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P-Doping of conjugated polymers based on an extended *m*-phenylenediamine motif produces a disperse population of ferromagnetically coupled spin clusters. To increase the average size of these spin clusters variations have been explored both in the structure of the polymer and in the method of doping. Introduction of ferromagnetic spin coupling '2,7 through the naphthalene nucleus' rather than '1,3 through the benzene nucleus' has been investigated as have variations in the aryl core/alkyl side chain ratio but the biggest improvements were achieved by adopting a doping procedure in which thin films of the polymer were exposed to gaseous antimony pentachloride. A thin film (*ca.* 1 μm thick) of the polymer obtained by the Pd⁰-mediated coupling of 1,3-dibromo-5-tetradecylbenzene with tris[2-butoxy-4-(dihydroxyboranyl)phenyl]amine was exposed to gaseous antimony pentachloride. Under these conditions 40–60% of the potentially dopable sites were oxidised to the ammonium ion (N⁺) level. A Brillouin function fit to the field dependence of the magnetisation of this doped polymer at 2 K corresponds to behaviour equivalent to a nonet ($S = 4$) pi multiradical.

Both butadiene **1** and trimethylenemethane (TMM) **2** have four pi electrons (Fig. 1). At the simplest level of theory the difference between these isomeric systems is obvious. A classical or Kekulé formula can be written for butadiene but not for TMM. In whatever way its structure is formulated, there are always two unpaired pi electrons. Hückel theory confirms this simple picture. Non-Kekulé pi systems like that of TMM, possess a degenerate pair of singly occupied non-bonding molecular orbitals and Hund's rule dictates that they should have a triplet ground state.¹ Paul Dowd was the first experimentalist to demonstrate the triplet nature of the two simplest non-Kekulé polyenes, TMM and TME.² Since then the triplet nature of many other non-Kekulé polyenes,³ non-Kekulé quinodimethanes⁴ and non-Kekulé polynuclear aromatics⁵ has been established. Non-Kekulé pi systems have also been synthesised with three, four, five, *etc.*, singly occupied orbitals giving quartet,^{6,7} quintet,^{8,9} sextet¹⁰ or even higher ground states.^{11,12} Many of the higher spin systems have exploited carbene or nitrene building blocks^{9,11} and radical ion (N^{•+} and B^{•-}) analogues^{6,13,14} of the simple systems have also been explored. These often prove more stable and more tractable than their neutral counterparts. The logical extension of this line of research would be to create macromolecules with very large ferromagnetically coupled spin clusters: polymers that exhibit bulk ferromagnetism.^{15,16} Most attempts to make 'polymer magnets'^{17–20} have exploited a repeat unit which is some sort of derivative of triplet *m*-quinodimethane (Fig. 2) or of the isoelectronic dication of *m*-phenyldiamine. Hence, oxidation of a solution of the networked polymer **5b** (Scheme 1) with NOBF₄ gives a distribution of spin states with 'average' behaviour close to $S = \frac{5}{2}$.^{17,18} Unfortunately this oxidation step is not very clean. Only 15–20% of the potential spin-bearing sites were successfully oxidised to the ammonium ion (N⁺) level. The average size of the ferromagnetically coupled spin clusters would presumably have been greater if this 'doping'/oxidation step had been more efficient. It has been suggested that the fact that doping levels are so low could be due to electrostatic factors but electrochemical studies on related oligomers have ruled this out.²¹ This led to the hypothesis that the low doping levels were related to structural factors: the difficulty of accommodating large counterions into a relatively rigid polymer network. This paper explores the creation of related polymers designed to accommodate the counterions more readily. This was only partly successful but, by changing the doping method, doping levels have been increased and new higher-spin polymers obtained.

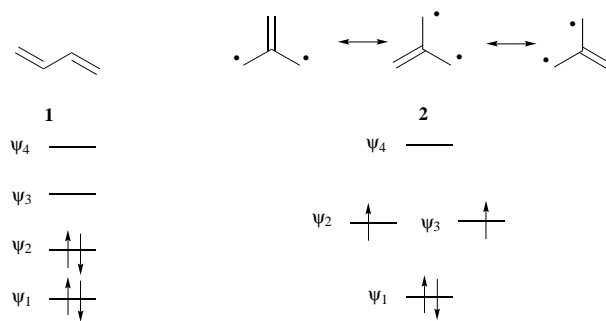
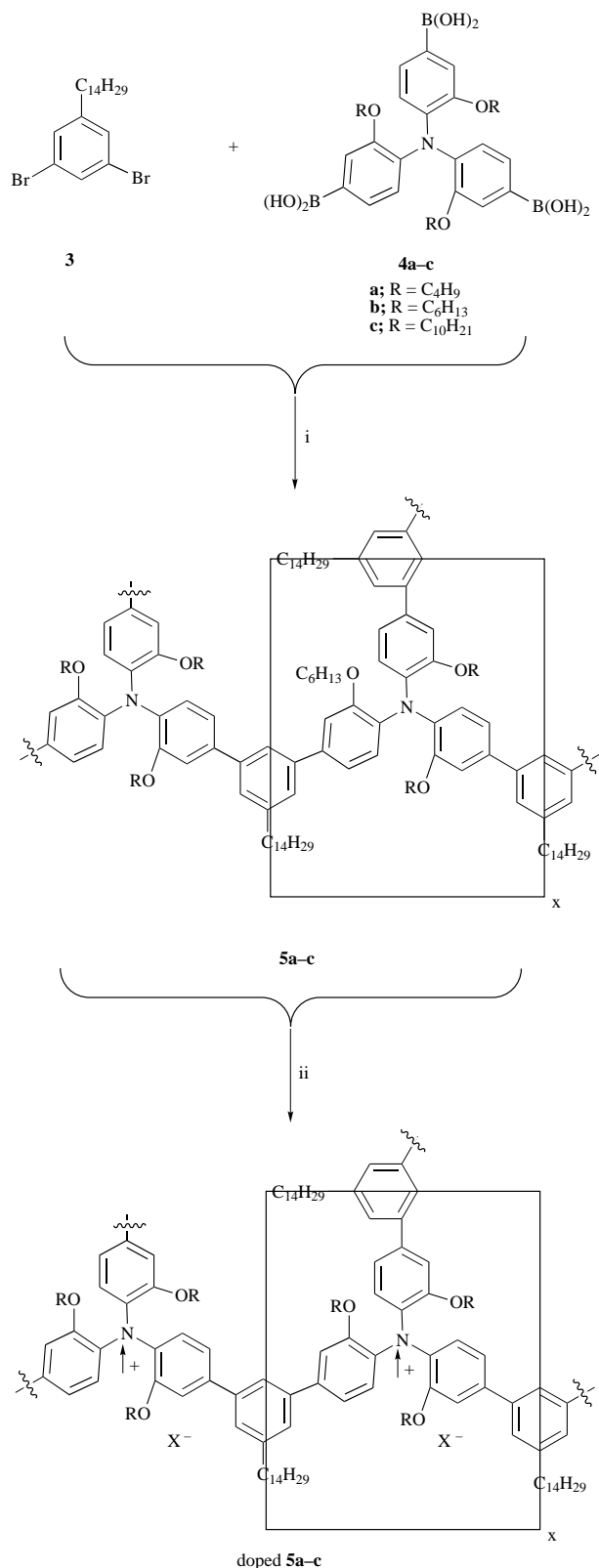


Fig. 1 A comparison of the Kekulé polyene butadiene **1** and its non-Kekulé isomer trimethylenemethane, TMM **2**

The synthesis of the polymers **5**, **11** and **12**

In all of the polymers described in this paper, the spin-bearing sites are triarylamminium (Ar₃N⁺) ions, branching/cross-linking is provided through the nitrogens and the ferromagnetic spin-coupling pathways exploited are 1,3 through the benzene nucleus⁴ and 2,7 through the naphthalene nucleus.²² These choices are based on the known high-spin nature of *m*-quinodimethane **6** and of 2,7-dimethylenenaphthalene **7**. As shown in Fig. 2, this is a consequence of the orthogonal coextensive nature of the singly occupied orbitals.^{1,18} The polymer **5b** was synthesised, as shown in Scheme 1 and this has been described previously.¹⁷ It involved a Suzuki coupling reaction²³ between the dibromide **3** and the trisboronic acid **4b**. This polymer may be thought of structurally as a rigid skeleton of jointed short polyphenylene rods with the space between the rods filled by disordered aliphatic alkyl and alkoxy side-chains. If we make the reasonable assumption that the cross-linking precludes significant swelling of the polymer, then, in the doped polymer, the counterions must displace alkyl chains and/or fill void volume. This may be difficult and the limiting factor in the doping may well be that of accommodating the counterions. To explore this suggestion further, we have synthesised a series of polymers with different lengths of side-chain, the polymers **5a** and **5c** (Scheme 1). These were made by coupling the boronic acids **4a** and **4c** with the dibromide **3**. In a complimentary approach we have tried to 'open out' the network by expanding the rigid aryl 'framework'. The polymers **11** and **12** (Scheme 2) were synthesised by coupling the boronic acid **4b** with the dibromides **8** and **9**. We have previously described the syntheses of the monomers **3**



Scheme 1 Synthesis of the polymers **5a-c**. (i) Pd(PPh₃)₄-toluene-aq. Na₂CO₃-reflux; (ii) NO⁺BF₄⁻-CH₂Cl₂ or SbCl₅ vapour. The polymer repeat unit is shown in the box. The extended structure is shown to illustrate the basic spin-coupling pathway.

and **4b**.¹⁷ The syntheses of the acids **4a** and **4c** were trivial variants on that of the acid **4b** and the syntheses of dibromides **8** and **9** were based on literature procedures for closely related compounds. All of the polymers were chloroform-soluble solids that were easily powdered except for polymer **5c**, which had a low molecular weight (Table 1) and which remained rather soft and jelly-like. All of the polymers used in the studies detailed below were purified and fractionated

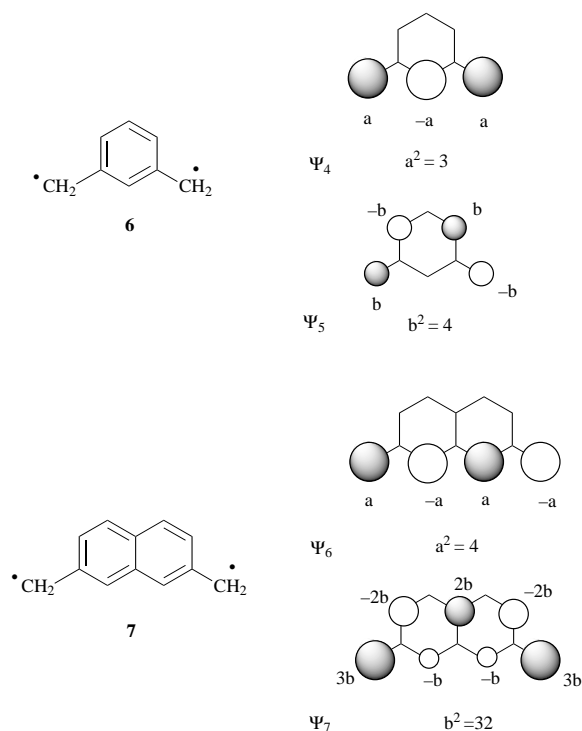
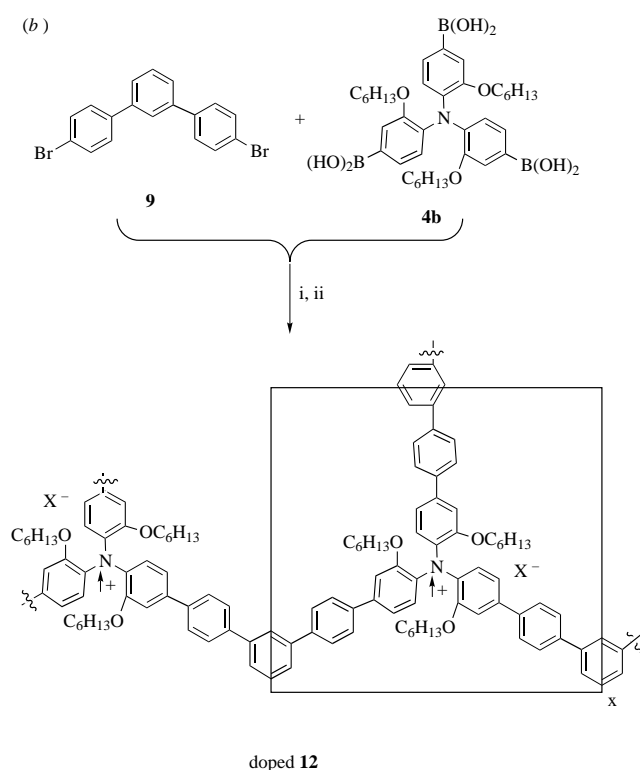
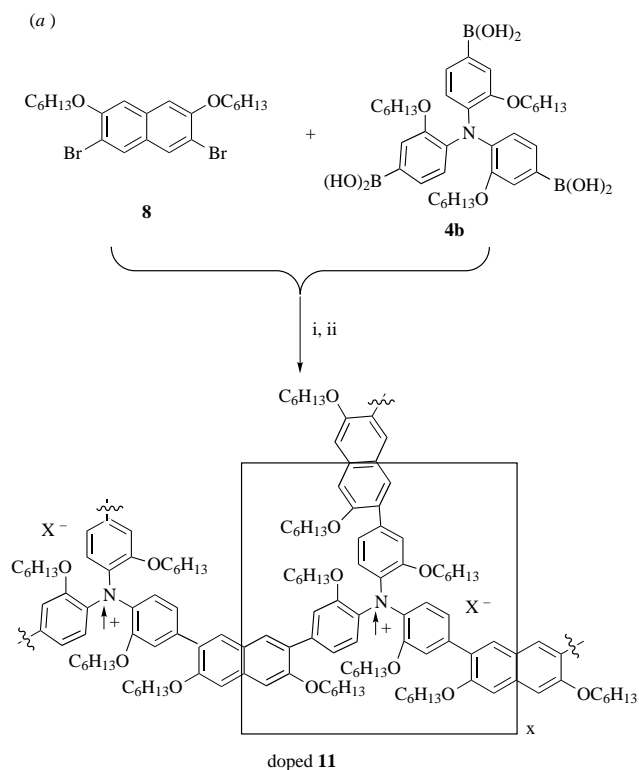


Fig. 2 Illustration of the pair of singly occupied Hückel molecular orbitals for the non-Kekulé quinodimethanes, *m*-quinodimethane **6** and 2,7-dimethylenenaphthalene **7**. For Hund's rule to apply and for a pi biradical to have a triplet ground state this pair of singly occupied orbitals have to be both orthogonal and coextensive (as in this case, sharing centres in common).¹ Extension of the conjugation of the pi systems by one or more additional *p*-phenylene or substitution of C by N^{•+} (as in some of these polymers) leaves the basic topology of the orbitals unaltered.

by repeated reprecipitation from chloroform with methanol and were handled under conditions that avoided contact with magnetic materials.

Oxidative doping of the polymers **5**, **11** and **12**

The results of various doping experiments of the polymers **5a-c**, **11** and **12** are summarised in Table 1. At first the doping of each polymer was investigated using the 'solution-doping' method described in our last publication.¹⁷ In this a solution of a known weight of the fractionated polymer in dichloromethane was treated with an excess of NOBF₄ in dichloromethane. The double integral of the resultant EPR signal was compared with that for a standard solution of DPPH (2,2-diphenyl-1-picrylhydrazyl) under identical spectrometer settings. From this a total number of spins per unit volume and hence a number of spins per gram of polymer and spins per repeat unit (the doping level) were calculated. None of the newly synthesised polymers gave higher doping levels than the polymer **5b**. Better results were obtained using a process based on *p*-doping of thin films of the polymers using gaseous antimony pentachloride.¹⁹ A solution of the polymer in chloroform was mixed with degreased glass wool and the solvent was removed using a rotary evaporator. Given the relative weights of the polymer and glass wool a (theoretical) quantitative even distribution under these conditions would have given a film of polymer on the glass which was ca. 1 μm thick. The glass wool was suspended in a tube and a stream of argon was passed over its surface, followed by argon saturated with antimony pentachloride vapour, followed by argon. Under an argon atmosphere the doped polymer was washed from the surface of the glass wool using dichloromethane and the concentration of radicals in the resulting solution was assessed by EPR spectroscopy. Conversion of these numbers into figures for the doping levels is not straightforward since the weight of the polymer in



Scheme 2 Synthesis of the polymers **11** (a) and **12** (b) (i) $\text{Pd}(\text{PPh}_3)_4$ -toluene-aq. Na_2CO_3 -reflux; (ii) NO^+BF_4^- - CH_2Cl_2 or SbCl_5 vapour. The polymer repeat unit is shown in the box. The extended structure is shown to illustrate the basic spin-coupling pathway.

solution is not accurately known. It had to be assumed that all of the polymer had been coated on the glass wool and all had been washed from its surface. This makes the doping levels given in Table 1 lower limit figures. The reproducibility of these figures was considerably poorer than those obtained for 'solution doping' but it is clear that doping by this method is considerably better than 'solution doping' and that polymer **5a** gives the highest doping levels.

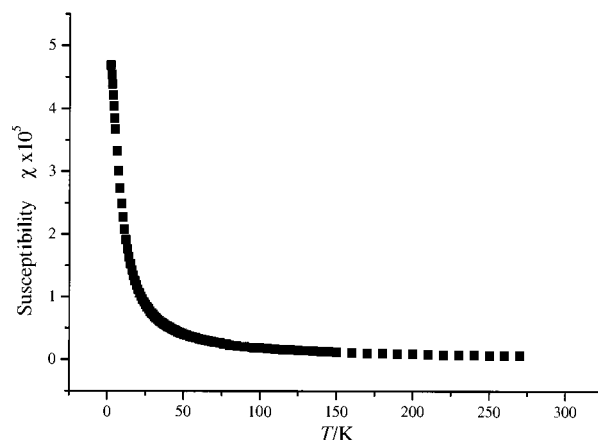
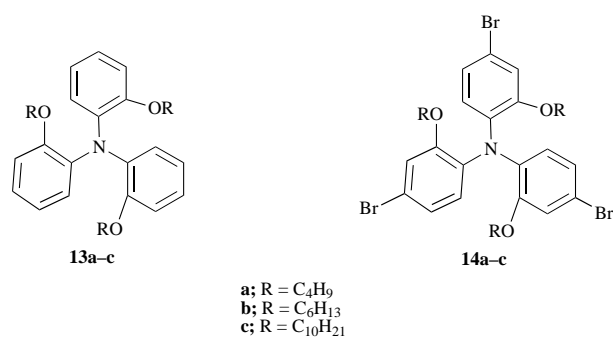


Fig. 3 Susceptibility χ of the polymer **5a** (expressed per gram of the doped polymer) doped with SbCl_5 (40%) as a function of temperature at a field of 5 T

Characterisation of the magnetic properties of the polymers **5a** and **5b** doped with gaseous antimony pentachloride

These polymers were designed to ensure ferromagnetic spin coupling between adjacent spin-bearing sites. After doping they should contain a non-interacting polydisperse population of $S = \frac{1}{2}, 1, \frac{3}{2}, 2, \text{etc.}$ spin clusters and, for the 'solution doped' polymers such a spread of spins has been confirmed by electron spin nutation methods.²⁴ There is no ideal way of characterising the distribution of spin states but, provided the spin clusters are non-interacting, comparison of the experimental dependence of magnetisation on applied field to theoretical Brillouin functions for monodisperse $S = \frac{1}{2}, 1, \frac{3}{2}, 2, \text{etc.}$ spin systems can be used as an empirical measure and as a method of comparing one polymer with another.¹⁷ This was the approach adopted. After doping a 1 μm thick film of the polymer it was washed from the surface of the glass wool with dichloromethane under an argon atmosphere, the solvent was removed under vacuum and the residue dried under vacuum. In a glove box the doped polymer was transferred to a sample holder under an atmosphere of dry nitrogen. Using a SQUID magnetometer the susceptibility of each doped polymer was measured as a function of temperature (2 K to room temperature) at constant field (5 T) and as a function of field (0–5 T) at constant temperature (*ca.* 2 K). The susceptibility measurements were corrected to allow for the diamagnetic contribution of the polymer and of the sample holder. The temperature dependence of the susceptibilities were very similar for both polymers. That for polymer **5a** doped with SbCl_5 is shown in Figs. 3 and 4. Within error limits, the Curie law is obeyed. The field dependence of the susceptibilities for polymers **5a** and **5b** are shown in Figs. 5 and 6 in which they are compared with theoretical Brillouin functions. However, it must be noted that, for a disperse spin system, an 'average' Brillouin function is never followed in a strict manner and typically the magnetisation tends to increase 'too rapidly' at low fields and 'too slowly' at high fields.¹⁹ Those for the doped polymer **5a** are closest to an $S = 4$ system (Fig. 5) and those for **5b** (Fig. 6) are closest to an $S = \frac{5}{2}$ system.

Table 1 Magnetic properties of the doped polymers

Polymers (monomers from which they were made)	$M_w/10^3$ ^a	'Solution doping'; % of sites doped using NOBF ₄ as estimated by EPR spectroscopy	'Thin-film doping'; % of sites doped ^b using SbCl ₅ as estimated by EPR spectroscopy	'Thin-film doping'; % of sites doped using SbCl ₅ as measured by SQUID magnetometry	'Thin-film doping'; \approx spin system S as estimated from Brillouin function fits (Figs. 5 and 6)
5a (3 + 4a)	34	13	60 ± 4 (3)	39, 40 ^c	4, 4 ^c
5b (3 + 4b)	80	21	50 ± 9 (4)	25	5/2
5c (3 + 4c)	4	16	43 ± 3 (4)	—	—
11 (8 + 4b)	—	11	31 ± 3 (2)	—	—
12 (9 + 4b)	—	6	21 ± 6 (2)	—	—

^a GPC against a polystyrene standard. ^b Average of 2, 3 or 4 preparations as indicated. ^c Two separate preparations.

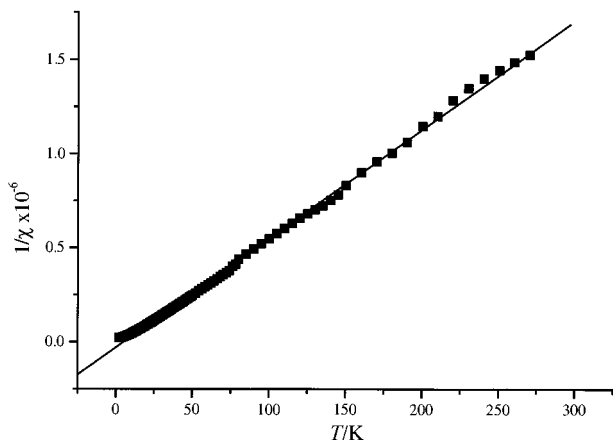


Fig. 4 $1/\chi$ for the polymer **5a** doped with SbCl₅ (40%) as a function of temperature at a field of 5 T

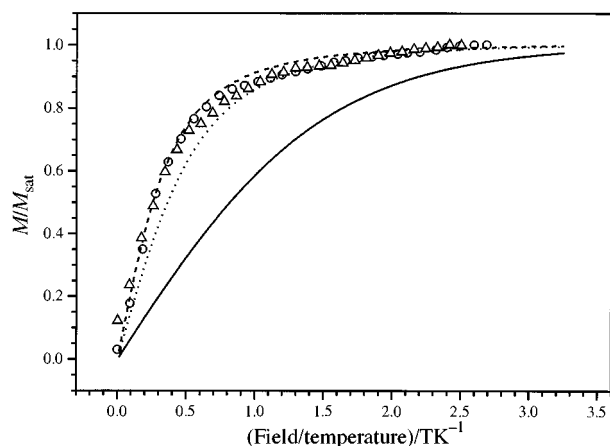


Fig. 5 Field dependence of the magnetisation of two separately prepared samples of the polymer **5a** doped with SbCl₅ (Δ , 39%; \circ , 40%) as a function of field at 2.0 K and 1.8 K, respectively compared with theoretical Brillouin functions for $S = \frac{1}{2}$ (solid line), $S = \frac{5}{2}$ (dotted line) and $S = \frac{3}{2}$ (dashed line) systems

Clearly, this method of doping the polymers induces higher-spin pi multiradical sites than the solution doping method but it gives more problems in terms of reproducibility. Using the solution doping method, results were very consistent run to run and concordant measurements of the levels of doping were achieved between the EPR experiments and SQUID magnetometer measurements.¹⁷ Using this 'film doping' approach the EPR experiments showed considerable variation in the doping levels achieved and measurements on the SQUID magnetometer always indicated lower doping levels than the EPR experiments. Some of this discrepancy is due to the difficulty of quantitatively adding and removing the polymer from the glass wool. However, it also became clear that, whilst bulk samples of the doped polymer are stable to some degree of exposure to the air, in a thin film format the doped polymer decays very rapidly

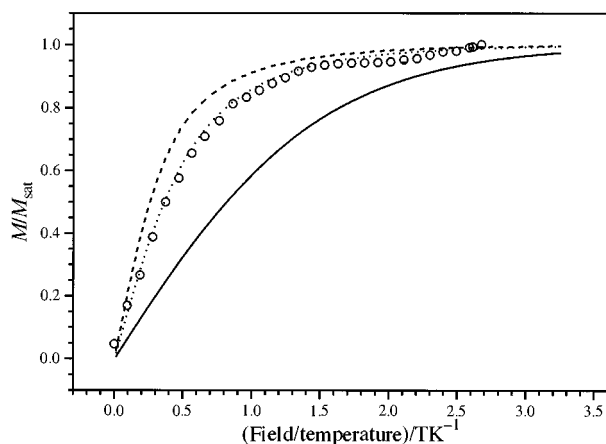


Fig. 6 Field dependence of the magnetisation of polymer **5b** doped with SbCl₅ (25%) as a function of field at 2.0 K compared with theoretical Brillouin functions for $S = \frac{1}{2}$ (solid line), $S = \frac{5}{2}$ (dotted line) and $S = \frac{3}{2}$ (dashed line) systems

on exposure to the air. The additional manipulations required in washing the polymer from the glass wool, evaporating the solution, *etc.*, to get it into the SQUID magnetometer sample holder inevitably resulted in some deterioration.

Conclusions

Oxidation of a thin film of the networked polymer **5a** (Scheme 1) with gaseous antimony pentachloride gives a distribution of spin states with overall behaviour close to $S = 4$. This represents an improvement over systems made previously¹⁷⁻²⁰ and higher spin systems could undoubtedly be produced by further optimisation of this system. Whether or not, at the percolation limit,¹⁸ there will be an onset of bulk ferromagnetic behaviour remains to be seen.

Experimental

Instrumentation and general procedures employed were described in detail in our last publication.¹⁷

Tris(2-butoxyphenyl)amine **13a**¹⁷

A mixture of tris(2-hydroxyphenyl)amine (3.00 g, 10.20 mmol),¹⁷ 1-bromobutane (7.00 g, 51 mmol) and powdered potassium carbonate (10.50 g, 76.40 mmol) was stirred and refluxed in dry ethanol (200 cm³) for 24 h. The reaction was cooled to room temperature after which the insoluble material was filtered off at the pump and the filtrate concentrated under reduced pressure to approximately 10 cm³. Dichloromethane (100 cm³) was added. The organic layer was washed with aqueous sodium hydroxide, water and brine and dried with magnesium sulfate. Solvent and excess bromobutane were removed under reduced pressure to give a pale brown oil. Column chromatography eluting with dichloromethane-hexane (50:50) gave the product **13a** as a pale brown oil (4.35 g,

92%) (Found: C, 78.0; H, 8.55; N, 3.0. $C_{30}H_{39}NO_3$ requires C, 78.11; H, 8.45; N, 3.05%); $\delta_H(\text{CDCl}_3)$ 0.88 (9 H, t, $J = 7.0$ Hz, Me), 1.03 (6 H, tq, $J = 7.0, 6.0$ Hz, CH_2CH_3), 1.24 (6 H, tt, $J = 6.0$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.78 (6 H, t, $J = 6.3$ Hz, OCH_2) and 6.7–6.98 (12 H, m, Ph); m/z 461 (M^+ , 100%), 347 (21), 291 (18) and 110 (11).

In a similar manner *tris*(2-decyloxyphenyl)amine **13c** was made using a mixture of *tris*(2-hydroxyphenyl)amine (2.00 g, 6.85 mmol), 1-bromodecane (5.30 g, 24.00 mmol) and powdered potassium carbonate (6.64 g, 48.10 mmol). Yield 4.51 g, 91% (Found: C, 80.5; H, 10.6; N, 1.85. $C_{48}H_{75}NO_3$ requires C, 80.70; H, 10.58; N, 1.96%); $\delta_H(\text{CDCl}_3)$ 0.88 (9 H, t, $J = 7.0$ Hz, Me), 0.97–1.26 (48 H, m, methylenes), 3.78 (6 H, t, $J = 6.0$ Hz, OCH_2) and 6.74–6.97 (12 H, m, Ph); m/z 713 (M^+ , 100%), 573 (78) and 111 (13).

Tris(4-bromo-2-butoxyphenyl)amine **14a**¹⁷

A solution of bromine (4.30 g, 26.70 mmol) in dry chloroform (40 cm^3) was added to a stirred solution of *tris*(2-butoxyphenyl)amine **13a** in dry chloroform (70 cm^3) at 0 °C over 30 min. After the addition, a blue–green reaction mixture formed which was allowed to warm to room temperature with stirring overnight. The reaction mixture then was washed with distilled water (2 \times 150 cm^3), dilute sodium metabisulfite solution, and brine, and dried with magnesium sulfate. The solvent was removed under reduced pressure to give a brown oil. The product was purified by column chromatography on silica gel, eluting with 30% dichloromethane in hexane to give the product **14a** as a colourless oil which crystallised on standing to give colourless needles (4.26 g, 69%) (Found: C, 51.6; H, 5.0; Br, 34.5; N, 1.9. $C_{30}H_{36}Br_3NO_3$ requires C, 51.62; H, 5.16; Br, 34.34; N, 2.01%); $\delta_H(\text{CDCl}_3)$ 0.88 (9 H, t, $J = 7.2$ Hz, Me), 1.01 (6 H, qt, $J = 7.2, 6.0$ Hz, CH_2CH_3), 1.28 (6 H, tt, $J = 6.0$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.72 (6 H, t, $J = 6.0$ Hz, OCH_2), 6.68 (3 H, d, $J = 6.0$ Hz, ArH) and 6.9 (6 H, dd, $J = 6.0, 1.0$ Hz, ArH); m/z 695 (M^+ , 33%), 668 (21), 646 (100), 590 (19), 417 (16) and 187 (10).

In a similar manner *tris*(4-bromo-2-decyloxyphenyl)amine **14c** was prepared from a solution of bromine (2.60 g, 16.10 mmol) in dry chloroform (50 cm^3) which was added to a stirred solution of *tris*(2-decyloxyphenyl)amine **13c** in dry chloroform (80 cm^3) at 0 °C. (Yield 3.7 g, 73%) (Found: C, 60.8; H, 7.5; Br, 25.4; N, 1.35. $C_{48}H_{72}Br_3NO_3$ requires C, 60.63; H, 7.63; Br, 25.21; N, 1.47%); $\delta_H(\text{CDCl}_3)$ 0.88 (9 H, t, $J = 6.5$ Hz, Me), 0.9–1.43 (48 H, m, methylenes), 3.70 (6 H, t, $J = 6.0$ Hz, OCH_2) 6.67 (3 H, d, $J = 8.0$ Hz, ArH) and 6.97 (6 H, dd, $J = 8.0, 1.0$ Hz, ArH); m/z (M^+ , 100%), 811 (22), 651 (31) and 80 (11).

Tris[2-butoxy-4-(dihydroxyboranyl)phenyl]amine **4a**¹⁷

n-Butyllithium in hexane (6.6 cm^3 , 1.3 M, 8.5 mmol) was added to a solution of *tris*(4-bromo-2-butoxyphenyl)amine **14a** (1.90 g, 2.7 mmol) in dry tetrahydrofuran (60 cm^3) under an atmosphere of argon at –78 °C over a period of 15 min. A yellow–green suspension formed. The suspension was stirred for a further 2 h at –78 °C. The cold suspension was cannulated into a solution of triisopropyl borate (9.0 g, 48.0 mmol) in tetrahydrofuran (30 cm^3) at –78 °C under argon, and the mixture was stirred for another 2 h before being warmed to room temperature overnight (*ca.* 12 h). The mixture was again cooled to –78 °C and the intermediate ester was hydrolysed by addition of 2 M hydrochloric acid (10 cm^3), slow warming to room temperature, and further stirring for 1 h before work-up. Diethyl ether (100 cm^3) was added and the ether layer separated. The aqueous layer was extracted with further ether (2 \times 20 cm^3). The combined ether layers were washed with water and dried with magnesium sulfate. The ether solution was concentrated to about 20 cm^3 under reduced pressure and without the use of heat. The product precipitated with added hexane (60 cm^3) and the pale green precipitate was collected by filtration under suction. The solid was washed with more ether–hexane (1:1) to give the product (1.16 g, 71%) as a pale green solid. The product

was insoluble in dichloromethane, chloroform and hexane but it was soluble in acetone and tetrahydrofuran (Found: C, 60.6; H, 7.4; N, 2.45. $C_{30}H_{42}B_3NO_9$ requires C, 60.70; H, 7.10; N, 2.40%); $\delta_H[(\text{CD}_3)_2\text{CO}]$ 0.88 (9 H, t, $J = 7.0$ Hz, Me), 1.04 (6 H, qt, $J = 7.0, 6.2$ Hz, CH_2CH_3), 1.27 (6 H, tt, $J = 6.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.76 (6 H, t, $J = 6.0$ Hz, OCH_2), 6.78 (3 H, d, $J = 7.5$ Hz, ArH), 7.00 [6 H, s, $\text{B}(\text{OH})_2$], 7.34 (3 H, d, $J = 7.9$ Hz, ArH) and 7.93 (3 H, s, Ph); m/z (from the ester formed by heating the product in the presence of ethanediol) 671 (M^+ , 100%), 541 (27), 322 (19) and 177 (21).

In a similar fashion, *tris*[2-decyloxy-4-(dihydroxyboranyl)phenyl]amine **4c** was produced from the addition of *n*-butyllithium in hexane (7.7 cm^3 , 1.6 M, 12.3 mmol) to a solution of *tris*(4-bromo-2-decyloxyphenyl)amine (**14c**) (2.90 g, 3.1 mmol) in dry tetrahydrofuran (90 cm^3). The product was obtained as a pale green powder (1.69 g, 65%) (Found: C, 68.2; H, 9.15; N, 1.45. $C_{48}H_{78}B_3NO_9$ requires C, 68.18; H, 9.25; N, 1.65%); $\delta_H(\text{CDCl}_3)$ (of the ester, formed by heating the product in the presence of ethanediol) 0.88 (9 H, t, $J = 6.5$ Hz, Me), 0.97–1.38 (48 H, m, methylenes), 3.74 (6 H, t, $J = 6.0$ Hz, OCH_2), 4.37 (12 H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 6.69 (3 H, d, $J = 8.0$ Hz, ArH) and 6.99 (6 H, dd, $J = 8.0, 1.0$ Hz, ArH); m/z (also of the ester) 923 (M^+ , 58%), 909 (38), 853 (16), 625 (15), 133 (59) and 57 (100).

2,7-Dihexyloxy-3,6-dibromonaphthalene **8**

A mixture of 3,6-dibromonaphthalene-2,7-diol (1.60 g, 5.00 mmol), prepared by the method of Cooke *et al.*,²⁵ 1-bromohexane (8.25 g, 0.05 mol) and powdered potassium carbonate (10.35 g, 0.075 mol) were heated at reflux with stirring in ethanol (100 cm^3) for 20 h. The reaction was cooled to room temperature after which residual insoluble material was filtered off at the pump and the filtrate concentrated under reduced pressure to approximately 10 cm^3 . Dichloromethane (100 cm^3) was added and the organic layer was washed with aqueous sodium hydroxide, water and brine, and dried with magnesium sulfate. Solvent and excess 1-bromohexane were removed under reduced pressure to give a light brown solid. Recrystallisation from dichloromethane–hexane (50:50) gave the product **8** as colourless needles (2.16 g, 89%) (Found: C, 54.2; H, 6.05; Br, 32.8. $C_{22}H_{30}Br_2O_2$ requires C, 54.35; H, 6.15; Br, 32.85%); $\delta_H(\text{CDCl}_3)$ 0.88 (9 H, t, $J = 7.0$ Hz, Me), 1.03 (6 H, tq, $J = 7.0, 6.0$ Hz, CH_2CH_3), 1.24 (6 H, tt, $J = 6.0$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.78 (6 H, t, $J = 6.3$ Hz, OCH_2) and 6.7–6.98 (12 H, m, Ph); m/z 461 (M^+ , 100%), 347 (21), 291 (18) and 110 (11).

4,4'-Dibromo-*m*-terphenyl **9**

This was prepared by the method of Woods *et al.*²⁶ (overall yield 37%) (Found: C, 56.0; H, 3.4; Br, 41.3. $C_{18}H_8Br_2$ requires C, 55.82; H, 3.09; Br, 41.30%); $\delta_H(\text{CDCl}_3)$ 7.52–7.55 (3 H, m, ArH), 7.54 (8 H, dd, $J = 6.0, 18.0$ Hz, ArH of 1,4-disubstituted aromatic rings) and 7.71 (1 H, s, ArH *ortho* to two aromatic rings).

Polymer **5a**¹⁷

A mixture of 1,3-dibromo-5-tetradecylbenzene **3** (1.64 g, 3.80 mmol) and tetrakis(triphenylphosphine)palladium (0.12 g, 0.11 mmol) was stirred for 10 min in dry toluene (70 cm^3) under argon. A solution of **4a** (1.50 g, 2.53 mmol) in dry ethanol (15 cm^3) was added followed by dilute sodium carbonate (2 M, 25 cm^3) and the entire mixture was heated at reflux under argon with stirring for 7 days. When cooled, the aqueous layer was removed and extracted with ether (2 \times 20 cm^3). A quantity of black 'gel' was found in the remaining organic layer which was also extracted with large amounts of ether. The combined organic layers were dried with magnesium sulfate and the solvent was removed under reduced pressure. The residual dark solid was dissolved in dichloromethane (15 cm^3) and the solution dropped into cold methanol (40 cm^3), causing precipitation of a grey powder which was collected at the pump. The process was repeated several times to remove impurities, eventually

yielding the polymer product as a grey powder (1.53 g, 60%) (Found: C, 82.8; H, 9.75; Br, <0.2; N, 1.75. Repeat unit $C_{60}H_{84}NO_3$ requires C, 83.10; H, 9.69; Br, 0.00; N, 1.94%; $\delta_H(CDCl_3)$ 0.79 (br m, CH_3 of C_4 alkyl chain), 0.88 (br m, CH_3 of C_{14} alkyl chain), 1.03–1.24 (br m, methylenes of both C_4 and C_{14} alkyl chains), 1.65 (br m, $Ph-CH_2CH_2$), 2.68 (br m, $PhCH_2$), 3.93 (br m, Ph and OCH_2), 6.98–7.18 (br m, ArH of arylamine groups) and 7.24–7.32 (br m, ArH of 1,3,5-trisubstituted benzene groups).

In a similar manner, polymer **5c** was produced from 1,3-dibromo-5-tetradecylbenzene **3** (0.65 g, 1.51 mmol), tetrakis(triphenylphosphine)palladium (0.05 g, 0.04 mmol) and a solution of **4c** (0.85 g, 1.01 mmol) in dry ethanol (10 cm^3) in dry toluene (40 cm^3) with dilute sodium carbonate (2 M, 10 cm^3). Precipitation from methanol yielded the polymer product as a sticky brown gum, collected by centrifugation (1.07 g, 95%) (Found: C, 81.9; H, 10.9; Br, <0.2; N, 1.45. Repeat unit $C_{78}H_{120}NO_3$ requires C, 83.66; H, 10.80; Br, 0.00; N, 1.25%; $\delta_H(CDCl_3)$ 0.79–0.98 (br m, CH_3 of both C_{10} and C_{14} alkyl chains), 0.99–1.24 (br m, methylenes of both C_{10} and C_{14} alkyl chains), 1.66 (br m, $PhCH_2CH_2$), 2.64 (br m, $PhCH_2$), 3.87 (br m, Ph and OCH_2), 6.91–7.20 (br m, ArH of arylamine groups) and 7.26–7.41 (br m, ArH of 1,3,5-trisubstituted benzene groups).

Polymer 11

This was produced from 2,7-dihexyloxy-3,6-dibromonaphthalene **8** (1.00 g, 2.06 mmol), tetrakis(triphenylphosphine)palladium (0.06 g, 0.05 mmol) and a solution of tris[2-hexyloxy-4-(dihydroxyboranyl)phenyl]amine **4b** (0.92 g, 1.36 mmol) in dry ethanol (10 cm^3), in dry toluene (40 cm^3) with dilute sodium carbonate (2 M, 12 cm^3) also using the same method. The polymer product was precipitated initially from methanol cooled to $-20^\circ C$, as a brown precipitate. Subsequent reprecipitation yielded a precipitate, collected at the pump as a grey powder (0.6 g, 50%) (Found: C, 79.7; H, 8.9; Br, 0.6; N, 1.25. Repeat unit $C_{69}H_{93}NO_6$ requires C, 80.26; H, 9.09; Br, 0.00; N, 1.36%; $\delta_H(CDCl_3)$ 0.79 (br m, CH_3 of aryl amine chains), 0.80–0.98 (br m, CH_3 of naphthyl alkyl chains), 1.02–1.98 (br m, methylenes of both C_6 chains), 3.83 (br m, OCH_2 due to arylamine subst.), 4.06 (br m, OCH_2 due to naphthyl subst.) and 6.9–7.80 (br m, ArH).

In a similar manner polymer **12** was formed from 4,4'-dibromo-*m*-terphenyl **9** (0.56 g, 1.44 mmol), tetrakis(triphenylphosphine)palladium (0.04 g, 0.03 mmol) and a solution of **4b** (0.61 g, 0.92 mmol) in dry ethanol (7 cm^3), in dry toluene (25 cm^3) with dilute sodium carbonate (2 M, 9 cm^3). The reaction was heated at reflux for 72 h after which the polymer was obtained by the usual method as a green powder (0.39 g, 48%) (Found: C, 83.9; H, 7.80; Br, 1.6; N, 1.40. Repeat unit $C_{63}H_{66}NO_3$ requires C, 85.38; H, 7.51; Br, 0.00; N, 1.58%; $\delta_H(CDCl_3)$ 0.83 (br m, CH_3), 0.98–1.45 (br m, methylenes), 3.84 (br m, OCH_2), 6.92–7.20 (br m, ArH due to aryl amine subst.) and 7.31–7.70 (br m, ArH due to terphenyl).

Studies of the oxidative doping of the polymers using EPR spectroscopy

Using $NOBF_4$ as the oxidant. In a typical doping experiment, the polymer (0.100 g) was dissolved in dry dichloromethane (100 cm^3) under an argon atmosphere to give a clear solution. A standard EPR tube was filled with the solution such that, as in the case of the calibration experiment, the depth of solution in the tube spanned the microwave cavity. Under a steady flow of argon and at a temperature of $-20^\circ C$, the solution was treated with an excess of powdered $NOBF_4$ causing a colour change to deep green. The EPR spectrum was recorded at room temperature on a Bruker ER 200 spectrometer with a Bruker ESP 1600 data acquisition system. The double integral of the resultant EPR signal was compared with that for a solution of DPPH standard under identical settings. The response

of the instrument was calibrated on a daily basis using the double integral of the signal from a fresh standard solution of DPPH (*ca.* 5 mg in 50 cm^3 of AR benzene) whose concentration was independently and accurately determined from the intensity of the absorption maximum at 530 nm ($\epsilon = 1.42 \times 10^4$ l mol $^{-1}$ cm $^{-1}$). From this a total number of spins per unit volume and hence a number of spins per gram of polymer and spins per repeat unit (the doping level) were calculated.

Using $SbCl_5$ as the oxidant. Typically, a solution of the polymer (0.100 g) in dry chloroform (10 cm^3) was mixed with 1 g of degreased glass wool. Removal of the solvent under reduced pressure using a rotary evaporator followed by an oil pump (10 $^{-2}$ mmHg) deposited a polymer film of thickness *ca.* 1 μm onto the glass wool surface [glass wool diameter = 1.5×10^{-3} cm; glass density = 2.6 g cm $^{-3}$; surface area of 1 g of glass wool = $\pi \times 1.5 \times 10^{-3} / 2.6 \times \pi \times (7.5 \times 10^{-4})^2 = 1.06 \times 10^3$ cm 2 ; film thickness for 0.1 g of polymer with a density of *ca.* 1 g cm $^{-3}$ coated onto 1 g of glass wool = $10^{-1} / 1.06 \times 10^3$ cm = *ca.* 1 μm]. The polymer-coated glass wool was suspended in a dry glass tube and the sample was flushed out with argon. A steady stream of argon saturated with antimony pentachloride was passed over its surface for 30 min or until the colour of the sample ceased to darken, whichever was the shorter. The system was again flushed with argon and thoroughly washed with dry dichloromethane (5 \times 10.0 cm^3), giving a dark green solution, the EPR spectrum of which was recorded as described above.

Characterisation of the magnetic properties of the doped polymers

Using $NOBF_4$ as the oxidant. Typical procedure: the polymer (100 mg) and dichloromethane (10 cm^3) were stirred together overnight under an argon atmosphere to give a clear solution. This was cooled to $-30^\circ C$ and powdered $NOBF_4$ (330 mg, a large excess) was added under argon. After 20 min at $-30^\circ C$ the solvent was initially removed by passing a steady stream of argon through the deep green solution and the residue dried at room temperature at *ca.* 10^{-4} mmHg overnight. In a glove bag, a portion of the doped polymer was transferred using a plastic spatula and a nitrogen atmosphere to a sealed sample holder which was immediately transferred to the SQUID magnetometer in which it was maintained under an atmosphere of helium.

Using $SbCl_5$ as the oxidant. The procedure adopted in this case was much the same as that described for the polymer in the EPR experiments detailed above. Once having washed the doped polymer from the wool surface, the solvent was 'bubbled' off with an argon flow leaving the polymer as a dark green gum. In this form, the polymer was transferred to its sealed sample holder, under nitrogen using non-metallic instruments. The polymer was then fully dried under vacuum at room temperature (*ca.* 10^{-4} mm) before transfer to the SQUID magnetometer, within which it was maintained under a helium atmosphere. Attempts fully to dry the polymer before transfer to the sample holder were less successful since the resultant polymer film was hard and very difficult to remove from the flask using non-metallic implements. The magnetisation data shown in Figs. 3–6 are corrected for the diamagnetism of the sample holder, the polymer and the excess reagent. The diamagnetic contribution for the sample holder (the largest part of the correction) and for undoped polymer were separately measured as a function of temperature and were assumed to scale linearly with field. The increase in weight upon doping (about twofold) was assumed to be wholly due to the reagent and the (very small) diamagnetic correction for this was estimated from standard tables. A sample of the polymer **5a** before doping showed C, 82.80; H, 9.75; N, 1.75%, figures within experimental error of those expected. Three samples of polymer, doped in the same way as for the magnetometer measurements, were submitted for combustion analysis with minimum exposure to the air.

They showed C, 45.25–46.75; H, 5.05–5.55; Cl, 22.55–23.30; N, 0.7–0.8%.

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References

- 1 W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1977, **99**, 4587; W. T. Borden, *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 195.
- 2 P. Dowd, *J. Am. Chem. Soc.*, 1966, **88**, 2587; P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, 1967, **89**, 715; P. Dowd, A. Gold and K. Sachdev, *J. Am. Chem. Soc.*, 1968, **90**, 2715; P. Dowd, *J. Am. Chem. Soc.*, 1970, **92**, 1066; R. J. Baseman, D. W. Pratt, M. Chow and P. Dowd, *J. Am. Chem. Soc.*, 1976, **98**, 5726; P. Dowd and M. Chow, *J. Am. Chem. Soc.*, 1977, **99**, 6438; P. Dowd, W. Chang and Y. H. Paik, *J. Am. Chem. Soc.*, 1986, **108**, 7416; P. Dowd, W. Chang and Y. H. Paik, *J. Am. Chem. Soc.*, 1987, **109**, 5284; Y. Choi, K. D. Jordan, Y. H. Paik, W. Chang and P. Dowd, *J. Am. Chem. Soc.*, 1988, **110**, 7575.
- 3 J. A. Berson, R. J. Bushby, J. M. McBride and M. Tremelling, *J. Am. Chem. Soc.*, 1971, **93**, 1544; W. R. Roth, M. Bierman, G. Erker, K. Jelich, W. Gerhartz and H. Gorner, *Chem. Ber.*, 1980, **113**, 586; W. R. Roth and B. P. Scholtz, *Chem. Ber.*, 1982, **115**, 1197; J. A. Berson, in *Diradicals*, ed. W. T. Borden, Wiley, New York, 1982; R. J. Bushby, M. V. Jesudason and S. Mann, *Tetrahedron Lett.*, 1983, **24**, 4743; R. J. Bushby, M. V. Jesudason and S. Mann, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2457; R. D. Little, *Chem. Rev.*, 1986, **86**, 875; R. J. Bushby and C. Jarecki, *Tetrahedron Lett.*, 1988, **27**, 2053; R. J. Bushby and C. Jarecki, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2335; R. J. Bushby and C. Jarecki, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2215.
- 4 M. S. Platz, in *Diradicals*, ed. W. T. Borden, Wiley, New York, 1982, p. 195; J. A. Berson, in *The Chemistry of the Quinonoid Compounds*, Vol. 2, Part 2, eds. S. Patai and Z. Rappoport, Wiley, New York, 1988, p. 455.
- 5 G. Allinson, R. J. Bushby, J.-L. Paillaud, D. Oduwole and K. Sales, *J. Am. Chem. Soc.*, 1993, **115**, 2062; G. Allinson, R. J. Bushby and J.-L. Paillaud, *J. Mater. Sci., Mater. Electron.*, 1994, **5**, 67; G. Allinson, R. J. Bushby, J.-L. Paillaud and M. Thornton-Pett, *J. Chem. Soc., Perkin Trans. 1*, 1995, 385; G. Allinson, R. J. Bushby, M. V. Jesudason, J.-L. Paillaud and N. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1997, 147.
- 6 N. Wilker, G. Kothe and H. Zimmermann, *Chem. Ber.*, 1975, **108**, 2124; M. Matsushita, T. Momose, T. Shida, Y. Teki, T. Takui and K. Itoh, *J. Am. Chem. Soc.*, 1990, **112**, 4700; A. Rajca, S. Utamapanya and J. Xu, *J. Am. Chem. Soc.*, 1991, **113**, 9235; K. Yoshizawa, A. Chano, A. Ito, K. Tanaka, T. Yamabe, H. Fujita, J. Yamauchi and M. Shiro, *J. Am. Chem. Soc.*, 1992, **114**, 5994; S. Rajca and A. Rajca, *J. Am. Chem. Soc.*, 1995, **117**, 9172.
- 7 K. Yoshizawa, M. Hatanaka, A. Ito, K. Tanaka and T. Yamabe, *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 323; K. R. Stickley and S. C. Blackstock, *J. Am. Chem. Soc.*, 1994, **116**, 11 576.
- 8 D. E. Seeger and J. A. Berson, *J. Am. Chem. Soc.*, 1983, **105**, 5144 and 5146; A. Rajca, *J. Am. Chem. Soc.*, 1990, **112**, 5890; S. J. Jacobs, D. A. Shultz, R. Jain, J. Novak and D. A. Dougherty, *J. Am. Chem. Soc.*, 1993, **115**, 1744; D. Dougherty, A. West and S. Silverman, *J. Am. Chem. Soc.*, 1996, **118**, 1452.
- 9 K. Itoh, *Chem. Phys. Lett.*, 1967, **1**, 235; E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo and G. Smolinsky, *J. Am. Chem. Soc.*, 1967, **89**, 5076; E. Wasserman, K. Scheuller and W. Yager, *Chem. Phys. Lett.*, 1968, **2**, 259; K. Itoh, *Pure Appl. Chem.*, 1978, **50**, 1251; H. Iwamura and S. Murata, *Mol. Cryst. Liq. Cryst.*, 1989, **176**, 33; K. Haider, N. Soundararajan, M. Shaffer and M. S. Platz, *Tetrahedron Lett.*, 1989, **30**, 1225; M. Okamoto, Y. Teki, T. Takui, T. Kinoshita and K. Itoh, *Chem. Phys. Lett.*, 1990, **173**, 265; S. Murata and H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 5547; S. Sasaki and H. Iwamura, *Chem. Lett.*, 1992, 1759; C. Ling, M. Minato, P. M. Lahti and H. van Willigen, *J. Am. Chem. Soc.*, 1992, **114**, 9959; H. Iwamura, *Pure Appl. Chem.*, 1993, **65**, 57; P. Lahti, C. Ling, N. Yoshioka, F. Rossitto and H. van Willigen, *Mol. Cryst. Liq. Cryst.*, 1993, **233**, 17; Y. Teki, I. Fujita, T. Takui, T. Kinoshita and K. Itoh, *J. Am. Chem. Soc.*, 1994, **116**, 11 499.
- 10 A. Buchachenko, *Stable Radicals*, AS USSR Publ. House, Moscow, 1963; A. Rajca, S. Rajca and R. Padmakumar, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2091; A. Rajca, S. Rajca and S. R. Desai, *J. Am. Chem. Soc.*, 1995, **117**, 806.
- 11 E. Wasserman, K. Scheuller and W. Yager, *Chem. Phys. Lett.*, 1968, **2**, 259; Y. Teki, T. Takui, K. Itoh, H. Iwamura and K. Kobayashi, *J. Am. Chem. Soc.*, 1983, **105**, 3722; T. Sugawara, S. Bandow, K. Kimura, H. Iwamura and K. Itoh, *J. Am. Chem. Soc.*, 1984, **106**, 6449; K. Itoh, Y. Teki, T. Takui, H. Yagi, K. Itoh and H. Iwamura, *J. Chem. Phys.*, 1985, **83**, 539; T. Sugawara, S. Bandow, K. Kimura, H. Iwamura and K. Itoh, *J. Am. Chem. Soc.*, 1986, **108**, 368; Y. Teki, T. Takui, K. Itoh, H. Iwamura and K. Kobayashi, *J. Am. Chem. Soc.*, 1986, **108**, 2147; I. Fujita, Y. Teki, T. Takui, T. Kinoshita, K. Itoh, F. Miko, Y. Sawaki, H. Iwamura, A. Izuoka and T. Sugawara, *J. Am. Chem. Soc.*, 1990, **112**, 4074; K. Itoh and H. Iwamura, in *Magnetic Molecular Materials*, eds. D. Gatteschi, O. Kahn, J. Miller and F. Palacio, Kluwer, Dordrecht, 1991; N. Nakamura, K. Inoue, H. Iwamura, T. Fujioka and Y. Sawaki, *J. Am. Chem. Soc.*, 1992, **114**, 1484; A. Rajca, S. Utamapanya and S. Thayumanavan, *J. Am. Chem. Soc.*, 1992, **114**, 1884; H. Iwamura, *Pure Appl. Chem.*, 1993, **65**, 57; N. Nakamura, K. Inoue and H. Iwamura, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 872; K. Matsuada, N. Nakamura, K. Takahashi, K. Inoue, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, 1995, **117**, 5550.
- 12 A. Rajca and S. Utamapanya, *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 305; A. Rajca and S. Utamapanya, *J. Am. Chem. Soc.*, 1993, **115**, 10 688; S. Utamapanya, H. Kakegawa, K. Bryant and A. Rajca, *Chem. Mater.*, 1993, **5**, 1053; A. Rajca, *Chem. Rev.*, 1994, **94**, 871; K. Matsuada, N. Nakamura, K. Takahashi, K. Inoue, N. Koga and H. Iwamura, *Chem. Eur. J.*, 1996, **2**, 259.
- 13 M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 1996, **118**, 10 626.
- 14 A. Rajca, S. Rajca and S. R. Desai, *J. Chem. Soc., Chem. Commun.*, 1995, 1959.
- 15 N. Mataga, *Theor. Chim. Acta*, 1968, **10**, 372; A. A. Ovchinnikov, *Theor. Chim. Acta*, 1978, **47**, 297; H. Fukutome, A. Takahashi and M. Ozaki, *Chem. Phys. Lett.*, 1987, **133**, 34.
- 16 R. J. Bushby and J.-L. Paillaud, in *An Introduction to Molecular Electronics*, eds. M. C. Petty, M. R. Bryce and D. Bloor, E. Arnold, London, 1995; H. S. Miller and A. J. Epstein, *Chem. Eng. News*, 1995, 30; J. S. Miller and A. J. Epstein, *Chem. Ind.*, 1996, 49.
- 17 R. J. Bushby and K. M. Ng, *Chem. Commun.*, 1996, 659; R. J. Bushby, D. R. McGill, K. M. Ng and N. Taylor, *J. Mater. Chem.*, in press.
- 18 R. J. Bushby, D. R. McGill and K. M. Ng, in *Magnetism: a Supramolecular Function*, ed. O. Kahn, Kluwer, Dordrecht, 1996, p. 181.
- 19 M. M. Murray, P. Kaszynski, D. A. Kaisaki, W. Chang and D. A. Dougherty, *J. Am. Chem. Soc.*, 1994, **116**, 8152.
- 20 P. M. Lahti, C. Ling, N. Yoshioka, F. C. Rossitto and H. van Willigen, *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 377; T. Kaneko, S. Toriu, Y. Kuzumaki, H. Nishide and E. Tsuchida, *Chem. Lett.*, 1994, 2135; S. Utamapanya, H. Kakegawa, L. Bryant and A. Rajca, *Chem. Mater.*, 1993, **5**, 1053; K. Yoshizawa, K. Tanaka, T. Yamabe and J. Yamauchi, *J. Chem. Phys.*, 1992, **96**, 5516; A. Ito, K. Ota, K. Tanaka, T. Yamabe and K. Yoshizawa, *Macromolecules*, 1995, **28**, 5618.
- 21 R. J. Bushby, D. R. McGill, K. M. Ng and N. Taylor, *Chem. Commun.*, 1996, 2641; R. J. Bushby, D. R. McGill, K. M. Ng and N. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1405.
- 22 M. C. Biewer, C. R. Biehn, M. S. Platz, A. Despres and E. Migirdicyan, *J. Am. Chem. Soc.*, 1991, **113**, 616.
- 23 Y. Hoshino, N. Miyaura and A. Suzuki, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3008.
- 24 D. Shiomi, K. Sato, T. Takui, K. Itoh, D. R. McGill, K. M. Ng and R. J. Bushby, *Synth. Met.*, 1997, **85**, 1721.
- 25 R. G. Cooke, B. L. Johnson and W. R. Owen, *Aust. J. Chem.*, 1960, **13**, 256.
- 26 G. F. Woods, D. D. Centola, H. E. Rushie and C. D. Miller, *J. Am. Chem. Soc.*, 1960, **82**, 5227.

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