Electron Transfer Through Molecular Bridges Between Reducible Pentakis(thiophenyl)benzene Subunits

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Abstract: "Dimers" **3**, **4** and **7**, which consist of two reducible pentakis(thiophenyl)benzene subunits linked by different molecular structures, have been synthesised as model compounds for reducible molecular-wire-type synthons to represent differences in the electron-transfer ability as a function of the bridging structure. The bridging units consist of *para*-divinylbenzene in **3**, bis-hydrazone in **4** and diacetylene in **7**. Their ability to transfer electrons from one reducible subunit to the other was investigated by electrochemical and spectroelectrochemical methods and, in the case of **4** and **7**, the solid-state structures support the experimental findings. The *para*-divinylbenzene bridge in **3** was found to completely isolate the reducible structures (Class I system). In contrast, the diacetylene bridge in **7** electronically connects the two reducible structures (Class III system) and, thus, demonstrates its potential application as a "molecular wire". The bis-hydrazone-linked compound **4** displayed only a low level of electronic connection between the subunits and was only observed in the spectroelectrochemical investigation.

Keywords: conjugation · electron transfer · mixed-valent compounds · molecular wires · polythiobenzenes

Introduction

Currently, a growing interest has been directed towards the design of molecular wires[1–4] and rods,[5, 6] since such structures may serve as building blocks for nanoscale chemical entities that are geometrically and dimensionally confined. They may act as connectors in molecular and supramolecular electronic and photonic devices.[7] A molecular bottom-up approach to complex functional entities, for example, electrical circuits or single-electron computing devices, depends strongly on the postulate that it may be possible to move single electrons between individual compartments.[8, 9] This simple function, namely the transfer of electrons from one subunit to another, has been a topic of interest for quite some time. Since the advent of the mixed-valence chemistry in 1967,[10] numerous structures have been studied that contain two or more active redox units, both inorganic[2] and organic, that are connected by molecular structures; their electron transport features have been discussed and analysed at various levels of detail.

Molecular wires based on pyridinium end-groups and carotenoid-type conjugated chains (termed caroviologens) have already been investigated in our laboratory and have been shown to induce electron transport through lipid vesicle membranes.[11] The structural reorganisation of anthracene-bridged stilbenoids by oxidation and reduction has also been studied.[12] Most of the molecular wires based on organic systems were, however, focused on electron-rich, oxidisable structures, such as thiophenes,[13] nitrogen-based mixed-valence systems,[14] pyrroles[15] and so forth. These oxidisable structures loose electrons and the mobility of the holes generated in the molecular structures was investigated. Reducible subunits take up additional electrons in their LUMO, which may lead to higher electronic mobility in the connecting molecular structure.

Poly(phenylthio)-substituted aromatic systems are well-known for their host–guest chemistry in the solid state[16] and

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have been shown to display remarkably low reduction potentials.[17] Therefore, they appear to be promising candidates to study the electron-transfer ability of molecular structures that contain connected reducible subunits. They have already been incorporated as electron-acceptor sites in a macrobicyclic ligand,[18] in reducible rod-like molecular wires[19] and in reducible nanosized macrocycles based on *meta*-diacetylene-linked poly(phenylthio)-substituted benzenes.[20]

We chose two pentakis(thiophenyl)benzene units connected by different conjugated π systems as bridges as the model compounds to investigate the electron-transfer ability in molecular structures that contain reducible subunits. A *para*-divinylbenzene bridge (1,4-bis(ethenyl)benzene-2′,2″-diyl) in **3**, a bis-hydrazone bridge (2,3-diazabuta-1,3-dien-1,4-diyl) in **4** and a diacetylene bridge (buta-1,3-diyne-1,4-diyl) in **7**[19] were investigated.

Herein we describe the synthesis of the model compounds **3**, **4** and **7**. Their electrochemical and spectroelectrochemical properties as well as, in part, their solid-state structures, are reported and discussed from the point of view of a possible electron transfer through the bridging structure.

Results and Discussion

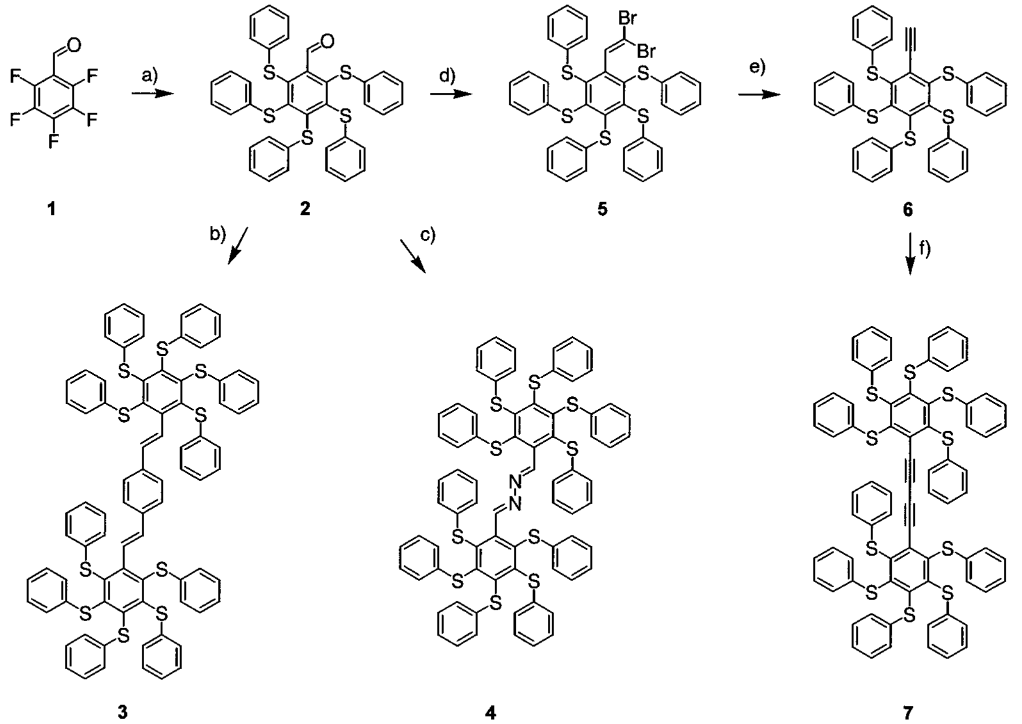
Synthetic procedures: The new compounds **3** and **4**, along with the previously described compound **7**,[19] each consisting of two reducible pentakis(thiophenyl)benzenes separated by different molecular spacers, were synthesised as shown in Scheme 1. All new compounds were characterised by ^{1}H and ^{13}C NMR spectroscopy, FAB-MS and microanalysis, as well as by single-crystal X-ray analysis for compounds **4** and **7**.

Starting with commercial pentafluorobenzaldehyde (**1**), the fluorine atoms were substituted by thiophenyl sodium salt in 1,3-dimethylimidazolidin-2-one (DMI) to give the pentakis(thiophenyl)benzaldehyde (**2**) in 75% yield. Compound **2** is the starting material for all three compounds **3**, **4** and **7**.

Treatment of **2** with *para*-xylylenebis(triphenylphosphonium bromide) in presence of a base gave the *para*-divinylbenzene-bridged *trans,trans*-1,4-bis-{[2′-(2″,3″,4″,5″,6″-pentathiophenyl)phenyl]ethenyl}benzene (**3**) in 49% yield. The *trans,trans* configuration of the bridging structure is proved by the coupling constant of $J = 16$ Hz between the ethenyl protons at $\delta = 6.86$ and 6.49, respectively. Compound **3** is a bright yellow solid and soluble in organic solvents, such as dichloromethane, chloroform, diethyl ether and toluene.

Treatment of **2** with hydrazine hydrate in acetonitrile heated under reflux gave *trans,trans*-decathiophenylbenzaldehyde azine **4** in 32% yield as a light yellow precipitate. The *trans,trans* configuration of the bridging structure was proved by single-crystal X-ray analysis. The light yellow solid is soluble in organic solvents, such as dichloromethane, chloroform, diethyl ether and toluene. Single crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of **4** in chloroform.[21]

In a Corey–Fuchs reaction sequence, the aldehyde **2** was first converted to the dibromoolefin **5**:[22] a CBr_4/PPh_3 solution was added to a solution of **2** in acetonitrile heated under reflux, and the desired dibromoolefin **5** was isolated in 69% yield. In later experiments, the reaction was repeated in dry dichloromethane at room temperature without changes in yield or quality of the product. Compound **5** is a brown-yellow solid that is very soluble in aprotic organic solvents. It is well characterised by ^{1}H and ^{13}C NMR spectroscopy and FAB-MS.



Scheme 1. Synthesis of the model compounds **3**, **4** and **7**. Reaction conditions: a) DMI, PhSNa, RT; b) $NaOH/CH_2Cl_2$, $Ph_3P^+CH_2(p\text{-}C_6H_4)CH_2P^+Ph_3 \cdot 2\,Br^-$; c) CH_3CN, $H_2NNH_2 \cdot H_2O$, reflux; d) CH_3CN, CBr_4, PPh_3, RT; e) THF, *n*BuLi, $-78\,^{\circ}C$, H_2O, RT; f) C_6H_5N, $CuAc_2 \cdot H_2O$, 55 °C.

However, several attempts to prepare a sample of **5** suitable for microanalysis failed. All microanalyses of **5** were consistently too high in carbon. Whether this error is caused by impurities or by the burning/combustion behaviour of **5** during the analysis could not be clarified. However, the quality of **5** was sufficient for the envisaged synthetic target and was therefore used without further purification. The acetylenic derivative **6** was prepared by reaction of **5** with *n*-butyllithium:[22] a solution of **5** in THF was treated with a 2.5 fold excess of *n*-butyllithium in hexane at −78 °C and quenched with aqueous ammonium chloride to give compound **6** in 65 % yield. 1-Ethinyl-2,3,4,5,6-pentakis(thiophenyl)benzene (**6**) is a yellow solid that is soluble in aprotic solvents. Oxidative coupling of **6** gave compound **7**:[23] compound **6** was heated to 55 °C with one equivalent of copper acetate monohydrate in pyridine to give the diacetylene-bridged **7** in 65 % yield as an intense orange solid that is moderately soluble in aprotic organic solvents, such as chloroform, methylene chloride, toluene or tetrahydrofuran. Crystallisation from hot toluene gave single crystals suitable for X-ray analysis.

Electrochemical studies: The redox behaviour of compounds **3**, **4** and **7**, which consist of two reducible subunits connected by a conjugated π system as a bridging unit is of particular interest, as it will reveal the electron-transfer ability of the different bridging structures and thereby their potential use as "molecular wires" between reducible subunits.

The electrochemical properties of compounds **3**, **4** and **7** were investigated by cyclic voltammetry (CV) at room temperature in anhydrous dimethylformamide (DMF) with tetra-*n*-butylammonium hexafluorophosphate (0.1 M $TBAPF_6$) as the supporting electrolyte. A three-electrode set-up was used with a platinum disk as the working electrode, a platinum wire as the counter-electrode and a silver wire as the dummy reference electrode. All samples were used at a concentration of 5×10^{-3} M and the formal reduction potentials ($(E_{pa} + E_{pc})/2$) were determined with respect to the ferrocenium/ferrocene (Fc^+/Fc) couple with $E^{\circ\prime}(Fc^+/Fc) = 0.5$ V versus SCE as the internal reference. The criterion applied for reversibility was 1.0 ± 0.5 for the ratio of the difference peak potential and the half-peak potential of the compound and ferrocene in the same measurement and no shift of the half-wave potential with varying scan rates (10–250 $mV\,s^{-1}$). The relative numbers of electrons were determined by measurements at limiting current with a rotating disk electrode. The plateau currents were compared to the plateau current of hexakis(*para*-*tert*-butylphenylthio)benzene as the internal standard for a one-electron reduction, assuming similar diffusion coefficients of the compound and the internal standard. The values are given in Table 1 as formal reduction potentials with respect to SCE.

The parent monomeric compound hexakis(phenylthio)benzene displays a reversible one-electron reduction at −1.56 V versus SCE under the same conditions.[17, 19] The two *para*-divinylbenzene-bridged reducible subunits in compound **3** display only one reversible reduction wave corresponding to two electrons at a formal potential of −1.39 V versus SCE. The bis-hydrazone-linked subunits in compound **4** display only one reduction wave corresponding to two electrons at −1.19 V at a scan rate of 100 $mV\,s^{-1}$. A more detailed analysis of the reduction wave showed a marginal shift of the reduction potential to more negative values with increasing scan rate (7 mV per 100 $mV\,s^{-1}$). However, the observation of a single reduction wave indicates that the two redox centres are independent and the bridging structure behaves rather as a non-conjugated spacer. In the classification for mixed-valence compounds from Robin and Day, compounds **3** and **4** with isolated redox centres are Class I derivatives.[10]

Table 1. Cyclic voltammetry data for $C_6(SPh)_6$, **3**, **4** and **7**.[a]

Compound	$E_2^{\circ\prime}$ [V][b]	$E_2^{\circ\prime}$ [V][b]
$C_6(SPh)_6$	−1.56[c]	–
3	−1.39[d]	–
4	−1.19[d]	–
7	−1.12[e]	−1.38[e]

[a] Platinum working electrode in 0.1 M $TBAPF_6$/DMF; scan rate: 100 $mV\,s^{-1}$. [b] In V versus SCE (Fc^+/Fc couple with $E^{\circ\prime}(Fc^+/Fc) = 0.5$ V versus SCE as internal standard), formal reduction potential $E^{\circ\prime} = (E_{pa} + E_{pc})/2$. [c] See Ref. [17]. [d] Two-electron reduction wave. [e] See Ref. [19].

The diacetylene-linked subunits in compound **7** display two reversible one-electron reduction waves at a formal potential of −1.12 and −1.38 V versus SCE, indicating that the first reduction yields a mono-anion stabilised by delocalisation over both electron-accepting subunits. The separation between the waves of 260 mV indicates that the mono-anion $\mathbf{7}^{\bullet-}$ is thermodynamically stabilised towards disproportionation to give **7** and $\mathbf{7}^{2-}$ by the comproportionation constant of $K_c = 2.55 \times 10^4$ which suggests **7** to be a Class II derivative.[10, 24] The diacetylene bridge connects the two subunits and facilitates active electron transfer: it displays its ability to function as electron-conducting spacer unit for molecular wire applications.

A more detailed analysis of the delocalisation of the first reducing electron over the "dimeric" structures **3**, **4** and **7** requires investigations on the single reduced species $\mathbf{3}^{\bullet-}$, $\mathbf{4}^{\bullet-}$ and $\mathbf{7}^{\bullet-}$, respectively, which were performed by spectroelectrochemical techniques.

Spectroelectrochemical studies: UV/VIS/NIR spectroelectrochemical investigations were performed under the conditions for electrochemistry (DMF, 0.1 M $TBAPF_6$, RT) in a cell described elsewhere.[25]

The radical anion of the parent monomeric compound hexakis(phenylthio)benzene displays two absorption maxima at $\lambda = 420$ and 590 nm and both have a bathochromic shift with respect to the lowest energy absorption maximum of the neutral species at $\lambda = 343$ nm. The uniformity of the process is demonstrated by isosbestic points at $\lambda = 313$ nm and 379 nm, and the reversibility, already observed in the CV experiment, is confirmed by recovery of the starting spectrum after reoxidation.

The *para*-divinylbenzene-bridged **3** displays only one reversible two-electron reduction wave in the CV experiment. The stepwise coulometric reduction to the dianion $\mathbf{3}^{2-}$ is shown by the increase in the intensity of the lowest energy absorption at $\lambda = 861$ nm and a concomitant decrease of the absorption at 331 nm from the neutral **3** (Figure 1). Isosbestic

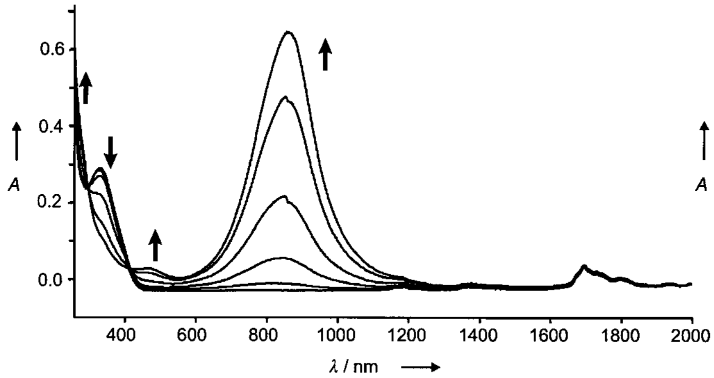


Figure 1. Spectroelectrochemistry of the reduction of **3** to $\mathbf{3}^{2-}$. Evolution of the UV/Vis/NIR spectrum; potential range: −1150 to −1300 mV.

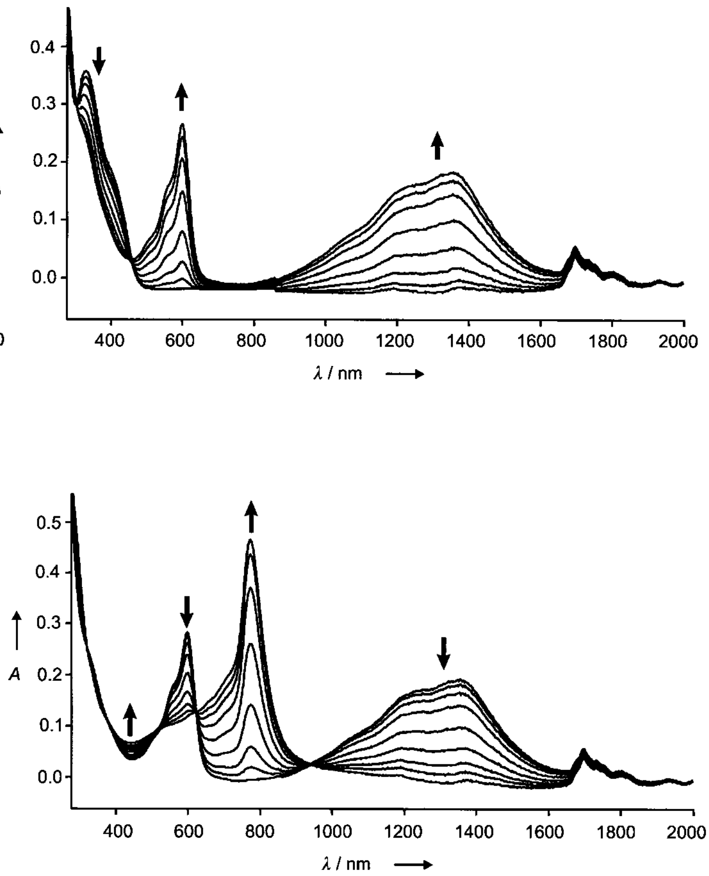


Figure 2. Spectroelectrochemistry of the reduction of **7** to $\mathbf{7}^{2-}$. Top: Evolution of the UV/Vis/NIR spectrum upon reduction of **7** to $\mathbf{7}^{\bullet-}$; potential range: −900 to −1070 mV. Bottom: Evolution of the UV/Vis/NIR spectrum upon further reduction of $\mathbf{7}^{\bullet-}$ to $\mathbf{7}^{2-}$; potential range: −1100 to −1300 mV.

points at $\lambda = 298$ and 418 nm show the uniformity of the process, while the recovered starting spectrum after reoxidation documents its reversibility. As already concluded from its CV, the two subunits are independent and, therefore, it can be confirmed that **3** is a Class I derivative.[10]

The spectroelectrochemical investigations of bis-hydrazone **4** performed in DMF demonstrate the limited reversibility of the reduction process within duration of the experiment (30 spectra each at 480 nm min^{-1}). The original spectrum is not completely restored. The CV of **4** displays only one reduction wave, which suggests that the two reducible units are electronically independent. However, it is interesting to note that two reductive processes can be detected in the spectroelectrochemical experiment: the first reduction step leads to new absorption bands at $\lambda = 517$, 622 and 1250 nm. The long-wavelength absorption at 1250 nm may either be attributed to a radical anion, or less likely, to a dianionic species. Based on structural considerations, we assign this band to a compound in which the central diazabutadiene spacer group acquires features of an azo group. Thus, the spacer unit is strongly reorganised in the first reduction step so that the second reduction step is much easier and very fast. This is in agreement with electrochemical studies and demonstrates that an increase in the scan rate causes the reduction wave to be slightly displaced to more negative values. Additionally, the ratio of anodic and cathodic currents is independent of the scan rate. The assignment to a radical anion is further supported by the disappearance of this long-wavelength absorption on extended reduction and leads to new absorption bands at $\lambda = 295$, 409 and 765 nm. The limited reversibility may be caused by protonation or elimination reactions.[26] Therefore, upon reduction of **4**, negative charge is not exclusively transferred into the reducible subunits, but to some extent into the spacer group.

The two separated reduction waves of the diacetylene-linked **7** observed by CV indicates the formation of a stable radical anion $\mathbf{7}^{\bullet-}$ allowing its spectroscopic characterisation (Figure 2). The spectroelectrochemical investigation confirms this finding and displays, as expected for coupled subunits, two separated reduction steps. During the first reduction process, the absorption bands of **7** at $\lambda = 346$ and 407 nm vanish, while bands of the radical anion $\mathbf{7}^{\bullet-}$ at $\lambda = 281$, 600 and 1310 nm appear. The 600 nm band has shoulders at 503 and 557 nm. Similar to $\mathbf{4}^{\bullet-}$, the lowest energy absorption of $\mathbf{7}^{\bullet-}$ at 1310 nm may be assigned to an intervalence charge-transfer (IV-CT) band. The uniformity of the process is demonstrated by isosbestic points at 298 and 457 nm, and the reversibility already observed in the CV experiment is confirmed by recovery of the starting spectrum after reoxidation.

On further reduction to the dianion $\mathbf{7}^{2-}$, the band at $\lambda = 600$ nm and its shoulders, as well as the broad band at 1310 nm, decrease, while the absorption spectrum of $\mathbf{7}^{2-}$ appears with absorptions at $\lambda = 267$ and 294 nm and an intense lowest energy band at 774 nm with two shoulders at 662 and 706 nm. Again, the isosbestic points at 317, 627 and 922 nm indicate the uniformity of the reduction process, and the regeneration of the starting spectrum documents its reversibility.

Analysis of the UV spectrum of $\mathbf{7}^{\bullet-}$ provides further insight into the electronic coupling in the mono-reduced state. For both Class II and III compounds, an absorption band in the near infrared region with low intensity is expected. For a Class II system, the electronic coupling integral H can be calculated according to the Hush approach.[27] For Class III systems with strong coupling, delocalisation occurs.

A plot of absorbance versus wavenumber of the low-energy transition at $\lambda = 1310$ nm of $\mathbf{7}^{\bullet-}$ leads to an unsymmetrical line shape with vibrational progression and an extinction coefficient of 19500 M^{-1}cm^{-1} (Figure 3). Consequently, the band

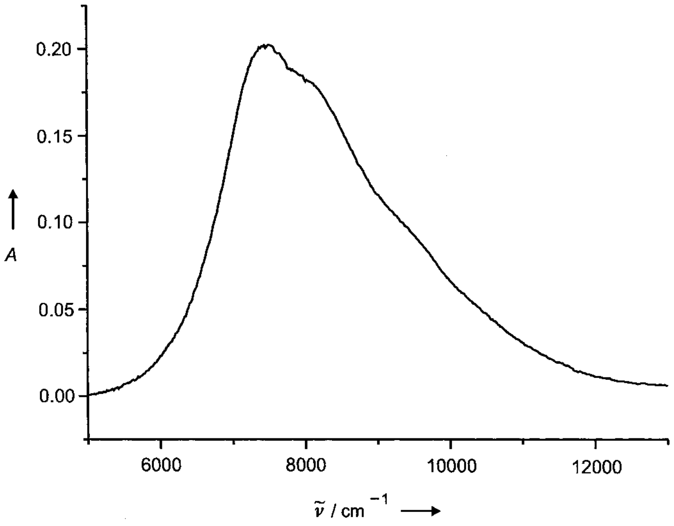


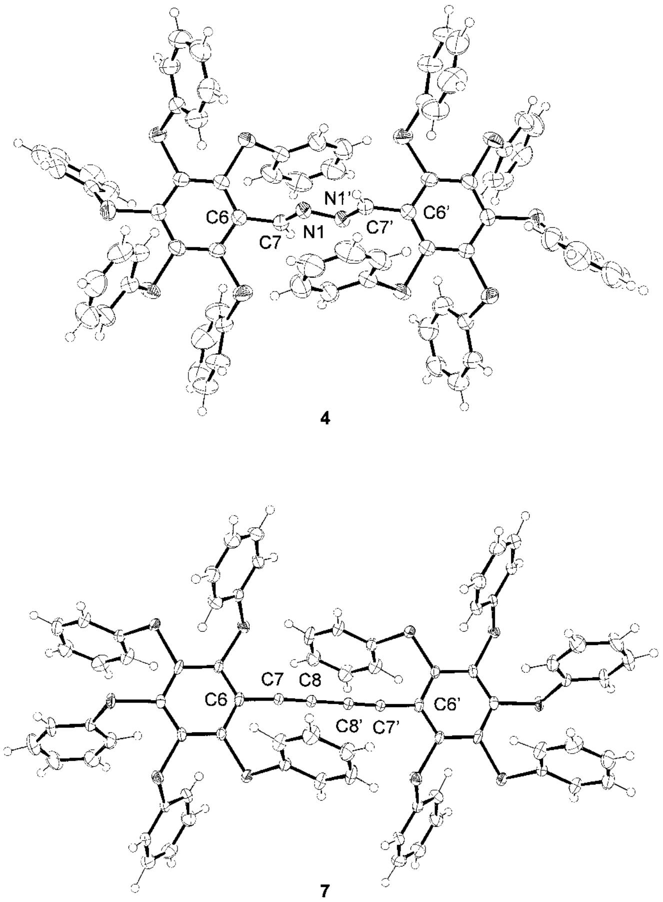
Figure 3. Plot of absorbance (A) versus $\tilde{\nu}$ for the IT band of $\mathbf{7}^{\bullet -}$.

shape is in agreement with either a vertical transition in a Class III system with a large vibrational progression or a cut-off Class II IV-CT band. Recently, Nelsen has analysed spectra of intervalence systems at the Class II/III borderline in detail.[28] The high extinction coefficient and the vibrational progression of the $\nu = 7500\ \mathrm{cm}^{-1}$ absorption of $\mathbf{7}^{\bullet -}$ account for an almost delocalised system, which has already passed the Class II/III borderline.

The spectra of the three doubly reduced compounds $\mathbf{3}^{2-}$, $\mathbf{4}^{2-}$ and $\mathbf{7}^{2-}$ resemble each other with absorptions at $\lambda = 861$, 765 and 774 nm, respectively. The hypsochromic shift of $\mathbf{7}^{2-}$ compared to $\mathbf{3}^{2-}$ is attributed to a more extended delocalisation in $\mathbf{3}^{2-}$.

Crystal structure of compounds 4 and 7: The solid-state structures of "dimers" **4** and **7** were determined by X-ray diffraction and are shown in Figure 4. They offer a deeper understanding of the ability of the reducing electrons to move from one subunit to the other. The reducing electron will, by definition, occupy the LUMO of the molecule which is part of the π system. Good electronic communication between subunits in a compound requires that their individual π systems have a considerable overlap. Particular attention will therefore be focused on the structural features of the π systems of the reducible subunit and the connected bridging structures.

The solid-state structure of **4** shows that the molecule consists of two reducible pentakis(thiophenyl)benzene subunits covalently linked by a *trans,trans*-CH=N-N=CH bridge with a crystallographic inversion centre in the middle of the N–N bond. The two reducible subunits are separated (centre to centre) by 8.7 Å and the central benzene cores are in parallel planes which are separated by 3.8 Å. The bond lengths in the bridging unit (C6C7=N1–N1′=C7′C6′) are 1.488 Å (C6–C7), 1.254 Å (C7–N1) and 1.421 Å (N1–N1′). The bridging angles of 120.4° (C6-C7-N1) and 111.1° (C7-N1-N1′) are as expected for a benzaldehyde-azine structure. Of particular interest, however, is the torsion angle of ≈72° between the C=N double bond and the central benzene plane of the terminal subunits. The planes of both benzene rings form an angle of 72° with the plane of the C=N bond, so that only a weak conjugation of these π systems is expected for the neutral species. This is confirmed by the CV experiments discussed above and the observable amounts of $\mathbf{4}^{\bullet -}$ may be the result of structural changes in the singly reduced species. The alternating "up" and "down" pattern (ududu) of the phenylthio substituents and the range of the sulfur angles (104–106°) agree with those found in the solid structure of the parent hexakis(phenylthio)benzene.[29]



4

7

Figure 4. Crystal structures of **4** (top) and **7** (bottom).

In spite of the fact that the *para*-divinylbenzene-bridged **3** is a crystalline compound, several attempts to obtain suitable single crystals of **3** failed. However, we assumed that, in analogy to **4**, the π systems of the bridging *para*-divinylbenzene unit and of the terminal pentakis(phenylthio)benzene units are more or less orthogonal and thus lead to little overlap. The CV and spectroelectrochemical investigations showed **3** to be a Class I compound with independent redox centres, which confirms such an assumption.

The solid-state structure of **7** shows that the molecule consists of two pentakis(thiophenyl)benzene units linked by a diacetylene bridge with a crystallographic inversion centre in the middle of the C8–C8′ central bond (Figure 4). The two central benzene cores of the reducible subunits are separated by 9.4 Å (centre to centre) and are in parallel planes separated by 0.75 Å. The bond length in the diacetylene bridge (C6–C7≡C8–C8′≡C7′–C6′) are 1.436 (C6–C7), 1.202

(C7–C8) and 1.372 Å (C8–C8′), and the bridge angles of 175.5 (C6-C7-C8) and 178.2° (C7-C8-C8′) deviate only slightly from linearity. The conformation of **7** shows the phenylthio groups in *para* and *ortho* positions to the diacetylene bridge point to the same side of the central benzene core to give an unexpected (udddu) pattern. However, this does not disturb the sulfur angles, which are in the expected range (104–106°). The overlap between the π system of the diacetylene bridging structure and the π system of the reducible subunits should be independent of the torsion angle of one subunit relative to the other. Even though both central benzene rings of **7** are in parallel planes, it is probably not a requirement for the electronic interaction between them. Evidently, the cylindrical acetylenic π system bears the advantage of this "rotational freedom". A stronger overlap would be expected for a conformationally optimised double-bond connector and in fact, the already mentioned bathochromic shift of the lowest energy absorption of the doubly reduced *para*-divinylbenzene-bridged structure $\mathbf{3}^{2-}$, in contrast to the doubly reduced diacetylene-bridged structure $\mathbf{7}^{2-}$, may be caused by such an effect in the doubly reduced form. Other redox centres connected by anthracene-bridged stilbenoids have been reported to display such conformational changes upon oxidation.[12]

Conclusions

The present results indicate the suitability of diacetylene connections as active electron-transfer linkers between molecular entities, while the *para*-divinylbenzene and the bishydrazone bridges probably require additional structural conditions for efficient electron transfer. The potential of the diacetylene connection is illustrated, to some extent, by the rapidly growing field of acetylene "scaffolding".[30, 31] Furthermore, they confirm the potential of poly(thiophenyl)-substituted aromatic compounds to act as reducible subunits in molecular structures and devices. This is the case for reducible molecular rigid rods,[19] reducible molecular macrocycles[20] and reducible macrobicyclic ligands[18] that contain such groups.

Experimental Section

General: All reaction vessels were flame-dried in an nitrogen atmosphere. Reactions were carried out under nitrogen with commercial reagents without further purification. THF: distilled over Na. CH_3CN: distilled over CaH_2. Column chromatography (CC): commercial-grade solvents, distilled; silica gel: Geduran SI 60 from Merck. Thin-layer chromatography (TLC): Macherey-Nagel pre-coated TLC plates SIL G-50 UV_{254}, visualisation by UV. Melting points: Büchi B-540, uncorrected. IR: Perkin–Elmer FT-IR 1600. ^1H NMR: Bruker AC200 (200 MHz); δ relative to the solvent signal: $CDCl_3$: $\delta H = 7.26$. ^{13}C NMR: Bruker AC200 (50 MHz); δ relative to the solvent signal: $CDCl_3$: $\delta C = 77.00$. The mass spectra were performed at the Laboratoire de Spectrométrie de Masse, Strasbourg (France).

Pentathiophenyl benzaldehyde (2): Thiophenyl sodium salt (18 g, 136.20 mmol) was dissolved in 1,3-dimethylimidazolidin-2-one (DMI; 100 mL) and pentafluorobenzaldehyde (3.81 g, 19.43 mmol) was added. The solution immediately turned orange and was stirred for 12 h at room temperature, poured into a saturated NaCl solution and extracted with toluene. The organic layer was separated and dried over $MgSO_4$. Evaporation of the solvent yielded **2** (9.49 g, 14.67 mmol, 75 %) as a yellow solid. M.p. 122 °C; IR (KBr): $\tilde{\nu} = 3051$ (w), 1704 (s), 1579 (m), 1476 (s), 1438 (s), 1288 (w), 1164 (w), 1080 (m), 1023 (m), 999 (w), 929 (w), 735 (s), 698 (m), 687 (s), 469 cm^{-1} (w); ^1H NMR ($CDCl_3$): $\delta = 6.85-7.35$ (m, 25 H), 9.87 (s, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 126.32$, 126.39, 126.83, 128.19, 128.48, 128.85, 128.96, 129.26, 136.32, 136.94, 137.23, 140.91, 146.57, 147.56, 150.72, 190.08; FAB-MS: *m*/*z* (%): 650 (8), 649 (21), 648 (46), 647 (75), 646 (100) $[M]^+$; elemental analysis calcd (%) for $C_{37}H_{26}OS_5$: C 68.70, H 4.05; found: C 68.81, H 4.07.

***trans,trans*-1,4-Bis-{[2′-(2″,3″,4″,5″,6″-pentathiophenyl)phenyl]ethenyl} benzene (3)**: A 50 % NaOH solution (4 mL) was added to pentathiophenyl benzaldehyde (0.21 g, 323 µmol) and *para*-xylylenebis(triphenylphosphonium bromide) (0.13 g, 163 µmol) in CH_2Cl_2 (8 mL). The colour changed immediately from yellow to red. After 20 h the reaction mixture was poured into water and extracted with CH_2Cl_2. Column chromatography (silica, benzene) yielded **3** (0.13 g, 79 µmol, 49 %) as light yellow solid. R_f (silica, xylene): 0.70; m.p. 76 °C; ^1H NMR ($CDCl_3$): $\delta = 6.95-7.5$ (*m*, 54 H), 6.86 (d, $J = 16$ Hz, 2 H), 6.49 (d, $J = 16$ Hz, 2 H); ^{13}C NMR ($CDCl_3$): $\delta =$ 149.32, 149.21, 147.49, 146.09, 142.64, 138.13, 137.60, 136.29, 134.39, 128.93, 128.35, 128.16, 127.99, 126.58, 126.02; FAB-MS: *m*/*z* (%): 1367 (20), 1366 (36), 1365 (69), 1364 (89), 1363 (100, molecular mass), 1362 (61) $[M]^+$, 1275 (33), 1274 (45), 1273 (50), 1272 (35); elemental analysis calcd (%) for $C_{82}H_{58}S_{10}$: C 72.21, H 4.29; found: C 72.36, H 4.44.

***trans,trans*-Decathiophenyl benzaldehyde azine (4)**: Pentathiophenyl benzaldehyde (0.532 g, 822 µmol) and hydrazine hydrate (0.016 g, 328 µmol) were refluxed in CH_3CN (12 mL) for 16 h. The light yellow precipitate was collected by filtration, washed with cold CH_3CN and dried under high vacuum to yield **4** (0.135 g, 105 µmol, 32 %) as a light yellow solid. R_f (silica, toluene/hexane 1:2): 0.31; m.p. 201 °C; ^1H NMR ($CDCl_3$): $\delta = 8.15$ (*s*, 2 H), 6.85–7.2 (*m*, 50 H); ^{13}C NMR ($CDCl_3$): $\delta = 159.25$, 149.24, 147.93, 144.59, 142.13, 137.60, 137.52, 136.92, 129.09, 128.94, 128.87, 128.61, 128.37, 128.10, 126.37, 126.21, 126.13; FAB-MS: *m*/*z* (%): 1293 (22), 1292 (44), 1291 (75), 1290 (79), 1289 (100) $[M]^+$, 1202 (34), 1201 (64), 1200 (71), 1199 (93), 1181 (34), 1180 (35), 1179 (47); elemental analysis calcd (%) for $C_{74}H_{52}N_2S_{10}$: C 68.91, H 4.06; found: C 68.83, H 4.15.

1-(2′,2′-Dibromoethenyl)-2,3,4,5,6-pentathiophenyl benzene (5): Pentathiophenyl benzaldehyde (0.839 g, 1.30 mmol) was heated under reflux in dry CH_3CN (30 mL). A solution of carbon tetrabromide (1.29 g, 3.89 mmol) and triphenyl phosphine (2.04 g, 7.78 mmol) in dry CH_3CN (10 mL) was added over a period of 5 min. After heating under reflux for 20 min, filtration and evaporation of the solvent gave a yellow solid as a crude product. Column chromatography (silica, toluene/hexane 1:1) yielded **5** (0.72 g, 0.897 mmol, 69 %) as a yellow dye. IR (film): $\tilde{\nu} = 3071$ (w), 1579 (m), 1476 (s), 1438 (s), 1323 (w), 1286 (w), 1080 (m), 1023 (m), 999 (w), 837 (m), 736 (s), 698 (s), 686 (s), 646 (m), 481 cm^{-1} (m); ^1H NMR ($CDCl_3$): $\delta = 7.15-7.52$ (m, 25 H), 6.70 (s, 1 H); ^{13}C NMR ($CDCl_3$): $\delta =$ 93.98, 125.92, 126.50, 127.71, 127.86, 128.01, 128.78, 128.92, 129.15, 136.13, 136.76, 137.46, 143.70, 145.72, 146.28, 147.16; FAB-MS: *m*/*z* (%): 805 (11), 804 (28), 803 (21), 802 (40), 801 (14), 800 (18), $[M]^+$, 725 (10), 724 (28), 723 (43), 722 (100), 721 (36), 720 (77) $[M - Br]^+$.

1-Ethinyl-2,3,4,5,6-pentathiophenyl benzene (6): Compound **5** (0.10 g, 0.125 mmol) was dissolved in absolute THF (10 mL) and cooled to −78 °C. *n*-Butyllithium (1.6 M in hexane, 0.2 mL, 0.32 mmol) was added dropwise. The mixture was stirred for 1 h under −70 °C, allowed to warm to room temperature and then stirred at this temperature for 1 h at. A saturated NaCl solution (40 mL) was added, and the mixture extracted with toluene (3 × 10 mL). The combined organic layers were dried over $MgSO_4$. Column chromatography (silica, toluene/hexane 1:2) yielded **6** (0.052 g, 0.08 mmol, 65 %) as a yellow dye. IR (film): $\tilde{\nu} = 3285$ (w), 2956 (w), 1582 (m), 1477 (s), 1437 (m), 1082 (m), 1024 (m), 735 (s), 687 cm^{-1} (s); ^1H NMR ($CDCl_3$): $\delta = 3.58$ (s, 1 H), 6.9–7.4 (m, 25 H); ^{13}C NMR ($CDCl_3$): $\delta = 80.37$, 88.35, 125.54, 125.76, 125.88, 126.72, 127.69, 128.15, 128.77, 128.96, 129.88, 137.34, 138.02, 138.41, 140.21, 145.14, 149.22, 153.81; FAB-MS: *m*/*z* (%): 645 (26), 644 (49), 643 (99), $[M]^+$, 642 (89), 641 (100), 565 (15), 457 (13), 456 (32), 454 (16), 424 (23), 422 (19), 379 (17), 378 (38), 377 (22), 348 (35), 347 (52), 346 (89), 327 (16), 316 (32), 315 (17), 314 (40); elemental analysis calcd (%) for $C_{38}H_{26}S_5$: C 70.99, H 4.08; found: C 70.88, H 4.22.

1,4-Di(pentathiophenyl)phenyl-buta-1,3-diyne (7): Compound **6** (0.115 g, 0.178 mmol) and copper(II) acetate monohydrate (0.039 g, 0.197 mmol, 1.1 equiv) were heated to 55 °C in pyridine (5 mL). After 1 h the reaction mixture was poured onto ice water and extracted with toluene. The organic layer was washed successively with 25 % AcOH, 1M $NaHCO_3$ and saturated NaCl, and dried over $MgSO_4$. Evaporation of the solvent yielded a crude product (0.139 g). Crystallisation from $CHCl_3$/hexane gave **7** (65 %) as orange crystals. M.p. 186 °C; IR (KBr): $\tilde{\nu} = 1581$ (m), 1477 (s), 1438 (m), 1311 (w), 1079 (m), 1023 (m), 999 (w), 741 (m), 732 (s), 697 (m), 686 cm^{-1} (m); ^1H NMR ($CDCl_3$): $\delta = 6.8-7.3$ (m, 50H); ^{13}C NMR ($CDCl_3$): $\delta =$ 83.01, 86.62, 126.23, 126.31, 126.52, 128.18, 128.40, 129.01, 129.28, 133.78, 136.48, 137.44, 137.80, 146.51, 146.59, 148.43; FAB-MS: m/z (%): 1287 (20), 1286 (41), 1285 (68), 1284 (88), 1283 (100), $[M]^+$, 1282 (66), 1281 (29), 1207 (29), 1206 (30), 1205 (28), 643 (50), 642 (44), 641 (83); elemental analysis calcd (%) for $C_{76}H_{50}S_{10}$: C 71.10, H 3.93; found: C 71.30, H 4.07.

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[21] Single-crystal data for **4**: $C_{74}H_{52}N_2S_{10}$, $M = 1289.78\ g\,mol^{-1}$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.614(2)$, $b = 10.578(2)$, $c = 17.080(3)$ Å, $V = 1570.8(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.363\ g\,cm^{-3}$, $F(000) = 670$, $T = 200$ K, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.397\ mm^{-1}$, $6.08 < 2\theta < 58.54°$, 9040 reflections of which 7615 unique and 7613 observed, 467 parameters refined, GOF(on F^2) = 1.038, $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0495$, $wR2 = 0.1348$ for $I > 2\sigma$ and $R1 = 0.0742$, $wR2 = 0.1534$ for all data. Crystals of **4** were measured on an Enraf–Nonius four-circle diffractometer at 200 K. The data collection was best for a crystal of 0.9 × 0.4 × 0.2 mm and an absorption correction by analytical integration. The structure was solved with direct methods and refined by full-matrix least-squares on F^2 with the SHELX-97 package. All heavy atoms were refined anisotropically. 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-147302. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk)..

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