Redox properties of polythiaarene derivatives. A novel class of electron acceptors

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A series of polythiaarene derivatives has been synthesised and their redox properties studied. The charge stabilizing effect of the aryl sulfide groups that surround the central aromatic core promotes nucleophilic substitution and markedly facilitates radical anion formation, leading to remarkably mild reduction potentials. Polythiaarene units may thus serve as electron accepting sites for the development of electron rich components for molecular electronic devices.

Introduction

There is currently a great deal of interest in the design of molecular electronic devices[1,2] and of novel organic redox substances. Sulfur containing compounds have been extensively studied as components of conducting organic materials, *e.g.* charge transfer salts.[3,4] In view of their relatively low oxidation potential, the sulfur species usually form the cationic part of the conducting material.[3] On the other hand, sulfur containing anions have found extensive use as versatile reagents in organic synthesis.

The ability of sulfur to stabilize negative charge suggested that polythia substances may represent a potential class of electron accepting units. Such groups could therefore be of interest as components of electron rich molecular electronic devices and of compounds of expanded atom type, like the 'cryptatium' entities.[5] To these ends, we turned our attention to perthiaarene compounds[6–8] which appeared to combine the electron delocalizing properties of the aromatic system with the negative charge stabilizing effect of the sulfur centres. All these molecules contain a central aromatic core surrounded by peripheral aromatic sulfide groups. A number of X-ray crystal structures have been reported,[8] revealing that these groups are often arranged in an ordered pattern. The unusual structures as well as the remarkably facile syntheses of these compounds in high yield prompted us to investigate their electronic properties further.

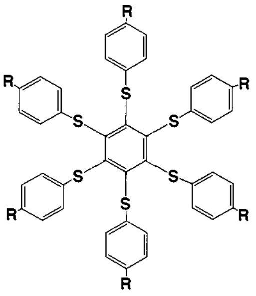
Results and discussion

Synthesis of model compounds

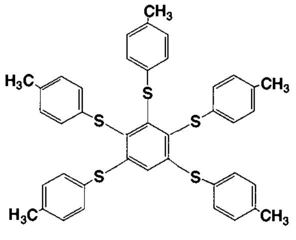
Using procedures based on those reported in the literature,[9] a range of compounds **1**–**6** were synthesised by varying the type and number of sulfide linkages to a central benzene core. Analogous compounds containing an ether **7**[10] or a seleno **8**[9] group were also obtained for the sake of comparison.

In a typical reaction, the treatment at room temperature of hexachlorobenzene (0.05 M) with 12 equiv. of sodium benzenethiolate (NaSPh) in 1,3-dimethylimidazolidin-2-one (DMI) produced an instantaneous reaction which went to completion in under 10 min, forming yellow **3** in high yield.

An analogous reaction using sodium benzenolate (PhONa) instead of PhSNa to form colourless **7** requires extended reaction times and high temperatures.[10] The rapid reaction with the thiolate implies that the sulfur groups as well as the chlorine atoms activate the central benzene towards nucleophilic substitution. In support of this, when compound **3** in DMI (0.03 M) was treated with 12 equiv. of sodium 4-methylbenzene-1-thiolate (MeC_6H_4SNa), mass spectrometry studies revealed that mixed species were obtained by displacement of a sulfide substituent already on the ring, as shown in reaction (1).



1 R = CH_3 **3** R = H
2 R = Br **4** R = OMe



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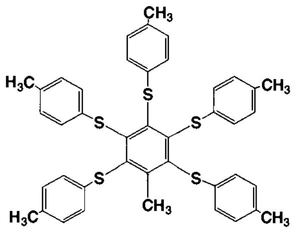
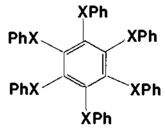
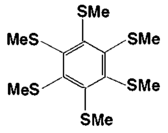


6



7 X = O
8 X = Se



9

$$\underset{\mathbf{3}}{C_6(SPh)_6} \xrightarrow[\text{DMI, 25 °C}]{12\ NaSC_6H_4Me} C_6(SC_6H_4Me)_x(SPh)_{6-x} \qquad (1)$$

After 24 h at room temperature, the major product was the tetrasubstituted species $C_6(SC_6H_4Me)_4(SPh)_2$. When the reaction was repeated under the same conditions at 120 °C, $C_6(C_6H_4Me)_4(SPh)_2$ was observed as the major product after only 10 min.

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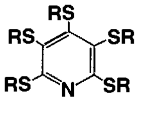
Table 1 Electrochemical data for compounds **1**–**9**[a]

	E/V		E/V
1	−1.62	**6**	−1.80
2	−1.42	**7**	*b*
3	−1.56	**8**	−1.65[c]
4	−1.69	**9**	−2.00[d]
5	−1.95		

[a] $E = \frac{1}{2}(E_{pa} - E_{pc})$ in V *vs.* SCE. The confidence limit is ±10 mV; for conditions see Experimental section. [b] No redox process observed up to −2.25 V. [c] Quasi-reversible redox process. [d] Irreversible reduction wave.

The polysulfur substances **10**–**12** with central aromatic cores other than benzene, were also synthesised following methodologies reported for related compounds.[7]



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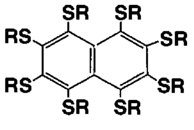

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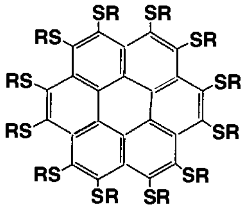
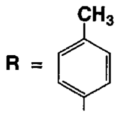


12



Electrochemical studies

The electrochemical properties of compounds **1**–**9** were investigated by cyclic voltammetry in anhydrous dimethylformamide (DMF). All the compounds containing substituted peripheral thiaarene groups gave a reversible one-electron redox wave ($I_{pa} = I_{pc}$, ΔE_p = 60–75 mV). The most likely explanation for this redox process is a one-electron reduction of the central benzene core. However, the redox potential of −1.62 V (*vs.* SCE) for **1** is at least 1 V more positive than that for the reduction of benzene itself.[11] This indicates that the peripheral sulfide groups are able to stabilise the radical anion $Ar^{\bullet -}$ by delocalising the negative charge. The data for compounds **1**–**9** in DMF are listed in Table 1 and displayed graphically in Fig. 1.

An inspection of these values reveals that the radical anion $Ar^{\bullet -}$ is further stabilised when the six OMe groups in **4** are replaced by substituents presenting increasing values of the Hammett σ_p parameter, CH_3 in **1**, H in **3** and Br in **2**.[12] The data for these four compounds show a linear Hammett relationship[12] with the σ_p parameters as shown in Fig. 2. The graph illustrates how the electron withdrawing effect of the six *para* substituents may affect both the properties of the sulfide groups and the central benzene unit.

One would expect compound **5** with only five SC_6H_4Me groups to be more difficult to reduce than **1**, which is indeed the case. However, the difference in redox potentials between **1** and **5** is surprisingly large (ΔE = 0.33 V). In addition, replacement of the proton on the central ring of **5** by a methyl group (**6**) results in a positive shift of + 0.15 V, which is the opposite to what is observed for compounds **1** and **3**.

These observations indicate that, in addition to electronic effects, steric factors may also contribute to the stabilisation of the radical anions formed. The X-ray crystal structure study of **3** reveals that the orientation of the six SPh groups alternates above and below the plane of the central benzene ring.[6,8] Variable temperature NMR studies[13] on hexa-substituted derivatives of this type suggest that this conformation is the only one found in solution, since rotation of the groups is strongly hindered. In this conformation, the negative charge must be able to delocalise effectively throughout the π system as well as on the S centres. For **5**, the weaker communication between the central and peripheral π systems implies that the extra freedom of orientation given to the five SC_6H_4Me groups reduces orbital interaction. When the CH_3 group is introduced on the central benzene ring as in **6**, steric hindrance would be expected to increase, thus making reduction easier, even though this group is more electron donating than the hydrogen in **5**. The linear Hammett relationship observed for compounds **1**–**4** holds presumably because the steric constraints are virtually identical for these persulfide derivatives.

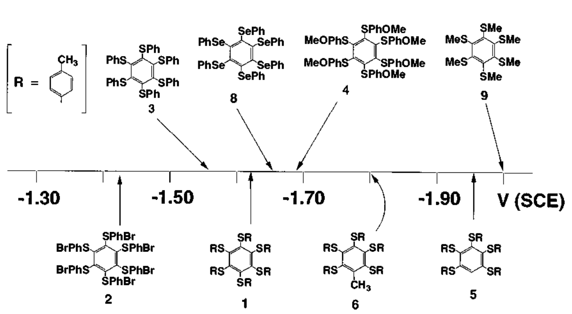


Fig. 1 Graphical representation of electrochemical data given in Table 1

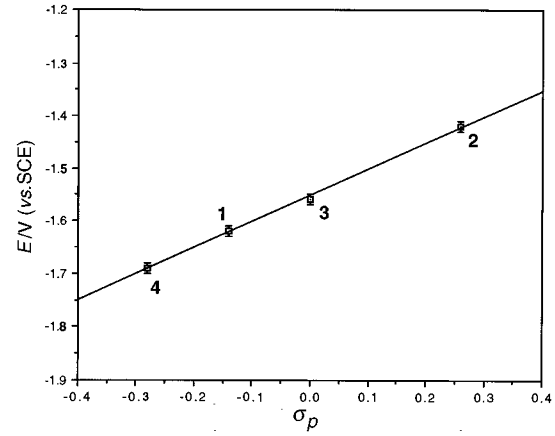


Fig. 2 Hammett correlation between the redox potentials (E) for compounds **1**–**4** and their corresponding substituent σ_p values

As expected, compound **9** with *S*-alkyl substituents is the most difficult to reduce and also yields an irreversible reduction wave, probably due to reduction cleavage of the S–C bond. Hexachlorobenzene gives several irreversible waves starting at *ca.* − 1.69 V. The oxygen analogue of **3**, **7**, shows no reduction wave up to − 2.25 V (*vs.* SCE) but the *quasi*-reversible redox wave at − 1.65 V for the corresponding selenium analogue **8** is very similar to that of **3**. Therefore oxygen, although more electronegative than both sulfur and selenium, is considerably less effective at delocalising the negative charge.

These observations appear to be in keeping with *ab initio* molecular orbital studies of α-sulfur stabilized carbanions[14] and the increased acidity of dimethyl thioether with respect to dimethyl ether.[15] Both polarization of the electron distribution and interaction with the antibonding σ*(C–S) orbital contribute to stabilisation of the negative charge. Furthermore the latter stereoelectronic effect is markedly conformation dependent.[14] Our electrochemical results suggest that the degree of radical anion stabilisation for the thiaarene derivatives is indeed affected by the rotameric orientation of the substituents.

All the compounds are yellow (**1**, λ_{max} = 326 nm, THF) except **5**, **7** and **9** which are white (**5**, λ_{max} = 290 nm, THF) and also the hardest to reduce. The electrochemical data would indicate that

Table 2 Electrochemical data[a] for compounds **10**–**12** and underivatised parent compounds

	E^1/V	E^2/V		E^1/V	E^2/V
10	−1.72[b]	—	Pyridine	−2.51[b,c]	—
11	−1.23	−1.73	Naphthalene	−2.53[c]	—
12	−1.02	−1.44	Coronene	−2.04[c]	−2.57[c]

[a] $E = \frac{1}{2}(E_{pa} - E_{pc})$ in V *vs.* SCE. The confidence limit is ±10 mV; for conditions see Experimental section. [b] Reversible two electron reduction. [c] Data from ref. 11.

the reduction of the HOMO–LUMO gap is primarily due to LUMO stabilisation.

Electrochemical studies in DMF carried out on the compounds that contain aromatic cores other than benzene (**10**–**12**) reveal that for **11** and **12**, two reversible one electron reduction steps are observed. The data for these compounds are listed in Table 2 along with the literature values for the underivatised parent compounds.[11] Once again, it can be seen that the reduced forms are strongly stabilised by the aromatic sulfur groups, presumably due to their effective delocalisation of the negative charge.

As found with the benzene derivatives, the first one-electron reductions for **11** and **12** are facilitated by over 1 V compared with the parent compounds. It is also interesting to compare these values with those for C_{60}, an efficient electron acceptor which can undergo six reversible one electron reductions.[16] The first two reductions for C_{60} occur at − 0.26 and − 0.72 V *vs.* SCE (in DMF), at still less negative potentials than even **12**.

Chemical reduction of 1

The addition of a slight excess of metallic sodium to a yellow solution of **1** in dry THF (0.01 M) under anaerobic conditions produced a burgundy red solution. The same reaction was then repeated in the presence of benzo-15-crown-5. The reduction product may be the corresponding radical anion or a doubly reduced species.

Dark red microcrystals of **13** were isolated by slow diffusion of hexane into the THF solution. Reduction in the presence of the crown ether was significantly faster than in its absence (15 min compared with 4 h) due to its cation binding power. Furthermore the product was also less soluble, probably caused by the formation of solvent separated ion pairs.

The treatment of the solution with dry, oxygen containing THF, resulted in the recovery of compound **1** (> 90% pure) as judged by ^{1}H NMR spectroscopy, which confirms the reversibility of the system. Further studies are required in order to characterize the nature of the reduced species generated.

Conclusions

Through synthetic, electrochemical and spectroscopic studies, it has been demonstrated that peripheral aromatic sulfide groups situated around a central aromatic core are able to distribute electron density effectively throughout the molecular system. These studies have also shown that the *para* substituent on the peripheral thiaarene groups affects the stability of the radical anion and that other factors of steric and orientational nature contribute to the overall stability of each anion. The present results indicate that such polythiaarene units may indeed serve as electron accepting and delocalizing sites for the development of electron rich components for molecular electronic devices.

Experimental

An inert atmosphere glove box and Schlenk-line techniques were used for the isolation of air sensitive compounds. Tetrahydrofuran and hexane were predried over 4 Å molecular sieves and were distilled from purple sodium–benzophenone under N_2. 1,3-Dimethylimidazolidin-2-one (DMI) was dried over 4 Å molecular sieves and degassed with N_2 prior to use. Sodium 4-methylbenzene-1-thiolate ($NaSC_6H_4Me$) was prepared from the corresponding thiol and sodium ethanolate in ethanol. All other reagents were obtained from commercial sources and were used as received. Melting points were determined in open capillary tubes and are uncorrected. IR samples were prepared as KBr pressings. UV–VIS spectra were recorded in 0.5 cm quartz cells. Elemental analyses were performed by the Centre de Microanalyses of the CNRS and mass spectra (EI, 70 e V) were performed within the Department of Chemistry at the Université Louis Pasteur (ULP), Strasbourg. ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded at ambient temperatures on a Bruker spectrometer at 200 or 250 and 50 or 62.9 MHz respectively, as well as on a Varian spectrometer at 600 and 150.9 MHz at the ULP or at the Centre d'Instrumentation, Université Libre de Bruxelles. Chemical shifts (δ) for ^{1}H NMR spectra are reported relative to TMS in the deuteriated solvent and for ^{13}C NMR spectra relative to carbons in the deuteriated solvent. EPR measurements were performed on a Bruker instrument at room temp. in the Institut Charles Sadron, Strasbourg.

Compounds **1**,[6] **3**,[6] **7**,[10] **8**[9], **9**[17] and dodecachlorocoronene[7] were prepared by literature methods.

Hexakis(4-methylphenylthio)benzene 1

DMI (100 ml) was added to hexachlorobenzene (1.425 g, 5.00 mmol) and $NaSC_6H_4Me$ (6.578 g, 45.00 mmol) under an atmosphere of argon. Immediately the colour turned dark orange and heat was evolved. A fine yellow precipitate had formed after stirring for 20 h at room temperature and a TLC analysis of the supernatant (silica gel, hexane–ethyl acetate 10:1) showed that no starting material remained. Toluene and aqueous 10% Na_2CO_3 were added to the mixture and the organic layer extracted twice with aqueous 10% Na_2CO_3 and once with aqueous 10% HCl. Drying ($MgSO_4$), removal of the solvent *in vacuo* and crystallization from hot toluene–ethanol afforded 3.68 g (91%) of the product as yellow microcrystals, mp 197–198 °C (lit.,[6] 197–200 °C); δ_H($CDCl_3$) 6.92 (12 H, d, ArH), 6.81 (12 H, d, ArH) and 2.26 (18 H, s, CH_3); λ_{max}(THF)/nm 247 (log ε 4.71), 254 (4.68), 291 (4.32) and 326 (4.29).

Hexakis(*p*-bromophenylthio)benzene 2

p-Bromobenzenethiol (10.0 g, 52.9 mmol) was placed in a dry flask. Dry DMI (30.0 ml) was injected under an argon atmosphere and the flask was cooled in an ice-bath. Sodium hydride (1.52 g, 63.5 mmol) was added in small portions over 30 min whilst stirring vigorously for *ca.* 15 min. Some foam is produced and an exothermic reaction resulted. Hexachlorobenzene was added in small amounts (1.255 g, 4.41 mmol). The mixture was allowed to stir at 0 °C for 2 h and then at room temperature for 14 h. The reaction first turned orange then deep red. Diethyl ether was poured into the flask (200 ml) followed by an aqueous solution of 2 M NaOH (100 ml). The aqueous phase was discarded and the organic phase was washed further with 2 M NaOH (3 × 50 ml). After drying the ethereal phase over Na_2SO_4–$MgSO_4$, filtration and evaporation of the solvent, a solid was recovered. Flash chromatography was carried out with toluene–hexane (3:7). Compound **2** was obtained as a bright yellow–orange solid (2.50 g, 48% yield), giving yellow crystals after recrystallization from toluene–hexane (3:7), mp 149.0–149.5 °C; δ_H($CDCl_3$) 7.28 [apparent d (AA′BB′), 12 H, ArH] and 6.75 [apparent d (AA′BB′), 12 H, ArH]; δ_C($CDCl_3$) 147.92, 136.01, 132.25, 130.00 and 120.86; *m/z* (FAB) 1199.2 (M^+, 100%) (Found: C, 42.41; H, 1.92. Calc. for $C_{42}H_{24}S_6Br_6$: C, 42.02; H, 2.02%).

Hexakis(*p*-methoxyphenylthio)benzene 4

Sodium hydride (0.60 g, 25 mmol) was added to DMI (20 ml) under an argon atmosphere. To this was carefully added *p*-methoxybenzenethiol (1.68 g, 12.0 mmol) and then hexachlorobenzene (0.276 g, 0.97 mmol). The mixture was allowed to stir at room temperature for 48 h before toluene and aqueous 10% Na_2CO_3 were added and the organic layer twice extracted with aqueous 10% Na_2CO_3. Drying (Na_2SO_4), removal of solvent *in vacuo* and crystallisation from hot benzene–ethanol (1:3) afforded the product **4** as bright yellow prisms (0.62 g, 70.5%), mp 158–159 °C; δ_H($CDCl_3$) 6.90 [apparent d (AA′BB′), 12 H, ArH], 6.67 [apparent d (AA′BB′), 12 H, ArH] and 3.76 (s, 18 H, OCH_3); δ_C($CDCl_3$) 158.42, 147.72, 130.88, 128.62, 114.46 and 55.23; *m/z* (EI) 907 (M^+, 94%) (Found: C, 62.93; H, 4.50. Calc. for $C_{48}H_{42}O_6S_6$: C, 63.55; H, 4.67%).

Pentakis(*p*-methylphenylthio)benzene 5

DMI (60 ml) was added to pentafluorobenzene (1.4 g, 8.33 mmol) and $NaSC_6H_4Me$ (10.3 g, 0.071 mol) under an atmosphere of argon. The mixture was stirred at room temperature for 48 h before toluene and aqueous 10% Na_2CO_3 were added and the organic layer was twice extracted with aqueous 10% Na_2CO_3 and once with 10% aqueous HCl. Drying ($MgSO_4$), removal of solvent *in vacuo* and crystallisation from hot toluene–ethanol afforded the product **5** as pale yellow fine needles (3.59 g, 63%), mp 149 °C; δ_H($CDCl_3$) 7.10 (d, 4 H, ArH), 7.05–6.90 (m, 16 H, ArH), 6.21 (s, 1 H, ArH), 2.38 (s, 6 H, CH_3), 2.29 (s, 6 H, CH_3) and 2.24 (s, 3 H, CH_3); *m/z* (FAB) 688 (M^+); λ_{max}(THF)/nm 238 (log ε 4.65), 264 (4.64) and 290 (4.54) (Found: C, 71.47; H, 5.32. Calc. for $C_{41}H_{33}S_5$: C, 71.47; H, 5.27%).

Pentakis(*p*-methylphenylthio)methylbenzene 6

DMI (30 ml) was added to pentabromotoluene (0.50 g, 1.027 mmol) and $NaSC_6H_4Me$ (1.502 g, 10.03 mmol). The colour turned orange and the mixture was stirred at room temperature for 48 h before toluene and aqueous 10% Na_2CO_3 were added and the organic layer twice extracted with aqueous 10% Na_2CO_3 and once with 10% aqueous HCl. Drying ($MgSO_4$), removal of solvent *in vacuo* and crystallisation from hot toluene–ethanol afforded the product **6** as a pale yellow precipitate (0.446 g, 62%), mp 133–135 °C; δ_H($CDCl_3$) 7.00–6.76 (m, 20 H, ArH), 2.43 (s, 3 H, CH_3) and 2.28 (s, 15 H, CH_3); δ_C($CDCl_3$) 149.6, 148.1, 142.6, 135.6, 135.4, 135.0, 134.9, 133.6, 129.7, 129.6, 129.5, 128.3, 127.5, 95.6, 92.7, 23.7 and 21.0; *m/z* (FAB) 702 (M^+, 100%) (Found: C, 70.44; H, 5.47. Calc. for $C_{42}H_{35}S_5$: C, 71.75; H, 5.45%).

Pentakis(*p*-methylphenylthio)pyridine 10

Pentafluoropyridine (0.300 g, 1.77 mmol) and toluene-*p*-thiol (2.71 g, 19.3 mmol) were added to a two-neck flask under argon. DMI (3.5 ml) was injected *via* a syringe and the flask was cooled in an ice-bath. Sodium hydride (350 mg, 14.6 mmol) was added in small portions under an argon stream while stirring vigorously. The bath was removed and stirring was continued for 15 days at 20 °C. Toluene and aqueous 10% Na_2CO_3 were added and the organic layer extracted twice with aqueous 10% Na_2CO_3. Drying (Na_2SO_4), removal of solvent *in vacuo* and crystallisation from hot benzene–ethanol afforded **10** as pale yellow crystals (0.800 g, 65%), mp 147–149 °C; δ_H($CDCl_3$) 7.10–6.80 (m, 20 H, ArH), 2.33 (s, 6 H, CH_3), 2.29 (s, 6 H, CH_3) and 2.25 (s, 3 H, CH_3); δ_C($CDCl_3$) 167.70, 158.18, 137.91, 136.68, 135.87, 134.73, 132.50, 132.22, 130.04, 129.70, 129.65, 129.29, 127.69, 126.82, 125.67, 21.44, 21.04 and 21.00; *m/z* (FAB) 689.0 (M^+, 100%) (Found: C, 69.55; H, 4.82. Calc. for $C_{40}H_{35}S_5N$: C, 69.63; H, 5.11%).

Octakis(*p*-methylphenylthio)naphthalene 11

Toluene-*p*-thiol (730 mg, 5.88 mmol) was added to a two-neck flask under argon. DMI (2.5 ml) was injected *via* a syringe and the flask was cooled in an ice-bath. Sodium hydride (1.69 mg, 7.06 mmol) was added under an argon stream followed by octafluoronaphthalene (100 mg, 0.368 mmol). The bath was removed and stirring was continued for 3 days at 20 °C. A deep red wine solution resulted. Toluene and a saturated solution of Na_2CO_3 were added. After discarding the aqueous phase, the organic layer was washed twice with the Na_2CO_3 solution. After drying the organic phase over Na_2SO_4–$MgSO_4$, evaporation and filtration, a red powder resulted which was triturated with *n*-hexane to afford pure **11** (286 mg, 70%) yield). Recrystallization by slow evaporation of a solution in chloroform gave red–orange prisms, mp 182 °C; δ_H($CDCl_3$) 6.95 [apparent d (AA′BB′), 8 H, ArH], 6.84 [apparent d (AA′BB′), 8 H, ArH], 6.80 [apparent d (AA′BB′), 8 H, ArH], 6.50 [apparent d (AA′BB′), 8 H, ArH], 2.32 (s, 12 H, CH_3) and 2.23 (s, 12 H, CH_3); δ_C($CDCl_3$) 144.10, 141.09, 139.66, 136.33, 136.10, 135.78, 134.63, 130.55, 129.84, 129.75, 128.32, 21.69 and 21.49; *m/z* (SIMS) 1104.1 (M^+, 30%) (Found: C, 71.94; H, 4.90. Calc. for $C_{66}H_{56}S_8$: C, 71.70; H, 5.11%).

Dodecakis(*p*-methylphenylthio)coronene 12

Toluene-*p*-thiol (209 mg, 19.3 mmol) was introduced into a two-necked flask under argon. DMI (4.0 ml) was injected *via* a syringe and the flask was cooled in an ice-bath. Sodium hydride (44.0 mg, 1.85 mmol) was added under an argon stream whilst stirring vigorously. Argon was bubbled into the solution for *ca.* 25 min before adding dodecachlorocoronene[7] (50.0 mg, 0.070 mmol). The bath was removed and stirring was continued for 4 days at 20 °C. A deep red wine solution and a red precipitate resulted. Toluene (*ca.* 150 ml) and a saturated solution of Na_2CO_3 (*ca.* 150 ml) were added. After discarding the aqueous phase, the organic layer was washed twice with the Na_2CO_3 solution (2 × 100 ml). The organic phases were combined and dried over Na_2SO_4–$MgSO_4$. After filtration and evaporation of the solvents, a red solid resulted, which was triturated under vigorous stirring with *n*-hexane–toluene (4:1) (10 ml) for 3 h at 20 °C. After filtration and drying the sample, a pure red powder of **12** resulted (87.6 mg, 71% yield), δ_H($CDCl_3$) 6.74 [apparent d (AA′BB′), 24 H, ArH], 6.46 [apparent d (AA′BB′), 24 H, ArH] and 2.21 (s, 36 H, CH_3); δ_C($CDCl_3$) 136.43, 134.74, 129.15, 127.02 and 123.90; *m/z* (FAB) 1766.2 (M^+, 100%).

Chemical reduction of 1

A specially made double Schlenk flask with internal frit and two Teflon valves was charged in a glove box with hexakis(*p*-methylphenylthio)benzene **1** (0.200 g, 0.247 mmol) and benzo-15-crown-5 (70 mg, 0.261 mmol). A piece of sodium (*ca.* 20 mg, 0.87 mmol) was placed in the side arm of the flask. Anhydrous, degassed THF (25 ml) was condensed on top of the starting materials and the piece of sodium was dropped into the solution after warming to room temperature. The hexakis(*p*-methylphenylthio)benzene started to dissolve immediately and after 15 min the solution had turned deep red. The solution was filtered into the other compartment of the reaction flask after another 1.5 h and hexane condensed into the other part of the apparatus. Over a period of 2 weeks the hexane was allowed to condense slowly into the THF solution to induce the formation of dark red crystals which were isolated by filtration (84 mg, 31%).

Quenching of the solution with dry, oxygen-containing THF resulted in an instant colour change to yellow. Filtration and removal of the solvent *in vacuo* gave a yellow compound which was identified as the starting material **1** (> 90% pure) by ^1H NMR spectroscopy.

Electrochemistry

Cyclic voltammograms were carried out at a scan rate of 200 mV s^{-1} in anhydrous DMF (5–10 ml) containing tetrabutylammonium hexafluorophosphate Bu_4NPF_6 (0.1 M), 1 mmol ferrocene and 1 mmol of substrate at 293 K. The following electrode system was used; Pt working electrode, Pt counter electrode and a Ag wire reference electrode. The data was initially internally referenced to ferrocene which was then converted to SCE by determining the value for ferrocene in DMF *vs.* SCE (0.50 V).

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