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Conceptual and Synthetic Strategies for the Preparation of Organic Magnets

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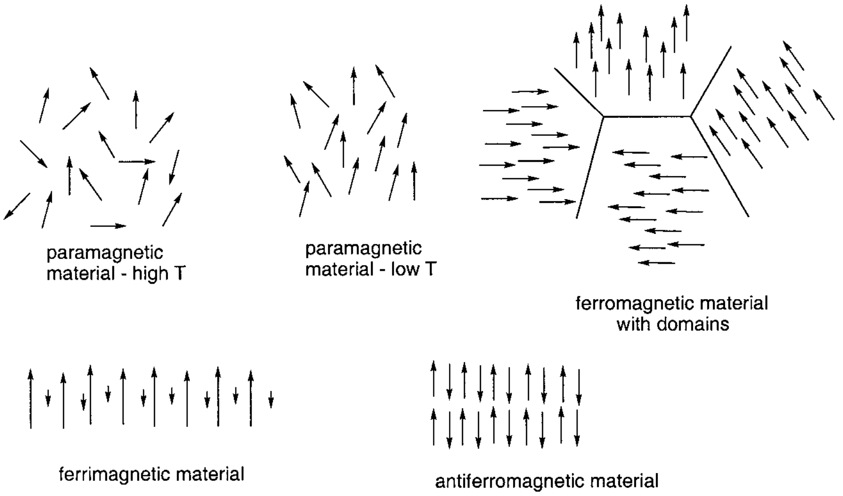


Figure 1. Schematic diagram showing the alignment of spins in paramagnetic, ferromagnetic, ferrimagnetic and antiferromagnetic materials.

1. Introductory Aspects of Magnetism

The earliest discovery of magnetic phenomena is not known for certain, although the word 'magnet' is probably derived from the Thessalian province of Magnesia where magnetite (lodestone, Fe_3O_4) was mined.[1] Magnetism is one of nature's most fascinating and evergreen phenomena. Magical powers to induce personal empathy and to attract gold, as well as various curative properties, were once attributed to lodestone. The application of magnets as primitive compasses for direction finding was first recorded in Europe in the 13th century, but the Chinese probably knew about the compass in 300–200 BC. The Earth's magnetic field continues to fascinate; recently it has been proposed that the Earth possesses a giant iron crystal at its core.[2] Electromagnets, dynamos and AC transformers have, of course, played key roles in modern technology. Luxury cars, for example, can contain up to 300 magnet-related components. Audio and video storage media were founded on magnetic tape technology. One of the most fascinating discoveries of the 20th century was the phenomenon of superconductivity in metals and alloys at liquid helium temperatures. Advanced applications of superconducting magnets have already been realised in NMR spectroscopy, magnetic resonance imaging and particle accelerators. Since their discovery in 1986, intense research effort has been devoted to 'high' temperature superconducting ceramic materials such as YBaCuO which are superconducting at temperatures above the boiling point of liquid nitrogen. A considerable technological problem with these ceramics is how to prepare wires for superconducting magnets out of an essentially brittle material. Recently, YBaCuO superconductors have been deposited as thin layers on a flexible metal tape,[3] that remains superconducting while carrying high current densities in the very high magnetic fields that are generated.

Meanwhile, new magnetic phenomena such as giant magnetoresistance,[4] have surprised physicists. The effect is most usually seen in magnetic multilayered structures, where two magnetic layers are closely separated by a thin spacer layer a few nanometres thick. It is analogous to a polarisation experiment, where aligned polarisers allow light to pass through, but crossed polarisers do not. The first magnetic layer allows electrons in only one spin state to pass through easily—if the second magnetic layer is aligned then that spin channel can easily pass through the structure, and the resistance is low. If the second magnetic layer is misaligned then neither spin channel can get through the structure easily and the electrical resistance is high. A related phenomenon is colossal magnetoresistance (CMR)[5] observed when $La_{1-x}Ca_xMnO_{3+d}$ is used as a ferroelectric layer. Commercial applications of giant magnetoresistance (GMR) are already being realised in the data storage industry and IBM were the first to the market with hard disks based on this technology, rather than on the ferroelectric effect used in conventional RAM.[6] Other applications of GMR are as diverse as on-chip sensors, solid-state compasses, automotive sensors, non-volatile magnetic memory and the detection of landmines. New technological applications of magnetic materials are being envisaged for imaging the new nanoscopic world: namely the magnetic force microscope and the magnetic resonance microscope.[7]

But today one of the greatest challenges in the field of magnetic materials research remains the design and preparation of organic ferromagnets.[8] The present article provides a review of the theoretical models that have been proposed in the development of organic ferromagnetic materials and the subsequent experimental and analytical work involved in evaluating them. It will, however, be necessary in the next section to briefly touch upon physical aspects of magnetism, and on transition metal ferromagnets, in order to place in context the challenge involved in designing organic ferromagnetic materials.

1.1. Types of bulk magnetism

The magnetic behaviour of solids is complex and many different types of magnetism have been distinguished: diamagnetism, paramagnetism, antiferromagnetism, ferrimagnetism, ferromagnetism, metamagnetism, etc. The many different forms of magnetic phenomena arise as a result of the diverse number of ways in which the moments of electrons in molecular and supramolecular arrays can be coupled together. In the presence of a magnetic field,

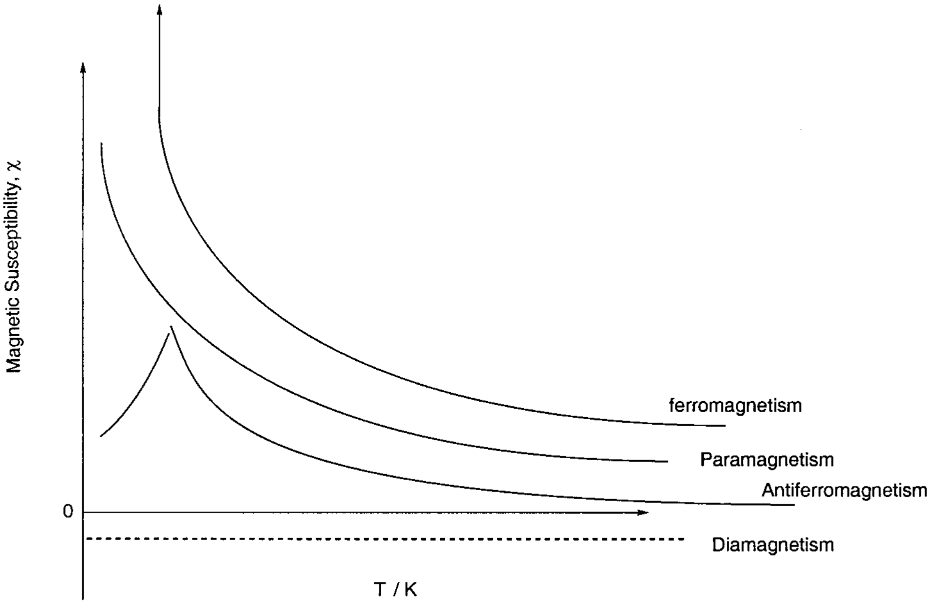


Figure 2. Temperature dependence of magnetic susceptibility in magnetic materials.

magnetic dipoles within a material become partially orientated. The magnetic dipole moment per unit volume is referred to as the magnetisation M. For isotropic substances the magnetic susceptibility χ is defined by $\chi=M/H$ where M and H are the magnitudes of the magnetisation and magnetic field vectors, respectively. Materials are classified as diamagnets, paramagnets or ferromagnets according to their bulk susceptibility. If a substance is diamagnetic, containing only spin-paired electrons, the magnetic response opposes the applied field and the magnetic susceptibility is small and negative. In a paramagnetic substance, namely one that contains unpaired electrons, the normally-randomised spin moments align with the external magnetic field, and the density of magnetic lines of force within the sample is intensified. The susceptibility, χ, is small, positive, independent of the magnetic field intensity, and decreases with increasing temperature. In a ferromagnetic substance, the spins are spontaneously parallel to one another in microscopic domains leading to a permanent magnetisation. In Fig. 1, the domains are shown when there is no applied magnetic field and the sample is not magnetised. The application of a magnetic field causes the domains to point along the field lines and this will lead to a magnetisation when the field is removed. The susceptibility, χ, is large and positive, dependent on the magnetic field, temperature, and the history of the sample. The related phenomenon, anti-ferromagnetism, occurs when neighbouring, *equal* spin moments couple in an anti-parallel fashion, leading to a lowering of magnetisation, while ferrimagnetism occurs when *unequal* spin moments couple in this way to leave a net magnetisation. Ferromagnetic, anti-ferromagnetic and ferrimagnetic materials often show hysteresis, that is irreversibility of magnetic behaviour as the applied magnetic field is changed.

Due to the thermal randomisation of the magnetic moments, the susceptibility of a paramagnetic material decreases smoothly with increasing absolute temperature (T) either according to the Curie law: $\chi=C/T$, or the Curie–Weiss law: $\chi=C/(T-\theta)$, in which C and θ are the Curie and Weiss constants, respectively. For a pure paramagnet (non-interacting spins) θ is zero and the Curie law applies but if local ferromagnetic coupling exists, θ is positive, whereas local anti-ferromagnetic coupling (anti-parallel spins) gives a negative value for θ. For substances that show bulk ferromagnetism a transition occurs at a temperature known as the Curie temperature, T_C, leading to a phase in which there is long-range parallel ordering of spins. Below this temperature the susceptibility rises abruptly to a very high value (Fig. 2).[9] Although ferromagnets below the Curie temperature exhibit long-range ordering of spins, a sample may still not behave like a magnet unless this ordering occurs within 'domains'. The domains themselves are randomly orientated and cancel each other out, however application of a magnetic field (i.e. the coercive field) will magnetise the sample. When the field is turned off the magnetisation curve shows hysteresis and the sample retains some magnetisation.

Detailed analysis and fitting of the temperature dependence of the magnetic susceptibility is possible using models based on the spin concentration and molecular parameters such as the exchange coupling constants and the average spin quantum number. The interested reader is referred to reviews covering these physical details.[8]

By far the most important class of materials from both the practical and theoretical viewpoints is the ferro-magnets. The applications, which these materials find, are very diverse. In engineering, for example, ferro-magnets are used because of their high permeabilities, which enable high magnetic inductions to be obtained with only modest magnetic fields. They also have the ability to retain magnetisation and thereby act as sources of fields. The few ferromagnetic elements in the periodic table are technologically vital.

1.2. Anticipated properties of organic magnetic materials[8]

The first obvious application would be the replacement of existing bulk magnets or magnetic recording devices. Values of the saturation magnetisation, M_s, for molecular/organic based magnets are comparable to metallic magnets on a mole basis. The inherently large molecular weight (per magnetic moment) and low densities, however, result in smaller saturation magnetisation on either a volume or mass basis, i.e. the spin concentration is low. In 1 cm^3 of metallic iron there thus are about 4×10^{23} spins, while in an organic ferromagnet it is less by 1–2 orders of magnitude. This results in lower magnetisations and small exchange energies (because of large interspin distances), and as a result in low temperatures of transition (T_C) to the ferromagnetic state. This means that molecular magnets are unlikely to compare well with existing magnets. A further disadvantage is the inherent chemical instability of organic materials and their 'ageing' with time.

Materials with magnetic moments parallel to the plane of a film or disk form the basis for magnetic tapes and discs. Increased data density requires materials with larger demagnetisation fields or larger coercive fields. Molecular based magnets, e.g. $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-+}$, have such large coercive fields. Magneto-optical discs, which have a higher data density than conventional disks, could be an increasingly important data storage system. Such technology relies upon the magneto-optical effect, which causes the magnetism of the medium to be changed when a high-power laser causes heating above the Curie temperature. The polarisation of the region of the disc can be read back by measuring the polarisation of the reflected light from a lower-powered laser. The degree of polarisation is dependent on the magnetisation of the target area (the Kerr effect) and is greatest when the magnetic moments are perpendicular to the plane of the substrate. Magneto-optic effects have yet to be studied for an organic/molecular magnet, and there are high expectations that molecular magnets will be useful. As a consequence of the insulating, and therefore transparent nature of organic magnetic materials a variety of optical properties may be expected, i.e. photomagnetic switches and polarised light manipulation in integrated optical devices. Finally, biocompatibility of organic magnetic materials may lead to several potential applications that include magnetic imaging and transducers for medical implants. In summary, the range of possible properties covers the following: (1) Insulating, (2) Low density, (3) Low magnetic anisotropy, (4) Optical changes, (5) Low elastic modulus, (6) Tuning of properties via organic chemistry, (7) Processability, (8) Low environmental contamination, (9) Solubility, and (10) Photomagnetic effect.

Other than commercial opportunities, the future realisation of the potential of organic ferromagnetism would be significant from a theoretical point of view, in which extended ferromagnetic exchange interactions through s and p orbitals may provide valuable insights into the very phenomenon of magnetism. From the synthetic chemist's perspective the extensive synthetic flexibilities offered by organic systems would enable the fine tuning of solid state magnetic characteristics. Further scientific and technological goals such as the fabrication of electronic devices containing such magnetic materials or molecules at a molecular level is an area of intense research activity with tempting possibilities for application in modern computer technology.[9]

1.3. Magnets based on organo-transition metal complexes

The mechanism of spin-coupling in molecular magnets differs from that in metals like iron. There are two distinct mechanisms: direct exchange and indirect exchange, or superexchange. A relevant example of direct exchange is Hund's rule of maximum multiplicity.[10] This predicts that atomic carbon will have a triplet ground state. Four of its six electrons are spin paired (in 1s and 2s orbitals) but the two remaining electrons, which occupy degenerate 2p orbitals, are predicted to have parallel spins. Hund's rule is also applicable to molecular and intermolecular situations; however, it must be applied with caution. In atomic, molecular or intermolecular situations, the interaction which lies behind the rule is only significant if the half-filled orbitals are orthogonal but represent electron distributions which overlap significantly in space. This 'orthogonal but coextensive' requirement is always met for co-centred atomic orbitals, but is not always fulfilled between molecular orbitals, and so the rule can break down. One of the main themes of research into high spin organic compounds has been the limitation of Hund's rule in situations where direct exchange dominates. The study of polynuclear transition metal complexes has shown a very different problem, namely that a strong coupling of spins may be observed over distances which are too great to be attributed to direct interactions between half filled metal ion d-orbitals. In cases where this exists the interaction is mediated through the ligands and the mechanism of spin-interaction is known as superexchange. An example of this type of interaction can be observed in the copper acetate complex $Cu_2(OAc)_4(H_2O)_2$. The crystal structure of this compound shows that it contains isolated dicopper molecules in which the copper atoms interact strongly through exchange forces, each pair forming a low energy singlet and a high energy triplet state.[11] This interaction occurs through the acetate ligands, not through direct bonding as the Cu–Cu distance is too great.

These ligand-mediated 'superexchange' interactions in bimetallic complexes have been the subject of a detailed systematic study by Kahn.[11] The sign and strength of the interaction varies widely from system to system but, as in direct exchange, it depends ultimately on the symmetry of the 'magnetic' orbitals and their overlap density, according to the Goodenough–Kanamori rules.[12] For example, comparison of the two complexes $CuVO(fsa)_2en{\cdot}CH_3OH$ (**1**) and $CuCu(fsa)_2en{\cdot}CH_3OH$ (**2**), where $(fsa)_2en^{4-}$ is the bichelating ligand derived from the Schiff base *N*,*N*-(2-hydroxy)-3-carboxybenzylidene-1,2-diamine, shows that the magnetic sites interact (Cu(II), $s=1/2$ and V(IV)O, $s=1/2$) to give rise to a singlet and a triplet ground state.

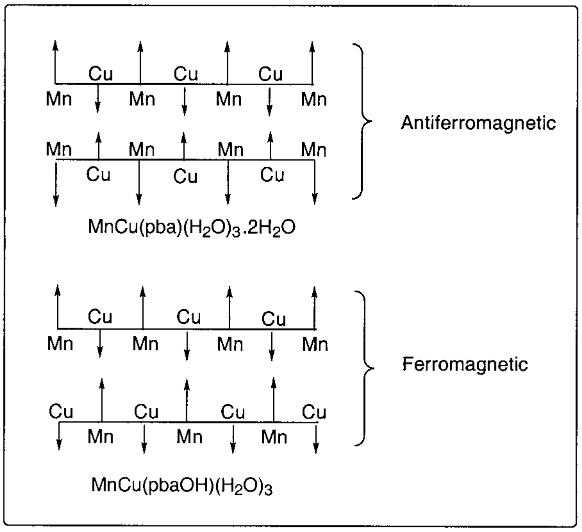
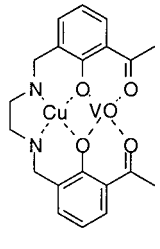


Figure 3. Magnetic interactions between neighbouring chains of metal ions.



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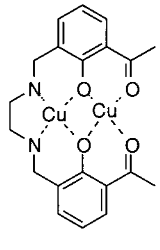


2

In compound **2** the magnetic orbitals have the same symmetry (containing $d_{x^2-y^2}$ orbital character) and overlap leading to a singlet ground state ($J=-650\ \mathrm{cm}^{-1}$). In compound **1**, however, the magnetic orbitals (containing Cu $d_{x^2-y^2}$ orbital and VO d_{xy} orbital character) are magnetic, orthogonal and co-extensive. This stabilises the triplet which becomes the ground state ($J=+120\ \mathrm{cm}^{-1}$).

The pairing of spins in dimeric complexes such as **2** would mean that a chain or polymer containing such copper units would tend to have zero aligned spin. If alternate coppers are replaced by Mn atoms, however, which have five unpaired electrons, then it would be possible to have an overall ferrimagnetic interaction along the chain as shown in Fig. 3 (top). When such chains are synthesised and crystallised it is generally found that *inter*chain interactions in the bulk crystal serve to cancel out the ferrimagnetism of the individual chains, and lead to an anti-ferromagnetic interaction between chains. Kahn[13] developed a strategy in the design of bimetallic chains containing metal ions of differing spins held together by bridging ligands. This approach produced one of the earliest true molecular magnets, namely $MnCu(pbaOH)(H_2O)_3$ [pabOH=2-hydroxy-1,3-propanediylbis(oxamato)] [$T_C=4.6$ K]. Its structure consists of alternating bimetallic chains assembled within the crystal lattice in such a way that along the chain axis the shortest interchain separations are Mn···Cu instead of Mn···Mn and Cu···Cu (Fig. 3, lower part). This strategy is reminiscent of an idea put forward by McConnell as early as 1963 (see Section 2.1).[14] The overall ferromagnetic coupling occurs through the interaction between strong positive and weak negative spin densities belonging to neighbouring ferrimagnetic chains. The positive and negative spin densities are provided by $S_{Mn}=5/2$ and $S_{Cu}=1/2$, respectively. The Mn(II)–Cu(II) interaction through the oxalato bridge of $MnCu(pba)(H_2O)_3{\cdot}2H_2O$, however, is strongly anti-ferromagnetic. This interpretation is substantiated by the fact that $MnCu(pba)(H_2O)_3{\cdot}2H_2O$ does not order ferromagnetically due to the fact that the shortest interchain interactions are now Mn···Mn and Cu···Cu.

Gatteschi developed this idea by choosing ligands which contain free radicals, namely nitroxides, and investigated the interactions between metal ions and the stable organic radicals.[15] When the nitroxide binds through its oxygen atom to a paramagnetic metal ion, the spins can orientate themselves anti-parallel to one another, or preferentially parallel to one another resulting in ferromagnetic coupling. The sign of the coupling from a nitroxide directly bound to a metal ion is again dependent on orbital overlap considerations as shown in Fig. 4, where only the interaction at the top

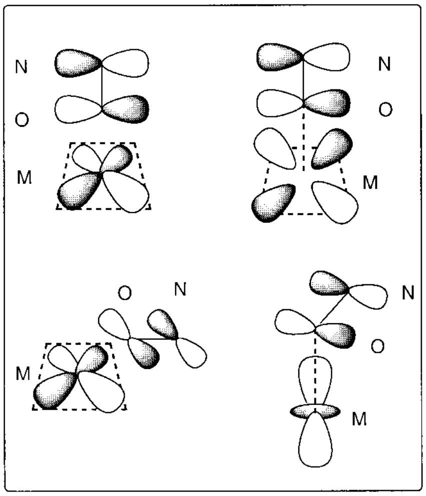
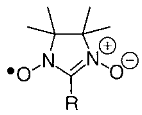


Figure 4. Potential orbital overlap scenarios between a nitroxide ligand and a central transition metal M.



3 R = aromatic

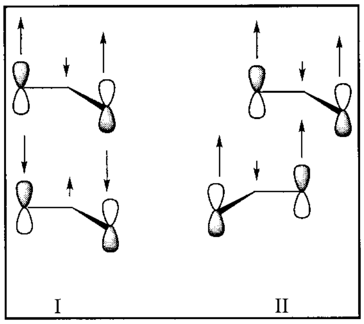


Figure 5. Schematic representation of the ideal alignment of spin densities in the McConnell model. Symmetric (I) and asymmetric (II) structures of the pair of allyl radicals. McConnell islets are present in structure II and absent in structure I.[19]

left is orthogonal and co-extensive. Simple nitroxides can interact with only one metal ion at a time and therefore cannot readily form extended magnetic structures. Gatteschi synthesised a series of compounds using bridging bidentate nitronyl nitroxide ligands, i.e. 2-alkyl-4,4′,5,5′-tetramethylimidazoline-1-oxyl-3-oxide (3).[16] If the two oxygens present in the NO groups bind to two different metal ions, a polymeric structure could be formed with effective pathways to transmit the magnetic interactions between the metal ions, leading to polymeric chains containing alternating spins on the metal and on the ligand. Gatteschi discovered that above 20 K manganese centres complexed to hexafluoroacetylacetonate (hfac) ligands behaved as typical ferromagnetic chains, but at low temperatures [T_C=7.6, 8.1, 8.6 K for R=*i*-Pr, Et, *n*-Pr] a three dimensional ferromagnetic ordering occurred and the magnetic moment rapidly increased. The ferromagnetic phase transition observed has been attributed to dipolar interactions between chains. A lower transition temperature was observed for the analogous Ni complexes and this was explained by the smaller spin of nickel, which makes the dipolar interaction less effective. The interaction between metal ions and radicals was very strong within the chains but, unfortunately, the chains were very well shielded from one another.

Since classical ferro- or ferri-magnetic order can be achieved only in three dimensions, because one dimensional materials order only at 0 K, the critical temperatures could only be increased if the interactions between the chains were enhanced. In order to achieve this Gatteschi chose to either introduce additional donor atoms on the NIT(R) radicals and hence to increase the number of metal ions to which an individual radical can be bridged, or to use co-ligands other than hfac, which favour the formation of adducts between the metal ions and the weak radical ligands, but very efficiently shield the chains from one another. The most encouraging results were found using $Mn[(pfbz)_2]_2 \cdot \mathbf{3}$ (pfbz=pentafluorobenzoate, and R=Me or Et) which ordered magnetically at temperatures as high as 20 K. Although the nature of the phase transition was not clear, there was evidence that these complexes behaved as weak ferromagnets.[15] The interested reader is directed to recent reviews in this area.[17,18]

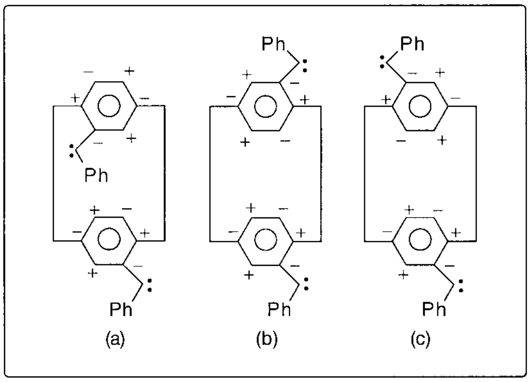


Figure 6. (a) Pseudo-*ortho*-, (b) pseudo-*meta*- and (c) pseudo-*para*-bis(phenylmethylenyl)-[2,2-*para*-cyclophanes].

2. Conceptual Models for Organic Molecular Magnets

Key models proposed for the development of organic ferromagnets, and the experimental work involved in evaluating these models will be described in this section. It is generally acknowledged that three models proposed in the 1960s form the basis for most of the discussion about how to design an organic magnet.

2.1. Negative spin density product model

The earliest proposal for achieving ferromagnetic interactions between organic free radicals was put forward by McConnell in 1963.[14] This model has only in the last few years received widespread interest in explaining through-space ferromagnetic interactions. McConnell stated that: "radicals with large positive and negative atomic π-spin densities which pancake such that atoms with positive spin density are exchange coupled to atoms with negative spin density should result in a ferromagnetic exchange interaction". McConnell's model therefore relies upon the construction of a crystal lattice of radicals in such a way that atoms with opposite spin densities are aligned side by side for each pair of radicals, as in the allyl radicals in Fig. 5. While anti-ferromagnetic interactions completely cancel the spins in (I), ferromagnetic interaction is possible if some atoms on the radicals have negative spin densities and the orientations of the radicals are such that spin densities of opposite sign couple most efficiently as in (II). It is thus possible to exploit an inherently anti-ferromagnetic coupling to produce bulk ferrimagnetism. In this way the McConnell model for organic π radicals is seen to be analogous to the Kahn model mentioned in the previous section.

The mechanism described above relates to pairwise ferromagnetic exchange, not to bulk ferromagnetism that requires ferromagnetic exchange in three dimensions. To achieve ferromagnetic exchange, routes to spin pairing must be avoided. This requires the use of stable species such as the radical anions from tetracyanoethylene $[TCNE]^{\cdot -}$ or tetracyano-*p*-quinodimethane $[TCNQ]^{\cdot -}$, which do not easily dimerise and contain atoms with unequal positive and negative spin densities such that it is conceivable that they might form a structure that complies with McConnell's requirement.[20] Of the numerous structures reported, however, the overlap required to satisfy the

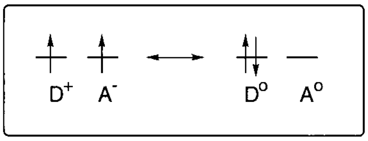


Figure 7. Radical ion CT complex with a singlet excited state.

McConnell model has never been achieved. Even stable radicals undergo dimerisation to form diamagnetic species.[21] A number of competing reactions such as carbon–carbon bond formation between $C(CN)_2$ moieties on adjacent TCNQ molecules have also been reported.[22] Expertly designed model cyclophane species with the required solid state packing were synthesised by Izuoka et al. in order to test McConnell's model (Fig. 6).[23]

Among the three isomers of bis(phenylmethylenyl) [2,2-*para*-cyclophanes] only the pseudo-*ortho* and pseudo-*para* isomers satisfy McConnell's condition in that the sign of the spin density product at each interacting site is negative, leading to ferromagnetic coupling of the two triplet carbenes and a quintet ground state, as observed by ESR. The overlapping mode in the pseudo-*meta* isomer leads to anti-ferromagnetic coupling and hence a singlet ground state. This provided the first experimental demonstration that the spin distribution of the π electrons in layered benzenoids can determine the ferro- or anti-ferromagnetic interaction between carbene units. The application of the McConnell-I model to this particular system has been investigated theoretically.[24]

2.2. Charge-transfer complex models

2.2.1. McConnell's model (II) and $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$. In 1967, at a Robert Welch Foundation Conference, Mulliken delivered a lecture on charge transfer complexes during which he considered spin interaction.[25] In normal ion radical charge-transfer solids, intermolecular spin pairing (antiferromagnetism) is a result of the mixing of a ground state and a singlet back charge-transfer state of a charge transfer pair (Fig. 7).

Following Mulliken's lecture McConnell proposed a detailed model utilising specific charge transfer complexes to produce molecular ferromagnets.[26] McConnell predicted that if an ionic charge transfer pair (D^+A^-) could be built that had a back charge-transfer excitation to a neutral triplet state, rather than to a singlet state, then the D^+A^- pair could also be a triplet due to mixing of the charge transfer state with the ground state (Fig. 8). If this mixing of a high spin arrangement could be organised between adjacent donors and acceptors in a multi-dimensional array within a solid, then macroscopic parallel alignment and thus ferromagnetic behaviour of solids should be possible.

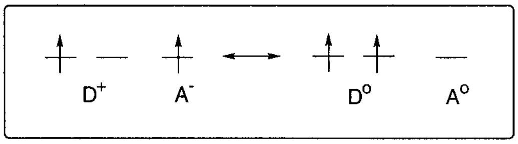


Figure 8. Back charge transfer to a triplet excited state.

Although Mulliken's lecture and McConnell's theories were published, they were not widely available, and as a result remained largely unknown until the work of Miller and Epstein[27] and of Breslow and co-workers.[28] McConnell's model relies on the following four basic criteria being fulfilled:

1. formation of a complex of the type $A^{\cdot-}$, $D^{\cdot+}$ where $A^{\cdot-}$ is the radical anion of the acceptor and $D^{\cdot+}$ is the radical cation of the donor;
2. crystallisation as mixed $(A^{\cdot-}, D^{\cdot+})_n$ not discrete $(A^{\cdot-})_n$ and $(D^{\cdot+})_n$ stacks;
3. significant admixture of the excited state A^{2-}, D^{2+}; and
4. either A^{2-} or D^{2+} to be a ground state triplet species.

By using Hund's rule as applied to molecules and biradicals,[29] the lowest energy excited state that can virtually admix with the ground state can be identified, thus enabling prediction of the magnetic coupling.[30]

For virtual forward charge transfer, excited states $EsFC^{D\rightarrow A}$, $EsAF^{D\rightarrow A}$, and $EsAC^{D\rightarrow A}$ are possible (Fig. 9). From Hund's rule the most easily lost $D^{\cdot+}$ electron has $m_s=-1/2$ and can only be transferred to the ferromagnetically coupled $A^{\cdot-}$ (Fig. 9(a)). Transfer of an $m_s=1/2$ electron to an anti-ferromagnetically coupled $A^{\cdot-}$ requires admixture of higher excited states (Fig. 9(b) and (c)). Forward charge transfer to the ferromagnetically coupled ground state may thus lead to ferromagnetic behaviour.

The seminal example of this was the complex $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ reported by Miller, Epstein and co-workers in which bulk ferrromagnetic behaviour was observed ($T_C=4.8$ K).[31] This was the first example of a magnet with spins residing in p-orbitals. It exhibited magnetic hysteresis, was soluble in organic solvents and did not require metallurgical preparative methods.[32] According to the McConnell mechanism the driving force behind its ferromagnetism is the triplet ground state character of $[Fe^{III}(C_5Me_5)_2]^{2+}$. This leads to ferromagnetic coupling between $[Fe^{III}(C_5Me_5)_2]^{\cdot+}$ and $[TCNE]^{\cdot-}$ both within the stack and between out of registry adjacent stacks giving the full three dimensional coupling of spins required for bulk ferromagnetism. Although the application of the McConnell II mechanism to these systems has been challenged,[33] it provides a simple rationalisation, if the direction of charge transfer is known, to the nature of the magnetic coupling. A variety of TCNE-based organic magnets have been discovered, including the remarkable $V^{II}(TCNE)_x{\cdot}y(CH_2Cl_2)$ which has a T_C above room temperature (ca. 400 K)[34] as well as $M(TCNE)_x{\cdot}y(CH_2Cl_2)$ types containing other transition metals and [Mn(porphyrin)][TCNE]-based magnets.[35] There is also a class of ferromagnetic materials with Prussian Blue structures, e.g. $V[Cr(CN)_6]_{0.86}{\cdot}2.8H_2O$ ($T_C=315$ K),[36] and the current record-holder with a T_C greater than 100°C, $KV[Cr(CN)_6]{\cdot}2H_2O$.[37]

2.2.2. Hexaminotriphenylene dication and hexaazaoctadecahydrocoronene complexes. Since the advent of McConnell's initial model, many adaptations have been linked to attempts to design synthetically accessible molecules to prove or disprove the model. In 1982

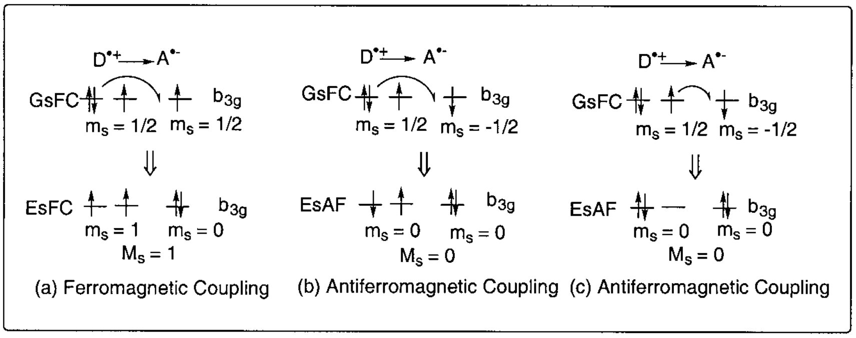
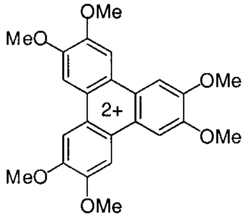


Figure 9. Donor–acceptor complex excited states (Es, lower half of diagram) derived from the ground states (Gs, upper half of diagram) by further transfer of charge from $D^{+\cdot}$ to $A^{\cdot-}$.

Breslow[28] suggested an improvement to the McConnell model that stemmed from his earlier work on cyclic conjugated systems with 4n π electrons. This led him to propose that 4n π electron cyclic conjugated systems had the potential to behave as ground state triplets, provided these systems had C_3 or greater symmetry. Such symmetry leads to orbital degeneracy in some molecules, while the presence of 4n π electrons causes half occupancy of a degenerate orbital pair with consequent spin unpairing and single occupancy of each orbital. There is no guarantee, however, that a symmetrical 4n π molecule will have a triplet ground state and therefore Curie Law studies (or similar) must be performed to ensure the ground state is not a singlet. Species such as $C_5H_5^+$ and $C_5Cl_5^+$ were known to have triplet ground states, but these molecules are chemically unstable. Following a report by Parker, in which it was claimed that the hexamethoxytriphenylene dication **4** had a triplet ground state,[38] Breslow synthesised[28] several triphenylene derivatives.



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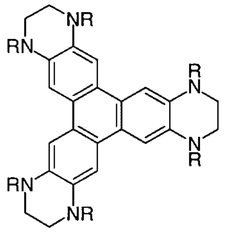
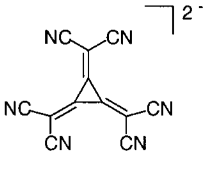


5 R = H, Et, CHF_2CH_2



6

The dication **4** had no real chemical stability and to form it required high positive potentials, thereby limiting the search for suitable anion acceptors. Breslow modified this molecule producing various hexaaminotriphenylene derivatives **5** which had greater stability and formed the relevant dication at much lower potentials, i.e. (**5**→**5**$^{2+}$ 0.27 V) compared to (**4**→**4**$^{2+}$ 0.85 V) [**5**=2,3,6,7,10,11-tris(*N*,*N*′-diethylenediamino)triphenylene]. Breslow claimed these species were ground state triplets and the dications were subsequently used in tests of Breslow's own model. When these dications have triplet spin multiplicity a forward charge transfer from D^+A^- to $D^{2+}A^{2-}$ is required (Fig. 10).

This leads to greater charge on the molecules than envisaged by McConnell's original proposal and favours the alternating donor–acceptor stacking required for donor–acceptor mixing. The interactions of donor and acceptor in the solid must induce substantial forward transfer and disfavour back charge transfer such that the neutral singlet charge transfer configuration is high in energy. For forward charge transfer to occur the donor and acceptor must be of similar potentials. It is also crucial that the donor has a stable triplet as one of its redox forms. The preference is for as large a triplet–singlet energy gap as possible in order to stabilise the spin parallel arrangement. Most challenging is maintaining the threefold symmetry of the donor, which effectively provides the degeneracy.

To test this model Breslow used the hexacyano compound **6** as an acceptor. This required alteration of the donor, with R=Et being replaced by the more electron withdrawing R=CHF_2CH_2, in order to match the donor/acceptor potentials, thus providing the correct amount of charge transfer in the solid. Despite satisfying the conditions of the model, namely alternating donor–acceptor stacking, partial second charge transfer and a triplet donor cation, the material was found to exhibit anti-ferromagnetic coupling. This may be a result of the instability of the triplet ground state of the donor, a loss of degeneracy resulting from a loss of symmetry of the donor in the complex (i.e. Jahn–Teller distortion) favouring the singlet ground state, or the intermolecular interactions may not be general or multidimensional enough.

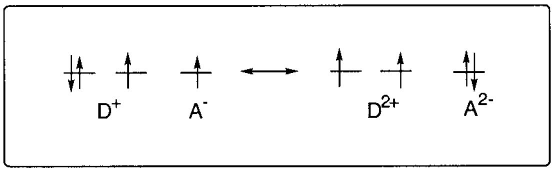


Figure 10. Forward charge transfer from symmetrical donor–acceptor complexes.

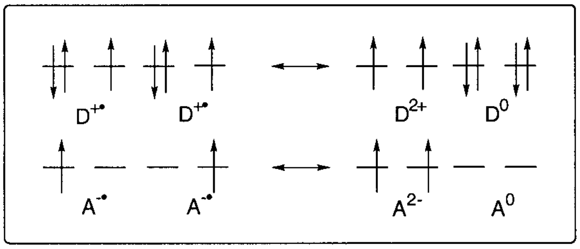
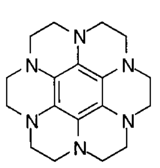
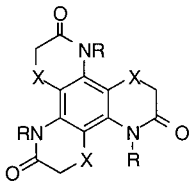


Figure 11. Torrance's model of orbital filling in cation/anion pairs.

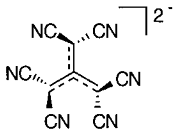


7

HOC



8 X = O, S
R = H, Me



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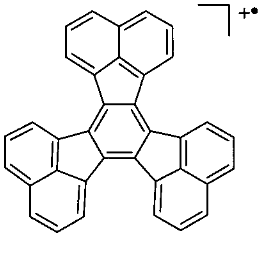
Breslow[39] turned his attention to hexaazaoctadecahydrocoronene (HOC) **7** which has a larger gap between the singlet and triplet energy states. He also examined variants of the tris(*N*,*N*′-diethylenediamino)triphenylene (**5**), such as **8**, because sulphur atoms on the edge of electrically conducting organic stacks can facilitate sideways interactions between the stacks. The non-planarity of these systems, however, made them much more difficult to oxidise. The dication of **7** was prepared and its role in charge transfer complexes was investigated by Miller and co-workers[40] who found that crystalline salts of $[\mathbf{7}]^{2+}$ with $(C_3[C(CN)_2]_3)^{2-}$, and of **9** with $(C_3[C(CN)_2]_3)^{2-}$ were in fact ground state singlets and that $[\mathbf{7}]^{\cdot+}[TCNE]^{\cdot-}$ showed strong anti-ferromagnetic interactions.

2.2.3. Decacyclene cation salts and symmetrical polyamines. Another modification of McConnell's model was proposed by Torrance[41] who suggested that a stack of highly symmetric radicals could have spins in degenerate orbitals which should have a triplet excited state as a consequence of the radical cation/anion of the molecule having the appropriate filling (Fig. 11).

Torrance made stable radical cation salts of decacyclene, **10**, with the anions shown. These salts had the stoichiometry $(decacyclene)_3X_2$ where X is the anion. Magnetic susceptibility measurements revealed, however, that these materials were not ferromagnetic.

n



BF_4^-, ClO_4^-, PF_6^-
AsF_6^-, ReO_4^-, SbF_6^-
TaF_6^-, HSO_4^-

10

This may be due to unknown complications in the structures of the complexes, distortions of the structures which destroy the symmetry, the widths of the bands formed by orbital overlap being too large compared to Hund's rule, intra-atomic exchange, or there may be complicating effects such as spin orbit interactions. Breslow's compounds were ideal candidates for Torrance's model but they were also found to be anti-ferromagnetic.

Torrance also suggested linking together symmetric polyamine type molecules in a way that maintained symmetry (Fig. 12). Oxidation of these structures was then used to produce spins.[42]

Torrance suggested that such a structure may have been produced in the reaction of triaminobenzene with iodine. This yielded a black insoluble polymer, which on rare occasions, showed the presence of small amounts of ferromagnetic material; however, these results proved irreproducible.

2.2.4. Complexes of TCNQ, PCCP, DDQ, etc. with various cations. Soos and co-workers tried to extend the

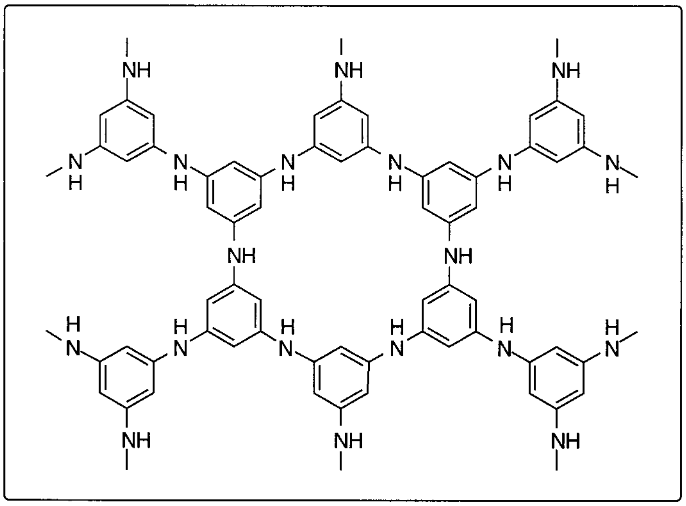


Figure 12. 2-D symmetric polyarylamine structure.

superexchange mechanism established for inorganic solids to organic stacked complexes.[43] In a mixed $R^{\cdot}SR^{\cdot}S$ stack, an excited triplet state may be obtained if the spacer molecule S has degenerate orbitals into which the spins of radical $R^{\cdot}$ are transferred during virtual excitation (Fig. 13). This requires the orbital degeneracy of S to be maintained in the solid complex and this is only possible if the orientation of $R^{\cdot}$ is such that the perturbations on the degenerate MOs of S are equal.

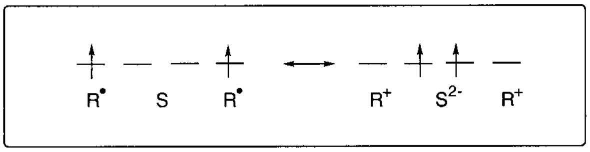
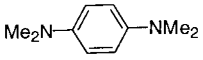
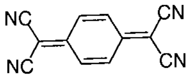


Figure 13. Spin transfer into the degenerate orbitals of a spacer molecule.

A spacer with a degenerate HOMO or LUMO should allow ferromagnetic coupling via charge transfer when radicals are orthogonal to each other. Soos et al. used ion radicals based on strong organic donors such as *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) **11** and strong organic acceptors such as tetracyanoquinodimethane (TCNQ) **12**.

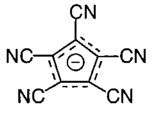


11 (TMPD)

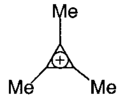


12 (TCNQ)

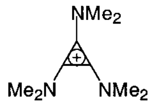
Appropriate spacers for the ion radicals are closed shell anions, X^-, like pentacyanocyclo-pentadienide (PCCP) **13** which has a degenerate HOMO, or cations, X^+, such as trimethylcyclopropenium (TMC) **14** or tris(dimethylamino)cyclopropenium (TDAC) **15** which have degenerate LUMOs.



13 (PCCP)$^-$



14 (TMC)$^+$



15 (TDAC)$^+$

The coulombic interactions present should promote mixed stacking $D^+X^-D^+X^-$ or AX^+AX^+. The preparation of a TMPD/PCCP complex in which the dihedral angle was 41° rather than the required 90° resulted in weakly antiferromagnetic interactions.[44]

Other complexes produced by Soos included a 1:1 TDAC/DDQ (2,3-dichlorodicyanobenzoquinone) complex. This was, however, found to have a dimerised stacking pattern of $X^+A^-A^-X^+$ by X-ray crystallography, which ruled out the possibility of superexchange.[44] It was proposed that this was the result of the strong tendency of DDQ^- ions to dimerise owing to strong dipolar attraction and exchange interactions. Replacing DDQ by TCNQ, which does not have a permanent dipole, however, failed to improve the situation.[45]

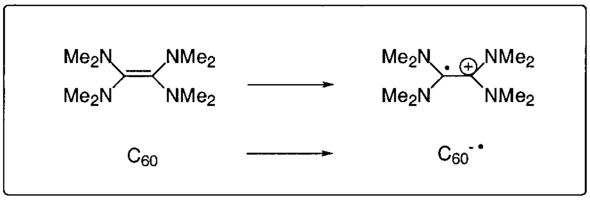


Figure 15. CT complex of TDAE and C_{60}.

2.2.5. CT complexes containing fullerenes. Wudl and coworkers proposed another variation of McConnell's model based on a ferromagnetic organic metal.[46] The design involved neutral diradicals, with the intent of generating neutral organic metals. Wudl suggested that the neutral donor could be a triplet and the acceptor could be the radical ion derived from the donor (Fig. 14). This would allow the generation of homomolecular stacks that could give rise to ferromagnetic organic molecules.

This differed from McConnell's model in that the stoichiometry was D_2A and species either side of the double arrow in Fig. 14 would be identical, thus satisfying the spin conservation rules. Wudl therefore required stable donor radicals, which had triplet ground states and would not dimerise or polymerise. A study of benzobisdithiazole (**16**) was prompted by the fact that cross-linking had never been observed in compounds containing $[-S-N-S-]^{\cdot}$ groups. Contrary to the favourable precedent, however, the biradical **16** was found to exist as an oligomer both in solution and in the solid state by ESR spectroscopy, which also indicated that if monomeric forms of **16** existed they would adopt a singlet rather than triplet ground state.

In 1991 it was discovered that buckminsterfullerene exhibited superconductivity upon doping with alkali metals.[47] Structural studies had shown that interstitial holes in the fullerene's face centred cubic structure could accommodate metal ions[48] and cyclic voltammetry had shown that C_{60} and C_{70} could easily be reduced.[49] Theoretical calculations had also established that the LUMO and HOMO of C_{60} were triply and five-fold degenerate, respectively.[46] It was proposed that such a

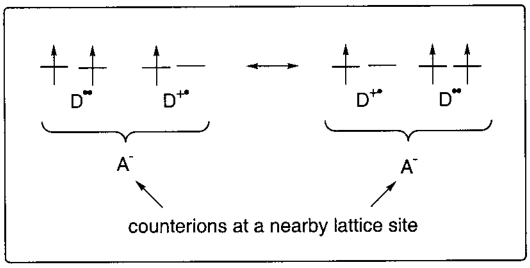
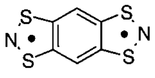


Figure 14. Orbital filling in homomolecular stacks of neutral and cationic donors.



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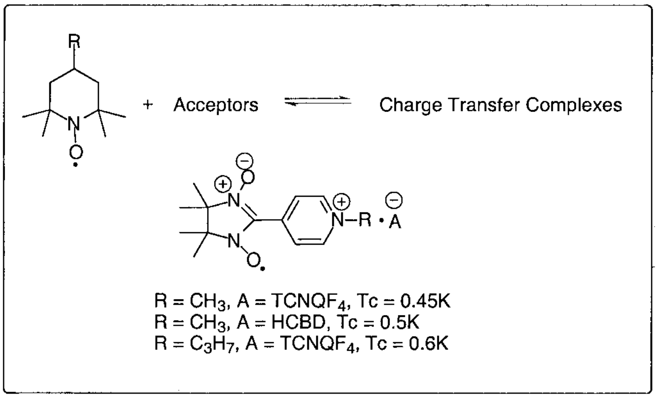


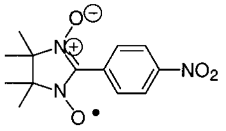
Figure 16. CT complexes containing nitroxide and nitronyl nitroxide donors.

large number of degenerate levels could lead to unusual electronic and magnetic properties. Wudl utilised the strong acceptor properties of C_{60} to form a 1:1 charge transfer complex with TDAE (Fig. 15).[50]

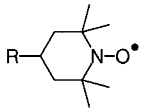
Magnetic susceptibility measurements established that this complex underwent a transition to a state in which the spins ordered ferromagnetically and that at 16 K the material showed magnetisation without remanance, i.e. without retention of magnetism outside an applied field. This was thought to indicate a transition to a soft itinerant ferromagnet.

2.3. Organomagnetic materials based on nitroxide radicals

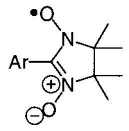
2.3.1. Mono-nitroxides, poly-nitroxides and nitronyl nitroxides. The discovery of *p*-nitrophenyl nitronyl nitroxide (**17**), the first ever bulk organic ferromagnet, was made by Kinoshita and co-workers in 1991.[51]



17 $T_c = 0.65$ K



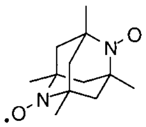
18 TEMPO



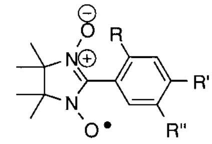
19 Nitronyl nitroxide

Today many of the over 20 known organic ferromagnets are nitroxide-containing materials. Nitroxide radicals have an inherently stable electronic configuration and can be further stabilised by conjugation with the π electrons of aromatic systems and/or by shielding with bulky substituents. Radicals such as TEMPO derivatives **18** and nitronyl nitroxides **19** have been central to the development of organomagnetic materials. The SOMOs of most mono-nitroxides are localised mainly on the N–O moiety and the unpaired electron resides there. In nitronyl nitroxides the unpaired electron is delocalised between nitrogen and oxygen and between both NO groups. The general strategy for designing nitroxide-containing magnetic materials has been to prepare molecules with large intramolecular spin polarisations, and to minimise the intermolecular overlap integrals between the SOMOs of adjacent radical centres, and the vacant or doubly occupied molecular orbitals of neighbouring molecules.

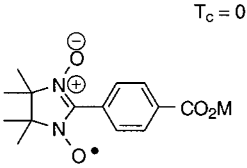
In 1993 Rassat and co-workers suggested that 1,3,5,7-tetramethyl-2,6-diazaadamantane-*N*,*N*′-dioxyl (**20**) in addition to exhibiting intramolecular ferromagnetic interactions, should also take part in intermolecular ferromagnetic interactions due to the three dimensional network of NO chains.[52] Further work followed in an attempt to either arrange the spin sources through hydrogen bonding effects in compounds such as **21**[53,54] or through control of the coulombic interactions, as in **22**, for which magnetic measurements indicated ferromagnetic interactions present in **22a** and **22c**.[55] The various design considerations in α-nitronyl nitroxide research have been reviewed recently.[56]



20 $T_c = 1.48$ K



21 R, R'' = OH, R' = H
$T_c = 0.5$ K



22 a. M = Li
b. M = Na
c. M = K

Multi-spin systems composed of nitroxide radicals have received significant attention in the design of molecular magnets. Iwamura and co-workers prepared the triradicals **23** and **24** and found that the tris-nitroxide **24** had a stronger intermolecular spin interaction than **23** and that **24** had a quartet ground state.[57] Despite many other attempts to produce crystalline radicals with high T_C values, the highest obtained remains 1.48 K for Rassat's radical (**20**).

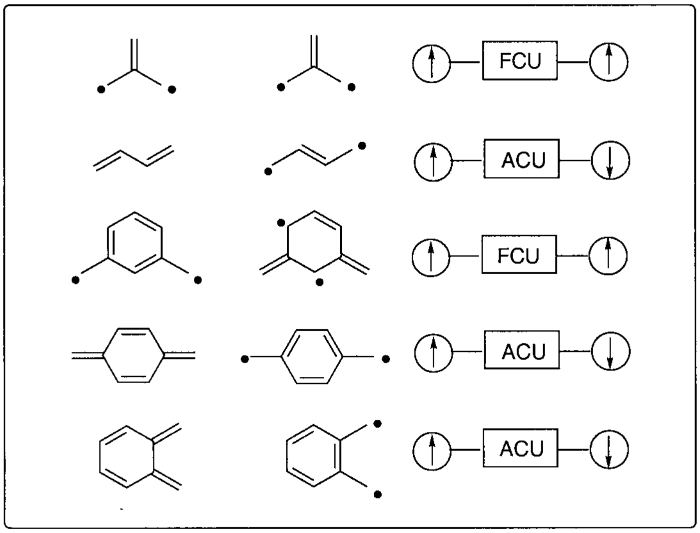
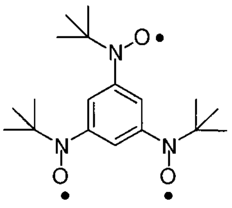


Figure 17. Molecular topology and spin coupling.



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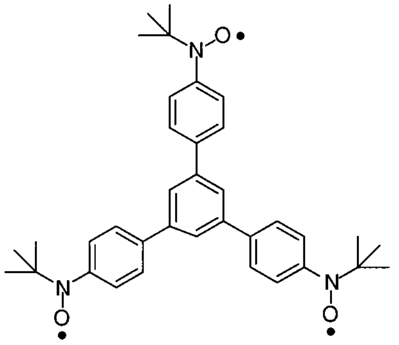

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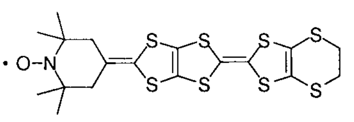

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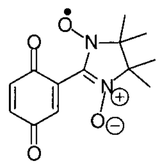

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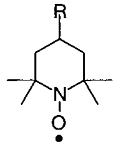

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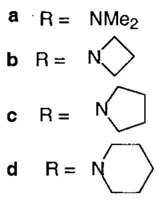


2.3.2. CT complexes containing nitroxide radicals. Recent attempts to produce charge transfer complexes employing acceptors paired with donors carrying nitroxide radicals have focused on tetrathiafulvalene (TTF) or aromatic alkyl amine donors functionalised with nitroxide radicals, coupled with DDQ or $TCNQF_4$ acceptors. These have mainly proved unsuccessful in producing ferromagnetic charge transfer salts. Sugimoto et al. succeeded in developing a ferromagnetic charge transfer salt based on pyridinium-substituted imadazolin-1-oxyl with $TCNQF_4$ or hexacyanobutadiene acceptors (Fig. 16).[58]

Recently the $Au(CN)_2^-$ salt of the extended TTF structure **25** was prepared and its crystal structure determined.[59] The coupling in $[\mathbf{25}]_2[Au(CN)_2]_3$ was, however, found to be anti-ferromagnetic due to strong spin–spin interaction via short O···O distances between donor sheets.

Limited success has also been achieved using acceptor molecules, most commonly benzoquinone derivatives, to carry stable nitroxide radicals. Sugawara and co-workers observed ferromagnetic interactions in a radical anion salt carrying a nitronyl nitroxide **26**, in the absence of a donor, i.e. the nitroxide radical itself acted as a donor.[60]

In their comprehensive review of this field Nakatsuji and Awzai[61] report preliminary results on alkylamino-TEMPO derivatives **27a–d** prepared by the reductive amination of 4-oxo-TEMPO with alkyl amines using sodium cyanoborohydride.[62] Compound **27d** exhibited ferromagnetic interactions with a Weiss constant of 0.5 K.

2.4. The topological model and applications to synthetic polyaryl-carbenes and polyaryl-radicals

2.4.1. Molecular topology and spin alignment. The topological model can be simply explained by considering the trimethylenemethane biradical, first reported by Dowd[63] as a ground state triplet, as predicted famously by Longuet-Higgins.[64] This biradical can be viewed as two methyl radicals connected 1,1 to ethylene. Alternatively, two methyl radicals connected 1,2 to ethylene will electronically reorganise to butadiene, which has a ground state singlet (Fig. 17). It follows that connectivity in molecular structures (topology) determines the nature of spin-coupling. Similar considerations apply to benzene-containing biradicals where *m*-benzoquinodimethane has a triplet ground state and acts as a strong ferromagnetic coupling unit (FCU) whereas its *ortho*- and *para*-isomers are ground state singlets and act as anti-ferromagnetic coupling units (ACU) (see Fig. 17).[65] Notice that all of the FCU groups are non-Kekulé

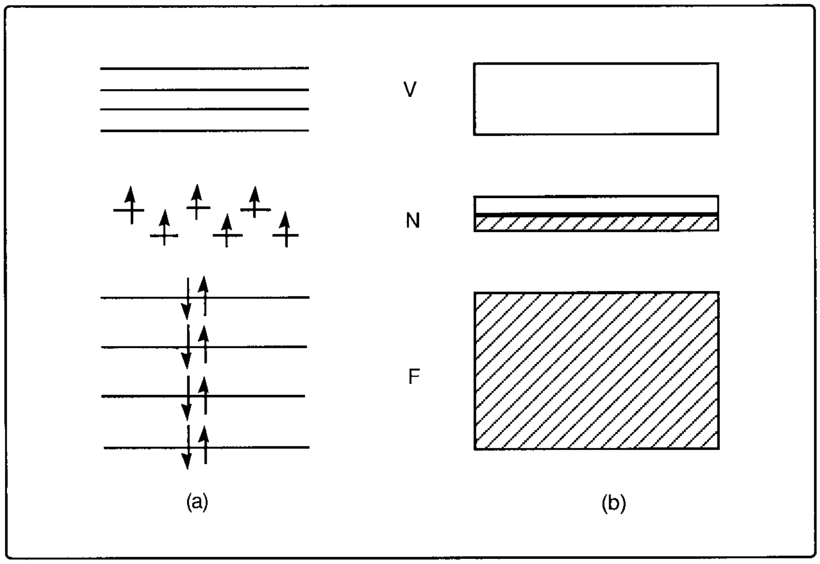
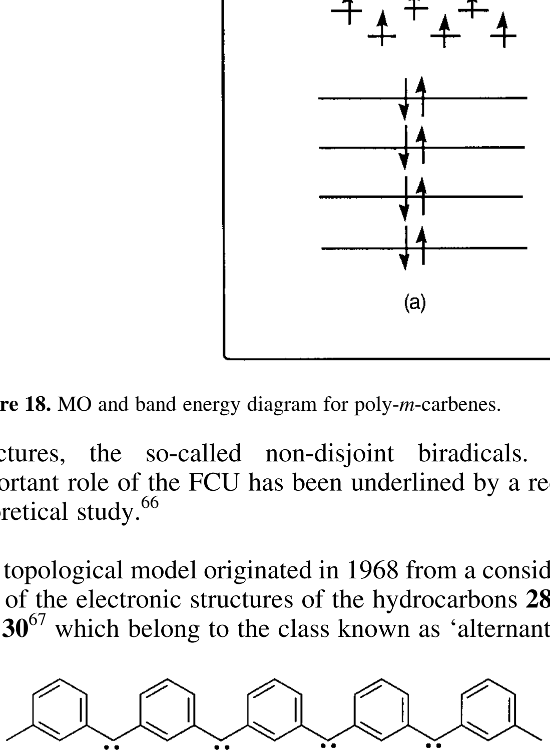


Figure 18. MO and band energy diagram for poly-*m*-carbenes.

structures, the so-called non-disjoint biradicals. The important role of the FCU has been underlined by a recent theoretical study.[66]

The topological model originated in 1968 from a consideration of the electronic structures of the hydrocarbons **28**, **29** and **30**[67] which belong to the class known as ‘alternant’.



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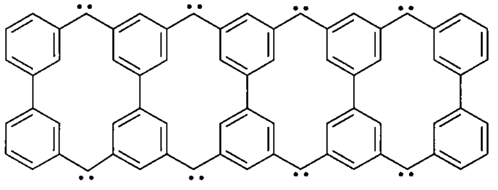

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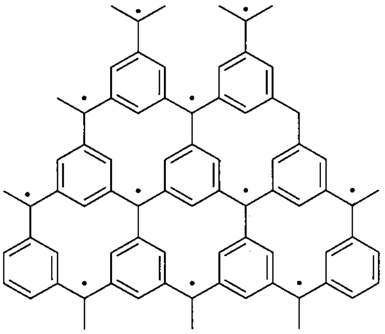

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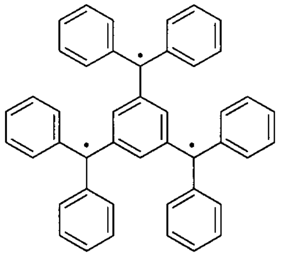
A conjugated π-system is defined as alternant if its atoms can be subdivided into two groups denoted by A and A* such that each A* atom is surrounded only by A atoms, and vice versa. In the case of the polycarbenes **28** and **29** it is assumed that one of the atomic orbitals of the divalent carbon participates in conjugation with the ring π system while the other remains as a σ-type orbital. If the assumption is made that these molecules are essentially planar then, according to Hückel MO theory, or Pariser–Parr–Pople (PPP) theory, these *meta*-substituted alternant hydrocarbons have multiple degenerate non-bonding π-molecular orbitals (NBMOs).[68] The number of π-NBMOs is equal to the number of carbons with unpaired electrons. The π-NBMOs and the σ-type NBMOs are not equal but are probably close in energy. The energy levels of these hydrocarbons will therefore be of the form shown in Fig. 18, where F indicates the π-MOs doubly occupied by electrons, V indicates the vacant π-MOs in the ground electronic state, and N indicates both the π-NBMOs and the σ-type NBMOs. If the orbital energy difference between the non-bonding electrons is sufficiently small then, according to Hund’s rule, electrons entering these orbitals will do so singly and with parallel spins as shown in Fig. 18(a). The spin pairing therefore depends on the exchange integral between the π-NBMOs and the σ-type NBMOs and the energy difference between these orbitals. Alternant hydrocarbons are clearly better for high-spin molecules since parallel spins are not on adjacent atoms. Mataga proposed that for sufficiently large molecules the orbital energies will become almost continuous bands as indicated in Fig. 18(b). Because of its non-bonding nature, however, the N band will remain sufficiently narrow to support degeneracy; hence parallel alignment of the spins of the electrons in this band can be expected. Alternatively, the band gaps between F, N, and V may become comparable to kT, so that ferromagnetism may only be supported at cryogenic temperatures.

Ovchinnikov proposed an even simpler model to predict ferromagnetic coupling in planar alternant hydrocarbons.[69] Based on the theorem of Lieb,[70] Ovchinnikov showed that if the number of starred (A*) and unstarred atoms (A) are not equal, the ground state spin, S, will be non-zero and equal to half the difference in their numbers, i.e. $S=|N^{*}-N^{0}|/2$. On the basis of this result Ovchinnikov suggested several hydrocarbons, such as **31** and the heterocycles **32**, **33**, which at infinite size could be expected to show ferromagnetic behaviour. The spin in polymers such as **32** would be proportional to the number of chain links.



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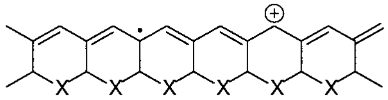
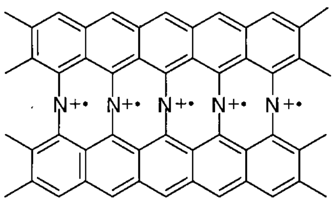


32 X = O, S



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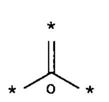

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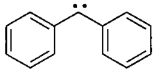
Klein et al.[71] supported the possibility of obtaining high spin hydrocarbons on the basis of valence bond models, as well as calculations using classical structures, MO theory, cluster expansions and PPP Hamiltonians. The simplest test for the odd alternant hydrocarbon model is again the trimethylenemethane biradical **34** for which the theory predicts $S=|N^*-N^0|/2\rightarrow(3-1)/2=1$, i.e. ground state triplet, which was confirmed by experiment.[63]

2.4.2. Poly(*m*-phenylene carbenes and nitrenes). Iwamura and Murata studied systems containing two phenyl nitrene units connected through acetylenic and diacetylenic bridges. It was observed that two triplet nitrenes at *meta*, *para′* and *meta*, *meta′* positions showed ferro- and anti-ferromagnetic interactions, respectively.[72] This validated the theory of Ovchinnikov[69] and Klein[71] and agreed with the rule proposed by Radhakrishnan,[73] which can be applied to biradicals, and states that if the number of atoms between radical sites is odd then ferromagnetic coupling occurs whereas if the number of atoms between sites is even, anti-ferromagnetic coupling occurs. This simple rule provides a useful guideline for the design of potential ferromagnetic coupling units.

Early experimental work had already proved that oligomeric derivatives of the model compounds proposed by Mataga, such as diphenylmethylene[74] **35** and *m*-phenylene-bis-phenylmethylene[75,76] **36**, have triplet and quintet ground states, respectively. Investigations of phenylene carbenes were initiated by Itoh and co-workers[76] who studied *m*-phenylene-bis-phenylmethylene **36**, formed by the photolysis of 1,3-bis-(alpha;-diazobenzyl)-benzene, and observed a quintet by EPR spectroscopy at 77 K.



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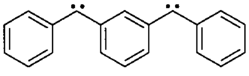

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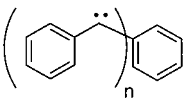
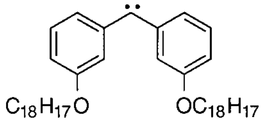


37 n = 4, **38** n = 5

Iwamura continued to study polycarbene compounds and in 1985 reported the nonet spin multiplicity of the ground state of the tetracarbene **37**. It was found that **37** displayed paramagnetic susceptibility with varying temperatures. This compound was termed a 'superparamagnet' because the electrons within the molecule were aligned in parallel but individual molecules behaved independently of one another, similar to a paramagnet. Iwamura claimed that partial intermolecular ferromagnetic interactions were observed in **39** because the dispersion forces due to the alkyl chains insulated the magnetic interactions between layers.[77]



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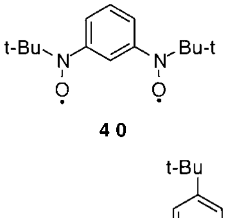
Theoretical work on Mataga's model continued using more accurate modelling packages which confirmed the expected ferromagnetic ground state in phenylene carbene polymers.[78] The synthesis of an $S=5$ carbene, **38**, was achieved by Iwamura[79] and its ground state was shown to be the expected undecet by EPR spectroscopy. In practical terms, however, the usefulness of polycarbene and nitrene compounds was restricted by their instability. Attention thus turned to analogous radical species capable of greater chemical stability.

2.4.3. *m*-Linked poly(aryl nitroxides). Calder et al.[80] utilised the stability of nitroxide radicals and linked these through a 1,3-substituted benzene ring to yield the biradical **40**, which was shown to be a ground state triplet by magnetic studies. The bis-nitroxide **40** was, however, not fully persistent and isomerised to an aminoquinone imine-*N*-oxide. Research was therefore diverted to more stable diaryl nitroxide polymers such as **41**. The poly-nitroxide **42** was synthesised and found to be stable at ambient temperature for several weeks.



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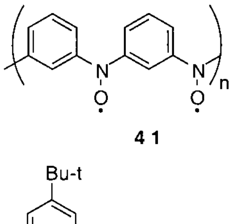

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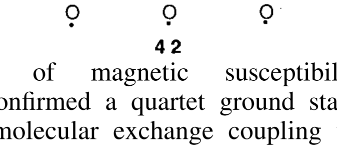

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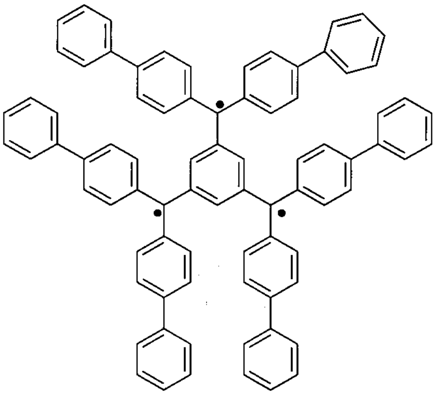
Measurements of magnetic susceptibility against temperature confirmed a quartet ground state indicating that the intramolecular exchange coupling was strongly ferromagnetic and that perturbation by heteroatoms did not affect the topological model.[81] Evidence of a band of degenerate NBMOs between bonding and anti-bonding MOs in polyphenylene nitroxides was provided by Tyutyulkov who also showed that these polymers suffer from a smaller degree of spin polarisation in the π-network compared to the analogous carbenes.[82] Smaller exchange interactions may indicate that high spin polynitroxides do not exist at ambient temperatures. An analogue of **40** with CF_3 groups in the 4- and 6-positions was quenched to the singlet state at 5 K.[83]

2.4.4. High spin hydrocarbons, chlorocarbons and heterocycles. Mataga also proposed that the triphenylmethyl type radicals could exhibit ferromagnetic coupling. Compound **43** was found to have a quartet ground state but was prone to rapid dimerisation.[84]



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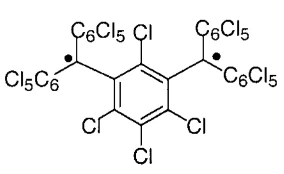
Since this observation, a series of related high spin hydrocarbons have been detected including 1,3,5-tris(phenylmethylene), $S=3$,[85] biphenyl-3,3′-bis(phenylmethylene), $S=0, 1, 2$,[86] 1,3,5-benzenetrityl[bis(biphenyl-4-yl)methyl], $S=3/2$,[87] and 3,3′-diphenylmethylene-bis-(phenylmethylene), $S=3$.[88]

In an endeavour to improve the stability of this type of compound, Palacio and co-workers produced a stable biradical (**44**) which had a triplet ground state and had a large separation between the triplet and singlet ground states.[89] The better stability was the result of the restricted rotation of the aryl groups, and also of the steric shielding provided by the Cl atoms.



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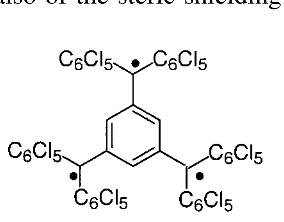

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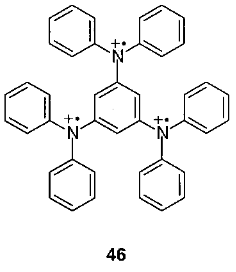

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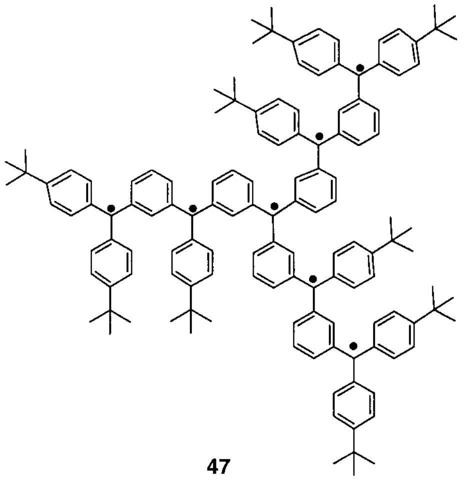
Extension to the triradical **45** produced a compound with a quartet ground state which was stable at 250°C in air.[90] The intramolecular exchange interactions were ferromagnetic and perturbation by electronegative heteroatoms, lack of planarity, and changes in symmetry had little effect on the coupling. It appears, therefore, that the topological model can be applied to highly distorted systems. Further evidence of this was provided by Tanaka et al. who observed a quartet ground state in the trication of 1,3,5-tris(diphenylamino)-benzene **46**.[91]

2.4.5. Star branched and dendritic aromatic polyradicals. Rajca's group has made significant progress in the design and synthesis of potential organic ferromagnets based on systems which are homologous to *m*-benzoquinodimethane.[92] Rajca designed and synthesised the heptaradical **47** and the decaradical **48** based on a 'star-branched' topology. These polyradicals showed high spin ground states with strong ferromagnetic coupling ($S=7/2$ and $S=5$). Magnetisation data suggested that the intermolecular interactions were ferromagnetic.[93]



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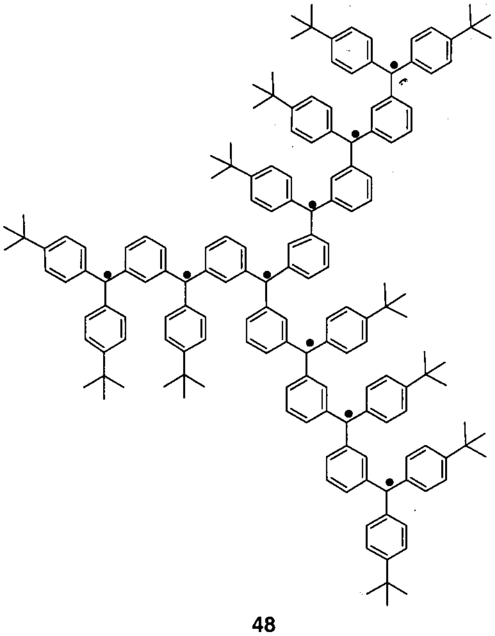

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Rajca also designed dendritic polyradicals including the heptaradical **49** as well as a pentadecaradical and a 31-radical

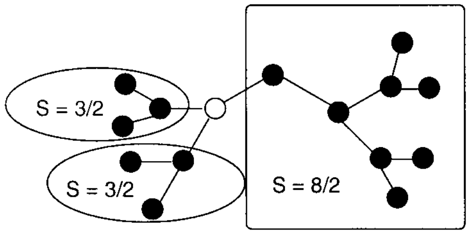
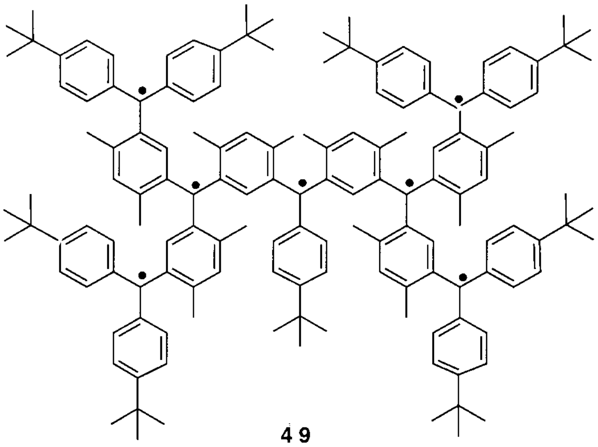


Figure 19. Inner-site defect in a polyradical.

dendrimer,[94] which were found to have average ground state spins of $S=3$, 7/2 and 5/2, respectively.



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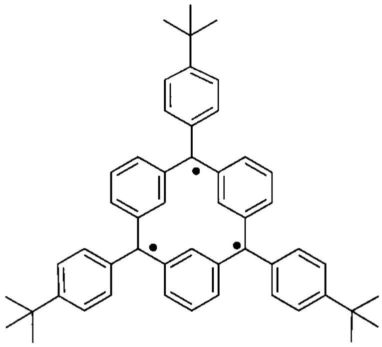
The observed spin deficiencies, known as spin defects, were due to the failure to generate spins at every potential site. Spin coupling in multi-site radicals such as these is extremely sensitive to these defects because they interrupt spin coupling paths.

2.4.6. Avoidance of spin defects via multiple coupling paths. It is difficult to overcome this problem unless improved methods of radical generation are developed. The site of the defect is also important, with defects at the inner sites being particularly detrimental. An inner site defect divides the polyradical into uncoupled parts with lower spin (Fig. 19), whereas defects at the peripheral sites are relatively innocuous (Fig. 20) (the circles represent spin sites and the lines are spin coupling paths).

Rajca attempted to overcome the problem of spin defects by designing molecules with multiple coupling paths, such as macrocyclic calixarenes, which are oblivious to one spin defect.[95] The triradical calix[3]arene **50** and the tetraradical calix[4]arene **51** were synthesised and, although **50** was found to dimerise readily, suggesting a lack of steric shielding of the radicals, the steric shielding in the calix[4]arene was sufficient to stabilise the tetraradical **51**. The out-of-plane twisting was moderate enough to preserve ferromagnetic coupling and therefore these macrocycles may be viable building blocks for defect resilient high spin polyradicals.



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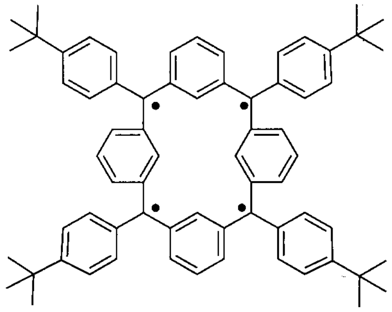

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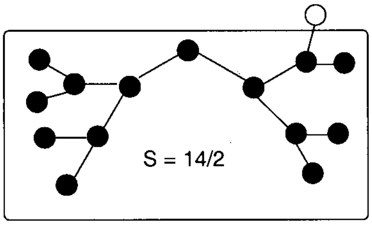


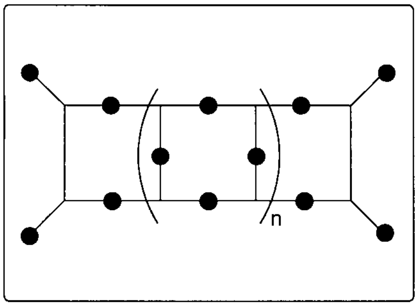
Figure 20. Peripheral site defect in a polyradical.

Highly annelated polymacrocyclic systems are difficult to synthesise, however, although oligomeric fragments which have two strands (see Fig. 21) are accessible by convergent synthetic routes and maintain π conjugation and ferromagnetic coupling in the presence of defects.[96]

Characterisation of **52** in THF-d_8/2-MeTHF by SQUID magnetometry indicated $S=6.2$, which is below the theoretical value of 7 expected for strong ferromagnetic coupling of 14 unpaired electrons. Quenching studies showed that approximately one deuterium atom from the solvent was incorporated in **52**, accounting in part for $S<7$. A study of the temperature dependence of the magnetisation disclosed that the ferromagnetic coupling between the spins was not very strong, probably because of an out-of-plane distortion of the π system. Rajca concluded that the development of 2-D and 3-D ferromagnets would require careful design to accommodate three considerations namely π conjugation, a connectivity compatible with ferromagnetic coupling and steric hindrance to stabilise radicals. These factors had to be compatible, of course, with a feasible synthetic strategy.

An alternative to the *m*-phenylene unit was examined by Rajca, who proposed that sterically unencumbered 3,4′-biphenyl units might possess a suitable size of spin coupling and might also stabilise radicals (Fig. 22).[97]

The biradical **53** was found to be thermally stable and to have a triplet ground state which showed that 3,4′-biphenyl could be used as a weak ferromagnetic coupling unit. Rajca then proposed that high spin modules should be linked to



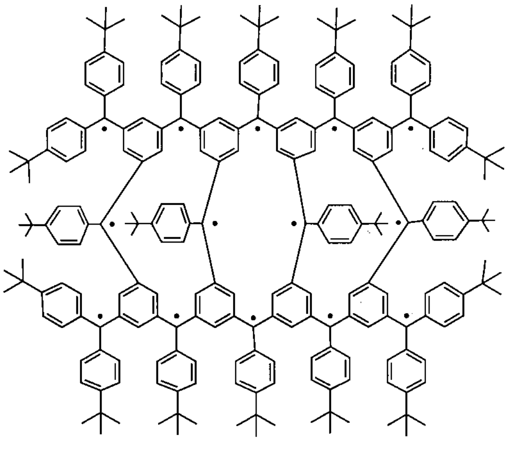


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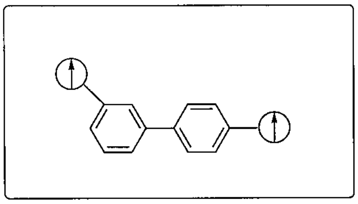
Figure 21. Two-strand polymacrocyclic systems.



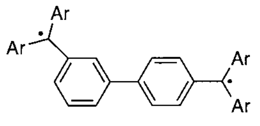


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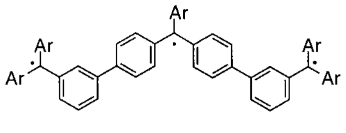
Figure 22. 3,4′-Biphenyl as a ferromagnetic coupling unit.

these weak FCUs to form the spin clusters **54**–**57**. In these spin clusters intramodular ferromagnetic coupling was very strong compared to the weak intermodular coupling through 3,4′-biphenyl units.[98] The polyradicals **54**–**56** possess only one site where a single defect may interrupt spin coupling whilst **57** has two such sites. The hydrocarbon **57** was potentially a hexadeca-radical and was found to have an impressive S=7.2. The estimated yield per site for the generation of unpaired electrons was as high as 98% and the development of spin clusters of this nature led to the synthesis of a polyradical with S=10.[99]



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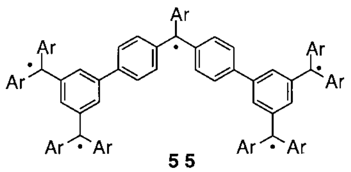

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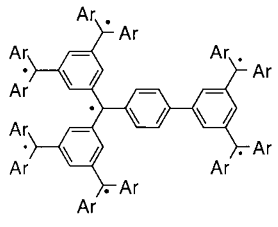

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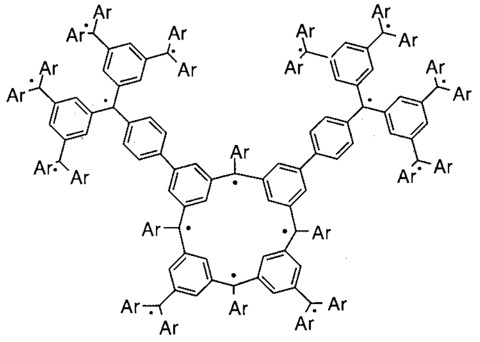

57

The four dendritic branches of the macropolyradical **58**, and the macrocyclic core, can be divided into component spins. The ferromagnetically coupled pentamer with S'=5/2, 5/2, 5/2, 5/2 and 2 should have an overall ground state with S=12 (Fig. 23).

A graph of M vs. H/T for **58** showed $S\sim10$ at 5 K. This is the highest spin recorded for an organic ferromagnet. The polyradical **58** benefits from the fact that only four of the 24 radical sites are defect sensitive. Rajca is currently working on analogues of **58** in which dendritic branches are replaced by macrocycles.

2.4.7. Polymers, oligomers or dendrimers with radical side-chain or pendant groups.

A variation of the topological model for preparing ferromagnetically coupled radical groups should not be overlooked. This approach,

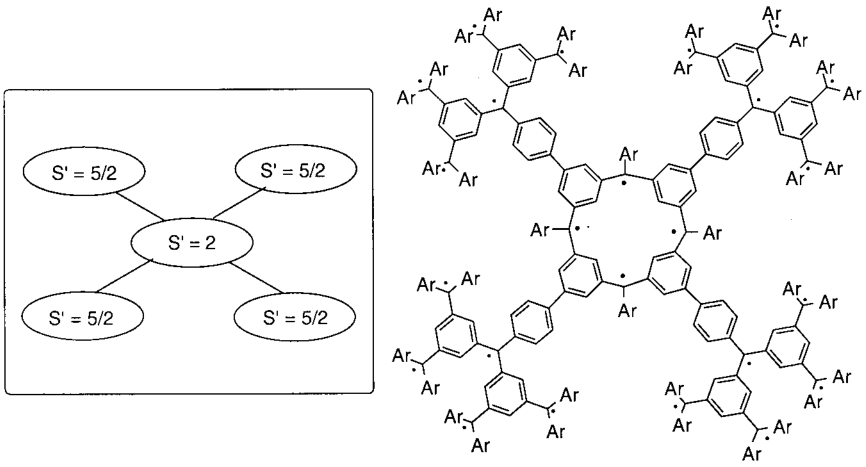

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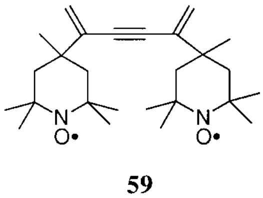
Figure 23. A macropolyradical with four dendritic branches.

proposed and first acted upon by Ovchinnikov, and later developed by Nishide and co-workers, introduces the radicals as pendant groups along a conducting polymer backbone, rather than embedding them in the chain or network. Unlike the systems mentioned in the previous section it is believed that pendant group polymers such as these can couple spins over the conjugated backbone even when there are defects (incomplete spin generation). Particular effort has been made to employ radical groups such as nitroxides and phenoxyls with greater stability than the carbon-based radical units described above. Earlier work, including systems with pendant radical groups attached to non-conjugated backbones, was described in a previous review by the authors.[100]

Ovchinnikov prepared the polymer from the diacetylene monomer **59**.[101] It was reported to display ferromagnetic interactions even at room temperature, but this claim was later challenged by Miller.[102] Other examples using this strategy have nevertheless been prepared since the Ovchinnikov paper appeared. For example, polyphenylacetylenes were prepared with various radical groups, including nitroxides, such as **60**. None of these polymers showed, however, any ferromagnetic interactions between the groups. There was only evidence of weak anti-ferromagnetic though-space interactions. The reasons for this were thought to be the non-planar nature of the polyacetylene backbone and the twisting of the pendant phenyl rings. Polyphenylene backbones would also suffer from twisting; however, polyphenylenevinylenes (PPVs) show evidence of considerable conjugation over several rings. PPV-backboned polymers with pendant nitroxide groups (e.g. **61**) were prepared by Heck head-to-tail coupling of the protected bromostyrene monomers, followed by removal of the protecting group and oxidation with PbO_2.[103] Magnetic measurements showed that *ortho*-linked **61** reached a spin concentration of 0.54 spins per monomer unit and had $S=1$. The related *para*-linked material was much less effective, despite the expected greater conjugation in the backbone. This was shown to be due to steric interactions between the pendant nitroxide groups and the chain, causing twisting out of planarity.[103]



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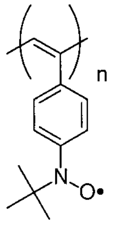

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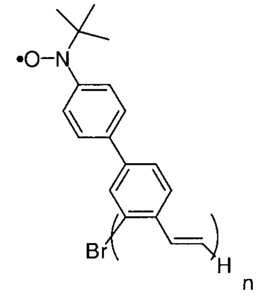

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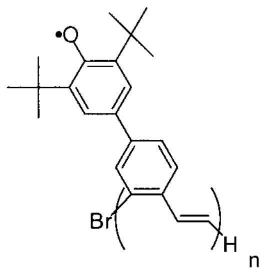
Phenoxide radicals were introduced onto the PPV backbone to give a protected polymer precursor which was subsequently deprotected and heterogeneously oxidised ($K_3Fe(CN)_6$) to **62**[104] with a degree of polymerisation $n=17$. SQUID magnetic measurements suggested that an average spin per monomer unit of 0.7 was achieved and that these coupled to give an effective spin quantum number of 4/2 to 5/2 at 2–15 K, indicating a high-spin ground state. Using electron-spin transient nutation spectroscopy based on pulsed ESR spectroscopy it is possible to resolve this bulk *S*-value into a mixture of spin components which include segments with *S* as high as 8/2 and 6/2.[105] Clearly, the move to the PPV backbone has thus proved to be a successful strategy in this area, provided that spin concentration levels can be optimised. Recently, similar star-shaped dendrimeric polymers with pendant polyphenoxyl radical units were derived from a 1,3,5-benzene core and magnetic susceptibility measurements gave an average *S* of >7/2.[106]



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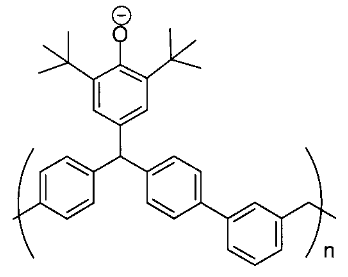


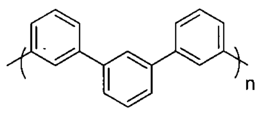
6 3

The most recent improvement of this approach has come from Dougherty who suggested that electrochemically doped poly(*m*-phenylenefuchsone), **63**, was an advance on other proposed systems in that it provided the first example of electrochemical doping in a polaronic ferromagnet, the first use of a radical anion in a polaronic ferromagnet, the first positive correlation between spin concentration and spin state, the first positive correlation between doping level and spin concentration and the first high spin polaronic system with $>50\%$ spin concentration.[107] Electrochemical doping (oxidation) of **63** in THF with *t*-butylammonium perchlorate as the supporting electrolyte resulted in $S\approx 2$ behaviour at a doping level of 61%. This is a significant result considering that each oligomer was found to be seven units long at most and therefore the maximum spin expected was 7/2.

2.5. The polaronic model: preparation of ferromagnetically coupled conjugated spin-containing segments

2.5.1. Fukotome's proposal of ferromagnetically coupled polarons. Fukutome proposed a new class of ferromagnetic conjugated polymers in which delocalised spins were to be generated by doping of conjugated segments. These polymers have an alternating A–B–A–B structure, where the A units are organic blocks which furnish polarons on doping (spin containing units, SCU) and the B units are blocks which couple the A block polaron spins in a ferromagnetic fashion (ferromagnetic coupling units, FCU) (Fig. 24).[108]

Fukutome suggested the use of oligomeric fragments of conducting conjugated polymers as SCUs, for example, *trans*-polyacetylene, poly-*p*-phenylene, polypyrrole or polythiophene, which all have degenerate or nearly degenerate band structures. On doping each conjugated segment with an electron or a hole, a series of polarons, which are ion-radicals trapped in local lattice distortions, can be produced. Examples of non-degenerate segments as suitable FCUs were suggested and these include poly-*m*-phenylene **64** and the polyketone **65**.



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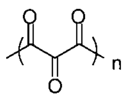
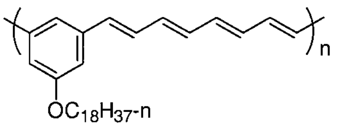


65

This polaronic model was supported by Tyutyulkov who maintained that the band structures of these polymers were analogous to those of odd alternant non-classical polymers.[109] The polaronic design had the potential to overcome the problems of instability associated with 'built in' radicals. The polaronic approach could separate the polymer synthesis stage from the introduction of spins, thus allowing full characterisation of the polymers, and hence ensuring that the desired topology for ferromagnetic coupling had been created, prior to the introduction of spins.

2.5.2. Dougherty's synthesis of poly(*m*-phenyleneoctatetraene). The first experimental approach to this model was undertaken by Dougherty and co-workers who employed *m*-phenylene as the FCU and a tetraene as the easily oxidised polaron precursor.[110] *O*-Alkyl groups were also attached at the 5-position of the phenylene ring to aid solubility. The poly(*m*-phenyleneoctatetraene) PMPOT-18, **66**, was lightly doped with AsF_5 to form polarons which were found to be stable at room temperature. Magnetic studies indicated $S\geq 2$, suggesting the existence of significant net ferromagnetic coupling in the system. It became clear that the doping was inhomogeneous and that regions of relatively heavier doping allowed significant ferromagnetic coupling of the spins, which were found to persist to at least 200 K. It could not be confirmed that these results were due to 1-D intramolecular couplings. Some intermolecular anti-ferromagnetic coupling was also observed at low temperatures.



66

On the basis of molecular orbital calculations and crystal orbital theory, Yamabe considered substituted polyacetylenes as potential 1-D ferromagnets.[111] Although the interactions of doped poly(4-oxyphenyl)acetylene were found to be anti-ferromagnetic, polyacetylene chains with phenoxyl radicals as pendants on each alternate site showed possible ferromagnetic couplings. Further theoretical work

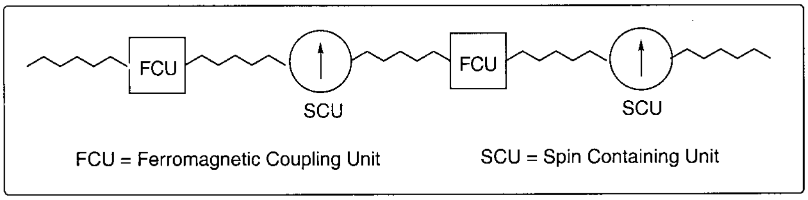
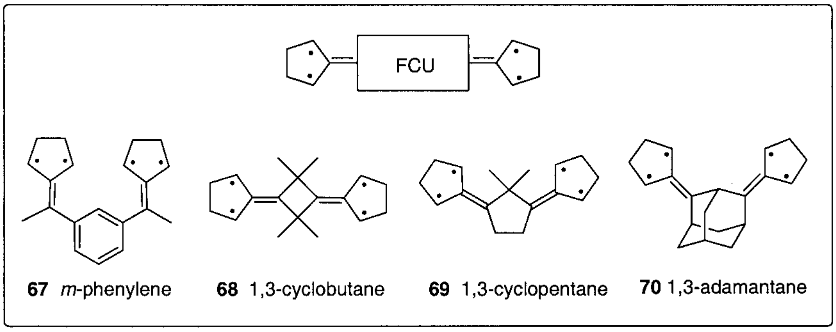


Figure 24. Conceptual model of a polaronic ferromagnet.



67 *m*-phenylene **68** 1,3-cyclobutane **69** 1,3-cyclopentane **70** 1,3-adamantane

Figure 25. Use of 2-alkylidene-1,3-cyclopentanediyl units for evaluating FCUs.

established that the interactions of $-C^{\cdot+}H$, $-N^{\cdot+}H$ and $N-O^{\cdot}$ linked through *m*-phenylene were much stronger than when coupled through a polyacetylene chain, and that the interactions would be ferromagnetic. It was also suggested that although bulk ferromagnetism in 1-D systems can only be observed at 0 K, there are always weak 3-D interactions such as interchain coupling. Ferro- or antiferro-magnetic ordering may therefore appear at a finite temperature.[112]

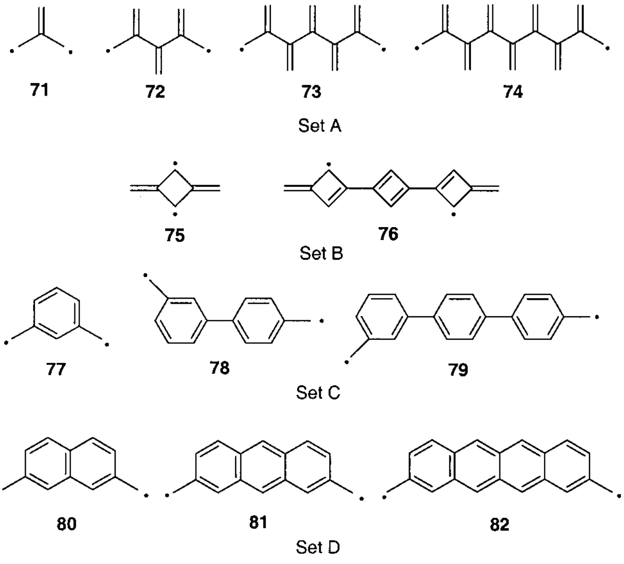
2.5.3. Measuring the effectiveness of ferromagnetic coupling units for use in polaronic model materials.

In the majority of polaronic models *m*-phenylene has been chosen as the ferromagnetic coupling unit since it is generally considered the most effective.[113] Dougherty surmised that the choice of ferromagnetic coupling units would be critical to design and began investigating various potential FCUs in the early 1990s. He concluded that magnetism arises when the overlap integral between orbitals is small but the exchange integral remains large. This is possible in fully conjugated, planar π systems with topologies that produce two or more NBMOs which are degenerate and where the critical issue is the extent to which these NBMOs overlap in space, rather than their relative energies. He devised a method of evaluating FCUs based on 2-alkylidene-1,3-cyclopentanediyl units which have a large triplet preference, are synthetically accessible, and are sufficiently thermally stable. These units provided robust triplets that could be linked via each potential FCU to enable the strength and nature of spin coupling to be determined by EPR spectroscopic and magnetic methods. Initial studies focused on the coupling units shown in Fig. 25.

When ferromagnetic coupling of the triplet spins occurs, a quintet should be observed by low temperature EPR spectroscopy. The species **67** and **68** were found to be good FCUs whilst **69** acted as a weak FCU. In **70**, however, the spins were coupled in an anti-ferromagnetic fashion. Studies on the strength of spin coupling have also been carried out by Li et al.,[114] using the effective valence bond model,[115] on the biradicals **71–82** (Sets A–D) that allowed the estimation of the singlet/triplet energy separation, ΔE_{ST}, which reflects the strength of spin coupling between two unpaired sites, and additionally relates to chemical reactivity (Scheme 1).

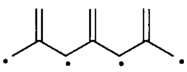
For Set A ΔE_{ST} decayed drastically with increasing topological distance between the spins; the same was found for Set B. For Set C, ΔE_{ST} also decreased, but in a more gradual manner. Interestingly, the coupling through three sequential benzene rings was still appreciable. Strong ferromagnetic coupling would appear to prevail in biradicals with short topological distances between spins and also where numerous spin-coupling paths and large delocalisation effects are present in the SCUs.

The same research group also investigated to what extent the coupling of the FCU in biradicals is maintained in polyradicals and ferromagnetic polymers, using the classical valence bond model based on vinylidene **83**, biphenyl **84**, and *m*-phenylene units **85**. It was found that the coupling through vinylidene decreased appreciably from the biradical to the linear triradical.



	ΔE_{ST}/eV			
Set A (71-74)	1.555	0.146	0.029	0.006
Set B (75,76)	1.492	0.248		
Set C (77-79)	1.146	0.380	0.147	
Set D (80-82)	0.842	0.634	0.487	

Scheme 1.



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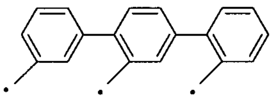

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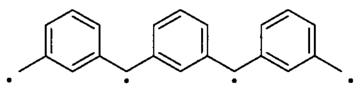
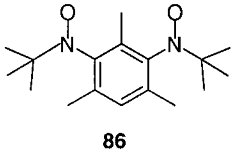


85

The spin coupling through *m*-phenylene in the biradical was reduced by one-third in the linear triradical. The magnitude of coupling through the central *m*-phenylene in a tetraradical was lower than the terminal *m*-phenylene and was taken to be a good approximation for a poly(*m*-phenylmethylene) system. The 2,3′-connected biphenyl unit was found to have a slightly greater coupling in the linear triradical **84** than in the biradical due to an amplification effect of the two outer spins on the central spin.

The effectiveness of intramolecular spin-coupling through *m*-phenylene has been extensively studied by means of several theoretical models and also by experiments.[116,117] On the whole, *m*-phenylene has proved to be by far the best FCU for constructing high spin molecules and for truly practical magnetic materials. In 1995, however, Iwamura argued that since thiophene rings are more electron rich than benzene, they are better equipped to stabilise radical cations. In addition, thiophene rings are sterically less demanding than benzene, which could result in the planarity of polymer backbones being maintained more easily. As an interesting alternative he coupled nitronyl nitroxides through 2,4-substituted thiophenes.[118] The interactions between the nitronyl nitroxides were found to be ferromagnetic and were larger than those observed through *m*-phenylene, presumably due to an increase in co-planarity and hence greater spin polarisation. Extension to bithienyl units, however, greatly weakened the interactions to the extent that degenerate singlet and triplet states were produced. This was accounted for by the poor delocalisation of the nitroxide's spin into the thiophene ring.

It would be advantageous to be able to estimate the effectiveness of *m*-phenylene in systems where the radical centres may be out of conjugation with the aromatic ring. Several groups have addressed this issue and have found that, in the highly crowded bisnitroxyls **86**[119] and **87**,[120] the two SCUs are twisted completely out of conjugation and the biradicals have singlet ground states. In contrast, the extremely congested polyaryl derivatives **88**[89] show high spin states despite a large degree of twisting.



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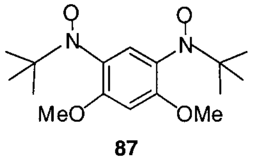

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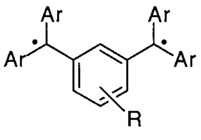
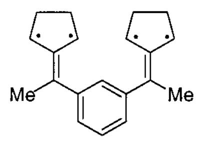


88 R = Cl

Using the bistrimethylenemethane strategy, Dougherty found that in conditions of modest twisting, the *m*-phenylene probe **89** remained an effective FCU. Completely twisting both SCUs out of conjugation with the *m*-phenylene the probe **90** led to no interaction whatsoever whereas having one SCU in plane and one completely out of plane in probe **91** still led to ferromagnetic coupling.[121] This was accounted for by a novel mechanism in which anti-ferromagnetic coupling between a centre of negative spin density and a centre of positive spin density gave overall ferromagnetic coupling.



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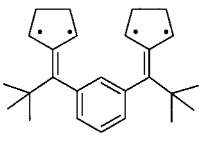

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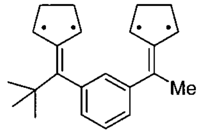
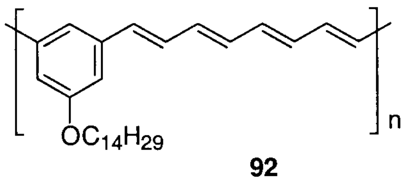


91

In addition to EPR spectroscopic and magnetic methods it may be possible to screen the degree of ferromagnetic coupling between spin-containing centres using electrochemical methods. As pointed out by Bushby et al. in structurally related bis(dialkyamino)benzene compounds (based on Fig. 22) the peak separation for the sequential oxidation of the two amino centres should be related to the degree of electron–electron repulsion, which will have both a coulombic component (assumed to be similar in structurally related compounds) and an exchange component (which will depend on whether the diradical SOMO is disjoint or non-disjoint (i.e. coextensive).[122] Schultz has shown that this electrochemical screening may also be useful for bis-quinones.[123]

2.5.4. Polymers containing conjugated segments linked through *m*-phenylene units. Dougherty continued his work on polaronic ferromagnets, proposing a range of potential polaronic magnets **92–98** in order to determine which conjugated segments were best suited to producing a large number of spins that would interact strongly through the FCU.[124] Although Dougherty's designs involved 1-D ferromagnets only, the structures shown were expected to display short range, high spin ordering. The polymers **92–98** were prepared by Wittig[125] or Suzuki[126] type polymerisation reactions that afforded materials with an average molecular weight of approximately 10,000 amu. This was a considerable achievement because insufficient solubility can result in oligomeric chains precipitating from solution. These polymers were doped using iodine or arsenic pentafluoride and subjected to magnetisation studies.



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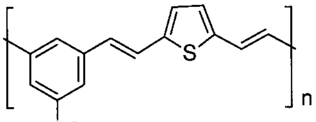

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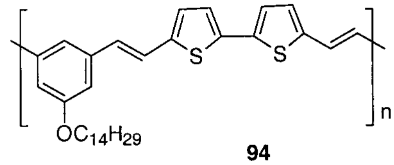

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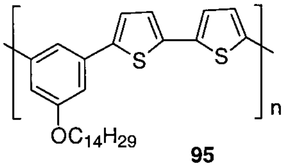

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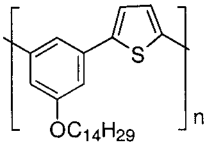

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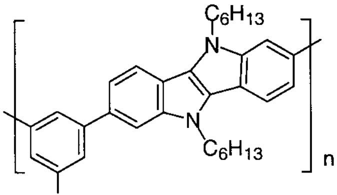

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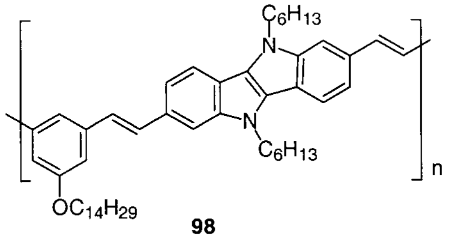
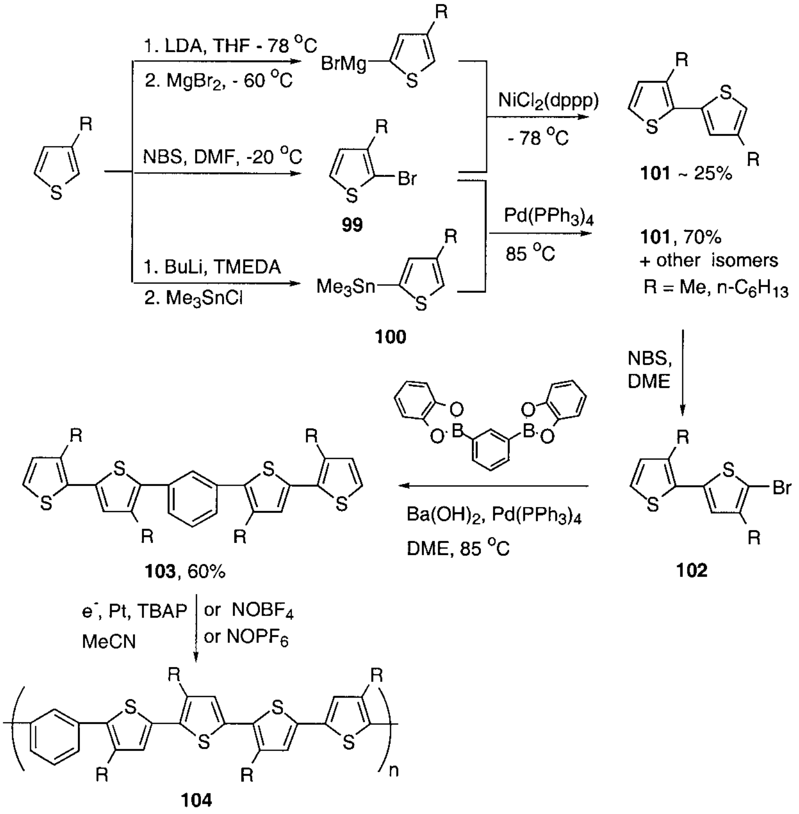


98

The best results were achieved for the polymer **97** in which one-third of the monomer units contained a spin. The spins produced were extremely stable with $S>1/2$ behaviour being observed. In general, however, less than one spin per chain was evident in these polymers. The magnetic behaviour was again explained by inhomogeneous doping which occurred due to the creation of a polar environment, which favoured further doping nearby.

A design consisting of tetrathiophene units *m*-coupled via phenylene FCUs (**104**) has recently been proposed.[127] The comparatively short, four-ring, SCU was chosen to minimise spinless bipolaron formation. Each thienyl ring was functionalised with an alkyl chain to promote solubility and processability. It was also expected that the large number of alkyl chains per polymer, and their siting in the conjugated sections of the backbone, would keep neighbouring chains apart and thus prevent π-dimerisation. Structural homogeneity and stereoregularity were necessary in order to maintain the backbone as close as possible to planar and hence to maximise polaron delocalisation. To achieve this, methods for the regioselective head-to-tail coupling of 3-alkylthiophenes were needed. Initially, the Ni catalysed coupling of a 2-bromo-3-alkylthiophene **99** with a 5-bromomagnesio-3-alkylthiophene was studied. This route delivered high regioselectivity but, despite

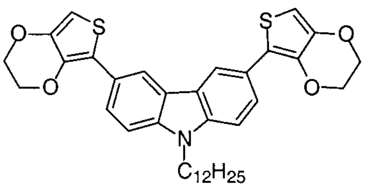


Scheme 2.

varying the coupling conditions, the ratio of reactants, the alkyl side chain and the catalyst, the yields of cross-coupled products **101** remained at ca. 25%. Satisfactory yields of **101** were obtained by Stille coupling of 2-trimethyltin-4-alkylthiophenes **100** with 2-bromo-3-alkylthiophene, but at the expense of lowered regioselectivity. The desired 5-bromo-3,4′-dialkyl-2,2′-bithiophene **102** was isolated in good yield by selective bromination of the isomeric mixture followed by column chromatography. Two molecules of **102** were successfully coupled to the *m*-bisboronic ester using modified Suzuki conditions to produce the monomer **103** in satisfactory yield (Scheme 2).

Electrochemical polymerisation of **103** (R=Me or H) with a Pt electrode gave polymers **104** containing the highest number of spins. Chemical polymerisation with NOBF$_4$ and NOPF$_6$ also produced satisfactory materials. UV–VIS and IR spectroscopy showed the formation of polarons on doping. The EPR spectra of these polymers were, however, consistent with paramagnetic materials except at low temperatures (<60 K) where some unusual features may indicate one-dimensional ferromagnet formation.[127,128]

Zotti et al. electropolymerised the monomer **105** to give a polymer with two distinct redox processes.[129] Localised oxidation of the bithiophene units occurred at +0.20 V, at which point a high spin density of 0.25 spins per unit was determined.

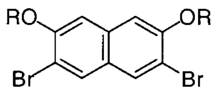


105

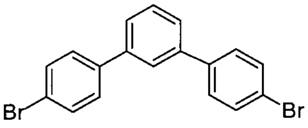
2.5.5. Polaronic poly(arylamines).

Although at first sight the rather localised oxidised amino groups of poly(arylamines) discussed in this section do not seem to be not entirely analogous to the extended polaronic SCUs described above, in fact these systems are closely related to the conducting polymer, polyaniline, in which the presence of delocalised spins is well established. Bushby et al. synthesised a polaronic polymer **108** with $S\sim5/2$ which featured aryl amines as spin containing units that were linked through *meta*-coupled benzene rings.[130] Unlike Dougherty's polymer, which was one dimensional, Bushby's polymer was cross-linked such that each SCU was ferromagnetically coupled to three others in order to counter the effects arising from incomplete doping. The percolation limit, the point at which all spins were aligned, for these systems was estimated to be 70%.[131] Bushby used spin bearing N$^{\cdot+}$ centres and 1,3,5-trisubstituted benzene rings to extend his structures in more than one dimension. The best results were achieved with a polymer obtained from the Suzuki reaction of the dibromide **106** with the trisboronic acid **107** (Scheme 3). Oxidation of **108** with NO$^+$BF$_4^-$ resulted in doping levels of ca. 15%, far short of the percolation limit and of the 10^3–10^4 spins required to sustain a ferromagnetic structure domain. A study of the magnetisation as a function of magnetic field strength suggested that **108** behaved most like an $S=5/2$ system. Further investigations by Bushby established that one reason for the poor doping levels was the difficulty of accommodating large counter ions in a rigid polymer, i.e. a steric rather than an electrostatic limitation.[132]

In an attempt to rectify this problem, Bushby linked the triarylammonium ions in the 2,7-naphthalene derivative **109** and the dibromide **110** rather than through 1,3-phenylene.

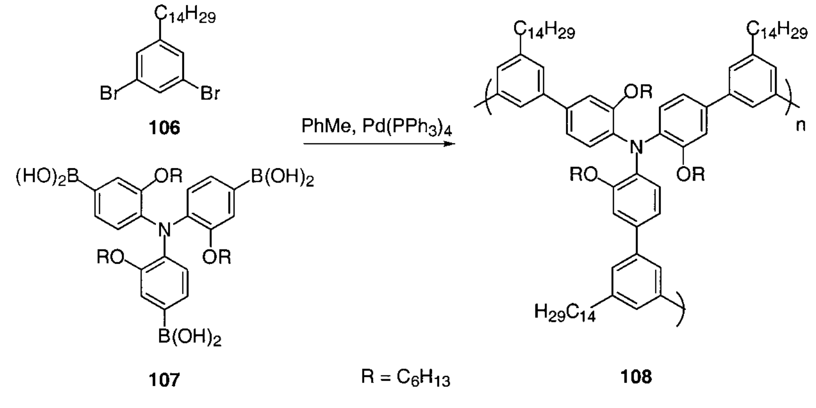


109 R = C$_6$H$_{13}$



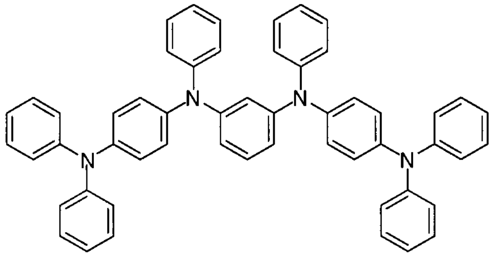
110

This 'spacing out' of the monomer units did not lead to higher doping levels with NO$^+$BF$_4^-$ in dichloromethane. A different doping technique using antimony pentachloride achieved higher doping levels but had poor reproducibility. It was also found that the thin polymer films required for this method of doping decayed rapidly. The polymer **108** could be doped to a level of 40% using SbCl$_5$ and it was then found to show $S=4$ behaviour.



Scheme 3.

It would appear that a significant problem associated with the polaronic model is achieving the necessary high levels of doping required for ferromagnetic coupling. The use of 'heavy' doping conditions can result in the formation of bipolarons which are spinless dications and thus detrimental to ferromagnetic design.[133] The emeraldine salt of polyaniline cannot accommodate bipolarons and may therefore be used as a basis for designing high spin density polymers. Janssen and co-workers[134] used this property in designing *N*-phenylaniline oligomers comprising alternate *meta*- and *para*-substituted rings to favour ferromagnetic coupling and radical cation stability, respectively.[135]



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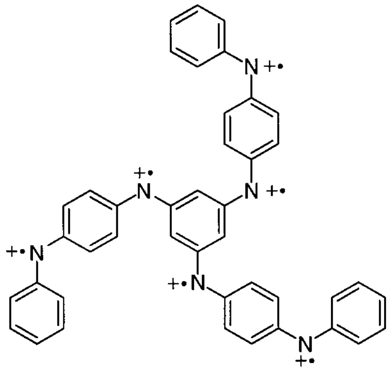
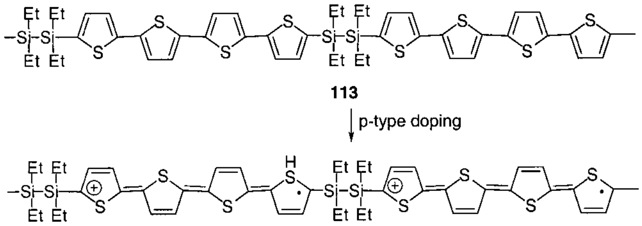


112

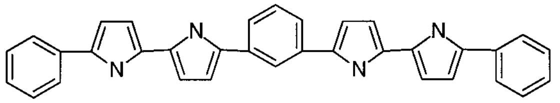
Oxidation of **111** with thianthrenium perchlorate afforded the dication radical, which was found to have a triplet ground state and showed no decay by EPR spectroscopy after several weeks. A study of **112** showed that it also had a high spin ground state. It was concluded therefore that these molecular types can be doped to produce stable triplet dication radicals.

The phenylenevinylene coupling unit has also been employed to good effect. The 3,4′-bis(diphenylamino)stilbene cationic diradical is sufficiently stable in the triplet state to permit SQUID measurements over a range of temperatures.[136] A polymeric analogue has also been reported.[137]

2.5.6. Other polaronic materials. A slightly different approach was adopted by Tanaka who constructed copolymers consisting of π conjugated units as the spin supplier and non-π conjugated units containing several sp^3 hybridised atoms as spacers.[138] The interactions between polaronic units could then be varied by altering the length and atomic structure of the spacer unit. The compounds prepared consisted of regularly aligned disilanylenes coupled with π conjugated units, the most promising of which appeared to be **113** containing quaterthiophene units. Doping the polymer **113** was unsuccessful as a result of oligothienylene units in the chain surrounding the dopant ion, hence resulting in a partially charged state. The consequent low spin concentrations hampered the formation of polaronic ferromagnetic interactions.



Janssen and co-workers examined thiophene and pyrrole oligomers such as **114** and **115**, which had been protected at the α-position. From these studies[139] Janssen claimed that cation radicals of oligopyrroles and oligothiophenes could form diamagnetic π dimers in the solid state and in solution and that the formation of these diamagnetic π dimers may provide an insight into the low spin concentrations observed in these systems as compared to inhomogeneous doping. Janssen concluded that it was not possible to obtain high spin molecules based on dopable π conjugated segments containing pyrrole or thiophene.



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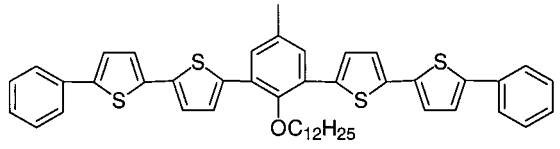
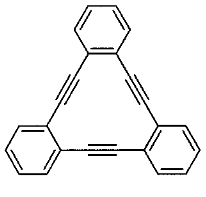


115

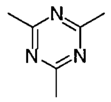
3. Conclusions and Future Prospects

It is remarkable to see how so much innovative and elegant synthetic work in this area has taken place over the last decade or so. Most of this work was inspired by the rather simple ideas of the 'through-space' McConnell models for building up bulk ferromagnetic interactions on the one hand, and the various topological models for 'through-bond', *intra*molecular interactions on the other. It is equally remarkable that all of these models have their place in the explanation of ferromagnetic interactions; indeed, in some cases more than one mechanism may be operating. Yet it may be some time before a reliable theoretical predictive method is available given the difficulties involved in calculations over several accessible open-shell configurations. It is here that the physicists may make a contribution in exploring the boundary between quantum and classical mechanics, as in the studies of single crystals of manganese acetate, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$.[140]

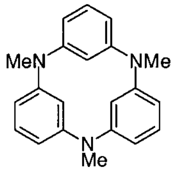
As far as it is possible to detect any trends in current synthetic endeavours, the following have been noted. New ferromagnetic coupling units (FCUs) other than those in Fig.17 are being investigated. For example, dehydro[12]-annulenes **116**,[141] *s*-triazines **117**,[142,143] cyclophanes **118**,[144] and even ferrocenes **119**:[145]



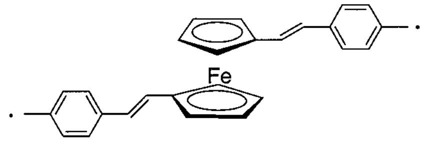
116



117



118



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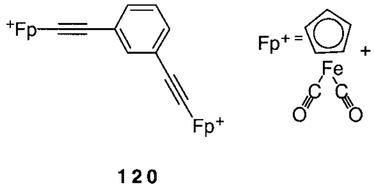
It is likely that the first commercial applications of organic ferromagnetic materials will involve polymeric materials of some sort.[146] A problem with the polymeric materials so far has been the twisting of the polymer chain due to steric interactions. The twisting prevents strong through-bond coupling along the conjugated chain between pendant radicals. Another problem is how to achieve high spin levels and stability at high temperatures. While the chemical and electrochemical treatment of precursor polymers has proved to be reasonably effective, there may be limits to this approach. For example, difficulties relating to the accommodation of charged centres and/or large counterions will hinder further oxidation.

Given the general rapid advances in dendrimer synthesis,[147] it is inevitable that this will become an even more popular approach to preparing and studying polyradical species of known size and disposition. Similarly, the possibility of using rapidly developing peptide synthesis techniques in connection with materials research has been proposed.[148] In the biological arena, the study of magnetic material inside living things, such as magnetotactic bacteria, has inspired several research groups to emulate these materials in the laboratory.[149]

Thanks to improved synthesis and crystal structure determination techniques interesting polymers are being prepared based on transition metal complexes. For example, the $[Co(pyrimidine)_2X_2]_n$ polymers are weakly ferromagnetic below 5 K.[150] Novel organometallic model diradical complexes, such as the 1,3-diethynylbenzene bridged $CpFe(CO)_2^+$ cations **120**,[151] or bis-porphyrins[152] open up a large array of possibilities.



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The world of buckyballs and buckytubes (nanotubes) continues to surprise and delight scientists. The ferromagnetic C_{60} charge-transfer salts were discussed earlier, and in the future it is possible that ferromagnetism may be observed with single-wall nanotubes, some of which are predicted and observed to be metallic, while others, such as the chiral examples, are semi-conducting.[153] Although electrons in a nanotube are generally considered to be non-interacting, contrary experimental evidence has recently emerged.[154] Indeed, spin-polarisation can be transferred to multiwalled nanotubes by contact.[155] Perhaps the through-bond topological model mentioned above could be applied to nanotubes. A nanotube that bites its own tail yields a torus (or 'crop circle'). These have been observed by several groups, usually in the nanotube soot mixture, although they have also been observed in the material obtained after pyrolysis of iron phthalocyanine.[156] The flow of electrons in this object will presumably also create its own magnetic field, analogous to the ring-current in benzene.[157] Ferromagnetic carbon nanotubes can be synthesised containing magnetic iron particles.[158] Cage structures and nanotubes can also be made out of layered materials such as boron nitride and even nickel chloride, with potentially interesting magnetic behaviour.[159]

There is, of course, much that remains to be discovered in the area of molecular magnetism. The effect of coupling familiar physical properties of organic materials and polymers, such as transparency and chirality,[160] with magnetic properties has hardly been examined. A note of caution should be struck, however, about the prospects of purely organic molecular magnets. So far, despite much research effort, the highest T_C recorded for a purely organic ferromagnet is 1.48 K for the Rassat diradical. There appears to be some barrier to high T_Cs related to the discussion above concerning spin density in organic materials. It is therefore likely that progress will only be made with a high-spin metal–organic hybrid complex crystal or polymer, as in the extraordinary $V^{II}(TCNE)_x \cdot y(CH_2Cl_2)$ complex which has its T_C above room temperature.

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References

1. Hellemans, A.; Bunch, B. Timetables of Science, Simon & Schuster: New York, 1988; p 19.
2. Stixrude, L.; Cohen, R. E. *Science* **1995**, *267* (5206), 1972–1975.
3. Finnemore, D. K.; Gray, K. E.; Maley, M. P.; Welch, D. O.; Christen, D. K.; Kroeger, D. M. *Physica C* **1999**, *320*, 1.
4. (a) de Boeck, J.; Borghs, G. *Phys. World* **1999**, *April*, 27. (b) http://www.stoner.leeds.ac.uk/research/gmr.htm
5. Kusters, R. M.; Singleton, J.; Keen, D. A.; McGreevy, R.; Hayes, W. *Phys. B* **1989**, *155*, 362; Fontcuberta, J. *Phys. World* **1999**, *12* (2), 33–38.
6. http://www.sciam.com/1999/0599issue/0599infocus.html
7. Hartmann, U. *Ann. Rev. Mater. Sci.* **1999**, *29*, 53.

8. (a) Kahn, O., Gatteschi, D., Miller, J. S., Palacio, F., Eds. *Magnetic Molecular Materials*; Kluwer: London, 1991. (b) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (c) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *23*, 34. (d) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385. (e) Gatteschi, D. *Adv. Mater.* **1994**, *9*, 635. (f) Turnbull, M. M., Sugimoto, T., Thompson, L. K., Eds. *Molecule-Based Magnetic Materials*; ACS Symposium Series 644; American Chemical Society: Washington, DC, 1996. (g) Iwamura, H.; Inoue, K.; Hayamizu, T. *Pure Appl. Chem.* **1996**, *68*, 243. (h) Miller, J. S.; Epstein, A. J. *Chem. Eng. News* **1995**, 2 October, 30.

9. Bushby, R. J.; Paillaud, J.-P. *Introduction to Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Edward Arnold: London, 1995; Chapter 4.

10. Hund, F. *Z. Phys.* **1927**, *43*, 805.

11. Kahn, O. *Struct. Bond.* **1987**, *68*, 89.

12. Goodenough, J. B. *Phys. Rev.* **1955**, *100*, 564; Kanamori, J. *J. Phys. Chem. Solids* **1959**, *10*, 87; Goodenough, J. B., *Magnetism and the Chemical Bond*; Oxford, 1963.

13. Nakatani, K.; Bergerat, P.; Codjovi, E.; Mathoniere, C.; Pei, Y.; Khan, O. *Inorg. Chem.* **1991**, *30*, 3977.

14. McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

15. Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392.

16. Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *J. Am. Chem. Soc.* **1989**, *111*, 785.

17. Nakatsuji, S.; Anzai, H. *J. Mater. Chem.* **1997**, *7*, 2161.

18. McCleverty, J. A.; Ward, M. D. *Acc. Chem. Res.* **1998**, *31*, 842.

19. From Dr Gleb D. Perekhodtse personal web-page at: http://center.chph.ras.ru/~perekhod/review6e.html.

20. Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 3656.

21. Isuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786. Azuma, N.; Yamauchi, J.; Mukai, K.; Nishiguchi, H. O.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2728; Agawa, K.; Sugano, T.; Kinoshita, M. *J. Chem. Phys.* **1986**, *85*, 2211.

22. Hoffmann, S. K.; Corvan, P. J.; Singh, P.; Sethulekshine, C. N.; Metzgar, R. M.; Hatfield, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4608.

23. Isuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786.

24. Deumal, M.; Novoa, J. J.; Berapark, M. J.; Celani, P.; Olivucci, M.; Robb, M. A. *J. Phys. Chem. A* **1998**, *102*, 8404.

25. Mulliken, R. W. *Proc. Robert A. Welch Found. Conf. Chem. Res.*; 1967; vol. 11, p 109.

26. McConnell, H. M. *Proc. Robert A. Welch Found. Conf. Chem. Res.*; 1967; vol. 11, p 144.

27. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201.

28. Breslow, R.; Juan, B.; Kluttz, R. Q.; Xia, C. Z. *Tetrahedron* **1982**, *38*, 863.

29. Lahti, P. M.; Rossiand, A.; Berson, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 1251.

30. Purcell, K. F. *Inorganic Chemistry*, W. B. Saunders: London, 1977; p 51.

31. Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittapedi, S. R.; Zhang, R. W.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

32. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Mol. Cryst. Liq. Cryst.* **1985**, *120*, 27; Miller, J. S.; Calabrese, J. C.; Epstein, A. J.; Bigelow, R. W.; Zhang, J. H.; Reiff, W. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1026.

33. Kollmar, C.; Couty, M.; Khan, O. *J. Am. Chem. Soc.* **1990**, *112*, 381.

34. Manriquez, J. M.; Yee, G. T.; Mclean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415.

35. Miller, J. S.; Epstein, A. J. *J. Chem. Soc., Chem. Commun.* **1998**, 1319–1325.

36. (a) Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701. (b) Verdaguer, M.; Bleuzen, A.; Marvaud; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Scuiller, A.; Train, C.; Garde R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *192*, 1023.

37. Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593.

38. Bechard, K.; Parker, V. *J. Am. Chem. Soc.* **1972**, *94*, 4749.

39. Thomaides, J.; Maslak, P.; Breslow, R. *J. Am Chem. Soc.* **1988**, *110*, 3970.

40. Miller, J. S.; Dixon, D. A.; Calabrese, J. C.; Vazquez, C.; Krusic, P. J.; Ward, N. D.; Wasserman, E.; Harlow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 381.

41. Torrance, J. B.; Bagus, I.; Nazzal, A. I.; Parkin, S. P. *J. Appl. Phys.* **1988**, *63*, 2962.

42. Torrance, J. B.; Oostra, S.; Nazzal, A. I. *Synth. Met.* **1986**, *19*, 709.

43. Radhakrishnan, T. P.; Soos, Z. G.; Endres, H.; Azevedo, J. L. *J. Chem. Phys.* **1986**, *85*, 1126.

44. Radhakrisnan, T. P.; Van Engen, D.; Soos, Z. G. *J. Phys. Chem.* **1987**, *91*, 3273.

45. Zanotti, G.; Del Pra, A.; Bozio, R. *Acta Crystallogr. B* **1982**, *38*, 1225.

46. Dorman, E.; Nowak, M. J.; Williams, K.; Angus, R. G.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594.

47. (a) Hadden, R. C. *Acc. Chem. Res.* **1992**, *25*, 127. (b) Cox, M. D.; Behal, S. M.; Disko, M.; Gorun, S.; Greaney, M.; Hsu, C. S.; Kollin, E.; Miliar, J.; Robbins, J.; Robbins, W.; Sherwood, R.; Tindall, P. *J. Am. Chem. Soc.* **1991**, *113*, 2940.

48. Fischer, J. E.; Heiney, P. A.; Smith, A. B. *Acc. Chem. Res.* **1992**, *25*, 112.

49. Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

50. Wudl, F.; Thompson, J. D. *J. Phys. Chem.* **1992**, *53*, 1449–1455.

51. Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401.

52. Chiarell, R.; Novak, M. A.; Rassat, A.; Tholence, J. L. *Nature* **1993**, *363*, 147.

53. Sugawara, T.; Matsushita, M. M.; Izuoka, A.; Wade, N.; Takeda, N.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1723.

54. Veciana, J.; Cirujeda, J.; Rovira, C.; Vidal-Gancedo, J. *Adv. Mater.* **1995**, *7*, 221.

55. Inoue, K.; Iwamura, H. *Chem. Phys. Lett.* **1993**, *207*, 551.

56. Deumal, M.; Cirujeda, J.; Veciana, J.; Novoa, J. J. *Adv. Mater.* **1998**, *10*, 1461.

57. Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Phys. Chem.* **1993**, *97*, 13267.

58. Sugimoto, T.; Tsujii, M.; Suga, T.; Hosoito, N.; Ishikawa, M.; Takeda, N.; Shiro, M. *Mol. Cryst. Liq. Cryst.* **1995**, *271*, A183.

59. Fujiwara, H.; Kobayashi, H. *Chem. Commun.* **2000**, 2417–2418.

60. Kumai, R.; Matsushita, M. M.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1994**, *116*, 4253.

61. Nakatsuji, S.; Anzai, H. *J. Mater. Chem.* **1997**, *7*, 2161.

62. Lane, C. F. *Synthesis* **1975**, 135.

63. Dowd, P. A. *J. Am. Chem. Soc.* **1966**, *88*, 2587.

64. Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.

65. Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

66. Lafuente, P.; Novoa, J. J.; Bearpark, M. J.; Celani, P.; Olivucci, M.; Robb, M. A. *Theor. Chem. Acc.* **1999**, *102*, 309.

67. Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372.

68. Salem, L. *Molecular Orbital Theory of Conjugated Systems*, W. A. Benjamin: New York, 1966; pp 36–43.

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

70. Lieb, E.; Mattis, D. C. *J. Math. Phys.* **1962**, *3*, 749.

71. Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, A. *J. Chem. Phys.* **1982**, *77*, 3101.

72. Iwamura, H.; Murata, S. *J. Am. Chem. Soc.* **1991**, *113*, 5547.

73. Radhakrishnan, T. P. *Tetrahedron Lett.* **1993**, *32*, 4601.

74. Murray, R. W.; Trozollo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3213.

75. Murray, R. W.; Trozollo, A. M.; Wasserman, E.; Yager, W. A.; Smolisky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5079.

76. Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235.

77. Sugawara, T.; Murata, S.; Kimura, K.; Sugawara, Y.; Iwasaki, H.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293.

78. Yoshizawa, K.; Hoffman, R. *Chem. Eur. J.* **1995**, *1*, 403 (and references therein).

79. Itoh, K.; Sawaki, Y.; Izuoka, A.; Sugawara, T.; Miko, F.; Iwamura, H. *J. Am. Chem. Soc.* **1990**, *112*, 4074.

80. Calder, A.; Forrester, A. R.; James, P. G.; Luckhurst, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3724.

81. Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238.

82. Tyutyulkov, N. N.; Ivanov, C. I.; Schopov, I.; Olbrich, G.; Polansky, O. E. *Int. J. Quantum Chem.* **1988**, *34*, 361.

83. Rajca, A.; Lu, K.; Rajca, S.; Ross II, C. R. *Chem. Commun.* **1999**, 1249.

84. Kothe, G.; Ohmes, E.; Brickman, J.; Zimmerman, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 938.

85. Takui, T.; Itoh, K. *Chem. Phys. Lett.* **1973**, *19*, 120.

86. Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251.

87. Kothe, G. *J. Chem. Phys.* **1985**, *83*, 539.

88. Teki, Y.; Takui, T.; Yagi, H.; Itoh, K.; Iwamura, H. *J. Chem. Phys.* **1985**, *83*, 547.

89. Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552.

90. Veciana, J.; Rovira, C.; Crespo, M. I.; Ventosa, N.; Palacio, F. *J. Am. Chem. Soc.* **1993**, *115*, 57.

91. Yoshizawa, K.; Chano, A.; Ito, A.; Tanaka, K.; Yamabe, T.; Fujita, H.; Yamauchi *J. Chem. Lett.* **1992**, 369.

92. Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

93. Rajca, A.; Utamapanya, S.; Thayumanavan, S. *J. Am. Chem. Soc.* **1992**, *14*, 1884.

94. (a) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 10688. (b) Rajca, A.; Utamapanya, S. *Liq. Cryst. Mol. Cryst.* **1993**, *232*, 305.

95. Rajca, A.; Rajca, S.; Desai, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 806.

96. Rajca, A.; Lu, K.; Rajca, S. *J. Am. Chem. Soc.* **1997**, *119*, 10335.

97. Rajca, A.; Rajca, S. *J. Am. Chem. Soc.* **1996**, *118*, 8121.

98. Rajca, A.; Wongsriratanakul, J.; Rajca, S. *J. Am. Chem. Soc.* **1997**, *119*, 11674.

99. Rajca, A.; Wongsriratanakul, J.; Rajca, S.; Cerny, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1229.

100. Crayston, J. A.; Iraqi, A.; Walton, J. C. *Chem. Soc. Rev.* **1994**, *23*, 147–153.

101. Korshak, U. V.; Madvedeva, T. V.; Ovchinnikov, A. A.; Spector, V. N. *Nature* **1987**, *326*, 370.

102. Miller, J. S. *Adv. Mater.* **1994**, *4*, 435.

103. Nishide, H.; Kaneko, T.; Toriu, S.; Kuzumaki, Y.; Tsuchida, E. *Bull. Chem. Soc. Jpn* **1996**, *69*, 499.

104. Nishide, H.; Kaneko, T.; Takeshi, N.; Katoh, K.; Tsuchida, E.; Lahti, P. M. *J. Am. Chem. Soc.* **1996**, *118*, 9695.

105. Sato, K.; Shiomi, D.; Takui, T.; Itoh, K.; Kaneko, E.; Tsuchida, E.; Nishide, H. *J. Spectrosc. Soc. Jpn* **1994**, *43*, 280.

106. Nishide, H.; Miyasaki, M.; Tsuchida, E. *J. Org. Chem.* **1998**, *63*, 7399.

107. Anderson, K. K.; Dougherty, D. A. *Adv. Mater.* **1998**, *10*, 688.

108. Fukutome, H.; Takahashi, A.; Ozaki, M. *Chem. Phys. Lett.* **1987**, *133*, 34.

109. Tyutyulkov, N. N. *Chem. Phys. Lett.* **1987**, *139*, 281.

110. Kaisaki, D. A.; Chang, W. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 2764.

111. Yoshizawa, K.; Tanaka, K.; Yamabe, T. *Int. J. Quantum Chem.* **1991**, *40*, 305.

112. Yoshizawa, K. *J. Phys. Chem.* **1994**, *98*, 1851.

113. Dougherty, D. A.; Novak, J.; Jain, R.; Schultz, D. A.; Jacobs, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 1744.

114. Li, S. M.; Ma, J.; Jiang, Y. S. *J. Phys. Chem. A* **1997**, *101*, 5567.

115. Malrieu, J. P.; Maynau, D. *J. Am. Chem. Soc.* **1982**, *104*, 3021.

116. Jacobs, S. J.; Schultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744; Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1791; Yoshizawa, K.; Tanaka, K.; Yamabe, T. *J. Phys. Chem.* **1994**, *98*, 1851; Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273.

117. Mitani, M.; Takano, Y.; Yoshioka, Y.; Yamaguchi, K. *J. Chem. Phys.* **1999**, *111*, 1309.

118. Mitsumori, T.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 2467.

119. Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 180.

120. Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847.

121. Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273.

122. Bushby, R. J.; McGill, D. R.; Ng, K. M.; Taylor, N. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1405.

123. Schultz, D. A.; Boal, A. K.; Farmer, G. T. *J. Org. Chem.* **1998**, *63*, 9462.

124. Dougherty, D. A.; Murray, M. M.; Chang, W. H. *J. Am. Chem. Soc.* **1994**, *116*, 8152.

125. Wittig, G. *Chem. Ber.* **1954**, *87*, 1318.

126. Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178.

127. Devine, J. N.; Crayston, J. A.; Walton, J. C. *Synth. Met.* **1999**, *103*, 2294–2295.

128. Devine, J. N.; Crayston, J. A.; Walton, J. C. Unpublished work.

129. Zotti, G.; Schiavon, G.; Zecchin, S.; Groenendaal, L. *Chem. Mater.* **1999**, *11*, 3624.

130. (a) Bushby, R. J.; Ng, K. M. *J. Chem. Soc., Chem. Commun.* **1996**, 267. (b) Bushby, R. J.; Gooding, D. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1069.

131. Stauffer, D.; Aharony, A. *Introduction to Percolation Theory*, Taylor & Francis: London, 1985.

132. Bushby, R. J.; McGill, D. R.; Ng, K. M.; Taylor, N. *J. Mater. Chem.* **1997**, *7*, 2343.

133. Bushby, R. J.; Gooding, D.; Vale, M. E. *Proc. Roy. Soc. A* **1999**, *357*, 2939–2957.

134. Janssen, R. A. J.; Wienk, M. W. *J. Chem. Soc., Chem. Commun.* **1996**, 267.

135. Stickley, K. R.; Blackstock, S. C. *J. Am. Chem. Soc.* **1994**, *166*, 11576.

136. Michinobu, T.; Takahashi, M.; Tsichida, E.; Nishide, H. *Chem. Mater.* **1999**, *11*, 1969.

137. Takahashi, M.; Nakawaza, T.; Tsichida, E.; Nishide, H. *Macromolecules* **1999**, *32*, 6383.

138. Ago, H.; Kuga, T.; Yamabe, T.; Tanaka, K. *Chem. Mater.* **1997**, *9*, 1159.

139. (a) van Haare, J. A. E. H.; van Boxtel, M.; Janssen, R. A. J.; *Chem. Mater.* **1998**, *10*, 1166. (b) van Haare, J. A. E. H.; Groenendaal, L.; Havinga, E. E.; Janssen, R. A. J.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 638.

140. Barbara, B.; Gunther, L. *Phys. World* **1999**, *March*, 35.

141. Nishide, H.; Takahashi, M.; Takashima, J.; Pu, Y.-J.; Tsuchide, E. *J. Org. Chem.* **1999**, *64*, 7375.

142. Ahang, J. P.; Wang, R. S.; Wang, L. X.; Baumgarten, M. *Chem. Phys.* **1999**, 209.

143. Selby, T. D.; Stickley, K. R.; Blackstock, S. C. *Org. Lett.* **2000**, 171.

144. Ito, A.; Ono, Y.; Tanaka, K. *J. Org. Chem.* **1999**, *64*, 8236.

145. Elsner, O.; Ruiz-Molina, D.; Vidal-Gancedo, J.; Rovira, C.; Veciana, J. *Chem. Commun.* **1999**, 579.

146. Bag, D. S.; Maiti, S. *J. Polym. Mater.* **1999**, *16*, 187.

147. Chow, H. F.; Mong, T. K. K.; Nongrum, M. F.; Wan, C. W. *Tetrahedron* **1998**, *54*, 8543.

148. Iwamura, H. *J. Phys. Org. Chem.* **1998**, *11*, 299.

149. Mann, S.; Burkett, S. L.; Davis, S. A.; Fowler, C. E.; Mendelson, N. H.; Sims, S. D.; Walsh, D.; Whilton, N. T. *Chem. Mater.* **1997**, *9*, 2300–2310.

150. Nakayama, K.; Ishida, T.; Takayama, R.; Hashizume, D.; Yasui, M.; Iwasaki, F.; Nogami, T. *Chem. Lett.* **1998**, 497.

151. Weyland, T.; Costuas, K.; Mari, A.; Halet, J. F.; Lapinte, C. *Organometallics* **1998**, *17*, 5569.

152. Schultz, D. A.; Lee, H.; Kumar, R. K.; Gwaltney, K. P. *J. Org. Chem.* **1999**, *64*, 9124.

153. Dresselhaus, M.; Dresselhaus, G.; Eklund, P.; Saito, R. *Phys. World* **1998**, *January*, 33.

154. Tans, S. J.; Devoret, M. H.; Groeneveld, R. J. A.; Dekker, C. *Nature* **1998**, *394*, 761.

155. Tsukagoshi, K.; Alphenaar, B. W.; Ago, H. *Nature* **1999**, *401*, 572.

156. Huang, S. M.; Dai, L. M.; Mau, A. W. H. *J. Mater. Chem.* **1999**, *9*, 1221.

157. Haddon, R. C. *Nature* **1997**, *388*, 31.

158. Satishkumar, B. C.; Govindaraj, A.; Rao, C. N. R. *Chem. Phys. Lett.* **1999**, *307*, 158.

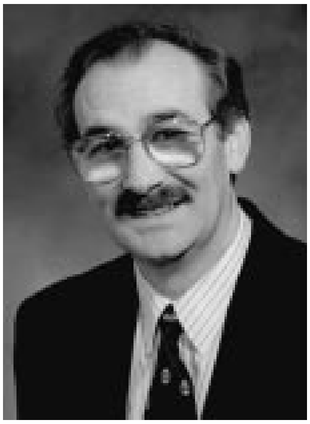
159. Rosenfeld Hacohen, Y.; Grunbaum, E.; Tenne, R.; Sloan, J.; Hutchison, J. L. *Nature* **1998**, *395*, 336.

160. Kaneko, T.; Yamamoto, T.; Aoki, T.; Oikawa, E. *Chem. Lett.* **1999**, 623.

Biographical Sketch

Joe Crayston was born in Cumbria, England in 1960. He received his degree from Cambridge University and his PhD in 1984 from the Nottingham University under the direction of Prof Jim Turner, Prof Martyn Poliakoff and Dr G. Davidson. He continued with a post-doctoral fellowship at MIT, working with Prof. Mark S. Wrighton on organometallic photochemistry and microelectrode voltammetry. In 1986, he joined the teaching staff at the University of St. Andrews. His current research interests include the electrochemistry of conducting polymers, modified electrodes and solar energy conversion. In 1990 he won the R.S.C. Harrison Medal and in 1995-6 he won a Fulbright award to work with Prof. Fred Anson at Caltech.

John Devine was born at Coatbridge in Lanarkshire, Scotland. He received his honours chemistry degree in 1995 from Glasgow University before moving to St. Andrews where he carried out research on functionalised poly(thienylphenylenes) as potential organic ferromagnets under the supervision of Professor Walton and Dr Crayston. He graduated PhD in 2000 and is currently working as a polymer research chemist for Victrex plc.



John Walton was born in St. Albans, England, in 1941. He graduated from Sheffield University in 1963 and studied for his PhD under the supervision of Lord John Tedder at Sheffield and Dundee Universities. He joined the faculty of the United College at St. Andrews University in 1970 as an assistant lecturer and became full Professor in 1997. His research has focused on synthetic, mechanistic and EPR spectroscopic aspects of free-radical chemistry and he was awarded the RSC prize for Organic Reaction Mechanisms in 1994. His current research interests include synthetic methods, cascade reactions and organic conducting and magnetic polymers.