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Does Charge Carrier Dimensionality Increase in Mixed-Valence Salts of Tetrathiafulvalene-Terminated Dendrimers?

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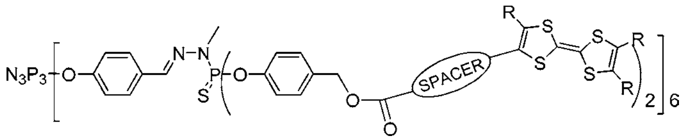
ABSTRACT



In four new dendrimers terminated by 12 electroactive tetrathiafulvalenyl substituents, the tridimensional character of the inter- and intradendrimeric charge and electron transfer, and hence of the electroconductivity, is evidenced by examination of the electronic spectra of their corresponding neutral state and cation radical, dication, and mixed-valence salts, including a closed-shell anion.

Most molecular organic conductors, such as those of the tetrathiafulvalene (TTF) series, possess properties of one-dimensional (1-D) conductors because the electrons (or holes) mainly travel along the columns formed by the π-stacking of the conjugated molecules.[1] Back in 1995, Miller and coworkers reported the first electrically conducting dendrimer, end-capped with diimide anion radicals, and pointed out the importance of interdendrimer (3-D) interactions in achieving high conductivity.[2]

A number of TTF end-capped dendrimers have previously been prepared,[3] and only in one instance[4] were charge-transfer salts with TCNQ studied. However, in that case it was impossible to conclude where the electroconductivity was originating from, since either oxidized TTF or reduced TCNQ species or both can give rise to the conductivity phenomenon. Moreover, despite some spectroscopic measurements that were carried out to monitor iodine oxidation of TTF-dendrimers in solution,[3d] the absorption band assignments appeared to be doubtful,[5] and, to the best of our

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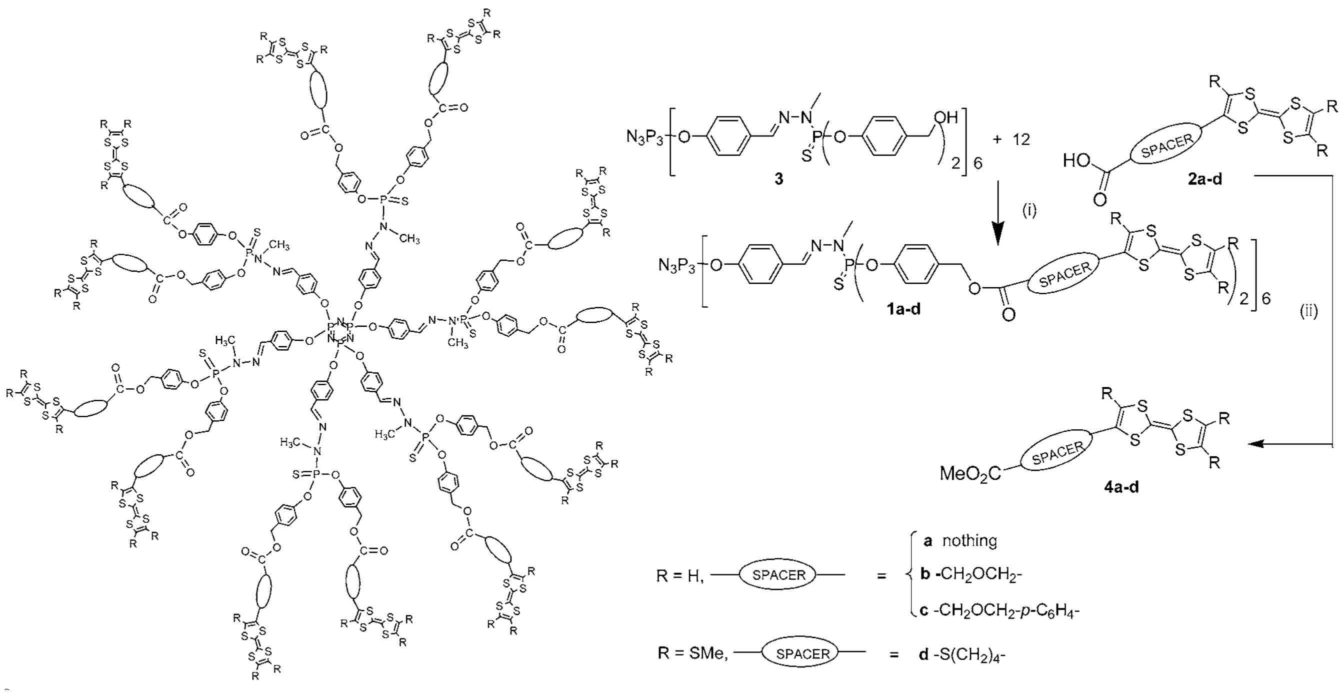
10.1021/ol049648x CCC: $27.50

Scheme 1. Synthesis of Targeted Compounds[a]



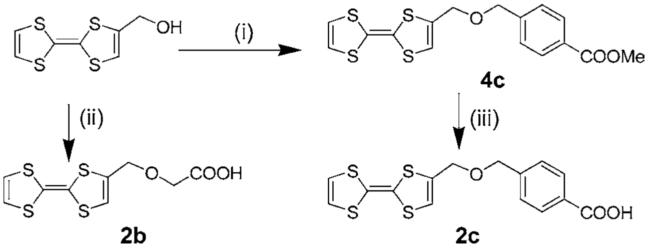
[a] Conditions: (i) DCC, DMAP, DCM, rt, 1−3 days; (ii) **2a−d**, DCC, DMAP, DCM, rt, 1−3 days + MeOH.

knowledge, no attempts to estimate the degree of interdendrimer interaction have been undertaken.

On these grounds, we have decided to study the electroconductive mixed-valence (MV) salts of TTF-terminated dendrimers with a closed-shell anion. Here we report on the synthesis and properties of four such new compounds built around the cyclotriphosphazene core,[6] i.e., **1a−d**, and present the results of the spectroscopic studies confirming the 3-D character of the conductivity of their mixed-valence salts.

In our synthetic route toward **1a−d** (Scheme 1), the varied TTF-pendant groups were branched on the surface of the dendrimer by DCC-DMAP esterification (yields 50−80%), by reaction of the corresponding carboxylic acids **2a−d** (prepared according to known procedures for **2a**[7] and **2d**[8] and Scheme 2 for **2b−c**) and dendrimer **3** bearing 12 outer alcohol functionalities. The latter new compound was prepared by $BH_3 \cdot SMe_2$ reduction of the corresponding dodecaaldehyde[9] in CH_2Cl_2 as a solvent and at 0 °C (91% yield). For comparison purposes, the "monomeric" Me-esters **4a−d** of related acids were also prepared. All derivatives **1a−d** gave satisfactory spectroscopic data after purification by chromatography on silica gel column. Thus, ^1H NMR and malditof mass spectrometry experiments unambiguously demonstrate the full functionalization of the 12 alcohol functionalities of the dendrimers. Moreover, in thin layer cyclic voltamperometry (Figure 1) of dendrimer **1d**,[10] the areas of the first and second peaks with respect to that of

Scheme 2. Synthesis of TTF-Carboxylic Acids **2c** and **2b**[a]



[a] Reagents and conditions: (i) $BrCH_2(p\text{-}C_6H_4)COOMe$, 18-Crown-6, DMSO, rt, 24 h; (ii) NaH, ICH_2COONa, 18-Crown-6, THF; (iii) 1 M KOH methanol solution, rt, 8 h.

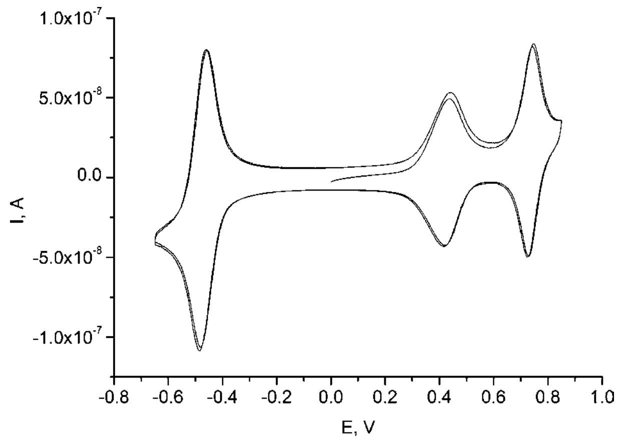


Figure 1. Thin-layer cyclic voltamperogram of **1d** (naphthoquinone as an internal standard).[9]

the internal standard naphthoquinone are in full agreement with 12 TTF units per dendrimer core. Dendrimers **1a−d** should be kept in a refrigerator in the absence of light, as they decompose in few days on exposure to light in the presence of moisture. Therefore, all UV−visible−NIR spectroscopic and electrochemical experiments were conducted on *freshly prepared* dendrimers.

Chemical oxidation of **1** into **5** [**1** $(CF_3SO_3)_6$], **6** [**1** $(CF_3SO_3)_{12}$], or **7** [**1** $(CF_3SO_3)_{24}$] (TTFs being in 1/2 MV, cation radical, or dication states, respectively) was best carried out by using $PhI(OAc)_2$ in the presence of CF_3SO_3H in dichloromethane (DCM) or in a mixture of DCM and acetonitrile and depended on the amount of the oxidizing reagent (1 mol per 2 mol of electrons).[11] The same procedure was also applied for esters **4**, which were converted into the corresponding cation radicals **8** and dication triflates **9**. Solid MV salts **5a−d** were precipitated after partial oxidation of **1a−d** by addition of diethyl ether to the reaction mixture. Four-probe conductivity measurements on compressed pellets reproducibly gave the values of $\sigma = (1.9, 1.3, 0.4, 0.6) \times 10^{-6}$ S cm^{-1} for **5a−d**, respectively. It is noteworthy that higher conductivities were found for the derivatives involving shorter spacers within the R = H series. On average, the conductivity increased by 3 orders of magnitude compared to that of precursors **1a−d**. The solid-state electronic spectra of **5** exhibit the expected broad MV bands in NIR (1600−1700 nm for **5a−c**, 2000 nm for **5d**) (Figure 2). They were also obtained by mixing equimolar amounts of **1** and **6** in DCM−acetonitrile solution and showed identical spectroscopic features.

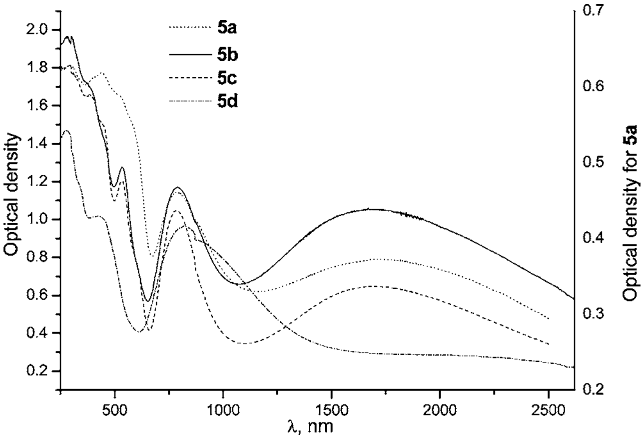


Figure 2. Spectra in the solid film of MV states **5a−d**.

To interpret the nature of the electronic interactions within the new materials, all oxidized forms of the dendrimers and the corresponding monomeric esters **4** were characterized by their UV−Vis−NIR spectra in solution. The simplest case is presented by the **d** series. Thus, portionwise addition of the oxidizing reagent ($PhI(OAc)_2/CF_3SO_3H$) to **1d** and **4d** was accompanied by the presence of isosbestic points and led to appearance of the long wave absorption band at about 846 nm characteristic of cation radicals of tetrathio-TTF derivatives.[5] Further oxidation afforded the corresponding dication characterized by a band at about 650 nm.

The spectra of the cation radicals of the **a−c** series are more complex. Thus, the spectrum of **8b** is similar to that of the TTF cation radicals and at concentrations higher than 10^{-3} M exhibits a weak band at about 780 nm (Figure 3). The intensity of this band does not obey Beer's law and depends on the counteranion.

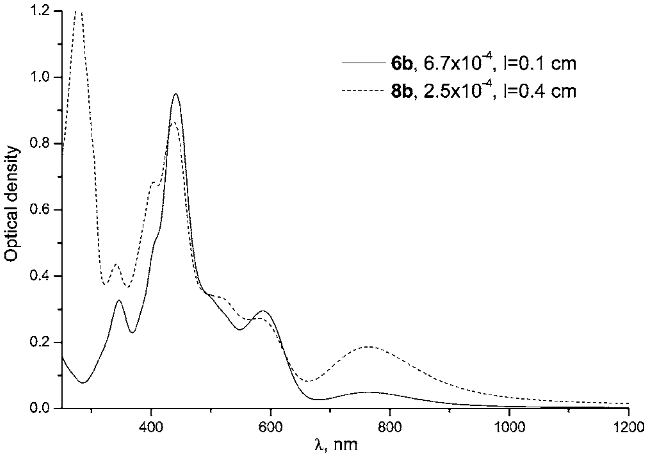


Figure 3. UV−vis−NIR spectra for cation radicals **6b** (2.5×10^{-4}, MeCN, $l = 0.4$ cm) and **8b** (6.7×10^{-4}, DCM, $l = 0.1$ cm).

A similar band was observed for TTF in the solid state;[12] therefore, it can be ascribed to the π-stacked aggregates. Stepwise oxidation of **1b** gave rise to **6b**, but no isosbestic points were observed. The spectrum of **6b** (Figure 3) presents an overlay of the features characteristic for the free cation radicals **8b** and the π-stacked TTF cation radicals. The optical densities of the bands corresponding to the aggregated TTF cation radicals (i.e., 780, 520, and 400 nm) upon dilution diminish proportionally with the decrease in the concentration, indicating that aggregation occurs within the dendrimers (intradendrimer π-stacking).

Oxidation of **1a−c** to **5a−c** or mixing **1a−c** with **6a−c** led to formation of the MV species in solution evidenced

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(8) Prepared from cyanoethylthiotris(methylthio)TTF by treatment with CsOH, alkylation of the Cs-thiolate with methyl 5-bromopentanoate, and saponification of resulting **4d** with LiOH according to the procedure given in: Becher, J.; Lau, J.; Leriche, P.; Mork, P.; Svenstrup, N. *J. Chem. Soc., Chem. Commun.* **1994**, 2715−2716.

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(10) Experimental conditions: 1/12 mM **1d** with 1.4 mM naphthoquinone as an internal standard, 0.4 M Bu_4NPF_6 in DCM−acetonitrile (4:1) E in V vs Ag/AgCl as the reference.

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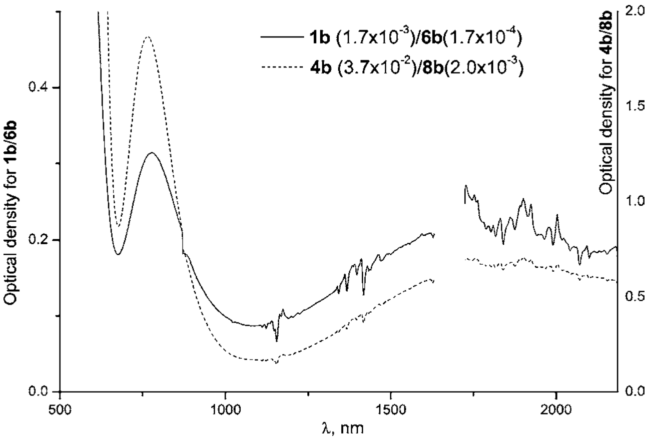

Figure 4. UV−vis−NIR spectra for mixed-valence states obtained by mixing of neutral dendrimer **1b** and monomer **4b** with corresponding cation radicals (**6b** and **8b**) (DCM, $l = 1.0$ cm).

by UV−vis−NIR spectra (Figure 4), similar to those obtained for the solid state (Figure 2). The behavior of **5b** serves as a typical example. Whereas intensities of the absorption bands corresponding to the MV salt generated by mixing **4b** and **8b** change in a highly nonlinear manner upon dilution (decreasing the concentration by a factor of 2 decreases the intensity by a factor of 3), the intensities of the corresponding bands of **5b** only change by factors of 2.2 (at 1600 nm) and 2.4 (at 780 nm). This behavior also indicates that the MV interaction within **5b** is mostly intradendrimeric, but there are still some interdendrimer (3-D) interactions, unlike in the case of the stoichiometric cation radicals **6b**. Apparently, longer and more flexible spacers in the series **a**−**c** increase the degree of intradendrimeric interaction and afford less conductive materials.

In conclusion, we have shown that mixed-valence cation radical salts of TTF-terminated dendrimers with closed-shell anion are conducting not only as a result of electron transfer between partially oxidized dendrimers but also due to the presence of interdendrimeric charge transfer (i.e., 3-D electronic interactions). The contribution of the latter is not large, but it can be increased by appropriate structural modifications of the dendrimers, e.g., by using shorter, rigid spacers. We are currently attempting to employ these features in light-harvesting devices.

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Supporting Information Available: General procedures for synthesis of dendrimers and their oxidation. This material is available free of charge via the Internet at http://pubs.acs.org.

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