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New *Bis*-Linked Tetrathiafulvalenes (TTFs) to [60]Fullerene: Spectral Investigations

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Extended spectral investigations of several new *bis*-linked tetrathiafulvalenes (TTFs) to [60]fullerene were performed. From VIS-NIR-IR spectra it was stated, that charge redistribution on C_{60} and TTFs moieties in the adducts occurs after their formation. This redistribution depends not only on the nature of a substituent but also on the number of bounded donors. Vibrational features of the polyadducts were also analyzed.

Key words: fullerene C_{60}, tetrathiafulvalene derivatives, C_{60} adducts, optical spectroscopy

Fullerene chemistry is a young field in the state of constant discovery and experiencing rapid developments. Most of the synthetic organic efforts, which were initiated since C_{60}, a new form of carbon [1] has become available in macroscopic quantities [2,3], have been so far concentrated on reactivity issues combining regio- and stereochemical aspects. There are a number of ambitious goals to be reached. In particular, a functionalization of C_{60} was initiated several years ago, which is connected with a variety of donors covalently bounded to C_{60} [4–7]. There are two main objectives concerning organic functionalization of C_{60}: one is focused on modification of their properties for easier handling and the other on combination of the fullerene properties with those of other materials. The last-mentioned aspect relates to design and construction of molecular systems, where electronic interactions take place between covalently linked components.

One of the strongest organic electron donor molecules that can be attached to C_{60} skeleton is tetrathiafulvalene (TTF) and its derivatives. To promote the electronic interactions, the Angers [8,9] and Barcelona [10,11] groups have developed the strategy consisting of linking C_{60} and TTFs by a rigid bridge. C_{60}–TTF fused systems have been designed in such a way that the C_{60} – acceptor and the TTF – donor are directly attached by two rigid σ-bonds, forming a cyclohexene ring. The fusion of two electroactive centers with a six-member ring provides a short distance and a controlled rigidification between TTFs and C_{60}, giving rise to a well-defined spacing and orientation of both moieties [11]. This kind of bridge has proven to be very efficient for mediating in electron transfer between two electroactive centers by a through-bond coupling mechanism [12].

Recently, we have investigated the spectral properties, mainly electron and vibrational spectra of several polyadducts of TTFs linked to C_{60} [13,14] arranged in four groups (Figure 1): **I**, where the TTF moiety is bearing an ethylenedithio group [13], as well as **II, III** and **IV** with two alkylsulfanyl $S(CH_2)_xCH_3$ groups bonded to TTF frame ($x = 0, 4$ or 11) [14]. It was shown that the charge redistribution on C_{60} and TTFs moieties occurs in these compounds after the adduct formation. This redistribution depends not only on the nature of a substituent but first of all on the number of bounded donors to C_{60}. A particularly strong effect was observed in the IR spectra of the double-substituted C_{60} molecules, where a new very strong and broad band appears at about 1100 cm^{-1}. The resonant origin of this band was suggested.

The aim of the present work is to provide supplementary information on electronic and vibrational properties of functionalized C_{60}. We have performed IR-NIR-VIS investigations of six new *bis*-linked adducts of C_{60} to TTF-derived donors with groups $-S(CH_2CH_2O)_xCH_3$, where $x = 3$ or 4. One of the goals of this paper is to understand the correlation between the structure of functionalized fullerenes and their spectral properties.

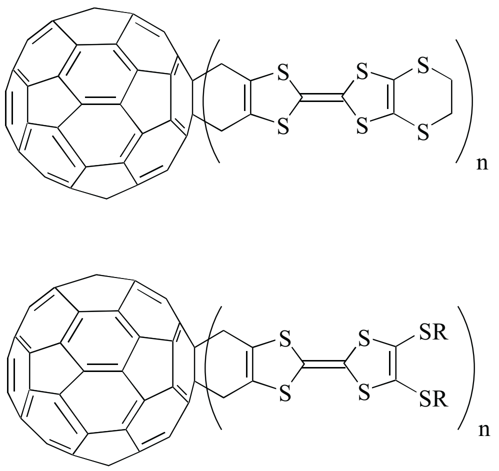
EXPERIMENTAL

The investigated TTF – C_{60} polyadducts **V/1, V/2, V/3, VI/1, VI/2,** and **VI/3,** having polyethersulfanyl $-S(CH_2CH_2O)_xCH_3$ groups with x = 3 and 4, are shown in Fig. 1. These compounds were synthesized using successive [4+2] Diels-Alder cycloadditions involving C_{60} and the transient 2,3-dimethyleneTTF, this latter being generated *in situ* by reductive elimination of the corresponding 2,3-*bis*(bromomethyl)TTF, according to the methodology recently reported [15]. Mono and polyadducts were purified and separated by silicagel column chromatography, di and tri-adducts being obtained as a mixture of numerous regioisomers. For the polyadducts the electronic (VIS-NIR) and vibrational (IR) spectra were investigated; an electrical conductivity was also evaluated. Complementary IR spectral studies of four selected TTFs derivatives with two polyethersulfanyl $-S(CH_2CH_2O)_xCH_3$ groups, where x = 3 and 4 (**A–D**) (Fig. 2), were performed.

Electronic absorption spectra in the range 200–2500 nm were recorded with Perkin Elmer UV-VIS-NIR Lamda 19 spectrometer, at room temperature. The spectra of powder samples were taken in KBr pellets containing dispersed compounds with concentration 1:2000 ÷ 1:8000, depending on the band intensities. Vibrational spectra in the spectral range 400–7000 cm^{-1} were recorded with FT IR Perkin Elmer 1725 X spectrometer, also at room temperature and in KBr pellets with typical concentration 1:1000.

Although the spectra were recorded in the large spectral range (400–50000 cm^{-1}), our interest was focused on the two ranges: the first one between 200 and 600 nm, where the electronic excitations of the fullerene and its derivatives are observed, and the second one between 400 and 1800 cm^{-1}, where the intramolecular vibrations of C_{60} and its derivatives occur. The latter one is also the range of the most characteristic vibrations of TTF and its derivatives. Between these two ranges only weak absorption typical for –CH groups is observed. It is necessary to notice that no spontaneous electron transfer band is observed in the investigated materials.

The d.c. electrical conductivity was evaluated using the two-probe technique. The powder samples were pressed up to a settlement of the conductivity value.



I : with **n = 1, 2** or **3**

II : **R = -CH_3** with **n = 1, 2** or **3**

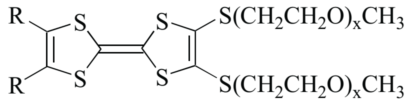
III : **R = -$(CH_2)_4CH_3$** with **n = 1, 2** or **3**

IV : **R = -$(CH_2)_{11}CH_3$** with **n = 1**

V : **R = -$(CH_2CH_2O)_3CH_3$**
V/1 : n = 1
V/2 : n = 2
V/3 : n = 3

VI : **R = -$(CH_2CH_2O)_4CH_3$**
VI/1 : n = 1
VI/2 : n = 2
VI/3 : n = 3

Figure 1. Chemical formulae of the *bis*-linked tetrathiafulvalenes (TTFs) to [60]fullerene from **I** to **VI**, for n = 1, 2 and 3.



A : x = 3, R = CO_2CH_3
B : x = 4, R = CO_2CH_3
C : x = 3, R = CH_2OH
D : x = 4, R = CH_2OH

Figure 2. Chemical formulae of the donors most suitable for analyses of the IR spectra of the adducts.

RESULTS AND DISCUSSION

Electronic spectra: Figure 3 presents the absorption spectra of the investigated compounds: **V/1, V/2, V/3** in the visible region; the spectrum of the pristine C_{60} is also shown for comparison (the spectra of **VI/1, VI/2, VI/3** display very similar tendency and are not shown here). Similarly as for previously investigated polyadducts [13,14] the spectra consist of three strong optical absorption bands resembling the bands identified as dipole-allowed transitions in C_{60} [16]. The bands: λ_1, below 264 nm, and λ_2, below 340 nm, undergo a blue shift in all investigated compounds and this shift is

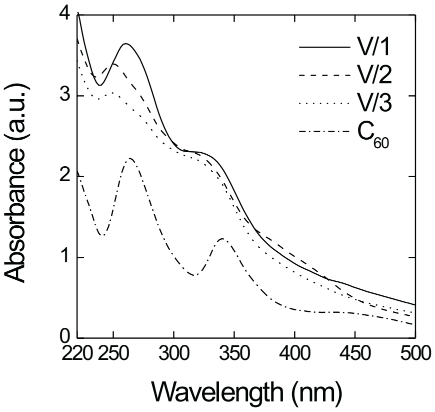


Figure 3. UV-VIS absorption spectra of the *bis*-linked TTF to C_{60} compounds: **V/1**, **V/2** and **V/3**, in KBr matrix, at room temperature. For comparison, the spectrum of C_{60} is given.

strongly dependent on the number of substituents; it also depends on their nature. The former band is shifted merely by 3÷4 nm for single substituted adducts (**V/1** and **VI/1**) but as much as 13÷15 nm for double-substituted (**V/2** and **VI/2**) and 14÷16 nm for triple-substituted samples (**V/3** and **VI/3**). The latter band is considerably shifted, by 14÷15 nm for **V/1** and **VI/1** compounds. This shift is slightly increased to 18÷20 nm in samples with n = 2 or 3 (**V/2, V/3, VI/2** and **VI/3**). Similar band shifts were observed previously [13,14] for the compounds of groups **I**÷**IV**. These results can be ascribed to the through-bond electronic interaction between the C_{60} moiety and the attached substituents but also to the through-space interaction to modify the electronic state of the fullerene [16]. Main consequences of the redistribution of charge on C_{60} are the energy change of the electronic levels of the C_{60} moiety and their widening. This effect increases with a number of substituents. It seems that the distribution of charge is significantly changed by addition of the second TTF-derived group (n = 2), and then changes slightly with addition of another TTF-derived group (n = 3).

Our conclusion from the studies of the electronic absorption spectra of the *bis*-linked fullerenes investigated as well in this paper as in the previous ones [13, 14] is that the electronic properties of the C_{60} adducts with TTF-derived substituents show characteristic changes depending not only on the molecular structure and properties of a substituent but first of all on the number of bounded donors.

Vibrational spectra: In order to perform a preliminary assignment of the vibrational bands of the polyadducts, the spectra of the materials containing the $-S(CH_2CH_2O)_xCH_3$ groups: **A** and **B** (with supplementary groups $-CO_2CH_3$) as well as **C** and **D** (with supplementary groups $-CH_2OH$) have been studied (Fig. 4). It is characteristic that they are nearly identical in spite of different number of $-CH_2CH_2O$ groups but show some specific features typical for both $-CO_2CH_3$ and $-CH_2OH$ groups. For example, a strong absorption band at 1731 cm^{-1} occurs only in the com-

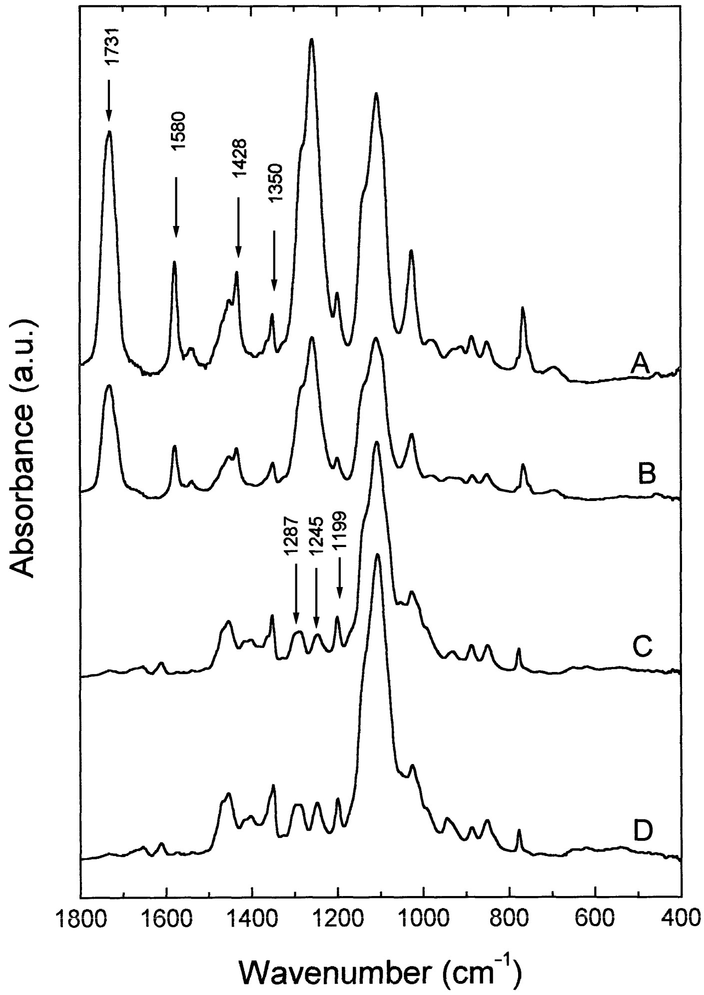
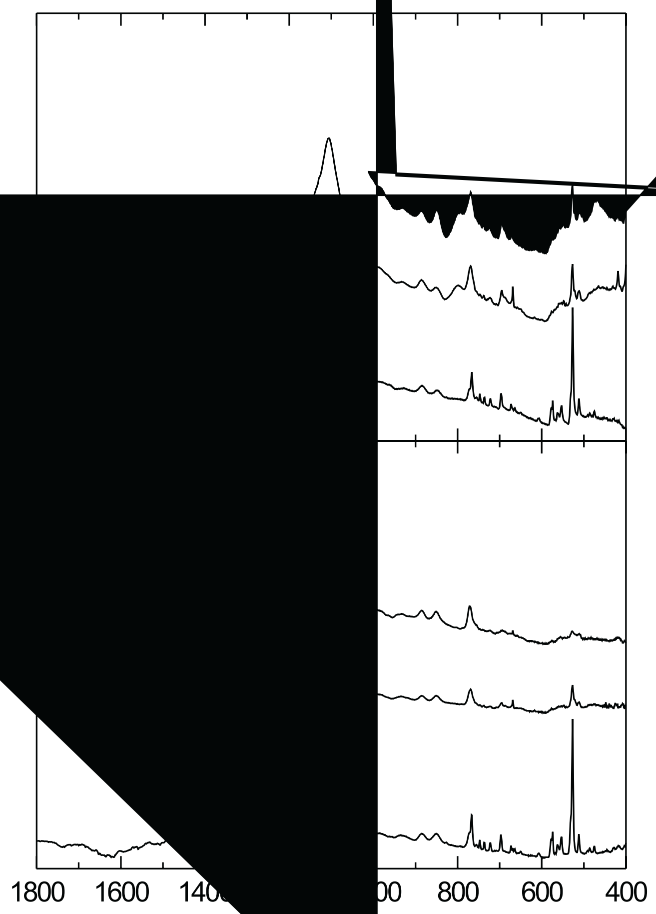


Figure 4. IR absorption spectra of the TTF-derived donors **A–D**, suitable for analyses of the IR spectra of the investigated polyadducts, in the KBr matrix (1:1000), at room temperature.

pounds **A** and **B** and is assigned to stretching vibrations of C=O group. Another strong band at 1257 cm^{-1} can be attributed to C–O stretching vibrations. In addition, the band 1580 cm^{-1}, relatively strong in these compounds, should be assigned to stretching vibrations of C=C group. The triplet 1287, 1245 and 1199 cm^{-1}, which appears in the compounds **C** and **D**, characterizes the stretching vibrations of C–OH groups. The strong band at 1107 cm^{-1} occurs in all compounds and is given by stretching vibrations of C–C groups of the substituents. This assignment is given taking into account the typical frequencies of organic molecules vibrations of a similar structure [17].

Fig. 5 shows the infrared (IR) spectra of investigated compounds. In general, the spectra of both types of polyadducts, **V** and **VI,** are alike and the resemblance within the same type of substituents is very close. The radial vibrations of C_{60} moiety at 527



and 576 cm^{-1} [18] are not disturbed after formation of the adducts; the former line is observed at 527 cm^{-1} in all compounds but the latter is insignificantly shifted and recorded between 574 and 577 cm^{-1}. A similar suppression of band positions were observed for polyadducts investigated previously [13,14]. The vibrations with domination of the tangential deformations of the fullerene [18] are more difficult to identify in the investigated polyadducts. The band corresponding to 1182 cm^{-1} in the fullerene coincides probably with the strong band centered at about 1107 cm^{-1} or appears as a shoulder in the high frequency slope of this band. The second one, at 1427 cm^{-1} in the neutral C_{60}, probably coincides with the large and structured band centered at about 1450 cm^{-1}. One can suppose that these bands of the adducts are distinctly shifted in relation to the normal fullerene bands because its tangential modes should be involved in vibrations of TTF-derived substituents [13,14,19,20].

The vibrational spectra of the polyadducts of families **V** and **VI** (Fig. 5) contain the strong band at 1107 cm^{-1}, which occurs in all compounds, and several bands of medium intensity. It refers mainly to such bands as: 1599, 1457*, 1449*, 1428*, 1350*, 1298*, 1247*, 1198*, 1030*, 933*, 886*, 851*, 769*, 747*, 737*, 722*, 697*, 670*, 575, 527*, 512* and 419 cm^{-1}; nearly all of them (marked here with *) occur in all investigated polyadducts. The frequencies of these bands are almost the same (+/–1 cm^{-1}) for all polyadducts with longer or shorter -S(CH$_2$CH$_2$O)$_x$CH$_3$ substituents; thus they are x-independent. The bands: 1599 and 419 cm^{-1} are observable only for some of the adducts **V,** and are probably due to contaminations. One should notice, that above 750 cm^{-1} the bands of the polyadducts marked with * have their counterparts in the spectra of the compounds **A÷D** but they are usually shifted to lower wavenumbers by a few cm^{-1} at the most. Thus, the polyadduct bands of medium intensities can be attributed to normal vibrations of substituents insignificantly disturbed by their bonding to C$_{60}$ moiety. Changes in the charge distribution on the substituents after the adducts formation result in the band frequency shifts by maximum +/–4 cm^{-1}.

In particular, we suggest that the bands between 1428 and 1457 cm^{-1} are given by bending vibrations of –CH$_3$ groups. The bands 1247, 1298 and 1350 cm^{-1} should be given by bending of –CH$_2$ and maybe –CH$_3$ groups. The strong band at 1107 cm^{-1} is given by stretching vibrations of C–C groups of the substituents. The band at about 933 cm^{-1} is probably given by bending of –CCS bonds and the bands 697 cm^{-1} as well as 722–769 cm^{-1} by stretching vibrations of –SCH groups. The band 512 cm^{-1} could be assigned to –CS stretching mode of TTF framework. However, normal mode calculations are needed for a detailed assignment of the bands of such complicated molecule as investigated adducts. Furthermore, the adducts usually appear as a mixture of several regioisomers [15], which makes the band attribution very complicated.

CONCLUSIONS

Based on the VIS-NIR-IR absorption spectra of the new *bis*-linked TTFs to C$_{60}$ compounds of **V** and **VI** groups it was stated that charge redistribution on fullerene and TTFs moieties occur after the polyadducts formation. This redistribution is detectable as a broadening and shifting of the electronic bands typical for fullerene molecule and shifting of some characteristic vibrational bands of both donor and acceptor parts. The spectral changes are similar for both groups of investigated polyadducts and they depend weakly on both the nature and the number of substituents.

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