p-Doped high spin polymers[1]

Richard J. Bushby,* David R. McGill, Kai M. Ng and Norman Taylor

School of Chemistry, The University Of Leeds, Leeds, UK LS2 9JT

High spin polymers have been created from p-doping of networked polyaryl and polyarylamine polymers which were synthesized using the Pd^0 mediated coupling reaction of aryl di- and tri-bromides with aryl bis- and tris-boronic acids. The doping procedures produce polyradical polycations in which (in the limit of 100% doping) each spin is coextensive in its spatial distribution with three neighbouring spins. Magnetic susceptibility studies show the expected ferromagnetic spin-coupling. In this respect the best of these systems is the polymer obtained by the Pd^0 mediated coupling of 1,3-dibromo-5-tetradecylbenzene with tris(4-boronic acid-2-hexyloxyphenyl)amine which was subsequently p-doped with $NO^+BF_4^-$. A Brillouin function fit to the field dependence of the magnetization of this doped polymer at 2 K corresponds to an average spin *S* of 5/2. The best levels of doping achieved so far are about 15% of the theoretical maximum. These are sufficient to demonstrate the genuine high-spin nature of these polymers but are well short of the *ca.* 70% percolation limit needed for bulk superparamagnetic or ferromagnetic behaviour. The low doping levels are attributed to steric rather than coulombic effects.

Almost thirty years ago, Mataga suggested that it might be possible to create ferromagnetic organic polymers by exploiting the strong ferromagnetic spin-coupling mechanism found in triplet ground state π-diradicals.[2] His idea was that a conjugated polymer in which the repeat unit was one of these triplets would possess a band structure in which a superdegenerate band occupied by ferromagnetically coupled unpaired electrons would lie between the valence and conduction bands.[3] This is illustrated schematically in Fig. 1 for the case in which the repeat unit is triplet *m*-quinodimethane. In principle, polymers with the same band structure can be written based on many other triplet non-Kekulé repeat units drawn from the non-Kekulé quinodimethane[4,5] and non-Kekulé polyene families.[4,6] This may appear to be an attractive idea, but many attempts by experimentalists to build on Mataga's suggestion have failed to produce a single genuine ferromagnetic polymer. In fact, the proposal shown in Fig. 1 is flawed. This polymer, like many of the later proposals by Ovchinnikov,[7] is essentially a proposal for a one-dimensional ferromagnet. Basic theory shows that this is not possible.[1,8] Also, non-Kekulé repeat units, such as *m*-quinodimethane, are far too unstable to make a practicable material.[9]

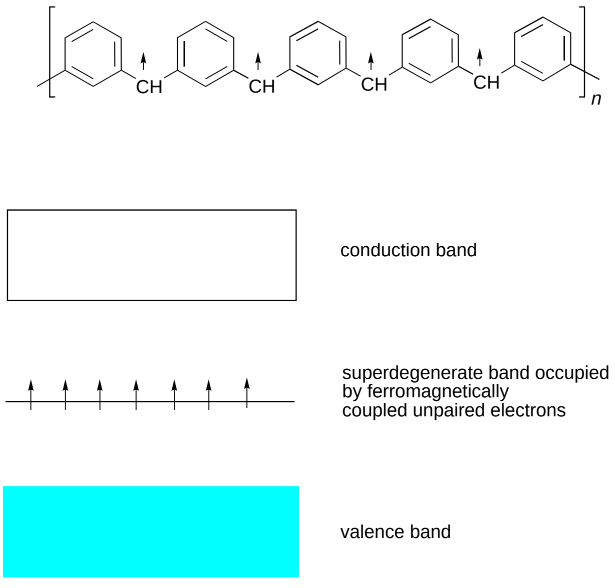


Fig. 1 Schematic representation of the band structure proposed for the hypothetical polymer poly(*m*-quinodimethane) (ref. 2)

A possible solution to these problems based on a 'doping' strategy is shown in Fig. 2.[1] This gets round the dimensionality problem by creating polymers which are randomly networked in three dimensions and solves the stability problem by using (relatively stable) radical-ion spin carriers.[1,4,10–13] For the polymers investigated in this paper, percolation theory[1,14] suggests that bulk ferromagnetic[15] or superparamagnetic behaviour requires a minimum of 70% of the sites to be 'doped'. We have not yet achieved this but we have succeeded in creating polymers with high degrees of ferromagnetic spin-coupling.

Synthesis

Based on literature precedents and our own experience with model oligomer systems[1,16] our polymer designs use 1,3,5-triarylbenzene,[17] 1,3,5-triaminobenzene[18] and 3,4′-diaminobiphenyl[19] to mediate the ferromagnetic spin-coupling[12] and aminium or aryl radical cation spin-carriers. The polymer syntheses use one of the very few reactions known to give a high yield in the formation of carbon–carbon single bonds between aromatic rings—the Suzuki reaction.[20] The syntheses of the aryl bromide and arylboronic acid monomers are summarized in Schemes 1–3.

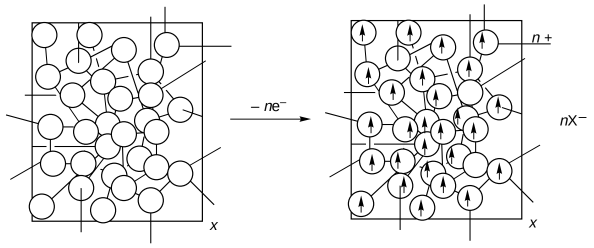
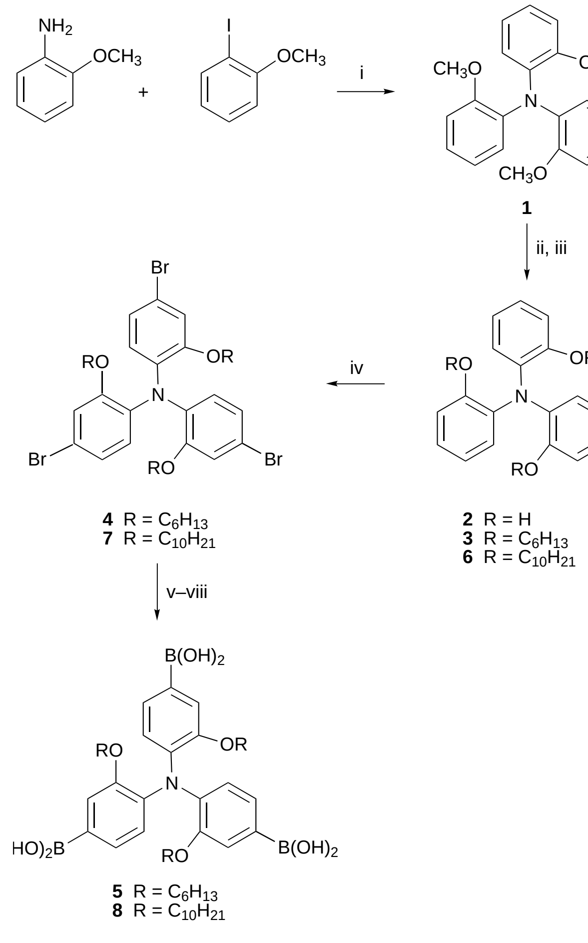
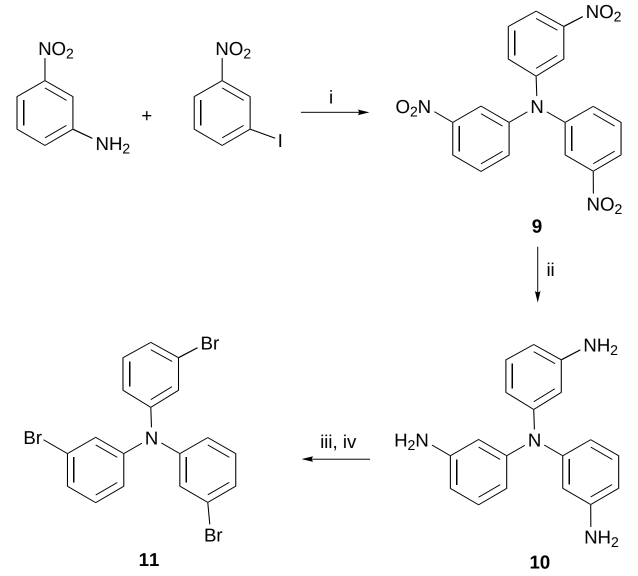


Fig. 2 Scheme for the production of a radical cation based high-spin/ferromagnetic polymer. The structure is randomly networked in three dimensions and arranged such that, following p-doping, each spin-bearing radical cation site is ferromagnetically coupled to up to three others. The dopable sites are represented by the circles and the bonding pathways through which the ferromagnetic spin coupling is mediated by the lines. Note that, because of the multiplicity of connecting pathways, the presence of a few undoped, non-spin-bearing centres is not fatal to the propagation of ferromagnetic spin coupling throughout the sample.

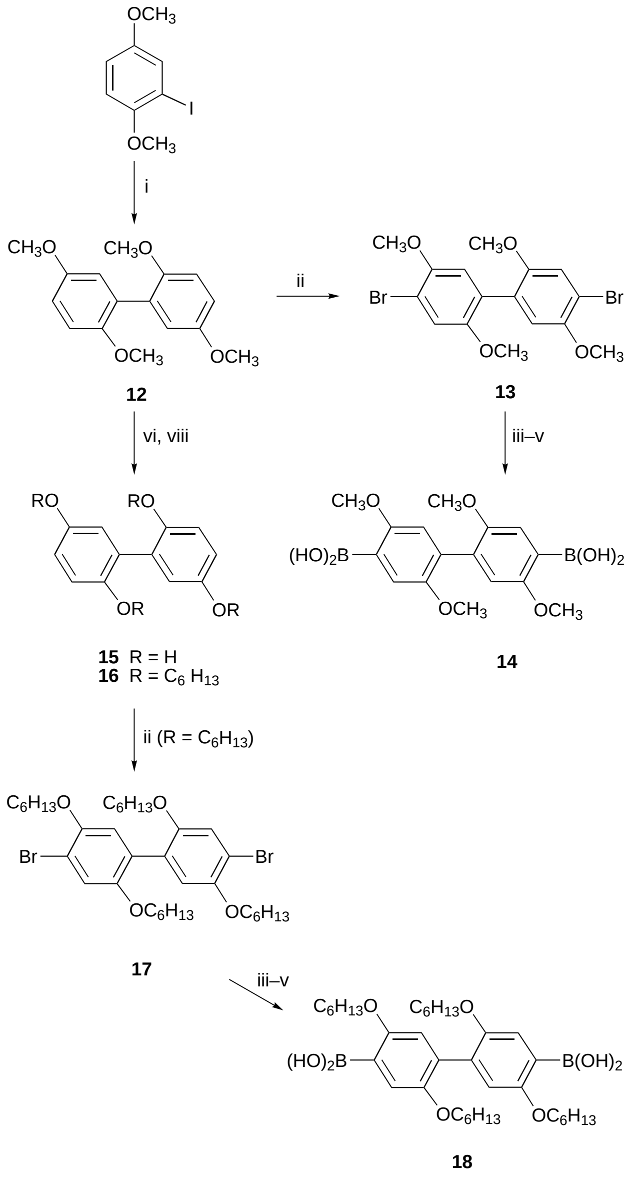


Scheme 1 *Reagents and conditions*: i, K_2CO_3, Cu, reflux; ii, BBr_3, $-78\,^{\circ}C$; iii, RBr, K_2CO_3, reflux; iv, Br_2, $CHCl_3$, 0 °C; v, BuLi, THF, $-78\,^{\circ}C$; vi, $(\mathrm{Pr^iO})_3B$, $-78\,^{\circ}C$; vii, HCl, H_2O



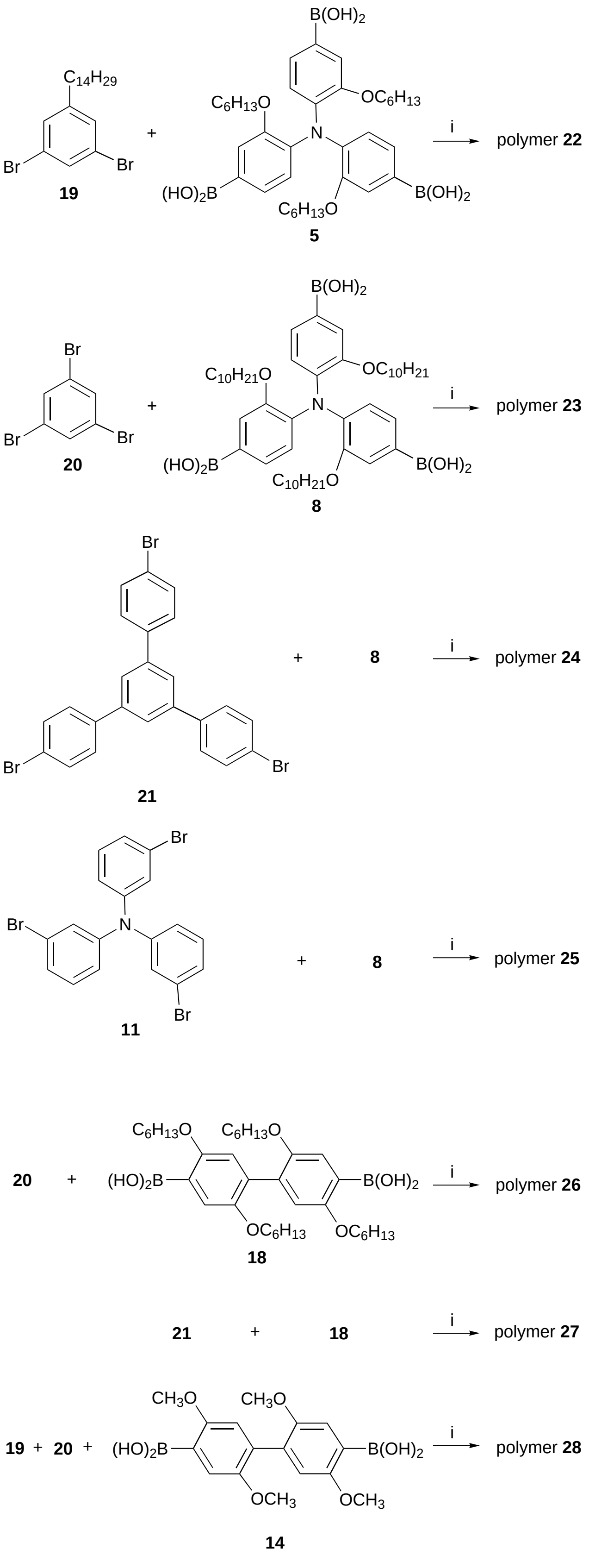
Scheme 2 *Reagents and conditions*: i, K_2CO_3, Cu, reflux, 18-crown-6; ii, Sn, HCl, EtOH, reflux; iii, HBr, $NaNO_2$, $-5\,^{\circ}C$; iv, CuBr, HBr

Most of the reactions used to make the monomers (Schemes 1–3) are quite simple and high-yielding. Of the (rather few) reactions that can be used to form triarylamines, the copper mediated reaction between primary aryl amines and aryl iodides in the presence of potassium carbonate,[21] whilst considered not high-yielding enough to use as the basis of the polymerization step, is perfectly satisfactory for making the monomers. On some occasions we have used a crown ether additive to aid the reaction but this is not essential. The regiochemistry of the bromination reactions of the substrates **3**, **6**, **12** and **16** is clearly critical to eventually achieving the desired coextensive, ferromagnetically coupled spin systems. In each case only a single regioisomer was obtained. In the case of compounds **12** and **16** its structure followed unambiguously from the proton NMR spectra (the absence of a *meta* coupling between the aromatic hydrogens). In the case of compounds **3** and **6** the proton NMR spectra showed that there was a 1,2,4-trisubstituted ring in the product. For compound **4** there was a doublet at $\delta 6.68$, $J = 8.3$ Hz, a double doublet at $\delta 6.89$, $J = 8.3$ and 2.2 Hz, and a doublet at $\delta 6.91$, $J = 2.2$ Hz. Given that, in non-planar aromatics (such as these) calculated chemical shifts can be an unreliable guide, such a spectrum would be consistent with bromination either *para* to the nitrogen or *para* to the alkoxy group. The desired structures (shown), in which bromination has occurred *para* to nitrogen, seemed *a priori* more probable and were confirmed by NOE experiments. In particular there was a strong NOE between the signal for the first methylene of the hexyloxy group and the signal at $\delta 6.91$ but none between this methylene and the signal at $\delta 6.68$.

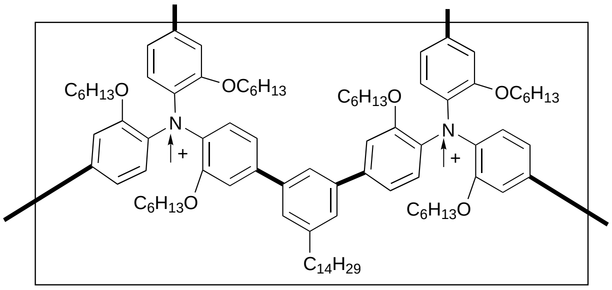


Scheme 3 *Reagents and conditions*: i, Cu, DMF, reflux; ii, Br_2, $CHCl_3$, 0 °C; iii, BuLi, THF, $-78\,^{\circ}C$; iv, $(\mathrm{Pr^iO})_3B$, $-78\,^{\circ}C$; v, HCl, H_2O; vi, BBr_3, CH_2Cl_2, $-78\,^{\circ}C$; vii, $C_6H_{13}Br$, EtOH, K_2CO_3, reflux

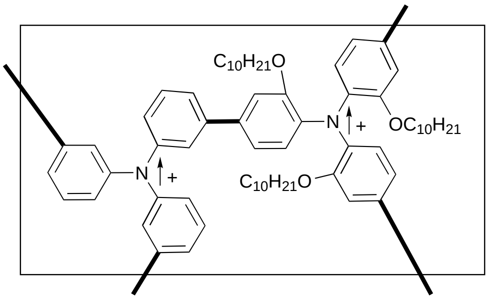
In principle, these monomers can be used as building blocks in many different combinations together with readily available 1,3-dibromobenzene derivatives (*e.g.* compound **19**), 1,3,5-tribromobenzene derivatives (*e.g.* compound **20**), suitable polybrominated polyphenylenes (*e.g.* compound **21**) or suitably polybrominated polynuclear aromatics to produce many different polymers that on doping are potentially high spin. The actual polymerization reactions we have carried out so far are representative and are summarized in Scheme 4, whereas Fig. 3 shows the essential ferromagnetic coupling entities in the doped polymers. The choice of the Suzuki reaction, a carbon–carbon bond forming reaction, for the synthesis of the polyaryl amines, rather than a carbon–nitrogen bond forming reaction, was dictated by the desire for high molecular masses, the known high-yielding nature of the Suzuki reaction and the known low-yielding nature of triarylamine-forming reactions in which formation of the carbon–nitrogen bond is the key step. Although some of our polymers (particularly **22–24**) are analogous to those made by Yoshizawa *et al.*[22] this alternative approach to the synthesis (Yoshizawa *et al.* employed the



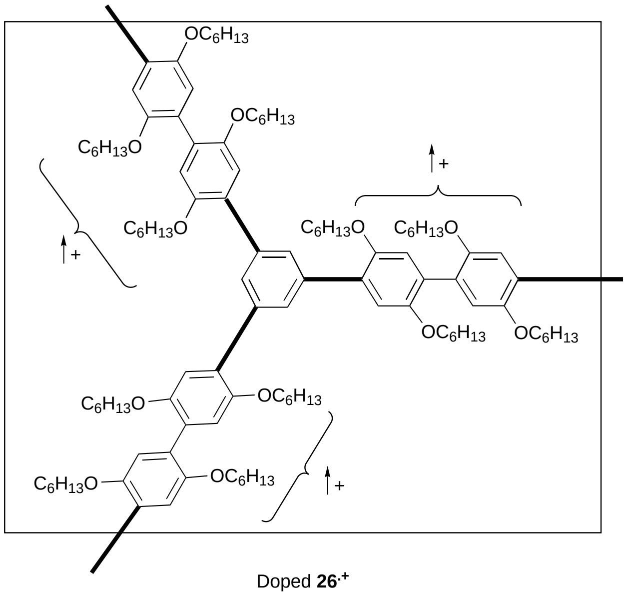
Scheme 4 *Reagents and conditions*: i, $Pd(PPh_3)_4$, toluene, aq. Na_2CO_3, reflux



Doped $\mathbf{22}^{\cdot +}$



Doped $\mathbf{25}^{\cdot +}$



Doped $\mathbf{26}^{\cdot +}$

Fig. 3 Part structures for the doped versions of the polymers **22**, **25** and **26** showing the essential ferromagnetic spin-coupling pathways in each case. In each formula the bonds formed in the Suzuki coupling step are shown in bold. In polymer **22** $N^{\cdot +}$ centres are ferromagnetically coupled 1,3 through benzene. Polymers **23** and **24** are simple variants on this theme. In polymer **25** $N^{\cdot +}$ centres are ferromagnetically coupled 3,4′ through biphenyl. In polymer **26** biphenyl radical cation moieties are ferromagnetically coupled 1,3 through benzene. Polymers **27** and **28** are simple variants on this theme. In all of the polymers, all of the doped/dopable sites are equivalent except for polymer **25** (as shown) and polymer **28**, because in this case a mixture of coupling units was employed.

carbon–nitrogen bond forming strategy) allows higher molecular masses to be achieved and the structure to be more easily varied, and enables us to produce networked rather than linear polymers. Furthermore, the extended conjugation in the polymers produced in this way (see particularly polymer **24**) means that the radical cations should be more stable and less prone to dimerization and other reactions. From the structural standpoint, each polymer can be thought of as a randomly networked array of fairly rigid jointed rods bearing flexible side-chains. In all cases, as shown in Fig. 3, the effective 'ferromagnetic coupling unit'[12] in the doped polymers is *m*-phenylene or a 3,4′-disubstituted biphenyl; the ferromagnetic spin coupling mechanism is analogous to that found in *m*-quinodimethane (Fig. 1) or 3,4′-dimethylenebiphenyl. Each polymer was based on a network in which it was intended that (after doping) each spin-bearing centre would be ferromagnetically coupled to three others. In the case of polymers **22** and **25** the networking/crosslinking is provided through the amino groups. In the case of polymers **26–28** it is provided through the 1,3,5-trisubstituted benzene residues and in the case of polymers **23** and **24** through both of these. All of the polymers used in the studies detailed below were purified and fractionated by repeated reprecipitation from chloroform, diethyl ether or dichloromethane with methanol. In some cases a substantial amount of a black chloroform-insoluble fraction was also obtained. This was presumably higher molecular mass polymer but it proved intractable and (on the basis of combustion analysis) difficult to free from contaminating solvent and reagents. During the fractionation and in all subsequent steps, contact with metallic implements such as spatulas was rigorously avoided. In each case, for solutions of the fractionated polymer in $CDCl_3$, clean ^1H NMR spectra were obtained with the correct integration and these are detailed in the Experimental section. The line widths, whilst too great to provide useful spin coupling information, were nonetheless narrow enough (down to 10 Hz) to suggest that these polymers are quite mobile in solution. The elemental analysis of the purified polymer **22** showed that it contained *ca.* 1% by mass of bromine which corresponds to about 4% unreacted 'end' groups. Elemental analyses, calculated analyses, estimates of the percentages of unreacted end groups, and molecular masses for all of the polymers are given in Table 1. The normalized C,H,N analyses, together with the NMR spectra confirm that, other than that some unreacted end-groups are present, all of the polymers were obtained in good purity. The molecular masses were determined by gel permeation chromatography against polystyrene standards. For such networked polymers this gives useful relative values but is known to substantially underestimate the absolute values.[23]

Electrochemical characterization of the polymers

From the electrochemical standpoint the polymers **22–28** are unusual: unlike either conventional conjugated polymers or polymers that contain isolated, non-conjugated electrophores.[28] The individual electrophores in these polymers are cross-conjugated so that, in the doped polymer, there is spatial overlap between the spin and hole distribution of each site but only the nearest neighbour sites.[1,24]

The electrooxidation of polymers **22–25** has been studied using cyclic voltammetry in dichloromethane solution using 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. A three electrode system was employed with platinum working and counter electrodes and a silver/saturated lithium chloride/chloroform reference electrode.[25] Convolution/deconvolution voltammetry using the semi-integral I_1 of the voltammetric current and time was used in the determination of the half-wave potentials.[26] Fig. 4(*a*)–(*d*) shows the results for the four polymers. Software correction of the potential axis was applied sufficient to yield a symmetrical peak for the ferrocene/ferrocenium couple (under identical conditions) the $E_{1/2}$ of which was also taken as the zero/reference point. For scans that only encompass the first oxidation step (0.3–0.7 V) both these polymers and the corresponding oligomers[24] give peaks for the forward and reverse scans that are well matched in amplitude showing that, under these conditions, the significant first oxidation step is not accompanied by chemical decomposition. The $E_{1/2}$ values also correspond to those seen in the corresponding oligomers. The polymers **22, 23** and **25** show a first oxidation peak at 220–270 mV as expected for triarylamine electrophores of the type $\{C_6H_5[C_6H_3(OR)]\}_3N$. The polymer **24** contains the extended triarylamine electrophore of the $\{C_6H_5C_6H_4[C_6H_3(OR)]\}_3N$ type and, not surprisingly, is oxidized at a lower potential: 210 mV. In the polymer **25** there are two types of electrophore. The oxidation of the electrophore $\{C_6H_5[C_6H_3(OR)]\}_3N$ occurs at 270 mV and that of the $(C_6H_5)_3N$ electrophore at 580 mV.[24,27] In all four cases the step corresponding to formal bipolaron/dication N^{2+} formation is at much higher potentials (>950 mV). A problem that was encountered for all of these polymers, and which is evident from Fig. 4(*a*)–(*d*), is that, once the solution containing the polymer had been subjected to one CV 'cycle', subsequent experiments suffered from a non-zero current at the initial potential. This phenomenon normally implies that, once oxidized, some polymer adheres to the surface of the electrode. The approximate widths at half height for the first oxidation step peaks on the first cycle are **22** = 240, **23** = 340, **24** = 200, and **25** = 500 mV. For a homogeneous polymer consisting of non-interacting electrochemically ident-

Table 1 Analytical data for polymers **22–28**

polymers (and the monomers from which they were made)	elemental analysis (calculated values)	normalised C,H,N elemental analysis (calculated values)	M_w[a] /10^3	approx. % unreacted end groups[b]
22 (5+19)	C: 83.2%; H: 10.4%; N: 1.3%; Br: <1% (C: 83.4%; H: 10.1%; N: 1.5%)	C: 87.6%; H: 11.0%; N: 1.5% (C: 87.8%; H: 10.6%; N: 1.6%)	80	<4
23 (8+20)	C: 77.8%; H: 9.3%; N: 1.5%; Br: 4.5% (C: 82.5%; H: 9.6%; N: 1.7%)	C: 87.8%; H: 10.4%; N: 1.6% (C: 87.9%; H: 10.1%; N: 1.8%)	42	16
24 (8+21)	C: 77.4%; H: 7.9%; N: 1.2%; Br: 9.4% (C: 85.3%; H: 8.6%; N: 1.4%)	C: 89.4%; H: 9.1%; N: 1.6% (C: 89.5%; H: 9.0%; N: 1.5%)	84	44
25 (8+11)	C: 80.6%; H: 8.9%; N: 2.6%; Br: 5.2% (C: 83.2%; H: 8.8%; N: 2.9%)	C: 87.5%; H: 9.6%; N: 2.8% (C: 87.6%; H: 9.3%; N: 3.1%)	104	21
26 (18+20)	C: 74.6%; H: 8.6%; Br: 6.4% (C: 79.7%; H: 9.6%)	C: 89.7%; H: 10.3% (C: 89.2%; H: 10.8%)	5.5	25
27 (18+21)	C: 80.3%; H: 8.2%; Br: 1.2% (C: 82.8%; H: 8.8%)	C: 90.7%; H: 9.3% (C: 90.4%; H: 9.6%)	115	6
28 (14+19 +20)[c]	C: 78.0%; H: 7.3%; Br: 1.8% (C: 77.1%; H: 7.3%)	C: 91.3%; H: 8.7% (C: 91.5%; H: 8.5%)	18	3

[a]GPC against polystyrene standards. [b]Based on bromine/carbon ratio. [c]Molar ratio of three parts of **19** to two of **20** to six of **14**.

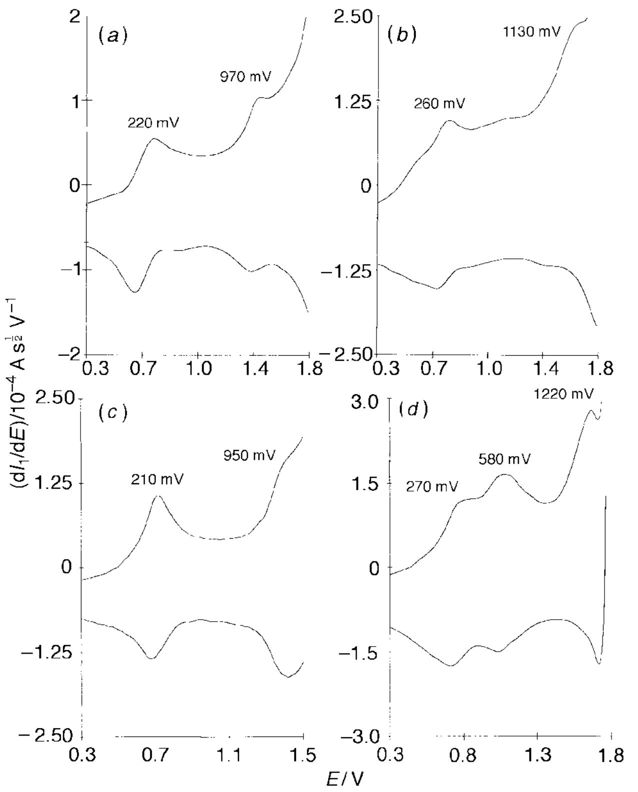


Fig. 4 Convolution/deconvolution cyclic voltammetry results (using the semi-integral I_1 of the voltammetric current and time) for polymers (*a*) **22**, (*b*) **23**, (*c*) **24** and (*d*) **25** in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The lower scale gives the potentials relative to the silver/saturated lithium chloride/chloroform reference electrode. The potentials written above each peak are the potentials relative to $E_{1/2}$ of the ferrocene/ferrocinum couple measured under identical conditions.

ical centres and fast reversible electron transfer we expect a width of *ca.* 90 mV at 300 K.[28] Studies of model oligomers have shown that coulombic interactions between sites.[28] account for a part of the broadening (up to *ca.* 100 mV).[24] Further broadening may result from the fact that we are short of the fast electron transfer limit or from structural inhomogeneities or (even in the first cycle) from build-up of the polymer film on the electrode surface.

Overall, these electrochemical studies show that these polymers should dope to the polaron $N^{\cdot +}$ level in a fairly straightforward manner giving stable radical cation products and having little or no tendency to oxidize to the spinless N^{2+} bipolaron level.

Studies of chemical doping of the polymers

The doping of each polymer was investigated for solutions in trifluoroacetic acid using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or thallium(III) trifluoracetate as the oxidant and in dichloromethane using $NOBF_4$, $NOPF_6$, or antimony pentachloride as the oxidant. In each case the doping levels achieved were assessed by EPR spectroscopy against a standard solution of diphenylpicrylhydrazyl (DPPH). The results of these experiments are summarized in Table 2. In most cases the best doping method for a solution of the polymer was treatment with an excess of $NOBF_4$. The EPR spectra of these $NOBF_4$ doped polymers (either as neat solids or as frozen solutions at 100 K) were very similar to those recently reported for the corresponding oligomers.[24] In the $\Delta m=1$ region they showed fairly narrow peaks with $\Delta H_{pp} < 20$ G, consistent in general width with the expected zero-field splitting parameters but too poorly resolved to provide meaningful values of $|D/hc|$ or $|E/hc|$. As expected the $\Delta m=2$ regions of most of these spectra showed no or barely detectable half field lines.[29] The exception was the doped polymer **25** for which the half field line was moderately strong.

Characterization of the magnetic properties of the doped polymers

Susceptibility studies on the purified, undoped polymers between 2 K and room temperature showed simple diamagnetic behaviour and that they were free from magnetic impurities. These polymers were designed with the hope that, when doped beyond the *ca.* 70% threshold, they would generate spin-clusters large enough to give ferromagnetic behaviour. At lower levels of doping (all that we have been able to achieve so far) they are expected to contain a non-interacting polydisperse population of $S=1/2$, 1, 3/2, 2 *etc.* spin clusters—to behave like other 'high-spin' polymers.[22,30–33] This proves to be the case although they are 'higher-spin' than most. After doping of a solution of the polymer with an excess of $NOBF_4$, the solvent was removed under vacuum and the residue dried for about 15 h at 10^{-3}–10^{-4} mmHg. The doped polymer was transferred to the 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 to 5 T) at constant temperature (2 K). The measurements were corrected to allow for the diamagnetic contribution of the polymer and of the sample holder. The levels of doping calculated on the basis of these magnetometer measurements were close to those determined in the model doping experiments (compare Tables 2 and 3). The results obtained from the temperature dependence studies were very similar for all of the polymers. Those for polymer **22** doped with $NOBF_4$ are shown in Figs. 5 and 6 and are typical. These are dilute spin systems and the small value of the paramagnetic term relative to the diamagnetic correction (particularly at higher temperatures) leads to relatively large errors but, within these error limits, the Curie law is obeyed. The main problem with these and all high-spin polymers is to characterize the extent of the ferromagnetic spin coupling and the distribution

Table 2 EPR studied of achievable levels of doping (expressed as spins per g of polymer × 10^{-19}) for polymers **22–28**

polymers (and the monomers from which they were made)	DDQ CF_3CO_2H	$NOBF_4$ DCM	$NOPF_6$ DCM	$Tl(O_2CCF_3)_3$ CF_3CO_2H	$SbCl_5$ DCM
22 (5+19)	6.2	10[a]	6.0	1.6	—
23 (8+20)	3.8	—	5.8[b]	5.9	—
24 (8+21)	0.99	4.9[c]	4.2	4.5	1.2
25 (8+11)	3.2	4.3[d]	4.2	3.3	5.5
26 (18+20)	6.3[e]	1.2	1.0	2.9	0.38
27 (18+21)	—	4.4[f]	0.31	2.0	2.8
28 (14+19+20)	7.7	6.8	—	—	16[g]

Percentages of sites doped: – [a]=16; [b]=8; [c]=8; [d]=3.4; [e]=9; [f]=6; [g]=11%.

Table 3 Magnetic properties of the doped polymers **22–28**

polymers (and the monomers: from which they were made)	doping agent	% of sites doped[a]	spin system S[a]
22 (**5**+**19**)	$NOBF_4$	15	5/2
23 (**8**+**20**)	$NOBF_4$	9.6	3/2
24 (**8**+**21**)	$NOBF_4$	9.9	1
25 (**8**+**11**)	$NOBF_4$	3.9	1/2
27 (**18**+**21**)	$NOBF_4$	16[b]	1
28 (**14**+**19**+**20**)	$SbCl_5$	15	1/2

[a] SQUID measurements at 2.0 K. [b] Based on EPR measurements at room temp.

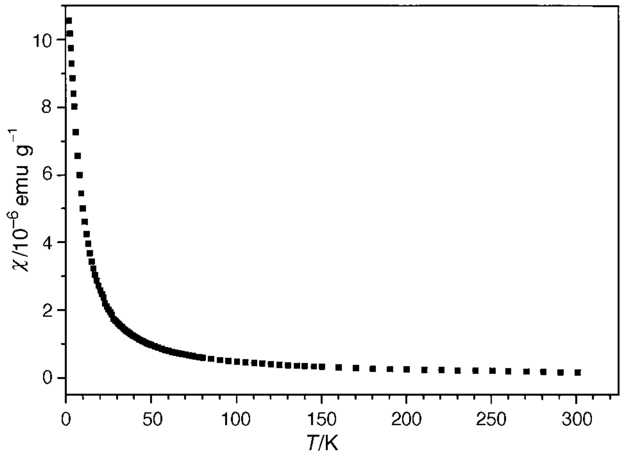


Fig. 5 Susceptibility χ of the polymer **22** doped with $NOBF_4$ as a function of temp. at a field of 5 T

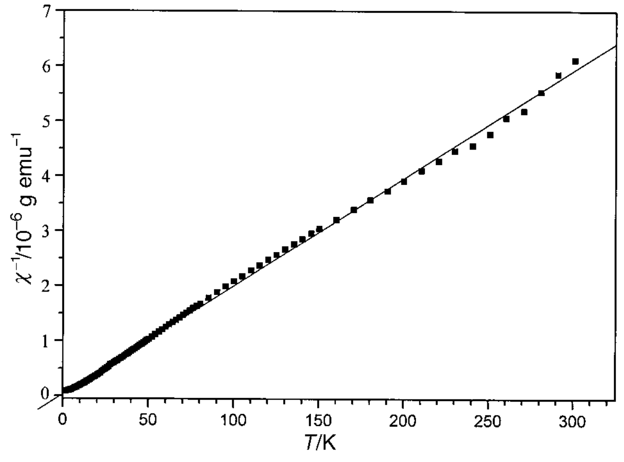


Fig. 6 χ^{-1} for the polymer **22** doped with $NOBF_4$ as a function of temp. at a field of 5 T

of spin clusters. There is no ideal way of doing this but, provided the clusters are non-interacting, an empirical measure is provided by comparing the experimental dependence of magnetization on applied field to theoretical Brillouin functions for monodisperse $S=1/2$, 1, 3/2, 2 *etc.* spin systems. However, it should be noted that, that for a disperse spin system, an 'average' Brillouin function is never followed in a strict manner and typically the magnetization tends to increase 'too rapidly' at low fields and 'too slowly' at high fields.[30] Typical plots are shown in Figs. 7–10. Fig. 7 shows behaviour for the doped polymer **28** which is indistinguishable from that for an $S=1/2$ system. The results for the doped polymer **25** were similar. The probable reason is that, in these two systems, not all of the sites that can be oxidized are the same or will have the same oxidation potential. This is clearly shown in the cyclic voltammetry study of polymer **25** [Fig. 4(*d*)]. Since, in this case, the high and low oxidation potential sites alternate within the network, at low doping levels only alternate sites carry a spin so that $S=1/2$ behaviour is inevitable. However, the doped polymers **22, 23, 24** and **27** showed evidence of the expected ferromagnetic spin coupling. Those for the doped polymers **24** (Fig. 8) and **27** are closest to an $S=1$ system, that for doped polymer **23** (Fig. 9) to an $S=3/2$ system, and that of doped polymer **22** to $S=5/2$ (Fig. 10).

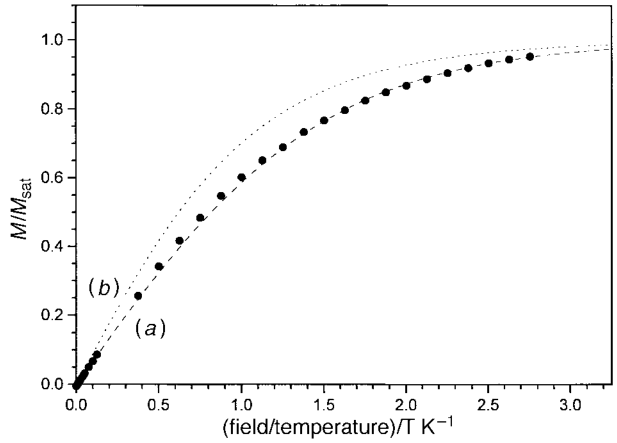


Fig. 7 Field dependence of the magnetization of polymer **28** doped with $SbCl_5$ (●) as a function of field at 2 K compared to theoretical Brillouin functions for (*a*) $S=1/2$ and (*b*) 1 systems

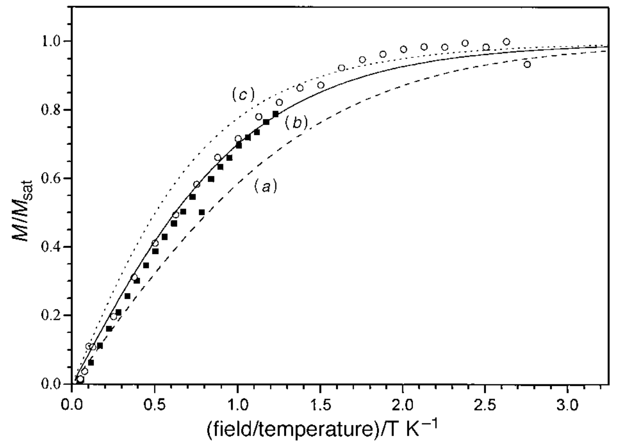


Fig. 8 Field dependence of the magnetization of polymer **24** doped with $NOBF_4$ as a function of field at (○) 2 and (■) 4.5 K, compared to theoretical Brillouin functions for (*a*) $S=1/2$, (*b*) 1 and (*c*) 3/2 systems

Conclusions

In terms of the extent of ferromagnetic spin coupling, the results for these new doped polymers are better than those previously reported for polyphenoxyl radicals,[31] for poly(*m*-phenylenediamine)s (maximum $S=1$),[22] for polymer derivatives of phenylenebis(*tert*-butyl nitroxide) (also maximum $S=1$),[32] for polymers of the poly(*m*-quinodimethane) type (maximum $S=2$)[33] and of most of the polymers reported by the group of Dougherty (mostly $S<5/2$)[30] but are short of their results for doped polymers based on a *m*-phenylenevinylenethienyl moiety (maximum S up to 9/2 'in some samples'). However, unlike Dougherty's polymers, which are linear, these new polymers are networked and so should display an attainable percolation limit. The biggest problem common to the polymers described in this paper and those studied by Dougherty is that the doping levels achieved are disappointingly low and

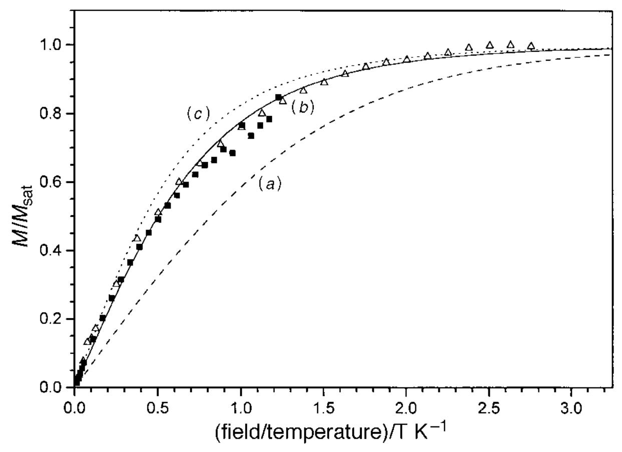


Fig. 9 Field dependence of the magnetization of polymer **23** doped with $NOBF_4$ as a function of field at (△) 2 and (■) 4.5 K, compared to theoretical Brillouin functions for (*a*) $S = 1/2$, (*b*) 3/2 and (*c*) 2 systems

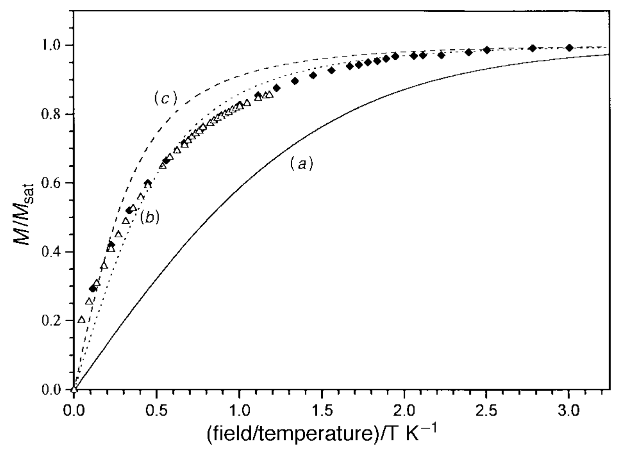


Fig. 10 Field dependence of the magnetization of polymer **22** doped with $NOBF_4$ as a function of field at (◆) 1.8 and (△) 4.5 K, compared to theoretical Brillouin functions for (*a*) $S = 1/2$, (*b*) 5/2 and (*c*) 4 systems

this is a problem that is proving difficult to solve. There seem to be two main possible explanations for the low doping levels. One possible explanation is electrostatic.[24] To ensure local ferromagnetic spin coupling, the local topology of the doped polymers has to mimic that of a coextensive diradical diion.[1,24,34] There has to be local spatial overlap of both the unpaired spin distributions and charges. Furthermore, the stronger the ferromagnetic coupling, the bigger the overlap, the bigger the local charge–charge repulsion, the more difficult it will be to achieve high doping levels. However, the fact that the oxidation 'peaks' shown in Fig. 4(*a*)–(*d*) are not very broad, together with the results of studies on model oligomers under a range of conditions suggest that this effect is not very great.[24] A much more feasible explanation is that the effect is steric; the difficulty of accommodating large counter-ions within these rather rigid polymer networks. Until the problem of low doping levels is solved and doping levels of *ca.* 70% are achieved we will not know whether this approach to 'molecular' magnets is a feasible alternative to those already explored.[35] If the problem is simply one of accommodation of the counter-ions this is one that it should be possible to overcome in redesigned polymers and experiments to this end are in progress.

Experimental

Melting points were determined on a Reichert hot stage apparatus and are uncorrected. Samples for combustion analysis were routinely dried by heating at 65 °C and 0.5 mmHg for 3 d. Column chromatography on silica refers to the use of Merck Kieselgel 7731 Type 60 and thin layer chromatography to Merck Kieselgel 7730 GF254. Routine concentration of solutions or removal of solvent was achieved using a Buchi rotary evaporator attached to a water pump.

Solvents were routinely purified according to the procedures recommended by Perrin.[36] Tetrahydrofuran was distilled from sodium and benzophenone. Toluene, dichloromethane (DCM), hexane and chloroform were distilled from calcium hydride. All other starting materials were used as purchased.

UV–VIS spectra were recorded using a Pye-Unicam PU8800 UV–VIS spectrophotometer. NMR spectra were recorded on a General Electric QE300 or a Bruker AM400 instrument. Chemical shifts are relative to tetramethylsilane; *J* values are in Hz. Mass spectra were obtained on a VG Autospec instrument. Gel permeation chromatography was performed on two mixed bed columns (Polymer Laboratories Ltd) using a Merck L-6000 pump, and a Varex light-scattering detector detector. Tetrahydrofuran (HPLC grade) was used as an eluent at a flow rate of 1 ml min^1. Molecular masses are reported relative to two narrow polystyrene standards. Magnetic susceptibility measurements were made on a Quantum Design MPMS SQUID magnetometer at fields between 0 and 55 kG and temperatures between 1.8 K and room temp. EPR measurements were made on an X-band ER-200 Bruker EPR spectrometer with spin concentrations being determined against standard DPPH in benzene at room temp.

Tris(2-methoxyphenyl)amine 1

A stirred mixture of freshly distilled 2-methoxyaniline (68–70 °C at 0.5 mmHg, 3.69 g, 30 mmol), 2-iodoanisole (16.3 g, 70 mmol), powdered anhydrous potassium carbonate (20.9 g, 151 mmol), copper powder (6.6 g, 100 mmol), 18-crown-6 (1.0 g, 3.78 mmol) and 1,2-dichlorobenzene (120 cm^3) was refluxed for 48 h. After cooling, the insoluble inorganic material was filtered off under suction and the dark brown filtrate collected. The insoluble material was washed with dichloromethane (4 × 500 cm^3). The combined filtrate and organic phase was washed with dilute aqueous ammonia and water and dried with magnesium sulfate. The solvent was removed under reduced pressure. After reprecipitation of the dark brown residues from hexane (50 cm^3) the crude solid was recrystallised from hexane–ethanol (2 : 1) to give the product **1** (9.2 g, 91%) as light brown crystals, mp 139.5–140 °C (Found: C, 75.30; H, 6.50; N, 3.95. $C_{21}H_{21}NO_3$ requires C, 75.20; H, 6.31; N, 4.17%); δ_H ($CDCl_3$) 3.56 (9H, s, —OMe), 6.79–6.86 (9H, m, ArH) and 6.99–7.05 (3H, m, ArH); δ_C ($CDCl_3$) 55.7, 112.5, 120.6, 123.7, 124.4, 137.7 and 153.1; *m*/*z* 335 (M^+, 100%) and 289 (97).

Tris(2-hydroxyphenyl)amine 2

A solution of boron tribromide (11.30 g, 45 mmol) in dry dichloromethane (40 cm^3) at −78 °C was added to a solution of tris(2-methoxyphenyl)amine **1** (5.02 g, 15 mmol) in dichloromethane (150 cm^3) at −78 °C over 15 min. The mixture was stirred at −78 °C. A white suspension formed over about 30 min. The temperature of the suspension was raised to ambient and the solid slowly redissolved. The resulting light purple–brown solution was stirred overnight. Water (200 cm^3) was added and the organic layer separated. The acidic aqueous solution was extracted with diethyl ether (3 × 50 cm^3) and the combined organic layer was dried with sodium sulfate. The solvent was removed to give a crude light brown solid. Recrystallization from ethanol–hexane (1 : 1) gave the product **2** (4.5 g, 97%) as white cubic crystals mp 167.5–168 °C (Found: C, 73.90; H, 5.25; N, 4.60. $C_{21}H_{21}NO_3$ requires C, 73.70; H, 5.15; N, 4.77%); δ_H($CDCl_3$) 5.51 (3H, s, —OH), 6.81–6.93 (9H, m, ArH) and 7.05 (3H, dt, *J* 8.2 and 1.6, ArH,); *m/z* 293 (M^+, 100%).

Tris(2-hexyloxyphenyl)amine 3

A mixture of tris(2-hydroxphenyl)amine **2** (4.30 g, 14.70 mmol), 1-bromohexane (10.90 g, 66 mmol) and powdered potassium carbonate (22.20 g, 160 mmol) was stirred and refluxed in dry ethanol (200 cm^3) for 12 h. After cooling to room temp. the insoluble material was filtered off and the filtrate collected. It was concentrated under reduced pressure to give a volume of about 20 cm^3. Dichloromethane (150 cm^3) was added. 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 yellow–brown oily residue. Column chromatography eluting with dichloromethane gave the product **3** as a pale yellow oil (6.41 g, 80%) (Found: C, 78.95; H, 9.65; N, 2.35. $C_{36}H_{51}NO_3$ requires C, 79.22; H, 9.41; N, 2.56%); δ_H ($CDCl_3$) 0.84 (9H, t, *J* 7.0, Me), 0.98–1.32 (24H, m, methylenes), 3.78 (6H, t, *J* 6.3, OCH_2-) and 6.7–7.5 (12H, m, Ph); δ_C ($CDCl_3$) 14.2, 22.6, 25.5, 29.4, 31.8, 68.5, 114.2, 120.8, 123.4, 124.9, 138.3 and 152.9; *m/z* 545 (M^+, 76%), 359 (25), 278 (18) and 110 (100).

Tris(4-bromo-2-hexyloxyphenyl)amine 4

A solution of bromine (5.0 g, 31.3 mmol) in chloroform (60 cm^3) was added to a stirred solution of tris(2-hexyloxyphenyl)amine **3** (8.0 g, 10.2 mmol) in chloroform (100 cm^3) at 0 °C over 30 min. After the addition, a blue–green reaction mixture was formed which was allowed to warm to room temp. After stirring for 12 h, the reaction mixture was washed with distilled water (2×200 cm^3), dilute sodium metabisulfite solution and brine, and then dried with magnesium sulfate. The solvent was removed to given a dark brown oil. The product was purified by column chromatography on silica gel, eluting with 30% dichloromethane in hexane to give the product **4** as a pale yellow oil (7.1 g, 91%) (Found: C, 55.40; H, 6.30; N, 1.70; Br, 30.50. $C_{36}H_{48}Br_3NO_3$ requires C, 55.26; H, 6.18; N, 1.79; Br, 30.63%); δ_H ($CDCl_3$) 0.87 (9H, t, *J* 7.2, Me), 0.98–1.42 (24H, m, methylene), 3.71 (6H, t, *J* 6.0, OCH_2-), 6.67 (3H, d, *J* 8.1, ArH) and 6.78–6.92 (6H, m, ArH); δ_C ($CDCl_3$) 14.1, 22.5, 25.3, 29.0, 31.6, 68.5, 116.0, 116.6, 123.4, 125.8, 136.2 and 153.4; *m/z* 783 (M^+, 100%) and 781 (97).

Tris[4-(dihydroxyboryl)-2-hexyloxyphenyl]amine 5

n-Butyllithium in hexane (8.13 cm^3, 1.6 M, 13 mmol) was added to a solution of tris(4-bromo-2-hexyloxyphenyl)amine **4** (3.13 g, 4 mmol) in dry tetrahydrofuran (120 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 (13.50 g, 71.0 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 temp. It was left to stand overnight (~12 h). The mixture was cooled to −78 °C and the intermediate ester was hydrolysed by adding 2 M hydrochloric acid, slowly warming to room temp., and stirring for a further 1 h before workup. Diethyl ether (100 cm^3) was added and the ether layer separated. The aqueous layer was extracted with more diethyl ether (2×20 cm^3). The combined ether layers were washed with water and dried with magnesium sulfate. The ether solution was concentrated to about 50 ml volume, and the product precipitated by adding hexane (60 cm^3). The white precipitate was collected by filtration under suction, and the solid was washed with more ether–hexane (1 : 1) to give the product **5** (2.16 g, 81%) as a white solid. The product is insoluble in dichloromethane, chloroform and hexane but it is soluble in acetone and tetrahydrofuran (Found: C, 62.95; H, 8.05; N, 1.60. $C_{36}H_{54}B_3NO_9$ requires C, 63.84; H, 8.03, N; 2.07%); δ_H ([$^2H_6$]acetone) 0.82 (9H, t, *J* 7.1, Me), 1.03–1.28 (24H, m, methylene), 3.79 (6H, t, *J* 6.1, OCH_2-), 6.76 (3H, d, *J* 7.7, ArH), 6.99 [6H, s, $B(OH)_2$], 7.34 (3H, d, *J* 7.9, ArH) and 7.43 (3H, s, Ph).

Tris(2-decyloxyphenyl)amine 6

A mixture of tris(2-hydroxphenyl)amine **2** (3.52 g, 12.0 mmol), 1-bromodecane (9.28 g, 42.0 mmol) and powdered potassium carbonate (11.6 g, 84.0 mmol) in ethanol (120 cm^3) was stirred and refluxed for 20 h. After cooling to room temp., insoluble materials were filtered off, the yellowish filtrate was concentrated to about 15 cm^3 and chloroform (200 cm^3) added. The organic layer was washed with 2 M aqueous sodium hydroxide, water and brine, and dried with magnesium sulfate. Solvent was removed to give a brownish oil. The product was purified by column chromatography eluting with dichloromethane–hexane (1 : 1) collecting the first main fraction **6** as a light orange oil (7.13 g, 83%)(Found: C, 80.60; H, 10.60; N, 1.85. $C_{48}H_{75}NO_3$ requires C, 80.73; H, 10.58; N, 1.96%); δ_H ($CDCl_3$) 0.88 (9H, t, *J* 6.4, Me), 0.97–1.26 (48H, m, methylene), 3.74 (6H, t, *J* 6.2, OCH_2-) and 6.74–6.97 (12H, m, ArH); δ_C ($CDCl_3$) 14.1 (1C), 22.7 (1C), 25.8 (1C), 29.4 (2C), 29.6 (2C), 29.7 (1C), 32.0 (1C), 68.5 (1C), 114.2 (1C), 120.8 (1C), 123.3 (1C), 124.9 (1C), 138.3 (1C) and 152.9 (1C); *m/z* 714 (62%), 713 (M^+, 100), 574 (40), 573 (78), 415 (37) and 275 (40).

Tris(4-bromo-2-decyloxyphenyl)amine 7

A solution of bromine (3.50 g, 21.8 mmol) in chloroform (80 cm^3) was slowly added to a solution of tris(2-decyloxyphenyl)amine **6** (6.7 g, 7 mmol) in chloroform (120 cm^3) at 0 °C to give a blue–green solution. The mixture was stirred at 0 °C for 3 h, and then at room temp. for a further 2 h. Water (200 cm^3) was added, the organic layer separated, washed with brine and dried with magnesium sulfate. Evaporation gave a green oily residue. Chromatography eluting with 10% dichloromethane in hexane gave the product **7** as a clear oil (5.30 g, 77%) (Found: C, 60.45; H, 7.50; N, 1.30; Br, 25.40. $C_{48}H_{72}Br_3NO_3$ requires C, 60.63; H, 7.63; N, 1.47; Br, 25.21%); δ_H ($CDCl_3$) 0.88 (9H, t, *J* 6.5, Me), 0.97–1.48 (48H, m, methylene), 3.70 (6H, t, *J* 6.1, OCH_2-), 6.67 (3H, d, *J* 8.1, ArH), 6.88 (3H, d, *J* 8.2, ArH) and 6.90 (3H, m, ArH); *m/z* 953 (49%), 951 (M^+, 100), 949 (98), 947 (39), 811 (22) and 809 (21).

Tris[4-(dihydroxyboryl)-2-decyloxyphenyl]amine 8

n-Butyllithium in hexane (4.45 cm^3, 1.6 M, 7.1 mmol) was added to a solution of tribromo compound **7** (2.10 g, 2.21 mmol) in dry tetrahydrofuran (70 cm^3) over a period of 15 min at −78 °C under an argon atmosphere. A yellowish suspension formed within 10 min. The suspension was stirred at −78 °C for 1 h. It was slowly added to a solution of triisopropyl borate (6.67 g, 35 mmol) in tetrahydrofuran (10 cm^3) at −78 °C *via* a cannula under argon. The resulting mixture was first stirred at −78 °C for 2 h and then stirred at room temp. overnight. The mixture was cooled to −78 °C and the intermediate ester was hydrolysed by adding 2 M hydrochloric acid**,** slowly warming to room temp., and stirring for a further 1 h before workup. Diethyl ether (50 cm^3) was added to the mixture and the organic layer was separated, washed with water and dried with magnesium sulfate. It was concentrated to about 5 cm^3 and the product precipitated with hexane. After drying for 24 h under high vacuum the boronic acid **8** was obtained as a nearly white solid (1.55 g, 83%). The product **8** is insoluble in dichloromethane, chloroform and hexane, but soluble in diethyl ether and tetrahydrofuran (Found: C, 68.15; H, 9.10; N, 1.45. $C_{48}H_{78}B_3NO_9$ requires C, 68.18; H, 9.29; N, 1.65%).

Tris[4-(ethylenedioxyboryl)-2-decyloxyphenyl]amine 8a

Trisboronic ester **8a** was prepared by heating the trisboronic acid **8** (0.2 g, 0.236 mmol) and ethane-1,2-diol at high temp. until it completely dissolved. The excess ethane-1,2-diol was removed under high vacuum to yield compound **8a** as a brownish oil (0.20 g, 87%). This boronic ester is soluble in all common organic solvents (Found C, 70.65; H, 9.50; N, 1.50. $C_{54}H_{84}B_3NO_9$ requires C, 70.17; H, 9.16; N, 1.51%); δ_H ($CDCl_3$) 0.88 (9H, t, *J* 6.5, Me), 0.97–1.24 (48H, m, methylene), 3.74 (6H, t, *J* 5.2, $-OCH_2-$), 4.35 [12H, s, $-O(CH_2)_2O-$], 6.84 (3H, d, *J* 7.8, ArH) and 7.24 (6H, d, *J* 8.4, ArH); *m/z* 924 (M^+, 57%), 923 (100), 922 (65), 854 (50), 853 (86) and 852 (44).

Tris(3-nitrophenyl)amine 9

3-Nitroaniline (2.76 g, 20 mmol), 3-iodonitrobenzene (11.0 g, 44.1 mmol), copper powder (2.80 g, 44.1 mmol), anhydrous potassium carbonate (12.0 g, 86.9 mmol) and a catalytic amount of 18-crown-6 (0.50 g, 1.8 mmol) were refluxed in 1,2-dichlorobenzene (40 cm^3). After 20 h the mixture was cooled to room temp., diethyl ether (300 cm^3) was added, and the insoluble materials filtered off. The organic layer was washed with 2 M hydrochloric acid (3×200 cm^3) and dilute ammonia solution (2×100 cm^3) and water, and dried with sodium sulfate. Removal of the solvent gave a solid residue which was washed with ethanol:hexane (1:1) and recrystallized from ethanol to give the product **9** as yellowish flat needles (3.27 g, 43%) mp 229.5–230.5 °C (Found: C, 56.70; H, 2.95. $C_{18}H_{12}N_4O_6$ requires C, 56.84; H, 3.15%); δ_H ($CDCl_3$) 7.43 (3H, dd, *J* 8.0 and 2.0, ArH), 7.54 (3H, t, *J* 8.1, ArH), 7.92 (3H, t, *J* 2.1, ArH) and 8.02 (3H, dd, *J* 8.1 and 2.1, ArH); δ_c ($CDCl_3$) 118.8, 119.5, 129.7, 130.9, 147.0 and 149.6 (Ph); *m/z* 380 (M^+, 100%), 288 (38), 287 (41) and 242 (49).

Tris(3-aminophenyl)amine 10

Tin powder (7.59 g, 64 mmol) was gradually added to a solution of tris(3-nitrophenyl)amine **9** (3.04 g, 8 mmol), conc. HCl (35 cm^3) and ethanol (150 cm^3). The mixture was refluxed for 2 h with stirring. After cooling, the volume was reduced to about 50 cm^3, the solution rendered basic with aqueous sodium hydroxide and extracted with diethyl ether (2×100 cm^3). Then the ether layer was washed with water and dried with sodium sulfate. Removal of the solvent gave the product **10** as a white solid (2.1 g, 90%) mp 205–207 °C. It was used directly for the next step without further purification (Found: C, 74.15; H, 6.15. $C_{18}H_{18}N_4$ requires C, 74.45; H, 6.25%); δ_H ($CDCl_3$) 3.54 (6H, s, $-NH_2$), 6.33 (3H, d, *J* 7.0, ArH), 6.42 (3H, s, ArH), 6.47 (3H, d, *J* 8.0, ArH) and 7.00 (3H, t, *J* 7.26, ArH); *m/z* 290 (M^+, 100%) and 273 (22).

Tris(3-bromophenyl)amine 11

Tris(3-aminophenyl)amine **10** (1.56 g, 5.3 mmol) was mixed with 48% aqueous hydrobromic acid (50 cm^3) to give a yellowish suspension. The diazonium salt was prepared by treating the acid salt with an aqueous solution of sodium nitrite (1.14 g, 16.5 mmol) in water (10 cm^3) at −5 °C to gave a brown–orange solution. A freshly prepared solution of copper(I) bromide (20.0 g, 139 mmol) in 48% aqueous hydrobromic acid (25 cm^3) was added at −5 °C. The mixture was stirred at room temp. for 10 h and extracted with dichloromethane (2×50 cm^3). The organic phase was washed with dilute hydrochloric acid, dilute aqueous sodium hydroxide and brine, and dried with magnesium sulfate. The solvent was removed to give a dark brown residue which was purified by column chromatography eluting with hexane. The product **11** was collected from the first main fraction as a white solid (0.95 g, 37%) mp 88–89 °C (Found: C, 45.35; H, 2.45; N, 2.85. $C_{18}H_{12}Br_3N$ requires C, 44.85; H, 2.51; N, 2.90%); δ_H ($CDCl_3$) 6.99 (3H, d, *J* 7.9, ArH), 7.14 (3H, t, *J* 7.8, ArH), 7.18 (3H, s, ArH) and 7.20 (3H, d, *J* 7.5, ArH); δ_c ($CDCl_3$) 122.8, 123.0, 126.76, 127.1, 130.7 and 148.0 (Ph); *m/z* 485 (85%), 483 (41), 481 (41) and 439 (10).

2,2′,5,5′-Tetramethoxybiphenyl 12

A stirred mixture of 2-iodo-1,4-dimethoxybenzene (11.27 g, 42.7 mmol), copper powder (15.0 g) and dry dimethylformamide (10 cm^3) was heated under reflux for 3 h. After cooling, benzene (100 cm^3) was added and insoluble solid was filtered off. The organic layer was washed with water and dried with magnesium sulfate. Solvent was removed under reduced pressure to give a light brown solid. Recrystallization from ethanol gave product **12** as light brown plates (3.90 g, 67%) mp 95.5–96.0 °C (Found: C, 70.20; H, 6.45. $C_{16}H_{18}O_4$ requires C, 70.05; H, 6.61%); δ_H ($CDCl_3$) 3.74 (6H, s, $-OMe$), 3.78 (6H, s, $-OMe$) and 6.84–6.89 (6H, m, ArH); δ_c ($CDCl_3$) 55.5 ($-OMe$), 56.3 ($-OMe$), 112.2, 113.2, 116.9, 128.4, 151.1 (OAr) and 153.1 (OAr).

4,4′-Dibromo-2,2′,5,5′-tetramethoxybiphenyl 13

A solution of bromine (7.60 g, 47.5 mmol) in chloroform (100 cm^3) was added dropwise to a stirred chloroform (100 cm^3) solution of 2,2′,5,5′-tetramethoxybiphenyl **12** (6.50 g, 23.7 mmol) over 1 h at 0 °C. After the addition was complete the mixture was stirred for a further 1 h at 0 °C. It was washed with water (3×200 cm^3), dilute aqueous ammonia and water, and dried with magnesium sulfate. The solvent was removed and the crude solid product was recrystallized from dichloromethane–hexane (2:1) to give compound **13** as a white crystals (7.70 g, 75%) mp 159–160 °C (Found: C, 44.30; H, 3.60; Br, 37.00. $C_{16}H_{16}Br_2O_4$ requires C, 44.47; H, 3.73; Br, 36.98%); δ_H ($CDCl_3$) 3.73 (6H, s, $-OMe$), 3.85 (6H, s, $-OMe$), 6.82 (2H, s, ArH) and 7.17 (2H, s, ArH); δ_c ($CDCl_3$) 56.6 ($-OMe$), 56.9 ($-OMe$), 110.9 (ArBr), 115.2, 116.9, 126.6, 149.8 (OAr) and 151.2 (OAr); *m/z* 433 (51%), 431 (100), 429 (51), 337 (25) and 335 (24).

4,4′-Bis(dihydroxyboryl)-2,2′,5,5′-tetramethoxybiphenyl 14

n-Butyllithium in hexane (6.98 cm^3, 1.6 M, 11.17 mmol) was added dropwise to a solution containing 4,4′-dibromo-2,2′,4,4′-tetramethoxybiphenyl **13** (2.20 g, 5.08 mmol) in dry tetrahydrofuran (40 cm^3) at −78 °C under an argon atmosphere. After the addition, the resulted pink suspension was kept at −78 °C with magnetic stirring for about 90 min. The cold suspension was slowly added *via* a cannula into a solution of triisopropyl borate (5.73 g, 30.48 mmol) in tetrahydrofuran (15 cm^3) at −78 °C under argon. The resulting mixture was stirred for a further 12 h at room temp. 10% Aqueous hydrochloric acid (30 cm^3) was added to the mixture and the aqueous layer was extracted with diethyl ether (2×25 cm^3). The organic phase was washed with water and dried with magnesium sulfate. Hexane (200 cm^3) was added to precipitate the product. The product **14** was obtained as a yellowish solid (0.78 g, 42%). It only dissolved in acetone, diethyl ether and tetrahydrofuran and was insoluble in other common organic solvents (Found: C, 53.25; H, 5.60. $C_{16}H_{20}B_2O_8$ requires C, 53.04; H, 5.56%); δ_H ([$^2H_6$]acetone) 3.72 (6H, s, $-OMe$), 3.89 (6H, s, $-OMe$), 6.92 (2H, s, ArH), 7.12 [4H, s, $-B(OH)_2$] and 7.45 (2H, s, ArH).

4,4′-Bis(ethylenedioxyboryl)-2,2′,5,5′-tetramethoxybiphenyl 14a

The bisboronic acid **14** (0.15 g, 4.1 mmol) and ethane-1,2-diol (0.50 cm^3) were heated until the solid dissolved. The excess solvent was distilled off under high vacuum to give the product **14a** as a white solid (0.13 g, 80 %). The cyclic ester **14a** is soluble in many common organic solvents (Found: C, 58.31; H, 6.10. $C_{20}H_{24}B_2O_8$ require C, 57.96; H, 5.83%); δ_H ($CDCl_3$) 3.77 (6H, s, $-OMe$), 3.86 (6H, s, $-OMe$), 4.41 (8H, s,

$\mathrm{-OCH_2CH_2O-}$), 6.85 (2H, s, ArH) and 7.37 (2H, s, ArH); *m*/*z* 414 ($\mathrm{M^+}$, 100%), 384 (8) and 344 (15).

2,2′,5,5′-Tetrahydroxybiphenyl 15

A solution of boron tribromide (13.20 g, 52.8 mmol) in dichloromethane (40 cm^3) was added to a cold (−78 °C) solution of 2,2′,5,5′-tetramethoxybiphenyl **12** (3.60 g, 13.1 mmol) in dichloromethane (120 cm^3). The reaction mixture was stirred at −78 °C for 5 h and then allowed warm to room temp. The mixture was poured onto water, the organic layer separated and the aqueous layer extracted with diethyl ether (3 × 50 cm^3). Removal of the solvent and drying gave product **15** as a greyish solid (2.0 g, 70%), mp 231–232 °C (Found: C, 65.80; H, 4.60. $\mathrm{C_{12}H_{10}O_4}$ requires C, 66.05; H, 4.62%); δ_H ([^{2}H$_6$]acetone) 6.72 (2H, dd, *J* 8.4 and 2.8, ArH), 6.75 (2H, d, *J* 2.8, ArH), 6.82 (2H, d, *J* 8.5, ArH), 7.89 (2H, s, $\mathrm{-OH}$) and 7.99 (2H, s, $\mathrm{-OH}$).

2,2′,5,5′-Tetrahexyloxybiphenyl 16

A mixture of 2,2′,5,5′-tetrahydroxybiphenyl **15** (2.0 g, 9.17 mmol), 1-bromohexane (9.1 g, 55 mmol) and powdered potassium carbonate (11.04 g, 80 mmol) in ethanol (120 cm^3) was refluxed for 15 h. After cooling, insoluble material was filtered off and the filtrate concentrated, diethyl ether (100 cm^3) was added, and the ether solution washed with dilute aqueous sodium hydroxide, water and brine, and dried with magnesium sulfate. Removal of the solvent gave a brownish oily residue. This was chromatographed on a large silica gel column eluting with 10% dichloromethane in hexane. The first main fraction gave an oil which solidified to give **16** as a waxy solid on cooling (4.05 g, 80%) mp 35–35.5 °C. (Found: C, 78.45; H, 10.45. $\mathrm{C_{36}H_{58}O_4}$ requires C, 77.93; H, 10.53%); δ_H (CDCl$_3$) 0.84–0.89 (12H, m, $\mathrm{-CH_3}$), 1.21–1.43 (24H, m, $\mathrm{-CH_2-}$), 1.57 (4H, t, *J* 6.1, $\mathrm{-CH_2-}$), 1.75 (4H, t, *J* 6.5, $\mathrm{-CH_2-}$), 3.81 (4H, t, *J* 6.2, $\mathrm{-OCH_2-}$), 3.90 (4H, t, *J* 6.4, $\mathrm{-OCH_2-}$) and 6.81–6.84 (6H, m, ArH); *m*/*z* 555 (17%), 554 ($\mathrm{M^+}$, 36), 278 (35) and 110 (100).

4,4′-Dibromo-2,2′,5,5′-tetrahexyloxybiphenyl 17

A solution of bromine (1.96 g, 12.2 mmol) in chloroform (20 cm^3) was added to a solution of 2,2′,5,5′-tetrahexyloxybiphenyl **17** (2.90 g, 5.23 mmol) in chloroform (40 cm^3) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and left at room temp. for 10 h. The organic layer was washed with water and dried with magnesium sulfate. Solvent was removed under reduced pressure to give a light brown oily residue. This was chromatographed on a short silica gel column eluting with hexane–dichloromethane (4:1). Removal of the solvent from the first fraction gave **17** as a near-white solid (3.10 g, 83%), mp 44–44.7 °C, which was used 'crude' for the next step. δ_H (CDCl$_3$) 0.85 (6H, t, *J* 7.1, $\mathrm{-CH_3}$), 0.89 (6H, t, *J* 6.7, $\mathrm{-CH_3}$), 1.23–1.82 (32H, m, $\mathrm{-CH_2-}$), 3.81 (4H, t, *J* 6.5, $\mathrm{-OCH_2-}$), 3.95 (4H, t, *J* 6.5, $\mathrm{-OCH_2-}$), 6.85 (2H, s, ArH) and 7.12 (2H, s, ArH); *m*/*z* 714 (62%), 712 ($\mathrm{M^+}$, 97%), 710 (57), 378 (21), 376 (39) and 374 (23).

4,4′-Bis(dihydroxyboryl)-2,2′,5,5′-tetrahexyloxybiphenyl 18

n-Butyllithium in hexane (5.93 cm^3, 1.6 M, 9.5 mmol) was added over a period of 15 min to a solution of 4,4′-dibromo-2,2′,5,5′-tetrahexyloxybiphenyl **17** (3.0 g, 4.21 mmol) in dry tetrahydrofuran (60 cm^3) at −78 °C under an argon atmosphere. The resulting white suspension was stirred at −78 °C under argon for 2 h. The cold suspension was slowly cannulated into a solution of triisopropyl borate (10.8 g, 57 mmol) in tetrahydrofuran (10 cm^3) at −78 °C under argon and stirred for 2 h when a yellowish mixture was formed. This was stirred at room temp. for about 10 h. The mixture was cooled to −78 °C and the intermediate ester was hydrolysed by adding 2 M hydrochloric acid, slowly warming to room temp., and stirring for a further 6 h. Water was added and the aqueous solution extracted with diethyl ether (2 × 50 cm^3). The organic phase was washed with water and dried with sodium sulfate. The solvent was removed under reduced pressure to give a yellowish waxy solid. Purification was by column chromatography using dichloromethane as the first eluent to remove a by-product and then 30% diethyl ether in dichloromethane After the solvent was removed the product **18** was obtained as a pale coloured solid (2.5g, 92%) (Found: C, 67.30; H, 9.81. $\mathrm{C_{36}H_{60}B_2O_8}$ requires C, 67.30; H, 10.10%); δ_H (CDCl$_3$) 0.84 (6H, t, *J* 6.7, $\mathrm{-CH_3}$), 0.90 (6H, t, *J* 6.6, $\mathrm{-CH_3}$), 0.95–1.85 (32H, m, $\mathrm{-CH_2-}$), 3.90 (4H, t, *J* 6.5, $\mathrm{-OCH_2-}$), 4.02 (4H, t, *J* 6.6, $\mathrm{-OCH_2-}$), 6.34 [4H, br s, $\mathrm{-B(OH)_2}$], 6.91 (2H, s, ArH) and 7.43 (2H, s, ArH, *ortho* to boron); *m*/*z* 638, 610, 570 and 554.

Polymers 22–28

1,3-Dibromo-5-tetradecylbenzene **19** (1.48 g, 3.42 mmol), tetrakis(triphenylphosphine)palladium (0.091 g, 7.85 × 10^{-5} mmol) and the trisboronic acid **5** (1.49 g, 2.25 mmol) in dry ethanol (10 cm^3) were added to stirred dry toluene (80 ml) followed, after 15 min, by aqueous sodium carbonate (20 cm^3, 2 M). The stirred inhomogeneous mixture was slowly heated to reflux temp. and refluxed under an argon atmosphere for 3 weeks. After cooling, insoluble black materials were filtered off and the layers were separated. The organic phase was washed with dilute hydrochloric acid and water and concentrated to about 15 cm^3. Methanol was added to precipitate a grey solid. This was redissolved in diethyl ether (50 cm^3) and the ether was added to methanol to give the polymer **22** (0.66g, 31%) as a light grey powder which decomposes at *ca.* 170 °C. Anal. Table 1; δ_H (CDCl$_3$) 0.7–1.0 (27H, br m, $\mathrm{-CH_3}$), 1.0–1.5 (108H, br m, $\mathrm{-CH_2-}$), 1.5–1.8 (12H, br s, $\mathrm{-OCH_2}C\mathit{H}_2\mathrm{-}$), 2.6–2.8 (6H, br s, $\mathrm{ArCH_2-}$), 3.8–4.0 (12H, br s, $\mathrm{-OCH_2-}$) and 6.9–7.7 (27H, br m, ArH).

In a similar manner 1,3,5-tribromobenzene **20** (0.374 g, 1.19 mmol), tetrakis(triphenylphosphine)palladium (0.041 g, 3.54 × 10^{-5} mmol) and a solution of trisboronic acid **8** (1.0g, 1.18 mmol) gave a product which was extracted with dichloromethane and reprecipitated with methanol. It was further extracted with tetrahydrofuran in a Soxhlet apparatus for 24 h. The resulting solution was allowed to cool to room temp. and concentrated, and the polymer **23** reprecipitated by adding to methanol, as a grey powder (0.60g, 65%). Anal. Table 1; δ_H (CDCl$_3$) 0.7–0.9 (12H, br s, $\mathrm{-CH_3}$), 1.0–1.4 (42H, br m, $\mathrm{-CH_2-}$), 1.4–1.7 (6H, br s, $\mathrm{-OCH_2}C\mathit{H}_2\mathrm{-}$), 2.6–2.8 (6H, br s, $\mathrm{ArCH_2-}$), 3.6–3.9 (6H, br s, $\mathrm{-OCH_2-}$) and 6.7–7.5 (12H, br m, ArH).

In a similar manner 1,3,5-tris(4-bromophenyl)benzene **21** (1.36 g, 2.5 mmol), tetrakis(triphenylphosphine)palladium (0.087 g, 7.5 × 10^{-5} mmol) and trisboronic ester **8** (2.31g, 2.5 mmol) gave the polymer **24** (1.5 g, 58%). Anal. Table 1; λ_max (dichloromethane) 363 nm; δ_H (CDCl$_3$) 0.7–0.9 (12H, br s, $\mathrm{-CH_3}$), 1.0–1.4 (42H, br m, $\mathrm{-CH_2-}$), 1.4–1.7 (6H, br s, $\mathrm{-OCH_2}C\mathit{H}_2\mathrm{-}$), 3.6–3.9 (6H, br s, $\mathrm{-OCH_2-}$) and 6.7–7.5 (24H, br m, ArH).

In a simillar manner, tris(3-bromophenyl)amine **11** (0.9 g, 1.87 mmol), tetrakis(triphenylphosphine)palladium (0.0645 g, 5.58 × 10^{-5} mmol) and trisboronic acid **8** (1.57 g, 1.86 mmol) gave a greenish solid which was dissolved in diethyl ether (20 cm^3) and reprecipitated with methanol giving the polymer **25** as a greenish powder (0.95g, 53%). Anal. Table 1; λ_max (dichloromethane) 330 nm; δ_H (CDCl$_3$) 0.7–0.9 (12H, br s, $\mathrm{-CH_3}$), 1.0–1.4 (42H, br m, $\mathrm{-CH_2-}$), 1.4–1.7 (6H, br s, $\mathrm{-OCH_2}C\mathit{H}_2\mathrm{-}$), 3.6–3.9 (6H, br s, $\mathrm{-OCH_2-}$) and 6.6–7.7 (21H, br m, ArH).

In a similar manner 1,3,5-tribromobenzene **20** (0.50 g, 1.57 mmol), tetrakis(triphenylphosphine)palladium (0.054 g,

4.68×10^{-5} mmol) and bisboronic acid **18** (1.51 g, 2.34 mmol) in degassed ethanol (10 cm^3) gave a solid which was dissolved in dichloromethane (20 cm^3) and reprecipitated with cold methanol to give the polymer **26** (1.01 g, 70%) as a pale coloured powder. The product is jelly-like at room temp. Anal. Table 1; δ_H ($CDCl_3$) 0.8–0.9 (36H, br m, $-CH_3$), 1.0–1.5 (72H, br m, $-CH_2-$), 1.5–1.7 (24H, br s, $-OCH_2CH_2-$), 3.7–3.9 (24H, br s, $-OCH_2-$) and 6.7–7.5 (18H, br m, ArH).

In a similar manner 1,3,5-tris(4-bromophenyl)benzene **21** (1.09 g, 2 mmol), tetrakis(triphenylphosphine)palladium (0.07 g, 6.0×10^{-5} mmol) and the bisboronic acid **18** (1.93 g, 3.0 mmol) gave a product which was redissolved in dichloromethane (30 cm^3) and reprecipitated with methanol giving the polymer **27** (1.0 g, 44%) as a light grey powder. Anal. Table 1; λ_{max} (dichloromethane) 327 nm; δ_H ($CDCl_3$) 0.8–0.9 (36H, br s, $-CH_3$), 1.0–1.5 (72H, br m, $-CH_2-$), 1.5–1.7 (24H, br s, $-OCH_2CH_2-$), 3.7–3.9 (24H, br s, $-OCH_2-$) and 6.7–7.5 (24H, br m, ArH).

In a similar manner 1,3-dibromo-5-tetradecylbenzene **19** (1.19 g, 2.75 mmol), 1,3,5-tribromobenzene **20** (0.58 g, 1.84 mmol), tetrakis(triphenylphosphine)palladium (0.127 g, 1.1×10^{-4} mmol) and a solution of bisboronic acid **14** (1.99 g, 5.5 mmol) gave a product which was dissolved in dichloromethane and reprecipitated with methanol, to give the white polymer **28** (0.65 g, 44%). Anal. Table 1; λ_{max} (dichloromethane) 310 nm; δ_H ($CDCl_3$) 0.8–0.9 (9H, br s, $-CH_3$), 1.1–1.5 (66H, br s, $-CH_2-$), 1.6–1.8 (6H, br m, $ArCH_2CH_2-$), 2.6–2.8 (6H, br m, $ArCH_2-$), 3.9 (72H, br s, $-OCH_3$) and 6.9–7.9 (24H, br m, ArH).

Electrochemical characterization of the polymers

These studies were carried out using a conventional three electrode system coupled to an EG & G Model 362 scanning potentiostat with the system controlled by an Amstrad PC 1640 personal computer running the 'Condecon 310' cyclic voltammetry software. The working electrode was a small platinum disc, the counter electrode a 1 cm square platinum sheet, and the reference electrode a silver wire immersed in a saturated lithium chloride–chloroform mixture containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The solutions were purged with argon prior to the start of data acquisition. Ferrocene was used as the standard and its oxidation potential checked before each new experiment for the particular solvent being used. For the voltammograms shown in Fig. 4 the concentrations were 1–2 mg cm^{-3}, the potential was swept in the anodic direction (upper trace) and the lower trace represents the reverse sweep in the cathodic direction.

Studies of the oxidative doping of the polymers using EPR spectroscopy

In a typical doping experiment a solution of polymer **22** (2.2 mg cm^{-3}) in dichloromethane was treated with an excess of $NOBF_4$ in dichloromethane such that, as in the case of the calibration experiment, the depth of solution in the tube spanned the cavity and a deep green solution formed. The double integral of the resultant signal under identical settings was compared to that for the standard, from which a total number of spins and hence a number of spins per gram of polmer and a percentage doping figure were calculated. These figures are summarized in Table 2. The EPR spectra were recorded at room temp. on a Bruker ER 200 spectrometer with a Bruker ESP 1600 data acquisition system. The response of the instrument was checked on a regular basis, under the conditions used for the spin-counting experiments, using the double integral of the signal from a fresh standard solution of DPPH (*ca.* 5 mg in 50 cm^3 of analytical grade benzene) whose concentration was independently and accurately determined from the intensity of the absorption maximum at 530 nm (ε 1.42×10^4 dm^3 mol^{-1} cm^{-1}).

Characterisation of the magnetic properties of the doped polymers

Typical procedure. Polymer **23** (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 °C and powdered $NOBF_4$ (330 mg, a large excess) was added under argon. After 20 min at -30 °C the solvent was removed from the deep green solution under vacuum and the residue dried at room temp. at *ca.* 10^{-4} mmHg overnight. Using a glove bag a portion 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. Although precautions were taken to protect these samples from air and moisture, prepared in this way, and in the presence of an excess of oxidizing agent it was found that some exposure to the air had little effect on the results. The magnetization data shown in Fig. 5–10 have been corrected for the diamagnetism of the sample holder, the polymer and the excess reagent.[28]

We thank the EPSRC for financial support Dr R. Luo for assistance with the electrochemical studies and Dr C. Frommen (University of Sheffield) for susceptibility measurements.

References

1 Preliminary communication: R. J. Bushby and K. M. Ng, *Chem. Commun.,* 1996, 659; R. J. Bushby, D. R. McGill and K. M. Ng, in *Magnetism: a Supramolecular Function* ed. O. Kahn, Kluwer, Dordrecht, 1996, p. 181.

2 N. Mataga, *Theoret. Chim. Acta*, 1968, **10**, 372.

3 T. Hughbanks and K. A. Yee, in *Magnetic Molecular Materials*, ed. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, Kluwer, Dordrecht, 1990, p. 133.

4 G. Allinson, R. J. Bushby and J.-L. Paillaud, *J. Mater. Sci., Mater. Electronics,* 1994, 67.

5 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* ed. S. Patai and Z. Rappoport, Wiley, New York, 1988, p. 455.

6 R. J. Bushby and C. Jarecki, *Tetrahedron Lett.*, 1988, 2715; R. J. Bushby and C. Jarecki, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2335.

7 A. A. Ovchinnikov, *Theor. Chim. Acta*, 1978, **47**, 297.

8 P. M. Chaikin, in *Synthesis and Properties of Low-Dimensional Materials* ed. J. S. Miller and A. J. Epstein, NY Acad. Sci., New York, 1978, p. 128.

9 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; H. Iwamura, S. Sasaki, N. Sasagawa, K. Inoue and N. Koga, in *Magnetic Molecular Materials* ed. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, Kluwer, Dordrecht, 1991, p. 53; K. Itoh, same volume, p. 67.

10 H. Fukutome, I. Takahashi and M. Ozaki, *Chem. Phys. Lett.*, 1987, **133**, 34.

11 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, J.-L. Paillaud and M. Thornton-Pett, *J. Chem. Soc., Perkin Trans. 1*, 1995, 385.

12 D. A. Dougherty, *Acc. Chem. Res.*, 1991, **24**, 88; A. Rajca, *Chem. Rev.*, 1994, **94**, 871.

13 Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita and M. Ishikawa, *Phys. Rev. B*, 1993, **46**, 8906; M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita, *Chem. Phys. Lett.*, 1991, **186**, 401; R. Chiarelli, M. A. Novak, A. Rassat and J. Tholence, *Nature*, 1993, **363**, 147.

14 D. Stauffer and A. Aharony, *Introduction to Percolation Theory* Taylor and Francis; London, 1994; T. C. Gibb, A. J. Herod, S. T. Lees and P. D. Battle, *J. Mater. Chem.*, 1995, **5**, 285.

15 C. Kittel, *Phys. Rev.* 1946, **70**, 965.

16 C. Halliwell, MSc Thesis, University of Leeds, 1994; D. R. McGill, PhD Thesis, University of Leeds, 1997.

17 R. E. Jesse, P. Biloen, R. Prins, J. D. W. van Voorst and G. J. Hoijtink, *Mol. Phys.*, 1963, **6**, 633; J. A. M. van Broekhoven, H. van Willigen and E. deBoer, *Mol. Phys.*, 1968, **15**, 101; H. Tukada, *J. Chem. Soc., Chem. Commun.*, 1994, 2293.

18 K. Yoshizawa, A. Chano, A. Ito, K. Tanaka, T. Yamabe, H. Fujita, J. Yamauchi and M. Shiro, *J. Am. Chem. Soc.,* 1992, **114**, 5994; K. R. Stickley and S. C. Blackstock, *J. Am. Chem. Soc.*, 1994, **116**, 11 576.

19 Y. Teki, I. Fujita, T. Takui, T. Kinoshita and K. Itoh, *J. Am. Chem. Soc.*, 1994, **116**, 11 499; M. Minato, P. M. Lathi and H. van Willigen, *J. Am. Chem. Soc.*, 1993, **115**, 4532.

20 Y. Hoshino, N. Miyaura and A. Suzuki, *Bull. Chem. Soc. Jpn*, 1988, **61**, 3008.

21 J. Lindley, *Tetrahdron,* 1984, **40**, 1433 and references therein.

22 K. Yoshizawa, K. Tanaka, T. Yamabe and J. Yamuchi, *J. Chem. Phys.*, 1992, **96**, 5516; A. Ito, K. Ota, K. Tanaka, T. Yamabe and K. Yoshizawa, *Macromolecules*, 1995, **28**, 5618.

23 K. E. Uhrich, C. J. Hawker, S. R. Turner and J. M. J. Frechet, *Macromolecules*, 1992, **25**, 4583.

24 R. J. Bushby, D. R. McGill, K. M. Ng and N. Taylor, *J. Chem. Soc., Chem. Commun.*, 1996, 2641; R. J. Bushby, D. R. McGill, K. M. Ng and N. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1405.

25 N. Taylor, T. Boddington, I. Dobson, B. Gill, R. Luo and B. L. Shaw, in *Molecular Electrochemistry of Inorganic, Bioorganic and Organometallic Compounds* ed. A. J. L. Pomberio and J. A. M. McCleverty, Kluwer, Dordrecht, 1993, p. 467; A. Blagg, S. W. Carr, G. R. Cooper, I. D. Dobson, J. B. Gill, D. C. Goodall, B. L. Shaw, N. Taylor and T. Boddington, *J. Chem. Soc., Dalton Trans.*, 1985**,** 1213; I. D. Dobson, PhD Thesis, University of Leeds, 1986.

26 K. B. Oldham and J. Spanier, *J. Electroanal. Chem.*, 1970, **26**, 331; K. B. Oldham, *Anal. Chem.*, 1972, **44**, 196; M. Grenness and K. B. Oldham, *Anal. Chem.*, 1972, **44**, 1121.

27 E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy and R. N. Adams, *J. Am. Chem. Soc.*, 1966, **88**, 3498; R. J. Bushby, D. R. McGill and N. Taylor, unpublished results.

28 J. B. Flanagan, S. Margel, A. J. Bard and F. C. Anson, *J. Am. Chem. Soc.*, 1978, **100**, 4248.

29 S. S. Eaton, K. M. More, B. M. Sawant and G. R. Eaton, *J. Am. Chem. Soc.*, 1983, **105**, 6560.

30 M. A. Murray, P. Kaszynski, D. A. Kaisaki, W.-H. Chang and D. A. Dougherty, *J. Am. Chem. Soc.*, 1994, **116,** 8152.

31 P. M. Lathi, C. Ling, N. Yoshioka, F. C. Rossitto and H. van Willigen, *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 377.

32 T. Kaneko, S. Toriu, Y. Kuzumaki, H. Nishida and E. Tsuchida, *Chem. Lett.*, 1994, 2135.

33 S. Utamapanya, H. Kakegawa, L. Bryant and A. Rajca, *Chem. Mater.*, 1993, **5**, 1053.

34 W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1977 **99**, 4587; W. T. Borden, *Mol. Cryst. Liq. Cryst.*, 1993, **232,** 195.

35 R. J. Bushby and J.-L. Paillaud, in *An Introduction to Molecular Electronics* ed. M. C. Petty, M. R. Bryce and D. Bloor, E. Arnold, London, 1995, J. S. Miller and A. J. Epstein, *Chem. Eng. News,* 1995, 30; J. S. Miller and A. J. Epstein, *Chem. Ind.*, 1996, 49.

36 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1980.

Paper 7/05076C; *Received* 15*th July*, 1997