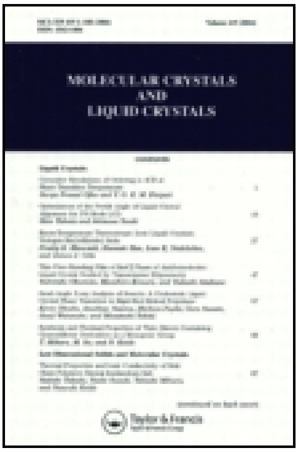


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Unusually Large Negative Spin Polarization of Hetero-Spin Composite High-Spin Carbenes as Models for Purely Organic Ferrimagnets: Topological Through-Bond Approaches and ESR/ENDOR Characterization

Takeji Takui [a] , Yoshio Teki [a] , Makoto Endoh [a] , Yukio Okudo [a] , Takamasa Kinoshita [a] & Koichi Itoh [a]

[a] Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka, 558, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Takeji Takui , Yoshio Teki , Makoto Endoh , Yukio Okudo , Takamasa Kinoshita & Koichi Itoh (1993): Unusually Large Negative Spin Polarization of Hetero-Spin Composite High-Spin Carbenes as Models for Purely Organic Ferrimagnets: Topological Through-Bond Approaches and ESR/ENDOR Characterization, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 232:1, 343-352

To link to this article: http://dx.doi.org/10.1080/10587259308035724

Mol. Cryst. Liq. Cryst. 1993, Vol. 232, pp. 343–352
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

UNUSUALLY LARGE NEGATIVE SPIN POLARIZATION OF HETERO-SPIN COMPOSITE HIGH-SPIN CARBENES AS MODELS FOR PURELY ORGANIC FERRIMAGNETS: TOPOLOGICAL THROUGH-BOND APPROACHES AND ESR/ENDOR CHARACTERIZATION

TAKEJI TAKUI, YOSHIO TEKI, MAKOTO ENDOH, YUKIO OKUDO, TAKAMASA KINOSHITA, and KOICHI ITOH
Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558, Japan

Abstract This paper deals with the topologically spin-controlled molecular design and spin structure of the first organic hetero-spin system, 4-(diphenylmethylene)-4'-(m-phenylenebis(phenylmethylene))-ether **1**, in which non-identical spins (S_i=1 and S_j=2) couple antiferromagnetically via an ether bridge in the ground state. The hetero spin system is a model for purely organic ferrimagnets via through-bond approaches, in which the underlining magnetic coupling is superexchange interaction via the bridge. The concept of the molecular design under study is associated with a counterpart of crystalline ferrimagnets via through-space approaches commonly exploited in magnetic materials. The single-crystal ENDOR spectroscopy has been applied to **1**, featuring an unusually large negative spin polarization in the spin density distribution for the ground state(S=1). The finding discloses a physical insight into organic ferrimagnetism. The unusual negative spin polarization strictly arises from a salient feature of organic hetero-spin systems in the electronic ground state, directly showing that one molecular spin moiety with $\mathbf{S}_i$(S_i=1) is inverted against the another with an inequivalent spin $\mathbf{S}_j$(S_j=2) in antiferromagnetically coupled hetero-spin systems. The spin inversion is responsible for such an unusually large negative spin polarization that chemistry so far has never expected. It is referred to a new aspect of negative spin polarization in chemistry.

INTRODUCTION

Organic molecular based magnetism[1-5] has been the current topic of intense and wide-increasing interest in many fields of both pure and applied sciences for the last decade. This is partly due to the rich variety of novel physical phenomena and properties which organic magnetic materials are expected to exhibit both macro- and mesoscopically and due to their potential applications as the future technology in materials science.[5,6] Also this is due to the fact that the study of organic magnetism has been conveying important conceptual advances in chemistry and physics. Typical examples are i) the topological degeneracy of π non-bonding orbitals in organic systems and the unlimitation of its degeneracy,[1b,c] ii) organic super high-spin states[7,8] characterized by extremely large spins in the ground or low-lying excited states, iii) polaronic organic ferromagnetism,[9,10] iv) hybrid molecular based magnets[5,11,12] via a through-space[5,11] or through-bond approach[12], and v) purely organic ferrimagnetism.[13,14] The concepts above have been taking their crucial part in particular aspects of the development in organic magnetism.[3-6]

Among the diverse variety of subjects in spin chemistry, purely organic crystalline and amorphous ferrimagnets have become the focus of the current topics in synthesizing organic magnetic materials. The essential reason is that antiferromagnetic coupling among molecular homo-spins commonly takes place in usual organic crystalline materials otherwise special tuning of crystal packing modes or chemical and physical modifications in spin control are made. Efforts have been made to overcome this disadvantage and to control the intermolecular spin alignment in solid until recently.[15] This apparent disadvantage is hampered by molecular hetero-spin systems forming higher-dimensional spin structures, in which antiferromagnetic coupling takes place only between the hetero-spins. Thus, the mixed crystalline approach is more useful and facile from a viewpoint of the strategy of crystal engineering. In fact, emphasizing the molecular and crystal engineering aspects of organic magnetism, chemistry in solid has been challenged in the designing and syntheses of mixed crystalline magnetic materials composed of only organic hetero-spins, aiming at through-space organic ferrimagnets.[14]

Purely organic ferrimagnetism, however, has not been fully characterized except for a simple scheme for the magnetic coupling between hetero-spins, nor the physical picture of organic ferrimagnets in terms of spin density distribution has been disclosed. It is of essential importance for the designing of organic crystalline and amorphous ferrimagnets to feature the spin structure of the ferrimagnetic state from a viewpoint of microscopic details.

Recently we have obtained the criteria of the spin control between molecular high-spin assemblages via functional bridges or spacers.[13] We have applied the criteria to the molecular design for a through-bond version of purely organic ferrimagnets, which is a counterpart of through-space crystalline ferrimagnets.[14] The organic system studied, (4-diphenylmethylene)-4'-(m-phenylenebis(phenylmethylene))-ether **1**, has been composed of two organic hetero-spins(S_i=1 and S_j=2) between which a through-bond antiferromagnetic coupling is introduced by exploiting the superexchange interaction via an ether bridge. The ground state of the hetero-spin system has been found to be the magnetic low-spin ground state(S=1) by ESR spectroscopy. The system **1** is the first prototype unit of purely organic ferrimagnets, showing the possible occurrence of the organic ferrimagnetism.

In this work we have determined the π spin density distribution of the first prototype molecule, a hetero-spin composite high-spin carbene **1** by single-crystal ^{1}H-ENDOR spectroscopy. It should be emphasized here that a breakthrough in the understanding of both rational designs of organic molecular magnetic materials and of mechanisms responsible for their particular magnetism is directly associated with the direct knowledge of the spin density distribution of the organic systems under study.[16-22] Among hybrid crystalline ferromagnets so far reported, an extensively studied example is decamethylferrocium(Fe(CpM$_5$)$_2$) tetracyanoethenide(TCNE) charge-transfer salt,[11] in which the ferromagnetism has been explained in terms of the McConnell mechanism.[2] An important experimental support, however, for an alternative interpretation has recently appeared.[21] This has been made in terms of the sign of the spin density of the Cp rings as determined by NMR spectroscopy,[20] showing the importance of the knowledge of the spin density distribution for studying the spin alignment in the hybrid systems as well. In the present work, the ENDOR characterization of the antiferromagnetically coupled organic hetero-spin system 1 has enable us to disclose the salient feature of the spin structure intrinsic to organic ferrimagnetic states, providing us with an essential and useful physical picture workable for both through-space and through-bond organic ferrimagnets.

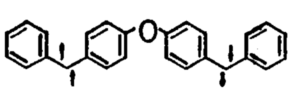
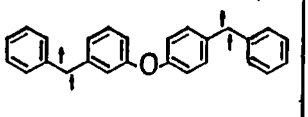
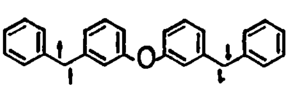
DESIGNING OF THROUGH-BOND ORGANIC FERRIMAGNETS:

Spin control between molecular homo-spins via superexchange interaction

Our strategy for obtaining purely organic molecular based magnetism has been mainly based on both the molecular design for organic high-spin assemblages exploiting the unlimitation of the degeneracy of π non-bonding orbitals in organic systems and the criteria of the spin control between the high-spin assemblages via functional bridges or spacers.[13]

Table I summarizes the experimental results obtained from the model compounds, a-, a'-bis(phenylmethylene)diphenylether(a-, a'-BPDE)(a,a'=3,4) in which spins in the two triplet moieties interact via an ether bridging a- and a'-positions of the two phenylmethylene moieties. The results clearly demonstrate that whether the effective exchange interaction J via the ether bridge is ferromagnetic or antiferromagnetic depends upon the connecting position of the bridge, indicating the importance of topology, i.e., modes of connectivity, similar to the topological symmetry which dictates the spin alignment through π electron network. The results and observed values for J have been satisfactorily interpreted by the Heisenberg model Hamiltonian approach[16b] combined with 180 degree superexchange interaction mechanism.[13,23] Our results also suggests that in favorable cases intramolecular ferromagnetic coupling is expected to dominate from 90 degree superexchange interaction. Molecular orbital calculations in various levels of approximation have been also carried out for such composite homo-spin carbenes.[22] It should be noted that the (4,4') connecting mode gives the most robust intramolecular coupling since the effective exchange interaction between the triplet spins can be nearly proportional to the product of the π spin densities of the two connecting carbon sites in the weak coupling scheme.[16d] The 4- and 4'-sites have a large positive π spin density, resulting in the robust antiferromagnetic coupling between the two

TABLE I Through-bond magnetic coupling via an ether bridge between two high-spin assemblages (superexchange interaction; charge transfer interaction via an oxygen atom). This table shows useful guiding principles for the topological control of the effective exchange interaction via an ether bridging high-spin moieties.

position (a,a')	isomer	order of energy levels	magnetic coupling
4 , 4'		J Q -J T -2J S	Antiferromag.
3 , 4'		-2J S -J T J Q	Ferromag.
3 , 3'		J Q -J T -2J S	Antiferromag.

homo-spins. This coupling mode is employed for the designing of the prototype unit of through-bond organic ferrimagnets.

Designing of units of through-bond organic ferrimagnets

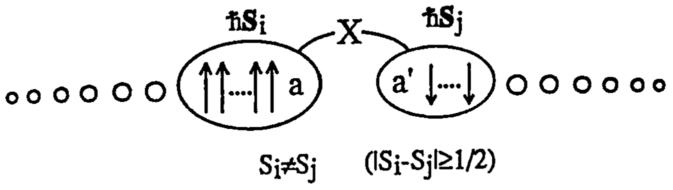
Our molecular design for units of through-bond organic ferrimagnets is based upon the following three guiding principles to control the sign of the intramolecular effective exchange interaction between hetero-spins.[13,24]

(i)Introduction of intramolecularly weak interactions between organic high-spin assemblages having non-identical spins S_i and S_j(S_i=S_j hetero-spin systems).

(ii)Through-bond chemical modification by functional groups(X) bridging the high-spin assemblages at particular positions(a,a'), which couples the spins antiferromagnetically(topological spin control by functional groups and a composite high-spin approach).

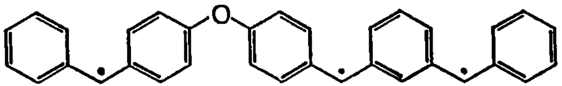
(iii)Utilization of the unlimitation of the degeneracy of π non-bonding orbitals in organic systems for the designing of the non-identical spins(high-spin assemblages as constituent spins of composite systems).

The resultant spin quantum numbers S arising from the through-bond antiferromagnetic coupling between two constituent hetero-spins S_i and S_j are given as $S= |S_j-S_i|, |S_j-S_i|-1, \cdots, S_j+S_i$ in order of

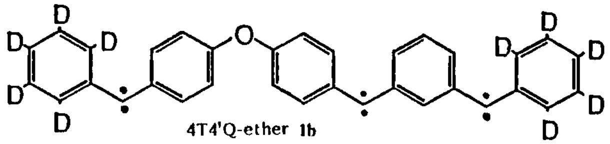


increasing energy. Since $S_j \neq S_i$, the net spin $|S_j - S_i|$ survives, while no net spin results in for antiferromagnetically coupled homo-spin systems.

We have chosen ground-state triplet diphenylmethylene($\mathbf{S}_i$) and ground-state quintet m-phenylenebis(phenylmethylene)($\mathbf{S}_j$) as the two constituent hetero-spins satisfying the requirement (iii), and we have introduced an ether bridging them at the 4- and 4'- carbon sites in order to obtain the intramolecular antiferromagnetic coupling according to the above criteria(for the requirements (i) and (ii)). The first prototype unit **1** of organic ferrimagnets so obtained is 4-(diphenylmethylene)-4'-(m-phenylenebis(phenylmethylene))-ether **1a**, which is abbreviated to 4T4'Q-ether, is shown below together with partially deuterated 4T4'Q-ether **1b**. The triplet ground state and the thermally accessible quintet and septet states have been detected by single-crystal ESR spectroscopy and a salient electronic and molecular structure have been characterized by the analysis of the fine structure spectra from **1a**.[24]



4T4'Q-ether **1a**



4T4'Q-ether **1b**

EXPERIMENTAL

4T4'Q-ether was generated at liquid helium temperatures by the photolysis of the corresponding trisdiazo precursor incorporated in benzophenone-d_{10} single crystals. The trisdiazo precursor was prepared from the corresponding a-hydroxybenzophenone and a'-bromodiketone via a sequence of reactions. We prepared the partially deuterium labeled trisdiazo precursor **1b** of 4T4'Q-ether and perdeuterated benzophenone-d_{10} in order to reduce ^{1}H-ENDOR spectral density and to facilitate the correct assignment of ^{1}H-ENDOR transitions. The deuterated compounds were synthesized from perdeuterated benzene-d_{10} (> 99.6 atom%D; Merk Sharp & Dohme Co., Inc.) as a starting material. A detailed description of the syntheses will be given elsewhere.

RESULTS and DISCUSSION

Figure 1 shows a typical ^{1}H-ENDOR spectrum observed at 2.3 K from **1b** oriented in the host benzophenone-d_{10} crystal with the static magnetic field applied parallel to the crystallographic a axis[24]. As shown below, the observed hyperfine couplings correspond to the five negative π spin carbon sites of **1a** and the observed negative ones to the seven positive sites. The unequivocal proton assignment of the ENDOR transitions observed from non-deuterated 4T4'Q-ether **1a** was made with the help of the complete spectral analysis for **1b**.

From the isotropic terms A_k^1 of the observed proton hyperfine

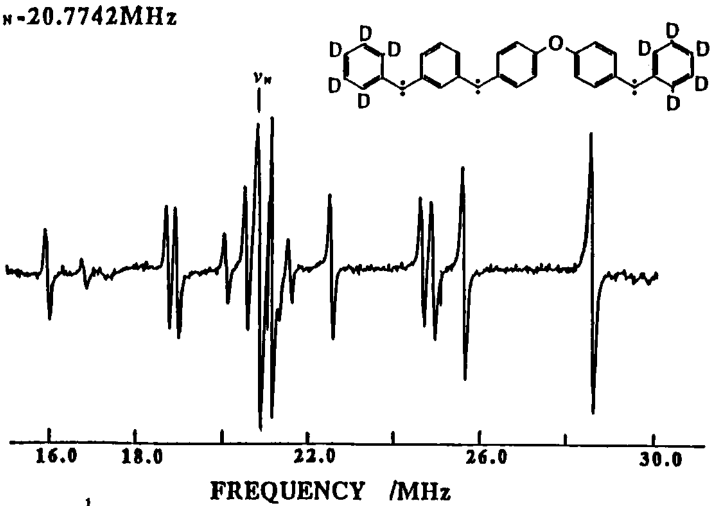


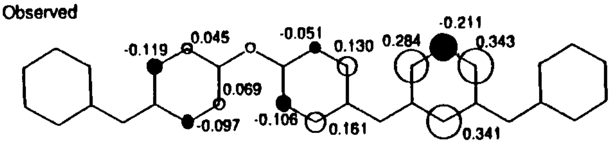
FIGURE 1 A ^{1}H-ENDOR spectrum of 4T4'Q-ether **1b** observed at 3K when the ESR Ms = 0 -- Ms = -1 transition was monitored with the external magnetic field parallel to the crystallographic a axis of the benzophenone-d_{10} host crystal. The free proton NMR frequency was 20.7742 MHz.

coupling tensors, the π spin densities ρ_k^i(k=A,B) of the carbon sites i bonded to the α-protons were determined using the well-established generalized McConnell relationship[26]

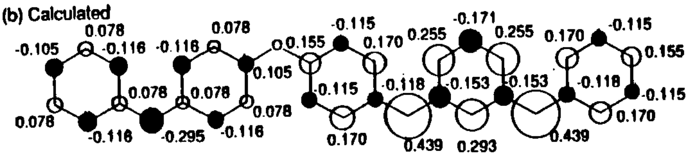
$$A_k^i = (2S)^{-1}Q\,\rho_k^i, \qquad k = A,\ B$$

where Q = -66.9MHz.[29] Figure 2(a) and 2(c) depict the experimentally determined π spin densities ρ_k^i of **1a** and **1b**, respectively. The spin

(a) Observed



(b) Calculated



(c) Observed

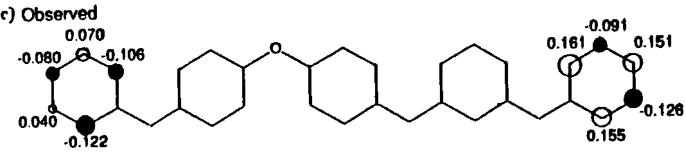


FIGURE 2 The π spin density distribution of 4T4'Q-ether **1** in the ground state(S=1). Open circles denote positive spin densities, and shaded ones negative spin densities, respectively. (a)The experimentally determined π spin densities on the carbon sites of partially deuterated 4T4'Q-ether **1b**. (b)The calculated π spin densities of 4T4'Q-ether **1** in terms of the generalized Hubbard model Hamiltonian. (c)The experimentally determined π spin densities of non-deuterated 4T4'Q-ether **1a**. Only those of the end terminal phenyl rings are shown.

densities of the carbon sites without α-protons were not derived from the present ^{1}H-ENDOR experiments.

It should be emphasized that the observed π negative spin densities in the diphenylmethylene moiety are larger than the observed positive ones, indicating that a great deal of negative spin polarization occurs in this hetero-spin system. Within the constituent moieties of the present weakly interacting hetero-spin systems the topological nature of the π spin-up and -down electron network(termed as a Spin Density Wave behavior in the molecule; pseudo π-SDW) should hold. This suggests that if the π spin network of the diphenylmethylene moiety of **1** is compared with that of the non-interacting ground-state triplet diphenylmethylene itself the spin densities on the corresponding carbon sites are opposite in sign, in other words the corresponding π-SDW is opposite in phase. The topologically controlled but sign-opposite π spin network appearing in the interacting diphenylmethylene triplet moiety of **1** gives rise to a large amount of negative spin density on the divalent carbon site of the interacting triplet moiety, amounting to somewhat reduced values but the same order of magnitude of the positive spin density on the divalent carbon site of the non-interacting ground-state triplet diphenylmethylene itself.

On the other hand, the observed π spin distribution of the quintet unit but larger than the negative ones in magnitude and the numbers of the positive and negative spins are consistent with those expected from the non-interacting quintet unit in the topologically densities are some what reduced in relative to the non-interacting quintet moiety is apparently normal, showing that the positive spin controlled "normal" spin polarization. Since the topological symmetry of the π electron network holds again for the quintet moiety in our weakly interacting model, the spin densities on the corresponding carbon sites are the same in sign if compared with the non-interacting ground-state quintet m-phenylenebis(phenylmethylene) itself. Thus, the above qualitative argument based on the experimental observation gives a simple but essential physical picture for the antiferromagnetically coupled hetero-spin system: the interacting triplet moiety($\mathbf{S}_i$) is inverted as a whole against the interacting quintet moiety($\mathbf{S}_j$). This up-side-down spin inversion is responsible for the observed unusually large negative spin polarization that chemistry has never expected so far, requiring some conceptual modification to spin polarization in chemistry. The derived physical picture in terms of spin density distribution is limited but also workable for the designing and understanding of both through-bond and through-space organic ferrimagnets.

A theoretical treatment based on quantum mechanical background has been carried out in order to predict and interpret the salient features of weakly coupled organic homo- and hetero-spin systems.[16d] Focussing upon the spin density of the resultant spin($\mathbf{S}=\mathbf{S}_i+\mathbf{S}_j$), the group theoretical calculation predicts that for the resultant triplet state($|S_i-S_j| =1$) in the present hetero-spin system the spin density of the interacting quintet moiety is reduced to be 3/4 of that of the non-interacting quintet constituent and the spin density of the interacting triplet moiety reduced to be -1/2 of that of the non-interacting triplet constituent. The reduction factor of the spin density for the resultant low spin state appears due to group-theoretical factorization and thus no reduction occurs for the resultant highest spin state. It also turns out that antiferromagnetic hetero-spin coupling arouses large negative spin density distribution. The calculated π spin densities on the carbon sites of **1** are given in Figure 2(b) for comparison with the experimental ones. The spin density distributions adopted here for the non-interacting two constituents were obtained by a generalized Hubbard model calculation.[28] In Figure 2 a satisfactory agreement is obtained between the experimental and theoretical values, showing that the triplet spin of the interacting diphenylmethylene moiety is opposite in direction to the interacting quintet spin and that the projected values of the resultant triplet spin($|S_i-S_j| = 1$) are reduced due to the group-theoretical factorization. Thus, the theoretical treatment for the weakly interacting hetero-spin systems has disclosed the complete quantitative details and salient features intrinsic to organic hetero-spin systems.

CONCLUSION

An unusually large negative spin polarization has been observed from an antiferromagnetically coupled organic hetero-spin system **1**, which is the first prototype unit of through-bond organic ferrimagnets. The antiferromagnetic coupling has been introduced by the through-bond superexchange interaction via an ether bridge which connects the triplet and quintet spins at the particular positions of the phenyl rings. The spin structure characteristic of the hetero-spin has been characterized in terms of spin density distribution, showing that the unusually large negative spin polarization directly arises from the inversion of the interacting triplet constituent in relative to the interacting quintet one in the ground state of the hetero-spin composite high-spin carbene **1**. A general theoretical treatment for weakly interacting spins predicts and elucidates the salient features of the spin structure in hetero-spin systems. It turns out that the occurrence of such large negative spin polarization is intrinsic to antiferromagnetically coupled organic hetero-spin systems. The finding gives an essential picture for both through-bond and through-space organic ferrimagnets. The picture is useful for the designing and understanding of organic ferrimagnetism.

This work was partly supported by Grant-in-Aid for Scientific Research on Priority Area(Grant Nos. 02205102 and 228/04242103(Molecular Magnetism)) and Grant-in-Aid for General Scientific Research(Grant Nos. 02453014 and 03640429) from the Ministry of Education, Science and Culture, Japan. The authors thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institutes for the use of the HITAC M680H computer.

REFERENCES

1. (a)S. Morimoto, F. Tanaka, K. IToh, N. Mataga, Preprints of T. TAKUI, Y. TEKI, M. ENDOH, Y. OKUDO, T. KINOSHITA, K. ITOH Symposium of Molecular Structure, 67(1968). (b)N. Mataga, Theor. Chim. Acta, **10**, 372(1968). (c)K. Itoh, Bussei, **12**, 635(1971). (d)K. Itoh, Pure Appl. Chem., **50**, 1251(1978). (e)K. Itoh, Chem. Phys. Letters, **1**, 235(1967). (f)E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, J. Am. Chem. Soc., **89**, 5076(1967). (g)A. A. Ovchinnikov, Theor. Chim. Acta, **47**, 297(1978).
2. (a)H. M. McConnell, Proc. R. A. Welch Found, Chem. Res., **11**, 144(1967). (b)H. M. McConnell, J. Chem. Phys., **39**, 1910(1963).
3. J. S. Miller and D. A. Dougherty, Eds., Mol. Cryst. Liq. Cryst., **176**, 1-562(1989).
4. L. Y. Chiang, R. M. Chaikin, D. O. Cowan, Eds., Advanced Organic Solid State Materials, **173**, 3-92(1989).
5. D. Gatteschi, O. Kahn, J. S. Miller, and F. Palacio, Eds., Molecular Magnetism, Kluwer Academic(1991).
6. (a)T. Takui and K. Itoh, Polyfile, No. 314, **27**, 49(1990). (b)C. P. Landee, D. Melville, and J. S. Miller, in Molecular Magnetism, D. Gattesche, O. Kahn, J. S. Miller, and F. Palacio, Eds., Kluwer Academic(1991). (c)T. Takui and K. Itoh, Zairyou Kagaku(Journal of Materials Science Society of Japan), **28**, 315(1991). (d)J. S. Miller, A. J. Epstein, Chemtech, **21**, 168(1991). (e)T. Takui, Polyfile, No. 334, **29**, 48(1992). (f)T. Takui, Kagaku(Chemistry), **47**, 167(1992). (g)J. S. Miller, Adv. Mater., **4**, in press.
7. (a)Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, J. Am. Chem. Soc., **108**, 2147(1986); ibid., **105**, 3722(1983). (b)Y. Teki, T. Takui, and K. Itoh, J. Chem. Phys., **88**, 6134(1988). (c)I. Fujita, Y. Teki, T. Takui, T. Kinoshita, K. Itoh, F. Miko, Y. Sawaki, H. Iwamura, A. Izuoka and T. Sugawara, J. Am. Chem. Soc., **112**, 4074(1990).
8. (a)A. Rajca, S. Utamapanya, and S. Thayumanavan, J. Am. Chem. Soc., **114**, 1884(1992). (b)N. Nakaumra, K. Inoue, H. Iwamura, T. Fujioka, and Y. Sawaki, J. Am. Chem. Soc., **114**, 1484(1992).
9. H. Fukutome, A. Takahashi, and M. Ozaki, Chem. Phys. Letters, **133**, 34(1986).
10. D. A. Kaisaki, W. Chang, and D. A. Dougherty, J. Am. Chem. Soc., **113**, 2764(1991).
11. (a)J. S. Miller, A. J. Epstein, and W. M. Reiff, Chem. Rev., **88**, 201(1988) and references therein. (b)J. Miller, A. J. Epstein, and W. M. Reiff, Acc. Chem. Research, **21**, 114(1988) and references therein. (c)P. M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruener, and J. D. Thompson, Science, **253**, 301(1991). (d)W. E. Broderick, J. A. Thompson, E. P. Day, B. M. Hoffman, Science, **249**, 401(1990). (e)J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein, and J. S. Miller, Science, **252**, 1415(1991). (f)G. T. Yee, J.

M. Manriquez, D. A. Dixon, R. S. McLean, D. M. Groski, R. B. Flippen, K. S. Narayan, A. J. Epstein, and J. S. Miller, Adv. Mater., **3**, 309(1991).

12. A. Ganeschi, D. Gatteschi, J. P. Renard, P. Rey, and R. Sessoli, Inorg. Chem., **27**, 1976(1989) and references therein.

13. K. Itoh, T. Takui, Y. Teki, and T. Kinoshita, Mol. Cryst. Liq. Cryst., **176**, 49(1989).

14. A. L. Buchachenko, Compt. Rend. Acad. Sci. USSR(Doklady), **244**, 1146(1979).

15.(a)M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe, Y. Maruyama, Chem. Letters, 1225(1991). (b)M. Takahashi, P. Turek, Y. Nakazawa, M. Tamura, K. Nozawa, D. Shiomi, M. Ishikawa, M. Kinoshita, Phys. Rev. Letters, **67**, 746(1991). (c)M. Kinoshita, et al., The proceedings of This Symposium.

16.(a)N. Nasu, Phys. Rev. **B33**, 330(1986). (b)Y. Teki, T. Takui, M. Kitano, and K. Itoh, Chem. Phys. Letters, **142**, 181(1987). (c)M. Okamoto, Y. Teki, T. Takui, T. Kinoshita, and K. Itoh, Chem. Phys. Letters, **173**, 265(1990). (d)Y. Teki, T. Takui, K. Sato, A. Yamashita, M. Okamoto, T. Kinoshita, and K. Itoh, The Proceedings of This Symposium.

17. T. Takui, S. Kita, S. Ichikawa, Y. Teki, T. Kinoshita, and K. Itoh, Mol. Cryst. Liq. Cryst. **176**, 67(1989).

18.(a)M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita, and K. Itoh, J. Am. Chem. Soc., **114**, 7470(1992). (b)M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita, and K. Itoh, Bull. Chem. Soc. Japan, submitted.

19.(a)J. Schweizer, The Proceedings of This Symposium. (b)A. Zheludev, A. Grand, E. Ressouche, J. Schweizer, A. J. Epstein, J. S. Miller, and B. G. Morin, The Proceedings of This Symposium. (c)R. J. Papoular, E. Ressouche, J. Schweizer, and A. Zheludev, The Proceedings of This Symposium.

20.(a)J. Bluemel, N. Hebendanz, P. Hudeczek, F. H. Koehler, and W. Strauss, J. Am. Chem. Soc., **114**, 4223(1992). (b)J. Bluemel, N. Hebendanz, P. Hudeczek, F. H. Koehler, and W. Strauss, The Proceedings of This Symposium.

21.(a)C. Kollmar, M. Couty, O. Kahn, J. Am. Chem. Soc., **113**, 7987(1991). (b)ibid., 7994(1991).

22. K. Yamaguchi et al., The Proceedings of This Symposium.

23. Y. Teki, T. Takui, and K. Itoh, to be published.

24. T. Takui, Y. Teki, H. Yagi, T. Kinoshita, and K. Itoh, to be published.

25. E. B. Fleisher, N. Sung and S. Hawkinson, J. Phys. Chem., **72**, 4311(1968).

26. Y. Teki, K. Sato, A. Yamashita, M. Okamoto, T. Takui, T. Kinoshita, and K. Itoh, Bull. Magn. Reson., **141**, in press(1992).

27. N. Hirota, C. A. Hutchinson Jr., and P. Palmer, J. Chem. Phys., **40**, 3717(1964).

28. Y. Teki, T. Takui, T. Kinoshita, S. Ichikawa, H. Yagi, and K. Itoh, Chem. Phys. Letters., **141**, 201(1987).