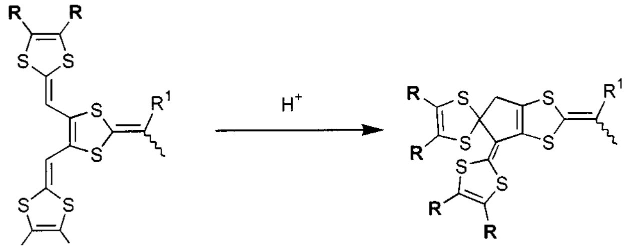
All these new donors undergo the acid-mediated intramolecular cyclization shown in Scheme 5.[12] For compounds **1**, **2aδ**, and **2bδ**, this reaction was very fast, and only a trace of acid was sufficient to provoke the cyclization. Thus, as



Scheme 3

Table 1. Names and yields of compounds **1** and **2**

Starting material	R^1	R^2	Akiba's reagent	Name	R or R−R	R′ or R′−R′	Yield
3a	Ph	H	**Wα**	**2aα**	CO_2Me	–	73%
3b	*p*-Me-C_6H_4	H	**Wα**	**2bα**	CO_2Me	–	81%
3d	H	Ph	**Wα**	**2dα**	CO_2Me	–	90%
3a	Ph	H	**Wβ**	**2aβ**	$-(CH=CH)_2-$	–	89%
3b	*p*-Me-C_6H_4	H	**Wβ**	**2bβ**	$-(CH=CH)_2-$	–	93%
3c	Me	Me	**Wβ**	**2cβ**	$-(CH=CH)_2-$	–	91%
3c	Me	Me	**Wγ**	**2cγ**	$-SCH_2-CH_2S-$	–	83%
3a	Ph	H	**Wδ**	**2aδ**	$-(CH_2)_4-$	–	91%
3b	*p*-Me-C_6H_4	H	**Wδ**	**2bδ**	$-(CH_2)_4-$	–	91%
3a	Ph	H	**Pβ**	**1aββ**	$-(CH=CH)_2-$	$-(CH=CH)_2-$	80%
3b	*p*-Me-C_6H_4	H	**Pβ**	**1bββ**	$-(CH=CH)_2-$	$-(CH=CH)_2-$	70%
2bβ	*p*-Me-C_6H_4	H	**Pγ**	**1bβγ**	$-(CH=CH)_2-$	$-SCH_2-CH_2S-$	85%
2cβ	Me	Me	**Pγ**	**1cβγ**	$-(CH=CH)_2-$	$-SCH_2-CH_2S-$	73%
2aδ	Ph	H	**Pβ**	**1aδβ**	$-(CH_2)_4-$	$-(CH=CH)_2-$	84%
2bδ	*p*-Me-C_6H_4	H	**Pγ**	**1bδγ**	$-(CH_2)_4-$	$-SCH_2-CH_2S-$	85%



2 or 1

cyclized form of **2 or 1**

Scheme 5

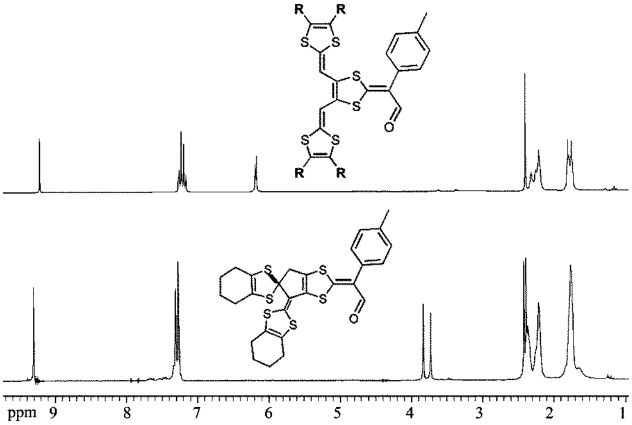
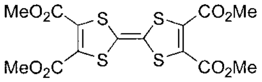
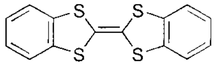
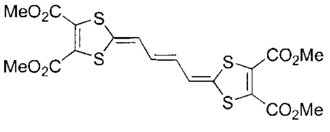
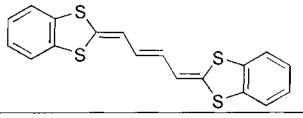


Figure 1. ^1H NMR spectra of **2bδ**: − in $CS_2 + C_6D_6$ (top); − after 5 min in $CDCl_3$ (bottom)

shown in Figure 1, the ^1H NMR spectrum of **2bδ** executed in $CDCl_3$, compared to one performed in a mixture of CS_2 and C_6D_6 led, after only 5 min, to a replacement of the ethylenic proton signals at δ = 6.5 by two singlets at δ = 3.8 and δ = 3.9, corresponding to the cyclized form of **2bδ**. For compounds **1**, the cyclizations were accompanied by the degradation of the molecules. In addition, the compounds are very thermally labile and light-sensitive, so they had to be stored in the dark at −20 °C.

The π-donor ability of compounds **1** and **2** was evaluated using cyclic voltammetry (CV) in dichloromethane as the solvent, previously filtered on a column of basic alumina. The CVs of compounds **2** exhibit two reversible one-electron waves with peak potentials Epa_1 and Epa_2 corresponding to the successive generation of the cation radical and dication, respectively. A comparison of the CV data collected in Table 2 shows that for a given R substituent on the dithiafulvalenyl moieties, the nature of the R^1 and R^2 groups exerts a weak influence on the Epa_1 and Epa_2 values only, while the electron donor effect of R strongly affects the π-donor character of compounds **2**. Thus, the replacement of the electron-withdrawing CO_2Me group by the

Table 2. Cyclic voltammetric data for compounds **2**; conditions: Bu_4NPF_6 0.1 M in CH_2Cl_2, scan rate v = 100 mV s^{-1}, vs. SCE

Compound	R^1; R^2	R or R–R	Epa_1 [V]	Epa_2 [V]	ΔEpa [V]
2aα	R^1 = Ph; R^2 = H	R = CO_2Me	0.69	0.82	0.13
2bα	R^1 = *p*-MeC_6H_4; R^2 = H	R = CO_2Me	0.70	0.83	0.13
2dα	R^1 = H; R^2 = *p*-MeC_6H_4	R = CO_2Me	0.65	0.82	0.17
2aβ	R^1 = Ph; R^2 = H	R–R = $(CH=CH)_2$	0.53	0.68	0.15
2bβ	R^1 = *p*-MeC_6H_4; R^2 = H	R–R = $(CH=CH)_2$	0.53	0.67	0.14
2cβ	R^1 = Me; R^2 = Me	R–R = $(CH=CH)_2$	0.50	0.65	0.15
2cγ	R^1 = Me; R^2 = Me	R–R = SCH_2CH_2S	0.38	0.50	0.12
2aδ	R^1 = Ph; R^2 = H	R–R = $(CH_2)_4$	0.33	0.45	0.12
2bδ	R^1 = *p*-MeC_6H_4; R^2 = H	R–R = $(CH_2)_4$	0.30	0.42	0.12
TTFα[13]			0.94	1.34	0.40
TTFβ[13]			0.72	1.06	0.34
V-TTFα[13]			0.64	0.76	0.12
V-TTFβ[13]			0.47	0.71	0.14

electron releasing $-(CH_2)_4-$ group produces a negative shift of Epa_1 values from 0.7 to 0.3 V. As shown in Table 2, the oxidation potentials of TTF derivatives **TTFα** and **TTFβ** are superior to those of compounds **2** bearing the same substituents R, while the vinylogs of tetrathiafulvalene **V-TTFα** and **V-TTFβ** present similar values.[13] In particular, the weak difference $\Delta E = Epa_2 - Epa_1$, is close to ca. 0.14V for compounds **2** compared to the parent TTF (about 0.3 V). This indicates a reduced intramolecular coulombic repulsion between the positive charges in the dication as in the case of **V-TTF**. Hence, despite the presence of electron-withdrawing carbonyl group, compounds **2** present a better π-donor ability than TTF core and nearly reach the electrochemical behavior of **V-TTF**.

The CVs of compounds **1** show three reversible one-electron oxidation waves followed by an irreversible one (Figure 2). Table 3 lists the values of the redox potentials (Epa_1, Epa_2, Epa_3, Epa_4) corresponding to the generation of the various cationic species. As expected, replacing the carbonyl group in **2** by the strongly electron-releasing dithiafulvalene group dramatically increased the π-donor character of compounds **1**. Thus the Epa_2 values of **1aββ** and **1bββ** corresponding to the formation of the dication $\mathbf{1}^{++}$ are inferior to the first oxidation potential Epa_1 of **V-TTFβ**. On the other hand, the large extension of the molecules and the multiplication of the dithiafulvalenyl substituents allow to reach multicationic states, such as a trication radical and a tetracation. The electrochemical properties mainly depend on the nature of the substituents R. In the presence of the most electron-donating $-(CH_2)_4-$ groups, the Epa_1 reaches a value as low as 0.06 V for **1bδγ**, which is among the lowest known in the TTF series.[14] The comparison between the data obtained for **1bβγ** and **1cβγ**, which differ in the R^1 and R^2 groups, shows a shift to a more positive potential of 0.12V for **1cβγ**. This result suggests a decrease in the conjugation for **1cβγ** owing to the distortion of the ethylenic spacers caused by steric hindrance between the close Me substituents.

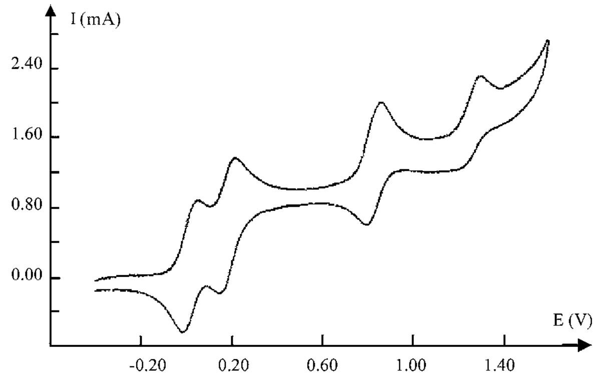


Figure 2. Cyclic voltammogram of compound **1bδγ** (ca. 10^{-4} mol L^{-1}) in 10^{-1} mol L^{-1} Bu_4NPF_6/CH_2Cl_2, scan rate 100 $mV \cdot s^{-1}$ vs. SCE

Compounds **1aββ**, **1bββ**, and **1bβγ** give small dark crystals by electrocrystallization under galvanostatic conditions in the presence of Bu_4NPF_6 or Bu_4NClO_4 in CH_2Cl_2. Although the poor quality of the crystals, the 1:1 stoichiometry and the structure of the cation radical salt namely **1bβγ·PF₆** was determined from X-ray diffraction.

As shown in Figure 3, the cation radical is characterized by the plane formed by the four dithiole rings, while the p-Me-C_6H_4 unit is located in a perpendicular plane. The two vicinal dithiafulvenyl arms and the central dithiole cycle present strong S···S intramolecular interactions characterized by the short distances d = 2.95 Å and d' = 2.98 Å. Such nonbonding 1−5 interactions between sulfur atoms of a dithiafulvene cycle and a central heterocycle have already been observed for neutral and cation radical states, allowing the planar conformation to be maintained during the oxidation process.[7,15]

As shown in Figure 4, the structure of **1bβγ·PF₆** is built up from sheets of molecules stacked along the O−A axis with an inclination of 22°. Intermolecular contacts (d_1 = 3.54 Å) between cations in the same layer are observed. The overlap mode, where a cation bridges the two others, minimizes the steric hindrance between bulky aryl units, and allows several close contacts between the neighboring donors. The distance between the planes in the stacking is about 3.6 Å.

Table 3. Cyclic voltammetric data for compounds **1**; conditions: Bu_4NPF_6 0.1 M in CH_2Cl_2, scan rate v = 100 mVs^{-1}, vs. SCE

Compound	R^1 and R^2	R−R and R′−R′	Epa_1 [V]	Epa_2 [V]	Epa_3 [V]	Epa_4 [V]
1aββ	R^1 = Ph R^2 = H	$R-R = -(CH=CH)_2-$ $R'-R' = -(CH=CH)_2-$	0.25	0.44	1.07	1.4 0
1bββ	R^1 = p-Me-C_6H_4 R^2 = H	$R-R = -(CH=CH)_2-$ $R'-R' = -(CH=CH)_2-$	0.23	0.43	1.10	1.40
1bβγ	R^1 = p-Me-C_6H_4 R^2 = H	$R-R = -(CH=CH)_2-$ $R'-R' = -SCH_2-CH_2S-$	0.22	0.39	1.03	1.37
1cβγ	R^1 = Me R^2 = Me	$R-R = -(CH=CH)_2-R'-R' = -SCH_2-CH_2S-$	0.34	0.50	1.10	1.40
1aδβ	R^1 = Ph R^2 = H	$R-R = -(CH_2)_4-$ $R'-R' = -(CH=CH)_2-$	0.12	0.30	0.94	1.30
1bδβ	R^1 = p-Me-C_6H_4 R^2 = H	$R-R = -(CH_2)_4-$ $R'-R' = -(CH=CH)_2-$	0.10	0.27	0.93	1.29
1bδγ	R^1 = p-Me-C_6H_4 R^2 = H	$R-R = -(CH_2)_4-$ $R'-R' = -SCH_2-CH_2S-$	0.06	0.23	0.85	1.26

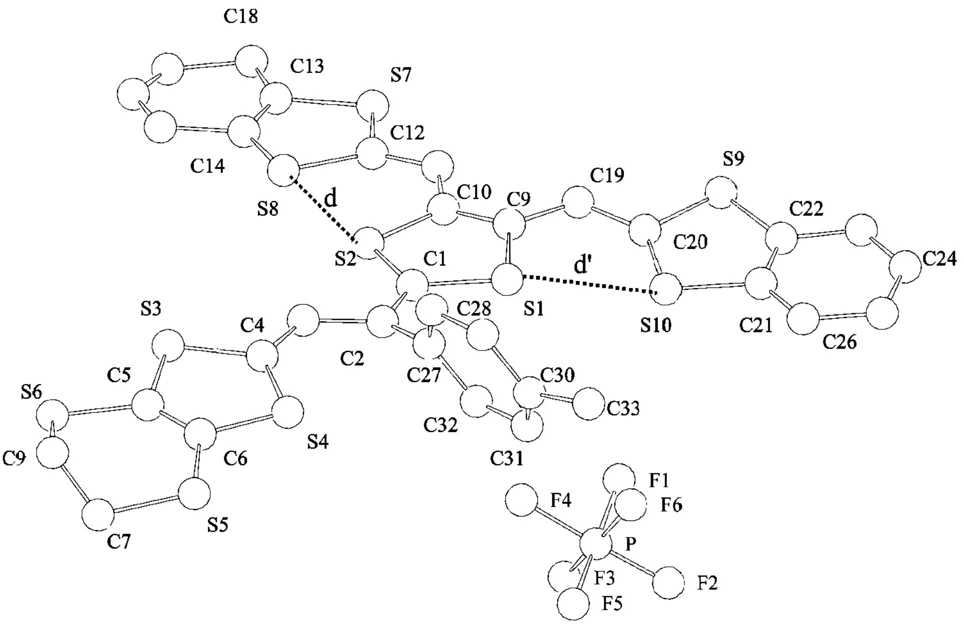


Figure 3. X-ray crystal structure of cation radical **1bβγ**$^{+\cdot}$

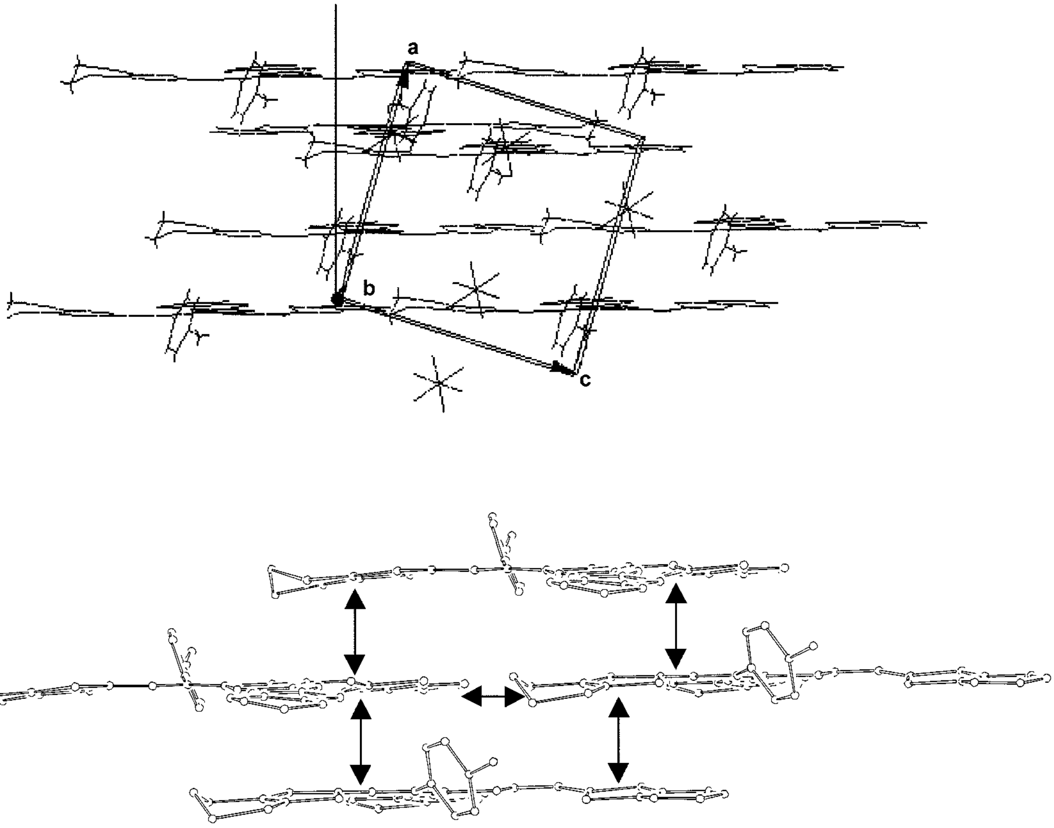


Figure 4. Overlap mode and close contacts of cation radicals in the salt **1bβγ·PF$_6$**

The conductivity measurements performed on powders of different salts gave values of ca. 10^{-1} S·cm^{-1}. Relatively high conductivity obtained for salts of 1:1 stoichiometry have already been observed for CRS of extended donors and are ascribed to decreasing coulombic repulsion.[7,14,16]

Conclusion

In conclusion, a new series of highly extended analogs of TTF **1** has been synthesized in one or two steps, using the difference in reactivity of ylides and phosphonate anions for the olefination of different carbonyl functionalities in compounds **3**. Their electrochemical properties reveal an exceptional π-donor ability associated to an access to polycationic states. In agreement with previous works, the cation radical salt obtained with a compound **1** confirms the rational approach in the design of extended- and sulfur-rich donors in order to enhance the dimensionality in the materials.

Experimental Section

General: ^{1}H NMR spectra were recorded with a Jeol GSX270WB spectrometer, operating at 270 MHz, and ^{13}C NMR with the same apparatus at 67.5 MHz; δ values are given in ppm (relative to TMS) and coupling constants in Hz. − Mass spectra were recorded under EI or FAB mode either with a Varian MAT 311 in the CRMPO (Rennes, France) or with a VG Autospec (Zaragoza, Spain). − Infrared spectra were recorded with a Perkin−Elmer 841 spectrometer. − Elemental analyses were performed by the service central d'analyse du CNRS (Vernaison, France).

Synthesis of Compounds 2: The ylides **W** were generated with a base (Et_3N at room temp. for **Wα** and BuLi at low temperature for **Wβ,γ,δ**) from the corresponding phosphonium salts, which were prepared according to literature procedures.[10]

Olefination with Ylide Wα: A dry THF/CH_3CN (30 mL/10 mL) solution containing the phosphonium salt (5 mmol) and the tricarbonyl compounds **3** (2 mmol) under nitrogen was treated dropwise with triethylamine (1 mL) at room temp., and a brown precipitate appeared immediately. The reaction mixture was stirred at room temp. for 30 min and the solvent was evaporated in vacuo. The precipitate was filtered off and washed with methanol, acetonitrile, and diethyl ether. The brown powders were recrystallized from a THF solution.

2aα (R^1 = Ph, R^2 = H, R = CO_2Me): M.p. 130−131 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1735, 1620 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 9.59 (s, 1 H), 7.57 (m, 5 H), 6.28 (s, 1 H), 6.22 (s, 1 H), 3.95−3.94−3.91−3.89 (4 s, 12 H). − ^{13}C NMR ($CDCl_3$): δ = 183.96, 159.65, 159.56, 159.52, 159.49, 157.50, 138.18, 137.93, 137.44, 134.16, 130.68, 130.07, 131.17, 128.32, 124.33, 121.83, 104.82, 104.20, 53.57, 53.53, 21.40. − $C_{27}H_{20}O_9S_6$: calcd. 679.94316 for [M^+], found 679.9416. − Elemental analysis: calcd. C 47.63, H 2.96, O 21.15, S 28.25; found C 47.89, H 3.07, O 21.34, S 28.00.

2bα (R^1 = *p*-Me-C_6H_4, R^2 = H, R = CO_2Me): M.p. 129 −130 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1733, 1616 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 9.35 (s, 1 H), 7.27 (m, 4 H), 6.13 (s, 1 H), 6.08 (s, 1 H), 3.85−3.84−3.82 (3 s, 12 H), 2.39 (s, 3 H). − $C_{28}H_{22}O_9S_6$: calcd. 693.9588 for [M^+], found 693.9547. − Elemental analysis: calcd. C 48.39, H 3.19, O 20.72, S 27.68; found C 48.36, H 3.15, O 20.82, S 27.18.

2dα (R^1 = H, R^2 = *p*-Me-C_6H_4, R = CO_2Me): M.p. 231 °C. − IR (Nujol): $\tilde{\nu}$ = 1730, 1710cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 8.06 (d, ^3J = 9.0 Hz, 2 H), 7.99 (s, 1 H), 7.60 (m, 3 H), 7.04 (s, 1 H), 6.99 (s, 1 H), 3.90−3.83−3.81 (3 s, 12 H). − $C_{27}H_{20}O_9S_6$: calcd. 679.94316 for [M^+], found 679.9402. − Elemental analysis: calcd. C 47.63, H 2.96, O 21.15, S 28.25; found C 47.53, H 3.11, O 20.97, S 26.80.

Olefination with Ylide Wβ, γ, δ: A dry THF solution containing the phosphonium salt (2 mmol), cooled to −78 °C under nitrogen, was treated dropwise with 1.24 mL of a 1.6 M BuLi in hexane solution. The yellow solution of **Wβ, γ, δ** was stirred for 10 min and 0.9 mmol of the tricarbonyl compound **3**, diluted in dry THF, was introduced dropwise at −78 °C. A brown precipitate appeared and the reaction mixture was allowed to warm to room temp. and concentrated in vacuo. The crude material was filtered off and washed with methanol, acetonitrile, and diethyl ether. The red powders were recrystallized from THF solutions.

2aβ [R^1 = Ph, R^2 = H, R−R = −(CH=CH)$_2$−]: M.p. 248 °C (dec.). − ^{1}H NMR (CS_2 + C_6D_6): δ = 9.13 (s, 1 H), 7.22−6.84 (m, 5 H), 6.11 (s, 1 H), 6.08 (s, 1 H). − $C_{27}H_{16}OS_6$: calcd. 547.95254 for [M^+], found 547.9527. − Elemental analysis: calcd. C 59.09, H 2.94; found C 59.10, H 3.13.

2aδ [R^1 = Ph, R^2 = H, R−R = −(CH_2)$_4$−]: M.p. 248 °C (dec.). − ^{1}H NMR (CS_2 + C_6D_6): δ = 9.14 (s, 1 H), 7.18−6.85 (m, 5 H), 6.03 (s, 1 H), 6.01 (s, 1 H), 2.03 (m, 8 H), 1.56 (m, 8 H). − $C_{27}H_{24}OS_6$: calcd. 556.0154 for [M^+], found 556.013. − Elemental analysis: calcd. C 58.23, H 4.34, O 2.87, S 34.55; found C 58.18, H 4.34, O 2.16, S 33.34.

2bβ [R^1 = *p*-Me-C_6H_4, R^2 = H, R−R = −(CH=CH)$_2$−]: M.p. 210 °C (dec.). − ^{1}H NMR (CS_2 + C_6D_6): δ = 9.23 (s, 1 H), 7.23−6.97 (m, 12 H), 6.24 (s, 1 H), 6.22 (s, 1 H), 2.35 (s, 3 H). − ^{13}C NMR (CS_2 + C_6D_6): δ = 182.04, 156.81, 139.33, 138.31, 137.59, 137.39, 135.77, 135.70, 134.95, 131.25, 130.24, 128.77, 126.41, 126.33, 126.19, 126.12, 122.33, 122.11, 121.41, 121.32, 121.11, 121.05, 21.88. − $C_{28}H_{18}OS_6$: calcd. 561.96819 for [M^+], found 561.9677.

2bδ [R^1 = *p*-Me-C_6H_4, R^2 = H, R−R = −(CH_2)$_4$−]: M.p. 210 °C (dec.). − ^{1}H NMR (CS_2 + C_6D_6): δ = 9.15 (s, 1 H), 7.15 (m, 4 H), 6.13 (s, 1 H), 6.10 (s, 1 H), 2.35 (s, 3 H) 2.18 (m, 8 H), 1.68 (m, 8 H). − FAB MS: *m*/*z* = 570 [M]. − $C_{28}H_{26}OS_6$ (570.9): calcd. C 58.91, H 4.59, O 2.80, S 33.70; found C 58.55, H 4.54, O 3.25, S 32.50.

2cβ [R^1 = Me, R^2 = Me, R−R = −(CH=CH)$_2$−]: M.p. 244 °C (dec.). − ^{1}H NMR (CS_2 + C_6D_6): δ = 7.11−6.98 (m, 8 H), 6.23 (s, 1 H), 6.20 (s, 1 H), 2.15 (s, 3 H) 2.10 (s, 3 H). − $C_{23}H_{16}OS_6$: calcd. 499.9525 for [M^+], found 499.9501.

2cγ [R^1 = Me, R^2 = Me, R−R = −S−CH_2−CH_2−S−]: M.p. 250 °C (dec.). − ^{1}H NMR (CS_2 + C_6D_6): δ = 6.13 (s, 1 H), 6.10 (s, 1 H), 3.24 (s, 8 H) 2.15 (s, 3 H), 2.08 (s, 3 H). − $C_{19}H_{16}OS_{10}$ (581.2): calcd. C 39.15, H 2.76; found C 39.65, H 3.10.

Synthesis of Compounds 1: A suspension of compounds **2** or **3** in dry THF with 2 or 4 equiv. of phosphonate, respectively, under nitrogen was treated dropwise with BuLi in hexane at room temp. The solution immediately darkened and was stirred for about 15 min at room temp. and then concentrated in vacuo. The crude material was treated with methanol to allow precipitation of the product. After filtration, the red brown powder was dissolved in a minimum of THF and was precipitated with methanol.

1aββ [R^1 = Ph, R^2 = H, R−R = R′−R′ = −(CH=CH)$_2$−]: M.p. 160 °C (dec.). − ^{1}H NMR (CS_2 + C_6D_6): δ = 7.45−6.85 (m, 17 H), 6.19 (s, 1 H), 6.17 (s, 1 H), 6.11 (s, 1 H). − FAB$^+$ MS: *m*/*z* =

684 [M]. − $C_{34}H_{20}S_8$ (685.2): calcd. C 59.61, H 2.94, S 37.44; found C 59.57, H 2.82, S 36.82.

1aδβ [R^1 = Ph, R^2 = H, R−R = $-(CH_2)_4-$, R′−R′ = $-(CH{=}CH)_2-$]: M.p. 165 °C. − ^1H NMR (CS_2 + C_6D_6): δ = 7.16 (m, 5 H), 6.54−6.83 (m, 4 H), 6.03 (s, 1 H), 5.97 (s, 1 H), 6.87 (s, 1 H), 2.00 (m, 8 H), 1.5 (m, 8 H). − $C_{34}H_{28}S_8$ (693.2): calcd. C 58.92, H 4.07; found C 59.12, H 4.21.

1bββ [R^1 = *p*-Me-C_6H_4, R^2 = H, R−R = R′−R′ = $-(CH{=}CH)_2-$]: M.p.120 °C (dec.). − ^1H NMR (CS_2 + C_6D_6): δ = 7.25−6.60 (m, 16 H), 6.16 (s, 1 H), 6.12 (s, 1 H), 6.10 (s, 1 H), 2.41 (s, 3 H). − FAB^+ MS: *m*/*z* = 698 [M].

1bβγ [R^1 = *p*-Me-C_6H_4, R^2 = H, R−R = $-(CH{=}CH)_2-$, R′−R′ = $-S-CH_2-CH_2-$]: M.p. 140 °C (dec.). − ^1H NMR (CS_2 + C_6D_6): δ = 7.13−6.92 (m, 12 H), 6.08 (s, 1 H), 6.02 (s, 1 H), 6.00 (s, 1 H), 3.01 (m, 4 H), 2.34 (s, 3 H). − FAB^+ MS: *m*/*z* = 750 [M].

1bδγ [R^1 = *p*-Me-C_6H_4, R^2 = H, R−R = $-(CH_2)_4-$, R′−R′ = $-S-CHS-$]: M.p. 192 °C (dec.). − ^1H NMR (CS_2 + C_6D_6): δ = 7.05 (m, 4 H), 5.94 (s, 1 H), 5.93 (s, 1 H), 5.88 (s, 1 H), 3.02 (m, 4 H), 2.33 (s, 3 H), 2.16 (m, 8 H), 1.70 (m, 8 H). − ^{13}C NMR (CS_2 + C_6D_6): δ = 138.05, 137.98, 137.64, 134.32, 130.13, 130.04, 126.42, 126.30, 125.47, 124.95, 124.83, 122.75, 113.69, 113.49, 110.39, 104.02, 103.90, 30.30, 30.19, 26.10, 26.00, 25.62, 25.57, 23.36, 23.31, 22.11. − FAB^+ MS: *m*/*z* = 746 [M]. − $C_{33}H_{30}S_{10}$ (747.4): calcd. C 53.04, H 4.04, S 42.91; found: C 52.99, H 4.07, S 42.03.

1cβγ [R^1 = Me, Me, R−R = $-(CH{=}CH)_2-$, R′−R′ = $-S-CH_2-CH_2-S-$]: M.p. 150 °C (dec.). − ^1H NMR (CS_2 + C_6D_6): δ = 7.07−6.95 (m, 8 H), 6.08 (s, 1 H), 6.07 (s, 1 H), 3.10 (m, 4 H), 1.74 (s, 6 H). − FAB^+ MS: *m*/*z* = 676 [M].

Electrocrystallizations: These were performed in 10^{-1} mol·L^{-1} of electrolyte support in dichloromethane, previously filtered through a column of basic alumina. The donor ($5 \cdot 10^{-4}$ mol·L^{-1}) was introduced into the anode compartment of a 50-mL H-shaped electrocrystallisation cell, separated from the cathode compartment by a porous glass frit. A constant current of 1 μA was applied for 10 d at room temperature between the two platinum electrodes (wire: 0.5 mm of diameter and 1.5 cm of length). Crystals or powders of cation-radical salt grew on the anode.

Crystal Data for 1bβγ·PF_6: *M* = 884.08, $C_{33}H_{22}F_6PS_{10}$, dark green needles (0.26 × 0.20 × 0.1 mm), monoclinic, space group $P2_1/n$, $a = 11.091(2)$ Å, $b = 30.807(5)$ Å, $c = 11.169(2)$ Å, $\beta = 91.92(3)°$, $V = 3814.1(12)$ Å^3, $\rho_{calcd.} = 1.540$, $Z = 4$, $2\theta_{max} = 55.94°$, Mo-K_α radiation ($\lambda = 0.71069$ Å), $T = 293(2)$ K. X-ray data are collected with an Enraf-Nonius CAD4 four-circle diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement on F^2 with SHELXL-97 converged with $R = 0.1028$ and $wR^2 = 0.2115$ for 9126 independent reflections with $I > 2\sigma(I)$ and 451 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-155908. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

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