Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: T. Takui, K. Sato, D. Shlomi, S. Nakazawa, M. Yano, T. Kinoshita, K. Abe, K. Itoh, T. Nakamura, T. Momose & T. Shida (1997): Molecular Designs for Polyionic Organic Ferromagnetics in Terms of Band Structure Calculation/ Crystal Orbital Approach; Exploitation of Topological Super Pseudo-Degeneracy of π-Bco's and π-Abco's with Hetero-Atomic Perturbation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 353-362

To link to this article: http://dx.doi.org/10.1080/10587259708044587

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 353–362
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MOLECULAR DESIGNS FOR POLYIONIC ORGANIC FERROMAGNETICS IN TERMS OF BAND STRUCTURE CALCULATION/ CRYSTAL ORBITAL APPROACH; EXPLOITATION OF TOPOLOGICAL SUPER PSEUDO-DEGENERACY OF π-BCO'S AND π-ABCO'S WITH HETERO-ATOMIC PERTURBATION

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Abstract One of the highlighted conceptual advances in organic magnetics and molecule-based magnetism has been that the use of topological-symmetry requirement in the π-electron network of "open-shell homoatomic neutral hydrocarbon systems" gives rise to the unlimited number of the degeneracy in non-bonding molecular orbitals (coined as topological degeneracy). This paper deals with the π-topological version of an approach to purely organic polyionic polymer ferromagnets, emphasizing that molecular design exploits the topological super pseudo-degeneracy of π-bonding and π-antibonding crystal orbitals (π-BCOs and π-ABCOs; π-bands) appearing close to zero energy in heteroatomic π-conjugated organic systems, for polycationic and polyanionic organic polymer ferromagnets, respectively. The appearance of the BCOs and ABCOs close to zero energy as well as their pseudo-degeneracy is due to heteroatomic perturbation. Their super degeneracy arises from the topological nature of the π-conjugated electron network of the elaborate molecular design. Oxidation and reduction states of polymers designed according to the topological approach are expected to undergo the additive operation of dynamic spin polarization, leading to high-spin ground states for polycationic and polyanionic model polymers, respectively. One-dimensional and two-dimensional star-burst model oligomers with heteroatoms in π-conjugation were designed as prototypical examples. Also, description of ferromagnetic or antiferromagnetic spin alignment depending on the topological symmetry in π-conjugation is given in terms of dynamic spin polarization.

INTRODUCTION

The last decade has found ever-increasing interest in organic magnetics/molecule-based magnetics from both the pure and applied sciences. The conceptual proposals of organic

magnetics in terms of non-charged open-shell molecular units were made at early times.[1, 2] The recent rapid development of this field is partly due to the rich variety of novel physical phenomena and properties which synthetic organomagnetic materials are expected to exhibit both macro- and meso-scopically[3a-c] and partly due to their underlying potential applications as future technology in materials science such as spin-manipulated electronics (spinics or spintronics).[4, 5]

The recent development of this field crucially owes the fact that the study of organic magnetics has conveyed important conceptual advances in chemistry and physics. Purely organic magnetics, defined typically as ferromagnetics originating in purely organic building spin-blocks composed of only light atoms such as C, H, N, O, and S, is apparently a controversial issue simply because organic substances are intrinsically diamagnetic. The search for organic magnetic materials is, thus, an important issue of the interplay between theory and experiment in physics and rapidly developing spin chemistry. Particularly, in view of magnetism and the appearance of quantum nature of electron spins in various forms from micro- to semimacro-scopic scale, high-spin chemistry has brought not only important issues in the quest for purely organic magnetics and intriguing related magnetic materials such as organic polymer magnets[1] and organic spin glasses[6] but also conceptual advances in chemistry and physics.

Topology Rule for Spin Alighment in Homoatomic vs. Heteroatomic π-Conjugation

One of the highlighted advances has been that the use of topological symmetry in the electron network of non-charged π-conjugated homoatomic hydrocarbons gives rise to the unlimited number of the degeneracy in nonbonding molecular orbitals (NBMOs) (coined as topological degeneracy),[1] which contrasts with the limitation of usual orbital degeneracy. The limitation of the latter essentially arises from the geometrical (group-theoretical) symmetry nature of organic systems comprised of multi-nuclear centers. In this context, group theoretical argument alone never predicts the possible existence of organic molecular high-spin systems with the spin multiplicity $2S+1$ greater than quartet in their electronic ground state.[1] The very exploitation of the π-topological degeneracy gives birth to purely organic neutral high-spin molecules with $S = 2$.[7] The topological approach for organic high-spin systems and organic magnetics underlies spin-prediction for electronic ground states in π-conjugated hydrocarbon systems, which is termed as "homo-topology spin-prediction" rule. Note that this homo-topology rule is applicable only to homoatomic hydrocarbon systems with π-conjugated electron network. Due care should be taken if the rule is applied to heterocyclic π-conjugated systems. Simple application or intuitive extension of the rule to the

heteroatomic systems cannot be justified without checking the occurrence of **topologically controlled dynamic spin polarization**, which dominates spin alignment of the systems under study. Wording of "violation of the topology rule applied to the spin prediction for heteroatomic π-conjugated systems" is not proper. The hetero-topology rule as a general spin-prediction rule is another thing and it should be established from both theoretical and experimental sides. In the documented literature referred to the violation there has been confusion with the application of the homo-topology rule.

Appearance of π-Topologically Controlled Superdegeneracy in π-Conjugation and Dynamic Spin Polarization

The viewpoint of the topological symmetry disclosed the possible occurrence of organic polymer superpara- and ferro-magnets,[1] following the appearance of the first organic high-spin quintet hydrocarbon.[7] It is important to realize that the through-bond approach to non-charged organic ferromagnetism is based on the topological nature of the through-bond linkage modes of π-conjugated spin systems. In Figure 1A and 2A are shown the hypothetical non-charged one- or two-dimensional polymer ferromagnets and super high-spin macromolecules with extremely large spins (assemblages of a great number of ferromagnetically exchange-coupled spins where the extended length of coherence in magnetic interactions is still short-range).[1a-c] Figure 1A shows the first documented band-structure calculation in terms of k-vector space representation revealing the possible occurrence of ferromagnetic ground states of purely organic polymeric spin systems.[1a, c] The molecular design of these first documented magnetic polymers was based on the through-bond approach (Itoh-Mataga approach).

In contrast to an extensive and continuing study of neutral molecular high-spin systems, it is not until recently that polyionic molecular high-spin systems have drawn attention as models for studying multi-charge fluctuation vs. spin polarization in homoatomic[8, 9] and heteroatomic polycationic[10-12] high-spin systems; the documented report and studies on polyanionic high-spin molecules and clusters appeared as early as 1970's,[13, 14] following Hirota and Weissman's pioneering work in 1960's on triplet ketyl-clusters formed by alkali-metal ion bridges.[15] Recently, diketone-based intermoelcular polyanionic clusters have been studied; metal bridge-based intermolecular quartet and quintet clusters with features of small zero-field splitting parameters have been claimed to be well characterized.[16] Stable polyionic magnetic systems[17] are the focus of current topics as models for multifunctionality molecule-based magnetic materials. Such systems have been regarded as models for organomagnetic metals, which arise from the interplay between spin polarization and charge

fluctuation. Hole or electron doped polyaromatic carbene-based systems have been theoretically studied as models for organic magnetic metals[18-21] before experimental challenges were carried out.[8]

In this work, we propose π-topology-based molecular design for one- and two-dimensionally extended polymeric super high-spin systems with multi-charge. The systems under study are of heteroatomic π-conjugation and expected to undergo dominant dynamic spin polarization which is π-topologically controlled for both polycationic and polyanionic cases, leading to super high-spin ground states or ferromagnetic ground states. In this context, the present work is a pluri-charge version of the topologically controlled through-bond approach to organic super high-spin or ferromagnetic polymeric systems. Instead of "topological degeneracy" used for π-NBMOs,[1a-c] a concept of "topologically super pseudo-degeneracy" of π-HOMOs or π-LUMOs is used, where "pseudo" and "super" degeneracy originate in heteroatomic perturbation and topological symmetry of π-conjugation network, respectively. Pseudo-degeneracy is essential for elaborate molecular designs of heteroatomic high-spin systems with π-conjugation.

MOLECULAR DESIGN; CRYSTAL ORBITAL APPROACH AND USE OF TOPOLOGICAL PSEUDO-DEGENERACY FOR ORGANIC SUPER HIGH-SPINS WITH MULTI-CHARGE

The first documented band-structure calculation,[1a, c] which showed the unlimitation of the degree of π-topological NBMO degeneracy for 1D neutral ferromagnetic polymer, appeared at earlier times before crystal orbital approach was established in polymer chemistry. Since then, theoretical studies of the possible occurrence of organic magnetic polymers or extended high-spin systems in terms of band structure calculation have been made in various levels of approximation.[18-27] The model calculation introduced in this section underlying molecular design for magnetic polymers with multi-charge is the simplest possible version for band structure calculations of π-conjugated polymeric systems and their inter-polymer interactions.[27] The extended interpolymer interactions in terms of topological considerations have not been documented. It has been shown that highly topological modulation of electronic band structures gives rise to intriguing spin-polarized magnetic properties of polymeric systems.[27]

The calculation was based on traveling wave (crystal orbital) approach, which corresponds to a description of mobile electrons with non-zero linear momentum in the periodic "lattice" comprised of the N-segment structure of the systems. Translation symmetry re-

quirements were assumed for potential terms and the corresponding Born-von Kármán's periodic boundary condition was also assumed for the total molecular orbital wave function describing the polymeric system under study. The tight binding approximation was used in

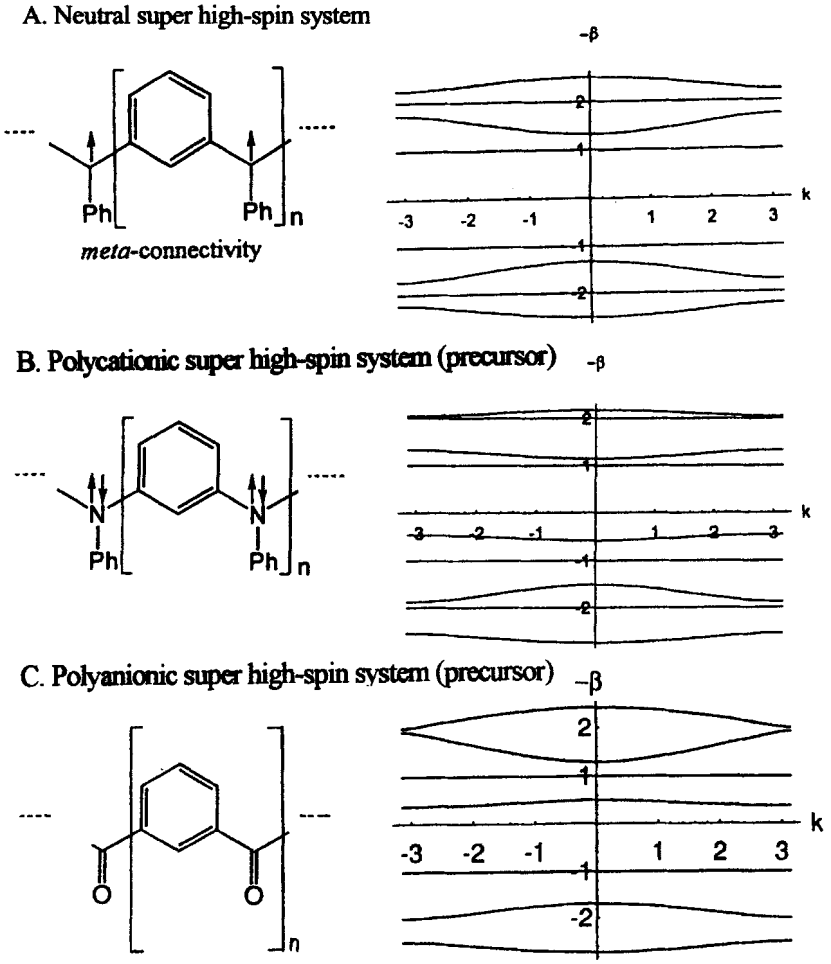


FIGURE 1. π-CO band structures of polymeric high-spin systems of 1D homoatomic π-conjugation (A), and heteroatomic π-conjugation for polycationic case (B) and polyanionic case (C), respectively.

order to facilitate the calculation by means of Rayleigh-Ritz linear variation method. Electron correlation was not included explicitly. Such improved treatment considering electron correlation has been demonstrated for a simpler segment structure.[27]

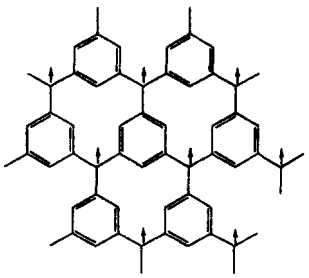
We stress that in some aspects of electronic spin structures of organic polymeric systems simple and intuitive extensions obtained from a finite systems to its extended system do not

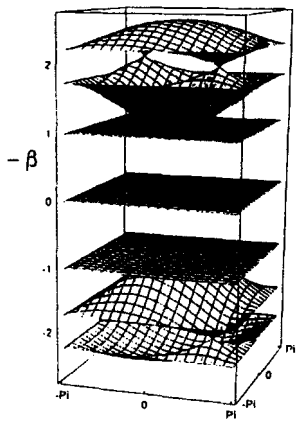
work.[27] We also stress that the theoretical model calculations in this section not only predict essential general features of electronic structures of the systems but also yield crucial aspects for their molecular design, despite the fact that simplified theoretical models only represent coarse qualitative features of physical properties.

Figure 1A and B show the π-crystal orbital band (π-CO band) structure in k wave vector space representation for a neutral extended system of 1D homoatomic π-conjugation and the corresponding one of a precursor extended system of 1D heteroatomic π-conjugation for polycationic high-spin cases, respectively. In the former A, complete N-fold superdegeneracy in the π-NBCO band at zero energy with N-electron occupancy appears due to the topology of *meta*-connectivity, leading to a ferromagnetic state at 0 K or a superparamagnetic state accommodating N parallel π-electrons. In the latter B, on the other hand, N-fold super pseudo-degeneracy in the π-HOCO (highest occupied π-crystal orbital) band completely filled with 2N electrons appears just below zero energy. The appearance of the both reduced energy and nonzero band width arises from heteroatomic perturbation, noticing that the ABCO (antibonding unoccupied π-crystal orbital) bands undergo much modulation due to the perturbation and considerable departure from the band structure of the homoatomic analog. The super pseudo-degeneracy in the HOCO band suggests that electron removal by partial or complete oxidation of the precursor generates polycationic high spin multiplets in their electronic ground state. This possible occurrence is essentially based on robust dynamic spin polarization taking place in the *meta*-connectivity-based polycationic system, considering electron repulsion on each carbon sites. The VB description of spin prediction in terms of MO/CO calculations can also give a rationale for the additive dynamic spin polarization dominating spin alignment in heteroatomic systems,[27] where the spin polarization competes with spin delocalization due to heteroatomic perturbation. The latter favors low-spin ground states. The band width of the HOCO band is typically less than 10^{-2} in units of -β.

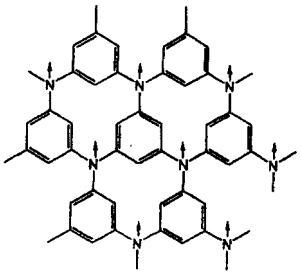
In Figure 1C is shown the π-CO band structure for a poly-1,3-ketone precursor of 1D heteroatomic π-conjugation. The super pseudo-degenerate LUCO (lowest unoccupied CO) band appears close to above zero energy in units of -β, suggesting the possible occurrence of polyanionic high-spin states by electron-doping the system. Dominant robust dynamic spin polarization is also the case for the occurrence of polyanionic super high-spin systems under study. Considerably large zerofield splitting parameters, *i.e.*, one order of magnitude larger than those of polycationic cases are anticipated for oligoketone-based intramolecular polyanionic high-spin systems. This is due to the expectation of a considerable contribution from one center n-π spin-spin interaction.

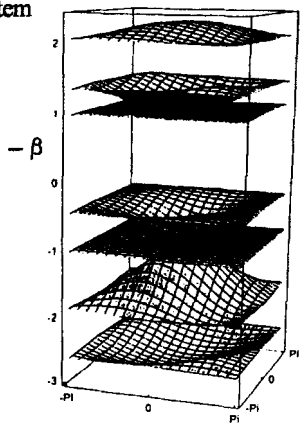
A. Neutral super high-spin system



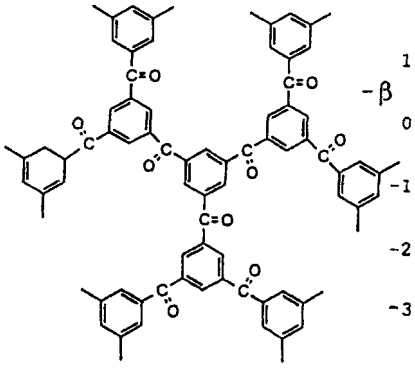


B. Polycationic super high-spin system





C. Polyanionic super high-spin system (precursor)



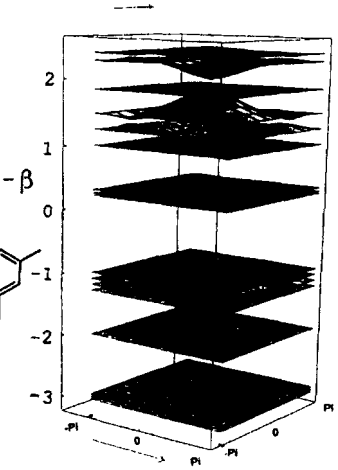


FIGURE 2. Crystal orbital picture in k-vector space for 2D extended systems in the ferromagnetic or super high-spin ground state. (A) Neutral, (B) polycationic, and (C) polyanionic case, respectively.

Figure 2 shows star-burst type 2D versions corresponding to those given in Figure 1, depicting complete topological degeneracy appearing at the π-NBCO band (A) for neutral cases and super pseudo-degeneracies of the π-HOCO band (B) and π-LUCO band (C) near zero energy for polycationic and polyanionic cases, respectively. The band structures in the k wave vector (k_x, k_y) representation reflect the translation symmetry of the systems as well as the topological symmetry. A ferromagnetic or super high-spin ground state is predicted for each 2D polymeric system since the topological 1,3,5-connectivity ensures the occurrence of robust dynamic spin polarization in the open-shell systems under study, *i.e.,* the triamino-benzene-based system for polycationic cases and the tribenzoylbenzene-based system for polyanionic cases. The band width of the HOCO or LUCO band depends highly on the topology of heteroatomic sites participating in π-conjugation and the Coulomb integral of heteroatoms themselves. Extension of the above approach to 3D polymeric high-spin systems or inter-polymer interactions can be made in order to understand topological nature of 3D electron network or inter-polymer contacts and to serve for molecular design for novel intriguing organic magnetic systems such as competing-interaction molecular systems. In these systems, electronic, optical, and magnetic anisotropies are based on spin quantum tunneling and spin-polarized phenomena appearing on semimacroscopic scale. Spin-polarized molecular devices can be termed as magnetic quantum well devices.[4]

CONCLUSIONS

A topological version for molecular design of polyionic high-spin polymeric systems has been proposed in terms of π-band structure calculations (crystal orbital approach) as prototypical models for organic magnetic metals. The molecular design has invoked the use of super pseudo-degeneracy appearing in π-HOCO and π-LUCO bands for polycationic and polyanionic cases, respectively. The pseudo-degeneracy instead of the complete degeneracy for homoatomic hydrocarbons arises from heteroatomic perturbation. The super degeneracy appearing in polymeric infinite systems originates in the topological nature of π-electron network based on elaborate molecular design. As far as robust spin polarization takes place in the topological electron network of the heteroatomic π-conjugation with partially filled MOs/COs, the highest spin multiplicity can be predicted. Otherwise, low-spin ground states can occur particularly for polycationic cases, where HOMO-LUMO energy gaps increase due to the stabilization by heteroatomic replacements of spin sites.

The prototypical model oligomers with pluri-charge have been designed and synthesized in order to exemplify the above prediction. Experimental studies along this line are under

way, together with the establishment of methodology for the unequivocal identification of their ground-state spin multiplicities of species generated by chemical oxidation or reduction of the corresponding precursors. A facile and powerful method is required for the spin discrimination between different spins in non-oriented media such as organic glasses.

Generation of ionic molecular high-spin systems by dry processes such as γ-irradiation is also planned, exemplifying metal-bridge free intermolecular polyanionic high-spin organic systems.

ACKNOWLEDGMENTS

This work has been partially supported by Grants-in-Aid for Scientific Research on Priority Areas "Molecular Magnetism" (Area No. 228/04 242 103 and 04 242 105) and Grants-in-Aid for Encouragement of Young Scientists (K. S. and D. S.) from the Ministry of Education, Science and Culture, Japan and also by the Ministry of International Trade and Industries (NEDO project "Organic Magnets").

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